DEVELOPMENT OF COMBINED FILTRATION AND BIORETENTION SYSTEM FOR THE TREATMENT OF URBAN STORMWATER RUNOFF

A Thesis Submitted
In Partial Fulfilment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

by

HARSH PIPIL
(2K19/PHDEN/02)

Under the joint supervision of

Prof. A. K. HARITASH
Delhi Technological University,
Delhi

Prof. KRISHNA R. REDDY
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Chicago, USA

DEPARTMENT OF ENVIRONMENTAL ENGINEERING

DELHI TECHNOLOGICAL UNIVERSITY
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CANDIDATE'S DECLARATION

I, Harsh Pipil, Roll No.: 2K19/PHDEN/02 student of Ph.D. (Environmental Engineering), hereby declare that the work which is being presented in the thesis entitled "Development of Combined Filtration and Bioretention System for the Treatment of Urban Stormwater Runoff" in partial fulfilment of the requirement for the award of Degree of Doctorate of Philosophy, submitted in the Department of Environmental Engineering, Delhi Technological University is an authentic record of my own work carried out during the period from August, 2019 to August, 2024 under the joint supervision of Prof. Anil Kumar Haritash (Delhi Technological University), and Prof. Krishna R. Reddy (University of Illinois, USA).

The matter presented in the thesis has not been submitted by me for the award of any degree of this or any other Institute.

Place: Delhi **(HARSH PIPIL)**
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CERTIFICATE BY THE SUPERVISORS

Certified that **Harsh Pipil** (2K19/PHDEN/02) has carried out the research work presented in this thesis entitled **"Development of Combined Filtration and Bioretention System for the Treatment of Urban Stormwater Runoff"** for the award of **Doctor of Philosophy** from Delhi Technological University, Delhi, under our supervision. The thesis embodies results of original work, and studies are carried out by the student himself and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

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ABSTRACT

Almost 97% of the world's available water is present in oceans but high concentration of salts renders the oceanic water unusable for domestic, agricultural, and industrial activities. Desalination techniques have been incorporated but it is a cost and energy intensive process to produce huge volume of freshwater, although, few regions on earth rely on this technique. On the other hand, freshwater resources are scarce out of which most of the freshwater is stored as glacier, and a very few percent which accounts to be 0.0072 % of world's total water budget is present in freshwater lakes and streams. As an alternative, the rainwater can be intercepted and utilised for non-potable application by providing minimal treatment since the rainwater is considered to be the purest form of water until it comes in contact with contaminants. These contaminants are the atmospheric impurities originating from natural and anthropogenic activities. Once the rainwater reaches earth's surface, it becomes stormwater which first gets infiltered into the ground surface and few portion of it becomes surface stormwater runoff. This surface stormwater runoff when comes in contact with the surface of earth and traverses its path, takes along floating, suspended, and dissolved impurities with it. Thus, the source characterisation of the rainwater and stormwater runoff was performed through various locations which include commercial, industrial, institutional, residential, and road/ highway. For this aim, the rainwater and stormwater samples were collected during year 2021 and 2022. The physico-chemical analysis of rainwater reveals that most of the chemical species are present in trace amount suggesting that chemical impurities are the result of atmospheric washing during the down pour. Also, no event of acid rain ($pH < 5.6$) was witnessed in Delhi. The physico-chemical analysis of stormwater runoff in Delhi for year 2021 and 2022 suggests wide variation among the different chemical and physical parameters from different land uses. Also, it revealed that total suspended solids are the major contributor in surface stormwater runoff which originated from road side sweeping, and surface runoff coming from construction sites. Nutrients (PO_4^{3-} and NO_3^-) are the second major contaminant found in the stormwater runoff samples which were found in higher concentration in the samples from residential areas. The heavy metals such as cobalt, chromium and lead were below the detection limit, but cadmium was found in trace amount at a few locations along to road/highway. The contaminant in stormwater runoff were identified followed by suitable treatment to make it usable. Initially, the filter media was identified on the basis of its availability and ability to remove the suspended as well as dissolved impurities. The pollutants in stormwater runoff were treated in batch process to remove dissolved nutrients using various filter media. The study indicated that phosphate removal by different materials follows the order iron filing > calcite > limestone > brick > hematite > biochar. Biochar being one of the filter media, was prepared in the lab using used and refused bamboo at 500 °C through pyrolysis. Biochar was not able to remove the nutrient in batch process suggested repulsion between electro-negatively charged nutrient and surface charge of biochar. Thus, biochar was treated with $FeCl_3$ to make its surface electro-positive to remove negatively charge nutrient (PO_4^{3-} and NO_3^-) from synthetically prepared and real stormwater runoff. The use of biochar in batch process at a dose of 5 g/L can remove upto 61 % of the phosphates at the initial PO_4^{3-} concentration of 5 mg/L when biochar treated with 10 % $FeCl_3$ solution was used. On the other hand, when biochar treated with 5 % $FeCl_3$ solution was used at a dose of 5 g/L, and the initial phosphate concentration was varied, suggested that removal efficiency increased when initial concentration of the phosphate was used to 2 mg/L. This underlines that removal of pollutant from is a function of pollutant initial concentration of contaminant and the dose of biochar. The adsorption capacity and performance of biochar are function of contact time. Followed by batch process, continuous flow filter was prepared using the identified filter media. The continuous flow study indicated that upto 97 % total suspended solids and phosphates upto 93 % can be removed from real stormwater runoff using filter media consisting of iron filing, calcite, limestone, brick, and hematite. Followed by identification of filter media for stormwater runoff treatment, bioretention system was designed consisting of different wetland macrophytes. In bioretention system, the available and total phosphate removal study was carried out which consisted of gap graded bed substrate for easy penetration of roots and easy movement of water. The available and total phosphate removal efficiency followed the order summer > spring > winter > autumn, for *Phragmites*, while it followed the order summer > spring > winter for available and total phosphate removal using *Cyperus alternifolius,* and *Canna lily*-based constructed wetland cell. Total phosphate removal efficiency using *Phragmites* based constructed wetland cell was of order 56.7 %, 80.6 %, 90.3 %, and 95.5 % for autumn, winter, spring, and summer season, respectively. Similarly, total phosphate removal efficiency of *Canna lily* based constructed wetland cell was of order 77.7 %, 82.5 %, and 88.7 %, respectively for winter, spring, and summer season. *Cyperus alternifolius* based constructed wetland cell indicated total phosphate removal efficiency of order 62.5 %, 74.0 %, and 81.7 %, during winter, spring, and summer season, respectively. Thus, the maximum total phosphate removal follows the order *Phragmites* > *Canna lily* > *Cyperus alternifolius* based constructed wetland during the respective season. In addition, similar trend was also shown by *Phragmites* > *Canna lily* > *Cyperus alternifolius* based constructed wetland during the respective season for available phosphate removal efficiency. The analysis of ferric to ferrous ratio in bioretention wetland cells was less than unity suggested that ferrous ions (Fe^{2+}) was present in the cell in major concentration while ferric ions (Fe^{3+}) were converted to ferrous by reduction. This rules out the removal and binding of phosphates with bed sediments and suggested that phosphate was removed by macrophytes. Lastly, a hybrid filter system was developed which consisted of filter media and the macrophytes in different cells. The selected filter media and the macrophytes are those which were suggested by previous experiments of same study. The hybrid filter was provided with vertical baffle walls such that polluted stormwater runoff flows above and below it while travelling from one chamber to another. The hybrid filter system reported almost 96 % removal of total suspended solids from stormwater runoff during continuous flow. The same filter was able to remove 55 % and 41 % of phosphates and nitrates, respectively, from synthetically prepared stormwater runoff when operated continuously. Thus, this is a promising design that can reduce the suspended solid load and dissolved nutrient load from stormwater runoff. The treated stormwater runoff from hybrid filter can be utilised for non-potable use which can reduce the dependence on freshwater and helps in bridging the demand and supply gap.

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List of Abbreviations

AAS	Atomic Absorption Spectrophotometry
AG	Above Ground
AP	Available Phosphate
APHA	American Public Health Association
ASTM	American Society for Testing And Materials
BCM	Billion Cubic Metre
BDL	Below Detection Level
BG	Below Ground
BMP	Best Management Practice
BOD	Biochemical Oxygen Demand
BTEX	Benzene, Toluene, Ethylbenzene, And Xylenes
CDOM	Coloured Dissolved Organic Matter
CEC	Contaminants Of Emerging Concerns
COD	Chemical Oxygen Demand
COVID	Corona Virus Disease
CW	Constructed Wetland
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
EC	Electrical Conductivity
EDTA	Ethylenediamine Tetraacetic Acid
EF	Enrichment Factor
FTIR	Fourier Transform Infrared
GDP	Gross Domestic Product
GI	Green Infrastructure
GPS	Global Positioning System
GPT	Gross Pollutant Trap

HCL	Hollow Cathode Lamp
HDS	Hydrodynamic Deflective Separation
HRT	Hydraulic Retention Time
IC	Inorganic Carbon
IMD	Indian Meteorological Department
ISE	Ion Specific Electrode
IUWM	Integrated Urban Water Management
LID	Low Impact Development
MLD	Million Litres Per Day
NF	Neutralization Factor
NMVOC	Non-Methane Volatile Organic Compounds
NSSF	Non-Sea-Salt Fraction
PAH	Polycyclic Aromatic Hydrocarbons
PCDD	Polychlorinated Dibenzo-Para-Dioxins
PCDF	Polychlorinated Dibenzofurans
POP	Persistent Organic Pollutants
RPM	Revolutions Per Minute
SCM	Storm Control Measures
SD	Standard Deviation
SDG	Sustainable development goal
SEM	Scanning Electron Microscopy
SOP	Synthetic Organic Pollutants
STP	Sewage Treatment Plants
SUDS	Sustainable Urban Drainage System
TC	Total Carbon
TDS	Total Dissolved Solids
TKN	Total Kjeldahl’s Nitrogen
TN	Total Nitrogen
TOC	Total Organic Carbon

TP	Total Phosphate
TSS	Total Suspended Solids
VOC	Volatile Organic Compounds
WSUD	Water Sensitive Urban Design
WTP	Water Treatment Plants
WTR	Water Treatment Residual

CHAPTER 1

INTRODUCTION

Almost 97% of the world’s water is present in ocean, however, the high concentration of dissolved salts in ocean water makes it almost unfit and unusable to municipal, agricultural and industrial applications. A very limited quantity of freshwater is available to us; hence, it is said that the water will become as valuable as crude oil in the present century, forcing us to think of its efficient management and usage so that water of acceptable quality is available to all and not only to specific group of population (Rezaei et al., 2017). For instance, in developing nations like India, the rural population is migrating towards urban areas for better lifestyle and job opportunities, leading to increase in demand of freshwater. Consequently, increasing the pressure on existing limited freshwater bodies. India is largely dependent upon monsoon for its agricultural growth, gross domestic product (GDP), and other socio-economic activities (Majumdar et al., 2022). The proper usage or over exploitation of freshwater leads to either depletion or generation of wastewater which cannot be used until it is given proper and desirable treatment making it fit for potable use. Although, rainwater is a source of freshwater, however, it gets polluted through atmospheric washing and as surface runoff over urban areas where it dissolves many impurities. Moreover, strength of pollutant in stormwater runoff is very less as compared to sewage water. The interception of this stormwater runoff before it gets mixed with sewage, its prevention to flows away from the urban area through natural drainage, and by providing minimal treatment so that stormwater runoff can be used for non-potable use in urban areas, such as, recreational activities, gardening, irrigation, and etc. Thus, stormwater runoff can be a good alternative for providing freshwater for non-potable use, and it can help in reducing the load on other freshwater bodies such as lakes, ponds or rivers in an urban area.

1.1 Background

The world’s water budget estimated and suggested that 1338x10^6 km^3 of water is stored in ocean which has dissolved salt, and accounts for 96.5 % of world water. Freshwater lakes, rivers, and streams have approximately 0.0072% of world’s total stock of water (≈93000 km^3) (Shiklomanov, 1993). There is more evaporation from ocean than precipitation while, there is more precipitation than evaporation over the land mass. The evaporation from ocean is of order 505 x10^3 km^3/year while evapotranspiration from land is of order 72 x10^3 km^3/year. Also, the precipitation on land is of the order 119 x10^3 km^3/year. The difference in amount of precipitation and evapotranspiration over the land mass is returned to ocean as surface flow or groundwater flow. India receives annual precipitation of about 3880 BCM out of which 1999 BCM of water becomes natural runoff and only 690 BCM of precipitation can be utilised as a source of surface water (Extraction of Groundwater 2020). Almost 70% of urban lands are paved with high runoff coefficient of 0.9, this causes high runoff volume, high peak flow, flooding in low lying areas, and limited groundwater recharge (Goel, 2011). Also, lack of adequate stormwater management practices leads to overflow of stormwater runoff in urban area, streets, basements, etc. during rainfall events. Moreover, the surface runoff scavenges the pollutants already present in the urban area and disposes it into the receiving waterbody which ultimately increases the contaminant concentrations. Based on the source of pollution, wastewater is broadly classified as stormwater runoff, agricultural runoff, industrial wastewater, and domestic wastewater; and the pollutants are broadly classified as physical, chemical, and biological in nature (Maurya et al., 2020). The problem of contamination of receiving waterbodies can be mitigated along with bridging the demand and gap of water in urban areas by providing an effective treatment to stormwater runoff.

1.2 Requirement of stormwater runoff treatment

The conventional water treatment plants are designed for treatment of sewage produced by the estimated population living in urban areas. In addition to this, the sewage conveyance systems were developed for poorly estimated population growth in urban areas leading to insufficient design and poor conveyance capacity. The absence of stormwater conveyance systems due lack of planning and capital investment, the stormwater gets mixed with sewage water. This conveyed sewage goes to sewage treatment plants (STP) which were not designed to handle the increased volume of receiving wastewater. Also, the rainwater is considered to be the purest form of water. As the wet precipitation takes place, it scavenges the pollutants suspended in atmosphere such as the resuspended dust particles, or dust particles in association with heavy metals, PAH, BTEX, nitrogen oxide (NO_x), carbon monoxide, sulphur dioxide (SO_2), etc. remains in suspension in atmosphere, leading to atmospheric washing and contamination of rainwater. The mixing of rainwater with suspended acidic species like SO_2 and NO_x can even lead to events of acid rain ($pH < 5.6$) (Kulshrestha et al., 2003). Depending upon the topography and meteorological conditions, the rainwater when comes in contact with the earth, it is further contaminated with the floating impurities like plastic, tree branch, paper, rags, leaves etc., and suspended impurities like dust, silt, and organic matter; and dissolved cations and anions leading to degradation of water quality. Thus, the quality of rainwater deteriorates as it traverses its path from atmosphere and over the terrestrial locations. However, the physico-chemical characteristics of runoff suggests that its quality is far better than wastewater and can be treated to meet the demand and supply gap.

1.3 Treatment methods and techniques

As the annual average temperature is increasing, resulting in the change in the climate and disturbed pattern of rainwater. There is an urgent need to design the water sensitive mechanisms and techniques in order to treat and reuse the contaminated storm water runoff. Despite being contaminated, the strength of impurities in storm water runoff is far less than the domestic/ municipal wastewater. Therefore, the surface runoff can be treated to make use of storm water most efficiently in order to reduce the load on the existing water resources and bridge the gap between the demand and supply of the freshwater. Several techniques and methods are being used in the developed countries like United States of America, New Zealand, and Australia, which include gross pollutant trap (GPT), vegetated swales, rain garden, wetlands, tree pits, etc. Such techniques have been implemented locally or as a centralized unit in these countries (Beza et al., 2018). These techniques and methods can also be used in India depending upon the prerequisites and requirement of the individual method are satisfied (Pipil et al., 2022a). The treated and untreated stormwater runoff received from catchment needs its management before it gets mixed with the sewage system and increase the load on the exiting low-capacity sewage treatment plants. Decentralised and sustainable stormwater treatment methods can be adopted to meet the demand of freshwater supply for gardening, street cleaning, washing and other potable use.

1.4 Management of stormwater runoff

India is the world's second most populous country with approximately 2.4% of the geographic area receives the annual precipitation of about 3880 BCM (Billion Cubic Metre) (Extraction of Groundwater, 2020). The precipitation is not uniform making few places to receive excessive rainwater and other places to receive scanty/ scarce rainwater. Hence, it can be said that distribution of water is uneven in India because of the limited resources of freshwater. Also, the rainwater which is received on earth, first fulfils the infiltration capacity (leading to interflow) of ground, fills the undulations (pits and ditches) on ground and it is affected by land use/ cover before it become stormwater runoff (Wang et al., 2021). Apart from it, there are fluctuations in the flow of stormwater due to differential precipitation every single time it rains. This in turn causes the variation in concentration of contaminants in the stormwater and so does the treatment efficiency of the treatment units (Rodziewicz et al., 2020). It raises the question on the requirement of the decentralized stormwater treatment. Nowadays, stormwater generally traverses through existing aging and inadequate conveyance systems and they are hardly given any treatment for their reuse. The stormwater runoff eventually meets the wastewater system and causes increase in the load on the existing relatively lower capacity centralized wastewater treatment plants. Thus, the present study focuses on physico-chemical chemical characterisation of stormwater runoff and suggesting the most suitable treatment method for the removal of contaminants through its treatment.

1.5 Objectives of the present study

Considering all the problems associated with the current management of stormwater, the following objectives were set forth for the research study:

(i) To characterize stormwater for its physical and chemical properties, and monitor typical flow characteristic in rainy season in Delhi.

(ii) To study the efficiency of different treatment filters towards removal of suspended and dissolved impurities from stormwater.

(iii) To study the efficacy of treatment system in combination with bio-treatment units.

(iv) To design and develop the most effective filter for treatment of stormwater.

CHAPTER 2

REVIEW OF LITERATURE

2.1 Introduction

The rapidly increasing global population at an average annual growth rate between 1 to 2% pose a threat in the coming future owing to the limited available fresh water resources, pressure on the sanitation system, and other environmental issues (Ezeh, 2012). Increasing population is leading to increase in urbanisation which causes the destruction of forest and vegetation for constructing impervious roads, pavements, houses, building, and rooftops. The exponential surge in impervious earth’s surface due to urbanisation have increase the stormwater runoff volume (Andoh and Declerck, 1997; Hogan and Walbridge, 2007), and subsequent decrease in groundwater recharge due to poor infiltration. In addition, the enormous size of India is the basis for non-uniform downpour leading to excessive rainfall over some parts of India and rest receiving the scanty rainfall (Ghosh et al., 2016). The majority of the Indian rural population is now migrating towards urban areas from rural area in search of employment, education and better lifestyle. As a consequence of which, the demand of potable water is increasing everyday leading to pressure on existing aquatic bodies and water treatment plants (WTP). The urbanisation is causing the release of pollutants from point and non-point anthropogenic sources that include various land uses, such as residential, commercial, industrial, institutional, road/highways, and open spaces (Kabir et al., 2014; Müller et al., 2020). When the rainwater falls over these various land use, its interaction with earth’s surface and infrastructure, causes sweeping of deposited sand/silt, clay, minerals, heavy, and other organic impurities in the stormwater runoff which is ultimately received by nearby water bodies (Pipil et al., 2022a). For instance, the capital city of India, New Delhi which is located next to river Yamuna receives the wastewater discharge from 21 different locations that comprises of treated, untreated and stormwater runoff, significantly increasing the faecal coliform level in the river (Jamwal et al., 2008). As a consequence, the water quality and health of receiving water body is deteriorated over a period of time, and it impacts both human life and aquatic ecosystem (Lee et al., 2007; Schwarzenbach et al., 2010; Björklund et al., 2018). Thus, the rainwater plays an important role in governing the stormwater runoff characteristics. Though, rainwater is the cleanest source of water but it also gets contaminated when it comes in contact with atmospheric impurities (Gonçalves et al., 2003). The atmospheric pollutants originate from natural sources such as volcanic eruption and forest fires; while anthropogenic sources contribute air pollutants from fossil fuel burning in thermal power plants, vehicular emissions, heating system, and other industrial activities (Kulshrestha et al., 2003). These pollutants emit SO_4^{2-} and NO_3^- that can lead to acid rain ($pH < 5.6$) on earth's surface. Heavy metals are also released through these activities which are different from organic waste in the sense that they do not degrade in environment on their own and becomes a part of food chain to cause bio magnification. Regulations have been imposed and policies were implemented, even though the management of stormwater runoff is still a challenge (Subramanian, 2016).

In ancient times, people used to collect and store stormwater from roofs, terraces and had specifically designed paved surfaces for the potable and non-potable use during the dry season (Gikas and Angelakis, 2009). Proper management of stormwater runoff prevent the mixing of pollutant in stormwater runoff along with its disposal into sewage and river, while, promoting its interception and treatment that could potentially fill the water demand and supply gap. Reusing the treated stormwater could reduce the dependence on other surface water resources further lessening the groundwater extraction, and helps in meeting the demand of water in many developing countries (Ashoori et al., 2019; Pipil et al., 2022a). Initially, stormwater management practice was implemented to attenuate the flood peak through flood routing using Muskingum method (1938) (Fenton, 2019). Efforts were made to reduce the contamination of stormwater runoff at the source which is a back-breaking practice, and decentralised water treatment units possess challenge of providing treatment units/ facilities in limited urban spaces (Brown and Farrelly, 2009). Moreover, stormwater runoff management in urban areas have been given distinct terms viz., water sensitive urban design (WSUD), storm control measures (SCM), sustainable urban drainage system (SUDS), green infrastructure (GI), best management practice (BMP) and low impact development (LID) (Fletcher et al., 2015). SCMs includes detention basins, constructed wetlands, bioretention system, sand filters, and grass swales (Urbonas, 1994); LID includes bioretention basins, raingardens, and permeable pavements (Dietz, 2007); whereas GI includes raingardens, permeable pavement, green roofs, and swales. Rainwater harvesting is another technique that can reduce the dependence on freshwater, easy to install, replenishes the groundwater, and reduces the stormwater runoff and flooding due to impervious surface (Melidis, 2007). These stormwater management techniques not only help in managing runoff volume but, improves the water quality as well. These techniques have garnered the attention in developed countries like United States of America, Canada, Australia, New Zealand and other European countries, but it lacks awareness as well as implementation in many developing countries (Kratky et al., 2017).

2.2 Bibliometric analysis

A comprehensive bibliometric analysis was performed on stormwater management strategies to manage stormwater runoff. Bibliometric analysis provides a basis to unveil the article publication trend, journal performance, and collaborations (Donthu et al., 2021). The study was based on the data retrieved from Scopus for duration year 2000 to 2023 which included the keywords “stormwater” OR “runoff” OR “stormwater treatment” OR “bioretention systems” OR “WSUD” OR “LID” OR “green infrastructure” searched under “Article title and Abstract” and provided a total of 828 articles. This provides the basis on which the progress in the field of stormwater management is can be estimated in last few decades in various countries. Over a period of last two decades, it can be seen that the popularity and attention towards the stormwater runoff management has increased significantly (Fig. 2.1).

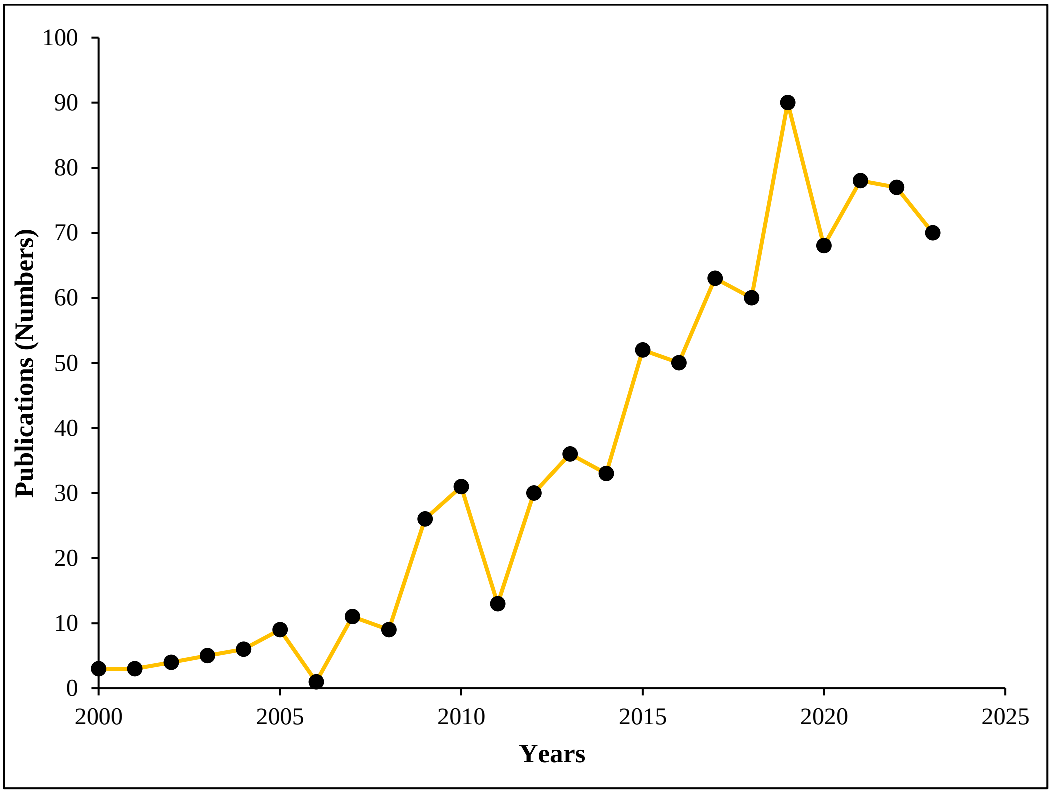

Fig. 2.1 Yearly publications on stormwater management

Until 2006, less than 10 articles were published which increased significantly to 90 articles in year 2019. However, a dip in number of articles published can be seen in year 2000 to 2023. Country/territory-wise publication of articles between 2000 to 2023 is shown in Fig. 2.2. Most of the articles (509) were published by the researchers in United States of America alone. The significant number of articles published in the defined time period by the countries follows the trend as Australia, China, United Kingdom, Canada, France, and Germany which have published 64, 47, 40, 35, 19 and 17 number of articles, respectively (Fig. 2.2). However, India has published 9 number of articles on stormwater runoff management from 2000 to 2023 which is a significant number among all the developing nations.

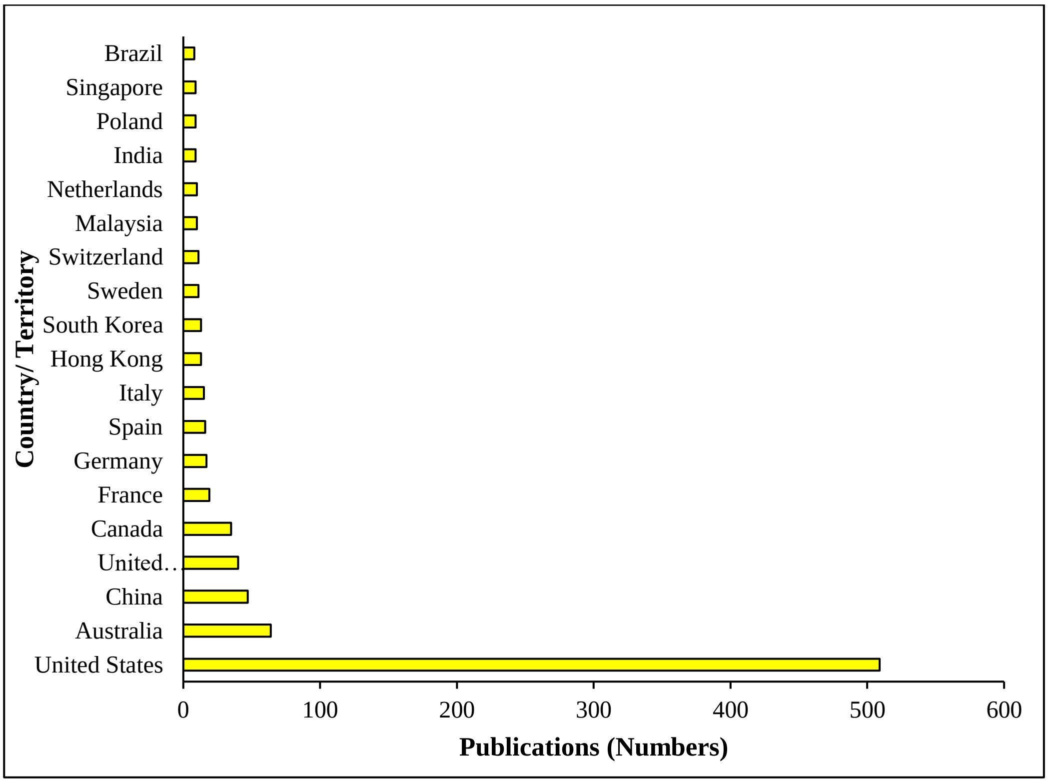

Fig. 2.2 Country/territory wise publications on stormwater management

2.3 Water resources

Due to vast variation of geological features, climatic conditions, and environmental factors, the distribution of water is non-uniform globally. Similarly, the size of India is enormous such that the distribution of freshwater is not equal. Some parts of the country are blessed with freshwater resources while other parts of the country face scarcity of water. The water resources are broadly classified as freshwater and saline water resources, where saline water, due to the presence of salts in it, has no application until certain treatment is not given to it as per the desired requirement. Freshwater resources, on the other hand are the main component of life on earth. Freshwater finds its application for human consumption, agricultural activity, industries, and sustaining freshwater ecology (Pimentel et al., 1997). The freshwater resources can be classified as the surface water resources which includes, rivers and streams, and lakes and ponds. Streams are the channels which feed their water into lakes or rivers. They discharge through streams are generally low which does not allow dependency on streams as a source of water for large population. However, rivers carry more discharge which can be used for public supply. Hence, this is the reason for settlement of major cities near river, including capital city of India, Delhi, which is located near river Yamuna (Profile of Delhi, 2023). Rivers are further classified as perennial in which the water flows throughout the year, while non-perennial rivers are those in which water flows intermittently (Wohl and Merritts, 2007). The perennial rivers can be a source of water for public supplies, for domestic, industrial, and agricultural use, though the quality of the water is not always reliable, thus might require a certain desired level of treatment. On the other hand, a large depression on earth’s surface when gets filled with water leads to formation of ponds and lakes. Ponds and lakes generally get the water from surface stormwater runoff and when the water table level rises to ground level. Larger and older lakes provide relatively better-quality water as compared to smaller and new lakes as a result of sedimentation although, algal growth, weed, and vegetation growth may impart colour, smell and taste in lake water. Underground water or groundwater is also a source of freshwater present inside the earth’s surface in an aquifer. Apart from all these sources of water, rainwater is also a fresh and pure source of water which has been neglected directly in urban areas where this water follows the natural ground slope and drains into river or stream. In developed nations, stormwater conveyance system has been designed and developed which drains away the stormwater runoff from urban areas. Although, if stormwater runoff can be intercepted and stored after providing minimal treatment, it can also be used as a source of non-potable water in urban areas of developing and developed nations (Poustie et al., 2015).

2.3.1 Water availability

It is said that around 60 % of the global population will experience the shortage of water supply by year 2050. The abundance of water differs across the various sources such that sea and ocean have 97.24 %, glacier and icecaps have 2.14 %, groundwater has 0.61 %, freshwater lakes have 0.009 %, inland seas have 0.008 %, soil has 0.005 %, and atmosphere has 0.001 % of the total water available on the earth (NOOA, 2023). Fresh water on the globe is not equally distributed which is also true for its unequal distribution in India. Ever increasing human population and migration of people to urban areas is increasing load on existing waterbodies, causing scarcity of fresh and potable water. Due to never ending demand for freshwater, the quality of available water is compromised as the desired degree of treatment could not be provided to raw water to be used as freshwater (Ehrlich and Ehrlich, 2009). Sometimes, disposal of used and wastewater is also a challenge which ultimately ends into finding its way into source of freshwater. It seems that water is available in abundance, however, only 1 % of the earth's water can be used to meet human demand (Longo and York, 2009).

2.3.2 Demand and supply gap

Water is an essential entity required to sustain life on earth. The demand for water consumption is far more than its current availability for a very large population globally. The population of India is second highest in the world constituting 1210 million of its population in the country having a total area of 3.3 million sq. km which is approximately 2.4% of the world's total land mass (Profile, 2022). The annual average rainfall over India has been estimated at 3880 BCM (Billion Cubic Metre) out of which 1999.20 BCM has been assessed as natural run-off after considering the evapotranspiration etc. The available stormwater is of order 1122 BCM which consists of 690 BCM of surface water and 432 BCM of total annual groundwater recharge taking into consideration the topography and hydrology (Extraction of Groundwater, 2020). Delhi, the metropolitan city, is classified as one of the most polluted cities around the globe. The city houses more than 20 million people in an area of 1484 square km with a population density of 13,500 people/km^2, thus raising a concern for public health and infrastructure development (Directorate of Economics and Statistics Office of Chief Registrar, 2023). It has demand of 5183 MLD of treated water against the supply of 4251 MLD creating a gap of 931 MLD, which projects to approximately 341,000 million litres on annual basis. Meanwhile, Delhi receives annual rainfall of approximately 650 mm per year. Considering 70% paved surfaces with runoff coefficient of 0.9, the city produces surface runoff of approximately 963,000 million litres annually which is approximately 2.8 times higher than the annual demand-supply gap. If only one third surface runoff is trapped, stored and utilised over the year, it can easily bridge the gap to meet the water demand of the city. Moreover, the utilisation of stormwater runoff would help overcome the problem of stormwater mixing with sewage, additional cost of treatment, and minimisation of secondary sewage sludge generation.

2.3.3 Water pollution

Water pollution is the contamination of waterbodies and water resources by pollutants such as floating (leaves, tree branches, bottles, platics, etc.); suspended (sand, silt, etc.); and dissolved (organic, ingoranic waste, heavy metals, nutrients, etc.) impurities beyond certain level.

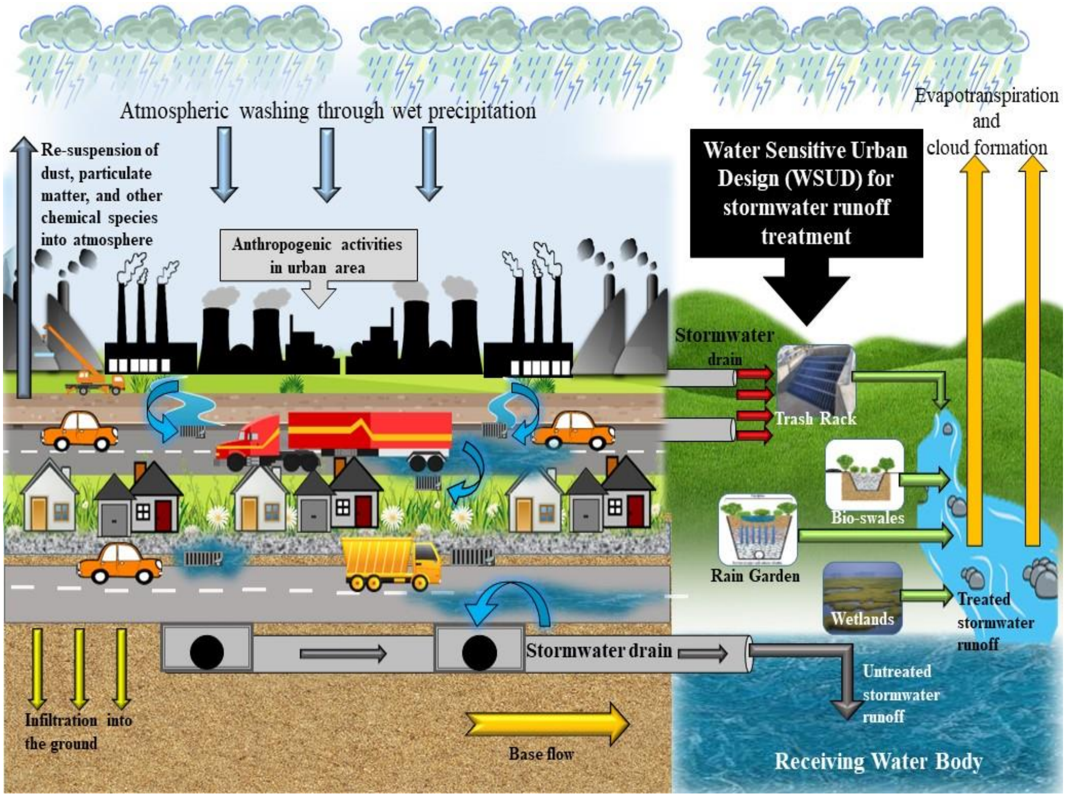

Fig. 2.3 Depiction of contamination of stormwater runoff through various activities in urban region and its possible treatment techniques

These pollutants becomes a part of waterbodies when they are discharged either directly, accidently or by some agency such as stormwater runoff. As a result, these contaminants impart detrimental harm to water body rendering it unfit for potable and non-potable use. Various activities such as indsustrial discharge, agricultural runoff, sewage overflow, oil spills, vehicular movement, etc. detoriate the quality of water (Fig. 2.3) These pollutants gets discharged directly into water bodies or sometimes, when the rainfalls over them, they get carried away with the stormwater runoff. The pollutants causes contamination of stormwater runoff first followed by its mixing with surface waterbodies, infiltration and leaching into land leading to groundwater pollution. However, the urban area have most of the surfaces paved, the contaminated stormwater runoff reached the surface waterbodies such as lakes, ponds or rivers.

2.4 Sources of stormwater contamination

2.4.1 Atmospheric fallout

Rainfall is considered to be the cleanest source of water until it comes in contact with atmospheric pollutants released either from natural or anthropogenic sources (Melidis et al., 2007). The downpour of first rainfall scavenges and dissolves all the atmospheric impurities with it, triggering the contamination of the rainfall thus changing its quality, chemical composition and pH, before it is received on earth (Al-Khashman, 2005), which in return plays a remarkable contribution towards the cleaning of atmosphere. The presence of sulphur dioxide, oxides of nitrogen, carboxylic and carbonic acid, acetic acid, organic acids, and other acidic precursors in the atmosphere causes decrease in the pH of rainfall, which results in acid rain for $pH < 5.6$ (De Mello, 2001; Migliavacca et al., 2005). The characteristics of rainfall highlights the impurities composition of stormwater and also the poor quality of the atmosphere from where it is scavenging these pollutants (Calvo et al., 2010). Volcanic eruption and forest fires are the natural source of CO_2, particulate matter, nitrogen and sulphur species such as sulphur dioxide (SO_2), hydrogen sulphide (H_2S), hydrogen chloride (HCl), halogen compounds, and aerosols (Giggenbach et al., 1996; Kumar et al., 2019).

Table 2.1 Various pollutants that result in contamination of wet precipitation during its downpour as reported by various published studies

Pollutant	**Reference**
Suspended Solids	Pipil et al., 2022b; Gunawardena et al., 2013; Kafi et al., 2008
Nutrients: N, P, Fe, Zn	Baker et al., 2007; Anderson and Downing, 2006; Koelliker et al., 2004;
Heavy metals: Fe, Cr, Mn, Ni, Cu, Zn, Cd, Pb, Hg	Liu et al., 2012; Gunawardena et al., 2013; Davis and Birch, 2011; Wicke et al., 2012; Bąk et al., 2019; Murphy et al., 2014; Lynam et al., 2014;
Organic Pollutants: Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF); Benzene, Toluene, Ethylbenzene and Xylenes (BTEX)	Lin et al., 2010; Lohmann and Jones, 1998; Halsall et al., 1997; Mohamed et at., 2020; Kirkok et al., 2020; Yu et al., 2022;

These pollutants originates from local or remote, anthropogenic source, such as vehicular movement, vehicular emission, terrestrial, naval and aerial pollution, releasing particulate matter, NO_3^-, SO_4^{2-}; carcinogenic species like polycyclic aromatic hydrocarbon (PAH), and persistent organic pollutants (POP); heavy metals, hydrocarbons, BTEX compounds (such as benzene, ethylbenzene and toluene), polychlorinated dibenzo-para-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (Yadav et al., 2023; Ryan and Gullett, 2000; Slezakova et al., 2013; Cortés et al., 2014; Adeyanju and Manohar, 2017) (Table2.1). Most of these pollutants are also categorised as criteria pollutants by United States Environmental Protection Agency (US EPA, 1983). Industrial activities utilise and burns fuel and coal for its energy requirement that releases CO_2, CO, hydrocarbon, aerosols etc.; oxidation of non-combustible species present in fuel (NO_x and SO_x); residue of fuel such as furnace bottom ash, soot, fly ash) that are released into the atmosphere. However, the release of pollutants from coal burning is many folds higher than the use of oil and natural gases for combustion. Heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), zinc (Zn) and vanadium (V) are also released into the atmosphere through industrial activities (Mishra et al., 2019). Other pollutants that contribute towards air pollution are volatile organic compounds (VOC's) originating from fuel, refrigerants, paints, and solvents; non-methane volatile organic compounds (NMVOC's) such as ketone and aldehydes (Wang et al., 2013; Liu et al., 2018). The emission of PCDD and PCDF from industrial activities depends highly on the combustion condition. These pollutants stay in the atmosphere of the urban area until they are washed out by wet precipitation.

2.4.2 Terrestrial pollution

As the rainfall reaches the earth's surface, it comes in contact with the pollutants which are already deposited on the various surfaces on earth, as a result of dry deposition under the effect of gravity. Due to presence of impervious surface, it traverses its path through roads, pavements, highways, buildings, roof tops, sheds, canopy, trees, open spaces, and green belts, from where stormwater runoff sweeps and mixes impurities in it, such as, floating, suspended, and dissolved.

2.4.2.1 Vehicular movement

The vehicular movement and its presence on the road cause the dispersion and re-deposition of contaminants over the paved surfaces and roads. The pollutants are released from the exhaust pipe of internal combustion engine gets deposited on road, dripping/ leakage of automotive fluid, vehicle washing, road accidents, and abrasion of pavement materials also contributes towards deposition of the pollutants (Markiewicz et al., 2017; Björklund, 2010). The cumulative contribution of the pollutants originating from vehicular movement cannot be estimated as several other sources also emits the contaminants. The pollutants contributing from vehicular movement included total suspended solids (TSS), PAH, BTEX, BOD, COD, nitrogen oxide (NO_x), carbon monoxide, sulphur dioxide (SO_2) and trace metals (Huber et al., 2016). The exhaust of vehicles equipped with catalytic converter that helps in reducing the air pollution, have been identified as the source of Rh, Pd, and Pt (Rauch et al., 2005). The leakage and seepage from the internal combustion engines emit PAH, whereas petrol refill stations are prominent hotspot source of BTEX (Liu et al., 2018). Vehicle washing releases various chemicals adhered to the vehicle's top or underbody, while rain falling on the vehicle also perform similar type action, and ultimately adds to the contamination of urban stormwater runoff. The tyre and brakes are also the source of heavy metals such as Zn, Cu, Cd, Ni, Pb, along with PAH and microplastics. The tyres and brakes worn out as a material on their application and gets deposited over the road with time. The abrasion of road material over a period of time also serves as the source of TSS along with the deposition of other suspended solids during dry spells. The presence of road side dust also contributes to TSS in urban stormwater, while the heavy metals, PAH and microplastics were also found in the road side suspended solid materials and in road dust (Müller et al., 2020). They also get pulverised between the tyre and pavement due to moving heavy vehicles that gets dispersed and acts as the non-point source of TSS pollution. Microplastics are also originated from the pavement material bitumen, and the paint used for road making (Horton et al., 2017). Moreover, the degree of abrasion is more for concrete pavement than bitumen-asphalt pavement resulting in higher concentration of heavy metals in road dust. The contribution of pollutants from traffic sources, the presence of type of vehicle composition (for instance, passenger car, trucks, buses, etc.), traffic density, hourly traffic volume, traffic behaviour (such as speeding and braking requirements), and pavement type needs to be considered as they play a vital role in defining the pollutant load of urban stormwater runoff. The flushing of the pavement surfaces, road side barriers, kerbs, delineators, and signage by rainfall takes along the contaminants from their surfaces which were deposited there during the dry season/ or spell of no rainfall. The roads having more braking, acceleration, deceleration contributed more heavy metal concentration along the road as compared to the other locations having similar traffic volume (Huber et al., 2016).

Hence, the stormwater runoff gets contaminated from the pollutants originating from the operation of vehicles, re-fuelling, traffic volume and its intensity; pollutants originating from exhaust, its maintenance; wear and tear of its components, etc. Thus, urban stormwater contamination can be reduced by switching to other alternate fuel, reducing the unnecessary trips, and using the materials pavement and vehicle that will help in reducing the pollutant concentration.

2.4.2.2 Industrial activities

Pollutants are emitted from the various industrial activities involved in production and manufacturing; vehicular movement for supply chain management, open storage units, etc. The pollutants from the industrial area are released in all the compartments of earth. Pollutants released into the air, comes to earth’s surface as dry deposition under the gravity or as wet deposition as a result of downpour. The washing of pollutant deposited over the ground surface, trees, road services, sheds, etc. remains either in suspension or in dissolved form in the stormwater runoff (Müller et al., 2020). The contribution of pollutant originating from the industry depends upon the type of industry, technology involved and its associated activity. Studies have reported the presence of heavy metals such as Pb, Cr, Cu, Hg, Cd, and Zn as high as 3223, 398, 2223, 24, 41 and 10083 ppb, respectively originating from auto salvage and scrap recycling yard (Line et al., 1996). The dust from cement manufacturing industries results in release of NO_x, SO_2, VOCs, mercury, toxic dioxins, furans and PCBs. The poor handling of raw material as well as finished products and improper management for their storage in open spaces can also contribute to stormwater runoff contamination. The storage of industrial raw materials in open spaces releases chemicals which gets mixed with stormwater runoff. In addition, the wastewater treatment facilities, their management, improper handling/ storage of sludge in open spaces, and their washing by rainfall can also contribute to stormwater runoff pollution. Moreover, the pollutants originating from the raw materials, clinker, pulverisation, and storage and handling gets deposited on the nearby land, tree leaves, and over buildings thus acting as another source of contaminating the stormwater runoff (Mohamad et al., 2021). Literature have reported the majority of the pollutants originating from vehicle movement, vehicle service area, and their parking facilities.

2.4.2.3 Construction activities

Construction practices vary from construction of small dwelling units to development of infrastructures like massive dams and never-ending roads. The activities involved during the construction phase such as cleaning, grading, stock piling near the site and excavation is known to produce dust, sand, and silt which when comes in contact with the stormwater, becomes resuspended and mobilises towards the drain and receiving water bodies. These resuspended silt and sand from the construction site carries along the organic matter, metals, oil and grease, nutrients, and bacteria, which mixes with the sewer system and finally discharged into the river or nearby receiving water body. The disposal of pollutants into the water body is toxic to aquatic ecosystem thus harming the aquatic life (Bang et al., 2020). During the construction phase, the natural vegetation canopy is stripped and the ground stabilising material is removed that increases the runoff volume, and carries along the soil because of erosion and scouring, contributing it to receiving water body. The intensity of rainfall, land use, gradient and slope of the land, type of soil, soil properties, etc. are the primary driver of the soil erosion (Gholami et al., 2021). In one of the studies carried out by Reed (1980), before and after road construction phase revealed that the sediment loads increased upto four folds in the stormwater runoff as compared to non-construction phase even if the soil erosion prevention measures were implemented on site. TSS and turbidity are the most documented parameter in stormwater water runoff originating majorly from the construction site all over the globe. In a study conducted by Pipil et al., (2022b), the construction activity taking place for the development of new infrastructure under the Central Vista Project in New Delhi, India has reported high TSS in stormwater runoff when compared to the runoff sample collected from other land use such as residential, industrial and institutional area.

2.4.2.4 Drain overflow

Modern cities are developed concerning the future expansion and scope for its inhabitants. Few cities have developed advanced sewage systems for the conveyance of the grey water whereas few other cities in developing nations rely on the conventional sewage system earlier designed to serve for lesser population. India being a developing nation has unauthorised settlements in the form of slums, colonies, clusters, etc. which is a home to a large population. The stormwater runoff commencing from these unauthorised localities contributes to total suspended solids (TSS), BOD_5, and faecal coliform as these areas does not have sanitation and lack properly laid underground sewage network (Jamwal et al., 2008). They rely upon the open sewage systems which when receives high intensity rainfall, has the tendency to overflow and mixes with the stormwater runoff causing its contamination.

2.4.2.5 Gardening and agricultural

India is a large country that has 3/4 of its population directly or indirectly dependent on agricultural activities and has a significant contribution (≈ 20%) in its gross domestic production (GDP) (Ministry of Agriculture & Farmers Welfare, 2022). The extent of agricultural activity and the production of stormwater runoff in a developing country like India can be understood. Residents around their dwelling in urban areas prefer to have some sort of gardening area maintained by them. Town planners also as a part of town aesthetics and ecological point of view, prefer to provide the green belt and open spaces for recreational activities, to preserve nature, and agricultural activities, etc. In the outskirts of the city, green belts are provided which surrounds the urban area and is being used for agricultural activities to fulfil the demand and need of the urban population. These areas are generally applied with the nutrients such as phosphate and nitrates in order to help plants and crops to grow more effectively and to also enhance the agricultural yield. Phosphates are considered as the critical pollutant that causes excessive nutrient loading of water bodies leading to eutrophication (Yadav et al., 2015; Haritash et al., 2017). The gardening and agricultural activities such as cutting, pruning, chipping, cropping of leaves and branches produces the organic waste that also contains the nutrients P and N, which might get deposited on the ground or nearby area and comes in contact with the stormwater runoff leading to deterioration of its quality.

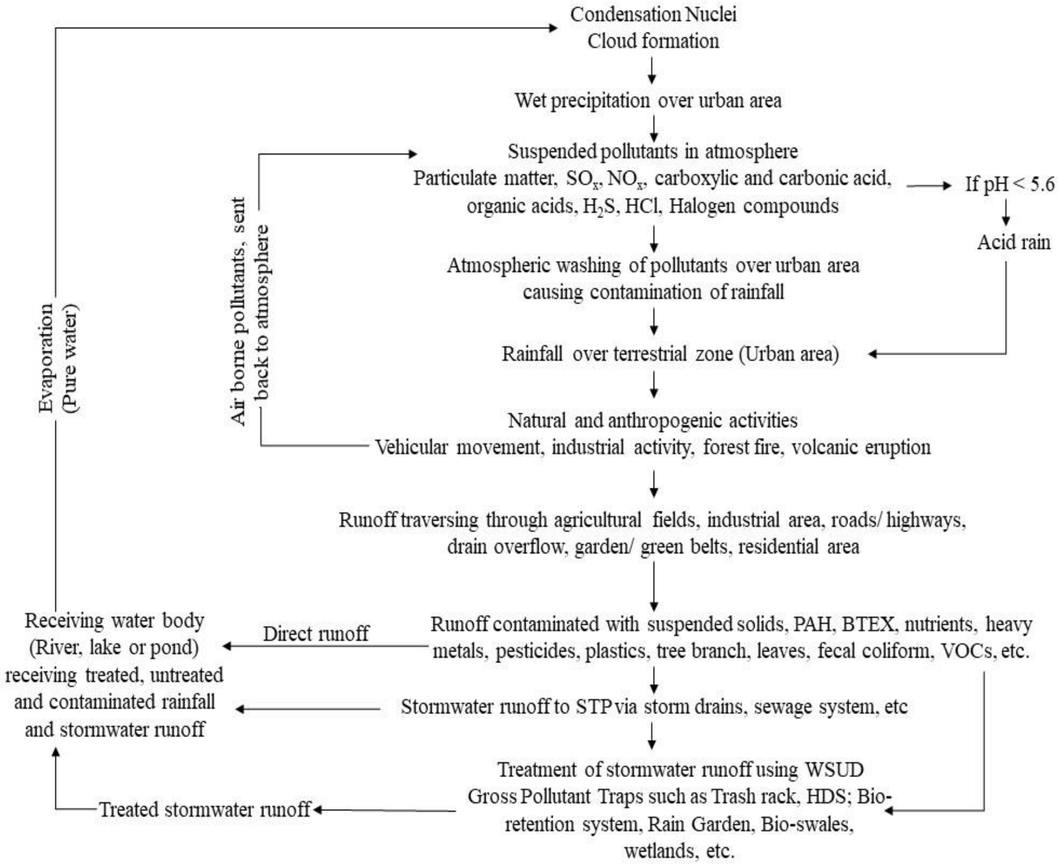

Fig. 2.4 Flow process of rainfall and stormwater runoff contamination, treatment techniques of stormwater runoff and re-introduction of treated water into atmosphere through evaporation

Once the infiltration capacity of the gardening area and agricultural field is fulfilled, the rainwater in excess become stormwater runoff that carry along the suspended solids, nutrients applied to the field (dominated by nitrogen and phosphate), and other organic matter present in the field (Malmqvist, 1983). Furthermore, pesticides, weedicides, and insecticides are being used tremendously in agricultural field to prevent pests, weeds and insects, respectively. These have the potential to degrade the quality of the stormwater runoff originating from gardening and agricultural practices (Bollmann et al., 2014). Pesticides such as organophosphates, organchlorines including diazinon, bifenthrin, chlordane, DDT (dichlorodiphenyltrichloroethane), DDD (dichlorodiphenyldichloroethane), and DDE (dichlorodiphenyldichloroethylene), and chlorpyrifos have been reported in the surface runoff originating from the fields (Mangiafico et al., 2009; Samuel et al., 2012; Yadav et al., 2023). A summary of contamination of rainwater and stormwater runoff through different polluting agencies has been described in Fig. 2.4.

2.5 Watershed Management

The urban population is increasing everyday which is enhancing the urbanisation all over the globe. This impacts both human beings and the limited water resources in urban area, thus requiring the management of urban stormwater runoff and natural drains in watershed (Fletcher et al., 2013). As a consequence of increasing population and expansion of urbanisation, the urban drainage and urban water cycle has changed over the last few decades. For the management of water resources and to fulfil the need of ever-growing urban population from the existing resources, few new techniques have been evolved in the last few decades across the globe for watershed management which include: Low Impact Development (LID), Water Sensitive Urban Design (WSUD), Integrated Urban Water Management (IUWM), Sustainable Urban Drainage System (SUDS), Best Management Practices (BMP), and Green Infrastructure (GI).

2.5.1 Low Impact Development (LID)

Low impact development was first introduced in USA by Barlow in year 1977 meant for land use planning and being popularly used in USA and New Zealand (Barlow et al., 1977). While conventional methods aim at intercepting and routing the stormwater runoff out of the catchment through a conveyance system of stormwater drains, LID focuses on keeping the stormwater runoff within the watershed and improve its water quality through various techniques (Davis, 2005). Low impact development tries to reduce the cost and minimise efforts towards stormwater management as a result of urban development over the watershed. It emphasises on use of natural hydrology of catchment during the pre-development phase of urban area (Fletcher et al., 2015). Earlier, the conventional stormwater management practices were focused on peak flow reduction to avoid flooding rather than improving the quality of stormwater runoff. It was achieved by re-routing the flow towards the natural drains or towards municipal facilities such as gutter and pipes. This conventional approach is still practiced in various urban areas around the globe. However, this approach to remove the stormwater runoff from urban catchment area has the drawback that it mixes along suspended as well as dissolved impurities and leads to contamination and pollution of downstream receiving waterbody (USEPA, 2000). The conventional system only prevents flooding and does not take into account of infiltration, groundwater recharge and treatment of stormwater runoff through its quality improvement. LID is implemented in such a way that stormwater runoff characteristics post-development does not vary significantly from the pre-development characteristics of the catchment. It takes into account the natural stormwater runoff, infiltration and evapotranspiration (USEPA, 2000). The main objective of LID is to reduce the stormwater runoff and increase the infiltration, groundwater recharge, stream protection and improved quality of water through pollutant removal techniques and mechanisms such as filtration, adsorption, absorption, detention, evapotranspiration, infiltration and biological processes like phytoremediation (Hunt et al., 2010). LID is known to have structural and non-structural small scale decentralised stormwater treatment techniques. Structural techniques which include, but not limited to bio-retention system, infiltration galleries, wetlands, permeable pavement, vegetated strips, swales and green roofs in order to achieve its goals. Non-structural LID techniques include increased preservation of catchment area to its natural feature with minimal changes, reduction of impervious surfaces, introduction of native plant species, etc (Ahiablame et al., 2012). Such LID techniques have been applied in developed nations such as New Zealand, Australia, Unites States of America, Canada, etc.

2.5.2 Water Sensitive Urban Design (WSUD)

The term water sensitive urban design (WSUD) came into existence in 1990s in Australia (Mouritz, 1992). Soon after, Western Australia released its report for guidelines (Whelans et al., 1994) and was later published in a book by Argue (2004) which included the basic concept, design, and techniques or WSUD. It works on the principle of capturing, diverting and retaining the stormwater runoff for its treatment in order to reduce the hydrological impact of urban development. WSUD techniques include infiltration systems, bio-retention system, vegetated swales, sand filters, permeable pavements, constructed wetlands, vegetated strips and rainwater tanks (Pipil et al., 2022a). Infiltration system is meant for infiltrating the stormwater runoff into the soil either directly or through the system of underlying drain having perforated drain pipes. The infiltration system is provided with filter media at top consisting of gravels of different gradations (Siriwardene et al., 2007). They provide temporary storage such that it attenuates the peak flood flow and reduces the stormwater runoff volume. However, the filtration technique is susceptible to get clogged which can be reduced by using pre-treatment units to prevent the entry of TSS into the infiltration system. Infiltration unit associated with loam and macrophytes is termed as bio-retention system in which filtration, adsorption, ion exchange and microbial decomposition takes place (Younos, 2011). Again, the purpose of such techniques is to reduce the stormwater runoff peak flow, reduction in stormwater runoff volume, promoting ground water recharge along with treatment of stormwater runoff. Bio-retention systems can effectively remove suspended sediments, nutrient, and heavy metals. Another WSUD techniques known as swales, vegetated swales or bio-swales, runs longitudinally along the roads, green land or industrial parks. It is a shallow drainage trench with sloping sides, filter media and vegetation used to reduce stormwater runoff peak and volume, suspended solids removal and treatment of runoff.

2.5.3 Integrated Urban Water Management (IUWM)

The conventional water service provisions and paradigm had unfortunate economic and environmental impacts, which are not restricted to damage to aquatic habitat, modification of ecosystem, waste disposal into streams, damage to native vegetation, unwanted loading of contaminants and nutrients leading to degraded quality of stream and coastal water. This requires high cost for repairing the damage and modification of conventional water systems which has reached end of its functional life (Mitchell, 2006). The authorities have developed water resources to meet the increasing urban water demand. However, due to limited water resources in urban area, the increase in supply of water comes across the constraints along with risk of climate change and decreased yield from the catchment (Marsalek et al., 2001). In order to overcome the shortcomings, Integrated Urban Water Management incorporate comprehensive role and interaction of various institutions involved as component in management of the water supply, groundwater, wastewater and stormwater (Fletcher et al., 2007). The word IUWM was first come into existence in 1990s and then onwards began discussing on new approaches of urban water management. It considers all the requirement of water for ecological use and human beings, originating from natural, constructed, surface and sub-surface water system considering them as an integrated system (Mitchell, 2006). The tools and techniques that are applied to IUWM include water conservation, urban land-use planning, urban landscaping, water sensitive planning, usage of roof runoff, stormwater runoff, greywater; stormwater and greywater pollution prevention; and non-conventional methods including education, pricing, and policy implementation.

2.5.4 Sustainable Urban Drainage System (SUDS)

Sustainable urban drainage system (SUDS) was initiated in Europe during 1990s, especially in Scotland as a parallel technique for LID and WSUD (Fletcher et al., 2015). The set of guideline documents and design manuals were published which included the term SUSD (CIRIA, 2000). SUSD uses techniques to drain stormwater runoff which are said to be more sustainable than conventional methods. It tries to replicate the natural and pre-development drainage. They try to mimic natural water cycle using retention basins, permeable surfaces, infiltration trenches, swales, water harvesting; and transpiration in wetlands of stormwater runoff (Elliott and Trowsdale, 2007). These units can be used individually or in combination of different series using different units. SUDS incorporate the role of both the structural and non-structural methods while it also makes use of centralised and decentralised techniques to combat point source and non-point source of pollution, respectively (Mitchell, 2005). SUDS employs structural devices includes wetlands and swales, while non-structural measures include educating people through knowledge, training, policies and laws; and using decentralised vegetations. Making use of pervious pavement and infiltration trenches, the runoff peak flow can be attenuated and can improve the water quality parameters along with providing the provision of recreational amenities in urban locality (Jayasuriya et al., 2007; Zhou et al., 2012). It also helps in reducing the risk of flooding by providing storage during the extreme rainfall when retention basins such as swales and filtration basins are employed (Stewart and Hytiris, 2008). The shortcomings of these techniques were also underlined that the stormwater infiltration trench is susceptible to get clogged easily due to sand and silt in much shorter time of life spam (Bergman et al., 2011). Geological and spatial limitations are also associated with soil erosion and water pollution in the catchment. It was found that increased hydraulic loading can reduce the effective working of SUDS units and reduction of flood volume is limited (Holman-Dodds et al., 2003; Nascimento et al., 1999).

2.5.5 Best Management Practices (BMP)

Initially, best management practices were being widely used to address water quality issues and hydrology related issues in urban and agricultural areas specifically in United States of America and Canada. In terms of urban drainage systems, BMP were applied for the management of wastewater drainage and treatment, and implementation of operator training and education, and maintenance of the structures. Nowadays, BMP have evolved into measures to prevent and reduce pollution by construction of engineered structures and preventing the impact of agricultural runoff caused due to application of pesticides and chemical fertilizers (Fletcher et al., 2015).

2.5.6 Green Infrastructure (GI)

The term green infrastructure (GI) originated in USA during 1990s which not only emphasize on stormwater runoff treatment but also take into consideration of both landscape architecture and landscape ecology (Benedict and McMahon, 2006). As the name suggests, this method makes maximum utilisation of green spaces and ecology of the catchment which is achieved through urban planning and layout of infrastructures. GI thus makes use of green roofs, permeable pavement, rain gardens, urban parks, raingarden, bioswales, wetlands and urban forests, etc. such that these techniques are aimed to capture and infiltrate the stormwater which ultimately help in reducing the stormwater runoff volume along with flood mitigation and improving the air quality (Fletcher et al., 2015). GI uses the soil and vegetative green cover for stormwater runoff management. The term BMP and LID is often used invariably and synonymous with GI for stormwater runoff and its management in any catchment area. GI is also being implemented by government and agencies which are responsible for stormwater management in the catchment through policy implementation that not only control stormwater runoff but is also beneficial to the humans, mitigating the climate change, providing recreational activities opportunity, along with improving the habitat and ecology (Tzoulas et al., 2007).

2.6 Characterisation of rainwater and stormwater

The growing demand of water for public supplies is becoming greater every day as compared to water reserve available. The quality of water in lakes, ponds, rivers, and streams are deteriorating rendering them unfit for use. This causes shortage in demand and supply. While on the other hand, rainwater is one of the purest forms of water which can be available to many of us, however, rainwater also gets contaminated dure to pollutants suspended in atmosphere, and hence, due to their atmospheric washing. Rainwater characterisation helps in understanding the source origin and relative contribution of soluble chemical species present in atmosphere (Kulshrestha et al., 2003). For instance, the tail pipe emission from roadways, railways, air and sea transport has been reported to be responsible for acid rain. Atmospheric washing by rainfall governs the sedimentation, chemistry, and biogeochemistry of aquatic ecosystem (Lawlor et al., 2003, Kieber et al., 2002). Local sources (natural as well as anthropogenic) influence the physico-chemical properties of precipitation (Brimblecombe, 1996). Around 40% of the Dissolved organic carbon (DOC) in rainwater is resistant to bacterial degradation, thus tend to travel long-distance (Wiley et al., 2000). In an urban environment, anthropogenic sources such as traffic, construction activities, industrial activities, waste generation has resulted in the emission of metals. The presence of organically complex metals like Cu, Cd, Ni, Zn, Pb, and Co in urban rainwater. These metals tend to persist and accumulate in the environment (Wong et al., 2006). A study reported the dominance of Al and Fe of crustal origin whereas enrichment factor revealed the moderate presence of As, Mn, Zn, Ni, Mo, Cr, Sn and Pb (Orlović-Leko et al., 2020). The EF value was higher in case of Cd, Cu and Sb, indicating anthropogenic origin. Since, rainwater is not contamination-free, and consist of various impurities mixed in it, including nutrients, oil and grease, organic compounds, particulate matter etc, the stormwater pollutants of natural and anthropogenic origin contribute to non-point source pollution. This runoff discharged into a local receiving waterbody degrades the health of aquatic ecosystem and pose threat to life (Pamuru et al., 2022). A study reported the presence of nutrients (N and P) in the rainfall, originating from the washing of terrestrial surfaces, further accumulates downstream and leads to eutrophication (US EPA, 2016). Although some heavy metals like Cu and Zn are not that lethal to human health, however are found toxic for aquatic life (Sakson et al., 2018). The stormwater composition is highly variable and depends on type of land use such as the drainage area, commercial, industrial or residential spaces. The variability and characterisation of stormwater are evaluated to determine the type of treatment or the feasibility of stormwater harvesting system required to achieve the water quality criteria of a certain place.

