

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The presence of several contaminants in the source of drinking water in rural area of India is of major concern due to their toxicity to many life forms. Ground water is the chief source of drinking water in India and this is only 0.61 % of the total available water on the Earth. It is reported that only 4% of world's freshwater resources are available in India while India inhabitants 14% of the world population. This shows scarcity of water in India. Article 47 of Indian Constitution rests the responsibility of providing safe drinking water to the public with the State Governments. According to one estimate 64% of rural population and 91% of the urban people have access to safe drinking water . The availability of water to India is almost fixed due to limited resources. But, with growing Indian population the per capita availability of water is steadily reducing; and when this drops below 1700 m³ / person / year, India will be water stressed. Due to over exploration of ground water in rural area for drinking as well as agriculture purpose, the concentration of the different contaminants are increasing day by day. Water quality is affected by both point and non-point sources of pollution. These include sewage discharge, discharge from industries, run-off from agricultural fields and urban run-off. Water quality is also affected by floods and droughts and can also arise from lack of awareness and education among users. The need for user involvement in maintaining water quality and looking at other aspects like hygiene, environment sanitation, storage and disposal are critical elements to maintain the quality of water resources.

This report is focusing on the characterization of the village drinking water quality based on experimental results, which bring out by different sample collection from one of the village in Haryana and on site sample testing with Jal Tara water quality testing Kit. According to the results, chloride content along with few other contaminants was found in excess, which encourage us to focus on chloride only for its removal with low cost techniques.

1.2 PRESENCE OF CHLORIDE AND ITS REMOVAL

Chloride is a salt compound resulting from the combination of Chlorine gas and a metal. The common chloride salts include Sodium Chloride (NaCl), and Magnesium Chloride (MgCl₂). Industrial processes such as battery manufacturing, pulp mills, bullion

refining, electroplating, pesticide manufacturing, a large number of small scale processing units etc are the main sources of chlorides in water. In majority of these industries, the main source of chlorides in the effluent is the use of Lime Ca(OH)_2 or Sodium Hydroxide (NaOH) for the neutralization of acidic effluents. At different instances, Acids like Hydrochloric Acid (HCl), or Sodium Hydroxide (NaOH) can be a major part of the industrial processes, where they are used for the initial de-coating of Oil film on the raw material. Naturally, they contribute substantially to the chlorides in wastewater. The major impact that chlorides impart on the receiving waters is the permanent hardness. They are also known to increase the rate of sedimentation and thereby decreasing the water column depth. When such effluents are disposed on land, chlorides tend to initially percolate some distance, but over a period of time, they cause surface salt formation, thereby causing increased alkalinity of the soil & thereby resulting in loss of soil fertility. In plants, chlorides tend to accumulate in the tissues, especially the leaves. Chloride accumulation in plants is closely related to the chlorine concentration in the external solution and the genotype (Hajrasuliha, 1979). It was also noted that when sodium and chloride, supplied via landfill leachate irrigation, is accumulated in high concentrations in the tissues of many plants like Populus (Zalesny et.al. 2007) A trace of chloride in water impart salty taste.

Various functionalized bio-adsorbents have affinity towards chloride ions. Congress grass / Gajar ghas / Parthenium sps is being low cost and easily available can be used in many chemical processes aiming several scientific and technical applications because of its low weight, high surface area during the reaction process. In the present work a Congress grass / Gajar ghas / Parthenium sps activated by thermal action. Main objective of the study is to determine the chloride removal capacity of this functionalized bio adsorbent through lab-scale investigation. Studies were conducted in batch with chloride concentrations. Effects of pH, dose of adsorbent and initial chloride ion concentration on chloride removal efficiency were investigated.

The study presented in this report is an effort for the availability of good quality of drinking water in the villages of India. India is being nourished by the people of Villages, who are working day and night in the agriculture field for goods productions. Good health of people of rural India will directly influence the Food production of India in a positive way. Water born disease in rural India is very common which attract the researcher and scientists for their studies. As this was the study of only a single village in India therefore we can't predict the same results from all over India. The results of this study cannot be utilized to implement to other villages.

As per the results of the tests conducted in the village during this study, no major impurity was found except high chloride level, TDS, Hardness, Phosphorus and Nitrate. The DO was found very low in pond water whereas the same was found sufficiently fine in the well water. In this study the main focus was given to chloride concentration and its removal by batch process and continuous flow using Bio-adsorbent.

Lab-scale study was conducted in batch mode and continuous flow mode with village pond water and well water containing excess chloride. A bio-adsorbent was prepared with Parthenium plant with required activation and employed for the removal of chloride ions. Water sample of chloride mixed village water is tested with activated bio-adsorbent prepared by Parthenium plant. The affectivity of the bio adsorbent is evaluated.