2.7 Treatment of stormwater runoff

Urban areas generally have impervious surfaces which leads to deposition of pollutants during dry period when no rainfall occurs. Imperious surfaces such as roads, parking area, roof tops have high coefficient of runoff leading to high stormwater runoff volume which mixes the contaminants from dry depositions, thus deteriorating the quality of stormwater runoff (US EPA, 2003). The stormwater runoff is a major source of water in urban areas which receives relatively more rainfall (Poustie et al., 2015). Also, due to limited supply of water from freshwater resources, there has been an increase in finding the alternatives to utilise stormwater runoff as a source of water supply in urban areas where this water can be used for non-potable use such as recreational activity, gardening, and irrigation (Lau et al., 2017). However, stormwater runoff mixes contaminants from non-point sources of pollution which poses its treatment challenge. Stormwater runoff has highly variable concentration of pollutants that ranges from suspended solids and nutrients to heavy metals which needs to be removed before it can be further used in urban areas (Poustie et al., 2015; Roy-Poirier et al., 2010). These pollutants in stormwater runoff are of major concern due to their toxicity, accumulation in environment, and non-biodegradability. Phosphates are the major pollutant in stormwater runoff which typically originates from fertilizers, atmospheric deposition, soil erosion, animal waste, and detergents (US EPA, 2003). Total phosphate in stormwater runoff may range from 0.08 mg/L to 17.9 mg/L (Koryto et al., 2018). The stormwater runoff thus, requires its treatment through filtration, absorption, adsorption, and ion exchange before it can be utilized in urban areas. The various methods and techniques for stormwater runoff treatment as discussed below.

2.7.1 Filtration/ Filter media

Filtration process using various filter media has been used for the treatment of stormwater runoff. Various filter media employed for this process includes zeolites, biochar, fly ash, iron filings, calcite, sand, etc. (Schifman et al., 2016). The various combinations of filter media for pollutants removal have been incorporated which includes layers and mixed combination of filter media. The removal efficiency by the filter media also depends upon the physical properties and hydraulic conductivity of filter, the type of filter media, and the concentration of the pollutant in stormwater runoff. Studies shows that heavy metals removal from stormwater runoff was upto 100 % for cadmium, copper, zinc and lead while using calcite, zeolite, and iron filings as the filter media (Reddy et al., 2014). Gravels and multi-layer filters are efficient in removal of suspended solids and particulate associated pollutants with consistent removal efficiency even with reduced hydraulic conductivity (Hatt et al., 2006). At the end of the treatment when the filter media gets exhausted from accumulation of pollutant, it requires periodic replacement of filter media with time leading to enhanced cost of maintenance and operation (Weiss et al., 2008).

2.7.2 Ion exchange

Ion exchange is a technique in which the ions between two electrolytes are exchanged. It is a process of purification and separation in an aqueous medium which are generally known as ion exchange resins, zeolites, or soil humus. The ion exchangers either exchange its positively charged cation or exchange negatively charged anion with the cationic or anionic species present in aqueous medium, respectively (Kansara et al., 2016). Ion exchange is generally present in resins through which the water to be treated is allowed to pass until it is saturated or exhausted, which means water coming out of the ion exchange system contains the ionic impurities in more than the desired level. The resins are then regenerated by process called backwashing to recharge the resins. Due to its capability and beneficial uses, ion exchange can be used for treatment of stormwater runoff (Zhang et al., 2023). The combination of ion exchange with constructed wetlands forms a hybrid bioretention system for the treatment of non-point stormwater runoff treatment. A study reported that nitrogen removal efficiency increased by 50 % when zeolites were incorporated as compared to CW cell without zeolites (Wen et al., 2012). Also, studies suggests that for columns of zeolites for stormwater runoff treatment, the removal efficiency of pollutants increases with the use of zeolites as compared to columns without zeolites. A study reported enhanced removal of NH_4^+ ions in column study while NH_4^+ ions were exchanged with Na^+, however, the salinity of the effluent increased due do exchange of ammonium ions with sodium ions (Jiang et al., 2019).

2.7.3 Adsorption

To increase the effectiveness of urban stormwater treatment methods, various adsorbents have been investigated for removal of runoff pollutants like nutrients, toxic heavy metals, synthetic organic pollutants (SOPs), sediments, etc (Deng, 2020). Low-cost adsorbents such as Biochar, fly ash, Zeolites, Sawdust, Scrap tires, iron filings, and water treatment residual (WTR) have gained attention because of their availability, affordability, cost-effectiveness. For instance, fly ash from coal combustion has been found effective in immobilizing heavy metals and phosphorus in stormwater (Genc Fuhrman et al., 2007; Zhang et al., 2008). Studies have reported the usefulness of incorporation of biochar into stormwater filtration systems. Biochar was found effective towards removal of numerous pollutants such as nitrogen and phosphates, trace organic contaminants, heavy metals Pb and Zn, polycyclic aromatic hydrocarbons (PAHs), and pathogenic indicators like *E. coli* (Mohanty and Boehm, 2014; Ulrich et al., 2015). Similarly, studies on used tyres have been extensively done as a viable sorbent for mitigating water pollutants since it can efficiently bind certain toxic metals, and various forms of nitrogen species in stormwater (Semerjian, 2010; Björklund and Li, 2015). Correspondingly, iron filings, derived from the grinding or milling of finished iron products, demonstrated excellent capability in capturing different metals and phosphate in stormwater (Erickson et al., 2012). Nevertheless, a single low-cost adsorbent is often inefficient to effectively adsorb all the pollutants. To increase the efficiency of adsorbents towards adhering and treating more contaminants, surface modification approach has been assessed in previous studies (Deng et al., 2020). For instance, impregnating aluminium hydroxide into biochar improved the sorption of arsenate in stormwater (Liu et al., 2019). Likewise, nano zero-valent iron integration with oak sawdust-derived biochar significantly enhanced the reduction of nitrobenzene (Wei et al., 2019). In another study, fixing zero-valent iron onto bentonite-fly ash pellets helped in the removal of Cd and Pb from water (Mwamulima et al., 2018). This approach thus enables the production of tailored adsorbents to meet specific stormwater treatment objectives. Thus, by combining adsorption with other treatment technologies can further enhanced the pollutant removal.

2.8 Water sensitive urban design (WSUD)

The stormwater runoff cannot be treated at the source from where it is originating, such as building, roods, highways, residential areas, due to limited availability of space. In earlier days, stormwater runoff was considered to be wastewater and limited emphasis was given towards its treatment and reusability (Ekka et al., 2021). Stormwater runoff was removed from the urban area as soon as possible through a network of stormwater drains. The stormwater gets contaminated as it traverses its path over various impervious surfaces from different land-use originating from non-point source. However, various stormwater treatment techniques have been employed for watershed management. Depending upon the function performed, the various WSUD treatment units can be classified as primary, secondary or tertiary as discussed below (Pipil et al., 2022a). Table 2.2 summarises the various functions performed by WDSU.

Table 2.2 The comparative functions performed by different WSUD techniques

WSUD Technique	**Various functions performed**				
	Flow Rate Reduction	Water Quality Management	Flood Management	Rainwater Harvesting	Biodiversity Improvement
Gross Pollutant Trap		✓			
Trash Rack		✓			
Swales	✓	✓	✓	✓	✓
Raingarden	✓	✓		✓	✓
Wetlands	✓	✓	✓	✓	✓

The pollutant load of stormwater can be significantly reduced in urban areas by adopting the techniques popularly known as water sensitive urban design (WSUD) in different configurations including gross pollutant trap (GPT), bioretention basins, bio-swales, raingarden and wetlands. These techniques can be adopted in urban areas in the developing country in order to bridge the demand and supply gap, and also to prevent the wastage of stormwater runoff as it meets natural drains.

2.9 Configuration of WSUD

2.9.1 Gross Pollutant Trap (GPT)

The visible and tangible solid arising from the urban environment has been termed as trash, debris, flotsam, jetsam, floatable, gross pollutants, rubbish or solid waste which composes the urban litter and becomes an integral part of the stormwater runoff thus possess threat to human health and ecology (Armitage, 2007). As stormwater runoff traverses its path along the urban area, it keeps the urban pollutant floating or as bed load in conveyance system. Such pollutant loads are not only aesthetically unattractive but are also devastating to the natural equilibrium and ecology of urban area, and thus significantly reduces the hydraulic performance of urban conveyance system (Ghani et al., 2011). Moreover, when these floating and suspended pollutants in stormwater runoff merge with natural waterways, becomes a threat to aquatic life as fishes can get entangled, suffocates, or ingest the litter while searching for food. Occurrence of toxins can interfere with terrestrial ecosystem, thus leading to imbalanced food chain (Wilson et al., 2009).

Hence, GPT is an engineered trap system designed to remove suspended as well as floating impurities from the stormwater runoff. They are installed on the existing conveyance system with an object to prevent the entry of floating and suspended impurities into the next treatment unit. Hence, they carry out the purpose of a pre-treatment unit (Pipil et al., 2022a). GPTs involves the mechanism of interception and retention of solids present in stormwater runoff. Their design demands the careful study of local hydrological processes, catchment area, pollutant load, size of conveyance system, and depends particularly on the cost of its operation and construction. With proper designing they have been reported to remove nutrients, trace metals, bacteria, and dissolved oxygen demanding pollutants (Wong and Walker, 2001). Many of the developed countries have adopted this technique for the improvement of quality of stormwater runoff with different configurations.

Table 2.3 Type of GPT configuration and removal of pollutant load from stormwater runoff at various locations

Type of GPT configuration	Country	Removal of pollutant	Reference
Hydrodynamic Deflective Separation (HDS)	Malaysia	Plastic, paper, vegetation, sediments	Sidek et al., 2016
Catch Basin Insert	Australia	Vegetation, plastic, newspaper, cardboard, food and drink package, cans, clothes, etc.	Alam et al., 2017
Gross Pollutant Trap with bioretention	Sweden	100–300 µm sized rubber, bitumen, and microplastics	Lange et al., 2021
Gross Pollutant Trap with bioretention and sand filter	Sweden	20–100 µm sized microplastics	Lange et al., 2022a
Gross Pollutant Trap followed by bioretention system	Sweden	Efficient removal of Pb (>76%), Cu (79%), and Zn (94%) when GTP and bioretention treatment train was used	Lange et al., 2022b
Gross Pollutant Trap	Australia	TSS, TN and TP removal	Nichols and Lucke, 2016
Gross Pollutant Trap	Malaysia	Floatable litter load	Asfi et al., 2023
Continuous Deflective Separation (CDS) Gross Pollutant Trap	Australia	TSS, TP, TN	Walker et al., 1999

The studies related to GPT are very limited which have reported the removal of suspended as well as floating impurities, however, Table 2.3 provides the summary of GPT configuration used for improving the quality of stormwater runoff in different locations around the globe. The various configurations of GPT are the one provided with baffle walls, trash rack, and hydrodynamic deflective separation (HDS) as discussed below.

2.9.2 Trash Rack

It is a type of GPT in which coarse metal screens facing towards the flow of storm water runoff are provided. The screens are made of parallel vertical metal bars with design specific centre-to-centre spacing. It can also be provided with a built-in trash collection unit (Fig. 2.5). It physically removes the floating anthropogenic impurities/ litter like plastics, bottles, paper, newspapers, etc. since, the clear opening between the screens are kept smaller than the trash in storm water runoff, and thus, prevents them from further entering and going downstream into the treatment system. Hence, they are recommended in high litter area and it results in storm water quality management (Hoban, 2018).

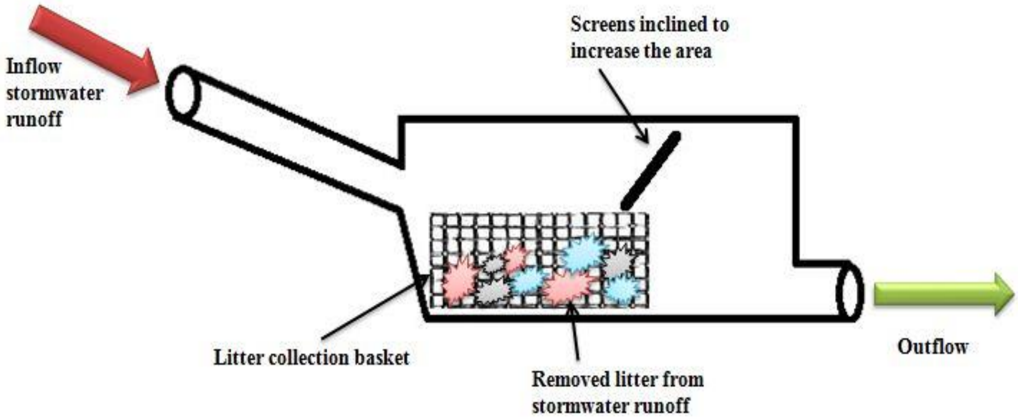

Fig. 2.5 Sectional view of a trash rack

2.9.3 Hydrodynamic deflective separation (HDS)

Hydrodynamic Deflective Separation (HDS) is another type of GPT, used to separate out the sediments, debris and litter from the storm water runoff through its continuously deflecting system. The incoming storm water runoff is allowed to pass through a system of screens provided at the centre of HDS to separate out the debris and litters, and it is collected at the sump at the centre from where it is removed later on. The incoming storm water runoff is acted upon by the centrifugal force, making a vortex, and treated storm water runoff exits the outlet (Hoban, 2018).

Hence, GPT can prevent a significant portion of impurities to enter the downstream treatment units such as wetlands. They do not increase the water level in upstream side as they do not block the flow of storm water runoff. However, it cannot remove the sediments having diameter smaller than 5mm. When it reaches the maximum capacity, the trapped debris can be remobilized. Poor maintenance reduces the working efficiency of the trap system and it can increase the pollutant such as phosphorus, nitrogen, COD and TSS in downstream side (Walker et al., 1999). They are usually unattractive and can cause odour problem due to poor maintenance that leads to decomposition of the wet organic litter and anaerobic conditions (Abood and Riley, 1997). Its performance depends upon rainfall and runoff characteristics. It can also cause health hazards to the workers handling the waste. In order to prevent these limitations, it is recommended to clean the GPT fortnightly or after 10mm downpour (Hunter, 2001).

2.9.4 Bioretention system

Bioretention system are also known as bio-filtration system comprising of media substrate made up of sand, gravel, slag, loam, etc. which is planted with suitable plant species. The stormwater runoff is treated through them via various processes such as filtration, infiltration, adsorption, ion exchange, and microbial degradation (Younos, 2011). Bioretention system such as bioswales, raingardens, and wetlands reduce the stormwater peak flow through volume attenuation, removes pollutants from stormwater runoff and recharge groundwater. Besides, the bioretention system also ameliorates the aesthetics of the urban area. Bioretention system are effective in removal of suspended sediments, heavy metals, and nutrients like phosphates and nitrates from stormwater runoff (Davis et al., 2006). In a bench-scale bioretention system, upto 96% of the phosphate was removed from stormwater runoff in India (Pipil et al., 2023). In another study conducted by Henderson et al., (2007) bioretention system removed 63 to 77% of nitrogen and 85 to 94% of phosphorus using vegetated column incorporated with varying substrate types (gravel, sand, loam). Another study conducted by Wadzuk et al., (2019) in USA in which five soil types: sandy loam, loamy sand, loam, silt loam, and clay loam was used to study nutrient removal through Lysimeters. The average total phosphate removal varied between 77 to 90.1% by this system. Another study conducted in Australia made use of large-scale column biofilter for stormwater treatment towards removal of N, P and TSS and reported removal of order 70%, 85% and 95%, respectively (Bratieres et al., 2008). The filter media, depth of filter, selection of plant species, filter area and influent pollutant concentration was varied. Bench-scale bioretention system with substrate depth of 25 cm was used to study its efficiency towards removal of heavy metals from stormwater runoff which exhibited upto 90% removal of Zn, Cu, Pd and Cd (Sun and Davis 2007). A study conducted by Du et al., (2021) in China showed average reduction of TSS, TN, and TP of order 20.8%–93.3%, 11.6%–54.8%, and 9.8%–47.3%, respectively, from stormwater runoff. Chisholm (2008) showed around 43%, 70%, 64%, and 87% reduction in Cu, Pb, Zn, and Phosphorus, respectively, in the bioretention system. Zhang et al., (2011) observed that plant species can remove 59 to 83% and 28 to 71% of N and P, respectively and suggested that the removal efficiency of pollutants in a bioretention system largely depends upon the substrate composition, type of vegetation, and symbiotic relationship with bacteria. Table 2.4 summarises the various studies conducted previously at various locations around the globe using various bioretention system for pollutant removal from stormwater runoff.

2.9.4.1 Bioswales

The stormwater runoff originating from roads and highways can be treated with one of the oldest and commonly implemented *in-situ* stormwater technique known as swales (Fig. 2.6). Swales are also popularly known as bioswales, vegetated swales, grassed swales, bio-filters, and filter strips (Ahiablame et al., 2012).

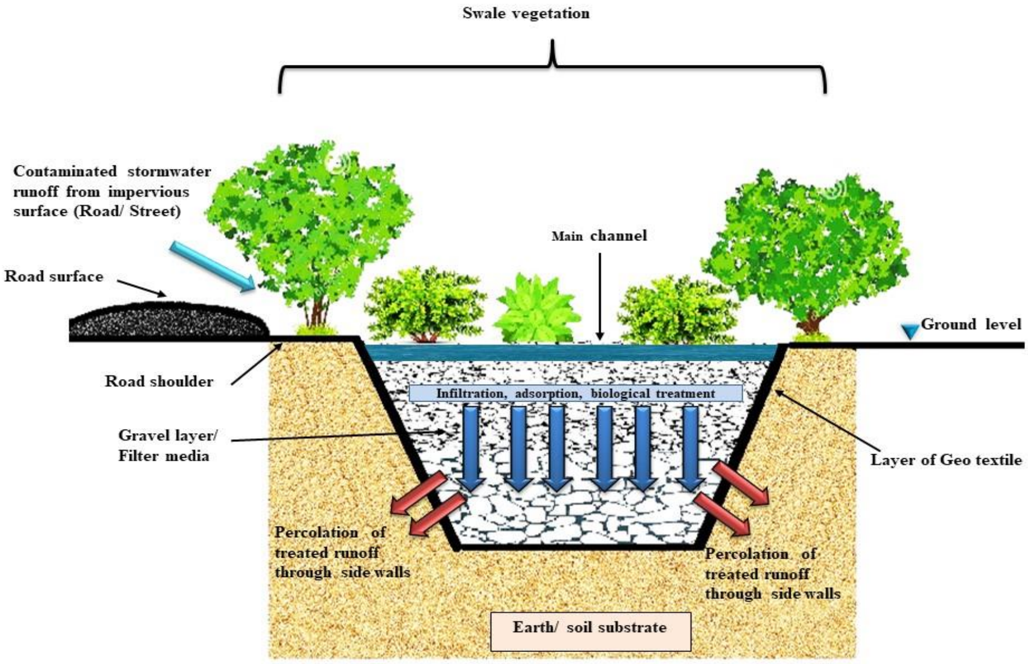

Fig. 2.6 Cross sectional view of a typical bioswale used to treat stormwater runoff originating from road/ highways

It is a technique for removal of pollutants, improving stormwater runoff quality, flow volume reduction, and it is a step towards making the urban cities more resilient. It involves a number of processes such as infiltration, filtration, sedimentation, and biological processes through which it treats stormwater runoff (Stagge et al., 2012). The swales consist of trenches which are provided with engineered media for infiltration of stormwater runoff and macrophytes for the improved removal efficiency of sediments, nutrients, and heavy metals removal. The macrophytes or vegetations provided are native to the location such that it can survive during dry season and helps in landscaping. It thus, helps in enhancing the urban biodiversity. Swales are effective stormwater techniques since they can effectively treat stormwater runoff for different seasons. The stormwater treatment efficiency of swales largely depends upon the healthy vegetations (Mazer and Ewing 2001). In a study conducted by Backstrom (2003) in Sweden, swale removed 70% of TSS from stormwater runoff. Stagge (2006a) conducted a study in USA and observed that swales can remove upto 90%, 45%, 38% and 80% of TSS, TN, TP and Zn, respectively. In another study conducted by Stagge (2006b) in USA, TSS and Zn removal varied between 65 to 71% and 30 to 60%, respectively. It was also observed that swales can reduce peak flow by 53% with peak flow delay of 34 minutes and flow volume reduction upto 54% (Stagge 2006a). Yu et al., (2001) suggested the maximum length of swales to be 75 m with 3% bed slope. However, another study conducted in USA suggested a bed length of 30 m, width 0.6 m with slope varying between 0.5 to 6% (Mazer and Ewing, 2001). Similarly, Deletic and Fletcher (2006) conducted study in Australia with a 65 m long swale at longitudinal slope of 1.6% and observed that average TSS, TN and TP removal rate was of order 69%, 56% and 46%, respectively. In another study conducted by Fletcher et al., (2002) in Australia, average pollutant removal varied between 57 to 88%, 40 to 72%, and 12 to 67%, respectively for TSS, TN and TP. In a study undertaken by Ismail et al., (2010) in Malaysia, demonstrated upto 96 % TSS removal from stormwater runoff and suggested that removal efficiency of swales depends upon substrate particle size, vegetation density, and surface slope.

2.9.4.2 Raingarden

Rain garden is a type of stormwater management system which treats the stormwater runoff through filtration via gravel media, sorption and denitrification if anaerobic conditions are present at the bottom. Rain garden is a low-lying land which consists of gravel media whose size increases from top to bottom which helps in physical removal of floating and suspended impurities, and they are planted with native vegetation to sustain in the local climate (Pipil et al., 2022a) (Fig. 2.7).

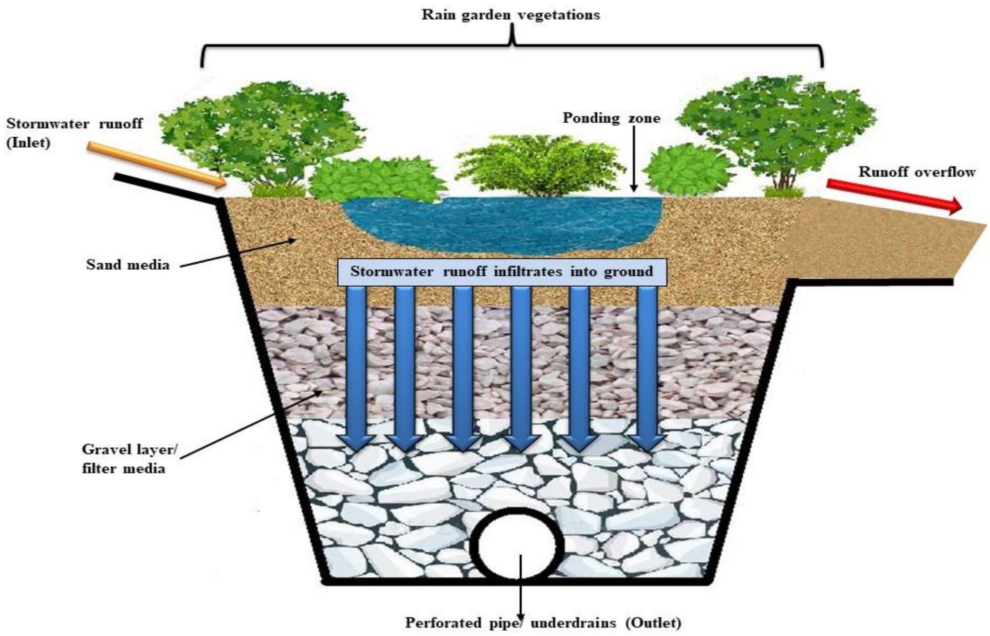

Fig. 2.7 Cross sectional of a typical raingarden for stormwater runoff treatment

The plants uptakes the nutrients present in stormwater runoff for their metabolic activities through photosynthesis (Nandakumar et al., 2019; Pipil et al., 2021, Pipil et al., 2023). The processes and mechanisms that takes place in rain garden include evapotranspiration, exfiltration, infiltration, adsorption, cation exchange towards the removal of pollutants from stormwater runoff. At the bottom of the rain garden, perforated pipe is provided which collects the partially treated stormwater runoff and send it to next treatment unit. The ponding in the rain garden provides the detention to stormwater runoff which is treated by native vegetation to remove dissolved impurities through sorption. The native plant species helps in beautification of landscape. The ponding or storage of stormwater runoff in rain garden also helps in flood management and peak flow attenuation. Rain garden also helps in infiltration of treated stormwater runoff and replenish the groundwater. The rain gardens are cheaper techniques to store and improve the quality of the stormwater runoff, requiring lesser land area with no specialized supervision, easily adaptable, can be constructed in backyard or commercial areas, thus making the rain garden obliging to urban people (Ishimatsu et al., 2017). They are widely used in developing countries to check stormwater runoff pollution. In a study undertaken by Du et al., (2021), raingardens have achieved average reduction of 20.8%–93.3%, 11.6%–54.8%, and 9.8%–47.3% in TSS, TN, and TP, respectively. Another study conducted by Chisholm (2008) in USA reported that 43%, 70%, 64%, and 87% reduction was observed in Cu, Pb, Zn, and Phosphorus, respectively. Trowsdale, and Simcock (2011) conducted a study on raingarden using Pennisetum clandestinum, a sub-tropical grass in New Zealand where 600 to 700 mm layer of sub-soil was used and was then covered with 300 to 400 mm deep topsoil. The study revealed NO_3^- removal up to 87% but lesser reduction in TSS and Zn. Also, another study conducted in New Zealand by Good et al., (2012) reported heavy metal reduction for Cu upto 83.3%, Zn upto 94.5%, and Pb upto 97.3% using raingardens. A study was conducted in USA using raingarden columns showed 89–100% PO_4^{3-} and 42–63% nitrate removal (Yang et al., 2010). Moreover, the ponding of stormwater runoff in raingarden provides storage and thus, helps in reducing the stormwater runoff volume and flow attenuation. Thus, raingardens have also been found efficient towards nutrient removal.

2.9.4.3 Wetlands

Wetlands are the distinctive type of ecosystem which remains submerged under water for most of the time of year. It has shallow water depth which is a habitat to various types of emergent, floating, or submerged type of macrophytes. Wetlands are also protected under Ramsar Convention on Wetlands in 1971 from the impact of anthropogenic activities such as agriculture, urbanization and waste disposal in wetlands (Stroud et al., 2022). The wetlands are classified as natural which involves lakes, flood plains, swamps, peatland, estuaries, mangrove, while constructed wetlands includes stormwater treatment wetlands, constructed canals, ponds, artificial lakes, fish and shrimp ponds. Natural wetlands are saturated with water permanently or seasonally leading to hydric soil which serves as habitat to flora and fauna, whereas, constructed wetlands are man-made which are provided with substrate and macrophytes that are transplanted to their new habitat from its native place.

The urban population is increasing everyday worldwide which results in threat to urban wetland by drain disposal, contamination and construction of dwellings and industries over the available land (McInnes and Everard, 2017). This also leads to disconnection, patchy and fragmented growth of urban wetlands which also reduces the biodiversity and affects the ecology. The urban wetlands are known as “city kidney” and “biodiversity library” due to the unique role it plays in urban ecology. Urban wetlands also provide scope for recreational activities and leisure sites for residing population. Correspondingly, urban wetlands are also used for stormwater runoff management in urban catchment. The change in catchment by uncontrolled construction of various structures increases the runoff volume and peak flow of runoff. However, wetlands provide detention to stormwater runoff which attenuates the peak runoff flow, absorbs the dissolved pollutants, prevents the erosion of soil, improves the water quality, and helps in groundwater recharge. Wetlands performs variety of physical, chemical and biological processes naturally that aids in purification of stormwater runoff. Moreover, the effective processes which are involved in purification of stormwater runoff includes sedimentation, filtration, adsorption, ion exchange, and biodegradation (Reddy and Gale, 1994). As the runoff flows over the catchment, it carries along the impurities which enters the wetlands through vegetations where ponding zone is provided for stormwater runoff retention that helps in velocity reduction and reduces the turbulence of runoff and thus, helps in removal of 90% of suspended impurities through sedimentation (Li et al., 2018). Also, dense vegetation of wetlands helps in removal of dissolved impurities as ponding helps in detention of stormwater runoff. The wetland macrophytes take up the nutrients for carrying out their metabolic activities (Nandakumar et al., 2019; Pipil et al., 2021). Wang et al., (2021) performed a study on nutrient removal from stormwater runoff using wetlands showed removal of 42% of TN and 35% of TP. Similarly, in another study conducted by Schmitt et al., (2015) in France, observed an average reduction of 90%, 79%, and 77% in TSS, TN, and TP respectively from stormwater runoff using wetlands. The wetlands are considered sustainable towards treatment of stormwater runoff and are preferred over conventional water treatment processes.

Table 2.4 Summary of pollutant removal from stormwater runoff by different bioretention systems

Type of bioretention system	**Type of pollutant**	**Pollutant removal**	**Study Location**	**Reference**
Swales	TSS, TN, TP and Zn	90%, 45%, 38% and 80% removal of TSS, TN, TP and Zn, respectively.	USA	Stagge, 2006a
	TSS and Zn	70% and 66% removal of TSS and Zn, respectively.	Sweden	Backstrom, 2003
	TSS, TN and TP	Average removal varied between 57 to 88%, 40 to 72%, and 12 to 67%, respectively for TSS, TN and TP.	Australia	Fletcher et al., 2002
	TSS and TP	83.5% and 81.3% removal of TSS and TP, respectively.	China	Zhao et al., 2016
	TSS and Zn	TSS and Zn removal varied between 65 to 71% and 30 to 60%, respectively.	USA	Stagge et al., 2006b

Raingarden	Cu, Pb, Zn, P, TKN, NO_3^-, ammonium	>92% removal in heavy metals; 80% in removal in P; 60–80% removal in ammonium; 65–75% removal in TKN	USA	Davis et al., 2001
	TP, TN, TKN, NH_3, NO_3^-, Cu, Pb, Zn	Higher removal of NH_3, TN than TP, TKN, NO_3^-, organic-N. Removal of Cu, Pb, Zn > 5, 5, 10 μg/L, respectively	USA	Dietz and Clausen, 2006
	Naphthalene toluene, HC	90% removal of all contaminants	USA	Hong et al., 2006
	Phosphorous	85% and 65% removal in high and low conductivity media	USA	Hsieh et al., 2007
	NO_3^-, PO_4^{3-}, atrazine	89–100% PO_4^{3-} 84–100% atrazine removal; 42–63% removal of nitrate.	USA	Yang et al., 2010
	Zn, TSS, NO_3^-, P	NO_3^- removal up to 87% Major reduction in P; Lesser reduction in TSS, Zn.	New Zealand	Trowsdale, and Simcock, 2011

	Zn, Pb, Cu	System with top-soil show 69.0%, 71.4% removal for Cu, Zn respectively; Sand and sand-top soil mix removed: Cu up to 83.3%; Zn upto 94.5%; Pb upto 97.3%	New Zealand	Good et al., 2012
	NO_3^-, PO_4^{3-}, Dicamba, Atrazine	Removal achieved was of order: Nitrate: 91%; PO_4^{3-}: 99%; Dicamba: 92%; Atrazine: 90%	USA	Yang et al., 2013
	Cd, Cu, Pb, Zn	Accumulated in top layer: Cd: >0.2–2.5 mg/kg; Cu: 3–290 mg/kg; Pb: <1–310 mg/kg; Zn: 11–3,900 mg/kg	Australia	Al-Ameri et al., 2018

	TN	52–89% removal	Colombia	Fajardo-Herrera et al., 2019
	TP, PO_4^{3-}	Average reduction in PO_4^{3-} is 93.6 to 96% Average reduction TP is 77 to 90.1%	USA	Wadzuk et al., 2021
	TSS, TP, Zn	59% TSS removal; 79% TP removal; 69% Zn removal	USA	Davis, 2007
	NH_3, NO_3^-, TKN, TN	Approximate 84%, 35%, 31% and 32% reduction of NH_3, NO_3^-, TKN, and TN, respectively.	USA	Dietz and Clausen, 2005
	Cu, Pb, Zn, Phosphorus	43%, 70%, 64%, and 87% reduction in Cu, Pb, Zn, and Phosphorus, respectively.	USA	Chisholm, 2008
	TSS, TN, TP	Average reduction of 20.8%–93.3%, 11.6%–54.8%, and 9.8%–47.3% in TSS, TN, and TP, respectively.	China	Du et al., 2021

Wetlands	TSS, TN, TP	Average reduction of 90%, 79%, and 77% in TSS, TN, and TP	France	Schmitt et al., 2015
	TN, TP	Reduction in TN: 42%; TP: 35%	USA	Wang et al., 2021
	TSS, BOD, COD, NO_3^-, NH_4^+, TN and TP	Average reduction of TSS, BOD, COD, NO_3^-, NH_4^+, TN and TP were of order 57%, 80%, 74%, 16%, 68%, 55%, 80%, respectively.	Latvia	Grinberga et al., 2021
	TSS, TN, TP	71.5%, 46%, and 55% reduction in TSS, TN, and TP, respectively.	South Korea	Choi et el., 2021
	TP and TN	Total phosphate and TN removal 39% and 67.5%, respectively.	Singapore	Chua et el., 2012
	TP and NH_4^+	TP removal by 95%; NH_4^+ removal by 94.5%	Argentina	Di Luca et al., 2019
	TSS, TP and TN	Removal of TSS, TP and TN of order 78%, 39% and 48%, respectively.	France	Ladislas et al., 2015
	TSS, BOD, COD, TN, TP, Cr, Pb, Zn	TSS: 50.84 to 67.58% BOD: 75.17 to 83.48%	Italy	Tuttolomondo et al., 2020

		COD: 62.52 to 68.88% TN: 58.96 to 66.50% TP: 20.95 to 32.66% Cr: 21.26 to 50.62% Pb: 13.17 to 46.27% Zn: 37.73 to 62.66%		
	BOD, NH_4, TP	Average removal of order 68%, 78% and 49% for BOD, NH_4, and TP, respectively.	Taiwan	Ko et al., 2010
	TP and TN	TP and TN removal ranged between 50.6 to 53% and 31.7 to 51.5%, respectively.	South Korea	Ham et al., 2010
	Cu, Pb, Zn and Ni	Removal efficiency of 23%, 61%, 59% and 33% for Cu, Pb, Zn and Ni, respectively.	Greece	Terzakis et al., 2008
	Ni and Cu	Ni and Cu removal efficiency varied between 81.5 to 89% and 95.5 to 97.3%, respectively.	Scotland	Lee and Scholz, 2007
	Nitrogen and Phosphorus	TN and PO_4^{3-} removal 82.1% and 84.3%, respectively.	Malaysia	Sim et al., 2008

2.10 Role of plants in the bioretention system

The role of plants in bioretention systems is crucial for their effectiveness in stormwater treatment. The selection of appropriate plant species, their specific roles in stormwater treatment, is a significant aspect of bioretention system design. Plants help regulate the water balance within the bioretention system and maintain a more consistent moisture content in the soil, promoting infiltration rates. Additionally, plants facilitate the cycling of nutrients within the system, converting them into less harmful or more readily utilized form (Fan et al., 2019). Presence of vegetation within bioretention systems aids in the physical filtration and retention of sediments and suspended solids present in contaminated stormwater runoff. The leaves, stems, and roots of plants act as natural filters, entrapping particles and promoting sedimentation. Nevertheless, plants also improve the green cover, adding aesthetic value to urban environments (Payne et al., 2018). They promote biodiversity within the system by providing habitat and food sources for various organisms, including insects, birds, and butterflies (Payne et al., 2018). Plants also supports the growth of certain microorganisms in the soil which can degrade organic compounds, break down nutrients, and remove certain stormwater pollutants through biological processes (Davis et al., 2010). The roots of plants in bioretention systems take up nutrients, including nitrogen and phosphorus, from stormwater runoff, reducing the nutrient loads in the water and thus prevent their release into receiving water bodies (Muerdter et al., 2018). The root system of plants binds the soil particles together, reducing the potential for erosion thus stabilizing the soil within the bioretention system. Stable soil conditions are effective during high-flow events when stormwater runoff can cause erosion and sediment transport (Water by Design, 2014). Thus, plants form a vital component in bioretention systems. Furthermore, practices such as pruning, weeding, and replanting are necessary to ensure the functionality of the vegetation within bioretention systems.

2.10.1 Nutrient removal

The efficiency of nutrient removal in bioretention systems is governed by factors such as hydraulic loading rates, vegetation health, soil conditions, and maintenance practices. Soil acts as a filter in bioretention systems and helps to bind and retain nutrients especially nitrogen and phosphorous when stormwater runoff flows through it. Nutrients are either retained or captured through processes like adsorption, ion exchange or indirectly by altering the soil biome including the soil microbial activity (Dagenais et al., 2018). The sediments settle, trap and accumulate the nutrients within the sediment layer, thus reducing the nutrient load. Plants, especially those with dense root systems, have the ability to absorb and utilize nitrogen and phosphorus (Nandakumar et al., 2019; Pipil et al., 2021). Plants facilitates higher nitrogen removal efficiency in the bioretention systems. Nitrogen is essential for vegetative growth of plants; thus, they assimilate nitrogen in the form of nitrates and ammonium ions (Muerdter et al., 2018). Certain wetland plants species such as cattails (*Typha spp.*) or rushes (*Juncus spp.*), *Bracharia*, *Phragmitis* are known to have a higher nutrient uptake capacity (Nandakumar et al., 2019; Pipil et al., 2021). The property to assimilate or uptake nutrients differ significantly from species to species. In a study, 20 different plant species were assessed for nutrient removal efficiency in bioretention systems. The study reported a 170-fold difference in nitrate or nitrite concentration whereas, around 570-fold difference in ammonium concentration (Read et al., 2008). A difference in biomass of shoot parts and root part was observed w.r.t. nitrogen transport in the bioretention system (Read et al., 2009; Barrett et al., 2013). In a similar study, *Typha latifolia*, *Juncus effusus* and *Cyperus papyrus* were investigated for phosphorus and nitrogen removal capabilities (Bebba et al., 2019). The results indicated that all plant species exhibited varying degrees of pollutant removal. *Juncus effusus* was found as maximum nitrogen removal efficient (95%) and *Typha latifolia* as best phosphorous removal (95%), thus displaying the maximum elimination rates. Other various studies have reported reduction of nitrogen load ranged from 7.8% using *Polygonum barbatum* (Chua et al., 2012) to nearly complete removal (99.4%) using *Rumex acetosa* (Zhou et al., 2012). Lynch et al., (2015) reported removal of phosphorous using *Juncus effusus* ranged from a low of 4% whereas Keizer-Vlek et al., (2014) observed around 92% removal efficiency for phosphorous using *Iris pseudacorus*. Five mono-culture of *Agrostis alba* (red top), *Canna* × *generalis* ‘Firebird’ (canna lily), *Carex stricta* (tussock sedge), *Iris ensata* ‘Rising Sun’ (Japanese water iris), *Panicum virgatum* (switchgrass were was assessed towards treatment of runoff from commercial nurseries (Spangler et al., 2019). *Panicum virgatum* was found most efficient and removed up to 64.7% Phosphorous and up to 82.4% Nitrogen, while other species remediation rates ranged from 25%-50% towards removal of Phosphorous and nearly 13% - 50% removal of Nitrogen.

2.10.2 Removal of Heavy Metals

Plants exhibit different extents of the uptake of metals and metalloids via different mechanisms like phytoremediation, metal adsorption/elution and complexation with the organic constituents (Glick, 2003). The effectiveness of metal removal in bioretention depends on type of metal, plant species metal tolerance, accumulation potential, and ability to thrive in the local environment as well as the sorption potential of growth substrate. The occurrence and abundance of metals in stormwater are generally location-specific and may exist either in dissolved form or gets bind with particulates (Sansalone and Buchberger, 1997). In bioretention system, sorption potential of growth substrate plays major role in removal of metals from stormwater whereas plants play secondary role, exhibiting different metals/metalloid uptake mechanisms. The later improves the quality of stormwater via processes such as phytoextraction, rhizofiltration, phytodegradation, phytostabilization etc (Dagenais et al., 2018). The root system of plants helps them accumulate metals in their shoot region (phytoextraction), which reduces the metal concentrations in the stormwater. The rhizosphere of the soil region surrounding the roots, (where interactions between roots, microorganisms, and soil occur) acts as a filter towards trapping and immobilizing metals, thus reducing their mobility and potential to transport (rhizofiltration). Plants with deep root systems can help stabilize metals in the subsurface layers, preventing the leaching into groundwater or sensitive ecosystems (phytostabilization) (Pipil et al., 2022a). The efficiency of *Dracaena marginata* in bioretention system was evaluated against an unvegetated system for treatment of stormwater containing various metals like Pb, Mg, Ca, Cu, Fe, Cd, Al, Cr, K, Na, Ni, and Zn (Vijayaraghavan and Parveen, 2016). Presence of vegetation significantly enhanced the overall removal performance of metals with remediation efficiency of 99.8% for all the metals post 245 mm of rainfall.

The reaction between soil, water and carbon dioxide (CO_2) from root transpiration resulted in the formation of carbonic acid (H_2CO_3), which released H^+ ions from the bioretention media. These H^+ ions occupy the functional sites previously occupied by other cations. Since mineral nutrients are essential for the growth of vegetation, the released inorganic ions were sorbed by the plant roots. This leaves the soil binding sites vacant, enabling the bioretention media to adsorb additional ions from the polluted runoff. The phytoremediation potential of a bioinfiltration system-integrated plant species, for the removal of heavy metals from stormwater runoff was investigated (Liu et al., 2019). Hyper-accumulative plant species such as *Iris pseudacorus*, *Juncus effusus*, and *Carex spp*. were studied using mixture of compost, sand and zeolite as filter media. The study reported effective contaminant removal of heavy metals like Cu, Zn, Pb, and Cd (Liu et al., 2019). In another study, the assessment of four different wetland plant species (*Phragmites australis*, *Typha angustifolia*, *Cyperus alternifolius*, and *Iris pseudacorus*) for removal of heavy metals, including copper (Cu), zinc (Zn), lead (Pb), and cadmium (Cd) was conducted. *Phragmites australis* and *Typha angustifolia* were predominantly effective in removing copper and zinc, whereas *Cyperus alternifolius* and *Iris pseudacorus* were more efficient in removing lead and cadmium. The study showcased the prominence of plant species selection towards attaining optimum removal of heavy metals primarily through plant uptake. Plants enhance the microbial activity in the soil, endorsing processes like metal reduction, precipitation, or transformation (Hsieh and Davis, 2005). Microorganisms in association with plant roots, interact with metals, causing immobilization or transformation of metals into less toxic forms. Plants secrete compounds called chelators or exudates from their roots, which bind to metals and form complexes that are least toxic, highly stable, thus reducing the bioavailability as well as mobility of metals (Agarwal et al., 2023). Implementation of green practices is a more sustainable and cost-effective approach for stormwater runoff control and pollution reduction compared to conventional gray infrastructure. The significance of integrating plants with green infrastructure in urban stormwater management strategies other than pollutant removal is ecological benefits. Vegetation boosts the biodiversity, providing habitat for wildlife, and promoting the ecological health as well as aesthetics of urban environments.

2.10.3 Bioretention Media

Bioretention media are green infrastructure practices, specially designed to manage and treat stormwater runoff by facilitating filtration, infiltration, pollutant removal and ascertaining the stability of bioretention system. Contemplating the comprehensive nature of these characteristics, it is impractical to form an ideal bioretention medium using single material bearing all these characteristics (Fassman-Beck et al., 2015). Often, combination of organic and inorganic constituents with respective properties at distinct ratios generates a substrate with specific properties. Bioretention media should be typically composed of materials that allow rapid infiltration and percolation of stormwater and improve the movement of water through the soil and into the underlying layers (Jiang et al., 2019). Conventional media reported effective remediation of stormwater runoff via either sorption or filtering impurities, suspended solids, sediments, heavy metals, nutrients (nitrogen and phosphorus), and organic matter (Shrestha et al., 2018). This helps improve water quality as runoff passes through the bioretention system. Conventional bioretention media composed of soil, sand and organic matter (Brown and Hunt, 2011). Organic matter enhances the nutrient-holding capacity and microbial activity. Organic matter enables the media to retain water and capture pollutants.

Bioretention media help mitigate the impacts of urbanization on stormwater management and water quality. The selection and design of bioretention media should consider local conditions, climate, hydrologic efficiency of bioretention system and pollutant loadings to optimize their performance in treating stormwater runoff (Liu et al., 2014). For instance, addition of bioretention substrate additives along with bioretention media has significantly enhanced the stormwater treatment. Different studies have reported effectiveness of additive substrate in bioretention systems including fly ash, biochar, vermiculite, zeolite and others (Kandel et. 2017; Soberg et al., 2019; Bratieres et al., 2008; Jiang et al., 2018; Sang et al., 2019). The use of organic matter additives like compost and peat moss have also found favourable towards treatment of runoff. Compost increases the water holding capacity as well as improves the nutrient retention, whereas peat moss enhanced the cation exchange capacity of media (Sharma and Malaviya, 2021). Some of the additives like zero-valent iron have the potential to reduce the nutrient pollution load like phosphorous in stormwater runoff (Ali et al., 2023). In addition, amendments of sulphur compounds and organic carbon enables the denitrification, reducing the nitrate concentration in stormwater runoff (Deng et al., 2020). Similarly, a standard sandy loam substrate with perlite/vermiculite resulted in removal of more than 70% nitrogen and around 80%-90% reduction in phosphate and total phosphorous load (Bratiers et al., 2008). In a study, optimized mixed substrate having red soil (50%), vermiculite (10%), fine sand (10%), coco-peat (10%), *Sargassum* biomass (10%) were used for *Dracaena marginata*-planted biofilter (Vijayaraghavan and Praveen, 2016). In comparison to the indigenous garden soil, the substrate mixture demonstrated higher sorption potential towards metal ions, high water holding capacity, air-filled porosity, and hydraulic conductivity, low bulk density. Location, topography, geological features, climatic and edaphic factors also determine the performance of substrate media additive Bioretention system. The same has been reported by Fassman-Beck et al., (2015) in which indigenous material of Auckland was used to prepare two commercial substrates. The system formed however failed to meet the international bioretention parameters.

2.10.4 Synergistic effect of Bioretention media and Biosorbents

The functioning of Bioretention systems majorly depends upon the sorption potential of susbtrate. The stormwater urban runoff majorly constitutes highly inorganic pollutant load (Vijayaraghavan et al., 2021). Although majority of the pollutants are significantly retained by the substrate, presence of inorganic impurities is a limiting factor to sorption potential. Substrates such as sand or native soil resulted in a meagre efficiency towards removal of heavy metals and nutrient (Kratky et al., 2017; Bratieres et al., 2008). Studies have reported that amendment of organic substrate other than compost and mulch, such as zeolites, biochar, seaweeds, crustacean shells, etc. are found effective in enhancing the sorption potential (Xiong et al., 2019; Vijayaraghavan and Praveen, 2016). Macroalgae are good assimilators of nutrients, thus it is an ecological and sustainable practice for the remediation of nutrient pollution (Aquilino et al., 2020). Moreover, the use of macroalgae for wastewater bioremediation offers the advantage of possible biomass recovery, since macroalgae are potential producers of substances useful in the pharmaceutical and cosmetic fields and are good candidates for production of fertilizers and biofuels (Aquilino et al., 2020). The algae *Chaetomorpha linum* and Cladophora prolifera exhibit high tolerance to a variety of environmental stress like pH, light intensity, temperature, salinity, nutrient concentrations and even heavy metals like Copper and Zinc (Aquilino et al., 2020; Ajjabi and Chouba, 2009). Similarly, Brown seaweeds has been reported as active biomonitoring agents for trace elements like copper and zinc in aquatic environments (Foday et al., 2021).

Another sorbent biochar has also been found efficient towards removal of contaminants of emerging concerns (CECs), organic impurities, heavy metals, microorganisms and reducing nutrient concentration (Ahmad et al., 2014; Mohanty and Boehm, 2014). The mechanism involved in pollutant adsorption includes physical adsorption, chemical reactions, and ion exchange. Wood-derived H_2SO_4 modified-biochar reported nearly complete removal of Escherichia coli from synthetic stormwater in the initial runoff infiltration and 92% efficiency was observed in the second cycle of runoff infiltration (Lau et al., 2017). In a study, iron-coated biochar amended media demonstrated around 95% reduction in COD, 98% removal for total nitrogen, and 90% removal of total phosphorous in stormwater treatment (Xiong et al., 2019). Biochar is a sustainable and ecofriendly sorbent owing to its production from biomass waste materials and potential for carbon sequestration in the soil (Yang et al., 2020). Biochar advances quite a few distinguishing attributes that make it suitable for implementing as bioretention media. These include (i) its cost-effectiveness because it can be produced from locally sourced biowastes; (ii) the potential for regeneration; (iii) its excellent chemical and thermal stability; (iv) significant water retention capacity (Yang et al., 2020). Furthermore, it can serve as a fertilizer for plant growth while inhibiting the leaching of nutrient (Inyang et al., 2016).

2.10.5 Regulating hydrological processes

Plants as well as substrate plays a crucial role in improving hydrological processes in various environmental matrices. They govern the water movement, storage, and quality, fostering a more sustainable and resilient hydrological system (Pipil et al., 2022a). Plants through their root systems and canopy, retain water in the soil. The roots act as binders, stabilizing the soil and causing gradual discharge/ release of water over the surface. This further prevents flood like situation and mitigates the impact of heavy rainfall and flooding events. The root system facilitates the groundwater levels through water infiltration and percolation of water in soil. The groundwater recharge thus reduces surface runoff (Vijayaraghavan and Raja, 2014). Plants take up nutrients from the soil and water and releasing them back when the plants decay. This helps in regulating the nutrient cycle (Pipil et al., 2021). The canopy of plants provides shade, regulates the temperature of the ground and water bodies, further supporting the sustenance of sensitive aquatic species and stimulating a healthier ecosystem. Riparian zones and wetlands habitats act as natural buffers, filtering out contaminants from runoff reaching the water body and reducing the influence of floods (Singh et al., 2021). Plants through photosynthesis helps in the carbon sequestration. By eliminating carbon dioxide from the atmosphere, plants functions in mitigating climate change and its impacts on hydrological cycles (Yadav et al., 2023). The presence of substrates aids in survival of vegetation. Bioretention media prepared from soil, wood chips, river sand along with fly ash, vermiculite and zeolites exhibited infiltration capacities more than that of undisturbed soil (Jiang et al., 2019). The water holding capacity of substrate influence plant life. Substrate with good water holding capacity decreases the reliance on irrigation thus improves the growth of vegetation (Pipil et al., 2022b). Nonetheless, exploration is required to assess their compatibility with different types of vegetation, modes of application, and their long-term impact on water and soil biome.

2.11 SWOT analysis of treatment methods

The current study focuses into the management and treatment of stormwater runoff in urban areas of developing nations through the application of different stormwater runoff treatment techniques as discussed above. The environmental performance of various treatment methods could be hampered because of certain factors regulating the treatment and pollutant removal efficiency from stormwater runoff (Pipil et al., 2022a). For instance, the hydraulic conductivity of the substrate can reduce due to its clogging, regular maintenance of the treatment unit is required for its better performance. Considering the various parameters and factors governing the treatment units towards the applicability, planning, and execution of these stormwater runoff treatment techniques, the strength, weakness, opportunity and threat (SWOT) analysis has been illustrated in Table 2.5.

Table 2.5 SWOT analysis of various stormwater treatment units

Type of treatment unit	Strength	Weakness	Opportunity	Threat
Gross Pollutant Trap (GPT)	• Energy-efficient as no energy is required; • Operates on gravitational and centrifugal force; • Can be retrofitted in existing stormwater drains; • Work as pre-treatment unit; • Generally low head is required;	• Aesthetically unattractive; • Doesn't not remove particles size less than 5.0 mm; • Requires regular maintenance; • Poor maintenance leads to foul smell; • Limited removal of dissolved impurities; • Disposal of removed waste from stormwater runoff;	• Can be installed in developing countries; • Design criteria can be developed as a code of practice;	• Perilous to person cleaning it; • Organic impurities can cause bad odour; • Resuspension and remobilisation of removed impurities;

Swales	• Improved aesthetics along the length of road; • Low cost of construction; • Augments the biodiversity; • Improved water quality down the slope; • Helps in reducing the peak runoff flow; • Infiltration from unlined sides helps in groundwater recharge; • Sustainable technique since no energy is required; • Prevents soil erosion; • Better aesthetic than gutter and kerbs;	• It takes time to stabilize; • Hydraulic conductivity reduces when silt from road enters swales; • It has high maintenance during development stage; • Fails to treat stormwater runoff during high intensity rainfall; • Steep slopes require small check dams;	• It does not require energy, thus, can be installed in developing countries; • Different vegetations can be used which are resistant to dry season; • Proper design can store larger stormwater runoff volume which can delay peak flow volume;	• Difficult to retain moisture; • Wilting of vegetation during dry period; • During high intensity, stormwater runoff can bypass them; • Earthen check dam may erode with flow; • Can be a mosquito breeding ground if correct slope is not provided; • Can produce bad odour;

Rain gardens	• Sustainable treatment process since it does not require energy; • Cheaper to construct; • Improved aesthetics and landscape; • Soil erosion prevention; • Increases ground water level; • Augment biodiversity; • Prevent flood through runoff detention; • Specialised supervision not required; • Easy to operate and maintain; • Can be installed in smaller land area;	• Hydraulic conductivity of media reduces with time due to its clogging; • Can effectively handle small stormwater runoff volume originating from catchment area; • Less effective in controlling floods; • It requires land which is expensive in urban area; • Takes time to establish fully;	• New species can be introduced which are can survive in dry season; • Can be installed in family houses; • Plant other than wetland vegetation can be used;	• Wilting of vegetation during dry season; • Can be a mosquito breeding site if not maintained properly; • Stormwater runoff can bypass rain garden during high discharge as a result of high intensity rainfall; • Filter media may clog;

Constructed wetlands	• It improves the aesthetic and vegetation cover; • Augmenting the biodiversity; • Carbon sequestration through photosynthesis; • Sustainable treatment method since no energy is required; • Prevents the flooding; • Reduces the peak stormwater runoff flow through peak attenuation; • Increases the ground water level; • Prevents soil erosion; • Easy to operate and no specialised supervision is required; • Can be operated throughout the year;	• Requires large land which is difficult to find in urban area; • Difficult to reach wetland for maintenance; • Requires time for its establishment; • Wrong selection of plant and substrate media; • Design of constructed wetland is empirical;	• Recreational and cultural activities; • Educational teaching and research work; • Water supply for irrigation, green belt; • Combinations in series, parallel, vertical and horizontal flow can be adopted; • Microbes can be fed to improve the pollutant removal;	• Cost of land is high in urban area; • Can be a breeding site for mosquitoes; • Poor removal efficiency when stormwater runoff flow is high and detention period is less; • Methane production at the bottom of wetlands; • Weed and unwanted vegetation can also grow; • Vegetations get shock when pollutant is toxic and concentration is high; • Vegetation wilting during high temperature and low stormwater runoff volume;

Sustainable development of urban area needs an awakening and awareness among the community as well as among local policy making agencies in developing nations like India. In India, the rural population is migrating towards urban area causing stress on scarce water resources. In order to make water fit for potable use or for industrial application, it is required to give treatment to raw water which cost hefty money to government. Even though, not everyone is providential to adequate supply and appreciable quality of treated water. The poor management and poor design capacity of wastewater conveyance system leads to contamination of fresh water resources. Thus, the dependence on limited water resources can be reduced by making proper utilization and management of stormwater runoff in catchment using Low Impact Development (LID), Water Sensitive Urban Design (WSUD), Integrated Urban Water Management (IUWM), Sustainable Urban Drainage System (SUDS), Best Management Practices (BMP), and Green Infrastructure (GI). Stormwater treatment methods and techniques are part of its management. Stormwater treatment is gaining importance nowadays because of their positive impacts on nature, environment, ecology and biodiversity. These techniques help in removing the floating, suspended, and dissolved impurities from stormwater runoff in a sustainable manner. The recent development and application of different stormwater treatment techniques such as gross pollutant trap, raingarden, bioswales, and wetlands in different countries vary in terms of pollutant removal mechanism, function, objective, and application. The selection of technique depends upon the local climate, type of soil, type of terrain, ground slope, laws of local governing authorities, presence of infrastructure and assent, etc. Thus, it can be said that not all the stormwater treatment methods can be adopted everywhere. These treatment methods improve stormwater runoff through removal of floating and suspended impurities, removal of organic (BOD) and nutrient (phosphate and nitrate) load, and other dissolved impurities. They also provide storage which reduced peak flow volume through attenuation which in return prevents flooding. The stored treated stormwater runoff can be used as a water resource that can increase the water capacity of the city and reduces the dependence of on other water resources for non-potable use, such as irrigation. Stormwater runoff management and treatment also augments the green cover, quality of life, increased ecology, and enhanced biodiversity. They also act as a sink of pollutants and helps in carbon sequestration. It also reduces the stress on existing combined conveyance system and wastewater treatment facility, and reduces the cost of stormwater drain laying. These treatment methods are sustainable as they do not require energy for their operation. These methods have been proven a success in developed countries and can find a way in coming future in developing nation like India.

CHAPTER 3

MATERIALS AND METHODS

3.1 Study area

The current study was undertaken in capital city of India, Delhi, which is situated between the latitudes of 28°-24’-17” and 28°-53’-00” North and longitudes of 76°-50’-24” and 77°-20’-37” East. Its maximum length and width are 51.9 km and 48.5 km, respectively and it is spanning over 1,484 km^2 (Profile of Delhi, 2023) (Fig. 3.1). Delhi is located in northern part of India which accommodates 16.8 million residents as per census of 2011 (Statistics at Glance, 2023). Delhi has river Yamuna which flows from north to south direction. River Yamuna initially originates from Yamnotri glacier in the Himalayas and then traverses its meandering path beginning from Tajewala. It enters Delhi near Palla village covering a total length of 22 km between Wazirabad barrage and Okhla barrage. River Yamuna collects all the stormwater and wastewater generated in Delhi and ultimately drains it into River Ganga. The terrain of Delhi is flat except for the regions of Aravalli hills. The river Yamuna, Aravalli hills, and plains between theses have alluvial deposits. Delhi ridge which is covered with forest has four sections, the northern, the central, the south central, and the southern which are the part of farthest extension of Aravalli hills.

With respect to climatic conditions, Delhi receives average annual rainfall of 692 mm during the monsoon rainfall in month of July, August and September with 35.7 rainy days annually. The average minimum temperature of Delhi was reported as 7.3 °C while average maximum temperature recorded as 40.7 °C. The annual average minimum and maximum temperature of Delhi was recorded as 19.2 and 31.7 °C (New Delhi, 2023).

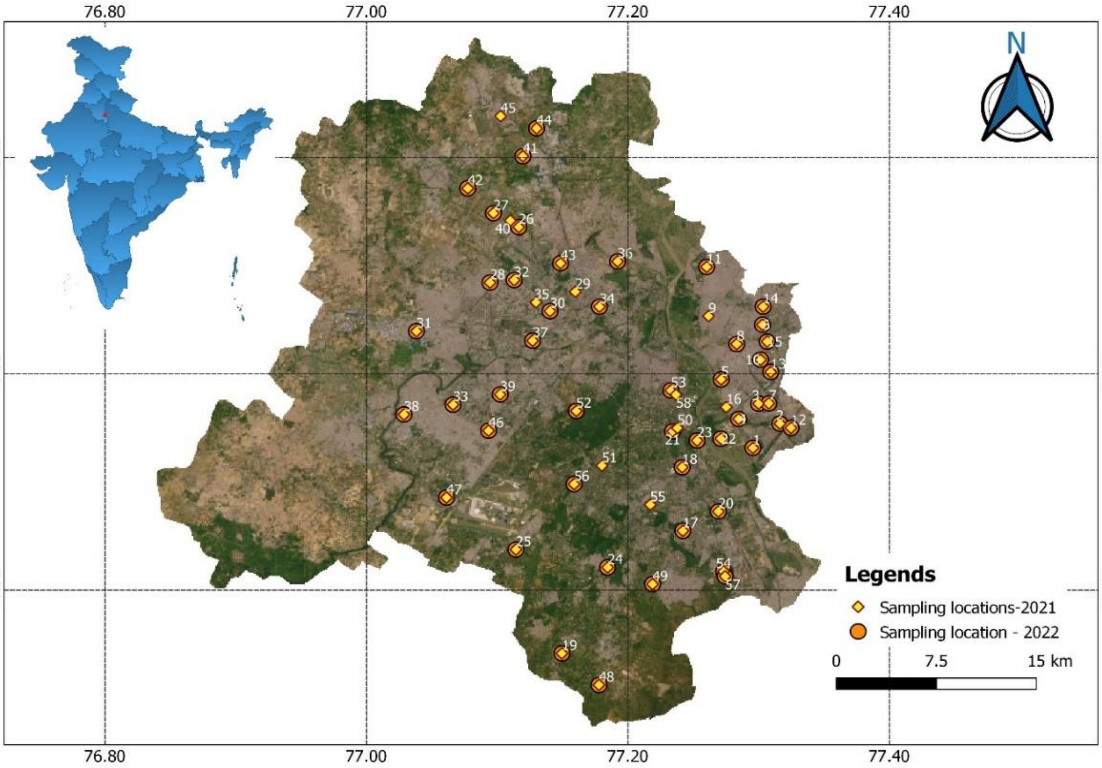

Fig. 3.1 Location of sampling points for stormwater runoff in Delhi, India, during 2021 and 2022

3.2 Collection of samples (rainwater and stormwater runoff) and its storage

The samples were collected during monsoon in year 2021 and 2022 during the study in order to compare physico-chemical characteristics of the rainfall and stormwater sample. The rainfall samples for their characterisation were collected on 19th May, 2021, as Delhi received its first downpour of the season after Tautae Cyclone hits the Indian subcontinent. Average rainfall on that day was observed to be 119.3 mm as per IMD, Delhi, which was one of the highest rainfalls in last 35 years in a day in the month of May. It was enough to cause the stormwater runoff on the impervious surfaces like roads and roof tops of houses. Being the first flushing of the season, it was expected to sweep more dissolved and suspended impurities along with it which was deposited over a period of time. Followed by it, the stormwater runoff samples were also collected from various locations and different land use including residential, industrial, commercial, institutional, and road/highways of Delhi. In year 2021, stormwater runoff samples were collected from four different rainfall events during 19th May (n=25); 14th July (n=14); 28th July (n=9); and 30th July (n=11). In year 2022, the runoff samples were collected from four different rainfall events occurred on 17th June (n=15); 30th June (n=11); 10th September (n=9); and 22nd September (n=13). The rainwater samples were also collected during 2021 and 2022 from the different location to assess the impact of atmospheric washing in terms of suspended and dissolved impurities of different anionic and cationic species. For the same, wet collector units were placed at 1 m height over the roof top to prevent collection of splashes. All the collected samples were taken to lab immediately for analysis. However, the samples were acidified and stored for later analysis of heavy metals using atomic absorption spectrophotometer.

3.3 Physico-chemical characterization

The various physico-chemical parameter that were analysed as per the details provided by manuals of American Public Health Association (APHA, 2012) during the study. The parameter, methods and associated instrument used during the study have been briefly summarised in the Table 3.1 below. The detailed description of each of the methods have been discussed below. Also, the flow velocity of the stormwater runoff was measured using Global Water Instrument (USA) make (Model: FP11).

Table 3.1 List of methods undertaken during the analysis of samples as per APHA 2012

Parameter	Standard method	Instrument/Make/Model/Method
pH	APHA 4500-H^+	Bench-top multiparameter Labman India/LMPH10
Electrical conductivity	APHA 2510	
Total dissolved solids	APHA 2540	

Total suspended solids	APHA 2540	Total Suspended Solids Dried at 103–105°C
Calcium	APHA 3500-Ca	Flame photometer/Systronics 128µC
Sodium	APHA 3500-Na	
Potassium	APHA 3500-K	
Lithium	APHA 3500-Li	
Magnesium	APHA 3500-Mg	Calculation method
Ammonium	APHA 4500-NH$_3$	Aquaread AP-7000
CDOM		
TKN	APHA 4500-NH$_3$	Titrimetric Method
Nitrate	APHA 4500-NO$_3^-$	UV-VIS Spectrophotometer/LABINDIA UV3092
Phosphate	APHA 4500-P	
Sulphate	APHA 4500-SO$_4^{2-}$	
Chloride	APHA 4500-Cl$^-$	Aquaread AP-7000
Total nitrogen		Shimadzu TOC analyzer/TOC-LCPH
Total organic carbon	APHA 5310 Total organic carbon (TOC)	
Total carbon		
Inorganic carbon		
Total Hardness	APHA 2340 Hardness	EDTA Titrimetric Method
Alkalinity	APHA 2320 Alkalinity	Titrimetric Method
Cobalt	APHA 3500-Co	

Chromium	APHA 3500-Cr	Flame atomic absorption spectrometric methods/ Analytik Jena novAA 350
Cadmium	APHA 3500-Cd	
Copper	APHA 3500-Cu	
Zinc	APHA 3500-Zn	
Iron	APHA 3500-Fe	
Lead	APHA 3500-Pb	

3.3.1 pH

The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. All the pH values were recorded as per APHA 4500-H^+ using electrometric method in which glass electrode was used that measures electromotive force (emf) produced in electrode system thus, varies linearly. The linear relationship is obtained by plotting the measured emf against the different pH buffer solutions. During present study, the pH was measured using Bench-top multiparameter Labman India/LMPH10 consisting of potentiometer, a glass electrode, a reference electrode and a temperature compensating device. A reference electrode is a half-cell that provides a constant electrode potential while the glass electrode is a sensor electrode consisting of bulb of glass containing a fixed concentration of HCl or a buffered chloride solution. The electrode system was calibrated using the standard buffer solution of known pH of 4.0, 7.0 and 10.0 (Metrohm make). Before the calibration, the electrode was washed with distilled water thoroughly, blot dry with a tissue paper and then dipped into the first known pH buffer solution. Similarly, the electrode was taken out of the first buffer solution, washed with distilled water thoroughly, blot dry with a tissue paper and then dipped into the second known pH buffer solution followed by repeating the process for third known pH buffer solution. Following calibration, the electrode was washed with distilled water thoroughly, blot dry with a tissue paper and then dipped into the unknown samples. Until the readings to get stabilised, and the pH was noted down. The process was repeated for all the samples. Also, keep electrodes wet by returning them to storage solution whenever pH meter is not in use.

3.3.2 Electrical conductivity (EC)

Electrical conductivity is a measure of the ability of an aqueous solution to carry an electric current which depends upon ion concentration, mobility, valency, and on the temperature of aqueous solution. During present study, the calibration of the instrument and measurement of electrical conductivity of the samples was performed as per APHA 2510-B using Bench-top multiparameter Labman India/LMPH10. The conductivity cell contains electrode of stainless steel. Before starting the experimentation, instrument was calibration using standard buffer solution of conductivity 1413 μS/cm and 12.9 mS/cm (Make: Thermo Scientific). During calibration, the electrode was thoroughly washed with distilled water and blotted dry with tissue paper. After selecting calibration mode in the instrument, the probe was immersed into 1413 μS/cm solution first such that the instrument will display 1412 µS/cm followed by immersing the electrode into 12.9 mS/cm buffer solution after washing the electrode in order to avoid any contamination of standard solutions. For measurement of EC for samples, the electrode was thoroughly washed and blotted dry with tissue paper followed by immersing electrode in the sample. Wait for the reading to get stabilized and note it down in the register. After the completion of experiment, electrode was rinsed thoroughly and kept immersed in distilled water when not in use.

3.3.3 Total dissolved solids (TDS)

Total dissolved solids (TDS) are a measurement of the total amount of inorganic and organic compounds that have been dissolved in aqueous solution. The ions present in the water sample conduct electricity which is proportioned to TDS of the sample. During present study, total dissolved solids were measured in the samples using Bench-top multiparameter Labman India/LMPH10. Before the start of experiment, the instrument was calibrated using standard buffer solution of strength 692 mg/L and 7230 mg/L as NaCl (Make: Thermo Scientific). The electrode used was thoroughly washed with distilled water and blotted dry with a tissue paper. After selecting calibration mode in the instrument, clean electrode was immersed first in 692 mg/L as NaCl standard buffer solution until stabilised reading is not displayed on the instrument. Same procedure was repeated for 7230 mg/L as NaCl standard buffer solution. After calibration is completed, the electrode was washed thoroughly with distilled water before immersing it in the sample. The stabilised readings of the samples were recorded. After the completion of experiment, electrode was rinsed thoroughly and kept immersed in distilled water when not in use.

3.3.4 Total suspended solids (TSS)

Total suspended solids in the samples were determined using gravimetric method as per APHA 2540-D. The membrane filters used were made up of cellulose nitrate having pore size of 0.45 µm. The initial weight (w_1) of the filter paper was recorded after keeping it inside the oven for 1 hour at 105 °C. This filter paper was placed over the Sartorius Microsart®e.jet with multi-branch filtration assembly using a forceps. The sample was agitated with the help of magnetic stirrer and known volume of sample was taken from this agitated sample with the help of a pipet. For homogenous sample, the sample was pipet out from approximate midpoint of container but not in vortex. The filtration assembly was turned on such that filtrate passes through it and residue remains on the filter paper. After filtration is completed, the filter paper was placed inside a hot air oven using forceps where it was heated at 105 °C for atleast 1 hour. After heating the filter paper, final weight (w_2) of filter paper and residue was observed on a weighing balance until no reduction in weight is observed between two consecutive observations. The TSS can be calculated using the equation (3.1):

$$Total\ Suspended\ Solids\ (mg/l) = \frac{(w_2 - w_1) \times 1000}{(volume\ of\ sample\ in\ ml)} \qquad \textbf{(3.1)}$$

Where, w_1 is weight (mg) of filter paper and w_2 is weight (mg) of filter paper and dried residue.

3.3.5 Calcium (Ca^{2+})

The calcium in stormwater runoff samples was estimated using the flame photometer (Make: Systronics; Model: 128µC) as per APHA 3500-Ca. The instrument was calibrated using standards having the strength of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, and 100 mg/L as calcium. The standard stock solution of calcium was prepared in laboratory by mixing 137.5 mg of $CaCl_2$ in 500 mL Type-I water to get 100 mg/L as calcium, followed by standards with the strength of calcium as 20 mg/L, 40 mg/L, 60 mg/L, and 80 mg/L which were prepared through serial dilution. For calibrating the flame photometer, flame was turned on carefully along with air compressor, and its flow was adjusted such that clear and sharp flame is visible. With the instrument, the input was given for calibration and Ca was selected in the instrument. Ultra-pure (Type-I) water was aspirated initially such that all the capillaries get cleaned before calibration was initiated. Each standard sample of known strength was aspirated as required by the instrument. After calibration was completed, the Type-I water (as reference solution) was aspirated before aspirating the stormwater runoff samples. The instrument provided the concentration of calcium in the stormwater runoff which was noted.

3.3.6 Sodium (Na^+)

The sodium in stormwater runoff samples was determined using the flame photometer (Make: Systronics; Model: 128µC) as per APHA 3500-Na. The instrument was calibrated using standards having the strength of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, and 100 mg/L as sodium. The standard stock solution of sodium was prepared in laboratory by mixing 132.8 mg of NaCl in 500 mL Type-I water to get 100 mg/L strength solution, followed by preparation of standards with the strength of sodium as 20 mg/L, 40 mg/L, 60 mg/L, and 80 mg/L through serial dilution. For calibrating the flame photometer, flame was turned on carefully along with air compressor, and its flow was adjusted such that clear and sharp flame is visible. With the instrument, the input was given for calibration and Na was selected in the instrument. Ultra-pure (Type-I) water was aspirated initially such that all the capillaries get cleaned before calibration was initiated. Each standard sample of known strength was aspirated as required by the instrument. After calibration was completed, the Type-I water (as reference solution) was aspirated before aspirating the stormwater runoff samples. The concentration of sodium in stormwater runoff was recorded.

3.3.7 Potassium (K^+)

The potassium in stormwater runoff samples was estimated using the flame photometer (Make: Systronics; Model: 128µC) as per APHA 3500-K. The instrument was calibrated using standards having the strength of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, and 100 mg/L as potassium. The standard solution of potassium was prepared in laboratory by mixing 95.5 mg of KCl in 500 mL Type-I water to get 100 mg/L strength solution, followed by preparation of standards with the strength of potassium as 20 mg/L, 40 mg/L, 60 mg/L, and 80 mg/L can be prepared through serial dilution. For calibrating the flame photometer, flame was turned on carefully along with air compressor, and its flow was adjusted such that clear and sharp flame is visible. With the instrument, the input was given for calibration and K was selected in the instrument. Ultra-pure (Type-I) water was aspirated initially as a reference solution such that all the capillaries get cleaned before calibration was initiated. Each standard sample of known strength was aspirated as required by the instrument. After calibration was completed, the Type-I water was aspirated before aspirating the stormwater runoff samples and the concentration of potassium in the stormwater runoff samples was recorded.

3.3.8 Lithium (Li^+)

The lithium in stormwater runoff samples was determined using the flame photometer (Make: Systronics; Model: 128µC) as per APHA 3500-Li. The instrument was calibrated using standards having the strength of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L as lithium. The standard solution of lithium was prepared in laboratory by mixing 555.7 mg of $LiCl_2$ in 500 mL Type-I water to get 50 mg/L strength solution, followed by preparation of standards with the strength of lithium as 10 mg/L, 20 mg/L, 30 mg/L, and 40 mg/L through serial dilution. For calibrating the flame photometer, flame was turned on carefully along with air compressor, and its flow was adjusted such that clear and sharp flame is visible. With the instrument, the input was given for calibration and Li was selected in the instrument. Ultra-pure (Type-I) water was aspirated initially such that all the capillaries get cleaned before calibration was initiated. Each standard sample of known strength was aspirated as required by the instrument. After calibration was completed, the Type-I water was aspirated as reference solution before aspirating the stormwater runoff samples. The instrument provided the concentration of lithium in the stormwater runoff which was recorded.

3.3.9 Magnesium (Mg^{2+})

Magnesium was estimated as the difference between total hardness and calcium as $CaCO_3$. Both total hardness and calcium hardness as $CaCO_3$ was determined using standard titrimetric method using EDTA (ethylenediamine tetraacetic acid) as titrant. Concertation of Mg^{2+} was calculated using the formula given in equation (3.2)

$$Mg^{2+}\ (mg/l) = \frac{(V_1 - V_2)\times 400.8}{V_S \times 1.645} \qquad \textbf{(3.2)}$$

Where, V_1 is volume (mL) of EDTA used for total hardness; V_2 is volume (mL) of EDTA used for Ca^{2+} hardness as $CaCO_3$; V_s is volume (mL) of sample used during titration.

3.3.10 Ammonium (NH_4^+)

The ammonium ions were determined in samples using ion specific electrode (ISE) as per APHA 4500-NH_3. The ISE was mounted on GPS enabled Aquaread AQUAPROBE AP-7000 instrument in which ISE was calibrated with standards of known strength having ammonium ion concentration of 10 mg/L and 100 mg/L. For preparation of standards, stock solution of NH_4Cl was prepared for which 296.5 mg of NH_4Cl salt was dissolved in 1000 mL Type-I water to get 100 mg/L as NH_4^+. From 100 mg/L as NH_4^+ solution, 10 mg/L as NH_4^+ was prepared through serial dilution. For calibration, the probe was attached to the handheld device in which the input for calibration was given. After the calibration, the probe was cleaned each time with Type-I water before dipping in the sample for measuring the NH_4^+ concentration. During this procedure, sample distillation is not required.

3.3.11 Coloured dissolved organic matter (CDOM)

CDOM was determined in the samples with the help of CDOM optical electrode mounted on Aquaread AQUAPROBE AP-7000 which was calibrated against the CDOM standard solution. The instrument was calibrated at two points, zero and 100 μg/l using Aquaread's CDOM-CAL solution provided by the manufacturer. For calibration, the probe was attached to the handheld device in which the input for calibration of CDOM was given. After the calibration, the probe was cleaned each time with Type-I water before dipping in the sample for measuring the CDOM concentration. The observations provided by the instrument was noted.

3.3.12 Total Kjeldahl's Nitrogen (TKN)

Ammonia of mineral origin is rare in natural waters. The most important source of ammonia in natural water is the ammonification of organic matter. Sewage is also an important source of ammonia. TKN process was used to analyse the organic nitrogen as well as ammonia in the wastewater sample. A micro Kjeldahl unit was used during the study to determine ammoniacal nitrogen in the samples. APHA 4500-NH_3 was followed for the preparation of reagents. 4% Borax buffer was prepared by adding 4.0 g of borax $Na_2B_4O_7$ in 100 mL of distilled water and heating it to mix the crystals well. Mixed indicator was prepared using bromocresol green (0.5%) and methyl red (0.1%) in 2:1 ratio in ethyl alcohol and volume was made upto 100 mL. Boric acid and mixed indicator solution was prepared using 4 g of boric acid and 5 mL of mix indicator followed by making total volume to 100 mL using distilled water. 0.01 N HCl was used as the titrant. First 1 N HCl solution was prepared using dilution and then it was further diluted in series to get 0.01 N HCl. For digestion of sample, 10 mL of sample was taken and 1 mL of borax was added for its digestion in micro TKN unit. 5 mL of mixed indicator was taken in another test tube where ammoniacal nitrogen is being collected as coming out from the condensation unit. The collected sample was titrated using 0.01 N HCl in which the end point is blue to wine red colour. The concentration of TKN (mg/L) was calculated using the following equation (3.3)

$$TKN\ (mg/l) = \frac{(Volume\ of\ titrant\ in\ ml) \times (normality\ of\ titrant) \times 14 \times 1000}{(Volume\ of\ sample\ taken\ in\ ml)} \qquad \textbf{(3.3)}$$

3.3.13 Nitrate (NO_3^-)

The presence of nitrate in the samples were determined using a double beam spectrophotometer LABINDIA make (Model: UV3092). The test procedure conforms to APHA 4500-NO_3^-. Initially, stock nitrate solution was prepared by mixing 721.8 mg of KNO_3^- in 1000 mL Type-I water. The stock solution was further diluted to 100 mg/L followed by 10 mg/L as NO_3^-. Using 10 mg/L as NO_3^- standard solution, lower strength standard solution of 1.0 mg/L, 2.0 mg/L, 3.0 mg/L, 4.0 mg/L, and 5.0 mg/L as NO_3^- was prepared. The calibration of instrument was done using the prepared standard solutions at 220 nm wavelength for which 10 mL standard solution was taken in a test tube and 0.2 mL 1.0 N HCl was added to it. The instrument was set to zero absorbance after placing sample in a cuvette which was filled with 0.2 mL 1.0 N HCl in 10 mL distilled water solution. The sample and standards were acidified by adding 0.2 mL of 1.0 N HCl in order to prevent interference from hydroxide or carbonate concentrations. The standard curve was prepared by the instrument software after calibration was over. For the analysis of stormwater runoff samples, 10 mL of each sample was taken in a test tube in which 0.2 mL of 1.0 N HCl was added followed by mixing the sample gently and taking the readings on spectrophotometer at wavelength of 220 nm. The reading of nitrate concentration for each sample was noted in register.

3.3.14 Phosphate (PO_4^{3-})

The presence of phosphates in the samples was determined with the help of stannous chloride method using LABINDIA make (Model: UV3092) UV-VIS spectrophotometer. The test procedure conforms to APHA 4500-P in which the absorbance was taken at 690 nm. This method follows the principle that molybdophospheric acid is formed which is reduced by stannous chloride to give blue coloured solution. For calibration, standard solution was prepared initially by mixing 143.3 mg of KH_2PO_4 in 1000 mL Type-I water to get 100 mg/L as PO_4^{3-}. This standard solution was diluted serially to get 1.0 mg/L as PO_4^{3-}. This solution was used to prepare standards ranging between 0.1 mg/L to 0.9 mg/L as PO_4^{3-}. The instrument was calibrated for phosphates standards of known strength of 0.1 mg/L, 0.2 mg/L, 0.3 mg/L, 0.4 mg/L, 0.5 mg/L, 0.6 mg/L, 0.7 mg/L, 0.8 mg/L, 0.9 mg/L, and 1.0 mg/L as PO_4^{3-}. Ammonium molybdate and stannous chloride were used as the reagents during phosphate analysis. Ammonium molybdate was prepared by taking 25.0 g of ammonium molybdate salt and dissolving it in 175 mL of Type-I water. In a separate conical flask, 280 mL of concentrated sulphuric acid was added to to 400 mL of distilled water. It was given some rest to cool since the reaction is exothermic. The above two solutions were mixed and the final volume was made to 1 litre. For preparation of stannous chloride, 2.5 g of stannous chloride was taken and it was dissolved in 100 mL of glycerol. The solution was heated over heating mantle with intermittent mixing using a glass rod until the mix appears transparent. Before initiating calibration, the instrument was set to zero absorbance by placing the cuvette having blank solution which was a mix of 10 mL distilled water with

0.4 mL ammonium molybdate and 2 drops of $SnCl_2$. For calibration, 10 mL of each standard solution was taken in test tubes in which 0.4 mL ammonium molybdate and 2 drops of $SnCl_2$ was added and was given a gentle mix until blue colour appears. The time interval between mixing of reagents and taking absorbance on the instrument was kept equal for all the standards and samples. The absorbance of each known standard solution was taken for plotting the calibration graph. After the calibration is over, 10 mL of each of the samples were taken in which 0.4 mL ammonium molybdate and 2 drops of $SnCl_2$ was added, followed by its mixing. As the blue colour appears, the absorbance in the instrument was taken at wavelength of 690 nm on a spectrophotometer to get phosphate concentration in mg/L.

3.3.15 Sulphate (SO_4^{2-})

The presence of sulphates in the samples were determined with the help of turbidity method using a double beam spectrophotometer LABINDIA make (Model: UV3092). The test procedure conforms to APHA 4500-SO_4^{2-} in which the absorbance was taken at 420 nm. For preparing standard sulphate solution of 100 mg/L as SO_4^{2-}, 147.9 mg of Na_2SO_4 was mixed in 1000 mL Type-I water. After the standard solution was prepared, lower strength of standard solution was prepared through serial dilution to get 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L as SO_4^{2-}. Conditioning reagent solution was used as standard reagent and barium chloride salts was also used. Conditioning reagent was prepared by adding 75 g of NaCl and 30 mL concentrated HCl in 100 mL 95% ethyl alcohol and by making its volume to 300 mL with distilled water followed by addition of 50 mL glycerol. A blank solution was prepared by taking 10 mL of Type-I water in a clean test tube and adding 0.4 mL of conditioning reagent and pinch of $BaCl_2$ and giving it a gentle mix. Before calibration was initiated, the instrument was set at zero absorbance after placing the cuvette having blank solution. For calibration, 10 mL of each standard solution was placed in clean test tubes in which 0.4 mL of conditioning reagent and pinch of $BaCl_2$ was added. The time interval between addition of reagents and taking absorbance in the instrument was kept equal for each standard solution and samples. After calibration was completed, calibration graph was obtained which was used for analysis of samples. During analysis of samples, 10 mL of each sample was taken in clean test tube in which 0.4 mL of conditioning reagent and pinch of $BaCl_2$ was added followed by its mixing. The readings in mg/L were noted as provided by spectrophotometer at wavelength of 420 nm.

3.3.16 Chloride (Cl^-)

The measurement of chloride involves the direct potentiometric measurement. Aquaread AQUAPROBE AP-7000 was used with solid state ion specific electrode (ISE) for chloride. This method conforms to APHA 4500-Cl^-. The standard chlorine solution was prepared by mixing 164.9 mg of NaCl in 1000 mL Type-I water to get 100 mg/L as Cl^-. Followed by this, 10 mg/L as Cl^- solution was prepared by serial dilution. The instrument with ISE was calibrated at 10 mg/L and 100 mg/L with the sensor specific calibration solution, while the third point intended to characterise the effect of temperature on that specific sensor. The third point is a second calibration at 10 mg/L in which this calibration point was at least 10 degrees colder than the initial point. The instrument was cleaned with Type-I water every time before it was used to for analysing chloride in samples. The instrument provided the strength of chlorides in mg/L which was noted.

3.3.17 Total nitrogen (TN)

Total nitrogen was analysed using Shimadzu TOC analyzer/TOC-LCPH at 720 °C during which TN decompose to nitrogen monoxide (NO). The instrument was calibrated using the standard total nitrogen solution. Standard TN solution was prepared by adding 7.219 g of potassium nitrate (KNO_3) in 1000 mL Type-I water. The calibration was done automatically with auto dilution of standard TN solution. Following the calibration, the samples were analysed for TN concentration and the strength given was noted.

3.3.18 Total organic carbon (TOC)

Total organic carbon was analysed using Shimadzu TOC analyzer/TOC-LCPH which conforms to APHA 5310 Total organic carbon (TOC). The instrument decomposes the organic matter by oxidation and measures the carbon dioxide generated. The instrument was calibrated using standard solution of total carbon (TC) and inorganic carbon (IC). The TC standard solution of strength 1000 mg/L was prepared by adding 2.125 g of potassium hydrogen phthalate ($C_8H_5KO_4$) in 1000 mL Type-I water. Similarly, IC standard solution of strength 1000 mg/L was prepared by adding 3.497 g of sodium hydrogen carbonate ($NaHCO_3$) and 4.412 g of sodium carbonate (Na_2CO_3) in 1000 mL Type-I water. The instrument was calibrated for TC and IC automatically with auto dilution, and TOC is measured as a difference between TC and IC using the instrument. Following calibration, the TOC strength in sample was analysed and noted.

3.3.19 Total Hardness

Total hardness of the samples was calculated using EDTA Titrimetric Method in which EDTA (Ethylenediaminetetraacetic acid) was used as a titrant. This test procedure conforms to APHA 2340 test for hardness in water samples. EDTA solution was prepared by adding 3.72 g of EDTA salt in 1000 mL distilled water to get 0.01 M EDTA solution. Ammonium buffer is another reagent which was prepared by dissolving 67.6 g of NH_4Cl salt in distilled water and by adding 570 mL ammonium solution to it and making the final volume to 1000 mL. During sample analysis, 20 mL of sample was taken, and 1 mL of freshly prepared ammonium buffer was added to it followed by adding pinch of Eriochrome Black-T (EBT) indicator which gives it a wine-red colour. After the titration, the end point was indicated when the sample turns blue. Total hardness as $CaCO_3$ in mg/L can be calculated by using the formula given in equation (3.4) below

$$Total\ hardness\ as\ CaCO_3\ (mg/l) = \frac{(volume\ of\ EDTA\ used\ in\ ml) \times 1000}{volume\ of\ sample\ in\ ml} \qquad \textbf{(3.4)}$$

3.3.20 Alkalinity

The alkalinity of the water samples was determined by titrimetric method which conforms to APHA 2320. The reagent used are 0.05 % methyl orange indicator, 0.02 N sulphuric acid, and phenolphthalein indicator. The methyl orange indicator was prepared by dissolving 0.5 g of methyl orange in 1000 mL distilled water, while phenolphthalein indicator was prepared by dissolving 5.0 g phenolphthalein in 500 mL ethyl alcohol and by adding 0.02 N NaOH dropwise such that as the pink colour appears, the volume was made to 1000 mL using distilled water. 0.02 N sulphuric acid was prepared from concentrated H_2SO_4 through serial dilution. During analysis, 20 mL of sample was taken in a conical flask and 2 drops of phenolphthalein indicator was added to it. If pink colour appears, it was titrated with 0.02 N H_2SO_4 to get colourless solution which is the end point of titration and the volume of titrant used was noted. Into the same flask, 2 drops of methyl orange indicator were added and titrated with 0.02 N H_2SO_4. The end point of the titration was represented by change of colour from orange to reddish orange. Total alkalinity as $CaCO_3$ in mg/L can be calculated using the equation (3.5) given below

$$Total\ alkalinity\ as\ CaCO_3 (mg/l) = \frac{(volume\ of\ titrant\ used\ in\ ml) \times 0.02N \times 1000 \times 50}{volume\ of\ sample\ in\ ml} \quad \textbf{(3.5)}$$

The alkalinity in terms of CO_3^{2-} and HCO_3^- can be computed using the formula given below

$$CO_3^{2-}(mg/l) = \frac{2a \times N \times (equivalent\ weight\ of\ CO_3^{2-}) \times 1000}{volume\ of\ sample\ in\ ml} \quad \textbf{(3.6)}$$

$$HCO_3^-(mg/l) = \frac{(b-2a) \times N \times (equivalent\ weight\ of\ HCO_3^-) \times 1000}{volume\ of\ sample\ in\ ml} \quad \textbf{(3.7)}$$

Where, a is volume (mL) of titrant used for phenolphthalein alkalinity, b is volume (mL) of titrant used for total alkalinity.

3.3.21 Cobalt (Co)

The presence of Co in samples was detected over atomic absorption spectrophotometry (AAS) using Analytik Jena make AAS (Model: novAA 350). The test procedure conforms to APHA 3500-Co. Initially, the standard stock Co solution of strength 100 mg/L as Co was prepared by mixing 422.9 mg cobalt acetate tetrahydrate $(CH_3COO)_2.Co.4H_2O$ with 1 mL conc. HCl and volume was made upto 1000 mL using Type-I water. The standard stock solution was further diluted through serial dilution to get lower strength standards ranging between 0.1 mg/L to 2 mg/L as Co. The instrument was then turned on and element specific hollow cathode lamp (HCL) was selected. The flame gases for Co were air and acetylene. The flame was ignited and method was developed for Co using the instrument software. The standard solutions were aspirated and calibration was carried out. Followed by calibration, the samples were aspirated to get Co concentration in mg/L.

3.3.22 Chromium (Cr)

The presence of Cr in samples was determined over atomic absorption spectrophotometry (AAS) using Analytik Jena make AAS (Model: novAA 350). The test procedure conforms to APHA 3500-Cr. Initially, the standard Cr solution of strength 100 mg/L as Cr was prepared by mixing 565.8 mg potassium dichromate $(K_2Cr_2O_7)$ with 1.0 mL conc. HNO_3 and the volume was made upto 1000 mL using Type-I water. The standard solution was further diluted through serial dilution to get standards ranging between 0.1 mg/L to 5 mg/L as Cr. The instrument was then turned on and element specific hollow cathode lamp (HCL) was selected. The flame gases for Cr were air and acetylene. The flame was ignited and method was developed for Cr using the instrument software. The standard solutions were aspirated and calibration was carried out. Followed by calibration, the samples were aspirated and Cr concentration in mg/L was noted.

3.3.23 Cadmium (Cd)

The presence of Cd in samples was determined over atomic absorption spectrophotometry (AAS) using Analytik Jena make AAS (Model: novAA 350). The test procedure conforms to APHA 3500-Cd. Initially, the standard Cd solution of strength 100 mg/L as Cd was prepared by mixing 163.1 mg cadmium chloride ($CdCl_2$) with 20 mL 1:1 HNO_3 and the volume was later made upto 1000 mL using Type-I water. The standard solution was further diluted through serial dilution to get standards ranging between 0.1 mg/L to 1 mg/L as Cd. The instrument was turned on and element specific hollow cathode lamp (HCL) was selected. The flame gases for Cd were air and acetylene. The flame was ignited and method was developed for Cd using the instrument software. The standard solutions were aspirated and calibration was carried out. Followed by calibration, the samples were aspirated to get Cd concentration in mg/L.

3.3.24 Copper (Cu)

The presence of Cu in samples was determined over atomic absorption spectrophotometry (AAS) using Analytik Jena make AAS (Model: novAA 350). The test procedure conforms to APHA 3500-Cu. Initially, the standard Cu solution of strength 100 mg/L as Cu was prepared by mixing 392.9 mg copper sulphate pentahydrate ($CuSO_4.5H_2O$) in 1000 mL Type-I water. The standard solution was further diluted through serial dilution to get standards ranging between 0.1 mg/L to 5 mg/L as Cu. Followed by this, the instrument was turned on and element specific hollow cathode lamp (HCL) was selected. The flame gases for Cu were air and acetylene. The flame was ignited and method was developed for Cu using the instrument software. The standard solutions were aspirated and calibration was carried out. Followed by calibration, the samples were aspirated and Cu concentration in mg/L was noted.

3.3.25 Zinc (Zn)

The presence of Zn in samples was detected over atomic absorption spectrophotometry (AAS) using Analytik Jena make AAS (Model: novAA 350). The test procedure conforms to APHA 3500-Zn. Initially, the standard Zn solution of strength 100 mg/L as Zn was prepared by mixing 100 mg zinc metal flakes with 20 mL 1:1 HCl and making the volume to 1000 mL using Type-I water. The standard solution was further diluted through serial dilution to get standards ranging between 0.1 mg/L to 1 mg/L as Zn. The instrument was turned on and element specific hollow cathode lamp (HCL) was selected. The flame gases for Zn were air and acetylene. The flame was ignited and method was developed for Zn using the instrument software. The standard solutions were aspirated and calibration was carried out. Followed by calibration, the samples were aspirated to get Zn concentration in mg/L was noted.

3.3.26 Iron (Fe)

The presence of Fe in samples was determined over atomic absorption spectrophotometry (AAS) using Analytik Jena make AAS (Model: novAA 350). The test procedure conforms to APHA 3500-Fe. Initially, the standard Fe solution of strength 100 mg/L as Fe was prepared by mixing 702.2 mg ammonium ferrous sulphate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) with 1.0 mL conc. HNO_3 and making the volume to 1000 mL using Type-I water. The standard solution was further diluted through serial dilution to get standards ranging between 0.1 mg/L to 5 mg/L as Fe. The instrument was turned on and element specific hollow cathode lamp (HCL) was selected. The flame gases for Fe were air and acetylene. The flame was ignited and method was developed for Fe using the instrument software. The standard solutions were aspirated and calibration was carried out. Followed by calibration, the samples were aspirated to get Fe concentration in mg/L.

3.3.27 Lead (Pb)

The presence of Pb in samples was detected over atomic absorption spectrophotometry (AAS) using Analytik Jena make (Model: novAA 350). The test procedure conforms to APHA 3500-Pb. Initially, the standard Pb solution of strength 100 mg/L as Pb was prepared by mixing 159.8 mg lead nitrate ($Pb(NO_3)_2$) with 20 mL 1:1 HNO_3, followed by making volume to 1000 mL using Type-I water. The standard solution was further diluted through serial dilution to get standards ranging between 0.1 mg/L to 2 mg/L as Pb. The instrument was turned on and element specific hollow cathode lamp (HCL) was selected. The flame gases for Pb were air and acetylene. The flame was ignited and method was developed for Pb using the instrument software. The standard solutions were aspirated and calibration was carried out. Followed by calibration, the samples were aspirated to get Pb concentration in mg/L and the concentration was recorded.

3.4 Source characterization of wet precipitation

Based on the results obtained for characterisation of wet precipitation, the relative abundance of acidic and alkaline ionic species, enrichment factor (EF), neutralization factor (NF), and source characterisation were also calculated. Enrichment factor for any species X in rainwater was calculated using equation (3.8):

$$\mathbf{EF_x = \{[X/Na]_{rain}\} / \{[X/Na]_{seawater}\}} \qquad \mathbf{(3.8)}$$

where, $[X/Na]_{rain}$ is the ratio of concentration of species X and sodium in rainwater.

Neutralization factor (NF_x) is another expression for any species X and was calculated for validating the neutralization of acids by bases using (3.9):

$$\mathbf{NF_x = [X] / [NO_3^- + SO_4^{2-}]} \qquad \mathbf{(3.9)}$$

To assess the role of local sea-salt resuspension or marine contribution towards the rain water quality, the non-sea-salt fraction (NSSF) of any species X in the rainwater was calculated using equation (3.10):

$$\mathbf{NSSF_x = [X_{rain}] - \{[Na_{rain}] * [X_{seawater} / Na_{seawater}]\}} \qquad \mathbf{(3.10)}$$

where, X_{rain} is the concentration of species X in rainwater, Na_{rain} is the concentration of sodium in rainwater.

3.5 Ion exchange

The study using cation exchange resins was conducted to assess its effectiveness towards removal of hardness from stormwater runoff at varying doses. For this purpose, the cation exchange resins were procured from Gokul Water Technologies, Delhi. Three columns were taken in which 0.5 g, 1.0 g, and 2.0 g of the resin was added such that the quantity of resin is just double the previous one. The flow rate was adjusted using three roller clamp one for each column. The hard water was supplied from constant head reservoir placed in the lab. The hardness of strength 1000 mg/L in synthetically prepared stormwater runoff was introduced using analytical grade $CaCO_3$ salt. The samples from each column were analysed at an interval of 30 minutes to check residual hardness. Once the resins are exhausted, it was regenerated using brine solution of strength 5% NaCl in which the resins were dipped for 24 hours and it was given a stirring. Next cycle of re-generated resin was run to again assess its efficacy towards removal of hardness from stormwater runoff.

3.6 Preparation of biochar

Old refused bamboo was collected from the university campus which was cleaned thoroughly with Type-I water. The pieces were cut out of it to prepare biochar in bulk quantity to have homogeneous characteristics. The bamboo samples were then dried in a hot air oven for 24 hours at 105 °C. The dried samples were then placed inside a muffle furnace at 500 °C for 30 minutes for torrefaction in an air-tight chamber to ensure the presence of zero oxygen. The temperature was raised in the muffle at a rate of 16.67 °C /minute for 30 minutes to attain a final pyrolysis temperature of 500 °C. The biochar so formed was allowed to cool freely inside the muffle. The produced biochar was crushed and passed through IS 4.75 mm sieve but retained on IS 2.35 mm sieve, which was the chosen grain size range for treatment. A solution of $FeCl_3$ of strength 1%, 5%, and 10% was prepared in which an equal quantity of prepared biochar was added. It was subjected to shaking in a bench-top shaker at an RPM of 150 and the temperature was set at 27 °C for 24 hours. In addition, one set of experiments were conducted with untreated biochar. This biochar impregnated with Fe(III) was then washed thrice thoroughly with Type-I water. It was then dried in a hot air oven at 105 °C for 24 hours. The untreated biochar is indicated with B0%, while biochar having 1%, 5%, and 10% $FeCl_3$ is named as B1%, B5%, and B10%, respectively. The percentage yield and the cost associated with the preparation of biochar were also calculated.

3.7 Characterisation of biochar

3.7.1 Proximate analysis

To estimate the moisture, volatile, fixed carbon and ash content of both biochar and raw bamboo, proximate analysis was conducted following ASTM (ASTM E871-82, ASTM E1755-01, ASTM E872-82) standard methods using ELTRA - Thermogravimetric Analyzer (manufacture in Germany). The temperature for moisture, volatile, fixed carbon, and ash content was fixed at 105 °C, 915 °C, 750 °C, and 750 °C, respectively. The thermogravimetric analysis was conducted using 1100 ± 10 mg of samples in the crucibles.

3.7.2 Elemental analysis

Elemental analysis was performed for the determination of carbon, hydrogen, nitrogen, and sulphur (CHNS) using Eurovector - EuroEA3000 Series elemental analyser at 950 °C. The calibration was conducted using L-Cystine as the reference standard material in tin capsules. CHNS analysis was conducted in duplicates using ≈ 2.5 mg samples in tin capsules.

3.7.3 Fourier Transform Infrared (FTIR) Spectroscopy

A non-destructive method was used to identify the various functional groups which are present in biochar. The FTIR was conducted for Fe (III) modified biochar and untreated biochar, before and after the experiments, to characterize the functional groups present. A Thermo Fisher Nicolet spectrometer enabled with KBr beam splitter was used in the mid-infrared region. All the samples were ground in a mortar pestle which was cleaned thoroughly with an organic solvent. Sample pellets were prepared in the ratio of 1:10 with KBr. Spectra of KBr were run initially to cancel out its effect and its spectrum in the final results. The spectra were collected in the range of 400 cm^{-1} and 4000 cm^{-1} with the resolution of 2 cm^{-1}.

3.7.4 Scanning Electron Microscopy (SEM)

A non-destructive method for Scanning Electron Microscopy was performed using Zeiss EVO 18 special (Zeiss, Germany). The biochar samples were used to analyse its structure before and after the adsorption in the experiment. The samples were dried in a hot air oven for 24 hours and then it was visualised on the copper coated grid after gold coating between 750x and 1500x magnification.

3.8 Nutrient removal study using biochar

Three combinations of concentration for both phosphate (PO_4^{3-}-P) and nitrate (NO_3^--N) were selected while preparing the mixed synthetically prepared stormwater runoff. Phosphate and nitrate were present in the mixed synthetically prepared stormwater having the concentration as 2mg/L PO_4^{3-}-P, 25mg/L NO_3^--N; 5mg/L PO_4^{3-}-P, 50mg/L NO_3^--N; and 10mg/L PO_4^{3-}-P, 75mg/L NO_3^--N. Initially, a dose of 1.0g/l of biochar was introduced for the treatment which was later increased to 5.0 g/l dose of biochar. The experiments were conducted in triplicates in a conical flask having 200 mL of synthetically prepared stormwater runoff and the respective doses of biochar. The sample with biochar was subject to shaking at 150 RPM at 27°C. 1.0 mL sample was extracted at every 1-hour time interval. Readings of pH, electrical conductivity, and total dissolved solids (TDS) were noted using Labman make (LMMP 30 model) bench-top multiparameter before and after the end of the experiment. The residual concentrations of phosphate was determined over single beam at λ_{max}= 690 nm (Labtronics make LT-290 Model) spectrophotometer and at λ_{max}= 220 nm for nitrate using double beam UV-Vis (Lab India make UV 3092 Model) spectrophotometer.

The removal efficiency of nutrients from synthetic and real stormwater runoff were calculated using the equation (3.11) given below:

$$\%\, Removal\ efficiency = \left[\frac{C_i - C_e}{C_i}\right] \times 100 \qquad \textbf{(3.11)}$$

Where C_i is the initial concentration in mg/L; C_e is the concentration after treatment in mg/L. The removal efficiency was calculated based on the extraction of samples at an interval of 1 hour which was extracted for up to 4 hours.

3.9 Adsorption Isotherm for biochar

To find the adsorption isotherm, both Langmuir and Freundlich isotherm models were applied. Langmuir isotherm in its linear form is represented by equation (3.12)

$$\frac{1}{q_e} = \frac{1}{K_L q_{max}} \frac{1}{C_e} + \frac{1}{q_{max}} \qquad \textbf{(3.12)}$$

Where q_e is the adsorption capacity of biochar at equilibrium in mg/g; q_{max} is the maximum adsorption capacity of biochar in mg/L; K_L is Langmuir's isotherm constant (L/mg).

The separation factor R_L is given by equation (3.13)

$$R_L = \frac{1}{1+C_i \times K_L} \qquad \textbf{(3.13)}$$

Where, R_L is Langmuir constant indicating the adsorption possibility which can be either favourable ($0 < R_L > 1.0$), unfavourable ($R_L > 1.0$), linear ($R_L = 1.0$) or irreversible ($R_L =0$).

Fruendlich isotherm in its linear form is represented by equation (3.14):

$$logq_e = logK_f + \frac{1}{n} logC_e \qquad \textbf{(3.14)}$$

Where, q_e is the adsorption capacity of biochar in at equilibrium mg/g; K_f is the Freundlich's constant ((mg/g) (L/mg)1/n); C_e is the concentration of nutrient at equilibrium after treatment in stormwater runoff in mg/L. In general, adsorption isotherm distinguishes the surface properties and affinity to adsorb the adsorbate.

3.10 Kinetics of removal for biochar

To find the kinetics of nutrient removal, pseudo-first order and pseudo-second order models were applied. Pseudo-first order kinetic model is given by equation (3.15)

$$\log(q_e - q_t) = logq_e - \frac{K_1 t}{2.303} \qquad \textbf{(3.15)}$$

Where q_e is the adsorption capacity of biochar at equilibrium in mg/g; q_t is the adsorption capacity of biochar in mg/g at any time t; K_1 is pseudo-first order rate constant (min^{-1}).

Pseudo-second order kinetic model is given by equation (3.16)

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad \textbf{(3.16)}$$

Where q_e is the adsorption capacity of biochar at equilibrium in mg/g; K_2 is pseudo-second order rate constant (g mg^{-1} min^{-1}) and t is time in minutes.

3.11 Adsorption capacity of biochar

The adsorption capacity q_e (mg/g) of the biochar was calculated using the equation (3.17)

$$q_e = \left[\frac{C_i - C_e}{W}\right] \times V \qquad \textbf{(3.17)}$$

Where q_e is the adsorption capacity of biochar at equilibrium in mg/g; C_i is the initial concentration of nutrients in stormwater runoff in mg/l; C_e is the concentration of nutrients at equilibrium after treatment in stormwater runoff in mg/l; V is the volume of sample used for analysis in litre; and W is the quantity of absorbent in g.

The adsorption capacity of biochar for a dose of 5.0 g/l was calculated in batch experiments for varying strength of phosphate in synthetic and real stormwater runoff which varied from 2.0 mg/L to 10 mg/L, and 0.4 mg/L to 3.2 mg/L, respectively.

3.12 Identification of filter media

Following the characterisation of stormwater runoff in Delhi, different filter media were identified such as biochar, brick, hematite, calcite, limestone, and iron filing. These filter media were chosen because of their easy availability, strength, stability, permeability and cost. The experiments were conducted using each of the media both in batch process as well as in continuous flow in an acrylic pipe. The major pollutants which were identified in stormwater runoff were suspended solids and nutrients. The removal of suspended solids was studied in continuous column process while removal of nutrients was studied in both batch as well as in column process. The filter media passing through IS 4.75 mm sieve but retaining on IS 2.36 mm sieve were selected for the treatment process. The filter media was initially given washing with distilled water such that all the loose impurities from the surface gets removed and does not affect the results. Following the washing, the filter media was dried at 105 °C for 24 hours in a hot air oven.

3.13 Nutrient removal study (batch process)

In the batch process of treatment, stormwater runoff having phosphate strength of 5 mg/L as PO_4^{3-} was prepared synthetically in the lab considering the pollutants presents in real stormwater runoff. The synthetically prepared stormwater runoff with volume 100 mL was then placed in six different conical flasks, each one for biochar, brick, hematite, calcite, limestone, and iron filing. The dose of filter media was kept fixed at 5 g/L. These conical flasks were then placed in bench top orbital shaker with shaking RPM set at 150. At an interval of 1 hour, the 10 mL sample from each conical flask was taken in cleaned test tubes for analysis. The experimental process was repeated for five hours. The standard analysis procedure for phosphate was adopted to estimate the reduction of phosphate concentration. Also, the removal efficiency of nutrients and total organic carbon (TOC) was also determined for the real stormwater runoff originating from road/highways which was collected during monsoon season. The removal efficiencies of pollutant from synthetic and real stormwater runoff were calculated using the equation (3.11).

3.14 Column filter unit (continuous process)

A column filter was designed to study the efficacy of filter media towards the removal of pollutants from stormwater runoff when being operated continuously under the action of gravity, similar to field conditions. The experimental setup comprises of a transparent acrylic pipe having different filter media inside and was placed vertically in the lab. The bottom end was provided with a valve for sample collection while the top was kept open. The total height of the column was 120 cm while the internal diameter of the pipe was 10 cm, thus providing the cross-sectional area of 78.5 cm^2. The filter media was packed in layer one over another inside the pipe to a depth of 15 cm for each media (Fig. 3.2). Starting from bottom to top, brick, limestone, calcite, iron filing, and biochar was placed, while stone dust was placed at the top having thickness of 2.0 cm which was packed between limestone to prevent its resuspension and prevent its disturbance due to flowing water. The filter media passing through IS 4.75 mm sieve but retaining on IS 2.36 mm sieve were selected for bottom five filter media layer, whereas, media passing through IS 2.36 mm sieve but retaining on IS 1.18 mm sieve was selected for stone dust, thus reducing the size for voids. Following the packing for the filter media, the column was flushed with 5 L distilled water. Initially, the infiltration rate was 50 mm/minute or 400 mL/minute through the cross-section of vertical column filter. The sample was allowed to pass through the vertical column filter which was collected from the bottom after 10 minutes in a beaker. The filter was allowed to work for 60 minutes during which 6 samples were collected for each run. Also, total seven runs of real stormwater runoff were involved during the present study. The removal efficiency of pollutant from real stormwater runoff were calculated using the equation (3.11).

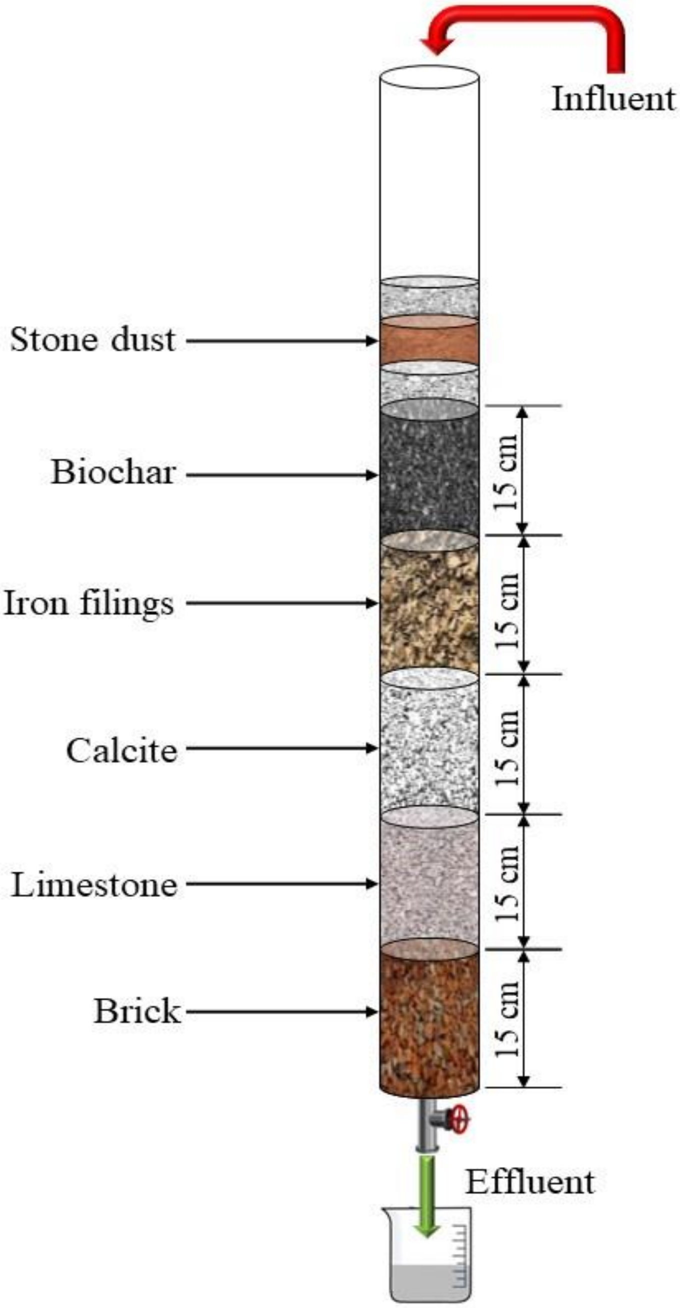

Fig. 3.2 Schematic experimental setup used to treat stormwater runoff through continuous column process

3.15 Pollutant removal study

The major pollutants identified were suspended solids and nutrients present in the stormwater runoff samples. The removal of suspended solids was studied majorly using the vertical column filter. However, the dissolved impurities such as nutrients present in stormwater runoff was studied using a bioretention system, bench scale constructed wetland (CW) cells. The major pollutant studied was removal of phosphate using three different types of macrophytes, namely, *Phragmites*, *Canna lily*, and *Cyperus alternifolius*. These emergent plant species were planted in individual wetland cells and retention time for stormwater runoff was provided to study their nutrient removal efficiency. Later, the efficacy of filter media and bioretention system was combined to develop a hybrid stormwater runoff treatment system.

3.16 Constructed wetland for pollutant removal

3.16.1 *Phragmites*-based CW Cell

The experiments were conducted for six months, dated from October, 2020 to April, 2021 on a constructed wetland made to work as a vertical sub-surface flow, located in Delhi Technological University (DTU), Delhi. *Phragmites* grass was taken out from the lake located within the campus of university. *Phragmites* was then again planted on the constructed wetland made up of brick masonry located strategically so as to replicate the natural conditions. This CW cell was filled with substrate media having a mixture of gravel-sand provided with a substrate media depth (d_s) of 0.35 m, and dimension of cell being 1.1 m in length (L), 0.80 m in width (B) with 0.45 m depth (H), thus the surface area (A) being 0.88 m^2 (Fig. 3.3).

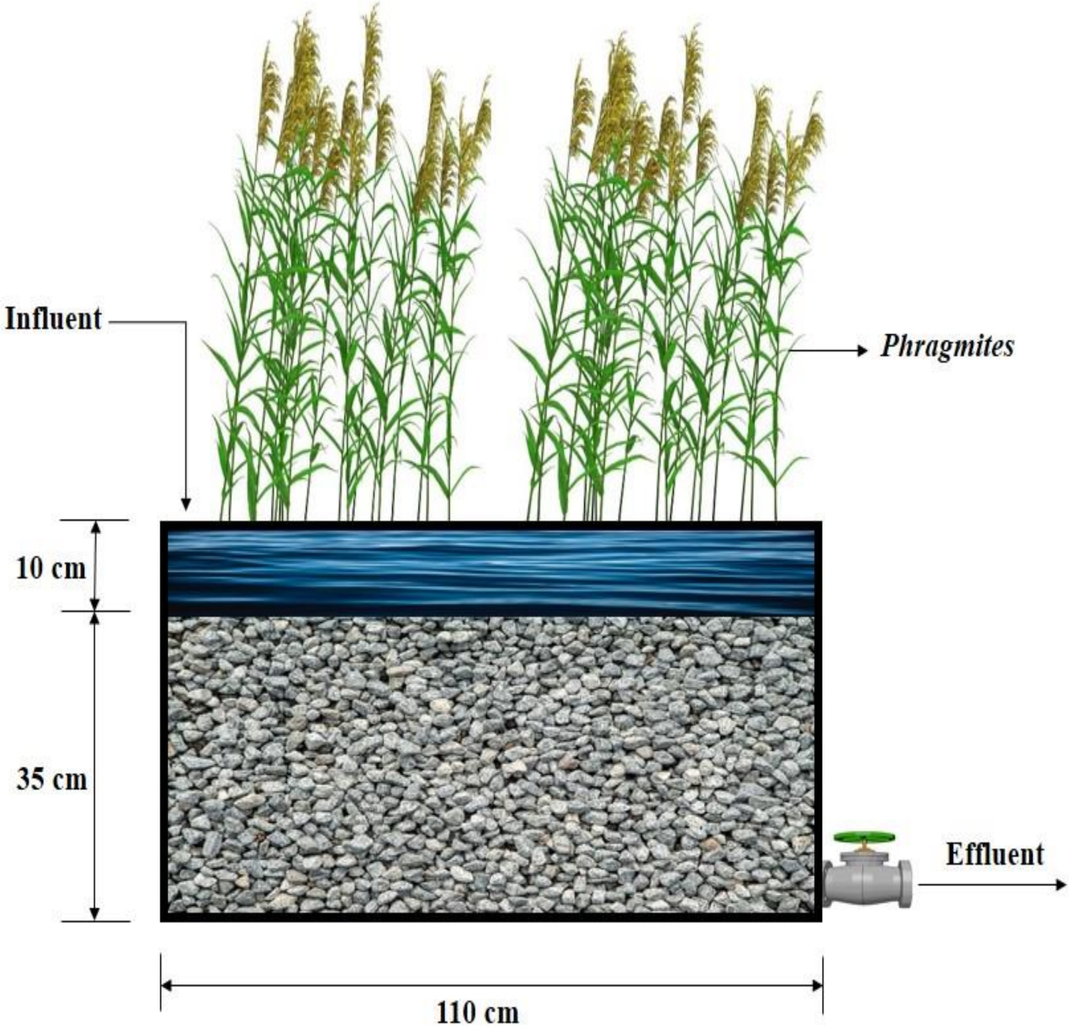

Fig. 3.3 Schematic diagram of *Phragmites*-based constructed wetland used during present study

The approximate volume (V) of the CW cell as determined was 400 litres. The media bed provided the suitable growth environment with easy root penetration, percolation of influent and gas exchange. Initially, 20 number of plant were planted in a grid pattern of 4x5 making the plant density of 22.7 plants/m^2 and a considerable time was given to *Phragmites* to adapt to its new habitat. In order to get stabilise to its new habitat, the CW cell was fed daily with water at the rate of

20 L/day. Fertilisers, such as, Di-ammonium phosphate and 50 g of urea were also fed in the system. Later, the system was fed with synthetically prepared stormwater runoff in the laboratory for which analytical grade di-hydrogen orthophosphate (KH_2PO_4) salt was used and dissolved in water. The synthetically prepared influent with initial phosphate concentration of 5mg/L as PO_4^{3-} which was later raised to 10mg/L and 20mg/L as PO_4^{3-}. Ammonium ions (NH_4^+) were also added to analyse the oxidation or reduction in system due to nitrification process. The synthetically prepared stormwater runoff was added every single day from the top in the morning, and the sample was collected next day from valve provided at the bottom of the CW cell before adding another batch in the morning, thus providing hydraulic retention time (HRT) of 24 hours. In order to conduct the study for phosphorous and nitrogen removal by *Phragmites*, 5 mg/L as PO_4^{3-} in spring season, 5 mg/L as PO_4^{3-} in winter season, 10 mg/L as PO_4^{3-} and 50 mg/L as NH_4^+ in spring; and 20 mg/L as PO_4^{3-} and 100 mg/L as NH_4^+ in summer season was added to the system. The concentration of phosphate was varied in order to determine the ability of *Phragmites* to remove the phosphates in varying concentration, and to assess its health and behaviour of the species towards the chemical shocks and threshold. Impact of variation of meteorological conditions, such as, ambient temperature, sunshine hours and rainfall were also studied.

After HRT of 24 hours, the sample collected from the valve provided at the bottom of the cell was analysed for phosphate as available phosphate (AP) and total phosphate (TP). Total Kjeldahl Nitrogen (TKN) was also assessed for organic nitrogen along with ammonia to find its presence in the wastewater sample. The sample was also analysed for the ratio of ferric to ferrous ion (Fe^{3+}/Fe^{2+}) in order to determine the reduction and oxidation state, if present in CW cell. The pollutant removal efficiencies were calculated using the equation (3.11).

3.16.2 *Canna lily*-based CW Cell

The study was undertaken from December 2021 to May 2022 for six months which included winter, spring and summer season using CW cells based on vertical flow located in Delhi, India. The study was undertaken. The CW cells were made up of HDPE drums in which *Canna lily* was planted. The top of drum was cut while the bottom remained intact. The bottom was provided with an outlet valve for collection of effluent. The internal diameter (D_i) of the CW cell was 0.55 m with overall height (H) of 0.43 m, thus, providing a surface area (A) of 0.24 m^2 and overall volume (V) of 0.1 m^3 (Fig. 3.4).

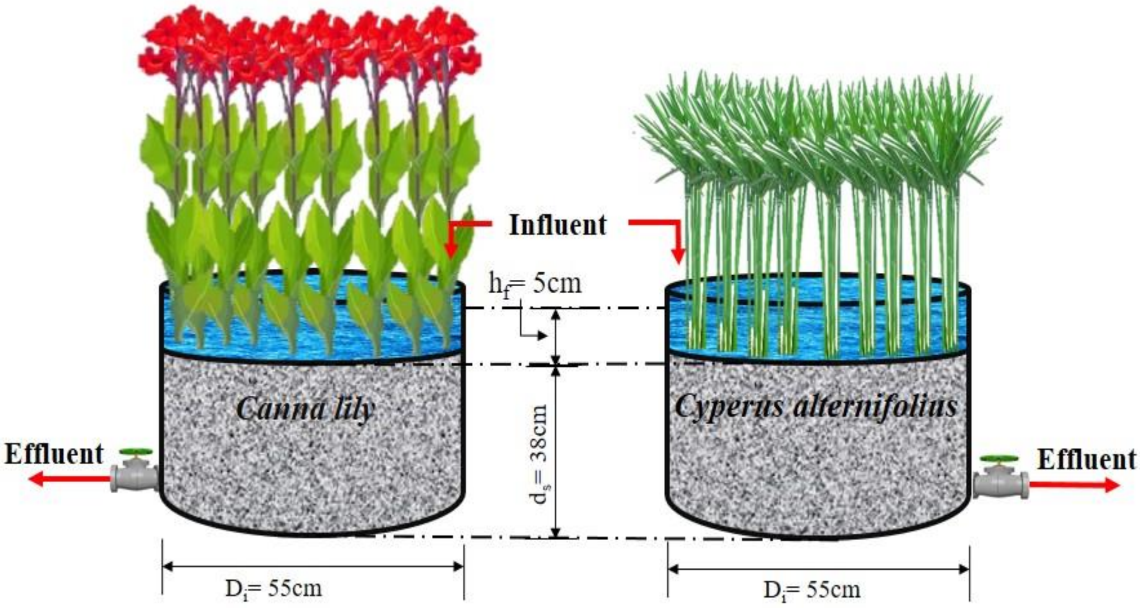

Fig. 3.4 Schematic diagram of *Canna lily* and *Cyperus alternifolius*-based constructed wetland used during present study

It was filled with substrate consisting of sandstone upto a depth (d_s) of 0.38 m having a freeboard (h_f) of 0.05 m in CW cell. The sieve analysis of the substrate was done as per ASTM D6913 (ASTM, 2009). Initially, plant density was 34 plants/m^2 which was later increased to 88 plants/m^2.

The CW cell was fed with 50 litres of water/day, urea and DAP initially and a considerable time was allowed for these *sp*. to get adapted to the new habitat. Following adaptation, the cell was flushed thoroughly with distilled water (100

L/day) followed by its flushing using Type-I (50 L/day) water continuously until no phosphate was obtained in the effluent of the CW cell before the start of experiment. During the study, the cell was irrigated with 50 L/day of synthetically prepared stormwater runoff for first 5 days and was reduced to feed of 17 L/day on daily basis for rest of the period. Synthetic stormwater runoff was prepared by using analytical grade potassium di-hydrogen orthophosphate (KH_2PO_4) salt dissolved in Type-I water. The strength of synthetically prepared runoff was kept at 5.0 mg/L PO_4^{3-}-P throughout the study. It was fed from the top of each CW cell as influent and was collected from the effluent valve provided at the bottom of each cell individually after an HRT of 24 hours, thus representing the down-gradient vertical flow. The samples of influent and effluent were collected on daily basis (HRT of 24 hours). Available phosphates (AP) and total phosphates (TP) were analysed for the collected samples in triplicates. The phosphate removal efficiency was calculated using equation (3.11). Meteorological data for, daily ambient temperature, sunshine hours, and rainfall were also obtained from Indian Meteorological Department (IMD), Delhi.

3.16.3 *Cyperus alternifolius*-based CW Cell

The study was undertaken for six months December 2021 to May 2022 using CW cells based on vertical flow which included winter, spring and summer seasons. The CW cells were made up of HDPE drums in which *Cyperus alternifolius* was planted. The top of drum was cut while the bottom remained intact. The bottom was provided with an outlet valve for collection of effluent. The internal diameter (D_i) of the CW cell was 0.55 m with overall height (H) of 0.43 m, thus, providing a surface area (A) of 0.24 m^2 and overall volume (V) of 0.1 m^3 (Fig. 3.4). It was filled with substrate consisting of sandstone upto a depth (d_s) of 0.38 m having a freeboard (h_f) of 0.05 m in CW cell. The sieve analysis of the substrate was done as per ASTM D6913 (ASTM, 2009). Initially, plant density was 42 plants/m^2 which was then increased to 261 plants/m^2.

The CW cell was fed with 50 litres of water/day, urea and DAP initially and a considerable time was allowed for these *sp*. to get adapted to the new habitat. Following adaptation, the cell was flushed thoroughly with distilled water (100 L/day) followed by its flushing using Type-I (50 L/day) water continuously until no phosphate was obtained in the effluent of the CW cell before the start of experiment. During the study, the cell was irrigated with 50 l/day of synthetically prepared stormwater runoff for first 5 days and was reduced to feed of 17 l/day on daily basis for rest of the period. Synthetic stormwater runoff was prepared by using analytical grade potassium di-hydrogen orthophosphate (KH_2PO_4) salt dissolved in Type-I water. The strength of synthetically prepared runoff was kept at 5.0 mg/L PO_4^{3-}-P throughout the study. It was fed from the top of each CW cell as influent was collected from the effluent valve provided at the bottom of each cell individually after an HRT of 24 hours, thus representing the down-gradient vertical flow. The samples of influent and effluent were collected on daily basis (HRT of 24 hours). Available phosphates (AP) and total phosphates (TP) were analysed for the collected samples in triplicates. The phosphate removal efficiency was calculated using equation (3.11). Meteorological data for, daily ambient temperature, sunshine hours, and rainfall were also obtained from Indian Meteorological Department (IMD), Delhi.

3.17 Development of hybrid filter

A bench-scale hybrid filter for the treatment of stormwater runoff was developed which comprised of filter media and bioretention system consisting of various macrophytes planted in individual cells. It was having six different cells which were divided by the baffle walls. The synthetically prepared stormwater runoff was following vertical up and down path for its flow while moving from one chamber to another. The stormwater runoff was fed from the first chamber from the top which was constituting purely filter media. Furthermore, following its path through bioretention system, the treated stormwater runoff was collected from the valve provided at the end of last chamber. Moreover, during continuous flow, the provision was made so that treated stormwater runoff can overflow and enter the drain from the last chamber. The width (B) of the entire treatment system was kept fixed at 0.6 m while the length (L) and height (H) varied for cells. Also, the height of succeeding cell was relatively lesser than the height of the previous cell in the direction of the flow.

The first cell was comprising of filter media which was placed in layers. The dimensions are such that its length (L) is 0.45 m and height (H) is 0.7 m, thus providing the surface area (A) of 0.27 m^2, and volume (V) as 0.19 m^3. Limestone being the bottom most layer, having thickness of 0.2 m, over which calcite having thickness of 0.2 m, and a layer consisting of biochar and iron filing having thickness of 0.1 m (Fig. 3.5). On top of all these, a 0.1 m thick layer of calcite was placed so that filter media bed doesn't get disturbed and biochar doesn't starts floating, thus making filter media as 0.6 m thick.

After the first cell of filter media, the following four cells were provided in which biological treatment method for which macrophytes are planted in a sequence of *Phragmites*, *Canna lily*, *Cyperus alternifolius*, and *Eichhornia* in individual cells. While *Phragmites*, *Canna lily*, and *Cyperus alternifolius* being emergent plant species, *Eichhornia* was the only floating species provided. The bed substrate of emergent plant species consists of majorly gravels of size 20 mm which are available easily in market. The depth of substrate for emergent plant species *Phragmites*, *Canna lily*, and *Cyperus alternifolius* was 0.45 m, 0.3 m, and 0.3 m, respectively.

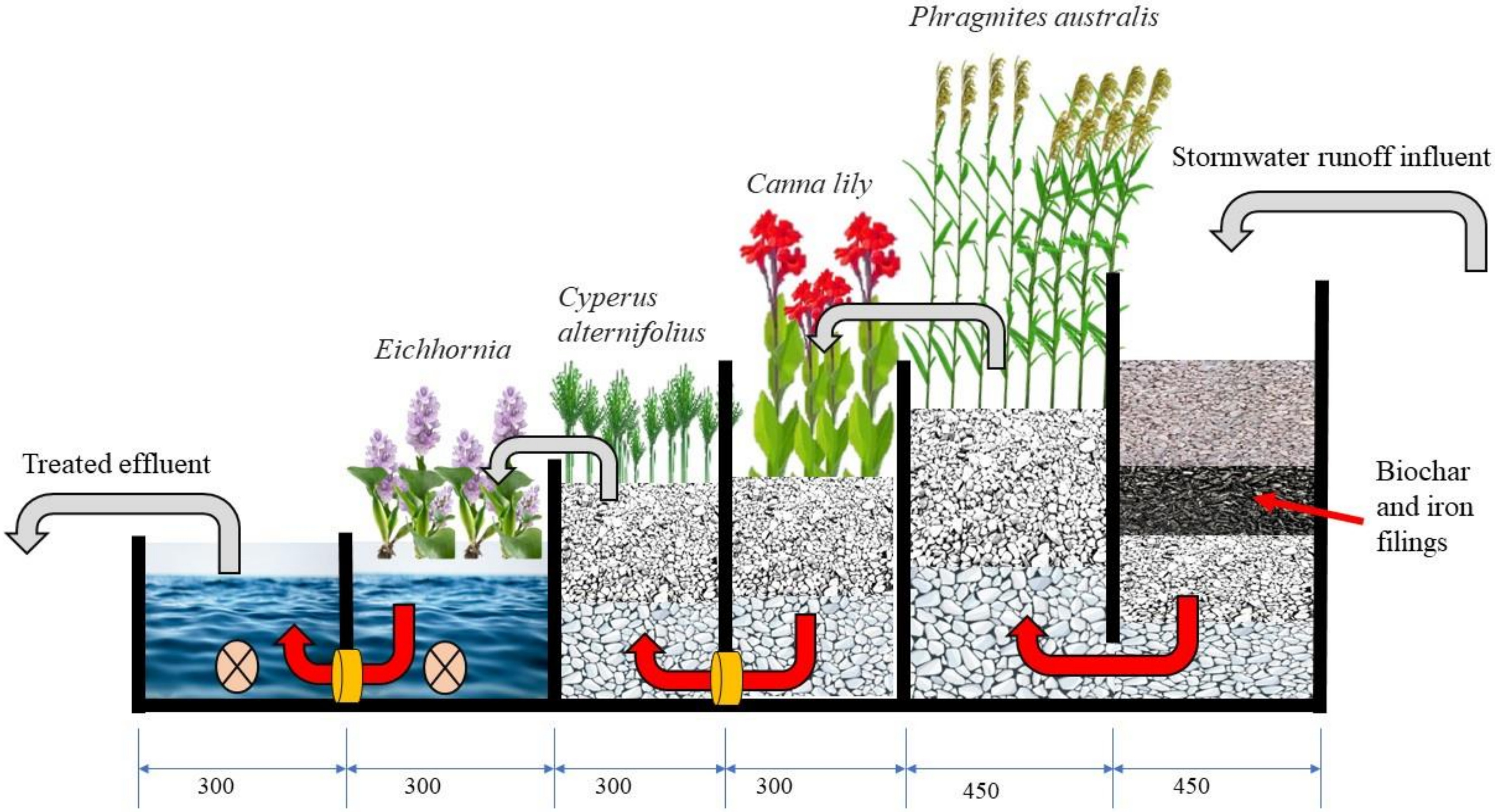

Fig. 3.5 Schematic diagram of hybrid filter system developed during the present study

3.18 Hybrid filter for pollutant removal study

As the macrophytes (*Phragmites*, *Canna lily*, *Cyperus alternifolius*, and *Eichhornia*) gets stabilised in the hybrid treatment system, the entire system was flushed initially with groundwater followed by its flushing with distilled water. During the experimentation, the system was fed with 80 litres synthetically prepared stormwater runoff which was prepared using garden soil in groundwater. The water was supplied continuously at 4 L/minute, and the outlet sample was collected from the valve provided at the effluent end after 20 minutes. The flow was kept continuous such that overflowing water exits the system from the very last cells. The parameters which were considered were TSS, phosphates, nitrates, TOC and TN. The pollutant removal efficiency of the system was calculated using the equation (3.11).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Physico-chemical characterization of rainwater and stormwater runoff samples

The present study aims to monitor the physico-chemical characteristics of both rainwater and stormwater runoff in Delhi, India, during year 2021 and 2022. The effect of different land use based on associated activity were studied towards finding the variations in the characteristics of samples.

4.1.1 Quality of rainwater

The physico-chemical characterization of rainfall revealed that most of the cationic and anionic species are present in trace concentration (Table 4.1). The average pH of rainwater was 6.6 ± 0.6 and 7.7 ± 0.2 during two rainfall events in year 2021, while, the average pH of rainwater during year 2022 was 7.3 ± 0.3 and 6.9 ± 0.4 for two different rainfall events revealing that alkaline species were available to neutralize acidic ions (SO_4^{2-} and NO_3^-). pH of 6.6 and 6.9 were observed during the present study owing to availability of acidic species present in atmosphere before monsoon and during intermediate rainfall events (due to higher level of air pollutants). The naturally originating alkaline species of crustal origin dominated during few monsoon rainfall events in year 2021 and 2022. The presence of higher level of alkaline species (Ca^{2+}, NH_4^+, Mg^{2+}, etc.) may be attributed towards alluvial nature of soil in Delhi region and its suspension in the atmosphere (Balachandran and Khillare 2001; Kulshrestha et al., 2003). Moreover, other similar studies on chemical composition of rainfall have confirmed the alkaline nature of suspended dust in Indian sub-continent (Khare et al., 2004). Also, no incident of acid rain ($pH < 5.6$) was observed in year 2021 and 2022 at any location during the study period in Delhi.

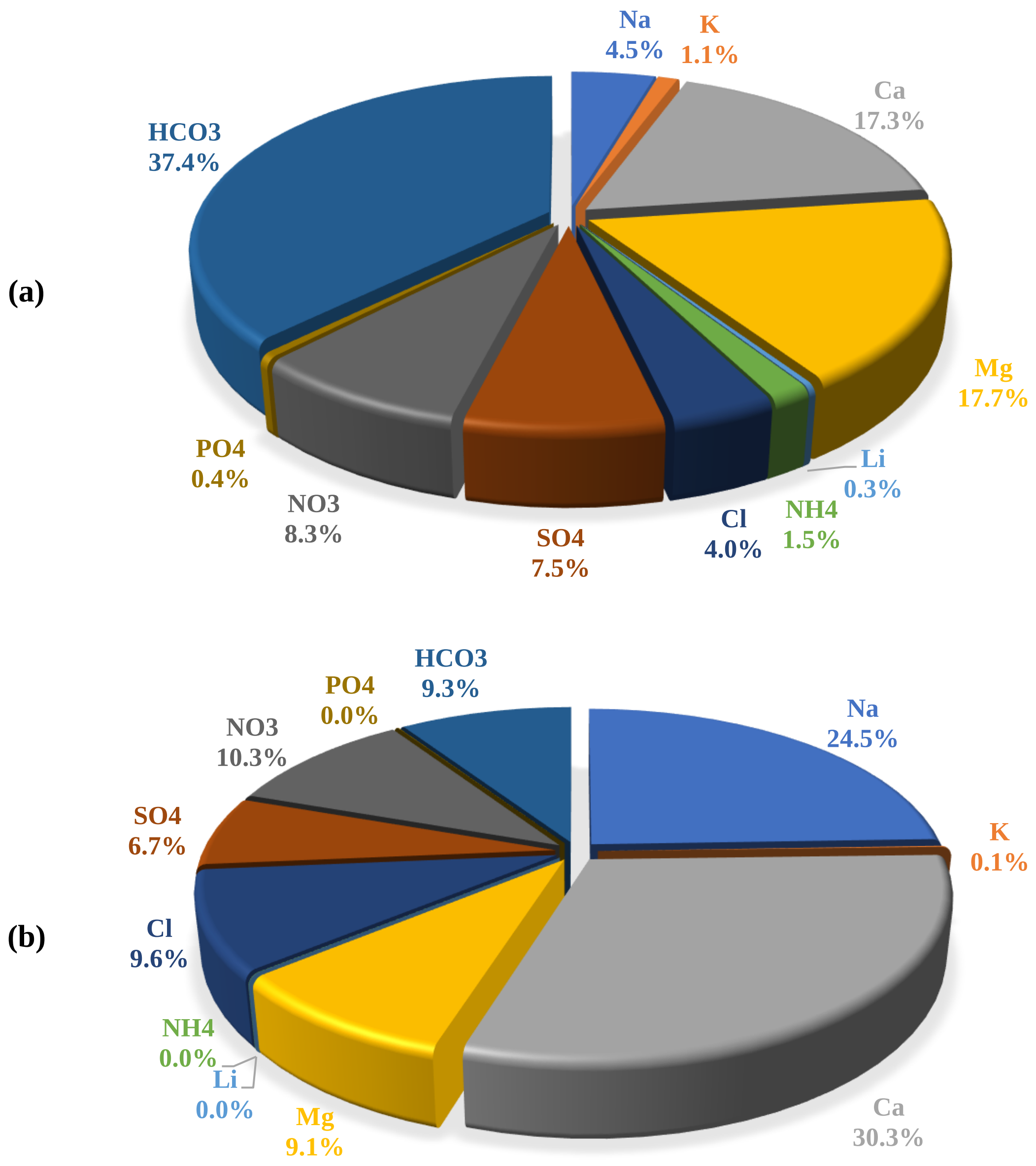

Fig. 4.1. Relative composition of cations and anions in rainwater during year (a) 2021, and (b) 2022

Atmospheric washing due to rainfall scavenges along the suspended atmospheric dust with it. This leads to presence of suspended solids in the sampled rainwater collected at various locations during 2021 and 2022. During a rainfall event in year 2021, the TSS level varied between 6 mg/L to 104 mg/L with an average of 43.2 ± 39.8 mg/L. While in same year but in different rainfall event, TSS level varied between 0 mg/L to 6 mg/L with an average concentration of 2.7 ± 3.1 mg/L. The higher level of TSS in rainfall can be ascribed to first rainfall of the season which was a result of tropical cyclone named Tautae. Also, during the rainfall event in year 2022, the TSS varied between 51 mg/L to 96 mg/L with an average of 73.5 ± 31.8 mg/L, while during another rainfall event in same year, the TSS level decreased significantly owing to cleaner atmosphere as a result of previous rainfall events. However, the TSS level during another rainfall event in 2022 varied between 8 mg/L to 16 mg/L with an average of 12 ± 5.7 mg/L.

The neutralising factor values greater than unity at all the locations indicated that alkaline species dominated over acidic species (Table 4.2). Neutralising factor (NF) revealed that calcium and magnesium as the major dominant alkaline species which contributed towards the neutralisation of acidic species. The relative abundance of chemical species, cations follow the trend $Mg^{2+} > Ca^{2+} > Na^{+} > NH_4^{+} > K^{+} > Li^{+}$, and $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+} > NH_4^{+} > Li^{+}$ for year 2021 and 2022, respectively, indicating the order of neutralising capacity of alkaline species present in rainwater. Similarly, the relative abundance of anions follows the trend $HCO_3^{-} > NO_3^{-} > SO_4^{2-} > Cl^{-} > PO_4^{3-}$ and $NO_3^{-} > Cl^{-} > HCO_{3-} > SO_4^{2-} > PO_4^{3-}$, respectively for year 2021 and 2022, showing the capacity of neutralising species (Fig. 4.1 (a) and (b)). The pH of the rainwater in different events was inclined more towards alkalinity, thus, attributing towards the presence of alkaline species. Later, dominant dusty environment resuspends the crustal dust dominated by Ca^{2+} and Mg^{2+} as represented by alkaline nature of the precipitation. The neutralisation factor with relative values lower than unity may signify relatively higher level of atmospheric acidic species (NO_3^{-} and SO_4^{2-}) while higher level of neutralising factor confirms scavenging of most of the acidic species present in atmosphere during the previous rainfall events.

Table 4.1 Physico-chemical characteristics of rainwater samples collected from different locations in Delhi, India, during year 2021 and 2022

	S. No.	pH	EC (µS/cm)	TDS (mg/L)	TSS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	PO_4^{2-} (mg/L)	HCO_3^- (mg/L)
2021	**1**	7.1	106.1	52.5	62	2.09	0.26	10.45	10	1.49	1.78	4.1	3.95	0.29	42.7
	2	7.1	65.9	33	22	4.88	0	67.64	11	0.45	2.25	1.1	4.45	0.13	30.5
	3	6.8	183.4	91.7	104	7.42	3.32	14.14	20	3.95	5.98	16.1	3.13	2.32	61.0
	4	6.5	243	121.6	22	10.52	1.56	16.7	3	0.08	0.82	5.4	0.69	0.21	18.3
	5	5.7	63.1	31.6	6	5.93	0.29	12.32	50	0.64	10.84	6.5	34.63	0.17	61.0
	Mean ± SD	6.6 ± 0.6	132.3 ± 78.7	66.1 ± 39.4	43.2 ± 39.8	6.2 ± 3.1	1.1 ± 1.4	24.3 ± 24.4	18.8 ± 18.5	1.3 ± 1.6	4.3 ± 4.1	6.6 ± 5.7	9.4 ± 14.2	0.6 ± 0.9	42.7 ± 18.8
2021	**1**	7.5	62.4	31.4	6	1.8	0.3	3.53	14	1.24	5.73	0.16	6.52	0.08	6.1
	2	7.9	36.3	18.56	2	1.08	0.19	2.69	10	1.86	1.83	0	3.5	0.07	30.5
	3	7.6	124.5	61.8	0	1.03	2.39	5.29	18	1.99	1.18	24.4	6.6	0.04	36.6
	Mean ± SD	7.7 ± 0.2	74.4 ± 45.3	37.3 ± 22.2	2.7 ± 3.1	1.3 ± 0.4	1.0 ± 1.2	3.8 ± 1.3	14.0 ± 4.0	1.7 ± 0.4	2.9 ± 2.5	8.2 ± 14.0	5.5 ± 1.8	0.1 ± 0.0	24.4 ± 16.1
2022	**1**	7.5	77	38	96	43.2	0	39.9	28	0.02	24.9	22.9	25.7	0.06	14.4
	2	7.1	57	29	51	33.7	0.2	35.2	26	0.02	17.8	16.3	21.4	0.02	16.2
	Mean ± SD	7.3 ± 0.3	67.0 ± 14.1	33.5 ± 6.4	73.5 ± 31.8	38.5 ± 6.7	0.1 ± 0.1	37.6 ± 3.3	27.0 ± 1.4	0.0 ± 0.0	21.4 ± 5.0	19.6 ± 4.7	23.6 ± 3.0	0.0 ± 0.0	15.3 ± 1.3
2022	**1**	7.1	17.5	8.7	8	44.5	0.3	59.8	0	0.04	8.3	0.3	7.1	0.08	10.1
	2	6.6	27.5	13.8	16	23.3	0.1	44.4	0	0.02	5.7	0.3	6.7	0.05	14.4
	Mean ± SD	6.9 ± 0.4	22.5 ± 7.1	11.3 ± 3.6	12.0 ± 5.7	33.9 ± 15.0	0.2 ± 0.1	52.1 ± 10.9	0.0 ± 0.0	0.0 ± 0.0	7.0 ± 1.8	0.3 ± 0.0	6.9 ± 0.3	0.1 ± 0.0	12.3 ± 3.0

SD= standard deviation; EC= electrical conductivity; TDS= total dissolved solids; TSS= total suspended solids

Table 4.2 Neutralising factor (NF) of major alkaline species present in rainwater

	Neutralising factor	**NH_4^+**	**HCO_3^-**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
2021	NF_1	0.25	2.42	0.10	4.18	5.34
	NF_2	0.36	1.54	0.09	0.74	4.43
2022	NF_3	0.00	0.31	0.00	2.38	2.82
	NF_4	0.01	1.68	0.04	22.12	0.00

1, 2, 3, and 4 are first, second, third, and fourth rainfall event.

Table 4.3 Equalization Factor (EF) of major chemical species present in rainwater

	Equalization Factor	**Cl^-/Na^+**	**SO_4^{2-}/Na^+**	**K^+/Na^+**	**Ca^{2+}/Na^+**	**Mg^{2+}/Na^+**
2021	EF_1	0.4	4.0	4.7	102.5	25.0
	EF_2	1.2	23.1	19.7	76.7	88.3
2022	EF_3	0.3	1.9	0.1	25.5	5.8
	EF_4	0.1	0.0	0.2	40.1	0.0

1, 2, 3, and 4 are first, second, third, and fourth rainfall event.

Table 4.4 Comparison seawater ratio and non-sea salt factor (NSSF) in rainwater

	Non-Sea Salf Factor	**Cl^-/Na^+**	**SO_4^{2-}/Na^+**	**K^+/Na^+**	**Ca^{2+}/Na^+**	**Mg^{2+}/Na^+**
	Rainwater	1.16	0.13	0.022	0.044	0.23
2021	R_1	-2.8	5.8	1.0	24.0	17.4
	R_2	1.4	8.0	0.9	3.8	13.7
2022	R_3	-23.3	14.6	-0.7	35.9	18.2
	R_4	-32.3	-4.1	-0.5	50.6	-7.8

1, 2, 3, and 4 are first, second, third, and fourth rainfall event.

The enrichment factor (EF) for different chemical species was calculated for the rainfall events occurred in year 2021 and 2022 (Table 4.3). The results confirms that Ca^{2+}, Mg^{2+} and SO_4^{2-} originated from local sources, i.e., the resuspension of dust. The resuspension of dust may occur from natural dust storms as well as fugitive emissions due to movement of vehicles. The negative values of NSSF (Table 4.4) shows no contribution of sea salt, whereas positive value of NSSF confirmed the resuspension of crustal dust and its role in alkaline nature of the rainwater. The distant location of Delhi from coastal areas may be the reason for no contribution of salt spray from sea. On the other hand, proximity to Thar desert of Rajasthan and dust load from limestone and sand stone mines of Haryana results in concentration of Ca^{2+} and Mg^{2+} in atmospheric dust (Ambastha and Haritash, 2021; Chitrakshi and Haritash, 2018).

4.1.2 Quality of stormwater runoff

The characterisation of stormwater runoff samples revealed that average pH of the samples was almost neutral. However, the pH of all the collected samples of stormwater runoff varied between 5.3 to 8.9 with an average of 7.1 ± 0.7 and 5.9 to 7.8 with an average of 6.9 ± 0.5 for year 2021 and 2022, respectively. The average pH in commercial, industrial, institutional, residential, and road/highway was of order 7.0 ± 0.6, 7.1 ± 0.3, 7.2 ± 0.6, 6.8 ± 0.7, and 7.3 ± 0.8, respectively for year 2021. While during year 2022, average pH in commercial, industrial, institutional, residential, and road/highway was of order 7.4 ± 0.4, 6.9 ± 0.6, 7.1 ± 0.5, 6.8 ± 0.6, and 6.8 ± 0.5, respectively. The characteristics of stormwater runoff shows that TDS level for the samples originating from commercial, industrial, institutional, residential, and road/highway was of order 136.7 ± 107.4 mg/L, 125.9 ± 77.1 mg/L, 113.2 ± 65.5 mg/L, 201.7 ± 218.5 mg/L, and 113.6 ± 99.6 mg/L, respectively for year 2021, whereas, the TDS level of stormwater runoff samples in year 2022, originating from commercial, industrial, institutional, residential, and road/highway was of order 139.4 ± 149.9 mg/L, 181.7 ± 188.0 mg/L, 98.6 ± 78.7 mg/L, 100.8 ± 97.9 mg/L, and 81.0 ± 43.8 mg/L, respectively. The runoff collected represented relatively higher level of TDS and EC which may be reasoned due to mixing of domestic wastewater (flow through open channels) with stormwater. The characteristics of stormwater runoff samples revealed that the maximum TDS level of the stormwater samples increased in year 2022 as compared to year 2021 for all the land use except for residential and road/highway, where a decrease in maximum TDS level was observed. The increase in TDS level in commercial, industrial and institutional areas can be rationalised in terms of the increased anthropogenic activities from year 2021 to 2022, since the activities were limited and restricted in year 2021 due to COVID-19 (Pipil et al., 2022b).

During year 2021, the TSS level of stormwater runoff samples varied between 48.0 mg/L to 800.0 mg/L, 52.0 mg/L to 1150.0 mg/L, 44.0 mg/L to 2308.0 mg/L, 20.0 mg/L to 2004.0 mg/L, and 18.0 mg/L to 3448.0 mg/L, respectively for commercial, industrial, institutional, residential, and road/highway. While during year 2022, the TSS level varied between 216.0 mg/L to 1215.0 mg/L, 184.0 mg/L to 5485.0 mg/L, 100.0 mg/L to 3125.0 mg/L, 10.0 mg/L to 1705.0 mg/L, and 376.0 mg/L to 2750.0 mg/L, respectively for commercial, industrial, institutional, residential, and road/highway area of Delhi. The level of TSS was observed high along the road/highways, industrial, and institutional areas which may be due to the suspension of deposited dust (during dry season) and accumulated street sweepings along the roads. The average TSS level follows the trend 692.2 ± 1114.5 mg/L > 504.9 ± 743.5 mg/L > 382.3 ± 574.5 mg/L > 374.2 ± 243.1 mg/L > 314.7 ± 416.1 mg/L for road/highway > institutional > residential > commercial > industrial during the year 2021; while it follows the trend 1671.4 ± 2222.1 mg/L > 903.6 ± 646.0 mg/L > 880.9 ± 899.5 mg/L > 739.5 ± 308.0 mg/L > 526.9 ± 472.9 mg/L for industrial > road/highway > institutional > commercial > residential during year 2022. The enhancement in TSS level in stormwater runoff from year 2021 to 2022 because of the suspension of silt and clay as a consequence of increased anthropogenic activity in year 2022 since the human activities were relatively restricted in year 2021 owing to COVID-19 lockdown.

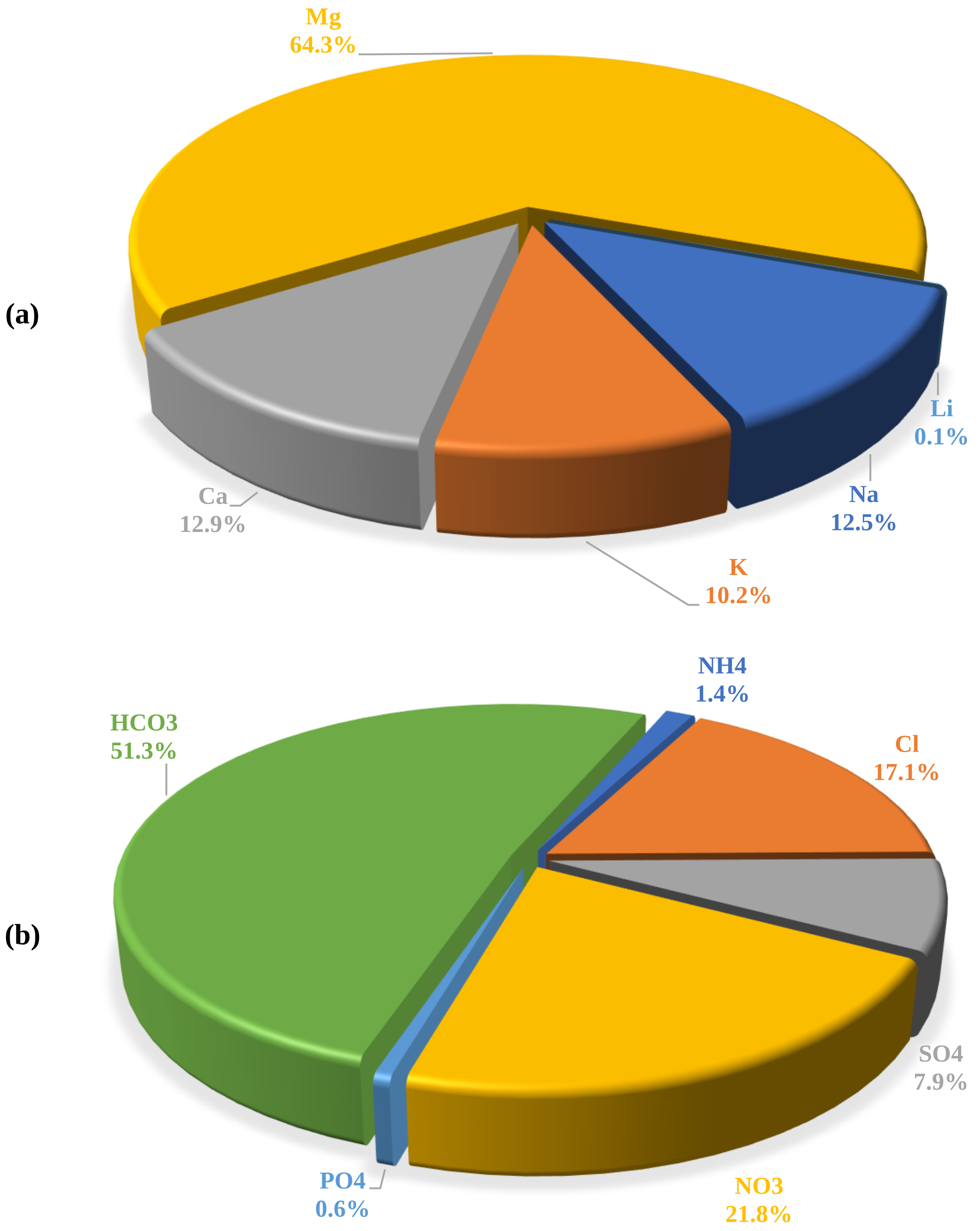

Fig. 4.2 The percent contribution of (a) cations, and (b) anions in stormwater runoff during year 2021

The characterisation of stormwater runoff from different locations in Delhi in year 2021 revealed relatively higher concentration of all the dissolved species except a slight decrease in Ca^{2+} concentration which may be attributed to indirect base-exchange upon interaction with soil. The major difference was observed in concentration of Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^- (Table 4.5). Cl^- and SO_4^{2-} are mainly contributed by mixing with domestic wastewater, and NO_3^- may be contributed from domestic wastewater, organic waste and compost/ fertiliser applied in lawns and parks, etc. Based on relative abundance, anions follow the trend as $HCO_3^- > NO_3^- > Cl^- > SO_4^{2-}$ while, cations follow the order $Mg^{2+} > Na^+ > Ca^{2+} > K^+$ during stormwater runoff in year 2021 (Fig. 4.2 (a) and (b)) indicating that the contribution of crustal origin, organic waste, and mixing of domestic wastewater significantly regulated the quality of stormwater runoff. Since the dust is a dominant feature of climate in India, its presence as TSS and Ca^{2+}, Mg^{2+}, HCO_3^-, etc. as dissolved impurities further confirm the source as natural.

The characterisation of stormwater runoff samples during year 2022 revealed increase in average concentration of Na^+, K^+, Ca^{2+}, Cl^- and SO_4^{2-}, while a slight decrease in average concentration of NH_4^+, HCO_3^-, TOC and Mg^{2+} was observed as compared to year 2021 (Table 4.6). The increase in Cl^-, SO_4^{2-}, and NO_3^- may be attributed towards the mixing of domestic sewage with stormwater runoff, application of fertilizers, mixing of organic waste, animal droppings on street, etc. Based on relative abundance, cation follows the trend as $Mg^{2+} > Na^+ > Ca^{2+} > K^+ > Li^+$, while anions follow the trend $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > PO_4^{2-}$ (Fig. 4.3 (a) and (b)). Also, the average TDS concentration increased from year 2021 to 2022 owing to more mixing of dust, sand, and silt with the stormwater runoff leading to enhanced level of dissolved impurities, along with increased TSS level due to enhanced human activity in year 2022.

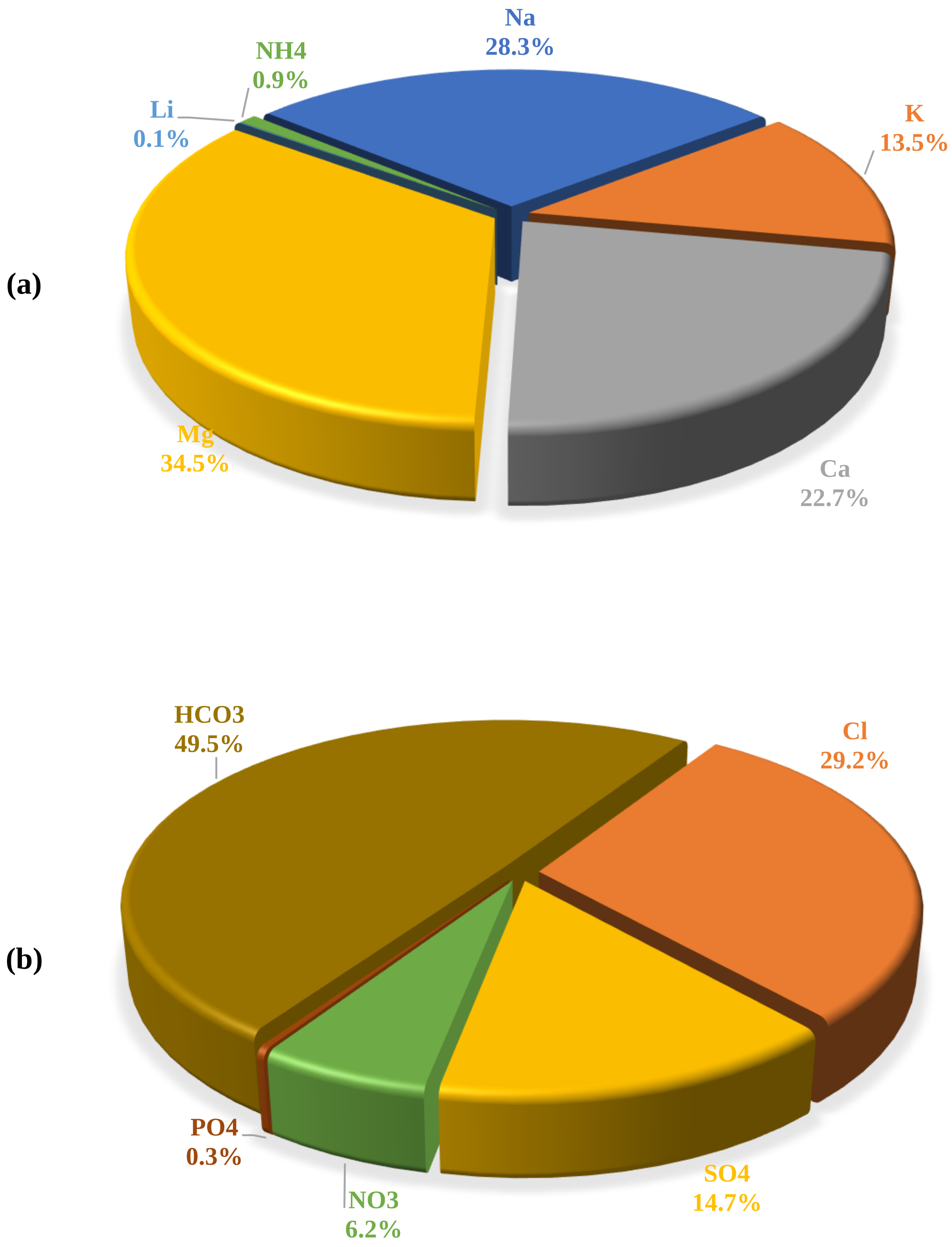

Fig. 4.3 The percent contribution of (a) cations, and (b) anions in stormwater runoff during year 2022

The characterisation of stormwater runoff during both the years 2021 and 2022, revealed the presence of nutrients such as phosphate and nitrates. The phosphates are critical pollutant for freshwater bodies that can cause eutrophication, while presence of nitrates leads pollution of marine waterbodies. The presence of phosphates in stormwater runoff during year 2021 follows the order 0.1 to 7.9 mg/L, 0.2 to 5.5 mg/L, 0.1 to 2.8 mg/L, 0 to 17.4 mg/L, and 0.1 to 3.2 mg/L for commercial, industrial, institutional, residential, and road/highway, respectively. The average concentration of phosphate during same year follows the trend 2.1 ± 4.2 mg/L > 1.9 ± 2.4 mg/L > 1.6 ± 2.0 mg/L > 1.1 ± 1.1 mg/L > 0.8 ± 0.9 mg/L for residential > commercial > industrial > road/highway > institutional area. During year 2022, the stormwater runoff characterisation revealed that the concentration of phosphate for commercial, industrial, institutional, residential, and road/highway follows the order 0.2 to 2.1 mg/L, 0.5 to 3.2 mg/L, 0.1 to 0.9 mg/L, 0.1 to 3.6 mg/L, and 0.2 to 0.7 mg/L, respectively, while it follows the trend 1.4 ± 1.2 mg/L > 0.8 ± 0.9 mg/L > 0.7 ± 0.7 mg/L > 0.6 ± 0.3 mg/L > 0.5 ± 0.1 mg/L for industrial > residential > commercial > institutional > road/highway.

The presence of nitrate in stormwater runoff samples during year 2021, between 2.1 to 122.8 mg/L, 1.9 to 72.8 mg/L, 2.3 to 62.0 mg/L, 2.3 to 478.8 mg/L, and 1.6 to 124.5 mg/L, respectively for commercial, industrial, institutional, residential, and road/highway. While during year 2022, nitrate concentration varied between 4.4 to 26.3 mg/L, 4.5 to 22.1 mg/L, 5.1 to 75.1 mg/L, 5.4 to 27.5 mg/L, and 9.1 to 21.3 mg/L for commercial, industrial, institutional, residential, and road/highway, respectively. The average concentration of nitrate follows the order residential > commercial > road/highway > institutional > industrial during year 2021, while, during year 2022, it follows the trend as institutional > road/highway > industrial > residential > commercial. It was observed that runoff from residential has relatively higher level of NH_4^+, NO_3^-, PO_4^{3-}, and TOC (Table 4.5 and Table 4.6) which may be attributed to the addition from organic matter, mulch, applied compost etc. in lawns, parks; littering of food waste, and excretory waste of stray animals and pets (Melidis et al., 2007; Gikas et al., 2012; Reddy et al., 2014).

Table 4.5 Physico-chemical characteristics of stormwater runoff from different land use areas in Delhi, India, during year 2021

Land use	**pH**	**EC (µS/cm)**	**TDS (mg/L)**	**TSS (mg/L)**	**Na$^+$ (mg/L)**	**K$^+$ (mg/L)**	**Ca^{2+} (mg/L)**	**Li$^+$ (mg/L)**	**NH$_4^+$ (mg/L)**	**Cl$^-$ (mg/L)**	**SO$_4^{2-}$ (mg/L)**	**NO$_3^-$ (mg/L)**	**PO$_4^{2-}$ (mg/L)**	**HCO$_3^-$ (mg/L)**	**TN (mg/L)**	**NH$_3$ TKN (mg/L)**	**CDOM (µg/l)**	**TOC (mg/L)**	**TC (mg/L)**	**IC (mg/L)**	**Total Hardness (mg/L)**	**Ca^{2+} Hardness (mg/L)**	**Mg $^{2+}$ Hardness (mg/L)**
Commercial	6.7	396	198	260.0	26.6	16.7	17.9	0.0	2.8	72.2	13.9	122.8	1.8	158.6	3.3	18.2	49.3	17.5	39.8	22.3	130.0	50.0	80.0
	6.8	215	107	800.0	5.2	5.2	9.6	0.0	2.9	11.5	7.9	109.1	1.6	143.4	3.4	14.0	57.5	19.6	39.2	19.7	110.0	62.0	48.0
	6.2	461	230	48.0	40.3	31.6	17.2	0.1	5.3	135.5	14.1	68.8	2.7	176.9	4.8	12.6	72.3	37.1	61.3	24.1	100.0	50.0	50.0
	6.4	724	365	536.0	48.6	19.8	28.3	0.1	6.8	236.8	13.4	59.1	1.8	311.1	5.0	14.0	53.8	44.6	99.6	55.0	275.0	100.0	175.0
	7.4	187	94	552.0	3.9	2.5	13.6	0.2	0.6	4.4	50.6	2.1	0.4	25.9	1.0	14.0	35.8	9.1	20.5	11.4	75.0	32.0	43.0
	7.4	130	66	68.0	4.0	7.5	15.2	0.1	0.7	3.7	11.1	2.1	7.9	91.5	0.9	4.2	27.2	14.8	26.6	11.8	65.0	26.0	39.0
	6.9	158	79	482.0	3.3	3.1	8.3	0.0	0.7	4.4	6.3	4.5	0.3	97.6	1.8	4.2	37.5	8.4	21.1	12.7	75.0	30.1	44.9
	7.4	81	41	330.0	0.8	2.7	4.1	0.0	1.2	4.7	9.3	6.6	0.1	48.8	1.9	11.2	35.3	4.6	9.9	5.4	25.0	20.0	5.0
	7.9	101	51	292.0	1.0	2.4	3.6	0.0	1.1	2.7	5.8	5.6	0.5	54.9	1.5	7.0	25.5	3.6	8.7	5.2	50.0	20.0	30.0
Minimum	6.2	81	41	48.0	0.8	2.4	3.6	0.0	0.6	2.7	5.8	2.1	0.1	25.9	0.9	4.2	25.5	3.6	8.7	5.2	25.0	20.0	5.0
Maximum	7.9	724	365	800.0	48.6	31.6	28.3	0.2	6.8	236.8	50.6	122.8	7.9	311.1	5.0	18.2	72.3	44.6	99.6	55.0	275.0	100.0	175.0
Mean ± SD	7.0 ± 0.6	272.7 ±213.4	136.7 ±107.4	374.2 ±243.1	14.9 ±18.6	10.2 ±10.3	13.1 ±7.8	0.1 ±0.1	2.5 ±2.2	52.9 ±82.7	14.7 ±13.8	42.3 ±49.0	1.9 ±2.4	123.2 ±87.4	2.6 ±1.6	11.0 ±4.9	43.8 ±15.5	17.7 ±14.3	36.3 ±28.9	18.6 ±15.2	100.6 ±72.6	43.3 ±25.8	57.2 ±48.3

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Land use	pH	EC (μS/cm)	TDS (mg/L)	TSS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Li^+ (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	PO_4^{2-} (mg/L)	HCO_3^- (mg/L)	TN (mg/L)	NH_3 TKN (mg/L)	CDOM (μg/l)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	Total Hardness (mg/L)	Ca^{2+} Hardness (mg/L)	Mg^{2+} Hardness (mg/L)
Industrial	6.7	379	189	276.0	21.2	15.0	15.0	0.0	2.3	131.8	6.9	72.8	2.0	170.8	3.0	7.0	69.8	20.6	48.3	27.7	143.0	68.0	74.0
	7.5	119	59	176.0	3.5	2.5	8.2	0.2	0.5	3.3	12.6	1.9	0.2	79.3	0.7	5.6	24.2	6.2	15.5	9.3	45.0	22.0	23.0
	7.3	118	60	128.0	5.6	3.2	9.0	0.0	0.2	3.4	9.9	4.7	0.6	79.3	1.8	7.0	27.5	3.7	11.0	7.2	40.0	22.0	18.0
	7.1	137	69	52.0	5.8	3.2	6.7	0.2	0.5	5.3	10.8	2.8	0.3	85.4	1.2	7.0	25.7	5.8	14.3	8.4	35.0	20.0	15.0
	6.8	485	242	1150.0	23.7	12.5	15.1	0.1	5.3	49.9	19.9	8.3	5.5	231.8	46.5	5.6	74.7	41.6	65.0	23.4	115.0	56.1	58.9
	7.2	273	137	106.0	8.4	7.4	10.5	0.1	2.0	16.8	57.4	5.0	1.1	122.0	7.0	4.2	39.8	12.3	30.7	18.4	90.0	38.1	51.9
Minimum	6.7	118	59	52.0	3.5	2.5	6.7	0.0	0.2	3.3	6.9	1.9	0.2	79.3	0.7	4.2	24.2	3.7	11.0	7.2	35.0	20.0	15.0
Maximum	7.5	485	242	1150.0	23.7	15.0	15.1	0.2	5.3	131.8	57.4	72.8	5.5	231.8	46.5	7.0	74.7	41.6	65.0	27.7	143.0	68.0	74.0
Mean ±SD	7.1 ±0.3	251.8 ±154.8	125.9 ±77.1	314.7 ±416.1	11.4 ±8.8	7.3 ±5.3	10.8 ±3.6	0.1 ±0.1	1.8 ±1.9	35.1 ±50.6	19.6 ±19.0	15.9 ±27.9	1.6 ±2.0	128.1 ±62.0	10.0 ±18.0	6.1 ±1.1	43.6 ±22.9	15.0 ±14.4	30.8 ±21.8	15.7 ±8.7	78.0 ±45.0	37.7 ±20.3	40.1 ±24.7

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Land use	pH	EC (µS/cm)	TDS (mg/L)	TSS (mg/L)	Na$^+$ (mg/L)	K$^+$ (mg/L)	Ca^{2+} (mg/L)	Li$^+$ (mg/L)	NH$_4^+$ (mg/L)	Cl$^-$ (mg/L)	SO$_4^{2-}$ (mg/L)	NO$_3^-$ (mg/L)	PO$_4^{2-}$ (mg/L)	HCO$_3^-$ (mg/L)	TN (mg/L)	NH$_3$ TKN (mg/L)	CDOM (µg/l)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	Total Hardness (mg/L)	Ca^{2+} Hardness (mg/L)	Mg $^{2+}$ Hardness (mg/L)
Institutional	6.0	403	199	132.0	28.1	26.3	17.0	0.0	3.3	88.8	14.9	59.6	2.8	198.3	3.8	8.4	58.3	30.9	60.3	29.4	388.0	61.0	326.0
	7.2	108	54	68.0	0.0	0.0	0.0	0.0	1.7	2.4	5.8	62.0	0.2	61.0	5.1	11.2	15.8	2.7	8.6	5.9	45.0	19.0	26.0
	6.8	137	79	44.0	5.1	1.0	7.5	0.0	1.6	4.6	16.6	57.0	0.2	70.2	4.4	8.4	22.2	3.3	12.8	9.5	75.0	26.0	49.0
	6.9	210	105	138.0	3.8	6.9	26.7	0.0	2.0	3.9	26.2	4.4	1.2	91.5	3.8	2.8	92.6	27.8	42.3	14.5	85.0	30.0	55.0
	7.5	476	238	2308.0	45.4	9.6	45.8	0.6	1.2	16.4	162.3	2.3	0.4	152.5	1.6	5.6	48.5	8.5	36.8	28.3	120.0	38.0	82.0
	7.2	162	81	292.0	2.8	3.8	33.0	0.1	2.4	2.5	17.7	2.8	1.2	73.2	4.1	5.6	88.3	15.5	26.6	11.0	60.0	24.0	36.0
	7.4	243	122	150.0	10.9	5.9	10.4	0.1	0.6	13.5	17.4	5.9	0.3	109.8	1.0	4.2	38.4	10.1	26.2	16.2	65.0	38.1	26.9
	7.9	200	100	358.0	10.4	6.0	8.4	0.1	0.7	10.3	18.8	5.2	0.4	85.4	0.8	2.8	36.4	4.5	16.9	12.5	60.0	18.0	42.0
	8.2	81	40	1054.0	1.5	1.7	5.0	0.0	1.0	3.4	7.3	6.1	0.1	36.6	1.7	16.8	11.9	2.1	6.3	4.2	20.0	12.0	8.0
Minimum	6.0	81	40	44.0	0.0	0.0	0.0	0.0	0.6	2.4	5.8	2.3	0.1	36.6	0.8	2.8	11.9	2.1	6.3	4.2	20.0	12.0	8.0
Maximum	8.2	476	238	2308.0	45.4	26.3	45.8	0.6	3.3	88.8	162.3	62.0	2.8	198.3	5.1	16.8	92.6	30.9	60.3	29.4	388.0	61.0	326.0
Mean ±SD	7.2 ±0.6	224.4 ±133.2	113.2 ±65.5	504.9 ±743.5	12.0 ±15.1	6.8 ±7.9	17.1 ±15.1	0.1 ±0.2	1.6 ±0.9	16.2 ±27.7	31.9 ±49.3	22.8 ±27.6	0.8 ±0.9	97.6 ±49.9	2.9 ±1.6	7.3 ±4.5	45.8 ±29.4	11.7 ±10.9	26.3 ±17.7	14.6 ±8.9	102.0 ±110.7	29.6 ±14.7	72.3 ±97.4

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Land use	**pH**	**EC (μS/cm)**	**TDS (mg/L)**	**TSS (mg/L)**	**Na^+ (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**Li^+ (mg/L)**	**NH_4^+ (mg/L)**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**	**NO_3^- (mg/L)**	**PO_4^{2-} (mg/L)**	**HCO_3^- (mg/L)**	**TN (mg/L)**	**NH_3 TKN (mg/L)**	**CDOM (μg/l)**	**TOC (mg/L)**	**TC (mg/L)**	**IC (mg/L)**	**Total Hardness (mg/L)**	**Ca^{2+} Hardness (mg/L)**	**Mg^{2+} Hardness (mg/L)**
Residential	6.2	648	421	260.0	41.5	19.2	22.8	0.1	9.8	260.0	23.2	109.5	6.7	271.5	6.3	11.2	67.6	19.2	70.4	51.1	225.0	70.0	155.0
	5.7	1375	686	2004.0	22.7	71.5	27.3	0.1	59.8	290.9	30.9	60.5	17.4	677.1	47.2	40.6	85.9	219.1	316.0	96.9	595.0	146.0	449.0
	6.2	440	220	228.0	24.7	29.7	16.4	0.0	7.5	85.4	10.7	62.5	3.1	201.3	4.1	21.0	72.3	43.6	73.8	30.2	125.0	34.0	91.0
	6.5	232	118	252.0	8.8	9.0	10.0	0.0	3.2	21.0	5.8	87.8	1.3	134.2	4.0	9.8	90.7	28.3	48.6	20.3	85.0	29.0	56.0
	5.3	1237	623	412.0	49.5	84.4	59.5	0.2	12.4	343.7	66.2	85.4	2.5	597.8	12.7	11.2	194.6	405.4	437.3	31.9	325.0	140.0	185.0
	6.8	98	49	60.0	2.2	0.0	4.6	0.0	0.6	6.3	2.8	223.2	0.1	70.2	1.7	8.4	12.9	3.0	11.5	8.5	43.0	18.0	24.0
	7.1	70	35	52.0	0.0	0.0	0.0	0.0	0.4	3.9	4.5	206.3	0.1	58.0	1.7	11.2	12.0	1.7	6.8	5.1	33.0	10.0	22.0
	6.2	56	28	60.0	1.4	2.2	3.0	0.0	0.5	13.7	1.9	323.3	0.1	39.7	1.7	7.0	14.8	11.8	15.7	3.9	23.0	8.0	14.0
	6.8	148	73	88.0	6.2	1.7	10.9	0.0	0.5	21.8	3.0	478.8	0.1	85.4	1.1	7.0	31.9	1002.5	1005.0	2.5	88.0	15.0	72.0
	6.5	155	77	20.0	7.1	3.1	7.0	0.0	1.1	10.7	12.6	134.2	0.0	73.2	1.2	8.4	28.8	6.2	13.8	7.6	50.0	18.0	32.0
	6.9	145	73	44.0	6.5	4.5	5.1	0.0	1.6	6.9	11.9	136.2	0.4	73.2	4.3	8.4	33.4	6.8	14.9	8.1	43.0	13.0	29.0
	6.7	115	58	28.0	2.0	1.8	6.0	0.0	1.3	1.4	9.9	108.1	0.1	61.0	5.0	9.8	14.7	2.4	8.3	6.0	25.0	15.0	10.0
	7.1	145	72	400.0	4.3	2.8	31.4	0.3	0.8	3.7	12.5	2.3	0.5	73.2	1.2	2.8	30.6	8.3	19.1	10.8	60.0	30.0	30.0
	6.9	1174	586	932.0	111.4	9.4	52.2	0.0	1.7	171.3	183.4	9.0	0.6	176.9	2.3	5.6	36.6	12.9	48.4	35.5	230.0	72.0	158.0
	7.6	259	131	1660.0	5.1	6.6	11.1	0.1	0.5	9.7	12.7	4.6	0.3	140.3	1.1	4.2	44.6	15.3	33.9	18.6	130.0	54.1	75.9
	7.5	389	194	64.0	20.2	16.2	11.7	0.1	3.8	35.3	44.1	11.5	2.9	91.5	13.7	4.2	70.7	23.1	36.8	13.7	100.0	26.1	73.9
	8.0	207	102	240.0	7.9	4.1	8.3	0.0	1.5	7.2	37.9	9.7	0.8	48.8	2.8	28.0	22.4	3.9	12.1	8.1	75.0	28.1	46.9
	7.7	178	84	78.0	5.3	7.2	6.2	0.0	1.1	6.9	16.1	4.9	0.4	73.2	2.1	15.4	57.0	18.1	31.2	13.2	80.0	16.0	64.0
Minimum	5.3	56	28	20.0	0.0	0.0	0.0	0.0	0.4	1.4	1.9	2.3	0.0	39.7	1.1	2.8	12.0	1.7	6.8	2.5	23.0	8.0	10.0
Maximum	8.0	1375	686	2004.0	111.4	84.4	59.5	0.3	59.8	343.7	183.4	478.8	17.4	677.1	47.2	40.6	194.6	1002.5	1005.0	96.9	595.0	146.0	449.0
Mean ±SD	6.8 ±0.7	392.8 ±427.1	201.7 ±218.5	382.3 ±574.5	18.2 ±27.2	15.2 ±24.2	16.3 ±16.7	0.1 ±0.1	6.0 ±13.9	72.2 ±112.7	27.2 ±42.5	114.3 ±127.0	2.1 ±4.2	163.7 ±183.1	6.3 ±10.8	11.9 ±9.4	51.2 ±43.9	101.7 ±246.8	122.4 ±248.7	20.7 ±23.1	129.7 ±141.8	41.2 ±41.6	88.2 ±103.8

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Land use	**pH**	**EC (μS/cm)**	**TDS (mg/L)**	**TSS (mg/L)**	**Na^+ (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**Li^+ (mg/L)**	**NH_4^+ (mg/L)**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**	**NO_3^- (mg/L)**	**PO_4^{2-} (mg/L)**	**HCO_3^- (mg/L)**	**TN (mg/L)**	**NH_3 TKN (mg/L)**	**CDOM (μg/l)**	**TOC (mg/L)**	**TC (mg/L)**	**IC (mg/L)**	**Total Hardness (mg/L)**	**Ca^{2+} Hardness (mg/L)**	**Mg $^{2+}$ Hardness (mg/L)**
Road/Highway	6.5	517	259	644.0	20.3	19.7	17.6	0.1	8.0	99.0	16.9	101.5	3.2	241.0	6.7	12.6	68.7	31.9	67.2	35.3	175.0	50.0	125.0
	6.3	467	233	552.0	24.0	18.4	18.1	0.0	6.8	87.8	14.5	57.9	3.2	210.5	6.2	9.8	71.9	50.1	79.3	29.2	160.0	50.0	110.0
	6.2	388	171	376.0	17.5	18.1	14.1	0.1	5.1	57.0	9.9	59.8	2.3	173.9	6.9	9.8	195.5	40.8	60.9	20.1	115.0	44.0	71.0
	6.6	547	273	416.0	22.9	34.1	19.3	0.1	4.9	72.7	11.7	107.1	2.3	262.3	4.6	8.4	124.7	30.2	69.1	38.9	188.0	65.0	122.0
	6.1	661	331	3176.0	15.4	24.1	21.1	0.1	10.2	40.7	11.7	124.5	2.2	408.7	7.6	11.2	18.4	45.0	98.9	54.0	355.0	105.0	250.0
	7.1	93	47	140.0	2.9	2.4	1.7	0.0	0.6	4.3	4.4	1.6	0.5	48.8	1.1	4.2	25.4	4.6	11.6	7.0	30.0	16.0	14.0
	7.1	100	50	34.0	3.6	2.6	0.0	0.2	0.6	3.8	6.5	1.6	0.6	54.9	1.2	4.2	27.5	5.9	13.9	8.0	45.0	18.0	27.0
	7.2	93	46	168.0	2.7	1.4	22.8	0.2	0.2	2.4	5.7	2.2	0.3	61.0	1.0	5.6	19.1	3.3	10.0	6.8	40.0	20.0	20.0
	6.7	86	43	18.0	3.2	5.9	4.4	0.0	1.0	2.5	5.1	1.9	0.7	30.5	2.0	2.8	29.1	7.5	13.8	6.3	20.0	6.0	14.0
	8.0	93	46	204.0	0.6	1.6	5.3	0.1	0.6	3.1	4.9	5.2	0.4	67.1	0.9	4.2	32.8	3.6	11.4	7.8	65.0	34.1	30.9
	7.7	235	117	18.0	7.9	5.9	9.8	0.1	1.0	11.8	11.7	4.7	0.8	85.4	3.4	2.8	40.1	11.7	29.5	17.9	90.0	40.1	49.9
	8.2	98	49	146.0	1.0	4.5	5.0	0.0	1.3	3.0	7.1	4.8	0.7	48.8	2.6	11.2	31.6	7.8	14.5	6.7	45.0	24.0	21.0
	8.1	166	87	163.0	0.8	3.9	4.8	0.0	1.4	1.9	7.9	4.7	0.6	48.8	2.2	19.6	27.2	6.6	13.6	6.8	20.0	14.0	6.0
	7.9	22	44	20.0	0.6	1.6	2.8	0.0	1.1	2.7	3.8	3.0	0.1	30.5	1.7	9.8	17.5	2.9	6.3	3.4	10.0	6.0	4.0
	7.2	49	24	38.0	0.4	1.3	3.2	0.0	1.1	1.0	6.1	2.6	0.1	24.4	1.6	9.8	21.9	2.9	6.6	3.7	25.0	10.0	15.0
	8.4	134	67	3448.0	2.2	3.9	5.9	0.0	0.8	1.8	8.9	3.5	0.3	67.1	1.2	14.0	49.8	3.7	13.1	9.2	45.0	30.1	14.9
	8.9	89	44	2206.0	3.9	4.4	2.6	0.0	0.9	3.4	10.9	6.0	0.6	61.0	1.3	11.2	42.8	3.3	9.9	6.5	60.0	14.0	46.0
Minimum	6.1	22	24	18.0	0.4	1.3	0.0	0.0	0.2	1.0	3.8	1.6	0.1	24.4	0.9	2.8	17.5	2.9	6.3	3.4	10.0	6.0	4.0
Maximum	8.9	661	331	3448.0	24.0	34.1	22.8	0.2	10.2	99.0	16.9	124.5	3.2	408.7	7.6	19.6	195.5	50.1	98.9	54.0	355.0	105.0	250.0
Mean ±SD	7.3 ±0.8	225.7 ±204.7	113.6 ±99.6	692.2 ±1114.5	7.6 ±8.6	9.0 ±9.9	9.3 ±7.7	0.1 ±0.1	2.7 ±3.1	23.5 ±34.1	8.7 ±3.8	29.0 ±43.4	1.1 ±1.1	113.2 ±108.1	3.1 ±2.4	8.9 ±4.5	49.6 ±46.3	15.4 ±16.8	31.2 ±30.6	15.7 ±14.9	87.5 ±89.0	32.1 ±25.5	55.3 ±64.3

SD= standard deviation; EC= electrical conductivity; TDS= total dissolved solids; TSS= total suspended solids; TN= total nitrogen; TKN= total Kjeldahl nitrogen; CDOM= colour dissolved organic matter; TOC= total organic carbon; TC= total carbon; IC= inorganic carbon.

Table 4.6 Physico-chemical characteristics of stormwater runoff from different land use areas in Delhi, India, during year 2022

Land use	pH	EC (μS/cm)	TDS (mg/L)	TSS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Li^+ (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	PO_4^{2-} (mg/L)	HCO_3^- (mg/L)	TN (mg/L)	NH_3 TKN (mg/L)	CDOM (μg/l)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	Total Hardness (mg/L)	Ca^{2+} Hardness (mg/L)	Mg^{2+} Hardness (mg/L)
Commercial	7.7	308	154	802.0	39.4	30.3	51.4	0.1	0.5	50.7	111.5	9.6	0.3	57.9	1.6	16.8	585.3	30.9	31.2	0.3	120.0	48.1	71.9
	7.6	274	137	820.0	36.1	20.7	39.8	0.1	0.2	60.8	119.5	8.6	0.2	36.6	2.6	14.0	818.4	31.6	32.3	0.6	110.0	74.1	35.9
	7.5	175	88	824.0	25.6	9.4	28.8	0.1	0.1	27.5	15.6	8.7	1.3	18.3	2.2	15.4	367.3	27.4	27.9	0.5	70.0	66.1	3.9
	7.4	142	71	980.0	33.1	7.7	23.9	0.0	0.2	3.4	4.6	5.4	0.6	85.4	2.8	12.6	215.1	8.7	20.8	12.1	65.0	24.1	40.9
	7.2	184	92	216.0	32.5	16.5	23.9	0.1	0.2	4.6	3.8	5.6	0.5	122.0	1.1	14.0	81.1	11.9	28.4	16.5	75.0	30.1	44.9
	6.5	992	496	514.0	229.4	181.5	112.2	0.8	36.6	117.2	162.3	26.3	2.1	512.4	48.4	49.0	1002.1	139.4	204.9	65.5	245.0	62.1	182.9
	7.2	67	33	545.0	25.1	6.5	28.7	0.1	0.4	3.9	4.2	4.9	0.2	61.0	1.5	2.8	317.1	12.1	21.9	9.8	50.0	54.0	26.0
	7.8	89	45	1215.0	30.3	8.5	30.4	0.1	0.1	6.6	25.7	4.4	0.5	170.8	1.2	1.4	336.5	11.8	27.5	15.7	90.0	50.1	39.9
Minimum	6.5	67	33	216.0	25.1	6.5	23.9	0.0	0.1	3.4	3.8	4.4	0.2	18.3	1.1	1.4	81.1	8.7	20.8	0.3	50.0	24.1	3.9
Maximum	7.8	992	496	1215.0	229.4	181.5	112.2	0.8	36.6	117.2	162.3	26.3	2.1	512.4	48.4	49.0	1002.1	139.4	204.9	65.5	245.0	74.1	182.9
Mean ±SD	7.4 ±0.4	278.8 ±299.8	139.4 ±149.9	739.5 ±308.0	56.4 ±70.1	35.1 ±59.7	42.4 ±29.7	0.2 ±0.3	4.8 ±12.9	34.3 ±40.4	55.9 ±64.4	9.2 ±7.2	0.7 ±0.7	133.1 ±160.8	7.7 ±16.5	15.8 ±14.6	465.4 ±313.0	34.2 ±43.5	49.4 ±63.0	15.1 ±21.5	103.1 ±61.9	51.1 ±17.2	55.8 ±54.8

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Land use	**pH**	**EC (µS/cm)**	**TDS (mg/L)**	**TSS (mg/L)**	**Na^+ (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**Li^+ (mg/L)**	**NH_4^+ (mg/L)**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**	**NO_3^- (mg/L)**	**PO_4^{2-} (mg/L)**	**HCO_3^- (mg/L)**	**TN (mg/L)**	**NH_3 TKN (mg/L)**	**CDOM (µg/l)**	**TOC (mg/L)**	**TC (mg/L)**	**IC (mg/L)**	**Total Hardness (mg/L)**	**Ca^{2+} Hardness (mg/L)**	**Mg^{2+} Hardness (mg/L)**
Industrial	7.4	1012	511	1772.0	69.1	19.9	61.1	0.1	0.5	716.8	231.3	22.1	3.2	51.8	2.8	16.8	755.1	51.9	57.7	5.8	145.0	38.1	106.9
	7.5	255	130	600.0	29.1	17.1	33.9	0.1	0.2	60.7	9.7	12.1	0.7	24.4	2.5	14.0	690.4	44.7	45.7	0.9	120.0	38.1	81.9
	6.9	147	74	184.0	35.2	9.4	22.1	0.0	0.1	4.7	4.1	4.5	0.5	103.7	0.8	19.4	196.5	11.1	23.2	21.1	70.0	22.1	47.9
	6.2	286	143	316.0	33.9	32.2	40.7	0.3	4.6	1.5	112.4	7.6	0.6	134.2	4.1	16.8	206.1	16.8	37.6	20.8	110.0	38.1	71.9
	6.5	102	51	5485.0	32.1	18.3	23.1	0.1	0.2	14.4	1.1	21.9	2.1	85.4	1.5	2.8	320.3	8.1	33.8	25.7	160.0	62.1	97.9
Minimum	6.2	102	51	184.0	29.1	9.4	22.1	0.0	0.1	1.5	1.1	4.5	0.5	24.4	0.8	2.8	196.5	8.1	23.2	0.9	70.0	22.1	47.9
Maximum	7.5	1012	511	5485.0	69.1	32.2	61.1	0.3	4.6	716.8	231.3	22.1	3.2	134.2	4.1	19.4	755.1	51.9	57.7	25.7	160.0	62.1	106.9
Mean	6.9	360.5	181.7	1671.4	39.9	19.4	36.2	0.1	1.1	159.6	71.7	13.6	1.4	79.9	2.4	14.0	433.7	26.5	39.6	14.9	121.0	39.7	81.3
±SD	±0.6	±372.0	±188.0	±2222.1	±16.5	±8.2	±15.9	±0.1	±2.0	±312.4	±100.7	±8.1	±1.2	±43.1	±1.3	±6.5	±269.3	±20.3	±13.0	±10.8	±34.7	±14.3	±23.1

Continued…

Land use	pH	EC (µS/cm)	TDS (mg/L)	TSS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Li^+ (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	PO_4^{2-} (mg/L)	HCO_3^- (mg/L)	TN (mg/L)	NH_3 TKN (mg/L)	CDOM (µg/l)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	Total Hardness (mg/L)	Ca^{2+} Hardness (mg/L)	Mg^{2+} Hardness (mg/L)
Institutional	7.5	181	91	936.0	25.5	10.7	28.9	0.1	0.1	35.3	1.9	16.7	0.7	152.5	3.2	12.6	961.5	20.7	21.2	0.5	70.0	24.0	46.0
	7.6	568	286	784.0	74.1	25.3	29.1	0.1	0.1	500.6	159.5	75.1	0.9	18.3	3.0	12.6	723.1	14.0	15.2	1.2	125.0	16.0	109.0
	7.7	180	88	832.0	35.5	9.1	26.8	0.2	0.1	30.1	4.9	21.6	0.8	12.2	2.2	16.8	1010.4	19.6	20.4	0.8	80.0	28.1	51.9
	6.9	90	45	656.0	112.8	2.8	80.2	0.0	0.1	1.8	1.7	5.3	0.6	79.3	0.9	18.2	97.3	5.3	14.1	8.8	40.0	16.0	24.0
	6.8	127	64	100.0	32.6	9.5	22.1	0.1	0.1	7.9	12.9	14.7	0.3	73.2	1.5	16.8	65.2	4.3	10.6	6.3	40.0	14.0	26.0
	6.6	89	44	168.0	133.9	5.6	92.6	0.0	0.0	3.4	1.9	7.9	0.4	67.1	0.5	18.2	148.8	2.5	11.8	9.3	40.0	16.0	24.0
	6.1	312	156	382.0	34.6	9.6	26.9	0.2	5.5	10.3	76.4	5.1	0.9	109.8	4.4	21.0	167.7	15.8	30.5	14.7	70.0	24.0	46.0
	7.4	84	42	945.0	28.8	16.3	24.5	0.1	0.3	5.9	12.9	7.5	0.7	128.1	1.2	4.2	305.1	14.3	30.9	16.6	40.0	34.1	5.6
	7.2	143	72	3125.0	30.6	29.5	26.9	0.1	0.2	98.5	12.8	8.4	0.1	353.8	0.8	2.8	276.1	13.6	35.1	21.5	105.0	62.1	42.9
Minimum	6.1	84	42	100.0	25.5	2.8	22.1	0.0	0.0	1.8	1.7	5.1	0.1	12.2	0.5	2.8	65.2	2.5	10.6	0.5	40.0	14.0	5.6
Maximum	7.7	568	286	3125.0	133.9	29.5	92.6	0.2	5.5	500.6	159.5	75.1	0.9	353.8	4.4	21.0	1010.4	20.7	35.1	21.5	125.0	62.1	109.0
Mean	7.1	197.1	98.6	880.9	56.5	13.2	39.8	0.1	0.7	77.1	31.7	18.0	0.6	110.5	2.0	13.7	417.2	12.2	21.1	8.9	67.8	26.0	41.7
±SD	±0.5	±156.2	±78.7	±899.5	±40.9	±8.9	±26.7	±0.1	±1.8	±161.7	±53.4	±22.1	±0.3	±102.3	±1.3	±6.4	±376.6	±6.6	±9.1	±7.5	±31.4	±15.1	±29.3

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Land use	pH	EC (µS/cm)	TDS (mg/L)	TSS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Li^+ (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	PO_4^{2-} (mg/L)	HCO_3^- (mg/L)	TN (mg/L)	NH_3 TKN (mg/L)	CDOM (µg/l)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	Total Hardness (mg/L)	Ca^{2+} Hardness (mg/L)	Mg^{2+} Hardness (mg/L)
Residential	7.5	360	180	328.0	58.9	46.3	47.8	0.4	0.2	175.6	9.8	22.5	0.6	24.4	2.9	14.0	998.3	55.1	55.6	0.5	110.0	44.1	65.9
	7.4	407	202	724.0	31.8	86.3	43.6	0.1	0.4	183.5	12.6	20.9	3.6	30.5	2.9	9.8	1397.3	57.5	58.3	0.8	125.0	42.1	82.9
	7.4	175	87	656.0	35.3	10.8	28.5	0.1	0.1	33.9	2.4	10.9	0.9	12.2	3.5	14.0	404.5	19.7	21.1	1.4	80.0	36.1	43.9
	7.3	279	140	280.0	29.2	24.3	35.6	0.1	0.1	92.5	65.9	21.9	0.9	213.5	2.1	14.0	733.2	21.7	22.1	0.4	90.0	32.1	57.9
	6.7	68	34	68.0	42.7	2.7	36.8	0.0	0.0	4.1	1.1	8.3	0.6	54.9	0.7	22.4	88.6	3.4	9.7	6.3	35.0	10.0	25.0
	6.5	110	55	500.0	63.6	9.9	22.3	0.1	0.0	6.9	0.9	9.4	0.4	85.4	1.1	15.4	205.6	4.2	14.6	10.4	35.0	20.1	14.9
	5.9	385	179	346.0	33.8	31.1	44.4	0.2	4.7	3.2	20.9	13.1	0.9	158.6	7.6	18.2	656.7	66.7	96.8	30.1	105.0	56.1	48.9
	5.9	700	350	756.0	84.6	62.9	61.3	0.4	5.6	97.8	59.9	27.5	0.2	323.3	14.6	19.6	968.2	161.1	217.9	56.8	285.0	98.2	186.8
	6.2	37	17	14.0	38.5	1.6	32.1	0.1	1.3	0.2	58.1	6.9	0.2	42.7	1.6	16.8	42.3	2.5	12.3	9.8	10.0	8.1	1.9
	6.1	24	12	10.0	35.9	3.1	20.5	0.1	1.2	0.4	16.9	6.1	0.3	85.4	1.5	9.8	41.9	2.1	9.1	7.0	10.0	8.1	1.9
	7.3	86	43	1705.0	26.1	14.4	27.4	0.1	0.3	27.7	55.3	10.9	0.6	85.4	2.2	2.8	220.3	12.9	25.8	12.9	60.0	20.0	40.0
	7.0	101	50	1085.0	25.8	22.1	30.3	0.1	0.3	39.8	15.3	7.3	0.7	122.0	1.5	1.4	327.1	20.5	36.9	16.4	80.0	32.1	47.9
	6.8	110	55	780.0	25.9	20.6	28.8	0.1	0.2	27.5	14.9	8.6	0.7	134.2	1.7	1.4	356.8	19.1	36.8	17.7	75.0	42.1	32.9
	6.9	14	7	125.0	23.3	3.9	9.8	0.1	0.1	7.6	0.1	5.4	0.1	128.1	1.2	1.4	151.6	1.4	5.9	4.5	10.0	2.0	8.0
Minimum	5.9	14	7	10.0	23.3	1.6	9.8	0.0	0.0	0.2	0.1	5.4	0.1	12.2	0.7	1.4	41.9	1.4	5.9	0.4	10.0	2.0	1.9
Maximum	7.5	700	350	1705.0	84.6	86.3	61.3	0.4	5.6	183.5	65.9	27.5	3.6	323.3	14.6	22.4	1397.3	161.1	217.9	56.8	285.0	98.2	186.8
Mean	6.8	204.0	100.8	526.9	39.7	24.3	33.5	0.1	1.0	50.1	23.9	12.8	0.8	107.2	3.2	11.5	470.9	32.0	44.5	12.5	79.3	32.2	47.1
±SD	±0.6	±197.7	±97.9	±472.9	±17.6	±25.1	±12.9	±0.1	±1.8	±63.2	±24.5	±7.2	±0.9	±84.2	±3.7	±7.2	±418.3	±43.2	±55.8	±15.2	±70.6	±25.0	±47.0

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Land use	pH	EC (μS/cm)	TDS (mg/L)	TSS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Li^+ (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	PO_4^{2-} (mg/L)	HCO_3^- (mg/L)	TN (mg/L)	NH_3 TKN (mg/L)	CDOM (μg/l)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	Total Hardness (mg/L)	Ca^{2+} Hardness (mg/L)	Mg^{2+} Hardness (mg/L)
Road/ Highway	7.4	252	126	376.0	24.6	19.9	33.1	0.1	0.1	128.8	24.5	18.8	0.5	213.5	4.3	12.6	793.7	38.2	39.3	0.1	100.0	28.1	71.9
	7.4	226	113	460.0	20.1	21.2	30.9	0.1	0.1	155.7	5.6	17.7	0.6	18.3	3.5	14.0	798.9	33.0	33.2	0.2	80.0	28.1	51.9
	7.3	200	101	404.0	20.9	9.7	29.2	0.1	0.0	126.3	8.2	17.9	0.6	21.4	2.6	14.0	500.2	21.2	21.5	0.3	90.0	24.0	66.0
	6.7	196	98	976.0	38.4	25.1	25.1	0.1	0.1	48.7	30.5	19.5	0.5	109.8	0.9	16.8	80.7	5.4	19.6	14.3	40.0	16.0	24.0
	6.6	126	63	752.0	37.9	4.4	21.5	0.0	0.0	17.8	3.2	10.9	0.4	91.5	1.1	16.8	25.1	9.8	21.6	11.8	60.0	22.1	37.9
	6.5	211	105	972.0	28.1	19.7	26.1	0.0	0.0	40.4	6.6	12.3	0.3	67.1	0.5	16.8	467.6	10.4	29.5	19.1	90.0	32.1	57.9
	5.9	336	168	2750.0	21.6	19.7	41.8	0.3	1.3	66.7	14.1	21.3	0.4	195.2	4.4	14.0	455.9	52.5	78.6	26.1	150.0	8.1	141.9
	5.9	108	54	708.0	32.3	11.1	30.3	0.1	1.4	4.7	34.9	16.5	0.5	140.3	3.2	15.4	382.3	15.4	32.2	16.8	90.0	40.1	49.9
	6.9	67	34	690.0	32.5	5.5	22.1	0.1	0.1	14.4	2.8	10.3	0.2	73.2	1.4	2.8	411.7	11.9	21.6	9.7	60.0	20.0	40.0
	6.8	82	41	1365.0	38.9	11.2	24.4	0.1	0.1	18.6	9.2	9.1	0.6	213.5	1.5	2.8	393.5	13.7	28.3	14.6	75.0	38.1	36.9
	6.9	72	36	555.0	35.1	9.4	21.4	0.1	0.1	17.7	3.9	14.6	0.7	97.6	1.9	2.8	415.8	12.2	23.5	11.3	60.0	28.1	31.9
	6.8	66	33	835.0	36.9	4.7	20.5	0.1	0.2	12.4	2.8	12.2	0.6	91.5	1.2	1.4	274.7	8.7	20.6	11.9	70.0	26.1	43.9
Minimum	5.9	66	33	376.0	20.1	4.4	20.5	0.0	0.0	4.7	2.8	9.1	0.2	18.3	0.5	1.4	25.1	5.4	19.6	0.1	40.0	8.1	24.0
Maximum	7.4	336.0	168.0	2750.0	38.9	25.1	41.8	0.3	1.4	155.7	34.9	21.3	0.7	213.5	4.4	16.8	798.9	52.5	78.6	26.1	150.0	40.1	141.9
Mean ±SD	6.8 ±0.5	161.9 ±87.6	81.0 ±43.8	903.6 ±646.0	30.6 ±7.2	13.5 ±7.3	27.2 ±6.2	0.1 ±0.1	0.3 ±0.5	54.4 ±53.2	12.2 ±11.4	15.1 ±4.1	0.5 ±0.1	111.1 ±67.3	2.2 ±1.3	10.9 ±6.3	416.7 ±231.1	19.4 ±14.4	30.8 ±16.3	11.4 ±8.0	80.4 ±27.8	25.9 ±8.9	54.5 ±30.8

SD= standard deviation; EC= electrical conductivity; TDS= total dissolved solids; TSS= total suspended solids; TN= total nitrogen; TKN= total Kjeldahl nitrogen; CDOM= colour dissolved organic matter; TOC= total organic carbon; TC= total carbon; IC= inorganic carbon.

Relative analysis of runoff collected from different rainfall events revealed that the average stormwater runoff quality remained almost same with minimal variations. Site specific activities associated with local environment represented variations with respect to a few parameters, e.g., the level of TSS was observed high owing to the construction activity of Central Vista Project in Central Delhi and construction activity taking place in Delhi Technological University campus. It was observed that the TSS, PO_4^{3-}, and NO_3^- were the major parameters that require the treatment before reuse of the treated runoff.

4.1.3 Heavy metal

The possibility of presence of heavy metals in stormwater runoff originating from various land use area in Delhi, was assessed using stormwater runoff samples. During year 2021, cobalt, chromium, cadmium and lead was in below detection level (BDL) in stormwater runoff sample originating from commercial, industrial, institutional, residential, and road/highway. The presence of copper and zinc in stormwater runoff was witnessed in the samples. The copper varies between 0.029 mg/L to 0.77 mg/L, 0.031 mg/L to 0.21 mg/L, 0.016 mg/L to 0.17 mg/L, 0.023 mg/L to 0.92 mg/L, and 0.016 mg/L to 0.14 mg/L for commercial, industrial, institutional, residential, and road/highway land use, respectively. The average concentration of copper follows 0.16 mg/L > 0.13 mg/L > 0.12 mg/L > 0.06 mg/L > 0.05 mg/L for commercial > industrial > residential > industrial > road/highways (Table 4.7). Copper is a common element which occurs naturally and spreads through natural phenomenon in the environment. As a nutrient, copper does not mobilise in soils, and in solution, it hydrolyses at about pH 7.5 (Adedeji et al., 2013). Copper in stormwater runoff could occur from the sources such as electrical equipment, heat exchangers, plumbing and roofing construction, alloys, and etc. Delhi is an urban area which is dominated by rapid urban expansion, leading to presence of copper in stormwater runoff through anthropogenic activities. Zinc in stormwater samples ranged between 0.1 mg/L to 1.4 mg/L, 0.119 mg/L to 2.41 mg/L, 0.11 mg/L to 2.77 mg/L, 0.23 mg/L to 1.56 mg/L, and 0.13 mg/L to 2.51 mg/L, respectively for commercial, industrial, institutional, residential, and road/highway land use. The average concentration of zinc in stormwater runoff follows the trend 1.43 mg/L > 1.14 mg/L > 1.088 mg/L > 1.006 mg/L > 0.78 mg/L for road/highway > industrial > institutional > residential > commercial land use. It can be observed that zinc in the most dominant metal among all the metals analysed for stormwater runoff in year 2021. Zinc is a common metal occurring naturally and its existence in stormwater runoff was also reported by other studies (Davis et al., 2001; Mangani et al., 2005; Karlén et al., 2003). It is worth noting that source of zinc originating from road/highway is dominating in terms of its average concentration. Similar results have been reported by other studies also in other parts of the world (Backstrom et al., 2003; Mangani et al., 2005). Zinc oxide is an important ingredient used for manufacturing of paints, rubber products, cosmetics, pharmaceuticals, plastics, printer inks, storage batteries, textiles products, electrical equipment, and other products which can contribute towards zinc in stormwater runoff.

Table 4.7 Heavy metals in stormwater runoff from different land use areas in Delhi, India, during year 2021

		Co (mg/L)	**Cr (mg/L)**	**Cu (mg/L)**	**Cd (mg/L)**	**Zn (mg/L)**	**Pb (mg/L)**
Commercial		BDL	BDL	0.076	BDL	0.100	BDL
		BDL	BDL	0.067	BDL	0.290	BDL
		BDL	BDL	0.770	BDL	1.147	BDL
		BDL	BDL	0.075	BDL	0.550	BDL
		BDL	BDL	0.140	BDL	1.360	BDL
		BDL	BDL	0.140	BDL	0.140	BDL
		BDL	BDL	0.029	BDL	1.250	BDL
		BDL	BDL	0.042	BDL	1.430	BDL
Minimum		-	-	0.029	-	0.100	-
Maximum		-	-	0.770	-	1.430	-
Average ± SD		-	-	0.167 ± 0.231	-	0.783 ± 0.534	-
Median		-	-	0.076	-	0.849	-
Skewness		-	-	2.680	-	-0.109	-

	Co (mg/L)	**Cr (mg/L)**	**Cu (mg/L)**	**Cd (mg/L)**	**Zn (mg/L)**	**Pb (mg/L)**
Industrial	BDL	BDL	0.110	BDL	2.140	BDL
	BDL	BDL	0.160	BDL	1.180	BDL
	BDL	BDL	0.180	BDL	0.119	BDL
	BDL	BDL	0.190	BDL	1.590	BDL
	BDL	BDL	0.210	BDL	1.440	BDL
	BDL	BDL	0.031	BDL	0.230	BDL
Minimum	-	-	0.031	-	0.119	-
Maximum	-	-	0.210	-	2.140	-
Average ± SD	-	-	0.132 ± 0.066	-	1.143 ± 0.675	-
Median	-	-	0.160	-	1.300	-
Skewness	-	-	-0.586	-	-0.434	-

	Co (mg/L)	**Cr (mg/L)**	**Cu (mg/L)**	**Cd (mg/L)**	**Zn (mg/L)**	**Pb (mg/L)**
Institutional	BDL	BDL	0.096	BDL	0.670	BDL
	BDL	BDL	0.073	BDL	0.570	BDL
	BDL	BDL	0.087	BDL	2.770	BDL
	BDL	BDL	0.170	BDL	1.430	BDL
	BDL	BDL	0.023	BDL	1.110	BDL
	BDL	BDL	0.045	BDL	1.300	BDL
	BDL	BDL	0.016	BDL	0.350	BDL
	BDL	BDL	0.031	BDL	0.110	BDL
	BDL	BDL	0.025	BDL	1.270	BDL
	BDL	BDL	0.045	BDL	1.300	BDL
Minimum	-	-	0.016	-	0.110	-
Maximum	-	-	0.170	-	2.770	-
Average ± SD	-	-	0.061 ± 0.045	-	1.088 ± 0.708	-
Median	-	-	0.045	-	1.190	-
Skewness	-	-	1.478	-	1.094	-

	Co (mg/L)	**Cr (mg/L)**	**Cu (mg/L)**	**Cd (mg/L)**	**Zn (mg/L)**	**Pb (mg/L)**
Residential	BDL	BDL	0.094	BDL	0.570	BDL
	BDL	BDL	0.084	BDL	0.630	BDL
	BDL	BDL	0.098	BDL	0.880	BDL
	BDL	BDL	0.099	BDL	0.870	BDL
	BDL	BDL	0.078	BDL	0.650	BDL
	BDL	BDL	0.920	BDL	0.870	BDL
	BDL	BDL	0.099	BDL	0.660	BDL
	BDL	BDL	0.103	BDL	1.010	BDL
	BDL	BDL	0.102	BDL	1.560	BDL
	BDL	BDL	0.120	BDL	0.990	BDL
	BDL	BDL	0.110	BDL	1.380	BDL
	BDL	BDL	0.110	BDL	0.920	BDL
	BDL	BDL	0.023	BDL	1.320	BDL
	BDL	BDL	0.026	BDL	0.230	BDL
	BDL	BDL	0.070	BDL	1.310	BDL
	BDL	BDL	0.047	BDL	1.390	BDL
	BDL	BDL	0.043	BDL	1.340	BDL
	BDL	BDL	0.045	BDL	1.530	BDL
Minimum	-	-	0.023	-	0.230	-
Maximum	-	-	0.920	-	1.560	-
Average ± SD	-	-	0.126 ± 0.195	-	1.006 ± 0.366	-
Median	-	-	0.096	-	0.955	-
Skewness	-	-	4.078	-	-0.222	-

	Co (mg/L)	**Cr (mg/L)**	**Cu (mg/L)**	**Cd (mg/L)**	**Zn (mg/L)**	**Pb (mg/L)**
Road/ Highway	BDL	BDL	0.120	BDL	2.510	BDL
	BDL	BDL	0.120	BDL	1.140	BDL
	BDL	BDL	0.130	BDL	2.080	BDL
	BDL	BDL	0.120	BDL	1.250	BDL
	BDL	BDL	0.140	BDL	1.140	BDL
	BDL	BDL	0.019	BDL	1.210	BDL
	BDL	BDL	0.018	BDL	0.130	BDL
	BDL	BDL	0.023	BDL	1.280	BDL
	BDL	BDL	0.016	BDL	1.310	BDL
	BDL	BDL	0.034	BDL	1.430	BDL
	BDL	BDL	0.037	BDL	2.390	BDL
	BDL	BDL	0.047	BDL	1.360	BDL
	BDL	BDL	0.031	BDL	1.360	BDL
	BDL	BDL	0.028	BDL	1.540	BDL
	BDL	BDL	0.034	BDL	1.400	BDL
	BDL	BDL	0.021	BDL	1.480	BDL
	BDL	BDL	0.047	BDL	1.360	BDL
Minimum	-	-	0.016	-	0.130	-
Maximum	-	-	0.140	-	2.510	-
Average ± SD	-	-	0.058 ± 0.045	-	1.434 ± 0.515	-
Median	-	-	0.034	-	1.360	-
Skewness	-	-	0.902	-	0.049	-

BDL= Below the Detection Limit (< 0.001 mg/L for Co; < 0.001 mg/L for Cr; < 0.003 mg/L for Cu, < 0.001 mg/L for Cd; < 0.001 mg/L for Zn; < 0.001 mg/L for Pb); SD= standard deviation*

The stormwater runoff samples for year 2022 reveals non-existence of cobalt in stormwater runoff samples. However, the cadmium which was not present in any stormwater runoff samples in year 2021, showed its existence in stormwater runoff samples from year 2022 for the samples originating from road/highway. Cadmium concentration varied between 0.001 mg/L to 0.006 mg/L with an average of 0.003 ± 0.002 mg/L for the samples from road/highway. The presence of cadmium in stormwater runoff samples can be ascribe to abrasion and disintegration of brake pads and tyres as its source (Flint and Davis, 2007). Here also, cobalt and lead were not found in the stormwater runoff samples from various land use during year 2022. However, zinc being a common metal occurring naturally was found in stormwater runoff samples ranging between 0.03 mg/L to 2.1 mg/L, 0.1 mg/L to 2.9 mg/L, 0.09 mg/L to 3.1 mg/L, 0.02 mg/L to 1.2 mg/L, and 1.1 mg/L to 3.1 mg/L for commercial, industrial, institutional, residential, and road/highway land use, respectively (Table 4.8). The average zinc concentration follows the order 1.77 mg/L > 0.93 mg/L > 0.69 mg/L > 0.53 mg/L > 0.46 mg/L for road/highway > institutional > industrial > residential > commercial land use. The average concentration of zinc is considerably higher for the stormwater runoff samples originating from road/highway owing to presence of zinc in the component of automobiles, such as brakes and tyres (Lau et al., 2009). Another metal assessed in stormwater runoff sample is iron. The concentration of iron in stormwater runoff samples for commercial, industrial, institutional, residential, and road/highway land use ranged between 0.3 mg/L to 1.1 mg/L, 0.14 mg/L to 1.02 mg/L, 0.07 mg/L to 1.2 mg/L, 0.09 mg/L to 1.6 mg/L, and 0.47 mg/L to 15.1 mg/L. The higher iron concentration was mainly sourced from stormwater runoff originating from road/highway. However, the average iron concentration in stormwater runoff follows the trend as 2.82 mg/L > 0.72 mg/L > 0.63 mg/L > 0.59 mg/L > 0.48 mg/L for road/highway > residential > institutional > commercial > industrial land use. Iron being an element originating from earth’s crust can be commonly found in all the stormwater runoff samples.

Table 4.8 Heavy metals in stormwater runoff from different land use areas in Delhi, India, during year 2022

	Co (mg/L)	**Cd (mg/L)**	**Zn (mg/L)**	**Fe (mg/L)**	**Pb (mg/L)**
Commercial	BDL	BDL	0.30	0.30	BDL
	BDL	BDL	0.40	0.40	BDL
	BDL	BDL	0.50	0.80	BDL
	BDL	BDL	2.10	1.10	BDL
	BDL	BDL	0.11	0.90	BDL
	BDL	BDL	0.20	0.32	BDL
	BDL	BDL	0.11	0.40	BDL
	BDL	BDL	0.03	0.50	BDL
Minimum	-	-	0.03	0.3	-
Maximum	-	-	2.1	1.1	-
Average ± SD	-	-	0.468 ± 0.634	0.59 ± 0.282	-
Median	-	-	0.25	0.45	-
Skewness	-	-	2.530	0.784	-
	Co (mg/L)	**Cd (mg/L)**	**Zn (mg/L)**	**Fe (mg/L)**	**Pb (mg/L)**
Industrial	BDL	BDL	0.20	0.50	BDL
	BDL	BDL	2.90	0.60	BDL
	BDL	BDL	0.13	1.02	BDL
	BDL	BDL	0.10	0.14	BDL
	BDL	BDL	0.16	0.14	BDL
Minimum	-	-	0.1	0.14	-
Maximum	-	-	2.9	1.02	-
Average ± SD	-	-	0.698 ± 1.101	0.48 ± 0.327	-
Median	-	-	0.16	0.5	-
Skewness	-	-	2.231	0.681	-

	Co (mg/L)	**Cd (mg/L)**	**Zn (mg/L)**	**Fe (mg/L)**	**Pb (mg/L)**
Institutional	BDL	BDL	3.10	0.60	BDL
	BDL	BDL	1.30	0.60	BDL
	BDL	BDL	0.80	0.80	BDL
	BDL	BDL	0.09	1.20	BDL
	BDL	BDL	0.80	1.20	BDL
	BDL	BDL	0.60	1.16	BDL
	BDL	BDL	0.09	0.22	BDL
	BDL	BDL	0.80	0.30	BDL
	BDL	BDL	0.80	0.07	BDL
Minimum	-	-	0.09	0.07	-
Maximum	-	-	3.1	1.2	-
Average ± SD	-	-	0.931 ± 0.845	0.683 ± 0.411	-
Median	-	-	0.8	0.6	-
Skewness	-	-	2.009	-0.003	-
	Co (mg/L)	**Cd (mg/L)**	**Zn (mg/L)**	**Fe (mg/L)**	**Pb (mg/L)**
Residential	BDL	BDL	0.02	1.60	BDL
	BDL	BDL	0.11	1.50	BDL
	BDL	BDL	0.90	0.90	BDL
	BDL	BDL	0.67	0.90	BDL
	BDL	BDL	0.90	1.41	BDL
	BDL	BDL	1.20	1.50	BDL
	BDL	BDL	0.11	0.20	BDL
	BDL	BDL	0.17	0.30	BDL
	BDL	BDL	0.23	0.17	BDL
	BDL	BDL	0.80	0.09	BDL
	BDL	BDL	0.07	0.20	BDL
	BDL	BDL	1.20	0.10	BDL
	BDL	BDL	0.90	1.10	BDL
	BDL	BDL	0.20	0.12	BDL

Minimum	-	-	0.02	0.09	-
Maximum	-	-	1.2	1.6	-
Average ± SD	-	-	0.534 ± 0.427	0.720 ± 0.587	-
Median	-	-	0.45	0.6	-
Skewness	-	-	0.263	0.312	-
	Co (mg/L)	**Cd (mg/L)**	**Zn (mg/L)**	**Fe (mg/L)**	**Pb (mg/L)**
Road/ Highway	BDL	0.0015	1.10	15.10	BDL
	BDL	0.0011	2.30	1.80	BDL
	BDL	0.006	1.90	0.90	BDL
	BDL	BDL	2.10	1.60	BDL
	BDL	BDL	1.30	2.10	BDL
	BDL	BDL	1.80	1.80	BDL
	BDL	BDL	1.10	0.47	BDL
	BDL	BDL	1.30	1.80	BDL
	BDL	BDL	3.10	1.51	BDL
	BDL	BDL	1.10	3.20	BDL
	BDL	BDL	2.30	1.40	BDL
	BDL	BDL	1.90	2.20	BDL
Minimum	-	0.001	1.10	0.47	-
Maximum	-	0.006	3.10	15.10	-
Average ± SD	-	0.003 ± 0.002	1.78 ± 0.60	2.82 ± 3.76	-
Median	-	0.002	1.85	1.80	-
Skewness	-	1.690	0.69	3.28	-

BDL*= Below the Detection Limit (< 0.001 mg/L for Co; < 0.001 mg/L for Cr; < 0.003 mg/L for Cu, < 0.001 mg/L for Cd; < 0.001 mg/L for Zn; < 0.001 mg/L for Pb); SD= standard deviation

4.2 Ion exchange

The ion exchange process for removal of hardness from the water was conducted in continuous process through three columns in which cation exchange resins in varying quantity was added. The synthetically prepared stormwater runoff was passed through the column until the resins get exhausted. The four cycles of removal of hardness were conducted in which the first cycle consisted of fresh resin while next three cycles were of regenerated resins. It was observed that the column with 0.5 g of cation exchange resin exhausted followed by 1.0 g and then 2.0 g. The observations of residual hardness from each column were obtained through titrimetric analysis. For first cycle where fresh resin was used reported that column with 0.5 g resin lasts for 120 minutes whereas, column with 1.0 g and 2.0 g resin lasted for 150 minutes and 180 minutes, respectively. Once resins were exhausted, they were regenerated using 5 % NaCl brine solution. In cycle 2, it was observed that the regenerated resins were less effective unlike fresh resins. The column with 0.5 g resin exhausted in 60 minutes as compared to 120 minutes ion first cycle. Column with 1.0 g resin showed no removal of hardness after 90 minutes as compared to 150 minutes for fresh resin. Similarly, column with 2.0 g resin lasted for 180 minutes. For third and fourth cycle, the column with 0.5 g regenerated resin lasted for 30 minutes beyond which no removal of hardness was observed. Correspondingly, the column with 1.0 g and 2.0 g regenerated resin lasted for 90 minutes and 150 minutes, respectively, beyond which no removal of hardness was observed. The maximum removal efficiency of hardness through these three columns is shown in Fig. 4.4. The maximum removal efficiency of 2.0 g resin is maximum. This can be ascribed to more dose as compared to that of 0.5 g resin column (almost four times) and 1.0 g resin (almost two times). It is also observed that regeneration of resin is not 100 % for cation exchange resins as compared to fresh resin. Similar results were also found in previous studies (Apell and Boyer, 2010).

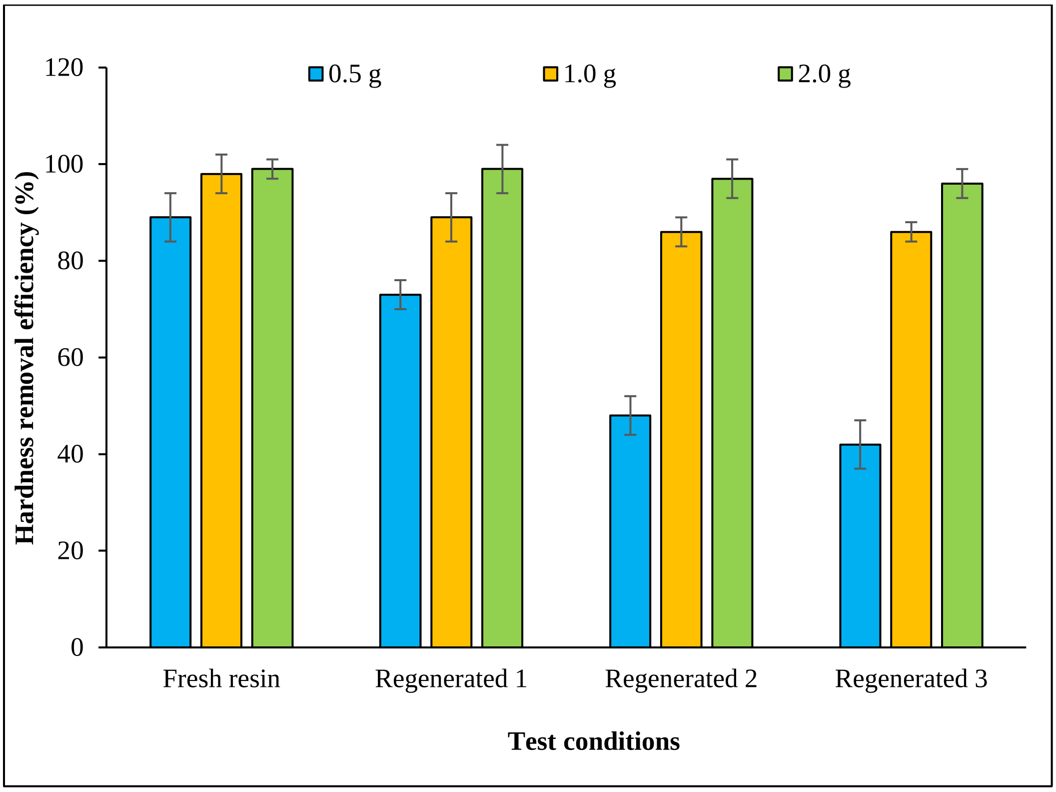


Fig. 4.4 Hardness removal efficiency (%) of fresh and regenerated resins

4.3 Characterisation of biochar

4.3.1 Yield of biochar

The yield of biochar produced during the experiment was calculated as the ratio of weight of carbonaceous biochar produced after pyrolysis to the weight of bamboo biomass before pyrolysis as given by the equation (4.1)

$$\%\ Biochar\ yield = \frac{weight\ of\ carbonaceous\ biochar\ produced\ after\ pyrolysis}{weight\ of\ bamboo\ biomass\ before\ pyrolysis} \text{ x } 100 \quad \textbf{(4.1)}$$

It was reported that approximately 40% biochar was produced from the initial bamboo biomass. The 60% of the initial mass loss can be attributed to the removal of moisture, the production of syngas, and the production of bio-oil during pyrolysis (Panwar and Pawar, 2020). It can also be commented that biomass with higher water content will lead to a poor yield of biochar due to enhanced initial weight and more loss of moisture during pyrolysis.

4.3.2 Proximate analysis

Based on thermogravimetric analysis, raw bamboo reported more moisture and volatile content while its biochar has more carbon and ash content as compared to raw bamboo (Table 4.9). Raw bamboo has moisture, fixed carbon, volatile, and ash content of 7.1%, 16.8%, 76.1%, and 5.1%, respectively. On the other hand, bamboo biochar has moisture, fixed carbon, volatile, and ash content of 3.5%, 59.6%, 17.4%, and 16.8%, respectively. During pyrolysis, as the temperature was raised from room temperature to a peak 500°C, the sample could have lost the moisture and water of hydration in the form of vapours, or the sample could have undergone decomposition which released complex organic compounds including CO_2, CO, H_2, CH_4 and other hydrocarbons in the form of syngas. This might have reduced the volatile content in biochar significantly. For the same reason of loss of moisture and hydration water, the moisture content also became half. The substantial increase in the fixed carbon content of bamboo biochar compared to raw bamboo is a result of loss of other volatile organics during the pyrolysis (Sun et al., 2014).

4.3.3 Elemental analysis

Based on elemental analysis, as presented in Table 4.9, it can be seen that pyrolysis has significantly changed the elemental composition of biochar. The carbon content of bamboo biochar increased to 73.2% from the 43.0% carbon content of raw bamboo. However, the hydrogen and oxygen content has reduced from 7.3% to 3.9% and 48.8% to 22.4%, respectively. Nitrogen and sulphur content remained <1.0% for both raw bamboo and bamboo biochar. O/C and H/C ratios reduced from 1.13 to 0.31 and 0.17 to 0.05, respectively, on the conversion of bamboo biomass to biochar. It is assumed that the lower the ratio, the greater the stability and degree of aromaticity within the biochar (Kumar et al., 2013).

Table 4.9 Proximate analysis and elemental analysis result of raw bamboo and bamboo biochar

Particular	**Proximate Analysis**				**Elemental Analysis**						
	Moisture (%)	**Fixed Carbon (%)**	**Volatile (%)**	**Ash (%)**	**Carbon (%)**	**Hydrogen (%)**	**Nitrogen (%)**	**Sulphur (%)**	**Oxygen* (%)**	**O/C ratio**	**H/C ratio**
Raw bamboo	7.1	16.8	76.1	5.1	43.0	7.3	0.9	0.01	48.8	1.13	0.17
Bamboo biochar	3.5	59.6	17.4	16.8	73.2	3.9	0.5	0.001	22.4	0.31	0.05

**Calculated on the basis of weight difference of elements during analysis assuming it consists of these elements only.*

4.3.4 Fourier Transform Infrared (FTIR) Spectroscopy

As a result of pyrolysis, the increase in temperature changes the functional groups in the biochar. Non-destructive FTIR spectroscopy shows the peak intensity of the various organic groups commonly observed in biochar (Table 4.10). Between 3550 cm^{-1} to 3200 cm^{-1} organic O-H stretching is a result of contribution from water retained in the biochar. C-H stretching between 3000 cm^{-1} to 2840 cm^{-1} corresponds to the presence of an alkane group. The peak between 2000 cm^{-1} to 1650 cm^{-1} is C=O stretching which consists of aromatic compounds, ketones, and amides for all the types of biochar. FTIR peak from 1400 cm^{-1} to 1000 cm^{-1} corresponds to C-H bending and C-O stretching that corresponds to the aldehyde and alcohol functional groups, respectively. 1000 cm^{-1} to 650 cm^{-1} corresponds to C=C stretching and C-H bending that relates to the alkene functional group (Fig. 4.5).

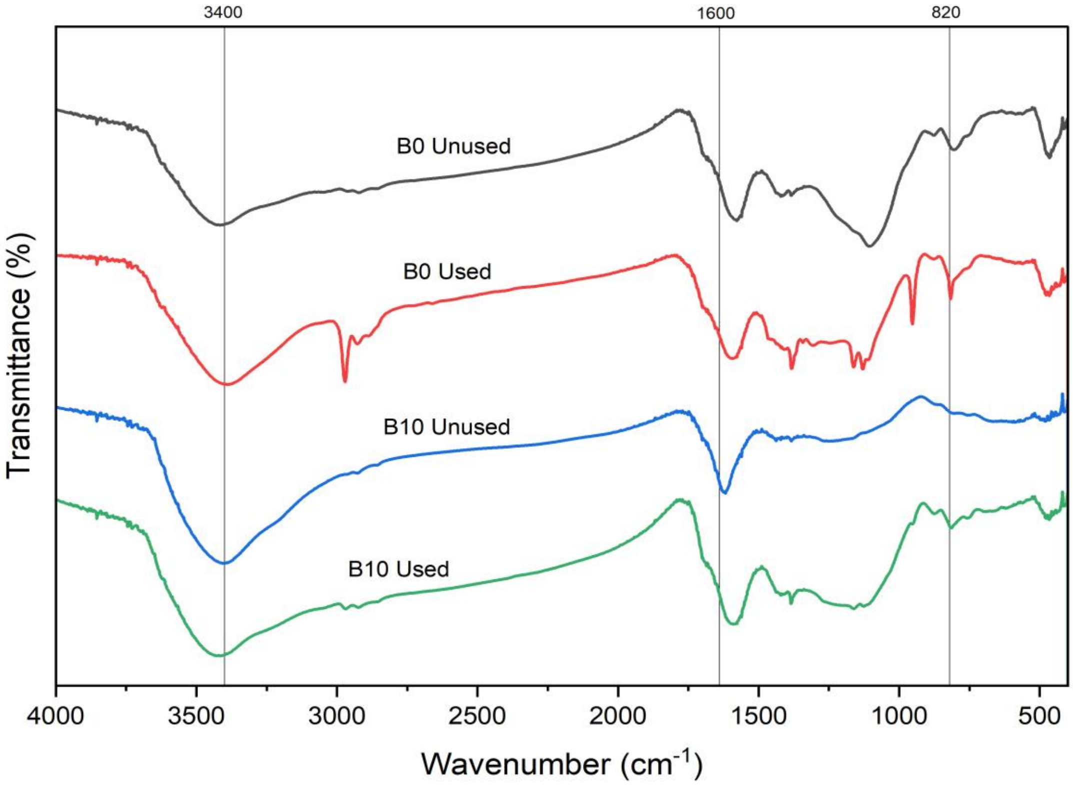


Fig. 4.5 FTIR spectrum of treated and untreated biochar before and after use

Table 4.10 Summary of functional group present in biochar samples

Functional group	**B10% used biochar**	**B10% unused biochar**	**B0% used biochar**	**B0% unused biochar**
	FTIR peak position Intensity	FTIR peak position Intensity	FTIR peak position Intensity	FTIR peak position Intensity
O-H stretch (alcohol)	3445cm^{-1} Intensity: Strong, broad	3413cm^{-1} Intensity: Strong, broad	3403cm^{-1} Intensity: Strong, broad	3439cm^{-1} Intensity: Strong, broad
C-H stretch (alkane)	2975cm^{-1} Intensity: Medium	2917cm^{-1} Intensity: Medium	2971cm^{-1} Intensity: Medium	2920cm^{-1} Intensity: Medium
C=O stretch (conjugated aldehyde)	1694cm^{-1} Intensity: Strong	1620cm^{-1} Intensity: Strong	1700cm^{-1} Intensity: Strong	1692cm^{-1} Intensity: Strong
C=C stretch (unsaturated ketone)	1594cm^{-1} Intensity: Strong	Peak not observed	1588cm^{-1} Intensity: Strong	Peak not observed
C-H bending (alkane)	Peak not observed	1437cm^{-1} Intensity: Medium	Peak not observed	Peak not observed
C-H bending (aldehyde)	1385cm^{-1} Intensity: Medium	1386cm^{-1} Intensity: Medium	1386cm^{-1} Intensity: Medium	1383cm^{-1} Intensity: Medium
C-O stretch (tertiary alcohol)	1151cm^{-1} Intensity: Strong	Peak not observed	1163cm^{-1} Intensity: Strong	1116cm^{-1} Intensity: Strong
C-O stretch (secondary alcohol)	1109cm^{-1} Intensity: Strong	Peak not observed	1127cm^{-1} Intensity: Strong	Peak not observed
C=C stretch (alkene)	961cm^{-1} Intensity: Strong	Peak not observed	952cm^{-1} Intensity: Strong	Peak not observed
C-H bending	882cm^{-1} Intensity: Strong	812cm^{-1} Intensity: Strong	817cm^{-1} Intensity: Strong	806cm^{-1} Intensity: Strong

4.4 Nutrient removal study using biochar

4.4.1 Removal from synthetically prepared stormwater runoff

Biochar is an excellent carbonaceous material for the pollutant removal through adsorption. It can be used as a filter material that can removal impurities from the stormwater runoff. The efficacy of laboratory prepared biochar was for pollutant removal was tested through series of experiments. For the phosphate strength of 5 mg/L, different types of biochar have shown different removal efficiencies. B0% biochar without any treatment was not able to remove the phosphate from synthetic stormwater runoff in a period of 4 hours.

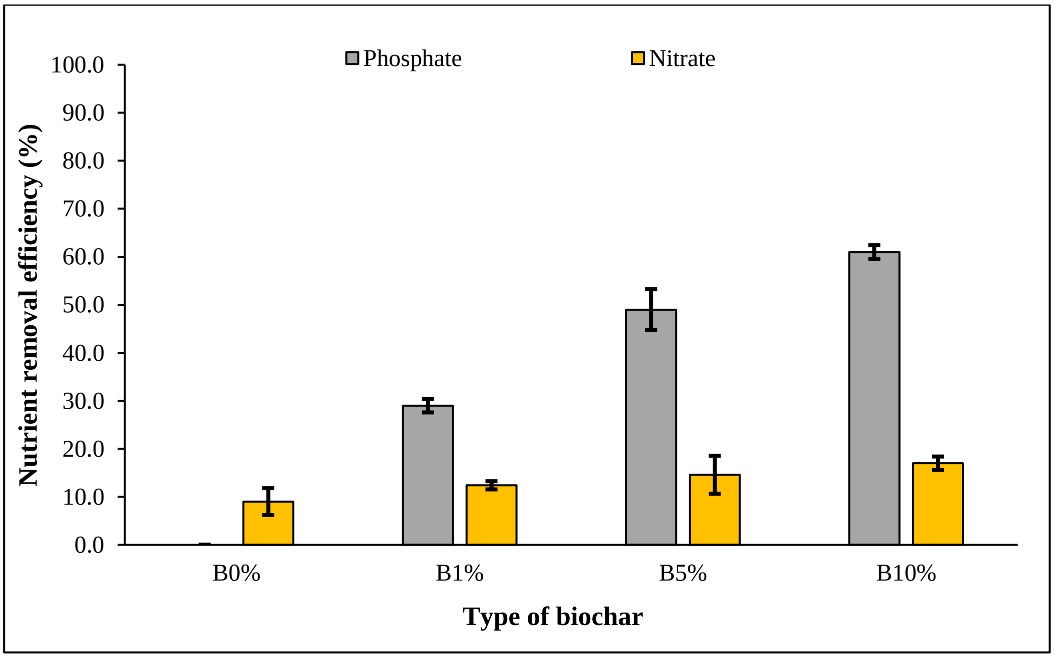


Fig. 4.6 Phosphate and nitrate removal efficiency of biochar from synthetically prepared stormwater runoff having PO_4^{3-} = 5mg/L and NO_3^- =50mg/L strength and biochar dose of 5 g/L

This could be attributed to the non-availability of adsorption sites on the surface of untreated biochar which are negatively charged. Negatively charged sites cannot remove anionic species. However, significant removal was observed in case of biochar which was pre-treated with $FeCl_3$. B1%, B5%, and B10% biochar removed 29%, 49%, and 61%, respectively, from synthetically prepared stormwater runoff when phosphate strength was 5 mg/L (Fig. 4.6). B10% treated biochar removed phosphate almost twice the B1% treated biochar. This could be attributed to the availability of sites having Fe (III) present on the porous surface of biochar that can easily remove phosphate from the sample. The increase in phosphate removal efficiency is almost 60 times for B10% treated biochar to that of the untreated B0% biochar in this study.

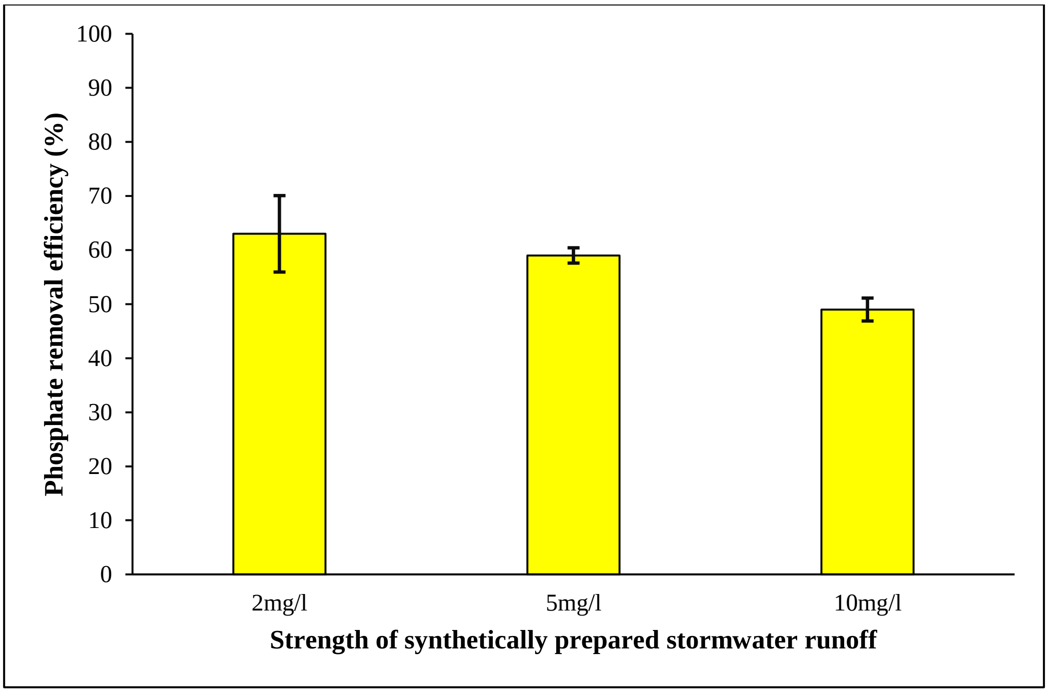


Fig. 4.7 Phosphate removal efficiency using B10% biochar with dose 5g/L

B10% biochar was further used to study its nutrient removal efficiency for different phosphate strengths of 2 mg/L, 5 mg/L, and 10 mg/L, and the results are presented in Fig. 4.7. It was observed that biochar can remove almost 63% of phosphate for the initial phosphate strength of 2 mg/L at a dose of 5.0 g/L absorbent and a contact period of 4 hours. At the same time, the removal efficiency of phosphates reduced with the increase in the strength of phosphate (Fig. 4.7). For the same dose and contact period, only 59% and 49% of phosphate were removed from synthetically prepared stormwater runoff of strength 5 mg/L and 10 mg/L, respectively. On the other hand, for the initial strength of nitrate as 50 mg/L, biochar without any given treatment was able to remove approximately 9%. The removal efficiency of nitrate using B1%, B5%, and B10% was of order 12.4%, 14.6%, and 17.0%, respectively. The lower adsorption of nitrate compared to phosphate can possibly be due to the preferential adsorption of phosphate over nitrate by Fe(III) modified biochar. Although, increasing Fe concentration in biochar did not show significant removal efficiency towards nitrate (Yadav et al., 2024).

4.4.2 Removal from field stormwater runoff

Based on the observations obtained for nutrient removal from synthetic stormwater, actual (field) stormwater runoff was also subjected to treated using B10% biochar, to examine the adsorption capacity in chemically complex field stormwater runoff. The phosphate removal efficiency of biochar for stormwater runoff collected from commercial, institutional, industrial, and road/highway areas of the Delhi region was of order 40.5%, 57.1%, 40.3%, and 59.1%, respectively (Fig. 4.8).

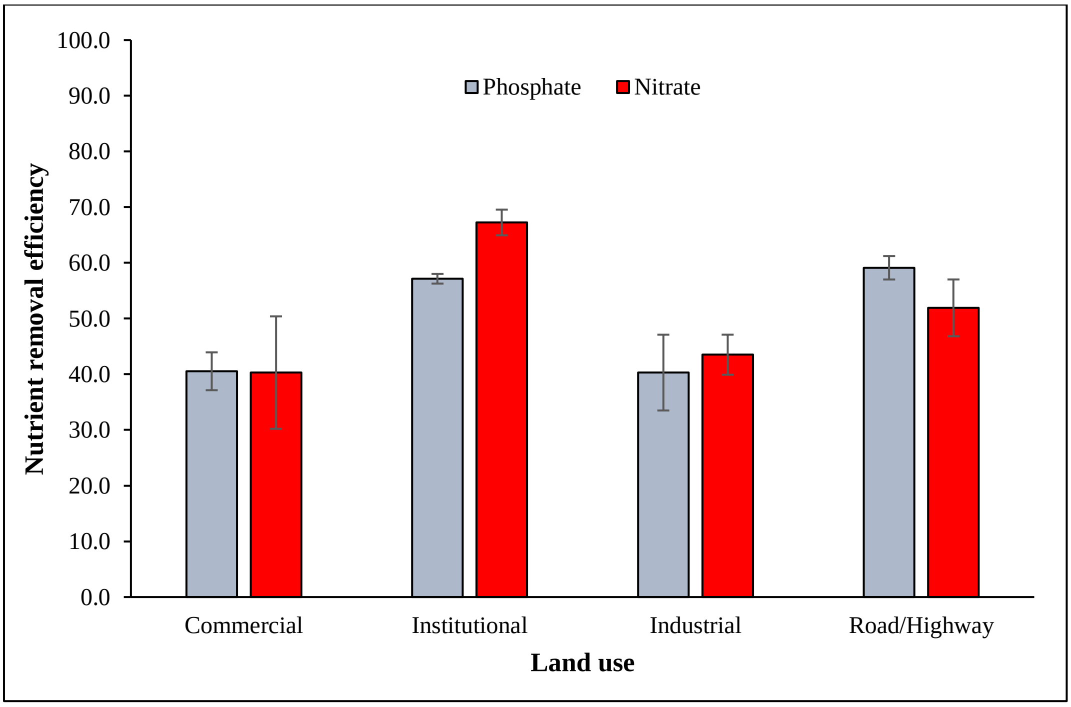


Fig. 4.8 Phosphate and nitrate removal efficiency (%) from stormwater runoff originating from different land use areas using B10% biochar

It shows that the removal efficiency observed is relatively similar to that of the synthetic stormwater runoff experiments. It was also observed that the biochar was not able to remove SO_4^{2-} chemical species though it is also an anionic species that was not absorbed on Fe (III) sites of biochar. Also, up to 67.3% of nitrate was removed from institutional area runoff. The removal efficiency depends upon the initial concentrations of the pollutants. The equilibrium of the reaction shifts towards another side that reverses and releases pollutants from the adsorbed surface of biochar. The shift of equilibrium depends upon the release of pollutants from the solid phase (biochar) to an aqueous phase.

4.5 Adsorption isotherm study

Adsorption isotherm distinguishes the surface properties and affinity to adsorb the adsorbate. Isotherms corresponding to B10% biochar were studied in order to understand the same. The best curve is obtained by the Langmuir isotherm model with R^2=0.9992 as against the Freundlich isotherm model with R^2=0.9933 (Fig. 4.9 (a) and (b)). The maximum adsorption capacity q_{max} was obtained as 11.57 mg/g for phosphate (Table 4.11). The calculated value of Langmuir constant R_L was less than 1.0 which suggests that the adsorption possibility is favourable (Ayub et al., 2020).

Table 4.11 Langmuir and Freundlich adsorption isotherm for B10% biochar

Isotherm	**Parameter**	**Unit**	**Values**
Langmuir	q_{max}	(mg/g)	11.5741
	K_L	(L/mg)	0.0469
	R_L	-	0.3473
	R^2	-	0.9992
Freundlich	K_f	(mg/g) (L/mg)$^{1/n}$	1.0097
	1/n	-	0.5531
	R^2	-	0.9933

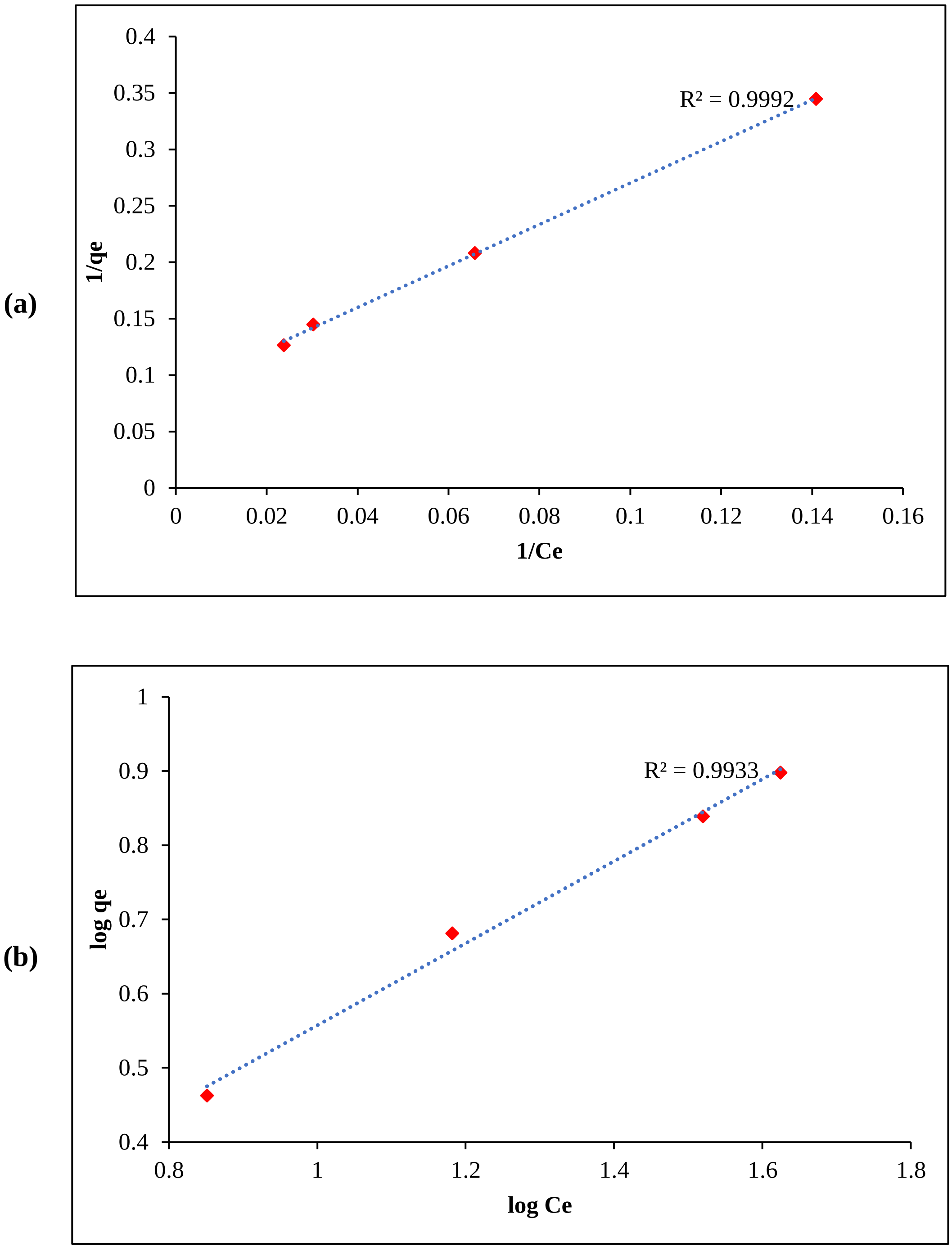


Fig. 4.9 (a) Langmuir isotherm (a) and (b) Freundlich isotherm fit for B10% biochar

4.6 Kinetics of removal

The plots of pseudo-first order and pseudo-second order models for the adsorption capacity of biochar are shown in Fig. 4.10 (a) and Fig. 4.10 (b) respectively.

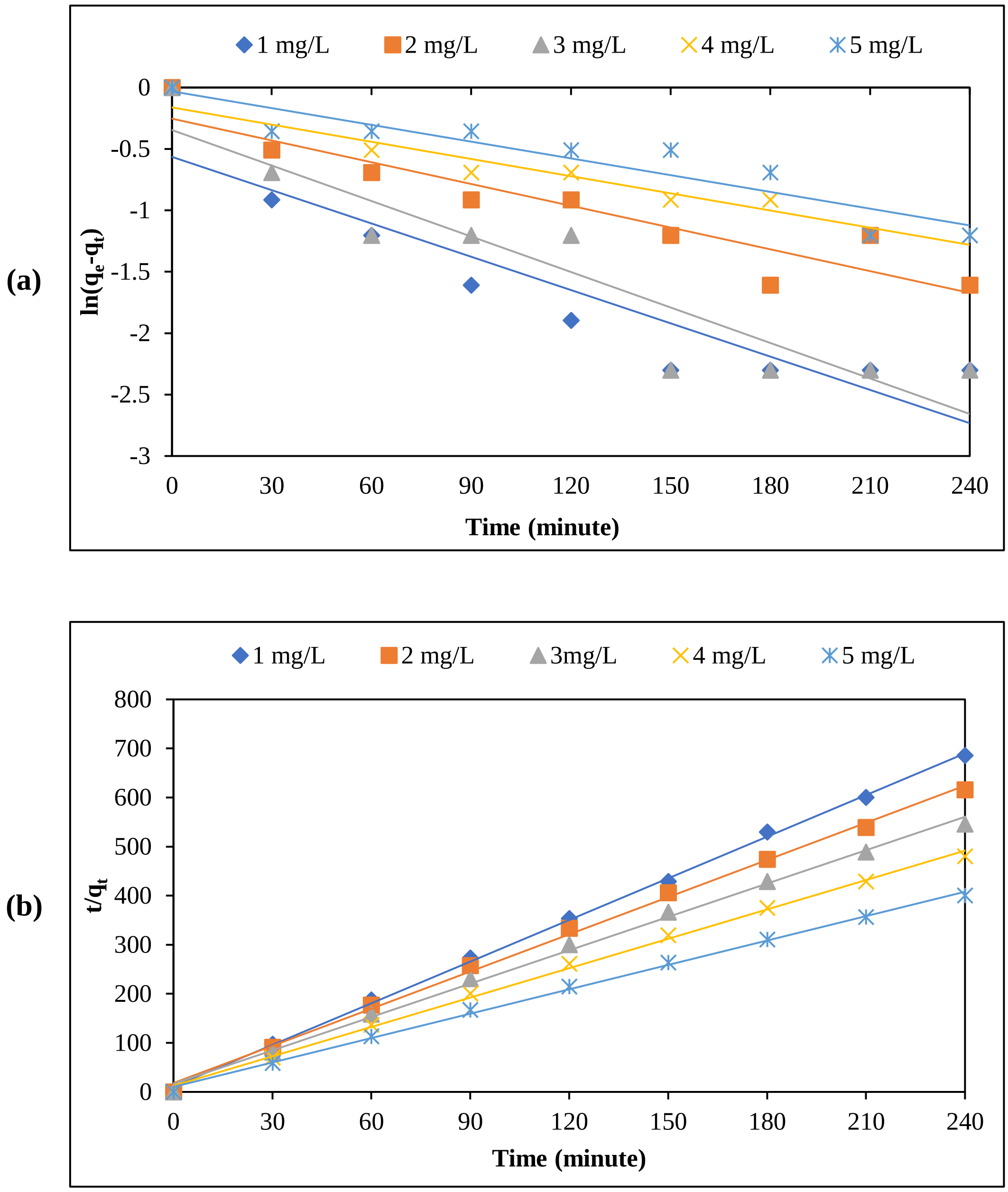


Fig. 4.10 (a) Pseudo first order kinetics and (b) Pseudo second order kinetics for removal phosphates using B10% biochar

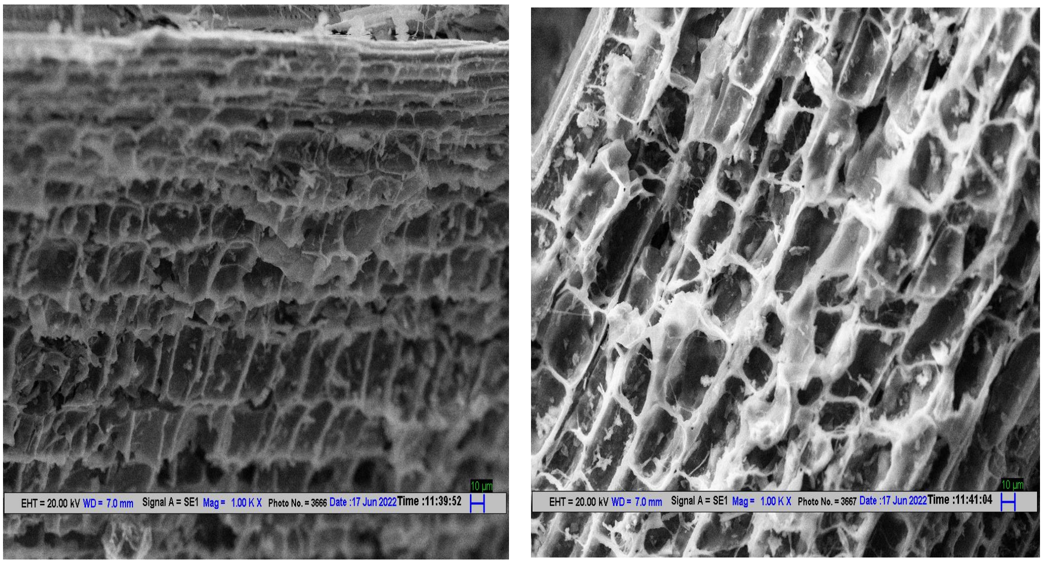
Table 4.12 Comparison of parameters for pseudo-first order and pseudo-second order reaction kinetics

Order of reaction	**Parameter**	**Unit**	**Concentration**				
			1.0 mg/L	**2.0 mg/L**	**3.0 mg/L**	**4.0 mg/L**	**5.0 mg/L**
-	$q_{e(exp)}$	mg/L	0.31	0.38	0.45	0.51	0.58
First Order	K_1	min^{-1}	-0.009	-0.0059	-0.0096	-0.0047	-0.0045
	$q_{e(cal)}$	mg/g	0.57	0.78	0.71	0.85	0.97
	R^2	-	0.8431	0.8727	0.8724	0.9457	0.8676
Second order	K_2	$g\ mg^{-1}\ min^{-1}$	0.73	0.35	0.31	0.31	0.27
	$q_{e(cal)}$	mg/g	0.35	0.40	0.44	0.50	0.60
	R^2	-	0.9991	0.9973	0.9968	0.9976	0.9981

The various parameters obtained from these models are given in the Table 4.12. Pseudo-first order model fits relatively poorly for the removal of phosphates in which the R^2 value varied from 0.867 to 0.945. Also, the adsorption capacity calculated at equilibrium ($q_{e(cal)}$) and adsorption capacity from the experiments ($qe_{(exp)}$) varied significantly. Thus, it shows that adsorption kinetics did not follow pseudo-first order kinetic model. On the other hand, the R^2 value for pseudo-second order kinetics varied between 0.999 to 0.996 which shows that the plot fits very well. Furthermore, adsorption capacity varied between 0.35 to 0.60 mg/g for phosphate. Similar results were found in experimental data for adsorption capacity. Thus, the adsorption of phosphate follows pseudo-second order rather than pseudo-first order kinetics (Zhang et al., 2012).

4.7 Scanning Electron Microscopy (SEM)

SEM images of biochar samples show the surface morphology of the biochar before and after treatment with $FeCl_3$. In both the biochar, complex surface morphology can be seen along with macro to micropores present over the surface which are produced as a result of a vascular bundle of raw biomass (Hernandez-Mena et al., 2014). However, in biochar treated with $FeCl_3$, agglomeration of this electropositive chemical can be seen (Yadav et al., 2024). Removal of chemical species by biochar depends upon the presence of adsorption sites over the surface which is correlated with the specific surface area of the biochar produced. The increase in temperature for biochar production by pyrolysis increases the specific surface area of biochar that enhances the removal of phosphates (Zeng et al., 2013). However, it was reported in earlier studies that biochar has an electro-negative charge over its surface, and it cannot remove anions (PO_4^{3-} and NO_3^-) by adsorption (Wang et al., 2015; Zeng et al., 2013).



(a) **(b)**

Fig. 4.11 SEM image of the biochar (a) before and (b) after impregnated with $FeCl_3$

The pyrolysis of biomass produces biochar having functional groups such as -OH and -COOH as shown by the FTIR spectrum peak at 3400 cm^{-1} and 1600 cm^{-1}, respectively (Fig. 4.11), which may result in negative surface charge. The net negative surface charge may lead to poor electrostatic attraction of PO_4^{3-} and NO_3^- with biochar and thus, require treatment with electro-positive chemical species like $FeCl_3$. The impregnation of $FeCl_3$ over the biochar surface has played a crucial role in nutrient removal. The SEM images before and after the adsorption (Fig. 4.11) suggest that the surface was smooth before adsorption while, after adsorption, the surface was occupied with adsorbed particles. This change in the surface morphology of biochar is an indicative that nutrients were removed by the action of electrostatic attraction between positively charged Fe(III) ions and negatively charged phosphate ions. FTIR spectrum peak at 1000 cm^{-1} after adsorption suggests the interaction of Fe-OH with P ions (Zhang et al., 2009).

4.8 Adsorption capacity of biochar

The adsorption capacity of biochar for a dose of 5.0 g/l was calculated in batch experiments for varying strength of phosphate in synthetic and real stormwater runoff which varied from 2.0 mg/L to 10 mg/L, and 0.4 mg/L to 3.2 mg/L, respectively. The experiment was conducted at 7.0 pH for synthetically prepared stormwater runoff at 27^{o}C temperature while the natural pH of real stormwater runoff is considered for this study.

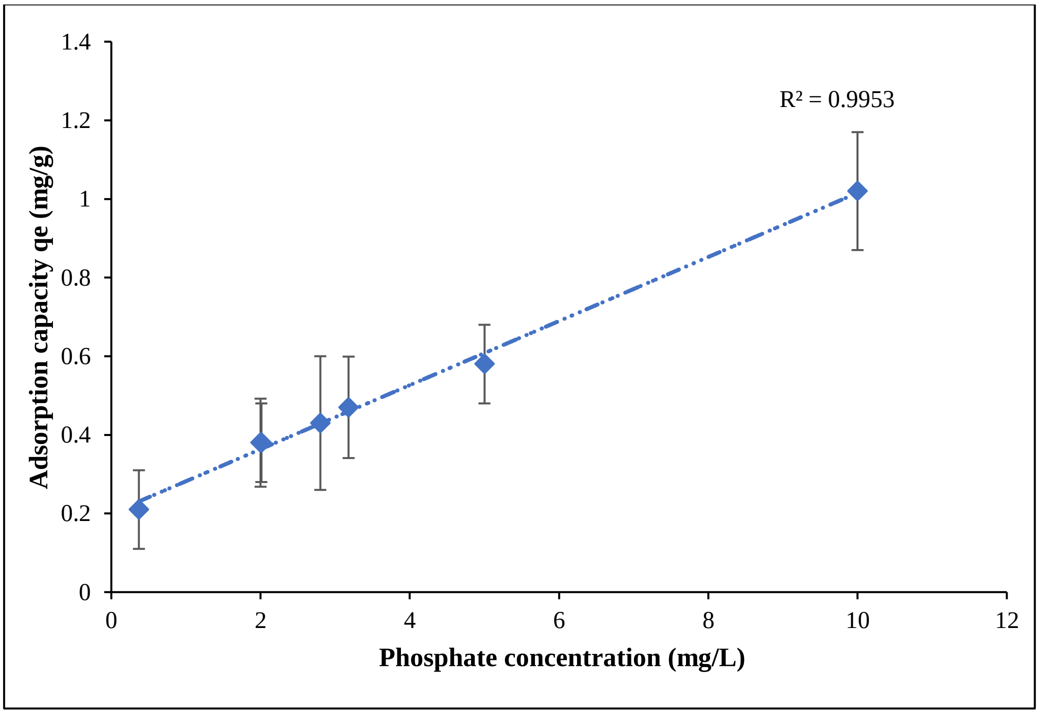


Fig. 4.12 Adsorption capacity of biochar for the removal of phosphate from synthetic and real stormwater runoff tested in a batch experiment

The dose of biochar was kept fixed at 5.0 g/l for Fe (III) treated B10% biochar for experimentation. The adsorption capacity of biochar increased with the increase in the concentration of phosphate which may be attributed to the availability of vacant sites for its adsorption which is represented by a strong correlation value (R^2>0.99) as shown in Fig. 4.12.

4.9 Nutrient removal study (batch process)

The removal efficiency of nutrient from synthetically prepared stormwater runoff was studied using six different filter media. The Fig. 4.13 shows the phosphate removal efficiency at initial phosphate concentrate of 5 mg/L. The experiment was carried out in batch in which the contact time of 5 hours between nutrients in synthetically prepared stormwater runoff and filter media was provided which is adequate where no storage is to be provided. The nutrient removal by each filter media at an interval of every hour is shown in Fig. 4.13 are obtained from replicate analysis of these samples. Controlled batch tests were conducted with each filter media using deionised water.

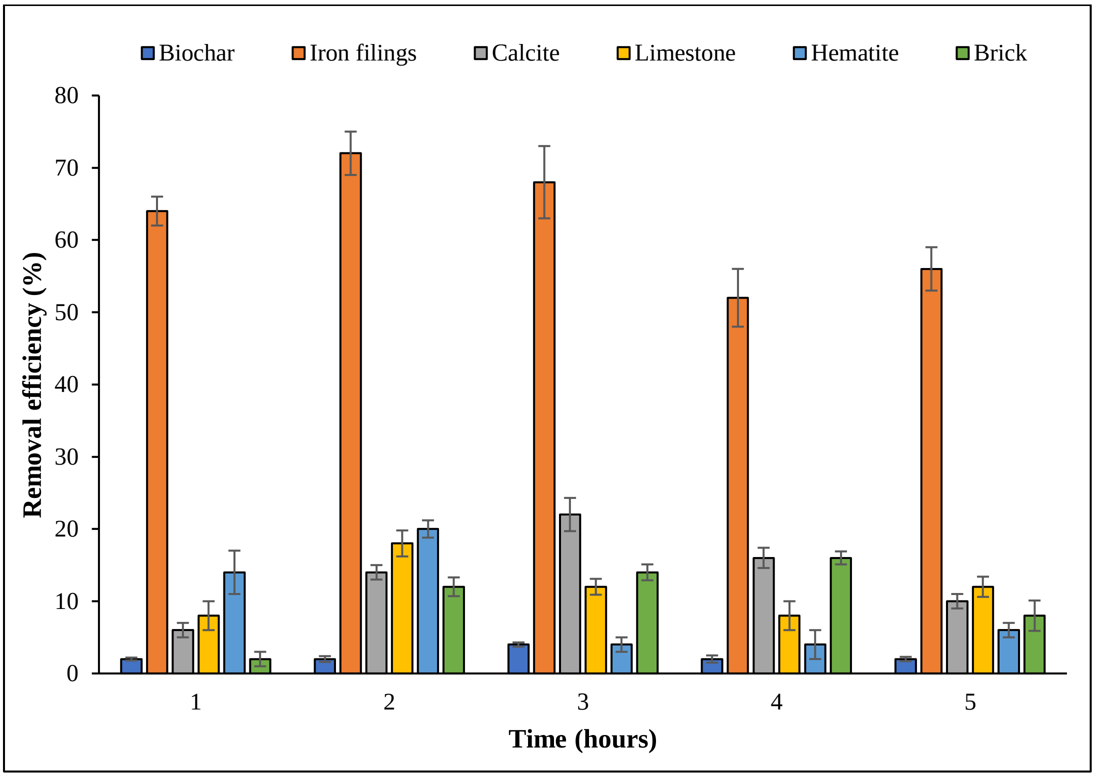


Fig. 4.13 Phosphate removal efficiency (%) using different filter media in batch (PO_4^{3-} = 5mg/L)

Table 4.13 Removal efficiency of different filter materials for initial phosphate concentration PO_4^{3-} = 5mg/L

Time (hours)	Biochar		Iron filings		Calcite		Limestone		Hematite		Brick	
	Residual PO_4^{3-} (mg/L)	Removal efficiency (%)	Residual PO_4^{3-} (mg/L)	Removal efficiency (%)	Residual PO_4^{3-} (mg/L)	Removal efficiency (%)	Residual PO_4^{3-} (mg/L)	Removal efficiency (%)	Residual PO_4^{3-} (mg/L)	Removal efficiency (%)	Residual PO_4^{3-} (mg/L)	Removal efficiency (%)
1	4.9	2.0	1.8	64.0	4.7	6.0	4.6	8.0	4.3	14.0	4.9	2.0
2	4.9	2.0	1.4	72.0	4.3	14.0	4.1	18.0	4.0	20.0	4.4	12.0
3	4.8	4.0	1.6	68.0	3.9	22.0	4.4	12.0	4.8	4.0	4.3	14.0
4	4.9	2.0	2.4	52.0	4.2	16.0	4.6	8.0	4.8	4.0	4.2	16.0
5	4.9	2.0	2.2	56.0	4.5	10.0	4.4	12.0	4.7	6.0	4.6	8.0
Minimum	4.8	2.0	1.4	52.0	3.9	6.0	4.1	8.0	4.0	4.0	4.2	2.0
Maximum	4.9	4.0	2.4	72.0	4.7	22.0	4.6	18.0	4.8	20.0	4.9	16.0
Average ± SD	4.9 ± 0.0	2.4 ± 0.9	1.9 ± 0.4	62.4 ± 8.3	4.3 ± 0.3	13.6 ± 6.1	4.4 ± 0.2	11.6 ± 4.1	4.5 ± 0.4	9.6 ± 7.1	4.5 ± 0.3	10.4 ± 5.5

SD= standard deviation

For the batch test, the average phosphate removal efficiency of the filter media follows the order 62.4 % > 13.6 % > 11.6 % > 10.4 % > 9.6 % > 2.4 % for iron filing > calcite > limestone > brick > hematite > biochar (Table 4.13; Fig. 4.13). For the iron filings, the phosphate removal efficiency ranged between 52 % to 72 %. The removal of phosphate increased followed by decrease in removal efficiency with time. The iron filings proved to be highly effective towards removal of phosphate from synthetically prepared stormwater runoff among all the filter media taken under consideration. This can be ascribed to electro-positive charge present in the iron filings which helped in binding of phosphates leading to its removal. For calcite, the phosphate removal efficiency varied between 6 % to 22 % which can be ascribed to slightly positive surface charge, thus, favouring anionic adsorption over the surface of calcite. Calcite is carbonate mineral consisting of stable calcium carbonate (Reddy et al., 2014). The calcium might dissolve in the aqueous phase at higher pH, as a result, the phosphate was removed by calcite may be due to formation of calcium phosphate precipitates. Also, the ligand exchange of phosphate with oxygen functional group present over the surface of calcite may also removes the phosphates from the sample. In the limestone batch test, the phosphate removal efficiency varied between 8 % to 18 %. The phosphate removal efficiency was relatively lower in case of limestone which may be due to non-availability of the adsorption sites over the surface of the limestone. It can also be inferred that shaking RPM in batch experiment also hinders the phosphate removal efficiency (Hussain et al., 2011). Another batch study using brick as an adsorbent for the phosphate removal efficiency was calculated which reported phosphate removal efficiency between 2 % to 16 %. For initial phosphate concentration of 5 mg/L, the phosphate removal efficiency increased with time upto 4 hours during the study, followed by its reduction in removal efficiency by almost 50 % at the end of 5th hour. The poor phosphate removal efficiency can be ascribed to lower concentration of Al_2O_3 and Fe_2O_3 chemical species in the brick clay (Jia et al., 2013). The batch study using hematite was able to remove 4 % to 20 % of the phosphate from synthetically prepared stormwater runoff. Initially, the removal rate was increasing upto 2 hours of study which then reduced to poor removal efficiency. The adsorption capacity and performance are function of contact time. The phosphate removal efficiency using hematite largely depends upon the hydroxyl groups and the surface area (Liu et al., 2013). The biochar used during the study was less efficient towards the removal of phosphates in aqueous medium when no surface treatment was provided to it. This is because of the presence of electro-negative surface charge, thus causing the non-availability of the adsorption sites over the surface of biochar.

4.10 Column filter unit for continuous process

The efficacy of the above-mentioned filter media which were studied individually in batch process, afterwards used to develop a continuous vertical flow column filter. These individual filter media were placed in layer in the vertical column through which the real stormwater runoff was fed. During the present study, stormwater runoff from seven different rainfall event was collected and passed through the column filter. Initially during Run 1 and Run 2, the layer of sand dust was not provided which caused poor removal of suspended solids as shown in Fig. 4.14. This can be ascribed to the size of voids which were larger than the particle of the suspended solids and thus, failed to get trapped in the voids. The TSS concentration of inflow for Run 1 was 210 mg/L while the TSS concentration at outlet varied between 78 mg/L to 150 mg/L (Table 4.14). Thus, the maximum suspended solid removal efficiency achieved was 62.9 % at the end of 60-minute cycle. Similarly, during Run 2 of another stormwater runoff treatment, the influent TSS concentration was 166 mg/L which was reduced to 42 mg/L to 92 mg/L during the treatment process. The suspended solid removal efficiency, however, increased slightly to 74.7 % which can be attributed towards clogging of filter media during previous run for treatment, thus, reducing the void size (Kandra et al., 2014). Due to reduced removal efficiency of suspended solids, a thin layer of stone dust was placed at the top of the column filter. In the following runs of stormwater runoff treatment, significant TSS removal efficiency was witnessed. The influent TSS concentration for Run 3, Run 4, Run 5, Run 6 and Run 7 was of order 64 mg/L, 48 mg/L, 64 mg/L, 110 mg/L and 154 mg/L. The suspended solids concentration at the effluent end varied between 4 mg/L to 30 mg/L, 4 mg/L to 8 mg/L, 6 mg/L to 12 mg/L, 8 mg/L to 21 mg/L, and 4 mg/L to 25 mg/L for Run 3, Run 4, Run 5, Run 6 and Run 7, respectively. During the treatment through column, the suspended solid removal efficiency followed the order 97.4 % > 93.8% > 92.7% > 91.7% > 90.6% for Run 7 > Run 3 > Run 6 > Run 4 > Run 5. The introduction of layer of stone dust caused significant reduction in the suspended solid concentration at the effluent end for consecutive runs. Although the suspended solid removal from stormwater runoff was significant, but the introduction of thin layer of stone dust leads to clogging and reduced hydraulic conductivity. Similar observations were highlighted in previous study as well (Kandra et al., 2014).

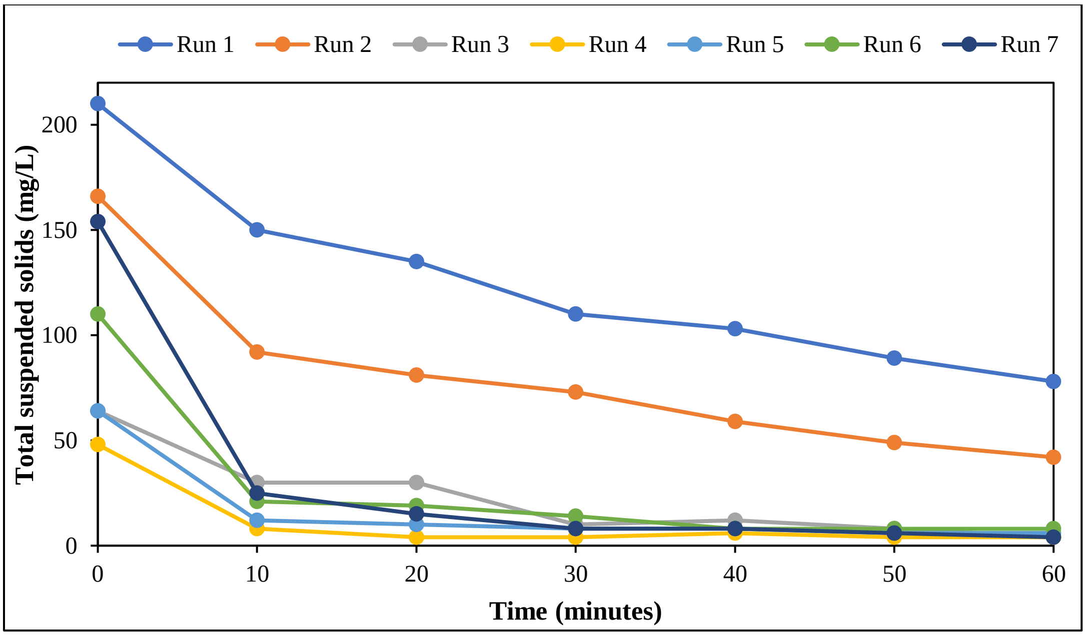


Fig. 4.14 Removal of total suspended solid using continuous vertical flow column filter

Presence of nutrients represents one of the major pollutants found in the stormwater runoff characterisation which is enough to cause eutrophication in waterbodies and disturb the ecological balance. Thus, the removal of phosphate and nitrates using continuous vertical flow column filter was studied for seven different rainfall events leading to stormwater runoff. The phosphate concentration in these seven stormwater runoff samples at the influent varied between 0.1 mg/L to 0.6 mg/L. The influent concentration of phosphate from seven different stormwater runoff samples was of order 0.13 mg/L, 0.6 mg/L, 0.2 mg/L, 0.3 mg/L, 0.6 mg/L, 0.6 mg/L, 0.4 mg/L, for Run 1, Run 2, Run 3, Run 4, Run 5, Run 6, and Run 7, respectively (Fig. 4.15). The phosphate concentration at the outlet was reported as 0.03 mg/L to 0.05 mg/L, 0.05 mg/L to 0.1 mg/L, 0.04 mg/L to 0.09 mg/L, 0.03 mg/L to 0.1 mg/L, 0.04 mg/L to 0.3 mg/L, 0.08 mg/L to 0.1 mg/L, and 0.04 mg/L to 0.1 mg/L for Run 1, Run 2, Run 3, Run 4, Run 5, Run 6, and Run 7, respectively. Thus, the maximum phosphate removal efficiency achieved was of order 76.9 %, 91.7 %, 80.0 %, 90.0 %, 93.3 %, 86.7 %, and 90.0 %, for Run 1, Run 2, Run 3, Run 4, Run 5, Run 6, and Run 7, respectively. The effective removal efficiency of phosphate can be attributed towards its binding with iron filings present in the vertical column along with hematite (Narayanasamydamodaran et al., 2021; Wen et al., 2020). Also, in comparison the phosphate removal efficiency of iron filing and hematite in batch experiment, the initial concentration of phosphate was of order 5.0 mg/L leading to its poor phosphate removal efficiency. On the other hand, the initial inlet concentration of real stormwater runoff was relatively many folds lesser than synthetically prepared stormwater runoff sample, leading to better performance of filter media and enhanced phosphate removal efficiency.

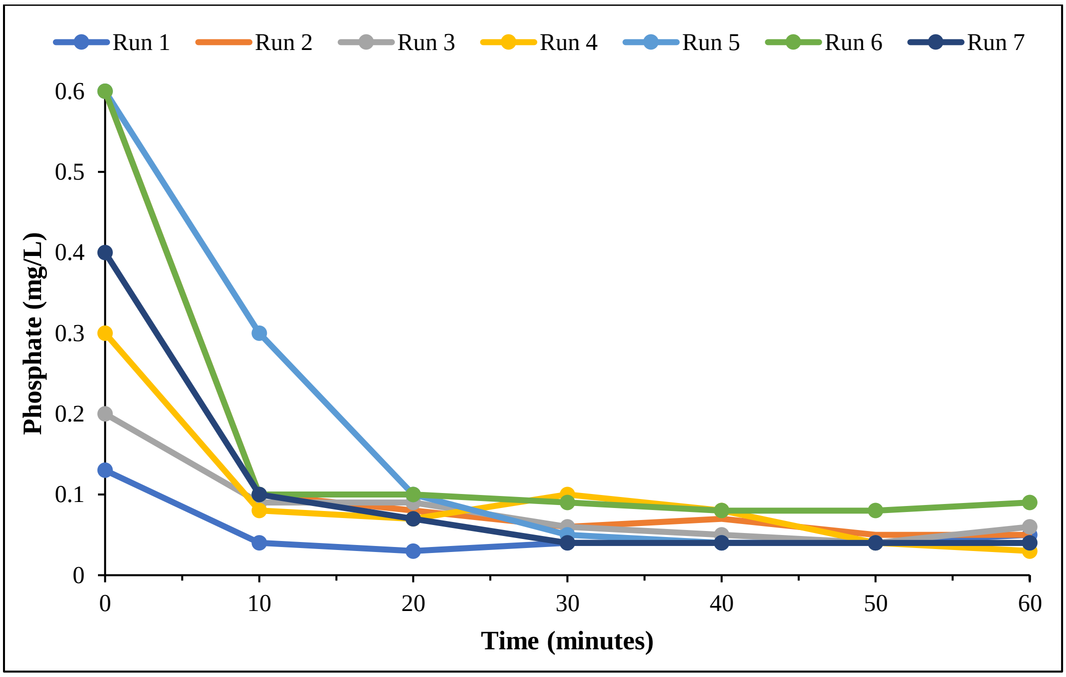


Fig. 4.15 Removal of phosphate using continuous vertical flow column filter

Another nutrient pollutant to marine waterbodies (NO_3^-) was investigated. The nitrates present in the stormwater runoff samples from seven different rainfall events were also removed using the continuous vertical flow column filter during the present study. The nitrate concentration at the inlet was varied as 22.9 mg/L, 18.8 mg/L, 14.9 mg/L, 13.9 mg/L, 14.7 mg/L, 15.5 mg/L, and 11.2 mg/L for Run 1, Run 2, Run 3, Run 4, Run 5, Run 6, and Run 7, respectively. The nitrate removal efficiency ranges widely between 75.2 % to 20.9 % during the present study. The nitrate removal efficiency from the vertical column filter follows the trend 75.2 % > 61.2 % > 56.3 % > 47.7 % > 33.3 % > 25.9 % > 20.9% for Run 3 > Run 2 > Run 7 > Run 6 > Run 5 > Run 4 > Run 1 (Fig. 4.16). This highly varying nitrate removal efficiency can be ascribed to complex chemistry and various chemical species present in stormwater runoff. Also, less availability of adsorption sites over calcite and limestone present in filter column, and affinity of nitrates towards making bond with iron filings could be a reason for varying result of nitrate removal efficiency (Reddy et al., 2014).

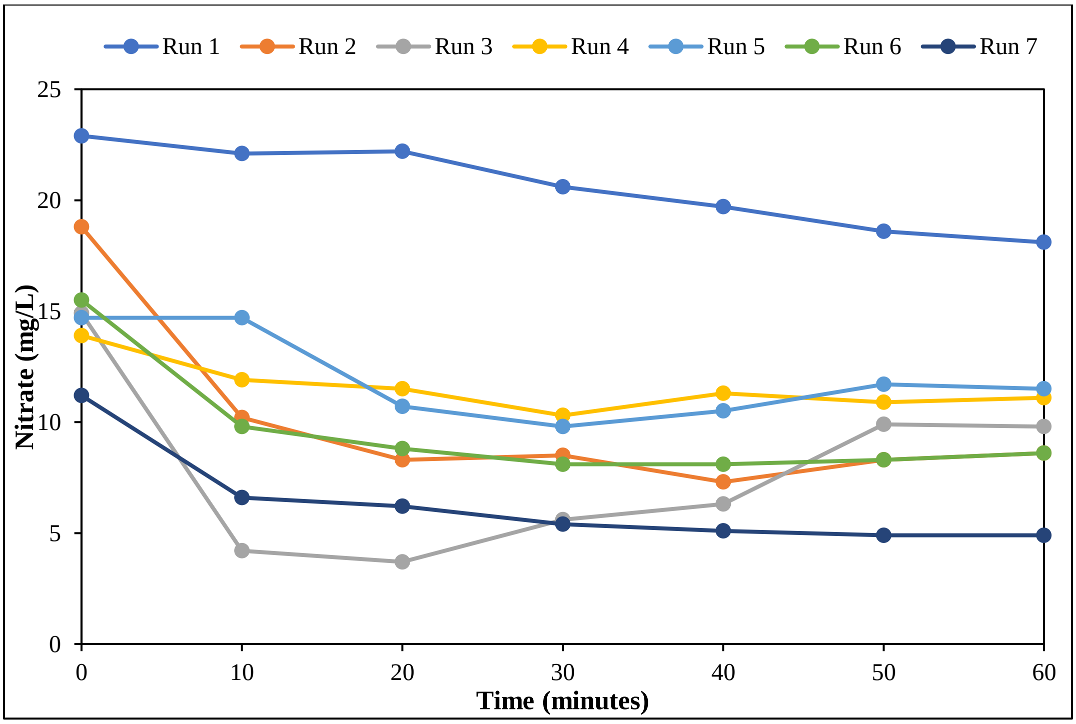


Fig. 4.16 Nitrate concentration during treatment with continuous vertical flow column filter

Table 4.14 Real stormwater runoff characteristics before and after treatment through continuous vertical flow column filter

Run 1	S. No.	pH	EC (μS/cm)	TDS (mg/L)	TSS (mg/L)	NO$_3^-$ (mg/L)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	TN (mg/L)	SO$_4^{2-}$ (mg/L)	PO$_4^{3-}$ (mg/L)
	Influent	7.8	176	88	210	22.9	1.9	18.8	16.9	3.5	127.9	0.13
	1	7.2	210	105	150	22.1	3.2	8.6	5.4	12.3	121.2	0.04
	2	7.2	213	107	135	22.2	3.3	8.9	5.6	12.3	115.3	0.03
	3	7.1	203	102	110	20.6	3.2	8.5	5.4	12.3	107.7	0.04
	4	6.9	208	104	103	19.7	3.1	8.6	5.5	12.1	101.2	0.04
	5	6.9	206	103	89	18.6	3.2	8.4	5.2	12.3	93.4	0.04
	6	6.7	200	100	78	18.1	3.1	8.3	5.2	12.3	89.1	0.05
	Minimum	6.7	200.0	100.0	78.0	18.1	3.1	8.3	5.2	12.1	89.1	0.0
	Maximum	7.2	213.0	107.0	150.0	22.2	3.3	8.9	5.6	12.3	121.2	0.1
	Average ± SD	7.0 ± 0.2	206.7 ± 4.3	103.5 ± 2.2	110.8 ± 24.9	20.2 ± 1.6	3.2 ± 0.1	8.6 ± 0.2	5.4 ± 0.1	12.3 ± 0.1	104.7 ± 11.4	0.0 ± 0.0

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	S. No.	**pH**	**EC (µS/cm)**	**TDS (mg/L)**	**TSS (mg/L)**	**NO_3^- (mg/L)**	**TOC (mg/L)**	**TC (mg/L)**	**IC (mg/L)**	**TN (mg/L)**	**SO_4^{2-} (mg/L)**	**PO_4^{3-} (mg/L)**
Run 2	**Influent**	8.6	477	239	166	18.8	1.5	14.9	13.4	8.4	190.5	0.6
	1	8.6	453	227	92	10.2	2.1	11.6	9.5	10.3	131.8	0.1
	2	8.5	443	223	81	8.3	2.2	11.7	9.5	9.9	125.3	0.08
	3	8.6	440	220	73	8.5	2.3	11.6	9.3	10.2	110.2	0.06
	4	8.5	453	227	59	7.3	2.2	11.4	9.2	10.2	105.8	0.07
	5	8.5	449	225	49	8.3	2.3	11.5	9.2	10.4	99.3	0.05
	6	8.5	447	224	42	8.6	2.3	11.4	9.1	10.8	83.9	0.05
	Minimum	8.5	440.0	220.0	42.0	7.3	2.1	11.4	9.1	9.9	83.9	0.1
	Maximum	8.6	453.0	227.0	92.0	10.2	2.3	11.7	9.5	10.8	131.8	0.1
	Average ± SD	8.5 ± 0.0	447.5 ± 4.8	224.3 ± 2.4	66.0 ± 17.6	8.5 ± 0.9	2.2 ± 0.1	11.5 ± 0.1	9.3 ± 0.2	10.3 ± 0.3	109.4 ± 15.9	0.1 ± 0.0

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	S. No.	**pH**	**EC (µS/cm)**	**TDS (mg/L)**	**TSS (mg/L)**	**NO$_3^-$ (mg/L)**	**TOC (mg/L)**	**TC (mg/L)**	**IC (mg/L)**	**TN (mg/L)**	**SO$_4^{2-}$ (mg/L)**	**PO$_4^{3-}$ (mg/L)**
Run 3	**Influent**	8.4	82	41	64	14.9	1.8	8.1	6.3	1.6	54.7	0.2
	1	8.8	158	78	30	4.2	3.1	17.9	14.8	2.9	34.7	0.09
	2	8.8	122	56	30	3.7	3.2	15.4	12.2	3.1	23.9	0.09
	3	8.7	115	57	10	5.6	3.3	14.1	10.8	2.3	16.8	0.06
	4	8.5	113	56	12	6.3	3.6	14.8	11.2	2.8	8.1	0.05
	5	8.4	112	56	8	9.9	3.2	14.1	10.9	2.4	6.9	0.04
	6	8.3	105	53	4	9.8	3.3	13.6	10.3	2.4	6.5	0.06
	Minimum	8.3	105.3	52.9	4.0	3.7	3.1	13.6	10.3	2.3	6.5	0.0
	Maximum	8.8	157.7	77.7	30.0	9.9	3.6	17.9	14.8	3.1	34.7	0.1
	Average ± SD	8.6 ± 0.2	120.6 ± 17.3	59.3 ± 8.4	15.7 ± 10.4	6.6 ± 2.5	3.3 ± 0.2	15.0 ± 1.4	11.7 ± 1.5	2.7 ± 0.3	16.2 ± 10.4	0.1 ± 0.0

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	S. No.	pH	EC (µS/cm)	TDS (mg/L)	TSS (mg/L)	NO$_3^-$ (mg/L)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	TN (mg/L)	SO$_4^{2-}$ (mg/L)	PO$_4^{3-}$ (mg/L)
Run 4	**Influent**	8.8	159	79	48	13.9	0.7	9.8	9.1	1.9	100.9	0.3
	1	8.3	203	102	8	11.9	3.1	18.5	15.4	8.4	97.6	0.08
	2	8.2	198	99	4	11.5	2.6	17.5	14.9	8.6	92.6	0.07
	3	8.1	201	101	4	10.3	3.2	18.7	15.5	8.6	82.2	0.1
	4	7.8	191	95	6	11.3	3.4	17.7	14.3	8.4	83.5	0.08
	5	7.6	187	93	4	10.9	3.3	17.4	14.1	7.5	70.1	0.04
	6	7.6	203	101	4	11.1	3.1	18.6	15.5	11.2	38.5	0.03
	Minimum	7.6	186.9	93.4	4.0	10.3	2.6	17.4	14.1	7.5	38.5	0.0
	Maximum	8.3	203.0	101.6	8.0	15.1	3.4	18.7	15.5	11.2	97.6	0.1
	Average ± SD	7.9 ± 0.3	197.2 ± 6.2	98.5 ± 3.2	5.0 ± 1.5	11.8 ± 1.6	3.1 ± 0.3	18.1 ± 0.5	15.0 ± 0.6	8.8 ± 1.1	77.4 ± 19.4	0.1 ± 0.0

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	S. No.	pH	EC (µS/cm)	TDS (mg/L)	TSS (mg/L)	NO_3^- (mg/L)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	TN (mg/L)	SO_4^{2-} (mg/L)	PO_4^{3-} (mg/L)
Run 5	**Influent**	8.5	195	97	64	14.7	2.3	13.1	10.8	2.5	156.9	0.6
	1	7.5	251	126	12	14.7	5.6	23.1	17.5	4.7	67.7	0.3
	2	7.4	225	113	10	10.7	4.5	19.1	14.6	4.9	60.7	0.1
	3	7.4	224	113	8	9.8	4.3	18.9	14.6	5.2	62.4	0.05
	4	7.4	223	112	8	10.5	4.5	18.9	14.5	5.2	63.7	0.04
	5	7.3	224	112	6	11.7	4.1	18.6	14.5	5.5	64.6	0.04
	6	7.3	223	112	6	11.5	4.5	18.9	14.4	5.2	65.4	0.04
	Minimum	7.3	223.0	111.8	6.0	9.8	4.1	18.6	14.4	4.7	60.7	0.0
	Maximum	7.5	251.0	126.0	12.0	14.7	5.6	23.1	17.5	5.5	67.7	0.3
	Average SD	7.4 ± 0.1	228.3 ± 10.2	114.6 ± 5.1	8.3 ± 2.1	11.5 ± 1.6	4.6 ± 0.5	19.6 ± 1.6	15.0 ± 1.1	5.1 ± 0.3	64.1 ± 2.2	0.1 ± 0.1

Continued…

Run 6	**S. No.**	**pH**	**EC (µS/cm)**	**TDS (mg/L)**	**TSS (mg/L)**	**NO_3^- (mg/L)**	**TOC (mg/L)**	**TC (mg/L)**	**IC (mg/L)**	**TN (mg/L)**	**SO_4^{2-} (mg/L)**	**PO_4^{3-} (mg/L)**
	Influent	8.4	153	77	110	15.5	2.1	16.7	14.6	4.5	115.9	0.6
	1	7.3	192	96	21	9.8	3.1	19.6	16.5	6.6	87.7	0.1
	2	7.3	210	105	19	8.8	2.9	18.7	18.5	6.3	88.1	0.1
	3	7.2	198	99	14	8.1	3.1	18.9	15.8	5.9	85.4	0.09
	4	7.3	200	100	8	8.1	3.2	18.4	15.2	6.2	86.2	0.08
	5	7.2	202	101	8	8.3	3.1	19.1	16	6.2	81.3	0.08
	6	7.1	203	102	8	8.6	3.2	18.9	15.7	6.2	79.8	0.09
	Minimum	7.1	192.0	96.0	8.0	8.1	2.9	18.4	15.2	5.9	79.8	0.1
	Maximum	7.3	210.0	105.0	21.0	9.8	3.2	19.6	18.5	6.6	88.1	0.1
	Average SD	7.2 ± 0.1	200.8 ± 5.4	100.5 ± 2.8	13.0 ± 5.4	8.6 ± 0.6	3.1 ± 0.1	18.9 ± 0.4	16.3 ± 1.1	6.2 ± 0.2	84.8 ± 3.1	0.1 ± 0.0

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Run 7	**S. No.**	**pH**	**EC (µS/cm)**	**TDS (mg/L)**	**TSS (mg/L)**	**NO_3^- (mg/L)**	**TOC (mg/L)**	**TC (mg/L)**	**IC (mg/L)**	**TN (mg/L)**	**SO_4^{2-} (mg/L)**	**PO_4^{3-} (mg/L)**
	Influent	8.6	220	110	154	11.2	4.3	11.4	7.1	2.8	111.5	0.4
	1	7.5	290	145	25	6.6	5.5	12.3	6.8	3.5	95.5	0.1
	2	7.4	292	146	15	6.2	5.4	12.9	7.5	3.2	93.2	0.07
	3	7.4	288	144	8	5.4	5.3	13.1	7.8	3.3	88.8	0.04
	4	7.3	290	145	8	5.1	4.9	12.8	7.9	3.4	89.2	0.04
	5	7.2	294	147	6	4.9	5.1	13	7.9	3.3	84.7	0.04
	6	7.1	294	147	4	4.9	5.2	12.9	7.7	3.3	82.2	0.04
	Minimum	7.1	288.0	144.0	4.0	4.9	4.9	12.3	6.8	3.2	82.2	0.0
	Maximum	7.5	294.0	147.0	25.0	6.6	5.5	13.1	7.9	3.5	95.5	0.1
	Average SD	7.3 ± 0.1	291.3 ± 2.2	145.7 ± 1.1	11.0 ± 7.1	5.5 ± 0.7	5.2 ± 0.2	12.8 ± 0.3	7.6 ± 0.4	3.3 ± 0.1	88.9 ± 4.6	0.1 ± 0.0

SD= standard deviation; EC= electrical conductivity; TDS= total dissolved solids; TSS= total suspended solids; TN= total nitrogen; TOC= total organic carbon; TC= total carbon; IC= inorganic carbon.

4.11 Pollutant removal study using macrophytes

The nutrients were the pollutants which were present as pollutant in stormwater runoff during the present study. The efficiency of *Phragmites*, *Canna lily* and *Cyperus alternifolius*-based constructed wetland were used during different seasons, and at varying influent phosphate concentration. The effect of increase concentration of phosphate towards its removal efficiency, and plant health were also monitored. The meteorological parameters were also monitored during the present study the nutrient removal efficiency.

4.12 Constructed wetland for pollutant removal

4.12.1 *Phragmites*-based constructed wetland

4.12.1.1 Ambient Temperature Profile

The ambient temperature profile for the period of almost seven months was studied from the month of October, 2020 to April, 2021 during pollutant removal study using *Phragmites*. The ambient temperature varied between 5 °C to 40 °C, while the average maximum and minimum temperature recorded during the study was 14 °C and 28 °C. The current study was conducted during different seasons i.e. autumn, winter, spring and summer. The ambient temperature varied between 9 °C to 34 °C; 5 °C to 29 °C; 11 °C to 34 °C; and 16 °C to 40 °C during autumn, winter, spring, and summer season, respectively (Annexure-I; Fig. 4.17). The average ambient temperature during the current study was 20.9 °C, 15.1 °C, 23.3 °C, and 28.6 °C for autumn, winter, spring, and summer season, respectively. The effect of ambient temperature profile on growth of *Phragmites* and its efficacy towards removal of nutrient was studied. The average sunshine hours varied between 8 to 10 hours.

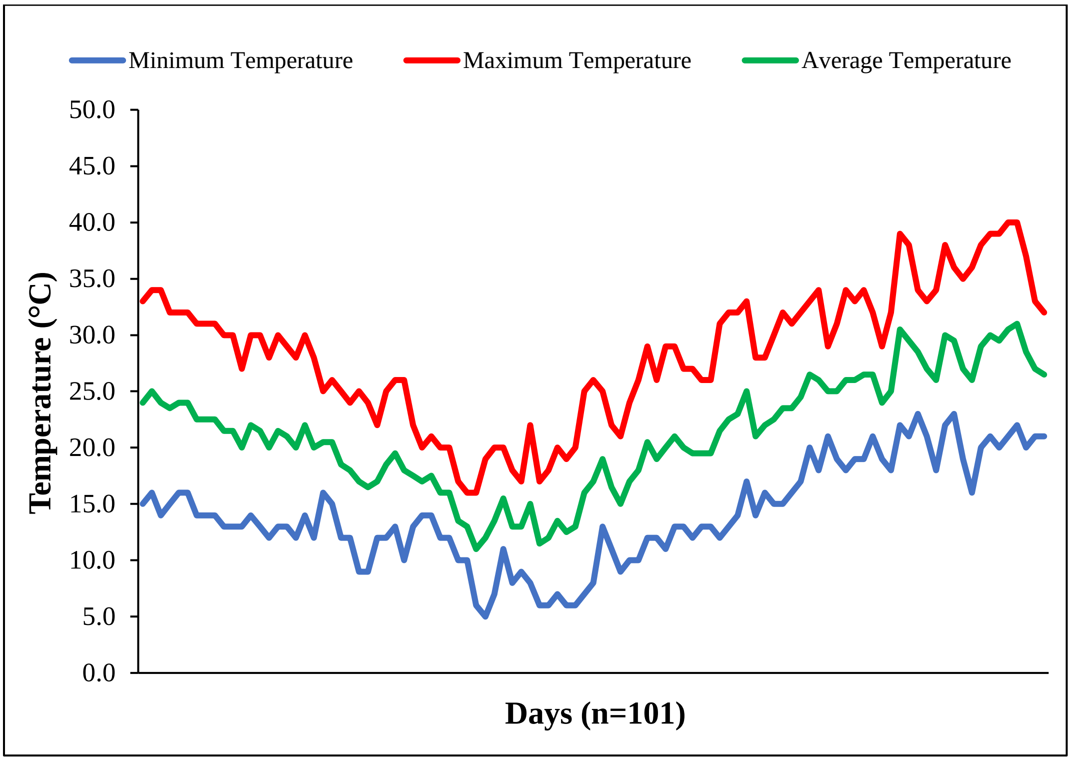

Fig. 4.17 Ambient temperature profile during pollutant removal study using *Phragmites*-based constructed wetland (October, 2020 to April, 2021)

4.12.1.2 Sediment analysis

The substrate bed of *Phragmites*-based constructed wetland cell was packed with gravel-sandy soil. The packing bed material has the specific gravity (G) as 2.74 with void ratio (e) equals to 0.77 and had a bulk density of (ρ) of 1782 kg/m^3. The packing material of CW cell has 62.4 % coarse aggregates retaining on 4.75 mm sieve, 37.4 % as fine aggregates passing through 4.75 mm sieve, and rest as silt retained on pan (Table 4.15). The packing material duplicates the type of bed usually found in natural wetlands. The gravels with voids form a porous medium and it helped in easy percolation of influent into the substrate and it made exchange of gases easy at root zone (rhizosphere).

Table 4.15 Sieve analysis of bed sediments used for *Phragmites*-based constructed wetland

Sieve size (mm)	Weight retained (g)	Percentage retained	Cumulative percentage	Percentage finer
25	321.3	21.3	21.3	78.7
19	40.9	2.7	24.0	76.0
12.5	211.8	14.0	38.0	62.0
9.5	7.5	0.5	38.5	61.5
4.75	360.3	23.9	62.4	37.6
2.36	104.6	6.9	69.4	30.6
1.18	84.4	5.6	75.0	25.0
0.3	299.9	19.9	94.8	5.2
0.15	55.6	3.7	98.5	1.5
0.075	19.0	1.3	99.8	0.2
Pan	3.3	0.2	100.0	0.0
Total (g)	1508.7	-	-	-

Gravels formed the bed so that clogging for the substrate can be prevented. The particle size distribution curve represents a gap graded soil in which intermediate size particles are missing (Fig. 4.18). A gap graded bed provides more hydraulic conductivity and also it helps in better and more efficient removal of nutrients (phosphate) from the stormwater runoff. Similar studies were also done by Vymazal (2005) for the study of nutrient removal through subsurface flow of wastewater.

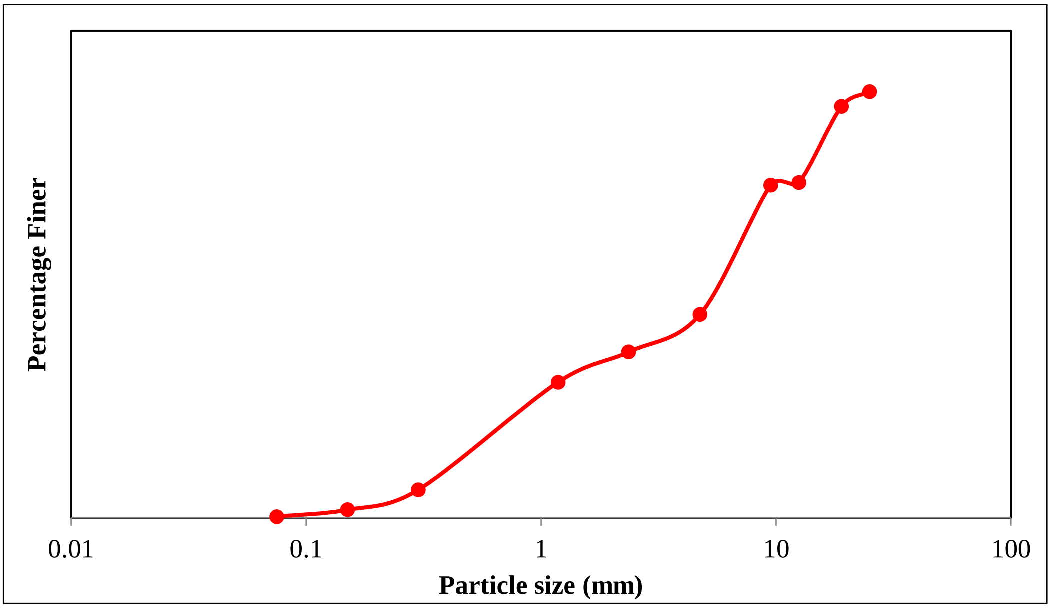

Fig. 4.18 Particle size distribution curve for bed sediments of *Phragmites*-based constructed wetland

4.12.1.3 Nutrient removal study in various seasons

Autumn season

The effectiveness of Phragmites-based constructed wetland was studied towards removal of phosphates (available phosphate and total phosphate) from stormwater runoff as tabulated in Table 4.16 and displayed in Fig. 4.19. The analysis was carried out from third week of October 2020 to November 2020. The initial concentrations of phosphate (AP_i) fed to the wetland cell range from 1.0 mg/L to 1.3 mg/L with an average of 1.1 ± 0.1 mg/L. Significant reduction in the phosphate concentration was observed at the effluent end with the residual concentrations (AP_o) ranging from 0.2 mg/L to 0.9 mg/L and average residual concentration of 0.4 ± 0.3 mg/L. Prominent removal of AP was observed with nearly 64 % average removal efficiency. Depending on the favourable conditions, the removal varied significantly, with a minimum of 17.0 % to a maximum of 85.2 % signifying a considerable variation in the treatment efficiency on different days at varying meteorological conditions.

Table 4.16 Removal efficiency (%) of phosphate PO_4^{3-}-P during autumn season using *Phragmites*-based constructed wetland

Date (n=30)	Available Phosphate			Total Phosphate		
	AP_i^* (mg/L)	AP_o^* (mg/L)	Removal Efficiency (%)	TP_i^* (mg/L)	TP_o^* (mg/L)	Removal Efficiency (%)
20-10-2020	1.1	0.3	77.3	3.0	1.2	61.6
21-10-2020	1.2	0.3	76.1	3.1	1.5	51.1
22-10-2020	1.2	0.3	77.4	2.4	0.9	64.0
23-10-2020	1.1	0.3	77.2	3.4	1.3	62.7
26-10-2020	1.1	0.2	79.6	3.4	1.2	64.2
27-10-2020	1.0	0.2	78.4	2.9	1.0	65.6
28-10-2020	1.1	0.2	78.5	3.2	1.2	64.5
29-10-2020	1.1	0.2	78.2	3.0	1.0	67.1
30-10-2020	1.1	0.2	78.8	2.9	1.0	67.0
02-11-2020	1.2	0.2	79.1	3.6	1.1	68.0
03-11-2020	1.0	0.2	79.4	3.4	1.1	67.5
04-11-2020	1.1	0.2	80.5	3.4	1.1	68.6
05-11-2020	1.1	0.2	80.0	3.2	1.0	67.6
06-11-2020	1.1	0.3	76.6	3.2	1.0	68.5
09-11-2020	1.0	0.2	77.0	3.5	1.1	68.1
10-11-2020	1.1	0.2	81.4	3.6	1.2	67.7
11-11-2020	1.2	0.2	81.5	3.1	1.1	65.0
12-11-2020	1.1	0.2	79.5	3.2	1.2	62.1
13-11-2020	1.1	0.2	81.7	3.3	1.2	64.3
16-11-2020	1.2	0.2	85.2	3.1	0.8	74.7
17-11-2020	1.1	0.2	82.0	3.3	1.0	70.2
18-11-2020	1.0	0.7	31.4	3.4	1.8	47.0
19-11-2020	1.1	0.8	25.7	3.2	1.9	41.3
20-11-2020	1.0	0.8	17.0	3.3	2.0	39.4

23-11-2020	1.2	0.9	25.8	3.2	2.1	34.4
24-11-2020	1.2	0.9	29.8	3.4	2.2	34.6
25-11-2020	1.2	0.9	24.8	3.4	2.3	31.6
26-11-2020	1.1	0.8	23.6	3.3	2.2	33.2
27-11-2020	1.1	0.8	29.1	3.4	2.4	29.1
30-11-2020	1.3	0.8	39.7	3.3	2.3	31.6
Minimum	1.0	0.2	17.0	2.4	0.8	29.1
Maximum	1.3	0.9	85.2	3.6	2.4	74.7
Mean ± SD	1.1 ± 0.1	0.4 ± 0.3	63.7 ± 24.5	3.2 ± 0.2	1.4 ± 0.5	56.7 ± 14.7

$^*AP_i$ = available phosphate at inlet; $^*AP_o$ = available phosphate at outlet; $^*TP_i$ = available phosphate at inlet; $^*TP_o$ = total phosphate at outlet

In case of total phosphate, initial concentrations (TP_i) were varied from 2.4 mg/L to 3.6 mg/L while the treated concentrations (TP_o) observed as residual concentration varied between 0.8 mg/L to 2.4 mg/L. The removal efficiency for total phosphate varied from nearly 30 % to 75 %, with an average removal of 56.7 ± 14.7%, demonstrating a relatively consistent but less varied effectiveness as compared to AP. This is because of the more readily availability of AP as it remains in the unbound form and plants can easily utilize it for carrying out its metabolic activities while using phosphate as nutrient. The variations in removal efficiency could be reasoned in terms of variations in composition of synthetically prepared stormwater runoff, functioning aspects of the wetland system or environmental conditions. Moreover, it was also observed that towards the end of the period, there's a noticeable decrease in the removal rate for both AP and TP. The removal rate was of increasing order during the initial phase of the treatment. However, it was slowed down in the later phase of autumn season. This might indicate system saturation, seasonal effects on plant performance, the existing stress conditions affecting the species productivity and metabolism. Since only phosphate was added as nutrient in the synthetically prepared stormwater runoff, the nitrogen-deficit induced stresses in the *Phragmites*. Furthermore, temperature variations also attribute to the changed removal efficacy. The average ambient temperature reduced along with reduction in average sunshine hours as the study proceeded from autumn to winter season.

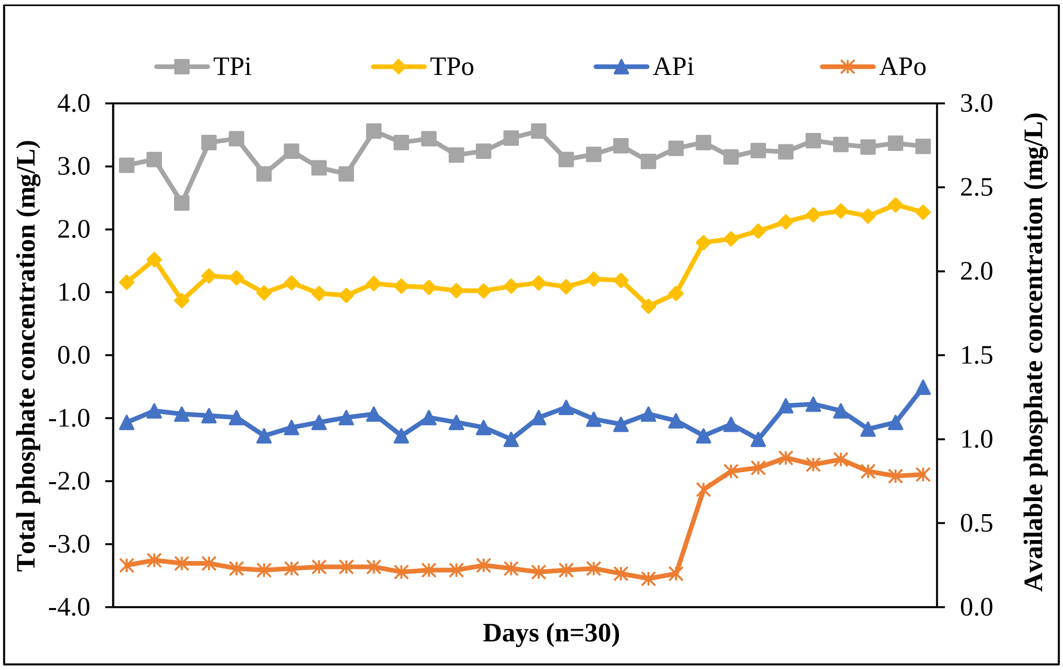

Fig. 4.19 Available and total phosphate concentration (mg/L) during autumn season for *Phragmites*-based constructed wetland

Winter season

The effect of temperature profile and plant growth was studied towards effective phosphate removal in winters from January 2021 to February 2021 as illustrated in Table 4.17; and depicted in Fig. 4.20. The average initial phosphate (AP_i) concentration of 1.7 ± 0.3 mg/L when varied between 1.2 mg/L to 2.7 mg/L, was fed to the constructed wetland cell. Notable reduction in the phosphate concentration of order 86 ± 6.1 % was observed in the outlet with the residual concentrations (AP_o) noted between 0.1 mg/L to 0.5 mg/L (average residual concentration of 0.2 ± 0.1 mg/L). The removal efficiency for AP varied from a minimum 75 % to almost removing all the phosphate from the system (~95% removal). Additionally, the removal of TP as observed was more efficient in winter season as compared to autumn, demonstrating an average removal efficacy of more than 80 ± 13.7 %. The TP removal peaked to a maximum removal of the order 92 % and minimum of 43 %. The removal efficiency of TP was slightly lesser as compared to AP due to readily availability of freely available and unbound form of AP for plant uptake for its metabolic activities. This could be attribute to the addition of nitrogen in the form of Di-ammonium phosphate (DAP) and urea regularly for 10 days which improved the health of *Phragmites* further enhancing the growth and metabolism of the plant.

Table 4.17 Removal efficiency (%) of phosphate PO_4^{3-}-P (mg/L) during winter season using *Phragmites*-based constructed wetland

Date (n=28)	**Available Phosphate**			**Total Phosphate**		
	AP_i^* (mg/L)	**AP_o^* (mg/L)**	**Removal Efficiency (%)**	**TP_i^* (mg/L)**	**TP_o^* (mg/L)**	**Removal Efficiency (%)**
04-01-2021	1.7	0.1	93.1	2.4	1.2	49.0
05-01-2021	1.6	0.1	94.5	2.5	1.0	61.8
06-01-2021	1.6	0.1	92.4	2.7	1.0	62.1
07-01-2021	1.7	0.3	83.9	2.9	1.1	63.2
08-01-2021	1.2	0.3	75.2	3.2	1.1	65.0
11-01-2021	1.2	0.1	88.4	3.2	1.9	42.6
12-01-2021	1.6	0.2	89.0	3.7	0.9	74.4
13-01-2021	1.6	0.2	89.0	3.7	0.8	77.1
14-01-2021	1.8	0.1	91.9	3.3	0.7	78.6
15-01-2021	1.8	0.2	90.5	3.0	0.7	78.1
18-01-2021	1.8	0.1	94.8	2.8	0.3	88.0
19-01-2021	1.9	0.2	91.5	2.8	0.3	88.8
20-01-2021	1.4	0.1	90.7	2.8	0.3	89.3
21-01-2021	1.2	0.1	89.5	3.4	0.3	91.5
22-01-2021	1.8	0.2	89.5	3.7	0.3	90.8
25-01-2021	1.7	0.2	86.0	3.8	0.4	88.9
27-01-2021	1.8	0.3	83.2	4.3	0.5	89.0
28-01-2021	1.6	0.3	83.0	4.2	0.4	89.9

29-01-2021	1.5	0.3	77.4	4.5	0.4	91.7
01-02-2021	1.6	0.3	78.5	4.0	0.4	90.4
02-02-2021	1.9	0.4	81.0	4.0	0.5	88.1
03-02-2021	1.6	0.4	75.6	4.6	0.5	88.5
04-02-2021	1.7	0.2	88.3	4.4	0.5	88.7
05-02-2021	1.6	0.4	76.5	3.8	0.4	88.7
08-02-2021	1.7	0.3	83.4	4.2	0.5	87.9
09-02-2021	2.7	0.4	85.6	4.7	0.5	89.7
10-02-2021	2.3	0.4	84.4	4.6	0.5	89.3
11-02-2021	2.0	0.5	76.1	4.5	0.6	85.6
Minimum	1.2	0.1	75.2	2.4	0.3	42.6
Maximum	2.7	0.5	94.8	4.7	1.9	91.7
Average ± SD	1.7 ± 0.3	0.2 ± 0.1	85.8 ± 6.1	3.6 ± 0.7	0.6 ± 0.4	80.6 ± 13.7

$^*AP_i$ = available phosphate at inlet; $^*AP_o$ = available phosphate at outlet; $^*TP_i$ = available phosphate at inlet; $^*TP_o$ = total phosphate at outlet

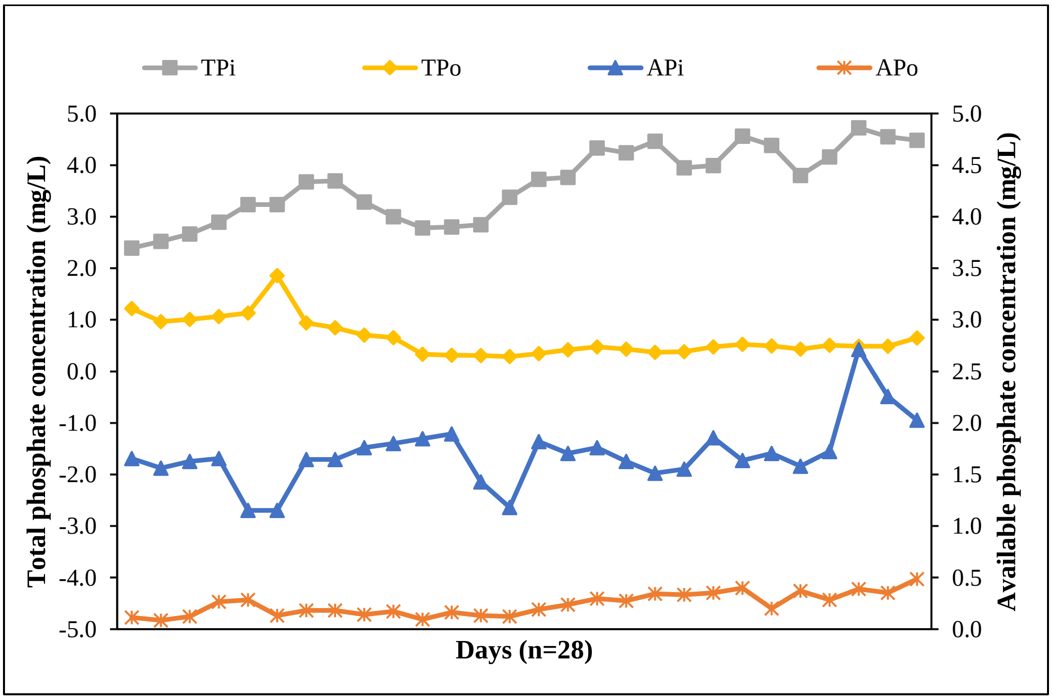

Fig. 4.20 Available and total phosphate concentration (mg/L) during winter season for *Phragmites*-based constructed wetland

Spring season

During autumn and winter season it was observed that in order to revive the plant from nitrogen deficit and stressful conditions, nitrogen is required by the plant as external nutrient. Therefore, during spring season (the period from mid-February, 2021 to March, 2021), the CW cell was amended with ammonium ions in the form of ammonium sulphate ($(NH_4)_2SO_4$) with the concentration of 50 mg/L to make an indirect inference of nitrifying conditions in CW cell. The initial concentration of phosphate in synthetically prepared stormwater runoff fed to the CW cell was also raised to 10 mg/L. Addition of nitrogen enhanced the removal of phosphate from synthetically prepared stormwater runoff samples resulting in an average removal efficiency of more than 90% for both AP as well as TP. For instance, the concentration of AP in outlet ranged from 0.0 mg/L to 2.2 mg/L with average of 0.3 ± 0.4 mg/L demonstrating the average removal efficiency of 91%. The AP removal efficiency from *Phragmites*-based CW was marginally higher than TP removal efficiency (Table 4.18; Fig. 4.21). The removal of phosphates from CW cell thus follows first order kinetics. The gradual increase in ambient temperature and average sunshine hours during the spring season escalated the removal rate. The minimum ambient temperature during spring season varied between 11 °C to 21 °C, while the maximum ambient temperature varied between 26 °C to 34 °C. Increasing temperature enhanced the rate of evapotranspiration causing an increased uptake of water from roots to the leaves of *Phragmites*. Evapotranspiration is, therefore, directly influence the removal efficiency of the plant as well the treatment. As favourable conditions persist, the phosphates in dissolved formed was taken up by plants along with the water and utilises it for its daily metabolic activity which was witnessed in terms of increased biomass. The increased plant density and growth of individual plant as a result of increased biomass also leads to enhanced phosphate removal from *Phragmites*-based CW cell.

Table 4.18 Removal efficiency (%) of phosphate PO_4^{3-}-P (mg/L) during spring season using *Phragmites*-based constructed wetland

Date (n=26)	Available Phosphate			Total Phosphate		
	AP_i^* (mg/L)	AP_o^* (mg/L)	Removal Efficiency (%)	TP_i^* (mg/L)	TP_o^* (mg/L)	Removal Efficiency (%)
15-02-2021	3.8	0.5	87.2	7.6	0.7	90.2
16-02-2021	3.4	0.4	87.0	6.8	0.6	90.6
17-02-2021	3.5	0.4	87.5	7.0	0.6	91.1
18-02-2021	3.7	0.3	91.5	7.9	0.6	92.7
19-02-2021	3.8	0.4	90.2	7.8	0.8	90.1
22-02-2021	3.6	0.3	90.7	8.2	0.7	91.3
23-02-2021	3.8	0.3	92.3	8.0	0.8	90.4
24-02-2021	2.7	0.2	94.1	9.4	0.2	98.2
25-02-2021	1.9	0.1	92.2	11.7	0.3	97.3
26-02-2021	4.0	0.2	95.8	12.5	2.9	76.9
01-03-2021	1.9	0.0	100.0	8.3	0.0	100.0
02-03-2021	1.3	0.3	78.2	10.5	0.5	95.5
03-03-2021	3.4	0.4	86.8	10.4	1.7	83.2
04-03-2021	4.9	0.0	99.5	10.9	0.1	99.1
05-03-2021	4.0	0.3	92.4	10.0	0.5	95.0
09-03-2021	3.3	0.3	90.9	11.0	1.6	85.2
10-03-2021	3.7	0.2	94.7	8.8	1.3	85.6
11-03-2021	4.6	0.2	95.4	10.8	1.0	90.9
12-03-2021	4.0	0.3	93.0	10.6	1.0	90.7
16-03-2021	4.2	0.2	94.4	9.3	0.9	90.3

17-03-2021	4.3	0.2	94.2	9.9	0.6	94.4
18-03-2021	3.8	0.1	98.2	9.8	0.1	98.7
19-03-2021	5.3	0.2	95.7	10.8	3.3	69.2
22-03-2021	2.3	0.3	88.8	10.3	0.5	95.6
23-03-2021	4.7	0.2	94.8	11.4	3.2	72.2
24-03-2021	5.6	2.2	60.3	11.3	0.6	94.6
Minimum	1.3	0.0	60.3	6.8	0.0	69.2
Maximum	5.6	2.2	100.0	12.5	3.3	100.0
Average ± SD	3.7 ± 1.0	0.3 ± 0.4	91.0 ± 7.8	9.6 ± 1.6	1.0 ± 0.9	90.3 ± 7.8

$^{*}AP_i$ = available phosphate at inlet; $^{*}AP_o$ = available phosphate at outlet; $^{*}TP_i$ = available phosphate at inlet; $^{*}TP_o$ = total phosphate at outlet

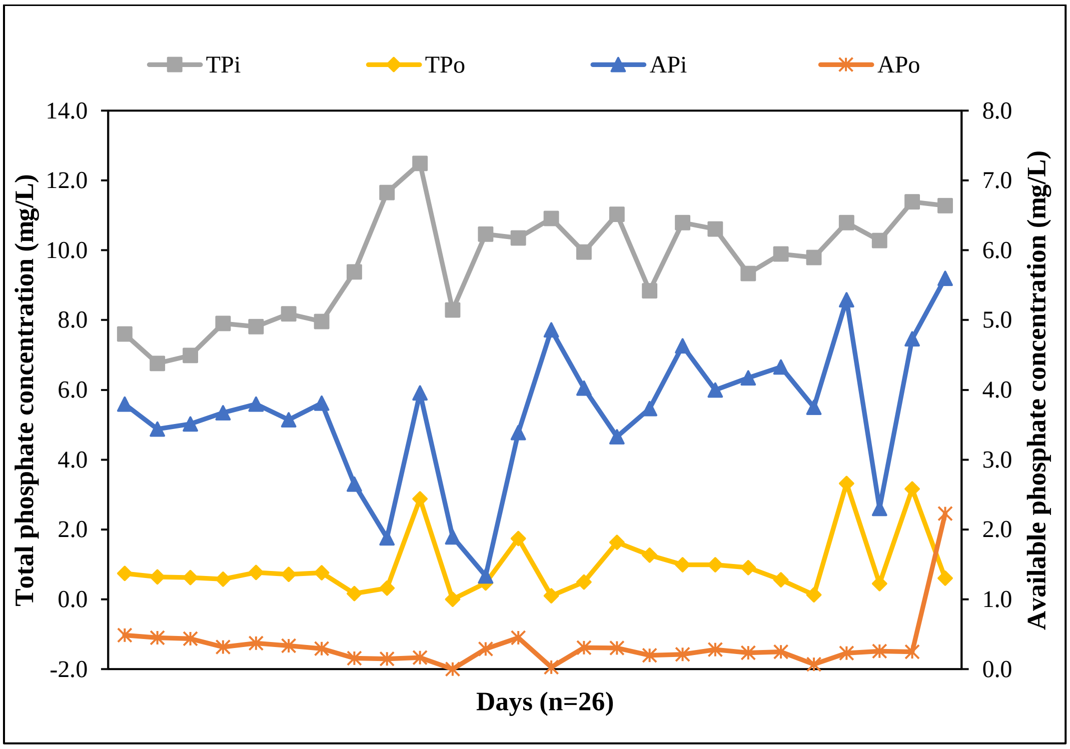

Fig. 4.21 Available and total phosphate concentration (mg/L) during spring season for *Phragmites*-based constructed wetland

Summer season

During the summer period (last week of March, 2021 to third week of April, 2021), phosphate (PO_4^{3-}) ions concentration of 20 mg/L was used in synthetically prepared stormwater runoff.

Table 4.19 Removal efficiency (%) of phosphate PO_4^{3-}-P (mg/L) during summer season using *Phragmites*-based constructed wetland

Date (n=17)	Available Phosphate			Total Phosphate		
	AP_i* (mg/L)	AP_o* (mg/L)	Removal Efficiency (%)	TP_i* (mg/L)	TP_o* (mg/L)	Removal Efficiency (%)
26-03-2014	3.0	0.1	97.6	11.2	0.7	93.3
27-03-2014	5.7	0.0	100.0	20.5	0.9	95.5
28-03-2014	13.2	0.2	98.7	21.8	0.9	95.7
31-03-2014	12.6	0.2	98.4	20.0	2.7	86.7
01-04-2014	7.3	0.2	96.9	23.1	0.5	97.8
02-04-2014	11.0	0.3	97.6	20.2	0.3	98.4
03-04-2014	10.2	0.1	98.6	19.9	1.6	91.7
04-04-2014	8.8	0.0	99.5	19.0	1.5	92.0
07-04-2014	8.9	0.1	98.7	20.6	0.9	95.5
12-04-2014	10.3	0.1	99.5	20.1	0.4	97.8
13-04-2014	18.0	0.4	97.7	18.2	1.5	92.0
15-04-2014	7.9	0.3	96.3	22.3	0.1	99.4
16-04-2014	6.6	0.0	100.0	23.3	0.1	99.4
17-04-2014	6.3	0.2	96.5	21.9	0.4	98.0
18-04-2014	17.8	0.1	99.3	23.6	0.5	97.9
19-04-2014	15.3	0.1	99.3	23.6	0.5	98.0
20-04-2014	14.7	0.1	99.5	22.7	1.1	95.0
Minimum	3.0	0.0	96.3	11.2	0.1	86.7
Maximum	18.0	0.4	100.0	23.6	2.7	99.4
Average ± SD	10.4 ± 4.3	0.1 ± 0.1	98.5 ± 1.2	20.7 ± 2.9	0.9 ± 0.7	95.5 ± 3.4

*AP_i = available phosphate at inlet; *AP_o = available phosphate at outlet; *TP_i = available phosphate at inlet; *TP_o = total phosphate at outlet

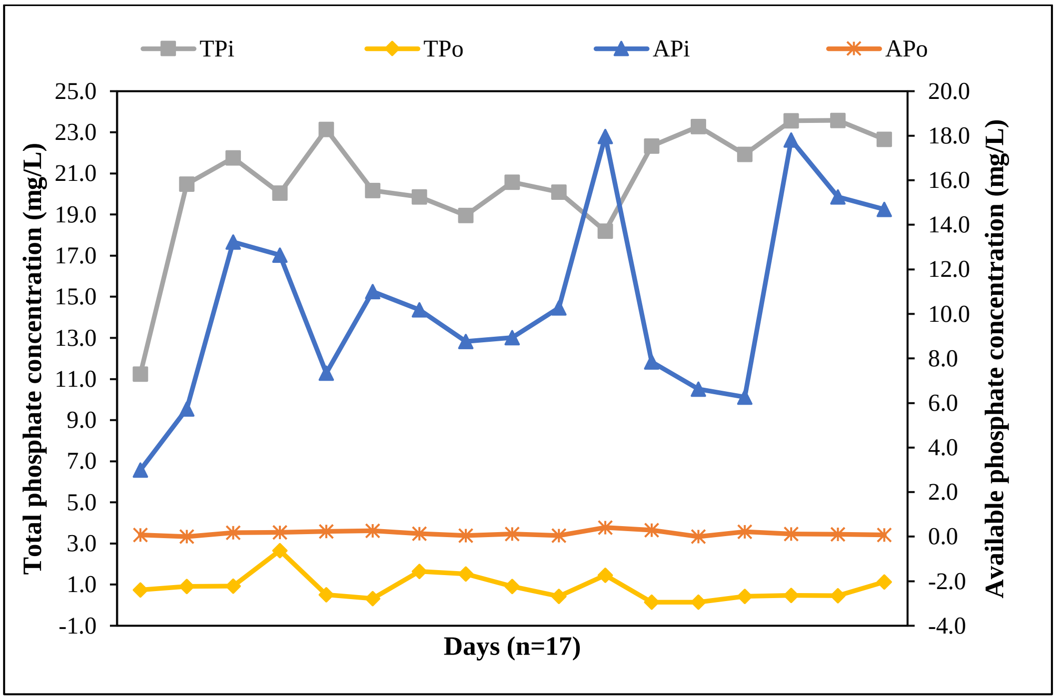

Fig. 4.22 Available and total phosphate concentration (mg/L) during summer season for *Phragmites*-based constructed wetland

The total phosphate of average concentration 21.0 ± 2.9 mg/L was fed to the inlet with concentration varying from 11.2 mg/L to 23.6 mg/L (Table 4.19; Fig. 4.22). Enhanced removal of TP was observed in summer season as compared to the rest other seasons. The concentration of TP in outlet ranged from 0.1 mg/L to 2.7 mg/L with an average value of 0.9 ± 0.7 mg/L, displaying an average removal efficiency of 96 %. On the other hand, average concentration of AP in outlet was 0.1 ± 0.1 mg/L against the average inlet concentration of 10 ± 4.3 mg/L. Available phosphate concentration at inlet varied between 3.0 mg/L to 18.0 mg/L while the AP concentration at outlet as observed varied between 0 mg/L to 0.4 mg/L. Almost complete removal of available phosphate was observed with average removal efficiency of 99% which varied between 96 % to 100%. The available phosphate removal efficiency was slightly higher than removal efficiency of TP. Increase in phosphate concentration increased the removal efficiency representing first order kinetics in summer season as well. Higher removal efficiency for AP is may be due to easy bio availability of AP to plants and microbes as compared to TP. TP is available to wetland vegetation only after its bio conversion to AP which was governed by pH of water and sediments, redox conditions in CW cell, availability of metals like Ca, Mg, Al, and Fe in sediments and stormwater runoff. Also, as the study proceeded, the biomass in terms of number of *Phragmites* plants also increased which also helps in effective and enhanced removal efficiency of phosphates from CW cell.

The removal of phosphate (AP and TP) by *Phragmites* is chiefly regulated by the environmental conditions. The changing seasons also governs the nutrient removal behaviour by the plants. The comparative analysis of both AP and TP removal efficiency in four different seasons is depicted in Fig. 4.23. For instance, temperature is a significant parameter influencing the removal rate for nutrients. Removal efficiency of phosphate was observed to be directly related to temperature. The removal efficiency increased with increasing temperature. Drop in temperature during late autumn reported nearly restricted AP and TP removal efficiency. With increase in the average ambient temperature during winters, the AP and TP removal efficiency also increased for *Phragmites*-based constructed wetland. Further, as the average temperature increased in spring season, a 10% surge in removal efficiency was observed i.e. 90% removal rate was there. Similarly, in summer season, increase in ambient average temperature and extended exposure to sunshine resulted in almost complete removal of the available phosphate. In case of autumn season, although temperature was around 20°C, higher than winter season, however, near 60% removal efficiency was observed. This is because of the stressful conditions resulted in lesser removal. Increasing temperature causes higher evapotranspiration, promoting more rate of uptake of water and nutrients from the CW cell for its metabolic activities. The seasonal removal efficiency of TP follows the following order: Summer (96%) > Spring (90%) > winters (81%) > autumn (57%). Similarly, available phosphate removal efficiency follows the trend summer > spring > winter > autumn for *Phragmites*-based constructed wetland cell.

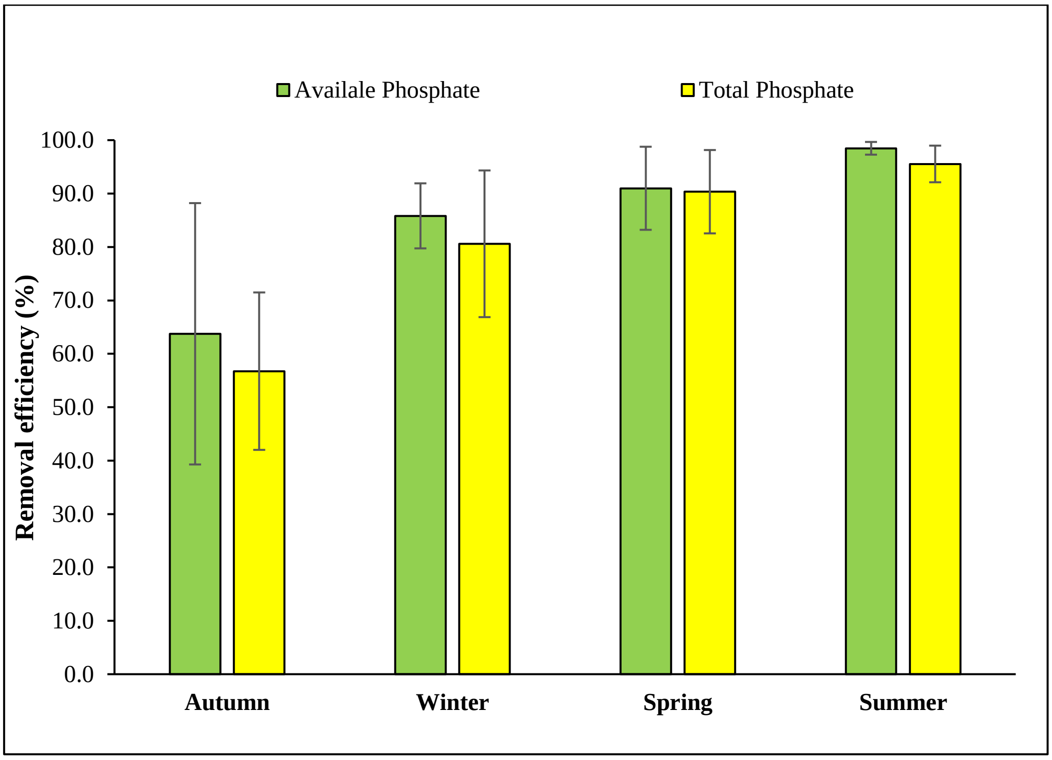

Fig. 4.23 Phosphate removal efficiency (%) of *Phragmites*-based constructed wetland during different seasons

4.12.1.4 Ferric/ Ferrous ratio

Various fractions of iron present in dissolved form as originated from bed sediments were also analysed in CW cell. The ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions had the average concentration of 1.34 ± 1.28 mg/L and 0.06 ± 0.04 mg/L, respectively. The Fe^{2+} concentration at effluent varied from 0.15 mg/L to 4.11 mg/L, while, concentration of Fe^{3+} varied between 0.01 mg/L to 0.14 mg/L. The ratio of ferric to ferrous (Fe^{3+} to Fe^{2+} ratio) was also calculated and had the average value 0.08 with slight deviation of ± 0.1 (Table 4.20). The ratio ranged from 0.01 to 0.37. The ratio had the values less than unity which indicates that most of the iron is present in the form of ferrous (Fe^{2+}) ions and ferric (Fe^{3+}) ions are being converted to ferrous by reduction. This comments upon the existence of aerobic conditions at the surface where oxidation is taking place, and at greater depth, anaerobic conditions might be existing.

Table 4.20 Ferric (Fe^{3+}) to Ferrous (Fe^{2+}) ratio from bed sediments

S. No. (n=22)	Ferrous (Fe^{2+}) (mg/L)	Ferric (Fe^{3+}) (mg/L)	Ferric/ Ferrous ratio
1.	0.24	0.02	0.09
2.	0.74	0.06	0.08
3.	0.64	0.05	0.07
4.	0.46	0.08	0.17
5.	0.72	0.05	0.06
6.	0.91	0.02	0.02
7.	0.58	0.05	0.08
8.	0.67	0.02	0.03
9.	1.27	0.09	0.07
10.	0.91	0.04	0.05
11.	0.89	0.05	0.06
12.	0.20	0.01	0.04
13.	1.38	0.05	0.03
14.	0.15	0.05	0.34
15.	4.11	0.08	0.02
16.	0.30	0.03	0.10
17.	2.30	0.14	0.06
18.	2.77	0.02	0.01
19.	0.17	0.06	0.37
20.	2.30	0.11	0.05
21.	3.69	0.10	0.03
22.	4.07	0.14	0.03
Minimum	0.15	0.01	0.01
Maximum	4.11	0.14	0.37
Average ± SD	1.34 ± 1.28	0.06 ± 0.04	0.08 ± 0.10

SD= standard deviation

When the anaerobic conditions are present in the CW cell at depths, much more ferrous ion acts as an alternate terminal electron acceptor (ATEA) and becomes more soluble ferrous iron and releases the phosphorus it had bound to while it was oxidised in the form of ferric. The reactivity of iron and its bonding with phosphate does not exist which can be said that the removal of phosphate from the CW cell was done by *Phragmites* for its metabolic activity. The iron being an alternate terminal electron acceptor gets reduced. Iron in the form of ferric (Fe^{3+}) forms the bond with phosphate (PO_4^{3-}) which is no more existed during the anaerobic conditions. This comments that phosphorus is not being removed by iron after forming a bond with the iron. The existence of anaerobic conditions forms the acid. Thus, slightly acidic conditions might have existed at depths (Pipil et al., 2021).

4.12.2 *Canna lily*-based constructed wetland

4.12.2.1 Ambient Temperature Profile

The ambient temperature profile for the period of six months was studied (December, 2021 to May, 2022) during pollutant removal study using *Canna lily*. The ambient temperature varied between 6 °C to 44 °C, while the average maximum and minimum temperature recorded during the study was 17.5 °C and 30 °C. The current study was conducted during winter, spring and summer seasons. The ambient temperature varied between 6 °C to 26 °C; 13 °C to 40 °C; and 22 °C to 44 °C during winter, spring, and summer season, respectively (Annexure-II; Fig. 4.24).

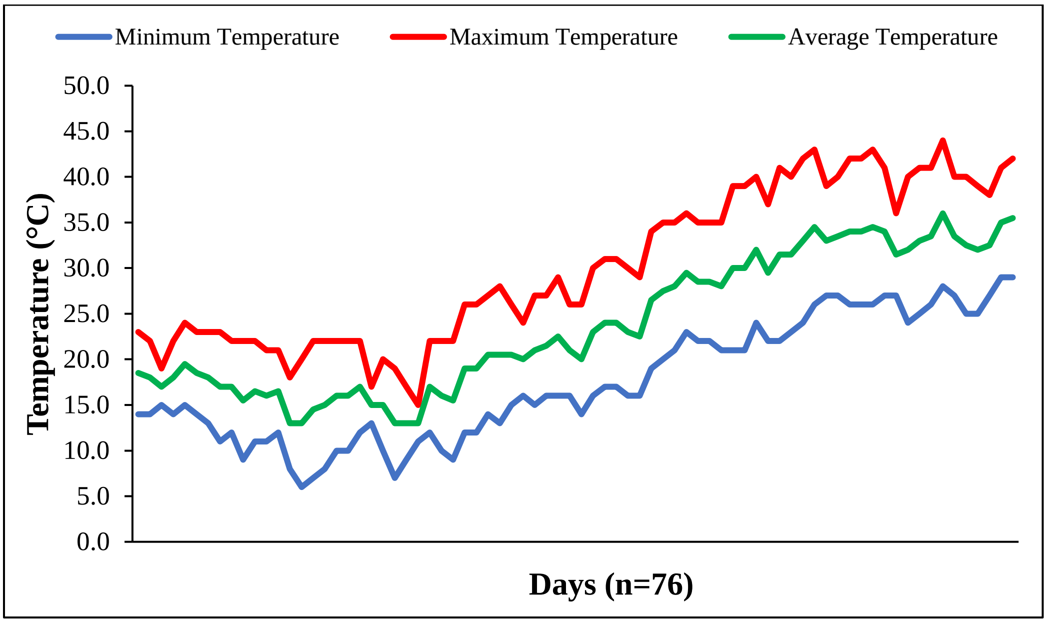

Fig. 4.24 Ambient temperature profile during pollutant removal study using *Canna lily*-based constructed wetland (December, 2021 to May, 2022)

The average ambient temperature during the current study was 16.2 °C, 24.7 °C, and 33.2 °C for winter, spring, and summer season, respectively. The effect of ambient temperature profile on growth of *Canna lily* and its efficacy towards removal of nutrient was studied. The average sunshine hours varied between 8 to 10 hours.

4.12.2.2 Sediment analysis

The substrate bed of *Canna lily*-based constructed wetland cell was packed with gravel-sandy soil. The packing bed material has the specific gravity (G) as 2.70 with void ratio (e) equals to 0.55 and had a bulk density of (ρ) of 1820 kg/m^3. The packing material of CW cell has 66.5 % coarse aggregates retaining on 4.75 mm sieve, 32.7 % as fine aggregates passing through 4.75 mm sieve, and rest as silt retained on pan (Table 4.21).

Table 4.21 Sieve analysis of bed sediments used for *Canna lily*-based constructed wetland

Sieve size (mm)	Weight retained (g)	Percentage Retained	Cumulative Percentage	Percentage Finer
19	364.0	20.2	20.2	79.8
12.5	270.0	15.0	35.2	64.8
6.3	472.0	26.2	61.4	38.6
4.75	92.0	5.1	66.5	33.5
2.36	92.0	5.1	71.6	28.4
1.18	184.0	10.2	81.8	18.2
0.6	102.0	5.7	87.4	12.6
0.3	56.0	3.1	90.5	9.5
0.15	53.0	2.9	93.5	6.5
0.09	102.0	5.7	99.1	0.9
Pan	15.0	0.9	100.0	0.0
Total (g)	1802.0	-	-	-

The packing material duplicates the type of bed usually found in natural wetlands. The gravels with voids form a porous medium and it helped in easy percolation of influent into the substrate and it made exchange of gases easy at root zone (rhizosphere). Gravels formed the bed so that clogging for the substrate can be avoided along with easy penetration of roots of macrophytes. The particle size distribution curve represents a gap graded soil in with intermediate size particles are missing (Fig. 4.25). A gap graded bed provides more hydraulic conductivity and also it helps in better and more efficient removal of nutrients (phosphate) from the wastewater. Similar studies were also done by Vymazal (2005) for the study of nutrient removal through subsurface flow of wastewater.

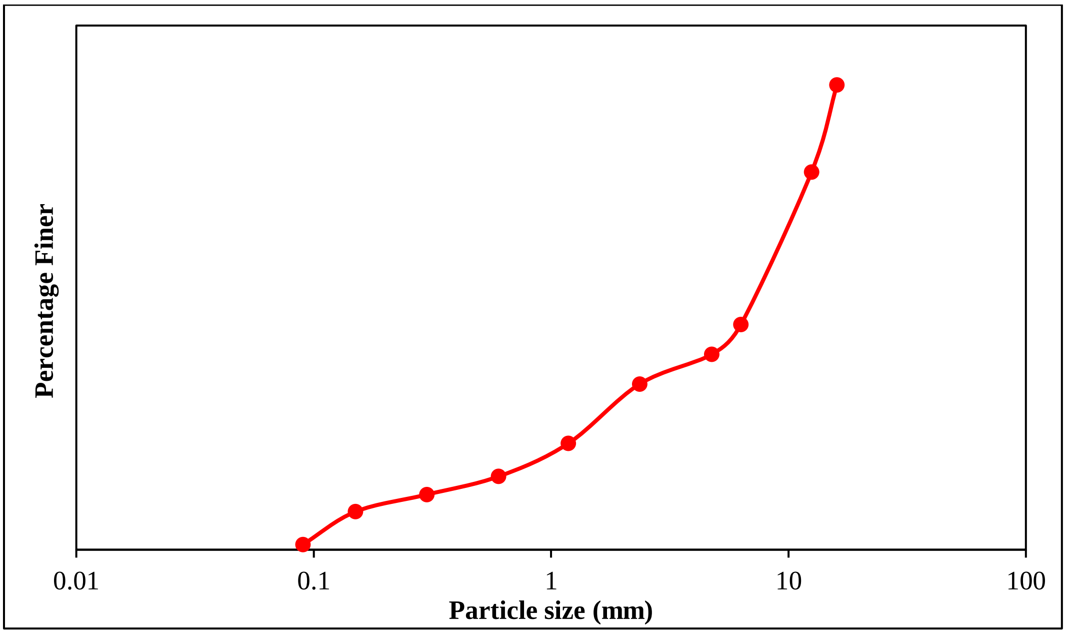

Fig. 4.25 Particle size distribution curve for bed sediments of *Canna lily*-based constructed wetland

4.12.2.3 Nutrient removal study in various seasons

Winter season

The impact of temperature variations and plant growth on efficient phosphate removal was investigated during the winter from December 2021 to February 2022, as detailed in Table 4.22 and illustrated in Fig. 4.26. An initial phosphate concentration (AP_i) in synthetically prepared stormwater runoff averaging 4.9 ± 0.4mg/L and ranging from 4.0 mg/L to 5.7 mg/L was introduced into the wetland cell. The significant reduction in available phosphate concentration at effluent end of the CW cell was observed ranging between 0.5 mg/L to 1.3 mg/L with an average of 0.8 ± 0.2 mg/L. This reveals a significant decrease in available phosphate concentration with nearly 84 % reduction at the effluent of *Canna*-based CW cell. On the other hand, the influent TP concentration ranged between 4.4 mg/L to 6.0 mg/L with an average of 5.3 ± 0.4 mg/L. A reduction in average TP concentration was observed at effluent end with an average of 1.2 ± 0.3 mg/L and the TP concentration ranged between 0.6 mg/L to 2.2 mg/L.

Table 4.22 Removal efficiency (%) of phosphate PO_4^{3-}-P during winter season using *Canna lily*-based constructed wetland

Date (n=30)	Available Phosphate			Total Phosphate		
	AP_i* (mg/L)	**AP_o* (mg/L)**	**Removal Efficiency (%)**	**TP_i* (mg/L)**	**TP_o* (mg/L)**	**Removal Efficiency (%)**
30-11-2021	4.9	1.3	73.3	5.5	2.2	60.9
01-12-2021	4.8	1.1	76.6	5.2	1.7	67.0
02-12-2021	4.9	0.7	86.4	5.2	1.2	76.7
03-12-2021	5.7	0.7	88.0	5.9	1.3	77.4
06-12-2021	5.4	0.9	83.6	6.0	1.3	79.0
07-12-2021	4.1	0.5	87.9	4.6	0.9	79.2
08-12-2021	5.0	0.7	86.9	5.1	1.2	76.7
09-12-2021	5.1	0.9	83.0	5.7	1.1	81.1
10-12-2021	5.1	0.8	83.7	5.7	1.2	79.3
13-12-2021	4.0	0.8	80.8	4.6	1.2	74.8
14-12-2021	4.0	0.7	82.0	4.6	1.0	78.5
15-12-2021	5.2	1.0	81.9	5.6	1.4	75.8
16-12-2021	4.8	0.8	83.3	5.0	1.6	68.8
17-12-2021	5.0	0.9	82.7	5.1	1.7	66.3
20-12-2021	5.0	0.7	86.3	5.1	1.2	77.0
21-12-2021	5.0	0.7	85.9	5.2	1.1	79.2
22-12-2021	5.0	0.8	83.3	5.2	1.3	74.6
23-12-2021	4.8	0.8	82.4	5.4	1.1	80.4
24-12-2021	5.1	0.7	85.7	5.3	0.9	82.1
27-12-2021	4.5	0.9	80.4	4.7	1.2	75.1
28-12-2021	4.3	0.9	79.8	4.4	1.1	74.5
29-12-2021	4.3	0.8	80.3	4.4	1.1	75.7
30-12-2021	5.4	0.9	83.9	5.8	1.1	80.2
31-12-2021	5.2	0.9	82.2	5.8	1.3	78.0
03-02-2022	5.2	0.6	88.7	5.7	0.6	88.9
09-02-2022	4.8	0.6	87.6	5.2	0.7	86.4

10-02-2022	4.9	0.6	87.5	5.3	0.6	88.0
11-02-2022	5.2	0.7	87.1	5.6	0.7	87.1
14-02-2022	4.9	0.8	83.7	5.6	1.1	80.8
15-02-2022	5.4	0.8	85.4	5.7	1.0	82.0
Minimum	4.0	0.5	73.3	4.4	0.6	60.9
Maximum	5.7	1.3	88.7	6.0	2.2	88.9
Average ± SD	4.9 ± 0.4	0.8 ± 0.2	83.7 ± 3.5	5.3 ± 0.4	1.2 ± 0.3	77.7 ± 6.2

$^{*}AP_i$ = available phosphate at inlet; $^{*}AP_o$ = available phosphate at outlet; $^{*}TP_i$ = available phosphate at inlet; $^{*}TP_o$ = total phosphate at outlet

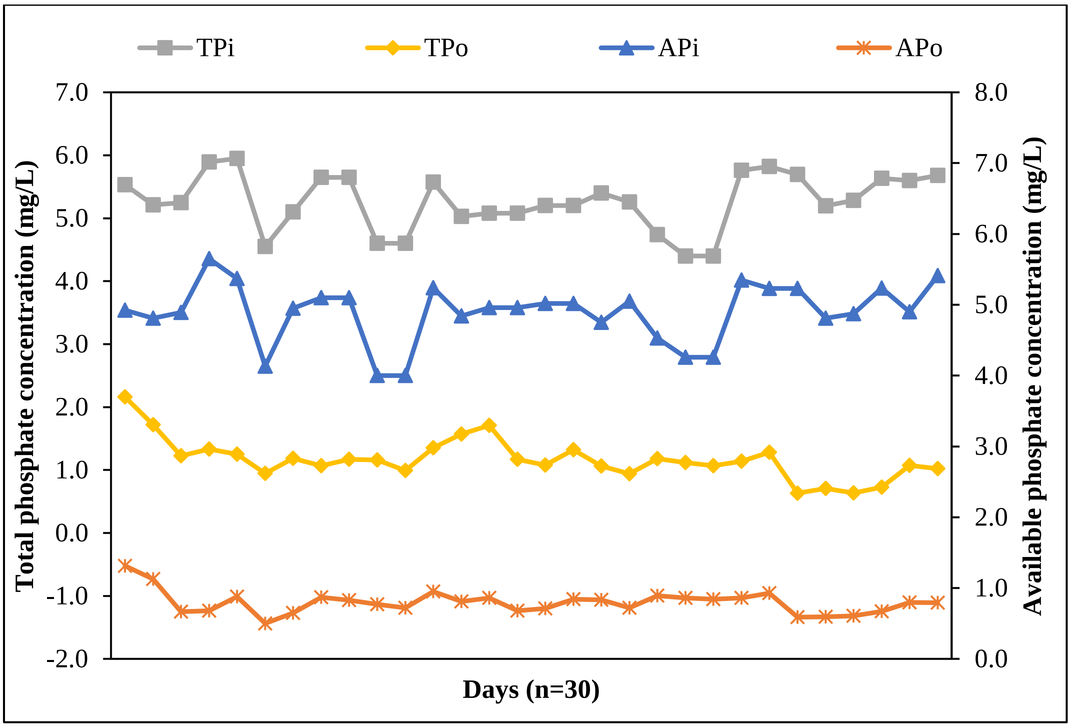

Fig. 4.26 Available and total phosphate concentration (mg/L) during winter season for *Canna lily*-based constructed wetland

This reported the TP removal efficiency was of order 77.7 ± 6.2 % with maximum and minimum total phosphate removal efficiency of 60.9 % to 88.9 %, respectively. The average TP phosphate removal efficiency was less than average available phosphate removal efficiency. The slight difference removal efficiency of TP compared to AP can be attributed to the availability of free and unbound AP to plant uptake for its metabolic activities.

Spring season

During the spring season (from mid-February 2021 to March 2021), the CW cell was fed with synthetically prepared stormwater runoff having phosphate strength of 5 mg/L. The available phosphate concentration at influent ranged between 4.0 mg/L to 5.8 mg/L with average inlet concentration of 4.6 ± 0.4 mg/L, while, the outlet AP concentration ranged from 0.2 mg/L to 0.8 mg/L, with an average of 0.6 ± 0.2 mg/L (Table 4.23; Fig. 4.27).

Table 4.23 Removal efficiency (%) phosphate PO_4^{3-}-P during spring season using *Canna lily*-based constructed wetland

Date (n=25)	Available Phosphate			Total Phosphate		
	AP_i^* (mg/L)	AP_o^* (mg/L)	Removal Efficiency (%)	TP_i^* (mg/L)	TP_o^* (mg/L)	Removal Efficiency (%)
17-02-2022	4.5	0.6	87.4	4.7	0.8	82.2
18-02-2022	4.0	0.6	84.7	4.6	0.7	84.1
22-02-2022	4.8	0.8	82.4	5.3	1.3	76.2
23-02-2022	4.8	0.8	83.8	5.5	1.5	73.7
24-02-2022	4.4	0.7	83.7	5.1	1.2	77.1
25-02-2022	4.8	0.8	83.8	5.5	1.4	75.1
03-03-2022	4.6	0.8	82.3	4.9	1.0	79.0
04-03-2022	4.3	0.7	84.5	4.7	0.9	80.2
05-03-2022	5.8	0.6	89.1	6.2	0.9	84.9
07-03-2022	4.3	0.7	83.1	5.0	1.1	77.2
08-03-2022	4.7	0.7	85.3	5.3	0.7	86.6
09-03-2022	4.6	0.2	95.6	5.0	0.5	89.7
10-03-2022	4.6	0.2	95.1	5.2	0.8	85.3
11-03-2022	4.3	0.7	84.6	4.9	0.7	85.4
14-03-2022	5.0	0.6	87.0	5.7	0.8	86.2
15-03-2022	5.0	0.4	91.8	5.5	0.7	88.1
16-03-2022	4.2	0.7	82.9	5.1	0.8	83.7
21-03-2022	4.2	0.7	83.1	4.5	0.8	81.9

23-03-2022	4.0	0.8	81.0	4.9	1.0	80.3
24-03-2022	4.5	0.6	86.9	5.3	0.7	87.8
25-03-2022	4.5	0.6	87.6	5.0	0.6	87.5
28-03-2022	5.2	0.7	86.6	5.4	1.0	82.3
29-03-2022	4.2	0.6	86.2	5.0	0.9	82.1
31-03-2022	5.1	0.7	87.1	5.5	0.9	83.8
Minimum	4.0	0.2	81.0	4.5	0.5	73.7
Maximum	5.8	0.8	95.6	6.2	1.5	89.7
Average ± SD	4.6 ± 0.4	0.6 ± 0.2	86.1 ± 3.8	5.2 ± 0.4	0.9 ± 0.2	82.5 ± 4.4

${}^{*}AP_i$ = available phosphate at inlet; ${}^{*}AP_o$ = available phosphate at outlet; ${}^{*}TP_i$ = available phosphate at inlet; ${}^{*}TP_o$ = total phosphate at outlet

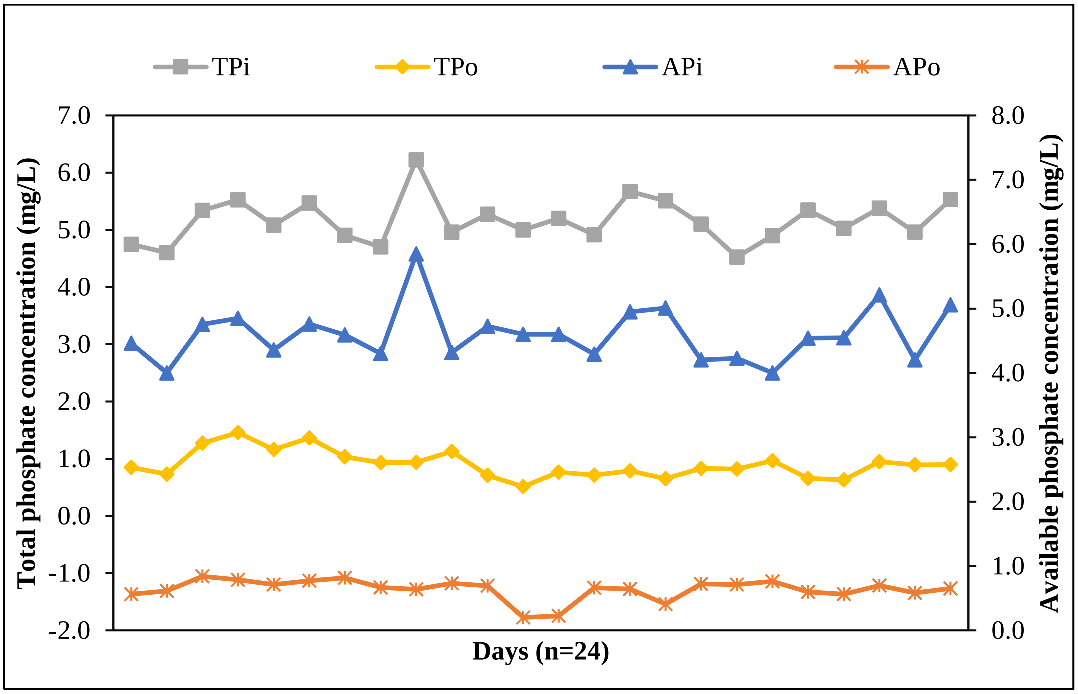

Fig. 4.27 Available and total phosphate concentration (mg/L) during spring season for *Canna lily*-based constructed wetland

This resulted in almost 86 ± 3.8 % removal of AP from *Canna*-based CW cell. On the other hand, the TP concentration at influent end varied between 4.5 mg/L to 6.2 mg/L while it ranged between 0.5 mg/L to 1.5 mg/L for TP at effluent end. The average TP removal efficiency was calculated as 82.5 ± 4.4 % as minimum and 73.7 % and 89.7 % as maximum TP removal efficiency. The AP removal efficiency was marginally higher than TP removal efficiency. This can be attributed towards non-availability and existence of TP in bound form with other chemical species within the CW cell. The available phosphates on the other hand, are readily available to be taken up by the plant species for its daily metabolic activities. Also, the average AP and TP removal efficiency was relatively higher in spring season as compared to winter season, owing to increase in average ambient temperature which ranged between 13 °C to 40 °C. In addition to this, the average sunshine hours and intensity of sun rays increases during spring season leading to more evapotranspiration and hence, more uptake of nutrients by *Canna*.

Summer season

During the summer period (April 2021 to mid-May 2021), synthetically prepared stormwater runoff having phosphate strength 5 mg/L was fed into the *Canna*-based CW cell. The inlet was fed with average AP concentration of 4.5 ± 0.3 mg/L which was varied between 4.0 mg/L and 5.0 mg/L (Table 4.24; Fig. 4.28).

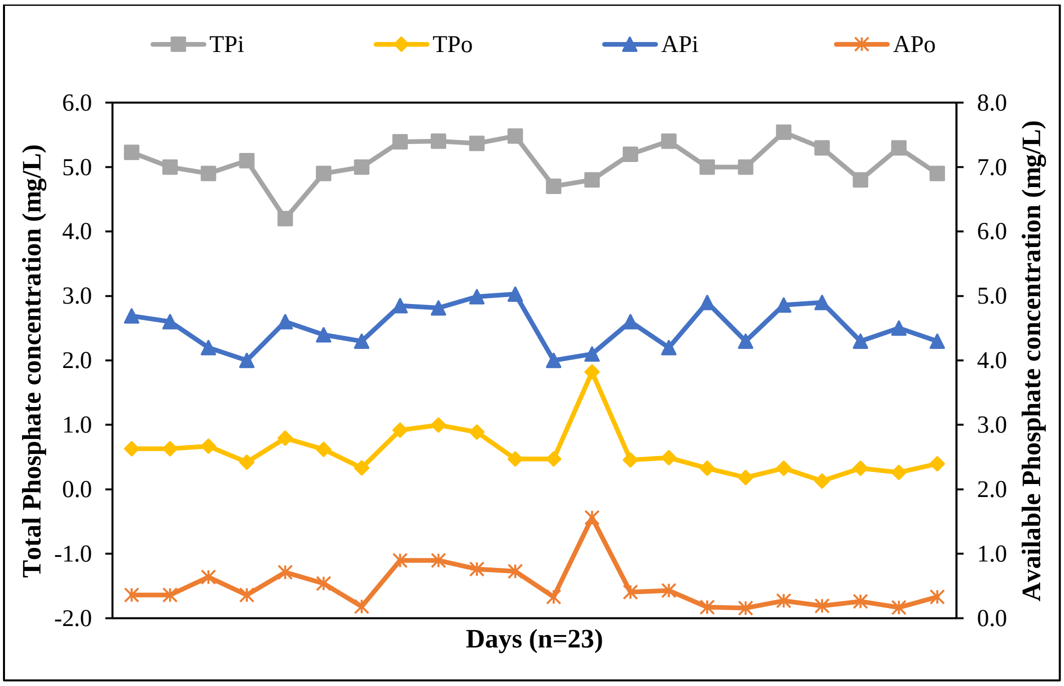

Fig. 4.28 Available and total phosphate concentration (mg/L) during summer season for *Canna lily*-based constructed wetland

The AP observed at effluent end varied between 0.2 mg/L to 1.6 mg/L. The average AP concentration at effluent end was 0.5 ± 0.3 mg/L. This highlights the average AP removal efficiency as 89.2 ± 7.8 % which varied between 61.9 % to 96.5 % owing to variation in environmental conditions. On the other hand, TP concentration at inlet varied between 4.2 mg/L to 5.5 mg/L whereas, TP concentration at effluent end as observed varied between 0.1 mg/L to 1.8 mg/L with an average TP concentration at effluent end as 0.6 ± 0.4 mg/L. Hence, the TP removal efficiency of *Canna*-based CW cell was 88.7 ± 7.6 % which varied between 62.1 % to 97.5 % depending upon the favourable conditions existing in CW cell, ambient temperature, and sunshine hours. Also, appreciably improved removal of Total Phosphate (TP) was recorded during the summer season compared to other seasons. Moreover, negligible difference in removal efficiency of AP and TP was witnessed. Since, evapotranspiration directly influences the removal efficiency of the plant as well as the treatment process, the rise in temperature heightened the evapotranspiration, leading to increased water uptake by *Canna* hence the enhanced removal of phosphate (Jain et al., 2024).

Table 4.24 Removal efficiency (%) phosphate PO_4^{3-}-P during summer season using *Canna lily*-based constructed wetland

Date (n=23)	Available Phosphate			Total Phosphate		
	AP_i^* (mg/L)	AP_o^* (mg/L)	Removal Efficiency (%)	TP_i^* (mg/L)	TP_o^* (mg/L)	Removal Efficiency (%)
01-04-2022	4.7	0.4	92.3	5.2	0.6	88.0
06-04-2022	4.6	0.4	92.2	5.0	0.6	87.4
07-04-2022	4.2	0.6	84.8	4.9	0.7	86.4
08-04-2022	4.0	0.4	91.0	5.1	0.4	91.8
11-04-2022	4.6	0.7	84.5	4.2	0.8	81.1
12-04-2022	4.4	0.5	87.7	4.9	0.6	87.3
14-04-2022	4.3	0.2	95.8	5.0	0.3	93.4
18-04-2022	4.9	0.9	81.5	5.4	0.9	82.9
19-04-2022	4.8	0.9	81.4	5.4	1.0	81.5

20-04-2022	5.0	0.8	84.7	5.4	0.9	83.5
21-04-2022	5.0	0.7	85.5	5.5	0.5	91.4
22-04-2022	4.0	0.3	91.8	4.7	0.5	90.0
25-04-2022	4.1	1.6	61.9	4.8	1.8	62.1
26-04-2022	4.6	0.4	91.2	5.2	0.5	91.3
27-04-2022	4.2	0.4	89.8	5.4	0.5	90.9
29-04-2022	4.9	0.2	96.5	5.0	0.3	93.5
02-05-2022	4.3	0.2	96.3	5.0	0.2	96.4
04-05-2022	4.9	0.3	94.4	5.5	0.3	94.1
05-05-2022	4.9	0.2	96.1	5.3	0.1	97.5
06-05-2022	4.3	0.3	93.9	4.8	0.3	93.2
09-05-2022	4.5	0.2	96.3	5.3	0.3	95.1
10-05-2022	4.3	0.3	92.3	4.9	0.4	91.9
Minimum	4.0	0.2	61.9	4.2	0.1	62.1
Maximum	5.0	1.6	96.5	5.5	1.8	97.5
Average ± SD	4.5 ± 0.3	0.5 ± 0.3	89.2 ± 7.8	5.1 ± 0.3	0.6 ± 0.4	88.7 ± 7.6

$^{*}AP_i$ = available phosphate at inlet; $^{*}AP_o$ = available phosphate at outlet; $^{*}TP_i$ = available phosphate at inlet; $^{*}TP_o$ = total phosphate at outlet

The seasonal analysis of *Canna lily* for removal of available and total phosphate from stormwater runoff reported no drastic change in the removal rate throughout the study period as compared to *Phragmites* (Fig. 4.29). Although slight difference in nutrient removal efficiency for AP and TP was seen. However, AP removal efficiency was greater than TP removal efficiency during all the season owing to the easy accessibility of unbound and free AP, making it readily available for plant as compared to bound TP. The TP removal efficiency of *Canna lily*-based CW follows the order as summer (89%) > spring (83%) > winter (78%). The AP phosphate removal efficiency for *Canna*-based CW cell follows as summer > spring > winter (% of Available Phosphate).

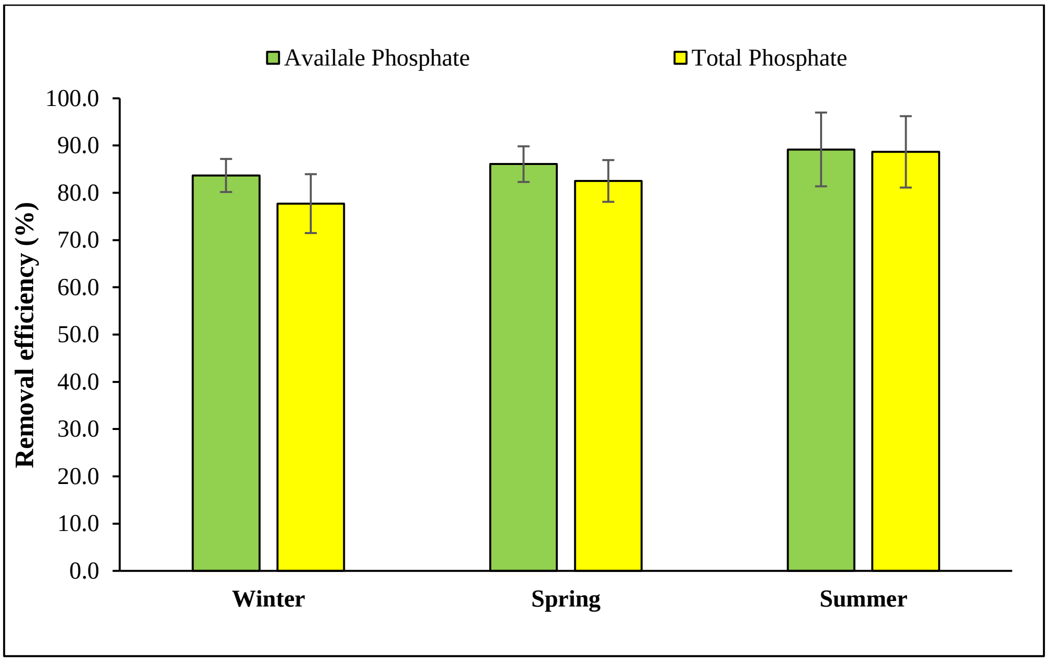

Fig. 4.29 Phosphate removal efficiency (%) of *Canna lily*-based constructed wetland during different seasons

4.12.3 *Cyperus alternifolius*-based constructed wetland

4.12.3.1 Ambient Temperature Profile

The ambient temperature profile for the period of six months was studied (December, 2021 to May, 2022) for pollutant removal study using *Cyperus alternifolius*. The ambient temperature varied between 6 °C to 44 °C, while the average maximum and minimum temperature recorded during the study was 17.5 °C and 30 °C. The current study was conducted during various seasons which are winter, spring and summer. The ambient temperature varied between 6 °C to 26 °C; 13 °C to 40 °C; and 22 °C to 44 °C during winter, spring, and summer season, respectively (Annexure-II; Fig. 4.30). The average ambient temperature during the current study was 16.2 °C, 24.7 °C, and 33.2 °C for winter, spring, and summer season, respectively. The effect of ambient temperature profile on growth of *Cyperus alternifolius* and its efficacy towards removal of nutrient was studied. The average sunshine hours varied between 8 to 10 hours.

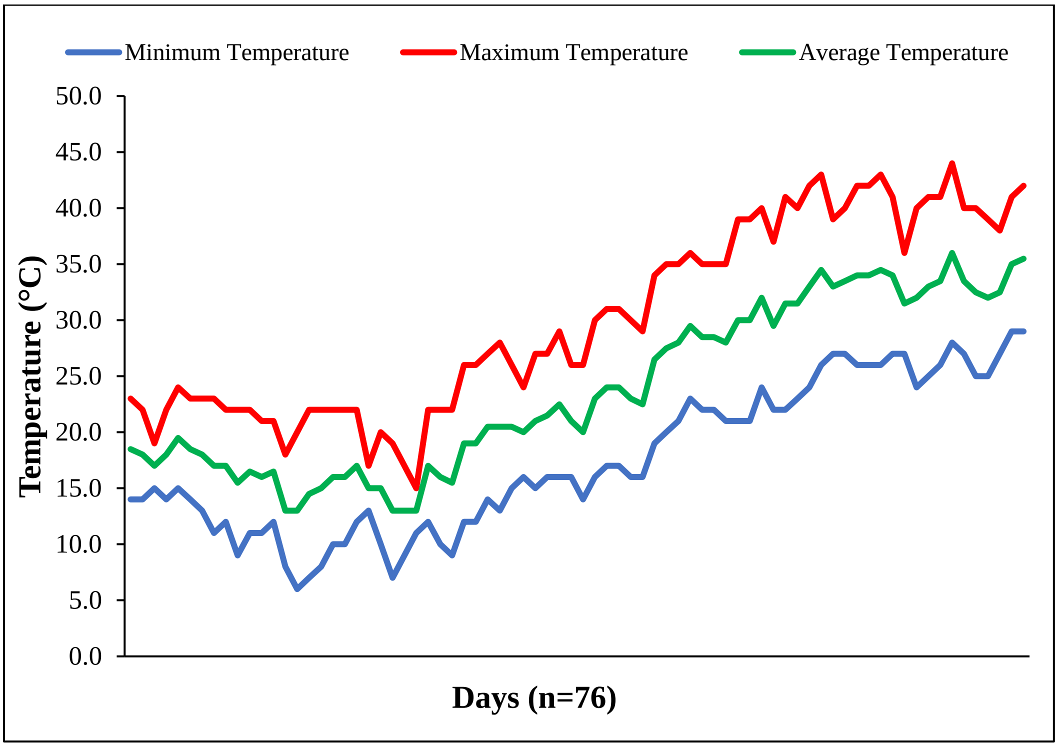

Fig. 4.30 Ambient temperature profile during pollutant removal study using *Cyperus alternifolius*-based constructed wetland (December, 2021 to May, 2022)

4.12.3.2 Sediment analysis

The substrate bed of Cyperus alternifolius-based constructed wetland cell was packed with gravel-sandy soil. The packing bed material has the specific gravity (G) as 2.70 with void ratio (e) equals to 0.55 and had a bulk density of (ρ) of 1820 kg/m3. The packing material of CW cell has 66.5 % coarse aggregates retaining on 4.75 mm sieve, 32.7 % as fine aggregates passing through 4.75 mm sieve, and rest as silt retained on pan (Table 4.25; Fig. 4.31). The packing material mimics the type of bed usually found in natural wetlands. The gravels with voids form a porous medium and it helped in easy percolation of influent into the substrate and it made exchange of gases easy at root zone (rhizosphere).

Table 4.25 Sieve analysis of bed sediments used for *Cyperus alternifolius*-based constructed wetland

Sieve size (mm)	**Weight retained (g)**	**Percentage Retained**	**Cumulative Percentage**	**Percentage Finer**
19	364.0	20.2	20.2	79.8
12.5	270.0	15.0	35.2	64.8
6.3	472.0	26.2	61.4	38.6
4.75	92.0	5.1	66.5	33.5
2.36	92.0	5.1	71.6	28.4
1.18	184.0	10.2	81.8	18.2
0.6	102.0	5.7	87.4	12.6
0.3	56.0	3.1	90.5	9,47
0.15	53.0	2.9	93.5	6.5
0.09	102.0	5.7	99.1	0.9
Pan	15.0	0.9	100.0	0.0
Total	1802.0	-	-	-

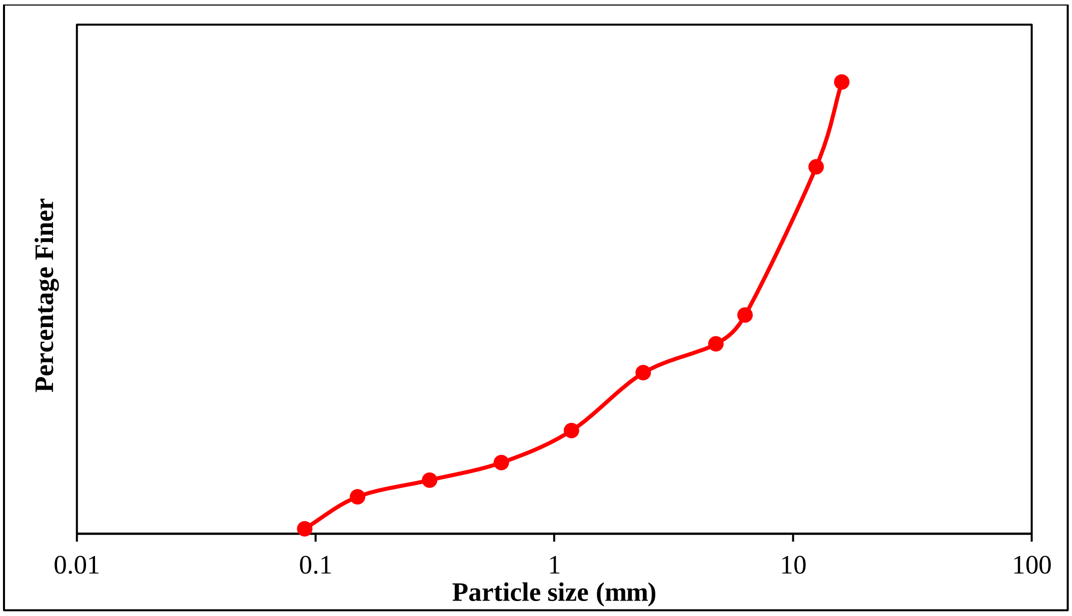

Fig. 4.31 Particle size distribution curve for bed sediments of *Cyperus alternifolius*-based constructed wetland

4.12.3.3 Nutrient removal study in various seasons

Winter season

The effective phosphate removal using *Cyperus alternifolius*-based constructed wetland was conducted from December 2021 to mid-February 2022, as outlined in Table 4.26 and depicted in Fig.4.32. The wetland cell was subjected to feeding with synthetically prepared stormwater runoff having average phosphate strength (AP_i) of 4.9 ± 0.4 mg/L with concentration ranging between 4.0 mg/L to 5.7mg/L. The phosphate concentration at effluent end following the treatment through CW cell ranged between 0.3 mg/L to 2.4 mg/L where average phosphate concentration was of order 1.6 ± 0.5 mg/L. Nearly 67 ± 9.9 % reduction in phosphate concentration was observed at the outlet, with maximum removal efficiency of order 95 % with a dip in removal efficiency to 56 %. This wide range in removal efficiency can be ascribe to reduction in average ambient temperature and reduction in sunshine hours during winter season. Similarly, the TP concentration at influent end was of order 4.4 to 6.0 mg/L with an average of 5.3 ± 0.4 mg/L. The average total phosphate concentration at effluent end after treatment was of order 2.0 ± 0.5 mg/L, ranging between 0.3 mg/L to 2.7 mg/L. The average TP concentration reduces significantly at effluent as compared to influent TP concentration, suggesting an average 63 % reduction. The TP removal efficiency ranged between 47.7 % to 94.1 % depending upon the favourable conditions for phosphate removal (Fig. 4.32). It is worth noting that TP removal efficiency is relatively lesser than AP removal efficiency which can be attributed to the easy availability of unbound AP fraction for plant uptake (Jain et al., 2024).

Table 4.26 Removal efficiency (%) of phosphate PO_4^{3-}-P during winter season using *Cyperus alternifolius*-based constructed wetland

Date (n=30)	Available Phosphate			Total Phosphate		
	AP_i^* (mg/L)	AP_o^* (mg/L)	Removal Efficiency (%)	TP_i^* (mg/L)	TP_o^* (mg/L)	Removal Efficiency (%)
30-11-2021	4.9	1.7	64.5	5.5	2.7	52.0
01-12-2021	4.8	1.5	68.6	5.2	2.2	58.0
02-12-2021	4.9	1.2	76.3	5.2	1.7	68.1
03-12-2021	5.7	1.5	74.0	5.9	1.7	71.3
06-12-2021	5.4	1.9	65.2	6.0	2.3	61.7
07-12-2021	4.1	1.9	55.2	4.6	2.3	49.5
08-12-2021	5.0	1.7	64.7	5.1	2.1	59.8
09-12-2021	5.1	1.7	66.3	5.7	2.1	62.1
10-12-2021	5.1	1.4	72.5	5.7	1.6	71.3
13-12-2021	4.0	1.1	72.0	4.6	1.5	68.3
14-12-2021	4.0	1.3	68.5	4.6	1.4	70.7
15-12-2021	5.2	1.7	67.8	5.6	2.0	65.0
16-12-2021	4.8	1.5	69.3	5.0	2.2	57.3
17-12-2021	5.0	1.8	64.3	5.1	2.1	59.4
20-12-2021	5.0	1.7	65.7	5.1	2.0	60.2
21-12-2021	5.0	1.8	65.1	5.2	2.2	58.7
22-12-2021	5.0	2.4	51.6	5.2	2.7	49.0
23-12-2021	4.8	2.3	51.8	5.4	2.7	49.6
24-12-2021	5.1	2.3	54.1	5.3	2.5	53.2
27-12-2021	4.5	1.8	59.8	4.7	2.2	54.6
28-12-2021	4.3	2.0	53.1	4.4	2.3	47.7
29-12-2021	4.3	1.8	58.2	4.4	2.1	53.4
30-12-2021	5.4	1.8	65.8	5.8	2.3	60.1

31-12-2021	5.2	2.0	61.0	5.8	2.4	58.4
03-02-2022	5.2	0.3	94.8	5.7	0.3	94.1
09-02-2022	4.8	1.1	78.2	5.2	1.5	70.4
10-02-2022	4.9	1.2	76.3	5.3	1.9	64.6
11-02-2022	5.2	0.9	83.5	5.6	1.0	82.2
14-02-2022	4.9	1.6	66.9	5.6	1.9	66.3
15-02-2022	5.4	1.0	81.4	5.7	1.2	78.5
Minimum	4.0	0.3	51.6	4.4	0.3	47.7
Maximum	5.7	2.4	94.8	6.0	2.7	94.1
Average ± SD	4.9 ± 0.4	1.6 ± 0.5	67.2 ± 9.9	5.3 ± 0.4	2.0 ± 0.5	62.5 ± 10.5

$^{*}AP_i$ = available phosphate at inlet; $^{*}AP_o$ = available phosphate at outlet; $^{*}TP_i$ = available phosphate at inlet; $^{*}TP_o$ = total phosphate at outlet

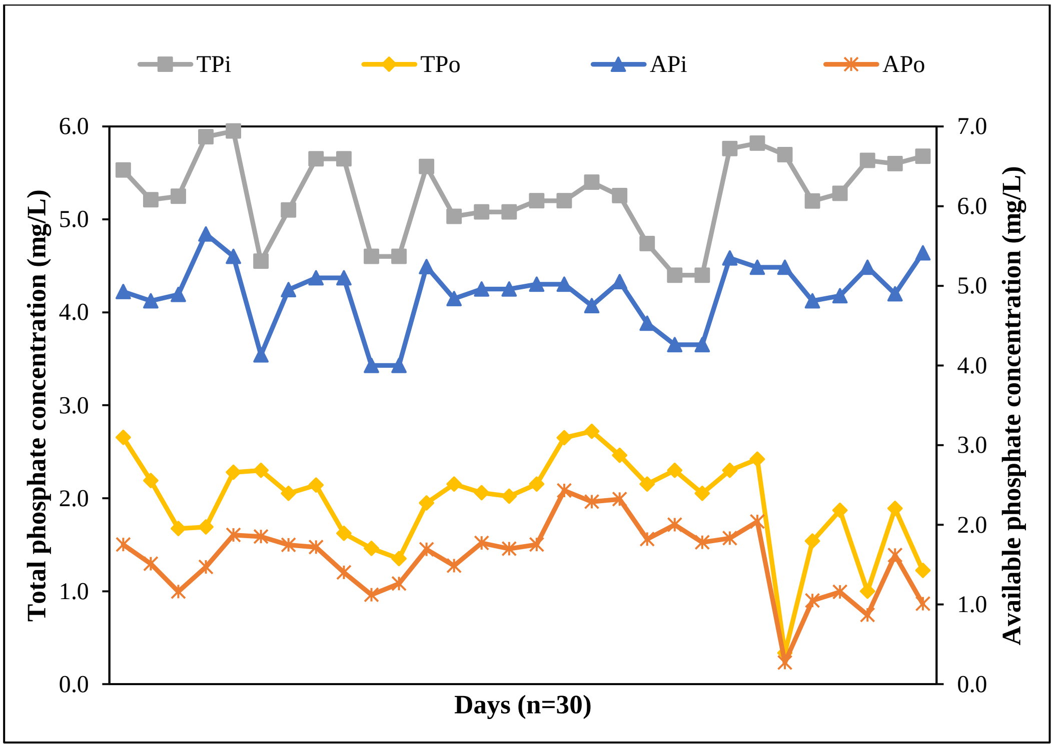

Fig. 4.32 Available and total phosphate concentration (mg/L) during winter season for *Cyperus alternifolius*-based constructed wetland

Spring season

The removal efficiency of phosphates using *Cyperus alternifolius*-based constructed wetland was conducted between mid-February 2021 to March 2021 for spring season. For an average available inlet concentration at influent end as 4.6 ± 0.4 mg/L, the average outlet Available Phosphate (AP) concentration observed as 1.1 ± 0.3 mg/L, representing slightly higher removal efficiency of 77 % as compared to AP removal efficiency in winter season (Table 4.27 and Fig. 4.33).

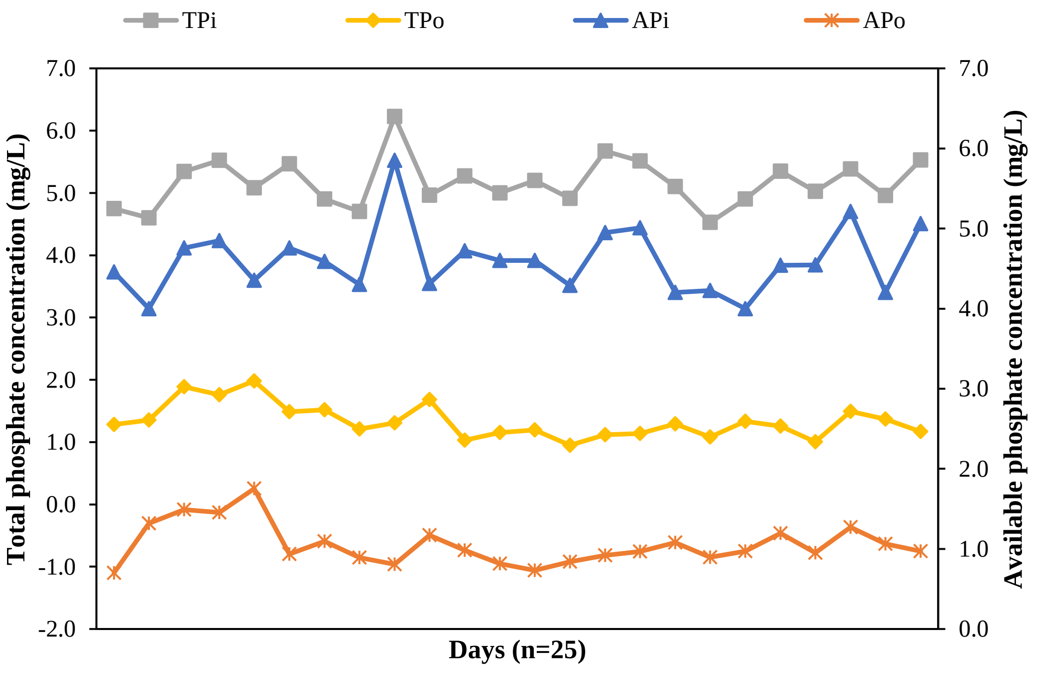

Fig. 4.33 Available and total phosphate concentration (mg/L) during spring season for *Cyperus alternifolius*-based constructed wetland

Also, the available phosphate removal efficiency ranged between 59.8 % to 86.2 % which is also slightly higher than AP removal efficiency during winter season. In case of TP, for an average inlet TP concentration of 5.2 ± 0.4 mg/L which ranged between 4.5 mg/L to 6.2 mg/L, whereas, the TP concentration at effluent end varied between 1.0 mg/L to 2.0 mg/L with an average concentration of 1.3 ±

0.3 mg/L. The reduction in TP concentration at effluent end resulted in 74 % removal efficiency of TP during spring season using *Cyperus alternifolius*-based constructed wetland. The temperature in spring season gradually increased, ranging from 13 °C to 40 °C along with increase in average sunshine hours, thus, promoted enhanced total phosphate removal as compared to winter season.

Table 4.27 Removal efficiency (%) of phosphate PO_4^{3-}-P during spring season using *Cyperus alternifolius*-based constructed wetland

Date (n=25)	**Available Phosphate**			**Total Phosphate**		
	AP_i^* (mg/L)	**AP_o^* (mg/L)**	**Removal Efficiency (%)**	**TP_i^* (mg/L)**	**TP_o^* (mg/L)**	**Removal Efficiency (%)**
17-02-2022	4.5	0.7	84.3	4.7	1.3	73.0
18-02-2022	4.0	1.3	67.0	4.6	1.4	70.6
22-02-2022	4.8	1.5	68.7	5.3	1.9	64.6
23-02-2022	4.8	1.5	70.0	5.5	1.8	68.2
24-02-2022	4.4	1.8	59.8	5.1	2.0	61.0
25-02-2022	4.8	0.9	80.4	5.5	1.5	72.8
03-03-2022	4.6	1.1	76.1	4.9	1.5	69.0
04-03-2022	4.3	0.9	79.3	4.7	1.2	74.3
05-03-2022	5.8	0.8	86.2	6.2	1.3	79.0
07-03-2022	4.3	1.2	72.9	5.0	1.7	66.1
08-03-2022	4.7	1.0	79.1	5.3	1.0	80.5
09-03-2022	4.6	0.8	82.3	5.0	1.2	76.9
10-03-2022	4.6	0.7	84.1	5.2	1.2	77.0
11-03-2022	4.3	0.8	80.4	4.9	1.0	80.7
14-03-2022	5.0	0.9	81.4	5.7	1.1	80.2
15-03-2022	5.0	1.0	80.7	5.5	1.1	79.3

16-03-2022	4.2	1.1	74.3	5.1	1.3	74.7
21-03-2022	4.2	0.9	78.8	4.5	1.1	76.1
23-03-2022	4.0	1.0	75.7	4.9	1.3	72.8
24-03-2022	4.5	1.2	73.7	5.3	1.3	76.5
25-03-2022	4.5	1.0	79.0	5.0	1.0	80.0
28-03-2022	5.2	1.3	75.6	5.4	1.5	72.3
29-03-2022	4.2	1.1	74.6	5.0	1.4	72.4
31-03-2022	5.1	1.0	80.8	5.5	1.2	78.8
Minimum	4.0	0.7	59.8	4.5	1.0	61.0
Maximum	5.8	1.8	86.2	6.2	2.0	80.7
Average ± SD	4.6 ± 0.4	1.1 ± 0.3	76.9 ± 6.1	5.2 ± 0.4	1.3 ± 0.3	74.0 ± 5.4

$^{*}AP_i$ *= available phosphate at inlet;* $^{*}AP_o$ *= available phosphate at outlet;* $^{*}TP_i$ *= available phosphate at inlet;* $^{*}TP_o$ *= total phosphate at outlet*

Summer season

Throughout the summer period (April 2021 to May 2021), phosphate ions having strength of 5 mg/L was introduced into the CW cell in the form of synthetically prepared stormwater runoff. The CW cell was amended with inlet average concentration of 4.5 ± 0.3 mg/L with minimum concentration of 4.0 mg/L and maximum concentration of 5.0 mg/L. At the effluent end, the available phosphate concentration ranged between 0.2 mg/L to 1.4 mg/L with an average of 0.8 ± 0.3 mg/L. Thus, the plant species was found efficient in removing around 83 % AP with 95 % maximal and 67 % minimum AP removal efficiency. Similarly, in case of total phosphate (TP) removal, for average inlet concentration of 5.1 ± 0.3 mg/L which ranged between 4.2 mg/L to 5.5 mg/L, while the average outlet concentration observed was 0.9 ± 0.4 mg/L which ranged between 0.3 mg/L to 1.5 mg/L. This resulted in 82 % reduction in TP removal efficiency at effluent end (Table 4.28; Fig. 4.34). Prominent enhancement in the removal of Total Phosphate (TP) was witnessed during the summer season in comparison to other seasons. Additionally, a minimal variation in the removal efficiencies of AP and TP was witnessed. Since summer season experienced a significant increase in temperature which rose to 44 °C during the study period, evapotranspiration directly impacts both plant removal efficiency and treatment processes. The increase in temperature fostered evapotranspiration, thereby escalating the water uptake by plants and subsequently increasing phosphate removal (Jain et al., 2024).

Table 4.28 Removal efficiency (%) of phosphate PO_4^{3-}-P during summer season using *Cyperus alternifolius*-based constructed wetland

Date (n=23)	Available Phosphate			Total Phosphate		
	AP_i* (mg/L)	AP_o* (mg/L)	Removal Efficiency (%)	TP_i* (mg/L)	TP_o* (mg/L)	Removal Efficiency (%)
01-04-2022	4.7	0.7	84.6	5.2	1.1	79.5
06-04-2022	4.6	1.2	75.0	5.0	1.1	78.6
07-04-2022	4.2	1.1	72.7	4.9	1.3	72.6
08-04-2022	4.0	0.4	89.0	5.1	0.5	90.3
11-04-2022	4.6	0.8	82.0	4.2	1.0	75.7
12-04-2022	4.4	0.9	79.2	4.9	1.1	76.7
14-04-2022	4.3	0.3	93.7	5.0	0.3	93.4
18-04-2022	4.9	1.3	72.4	5.4	1.5	71.6
19-04-2022	4.8	1.1	76.5	5.4	1.5	72.2
20-04-2022	5.0	1.3	74.3	5.4	1.5	72.6
21-04-2022	5.0	1.1	78.0	5.5	1.4	73.9
22-04-2022	4.0	0.7	82.8	4.7	0.7	84.9
25-04-2022	4.1	1.4	67.1	4.8	1.5	69.2
26-04-2022	4.6	0.6	87.6	5.2	0.9	83.2
27-04-2022	4.2	0.5	87.6	5.4	0.6	89.4
29-04-2022	4.9	0.2	95.0	5.0	0.6	88.2

02-05-2022	4.3	0.5	88.1	5.0	0.6	87.5
04-05-2022	4.9	0.4	91.1	5.5	0.6	88.7
05-05-2022	4.9	0.6	87.4	5.3	0.7	87.2
06-05-2022	4.3	0.5	88.7	4.8	0.5	89.1
09-05-2022	4.5	0.6	86.3	5.3	0.8	85.5
10-05-2022	4.3	0.6	86.1	4.9	0.6	87.0
Minimum	4.0	0.2	67.1	4.2	0.3	69.2
Maximum	5.0	1.4	95.0	5.5	1.5	93.4
Average ± SD	4.5 ± 0.3	0.8 ± 0.3	83.0 ± 7.6	5.1 ± 0.3	0.9 ± 0.4	81.7 ± 7.5

$^{*}AP_i$ = available phosphate at inlet; $^{*}AP_o$ = available phosphate at outlet; $^{*}TP_i$ = available phosphate at inlet; $^{*}TP_o$ = total phosphate at outlet

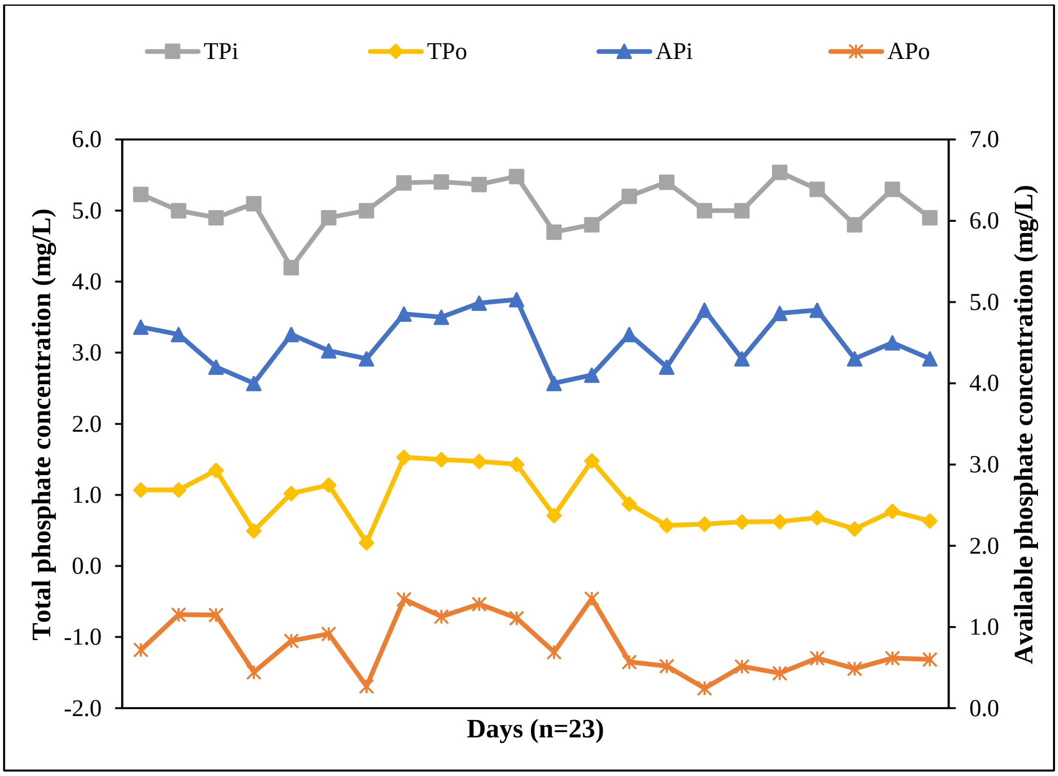

Fig. 4.34 Available and total phosphate concentration (mg/L) during summer season for *Cyperus alternifolius*-based constructed wetland

The overall performance of *Cyperus alternifolius*-based constructed wetland can be summarized from Fig. 4.35 representing the removal efficiency for different seasons. It can be observed that summer season reported maximum available and total removal efficiency followed by spring season and winter season respectively. The temperature directly influences the growth and metabolism of the plant. During winter season, cold environment might inhibit the plant cell metabolism and reduced sunshine hours leads to lesser photosynthesis and associated activities. Increase in the temperature during spring and summer season increased the nutrient uptake by the plant species, hence increasing the removal efficiency of the CW cell.

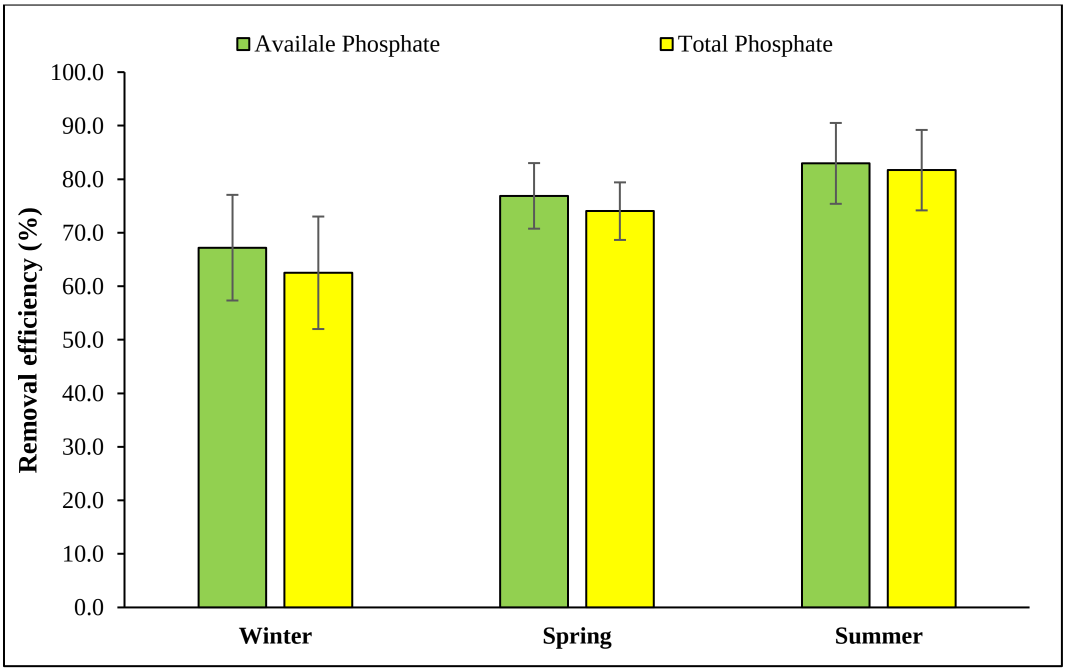

Fig. 4.35 Phosphate removal efficiency (%) for *Cyperus alternifolius*-based constructed wetland during different seasons

4.13 Effect of temperature and season

The variation in available phosphate removal efficiency during autumn, winter, spring and summer for *Phragmites*, *Canna lily*, and *Cyperus alternifolius*-based constructed wetland can be seen in Fig. 4.36. The study was conducted during autumn season only for *Phragmites*-based constructed wetland. However, the available phosphate removal efficiency was maximum for *Phragmites*, followed by *Canna lily*, and *Cyperus alternifolius*-based constructed wetland during winter season. Similar trend was followed for spring and summer season where available phosphate removal efficiency followed the order *Phragmites* > *Canna lily* > *Cyperus alternifolius*. Hence, it can be suggested that *Phragmites* species suits better to remove available phosphates from stormwater runoff among all the seasons when compared with *Canna lily* and *Cyperus alternifolius*-based constructed wetland.

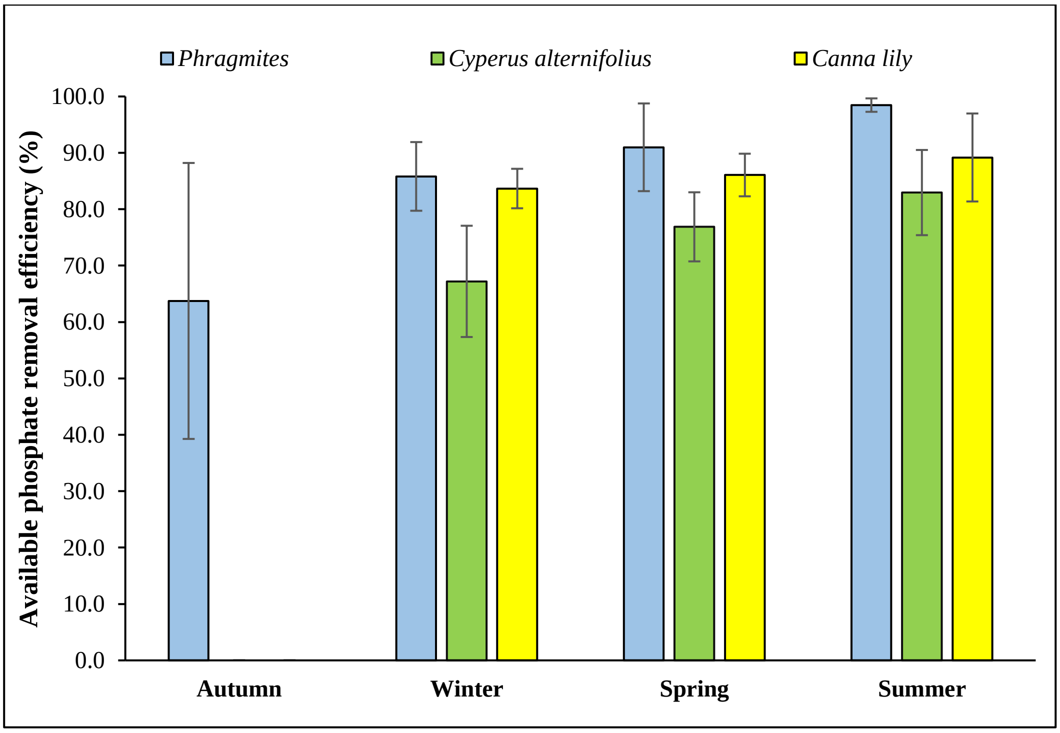

Fig. 4.36 Available phosphate removal efficiency (%) using *Phragmites*, *Canna lily*, and *Cyperus alternifolius*-based constructed wetland during different seasons

The variation in total phosphate removal efficiency during autumn, winter, spring and summer for *Phragmites*, *Canna lily*, and *Cyperus alternifolius*-based constructed wetland can be seen in Fig. 4.37. Here also, the study was conducted during autumn season only for *Phragmites*-based constructed wetland. However, the total phosphate removal efficiency was maximum for *Phragmites*, followed by *Canna lily*, and *Cyperus alternifolius*-based constructed wetland during winter season. Similarly, for spring and summer season where total phosphate removal efficiency followed the order *Phragmites* > *Canna lily* > *Cyperus alternifolius*. Hence, it can be suggested that *Phragmites* species suits better to remove total phosphates from stormwater runoff among all the seasons when compared with *Canna lily* and *Cyperus alternifolius*-based constructed wetland.

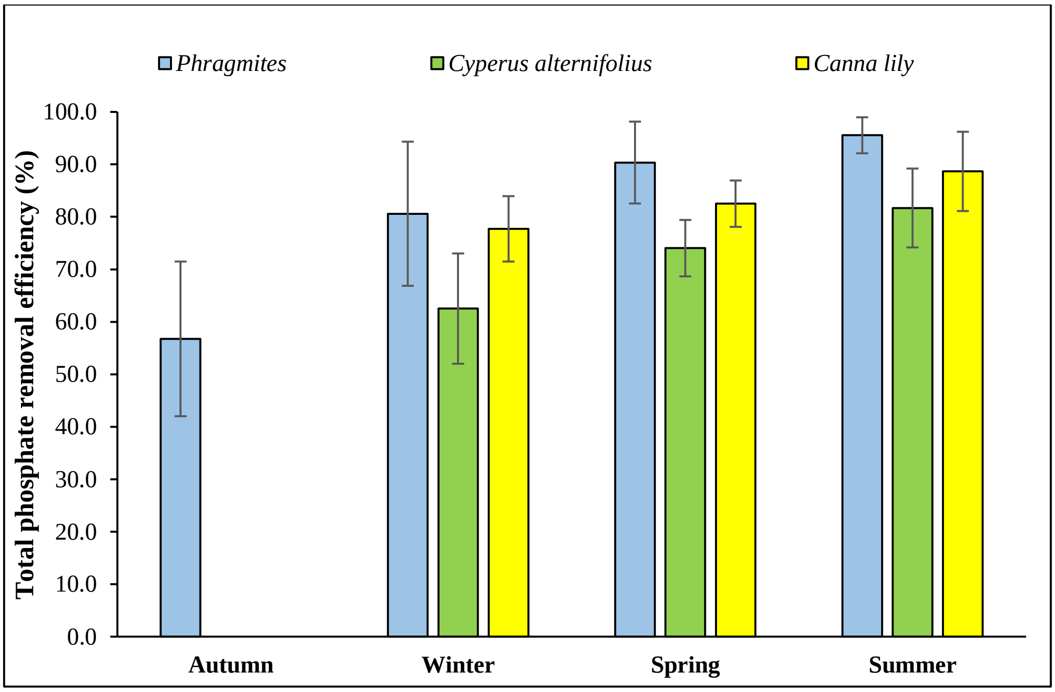

Fig. 4.37 Total phosphate removal efficiency (%) using *Phragmites*, *Canna lily*, and *Cyperus alternifolius*-based constructed wetland during different seasons

4.14 Phosphate in plant tissue

The removal efficiency primarily depends upon the nutrient uptake by the plant sp. which is correlated with its accumulation in biomass as suggested by Jiang et al., (2011). Hence, analysis of plant tissue is necessary to study translocation and accumulation of phosphate in different plant tissues of *Canna lily* and *Cyperus alternifolius* in the present study. The accumulation in tissue helps in preventing recirculation and reintroduction of phosphate into the CW cell once it is removed by plant. The analysis of plant tissues (roots, stems, leaves and flower) for *Canna lily* and (roots, stems and leaves) *Cyperus alternifolius* was investigated for accumulated phosphate concentration. Maximum accumulation of phosphate was observed in stem, followed by flowers, roots and leaves of *Canna lily*. Compared to the initial concentration, the phosphate concentration was more than twice for roots and stems while it increased 23 and 4.7 times in leaves and flowers, respectively. On the other hand, for *Cyperus alternifolius*, maximum accumulation of phosphate was observed in stem followed by roots and leaves. The increase in final phosphate concentration was observed as 5.3, 2.7 and 1.5 times that of initial concentration in roots, stem, and leaves, respectively (Table 4.29). In present study, the removal of phosphate from CW cell is correlated with increase in biomass. Similar results have also been reported by other studies (Iamchaturapatr et al., 2007; Jiang et al., 2011; Kyambadde et al., 2004). In present study, the ratio of Above ground: Below ground (AG:BG) > 1.0 for both the plant *sp.* which means above ground tissue have stored more phosphate than below ground tissue. Hence, in order to prevent the re-entry and re-circulation of phosphate via felling of leaves, flowers and dead biomass into the wetland system, its harvesting is necessary at regular interval leading to nutrient export away from wetland system as suggested by Haritash et al., (2017) and Jain et al., (2024).

Table 4.29 Total phosphate concentration (mg/g) in different plant tissues before and after the study

Plant tissue		***Canna lily***		***Cyperus alternifolius***	
		Initial (mg/g)	**Final (mg/g)**	**Initial (mg/g)**	**Final (mg/g)**
Roots	BG	1.7 ± 0.3	3.9 ± 0.3	0.4 ± 0.1	2.1 ± 0.2
Stems	AG	4.4 ± 0.1	9.1 ± 0.2	2.9 ± 0.2	7.9 ± 0.3
Leaves		0.1 ± 0.1	2.3 ± 0.1	1.1 ± 0.3	1.7 ± 0.2
Flowers		0.9 ± 0.2	4.2 ± 0.2	NA	NA

**NA= Not applicable*

4.15 Pollutant removal study by using hybrid filter system

A combination of filter media and macrophytes which includes *Phragmites*, *Canna lily*, *Cyperus alternifolius*, and *Eichhornia* in individual but connected cells were used to assess the efficacy of hybrid filter towards the treatment of synthetically prepared stormwater runoff. The experiment was conducted for 28 days during the present study. The synthetically prepared stormwater runoff was fed from the influent end. It was fed continuously such that after 20 minutes, the treated effluent was collected in a beaker. One of the major pollutants found in stormwater runoff was suspended solids. During the present study, the influent TSS concentration varied between 200 mg/L to 3175 mg/L with an average of 1154.7 ± 801.8 mg/L. However, the effluent concentration of TSS varied between 5 mg/L to 135 mg/L with an average of 35.7 ± 28.4 mg/L (Table 4.30). The minimum TSS removal efficiency obtained during the current study was 88.2 % while the maximum TSS removal efficiency obtained was 99.5 %. The average of TSS removal efficiency using the hybrid filter system was 96.3 ± 2.4 % (Fig. 4.38) suggests that this system is highly effective and efficient towards removal of suspended solids from stormwater runoff. The effective TSS removal efficiency can be ascribed to void spaces which reduces the turbulence of flowing stormwater runoff, and also to the flow in direction vertically downward and upward through all the cells provided in the hybrid filter system. Phosphate being a pollutant was also removed effectively using hybrid filter. The filtration unit in the first cell was provided with calcite, limestone, biochar, and iron filings which in synergy with four different macrophytes was able to remove phosphates during the continuous operation. The influent phosphate concentration varied between 0.09 mg/L to 0.41 mg/L, while the average influent phosphate concentration during the experiment obtained was 0.23 ± 0.08 mg/L. The phosphate removal efficiency obtained was varied between 38.9 % to 76.3 % with an average of 54.3 ± 10.0 % (Table 4.31; Fig. 4.39).

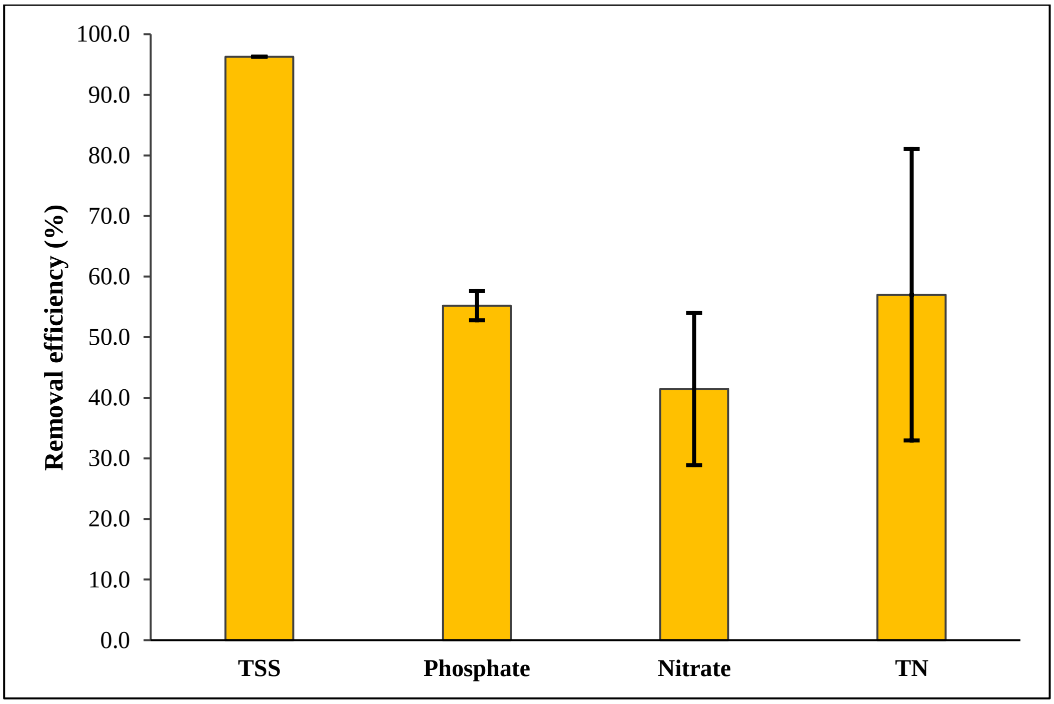

Fig. 4.38 Removal efficiency of TSS, phosphate, nitrate and TN from bench-scale WSUD

During certain days, when the phosphate removal efficiency was less, it can be ascribed to shift in chemical equilibrium and release of bound phosphate from iron filings when the form iron changes from Fe^{3+} to Fe^{2+}. Removal of nitrate was also studied using the hybrid filter system. The influent nitrate concentration in synthetically prepared stormwater runoff varied between 1.9 mg/L to 7.1 mg/L with an average of 3.9 ± 1.2 mg/L. On the other hand, the nitrate concentration at effluent after the treatment ranged between 0.1 mg/L and 4.9 mg/L with an average of 2.4 ± 1.3 mg/L. While the hybrid system was operated continuously, the nitrate removal efficiency ranged between 10.3 % to 95.5 %. The average nitrate removal efficiency was of order 41.4 ± 24.0 %. The nitrate was removed from the hybrid system can be attributed towards uptake by the plant species (Kadlec et al., 2012). Nitrogen conversions in wetlands include the formation of oxidized nitrogen which results in its removal. Based on results from prior studies, it is most likely that the predominant removal mechanism could be denitrification (Karpuzcu and Stringfellow, 2012). Total nitrogen (TN) removal was also studied using hybrid filter system. TN concentration at influent varied between 0.5 mg/L to 1.3 mg/L with an average of 0.8 ± 0.2 mg/L. Post treatment, the TN concentration at effluent was found to be 0.1 mg/L to 0.8 mg/L with an average of 0.3 ± 0.2 mg/L. The TN removal efficiency varied between the range 14.3 % to 88.9 % with an average TN removal efficiency of 57 ± 20.0 %.

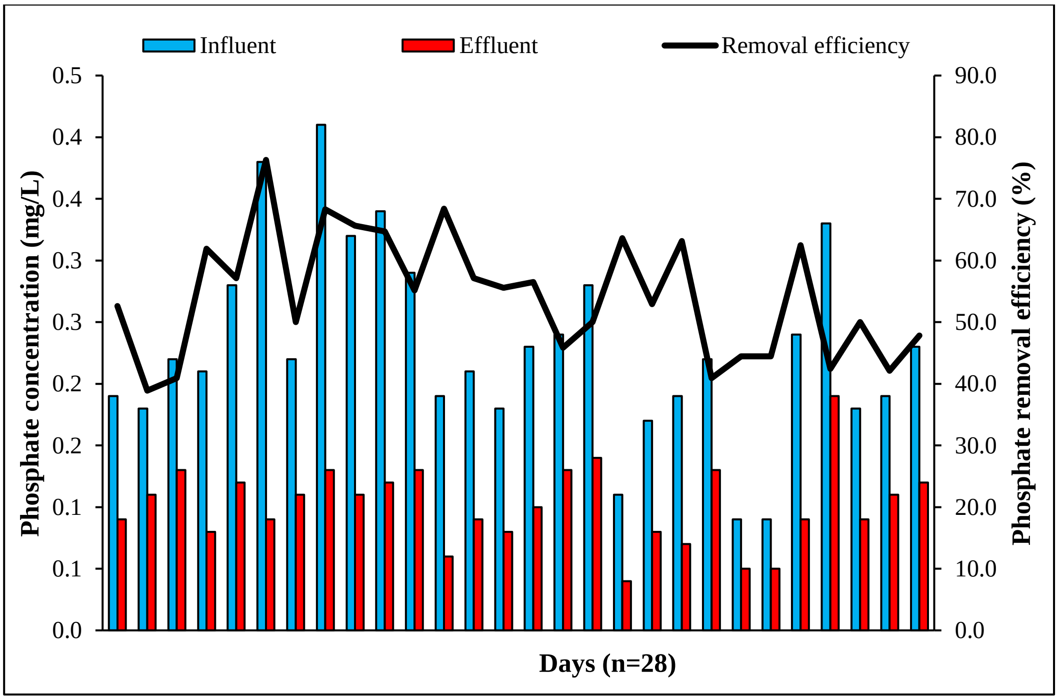

Fig. 4.39 Influent and effluent phosphate concentration (mg/L) and its removal efficiency using a bench-scale hybrid filter system

The TN removal efficiency can be ascertained to nitrification and denitrification processes while the hybrid system was amended with biochar. Similar results were also obtained by previous studies (Guo et al., 2023). The experimentation during present study suggests a proper design and code of practice for the development of such hybrid filter systems that can efficiently remove suspended solids and nutrients from the urban stormwater runoff. This can help in mitigating sedimentation and silting in natural as well as in man-made drains which reduces its capacity to carry water. It can also help in reducing the nutrient content of freshwater bodies which leads to its eutrophication.

Table 4.30 Influent and effluent characteristics of synthetically prepared stormwater runoff using a hybrid filtration system

S. No.	**pH**		**EC**		**TDS**		**TSS**		
	Inlet	**Outlet**	**Inlet (μS/cm)**	**Outlet (μS/cm)**	**Inlet (mg/L)**	**Outlet (mg/L)**	**Inlet (mg/L)**	**Outlet (mg/L)**	**Removal efficiency (%)**
1	6.6	6.8	900	896	450	448	200	5	97.5
2	6.1	6.5	806	1116	403	558	2450	135	94.5
3	6.6	6.8	904	1125	452	562	2796	85	97.0
4	6.9	6.7	870	1114	435	555	1196	50	95.8
5	6.4	6.6	920	1050	460	525	210	15	92.9
6	6.5	6.8	920	970	460	485	805	95	88.2
7	6.3	7.0	950	1010	475	505	980	15	98.5
8	6.5	6.7	960	1070	480	535	3175	60	98.1
9	6.7	6.9	950	980	475	490	720	20	97.2
10	6.3	6.7	850	910	425	455	1125	45	96.0
11	6.7	7.0	880	970	440	485	1870	45	97.6
12	6.9	6.9	980	950	490	475	1150	20	98.3
13	6.3	6.6	940	923	470	460	752	38	94.9
14	6.2	6.5	923	910	459	455	392	26	93.4
15	6.6	6.8	995	1040	499	519	960	30	96.9

16	6.7	6.9	962	925	478	462	315	25	92.1
17	6.4	6.7	928	977	464	489	450	20	95.6
18	6.2	6.6	926	911	463	456	550	20	96.4
19	6.9	6.8	940	1040	470	520	790	25	96.8
20	6.9	7.0	950	970	475	485	540	25	95.4
21	6.3	6.8	930	965	466	481	745	15	98.0
22	6.4	6.7	955	924	477	462	1010	25	97.5
23	6.4	6.6	934	928	462	464	1265	20	98.4
24	6.5	6.6	943	947	473	474	2815	15	99.5
25	6.3	6.5	900	1040	450	520	1125	25	97.8
26	6.5	6.8	940	976	470	488	1010	20	98.0
27	6.4	6.7	909	932	455	463	1145	50	95.6
28	6.5	7.1	949	903	474	451	1790	30	98.3
Minimum	6.1	6.5	806.0	896.0	403.0	448.0	200.0	5.0	88.2
Maximum	6.9	7.1	995.0	1125.0	499.0	562.0	3175.0	135.0	99.5
Average ± SD	6.5 ± 0.2	6.8 ± 0.2	925.5 ± 39.4	981.1 ± 68.5	462.5 ± 19.7	490.3 ± 34.2	1154.7 ± 801.8	35.7 ± 28.4	96.3 ± 2.4

EC= Electrical Conductivity; TDS= Total Dissolved Solids; TSS= Total Suspended Solids; SD= Standard deviation.

Table 4.31 Influent and effluent characteristics of synthetically prepared stormwater runoff using a hybrid filtration system

S. No.	Phosphate (PO_4^{3-})			Nitrate (NO_3^-)			TOC		TN		
	Inlet (mg/L)	Outlet (mg/L)	Removal efficiency (%)	Inlet (mg/L)	Outlet (mg/L)	Removal efficiency (%)	Inlet (mg/L)	Outlet (mg/L)	Inlet (mg/L)	Outlet (mg/L)	Removal efficiency (%)
1	0.2	0.1	52.6	7.1	4.9	31.0	1.1	1.7	0.9	0.2	77.8
2	0.2	0.1	38.9	5.2	3.5	32.7	1.9	9.3	0.6	0.4	33.3
3	0.2	0.1	40.9	5.5	4.2	23.6	2.7	9.9	1.2	0.6	50.0
4	0.2	0.1	61.9	6.2	4.1	33.9	4.3	13.1	1.3	0.8	38.5
5	0.3	0.1	57.1	4.3	3.2	25.6	1.9	5.1	0.7	0.3	57.1
6	0.4	0.1	76.3	3.1	2.7	12.9	1.5	4.5	0.6	0.3	50.0
7	0.2	0.1	50.0	3.8	3.2	15.8	1.1	4.7	0.6	0.3	50.0
8	0.4	0.1	68.3	4.4	3.7	15.9	2.1	8.1	0.8	0.3	62.5
9	0.3	0.1	65.6	2.7	1.8	33.3	1.1	4.2	0.5	0.2	60.0
10	0.3	0.1	64.7	3.9	3.5	10.3	2.3	4.9	1.1	0.6	45.5
11	0.3	0.1	55.2	5.2	2.7	48.1	1.6	5.1	0.7	0.3	57.1
12	0.2	0.1	68.4	3.5	1.5	57.1	2.1	4	0.6	0.1	83.3
13	0.2	0.1	57.1	1.9	0.1	94.7	3.3	3.6	0.6	0.1	83.3
14	0.2	0.1	55.6	2.2	0.1	95.5	3.2	4.1	0.6	0.2	66.7
15	0.2	0.1	56.5	4.4	2.8	36.4	1.6	7.6	0.7	0.6	14.3

16	0.2	0.1	45.8	3.2	1.2	62.5	3.5	4.9	0.6	0.1	83.3
17	0.3	0.1	50.0	3	2.1	30.0	2.8	8.1	0.7	0.4	42.9
18	0.1	0.0	63.6	3.6	0.7	80.6	3.5	4.8	0.8	0.1	87.5
19	0.2	0.1	52.9	3.8	2.9	23.7	2.6	7.1	0.8	0.5	37.5
20	0.2	0.1	63.2	2.4	0.5	79.2	4.2	4.7	0.5	0.3	40.0
21	0.2	0.1	40.9	2.7	1.2	55.6	3.8	4.5	0.8	0.2	75.0
22	0.1	0.1	44.4	2.7	1.1	59.3	3.7	4.5	0.6	0.2	66.7
23	0.1	0.1	44.4	5.2	3.1	40.4	3.8	3.9	0.9	0.1	88.9
24	0.2	0.1	62.5	4.4	2.3	47.7	3.8	4.8	0.6	0.3	50.0
25	0.3	0.2	42.4	4.4	3.3	25.0	1.8	5.8	0.7	0.6	14.3
26	0.2	0.1	50.0	3.5	2.1	40.0	1.7	5.1	0.8	0.3	62.5
27	0.2	0.1	42.1	3.4	3	11.8	3.2	5.3	0.9	0.4	55.6
28	0.2	0.1	47.8	4.2	2.6	38.1	3.4	3.9	0.8	0.3	62.5
Minimum	0.09	0.04	38.9	1.9	0.1	10.3	1.1	1.7	0.5	0.1	14.3
Maximum	0.41	0.19	76.3	7.1	4.9	95.5	4.3	13.1	1.3	0.8	88.9
Average ± SD	0.23 ± 0.08	0.10 ± 0.03	54.3 ± 10.0	3.9 ± 1.2	2.4 ± 1.3	41.4 ± 24.0	2.6 ± 1.0	5.6 ± 2.3	0.8 ± 0.2	0.3 ± 0.2	57.0 ± 20.0

TOC=Total Organic Carbon; TN= Total Nitrogen; SD= Standard deviation.

4.16 Significance of the study

Capturing, intercepting, treating, and using treated stormwater runoff could have several positive impacts on the environment as well as on the society. The present study also aligns with the targets and indicators of the United Nations's Sustainable Development Goals (SDGs) which are shown in Fig. 4.40. The following are the environmental and social impacts which the present study can make:

4.16.1 Environmental impacts

- Properly managed stormwater runoff treatment method, such as a wetland, rain garden, bioswales, etc. can treat and at the same time, provide an area for storing the stormwater runoff, which helps in reducing the peak runoff volume, and reduces the probability of occurrence of flooding. The stored water undergoes sequence of treatment methods during its detention in the wetlands which can be utilised later for non-potable usage. The treated water also percolates to join with the water table to increase its level. The availability of water can be assured over a period of time. Thus, it reduces the dependence on freshwater and it aligns with the targets of 6th Sustainable Development Goal: Clean Water and Sanitation.

- At the level of authorities, if the stormwater water treatment units can be installed in the urban areas which if provided with tertiary level treatment, it can certainly reduce demand and supply gap of the treated water supplied by authorities while utilising the treated stormwater runoff. At places where meter system has been installed for freshwater supply, it reduces dependence on freshwater which can help in saving money. The loss of runoff while following its natural path can be reduced by providing storage for the treated stormwater runoff. This can be implemented to reduce the impact on environment and thus, align with the targets of 11th Sustainable Development Goal: Sustainable Cities and Communities.

- The treated stormwater runoff through a sequence of treatment methods and techniques, helps in reducing the pollutant concentration in the water body which receives treated stormwater runoff. If no treatment is provided, the stormwater runoff from urban areas will pollute and contaminate the receiving water body. For instance, if riparian buffers are provided along the rivers that receives urban stormwater runoff, the pollutant load of the reiver will reduce which will help in protecting the sensitive aquatic species. Saving the aquatic species could be a pride to nation and its citizen. Thus, this aligns with the 14th Sustainable Development Goal: Life Below Water.

- The bioretention basin such as wetlands and raingarden, not only increases the aesthetics of the surrounding, but also improves the biodiversity of the region. It helps in augmenting the diversity of flora and fauna by providing them the habitat and food. The wetlands used for treatment of stormwater runoff can restore the freshwater ecosystem and provides protections to the biodiversity. The people in that region can feel proud and can utilise such pride to develop the tourism in that region with the help of local authorities and administration. Such methods and techniques are the indicators of 15th Sustainable Development Goal: Life on Land.

- Treatment units such as swales, wetlands, rain garden, etc. are provided with various species of macrophyte suitable for the regional climatic conditions can act as the sink of carbon dioxide, thus reduces the carbon dioxide from the atmosphere through carbon sequestration.

- Such treatment techniques are provided with sustainable method for pollutant removal using various species of macrophytes. These macrophytes increases the vegetative cover over the urban areas which can help in cooling the urban environments by reducing the urban heat island effect.

Fig. 4.40 Highlighted United Nation's sustainable development goals (SDGs) aligning with the present study

4.16.2 Social impacts

- Design, development, and maintenance of stormwater runoff treatment infrastructure can generate job opportunities in terms of its construction, landscaping, etc. in specialisation linked with it. Such chances will increase the work opportunity, thereby reducing the inequality in terms of income. Such techniques from developed nations can be implemented in the developing nations through transfer of technology, thus, promoting 10th Sustainable Development Goal: Reduced Inequality.

- The bioretention systems are not provided with lining at the bottom. The water stored and being treated will infiltrate and it can further percolate from the ground surface to recharge the aquifers, and thus, helps in increasing the water table level. People living in areas with scarce freshwater supplies can depend upon it which will reduce the time and energy wasted in acquiring fresh water from distant water resources.

- Due to availability of treated stormwater runoff, it can be used for non-potable domestic applications such that flushing system can be provided in the dwelling units which helps in ending open defecation. It also provides social sense of security to the women of the society in developing nations where sanitation and hygiene is still a challenge for the government.

- Installation of treatment technique such as a rain garden in the premisses of dwelling unit, it adds value to the property, hence, increasing the property value of the owner. Rain garden not only treats stormwater runoff, it can also enhance the aesthetics of the property.

- In India, the water resources are sacred which connects various cultural and spiritual diversities. Maintaining the aesthetics of the water bodies like holy rivers and ponds promote the sense of preserving the cultural customs and rituals of the society which beholds the people together.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

On the basis of the outcome of the current study, the following conclusions can be made

- The physicochemical characteristics of rainwater samples during year 2021 and 2022 shows that chemicals species were present in trace amount. The presence of chemical species originating from alluvial dust of region surrounding Delhi can neutralise each other making the rainfall pH almost neutral for most of the rainfall events. As a result of which, no event of acid rain ($pH < 5.6$) was observed over Delhi. Also, there was no contribution from sea salts owning to NSSF factor and distance of Delhi from seas.

- The atmospheric washing as a result of rainfall event leads to presence of suspended solids in the rainwater samples as it scavenges suspended dust particles. The subsequent rainfall events did not show presence of suspended solids and the concentration of various cationic and anionic species reduced in following rainfall events.

- The physicochemical characteristics of stormwater runoff from year 2021 and 2022 in Delhi, India, suggested that pH and total dissolved solids (TDS) varies significantly among the various land use areas. Also, major pollutant in stormwater runoff originating from commercial, industrial, institutional, residential, and road/highway was total suspended solids and nutrients which requires it efficient treatment to make it usable for non-potable use.

- Majority of heavy metals were not found in the stormwater runoff samples collected from Delhi, India. However, the presence of copper, zinc and iron was observed in varying concentration in all the land use areas. The presence of cadmium was observed in stormwater runoff samples originating from road/highways owing to its presence in tyres and brake pads with disintegrates with time on its application.

- Bamboo which was used to produce biochar in the lab for the treatment of stormwater runoff has a yield of approximately 40 %. The loss in weight during its production was due to loss of moisture, syngas, and production of bio-oil. Due to its electro-negative surface charge, surface of biochar was modified with chemical species using $FeCl_3$ that imparted electro-positive charge before treatment. Biochar treated with 10 % $FeCl_3$ solution resulted in 61 % phosphate removal efficiency when the strength of synthetically prepared stormwater runoff was 5 mg/L as PO_4^{3-}.

- The removal efficiency of biochar is a function of surface chemical treatment with electro-positive chemical species, dose of biochar in the aqueous solution, its contact time, and initial concentration of nutrient (phosphate) in the synthetically prepared stormwater runoff solution.

- The adsorption isotherm study suggested the removal of nutrient follows Langmuir isotherm model. Kinetics of phosphate removal using biochar follows pseudo-second order as suggested by best fit curve. In addition to this, removal of phosphates by biochar depends upon the presence of adsorption sites over the surface which is correlated with the specific surface area of the biochar produced.

- The batch study of different filter media suggested the phosphate removal efficiency follows the trend iron filing > calcite > limestone > brick > hematite > biochar. The adsorption capacity and performance are function of contact time. The maximum phosphate was removed by iron which can be ascribed to electro-positive charge presented in the iron filings that helped in binding of phosphates leading to its removal.

- The continuous vertical flow column filter shows that upto 97 % of the total suspended solids can be removed from real stormwater runoff samples. Due to the presence of various filter media in layers in series, the maximum phosphate removal efficiency achieved was of order 93 %, whereas, the filter achieved almost 75 % removal of nitrate from real stormwater runoff samples.

- The phosphate removal efficiency from synthetically prepared stormwater runoff using *Phragmites*-based CW cell shows trend summer > spring > winter > autumn for both available. In case of total phosphate removal efficiency, the *Phragmites*-based CW cell follows the same trend summer > spring > winter > autumn. Also, the removal efficiency of available phosphates was higher owing to its unbound form and free availability in aqueous medium.

- The available phosphate removal efficiency of *Canna lily*-based constructed wetland cells suggested maximum removal efficiency was achieved in summer season, followed by spring and winter season. In addition to this, the total phosphate removal efficiency shows the TP removal efficiency trend as summer > spring > winter season. Also, the removal efficiency of AP was more than TP among all the seasons during the study.

- *Cyperus alternifolius*-based constructed wetland cell suggested that maximum available phosphate removal efficiency was achieved in summer season followed by spring and winter. The total phosphate removal efficiency also follows the trend summer > spring > winter season. Also, the removal efficiency of AP was greater than TP owing to easy availability of available phosphates in unbound form to the plant which can be utilised for its metabolic activity.

- The phosphate removal efficiency using macrophytes in constructed wetland cells suggested that its removal efficiency is a function of ambient temperature, average sunshine hours, and other environmental conditions. However, the nutrient (phosphate) removal efficiency in *Phragmites*-based CW cell was highest among all the seasons followed by *Canna lily* and *Cyperus alternifolius* for both available phosphates and total phosphates during the present study.

- The hybrid filter system can remove almost 99.5 % total suspended solids from synthetically prepared stormwater runoff. The average phosphate removal efficiency of phosphate in hybrid filter system was of order 55 % with maximum phosphate removal efficiency achieved as 80 % when no retention time was given and the cell was being operated continuously. Whereas, the removal efficiency of nitrate was of order 41 % with maximum nitrate removal efficiency achieved as 95 %.

5.2 Recommendation

Based on the outcomes of the present study, the following recommendations are suggested aiming to make better use of stormwater runoff and reduce the water scarcity in urban areas.

- On the basis of physicochemical characterisation of stormwater runoff, it is evident that stormwater runoff has relatively less contamination which can be treated easily. Hence, stormwater runoff should be intercepted and stored wherever possible, so that it can be used in urban areas of Delhi for non-potable use. This can also help in bridging the demand and supply gap.

- Although, there are Indian standards for disposal of treated sewage and treated industrial effluents over the land and into the rivers/streams. However, there are no standard developed in India to categorise the quality of stormwater runoff. Hence, it is recommended to develop water quality standards, categories and indices for stormwater runoff characteristics.

- The natural slope of urban area can be estimated using contour maps to track the flow of stormwater runoff before it gets mixed with river and streams and disposes of. The same can be utilized to develop wetlands and provide the desired level of treatment to stormwater runoff such that it will help in capacity building of urban areas and provide the storage for its later non-potable use.

- Stormwater runoff simulation models can be adopted for predicting the flow volume for which the infrastructure of optimum capacity can be developed through model testing and validation with real world problem.

- The economic analysis of the infrastructure and treatment cost that can occur towards treatment of stormwater runoff is rare and limited. If the economic analysis can be provided, then cost benefit analysis, life cycle cost, breakeven period, and net asset value can be calculated for its application in developing nations where the shortage of funds remains for capital investment.

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ANNEXURE-I

Table 1 Ambient temperature during the study (October, 2020 to April, 2021)

Date	Minimum Temperature (°C)	Maximum Temperature (°C)	Average Temperature (°C)
20-10-2020	15.0	33.0	24.0
21-10-2020	16.0	34.0	25.0
22-10-2020	14.0	34.0	24.0
23-10-2020	15.0	32.0	23.5
26-10-2020	16.0	32.0	24.0
27-10-2020	16.0	32.0	24.0
28-10-2020	14.0	31.0	22.5
29-10-2020	14.0	31.0	22.5
30-10-2020	14.0	31.0	22.5
02-11-2020	13.0	30.0	21.5
03-11-2020	13.0	30.0	21.5
04-11-2020	13.0	27.0	20.0
05-11-2020	14.0	30.0	22.0
06-11-2020	13.0	30.0	21.5
09-11-2020	12.0	28.0	20.0
10-11-2020	13.0	30.0	21.5
11-11-2020	13.0	29.0	21.0
12-11-2020	12.0	28.0	20.0
13-11-2020	14.0	30.0	22.0
16-11-2020	12.0	28.0	20.0
17-11-2020	16.0	25.0	20.5
18-11-2020	15.0	26.0	20.5
19-11-2020	12.0	25.0	18.5
20-11-2020	12.0	24.0	18.0
23-11-2020	9.0	25.0	17.0
24-11-2020	9.0	24.0	16.5
25-11-2020	12.0	22.0	17.0

26-11-2020	12.0	25.0	18.5
27-11-2020	13.0	26.0	19.5
30-11-2020	10.0	26.0	18.0
04-01-2021	13.0	22.0	17.5
05-01-2021	14.0	20.0	17.0
06-01-2021	14.0	21.0	17.5
07-01-2021	12.0	20.0	16.0
08-01-2021	12.0	20.0	16.0
11-01-2021	10.0	17.0	13.5
12-01-2021	10.0	16.0	13.0
13-01-2021	6.0	16.0	11.0
14-01-2021	5.0	19.0	12.0
15-01-2021	7.0	20.0	13.5
18-01-2021	11.0	20.0	15.5
19-01-2021	8.0	18.0	13.0
20-01-2021	9.0	17.0	13.0
21-01-2021	8.0	22.0	15.0
22-01-2021	6.0	17.0	11.5
25-01-2021	6.0	18.0	12.0
27-01-2021	7.0	20.0	13.5
28-01-2021	6.0	19.0	12.5
29-01-2021	6.0	20.0	13.0
01-02-2021	7.0	25.0	16.0
02-02-2021	8.0	26.0	17.0
03-02-2021	13.0	25.0	19.0
04-02-2021	11.0	22.0	16.5
05-02-2021	9.0	21.0	15.0
08-02-2021	10.0	24.0	17.0
09-02-2021	10.0	26.0	18.0
10-02-2021	12.0	29.0	20.5
11-02-2021	12.0	26.0	19.0
15-02-2021	11.0	29.0	20.0

16-02-2021	13.0	29.0	21.0
17-02-2021	13.0	27.0	20.0
18-02-2021	12.0	27.0	19.5
19-02-2021	13.0	26.0	19.5
22-02-2021	13.0	26.0	19.5
23-02-2021	12.0	31.0	21.5
24-02-2021	13.0	32.0	22.5
25-02-2021	14.0	32.0	23.0
26-02-2021	17.0	33.0	25.0
01-03-2021	14.0	28.0	21.0
02-03-2021	16.0	28.0	22.0
03-03-2021	15.0	30.0	22.5
04-03-2021	15.0	32.0	23.5
05-03-2021	16.0	31.0	23.5
09-03-2021	17.0	32.0	24.5
10-03-2021	20.0	33.0	26.5
11-03-2021	18.0	34.0	26.0
12-03-2021	21.0	29.0	25.0
16-03-2021	19.0	31.0	25.0
17-03-2021	18.0	34.0	26.0
18-03-2021	19.0	33.0	26.0
19-03-2021	19.0	34.0	26.5
22-03-2021	21.0	32.0	26.5
23-03-2021	19.0	29.0	24.0
24-03-2021	18.0	32.0	25.0
29-03-2021	22.0	39.0	30.5
30-03-2021	21.0	38.0	29.5
31-03-2021	23.0	34.0	28.5
01-04-2021	21.0	33.0	27.0
02-04-2021	18.0	34.0	26.0
06-04-2021	22.0	38.0	30.0
07-04-2021	23.0	36.0	29.5

08-04-2021	19.0	35.0	27.0
09-04-2021	16.0	36.0	26.0
12-04-2021	20.0	38.0	29.0
13-04-2021	21.0	39.0	30.0
14-04-2021	20.0	39.0	29.5
15-04-2021	21.0	40.0	30.5
16-04-2021	22.0	40.0	31.0
19-04-2021	20.0	37.0	28.5
20-04-2021	21.0	33.0	27.0
21-04-2021	21.0	32.0	26.5

ANNEXURE-II

Table 2 Ambient temperature during the study (December, 2021 to May, 2022)

Date	Minimum Temperature (°C)	Maximum Temperature (°C)	Average Temperature (°C)
30-11-2021	14.0	23.0	18.5
01-12-2021	14.0	22.0	18.0
02-12-2021	15.0	19.0	17.0
03-12-2021	14.0	22.0	18.0
06-12-2021	15.0	24.0	19.5
07-12-2021	14.0	23.0	18.5
08-12-2021	13.0	23.0	18.0
09-12-2021	11.0	23.0	17.0
10-12-2021	12.0	22.0	17.0
13-12-2021	9.0	22.0	15.5
14-12-2021	11.0	22.0	16.5
15-12-2021	11.0	21.0	16.0
16-12-2021	12.0	21.0	16.5
17-12-2021	8.0	18.0	13.0
20-12-2021	6.0	20.0	13.0
21-12-2021	7.0	22.0	14.5
22-12-2021	8.0	22.0	15.0
23-12-2021	10.0	22.0	16.0
24-12-2021	10.0	22.0	16.0
27-12-2021	12.0	22.0	17.0
28-12-2021	13.0	17.0	15.0
29-12-2021	10.0	20.0	15.0
30-12-2021	7.0	19.0	13.0
31-12-2021	9.0	17.0	13.0
03-02-2022	11.0	15.0	13.0
09-02-2022	12.0	22.0	17.0
10-02-2022	10.0	22.0	16.0

11-02-2022	9.0	22.0	15.5
14-02-2022	12.0	26.0	19.0
15-02-2022	12.0	26.0	19.0
17-02-2022	14.0	27.0	20.5
18-02-2022	13.0	28.0	20.5
22-02-2022	15.0	26.0	20.5
23-02-2022	16.0	24.0	20.0
24-02-2022	15.0	27.0	21.0
25-02-2022	16.0	27.0	21.5
03-03-2022	16.0	29.0	22.5
04-03-2022	16.0	26.0	21.0
05-03-2022	14.0	26.0	20.0
07-03-2022	16.0	30.0	23.0
08-03-2022	17.0	31.0	24.0
09-03-2022	17.0	31.0	24.0
10-03-2022	16.0	30.0	23.0
11-03-2022	16.0	29.0	22.5
14-03-2022	19.0	34.0	26.5
15-03-2022	20.0	35.0	27.5
16-03-2022	21.0	35.0	28.0
21-03-2022	23.0	36.0	29.5
23-03-2022	22.0	35.0	28.5
24-03-2022	22.0	35.0	28.5
25-03-2022	21.0	35.0	28.0
28-03-2022	21.0	39.0	30.0
29-03-2022	21.0	39.0	30.0
31-03-2022	24.0	40.0	32.0
01-04-2022	22.0	37.0	29.5
06-04-2022	22.0	41.0	31.5
07-04-2022	23.0	40.0	31.5
08-04-2022	24.0	42.0	33.0
11-04-2022	26.0	43.0	34.5

12-04-2022	27.0	39.0	33.0
14-04-2022	27.0	40.0	33.5
18-04-2022	26.0	42.0	34.0
19-04-2022	26.0	42.0	34.0
20-04-2022	26.0	43.0	34.5
21-04-2022	27.0	41.0	34.0
22-04-2022	27.0	36.0	31.5
25-04-2022	24.0	40.0	32.0
26-04-2022	25.0	41.0	33.0
27-04-2022	26.0	41.0	33.5
29-04-2022	28.0	44.0	36.0
02-05-2022	27.0	40.0	33.5
04-05-2022	25.0	40.0	32.5
05-05-2022	25.0	39.0	32.0
06-05-2022	27.0	38.0	32.5
09-05-2022	29.0	41.0	35.0
10-05-2022	29.0	42.0	35.5

LIST OF PUBLICATIONS

Research Papers:

SCI/ SCIE Index Publications:

1. Yadav, S., Pipil, H., Haritash, A.K. Reddy, K.R. (2024). Fe(III)-modified bamboo biochar for the removal of phosphate from synthetic and field stormwater runoff. Sustain. Water Resour. Manag. 10, 140. https://doi.org/10.1007/s40899-024-01123-1

2. Jain, N., Yadav, S., Taneja, S., Ray, S., Haritash, A. K., Pipil, H. (2024). Phosphate removal from urban stormwater runoff using Canna lily and Cyperus alternifolius-based bioretention system. *Sustainable Water Resources Management*, *10*(2), 1-10. https://doi.org/10.1007/s40899-024-01076-5

3. Pipil, H., Haritash, A. K., Reddy, K. R. (2022). Spatio-temporal variations of quality of rainwater and stormwater and treatment of stormwater runoff using sand–gravel filters: case study of Delhi, India. *Rendiconti Lincei. Scienze Fisiche e Naturali*, 1-8. https://doi.org/10.1007/s12210-021-01038-5

4. Pipil, H., Haritash, A. K., Reddy, K. R. (2021). Seasonal variability and kinetics of phosphate removal in a Phragmites-based engineered wetland. Rend Lincei Sci Fis Nat. 1–7. https://doi.org/10.1007/s12210-021-01017-w

Conference Papers:

1. Pipil, H., Yadav, S., Taneja, S., Chawla, H., Haritash, A. K., Reddy, K. R. (2022). Removal of Phosphate from Stormwater Runoff Using Bench Scale Constructed Wetland. In *International Conference on Environmental Geotechnology, Recycled Waste Materials and Sustainable Engineering* (pp.

443-449). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-99-4041-7_39

2. Pipil, H., Yadav, S., Taneja, S., Chawla, H., Haritash, A. K., Reddy, K. R. (2022). Water sensitive urban design (WSUD) for treatment of storm water runoff. In *Proceedings of International Conference on Innovative Technologies for Clean and Sustainable Development (ICITCSD–2021)* (pp. 49-61). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-93936-6_5

CIRCULAR VITAE

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Educational Qualifications:

Period	Board/ University/ Institute	Degree/ Certificate	Subject	Percentage %
2019-Present	Delhi Technological University	Ph. D.	Environmental Engineering	-
2015-2016	Unitec Institute, Auckland	Grad. Diploma in Construction Project Management	Construction Project Management	75
2012-2014	Delhi Technological University	M. Tech.	Environmental Engineering	81.15
2008-2012	Gautam Buddha Technical University	B. Tech.	Civil Engineering	72.84
2007-2008	C.B.S.E.	Twelfth Standard	Mathematics, Physics, Chemistry, Computer Science, English	70.20
2005-2006	C.B.S.E.	Tenth Standard	English, Hindi, Mathematics, Social Studies, Science	66.2

Publications:

SCI/ SCIE Index Publications:

1. Yadav, S., **Pipil, H.**, Haritash, A.K. Reddy, K.R. (2024). Fe(III)-modified bamboo biochar for the removal of phosphate from synthetic and field stormwater runoff. *Sustain. Water Resour. Manag.* 10, 140. https://doi.org/10.1007/s40899-024-01123-1

2. Jain, N., Yadav, S., Taneja, S., Ray, S., Haritash, A. K., **Pipil, H**. (2024). Phosphate removal from urban stormwater runoff using Canna lily and Cyperus alternifolius-based bioretention system. *Sustainable Water Resources Management*, 10(2), 1-10. https://doi.org/10.1007/s40899-024-01076-5

3. **Pipil, H.**, Yadav, S., Kumar, S., Haritash, A. K. (2024). Evaluating the photocatalytic degradation efficacy of 2, 4, 6-trichlorophenol: performance evaluation and influencing factors. *Journal of Water and Climate Change*, jwc2024483. https://doi.org/10.2166/wcc.2024.483

4. **Pipil, H.**, Yadav, S., Kumar, S., Haritash, A. K. (2024). Synergistic potency of ultrasound and solar energy towards oxidation of 2, 4-dichlorophenol: a chemometrics approach. *Environmental Science and Pollution Research*, 1-24. https://doi.org/10.1007/s11356-023-31598-y

5. Radhakrishnan, N., Taneja, S., Ambastha, S., **Pipil, H**., Haritash, A. K. (2023). Heavy metal profile, mobility, and source characterization in size-fractionated bed-sediments of River Ganga, India. *Marine Pollution Bulletin*, 188, 114650. https://doi.org/10.1016/j.marpolbul.2023.114650

6. **Pipil, H**., Haritash, A. K., Reddy, K. R. (2022). Spatio-temporal variations of quality of rainwater and stormwater and treatment of stormwater runoff using sand–gravel filters: case study of Delhi, India. *Rendiconti Lincei. Scienze Fisiche e Naturali*, 1-8. https://doi.org/10.1007/s12210-021-01038-5

7. **Pipil, H**., Yadav, S., Chawla, H., Taneja, S., Verma, M., Singla, N., Haritash, A. K. (2022). Comparison of TiO_2 catalysis and Fenton's treatment for rapid degradation of Remazol Red Dye in textile industry effluent. *Rendiconti Lincei. Scienze Fisiche e Naturali*, 33(1), 105-114. https://doi.org/10.1007/s12210-021-01040-x

8. **Pipil, H**., Haritash, A. K., Reddy, K. R. (2021). Seasonal variability and kinetics of phosphate removal in a *Phragmites*-based engineered wetland. *Rendiconti Lincei. Scienze Fisiche e Naturali*, 32(4), 729-735. https://doi.org/10.1007/s12210-021-01017-w

9. Nandakumar, S., **Pipil, H**., Ray, S., Haritash, A. K. (2019). Removal of phosphorous and nitrogen from wastewater in *Brachiaria*-based constructed wetland. *Chemosphere*, 233, 216-222. https://doi.org/10.1016/j.chemosphere.2019.05.240

Book Chapters:

1. Yadav, S., **Pipil, H.**, Kumar, S., Reddy, K.R., Haritash, A.K. (2024). Photocatalytic Degradation of 2,4,6-Trichlorophenol Using P-25 TiO2. In: Agnihotri, A.K., Reddy, K.R., Bansal, A. (eds) *Sustainable Materials. EGRWSE 2023.* Lecture Notes in Civil Engineering, vol 509. Springer, Singapore. https://doi.org/10.1007/978-981-97-3153-4_8

2. **Pipil, H**., Yadav, S., Taneja, S., Chawla, H., Haritash, A.K., Reddy, K.R. (2023). Removal of Phosphate from Stormwater Runoff Using Bench Scale Constructed Wetland. In: Yukselen-Aksoy, Y., Reddy, K.R., Agnihotri, A.K. (eds) *Sustainable Earth and Beyond. EGRWSE 2022*. Lecture Notes in Civil

Engineering, vol 370. Springer, Singapore. https://doi.org/10.1007/978-981-99-4041-7_39

3. Taneja, S., Yadav, S., **Pipil, H**., Karaca, O., Haritash, A. K. (2023). Soil–Water Interactions and Arsenic Enrichment in Groundwater. *Hydrogeochemistry of Aquatic Ecosystems*, 97-120. https://doi.org/10.1002/9781119870562.ch5

4. **Pipil, H**., Yadav, S., Taneja, S., Chawla, H., Haritash, A. K., Reddy, K. R. (2022, April). Water Sensitive Urban Design (WSUD) for Treatment of Storm Water Runoff. *In Proceedings of International Conference on Innovative Technologies for Clean and Sustainable Development (ICITCSD–2021)* (pp. 49-61). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-93936-6_5

5. Yadav, S., **Pipil, H**., Chawla, H., Taneja, S., Kumar, S., Haritash, A. K. (2022, April). Textile Industry Wastewater Treatment Using Eco-Friendly Techniques. *In Proceedings of International Conference on Innovative Technologies for Clean and Sustainable Development (ICITCSD–2021)* (pp. 63-74). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-93936-6_6

6. Taneja, S., Chawla, H., **Pipil, H**., Yadav, S., Karaca, O., Haritash, A. K. (2022, April). Sustainable treatment of metal-contaminated soil by electrokinetic remediation. *In Proceedings of International Conference on Innovative Technologies for Clean and Sustainable Development (ICITCSD–2021)* (pp. 75-84). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-93936-6_7

7. Chawla, H., Taneja, S., Yadav, S., **Pipil, H**., Singla, N., Haritash, A. K. (2022, April). Eco-Restoration of Lakes and Water Sustainability in Urban Areas. *In Proceedings of International Conference on Innovative Technologies for Clean and Sustainable Development (ICITCSD–2021)* (pp. 85-94). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-93936-6_8

Work Experience:

Period	Organization	Location	Designation	Responsibility
17th August 2016 to 11th August 2017	YJC Building Solutions Limited	Auckland, New Zealand	Junior Site Manager	Supervision of construction activities, laying of sewer and water harvesting pipes, estimation of quantities.
16th December 2014 to 12th February, 2015	Military Engineer Services (MES)	Jaipur, India	Junior Engineer	Execution of various construction activities, estimation of quantities.

Other Responsibilities:

1. Member of Monitoring/Inspection Team of Gross Polluting Industries (GPI) conducted by Central Pollution Control Board (CPCB), 2023.
2. Team member of Remediation and Drain Management of DDA Drains in Delhi, 2020.
3. Member of Monitoring/Inspection Team of Gross Polluting Industries (GPI) conducted by Central Pollution Control Board (CPCB), 2020.

Academic Achievements:

1. UGC-NET Qualified: June 2020 (Environmental Sciences)
2. UGC-NET Qualified: December 2020 (Environmental Sciences)

Strength:

- Good hands-on analytical instruments including Atomic Absorption Spectrophotometer (AAS), High Performance Liquid Chromatography (HPLC), Elemental Analyser, Proximate Analyser, UV-Vis Spectrophotometer, water quality monitoring Hand-held instruments.
- Good verbal and written communication skills.
- Hard working, sincere, leadership quality and dedicated towards my work.

Personal Information:

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