1.3 OBJECTIVE OF THE STUDY

Due to Poor quality of water and presence of chemical/ bacteriological contamination, any water borne diseases are spread, which causes untold misery, and in several cases even death, thereby adversely affecting the socio-economic progress of the country. From an estimate by Water Aid, it has come out that these diseases negatively affect health and education in children, and further what is worse, 180 million man days approximately are lost in the working population to India every year.

Water-related diseases put an economic burden on both the household and the nation's economy. At household levels, the economic loss includes cost of medical treatment and wage loss during sickness. Loss of working days affects national productivity. Government spends a considerable amount undertaking water supply projects including water purification and providing safe drinking water to all in rural India in adequate quantity and within minimum distance, including piped supply to within the household. These are challenging and enormous tasks. Given the diversity of the country, solutions have to be diverse, and given the quantum of biological and chemical contamination in water in rural India, an all out effort is required by all concerned to solve this gigantic problem which will improve the overall health and thereby the productivity of the Nation. It is in this context that interventions by Central Public Sector Units and Corporate Houses under Corporate Social Responsibility become relevant.

The primary objective of the study presented here is to first determine the water quality of village Pond and adjacent well by assessing the drinking water quality parameters.

Main Objectives of the study are:

1. To study the quality of water in village Kharak kalan, District Bhiwani, Haryana for its water supply

2. To study removal of chloride by bio-adsorbents for drinking water in rural area.
3. Study in batch mode varying the following parameters.
 - a. Reaction pH.
 - b. Dose of Bio-adsorbent.
 - c. Concentration of chloride in solution.
4. Identification of appropriate adsorption isotherms and kinetic model for removal of chloride ions.
5. Comparison with continuous flow mode or column method with batch mode.

CHAPTER 2

LITERATURE REVIEW

2.1 CONTAMINATION OF DRINKING WATER

Water pollution is one of the major and most urgent problems of the modern world. Many pollutants and their breakdown products are harmful to life and property. Rural water sources have different type of pollution sources compare to urban scenario. Most of the rural area in the country is being supplied with the untreated ground as well as surface water for drinking. This water is not safe being having physical, chemical and biological contaminations. Drinking water is contaminated if it contains suspension or dissolved impurities beyond toxic limit. The toxicity limits as per Indian standards are listed in Table 2.1. Following are the major categories of contaminants found in raw water.

- **Suspension and Colloidal Particles:** Unlike dissolved inorganic impurities some pollutants are much larger in size. They appear as colloids or suspension, these are called particulate matter. If they settle in the body of water, they will cause added problems of toxicity. Suspended particles could be silt and colloidal particles might be organic or inorganic matter causing turbidity. Safe drinking water must be free from both.
- **Dissolved Inorganic Solids:** When rain water or water coming from a point source or nonpoint source percolates through soil, certain inorganic matters are most likely to dissolve. Run off from agricultural lands may have concentrations of phosphorus and nitrogen containing salts issuing from fertilizers. Also, insecticides or pesticides used in agriculture, and preservatives and insecticides used in households may find way into water. They are toxic for human-beings as well as other living organisms. Industrial release is another source of contamination. Many chemicals from industries such as toxic inorganic salts and solvents and many chemicals formed from the breakdown of sewage wastes are hazardous. Pesticides used in agriculture and preservatives and insecticides for controlling insects and weeds may also find way into water. They are toxic chemicals for all the living organisms.
- **Dissolved Organics:** Organic impurities originate from the decay of vegetable matter, agricultural farms and various industrial and domestic wastes. In addition, water-borne organics are formed from improper storage conditions and inadequate sanitation. Detergents and oils and many other chemicals, which had odor may also be present as pollutants in water.

- **Microorganisms:** Many biodegradable wastes may be good for environment, but they provide food to microorganisms like bacteria to grow. The elements P and N are present in fertilizers. They are plenty in untreated agricultural wastes. If they find entry into streams of water, they cause growth of algae and unwanted weeds. They can cause problems for safe water.
- **Storm sewage:** Storm water is the runoff from precipitation that is collected in a system of pipes or open channels. Such sewage carries organic materials, suspended and dissolved solid and other substance picked up as the water travels over the ground. Sewage discharge from domestic, municipal, food processing and other industrial concerns contains a variety of pollutants detrimental to water quality.
- **Agricultural sources:** Agricultural wastes, generally, consists of organic products. Fertilizers and other chemicals are spread over agricultural lands. These materials and crop, animal and chemical wastes enter water bodies, mainly in runoff from watershed lands and cause pollution. The inflow of manures from livestock feed lots also adds to organic pollution. Many of the pesticides, fungicides, herbicides and other industrial chemicals are highly toxic. They are carcinogenic and mutagenic.

The contamination of drinking water by pathogens causing diarrhea disease is the most Common. In many developing countries, cholera and typhoid are still known. These diseases are spread from contaminated water containing fecal matter with pathogenic organisms. Therefore the low cost water treatment is very essential to remove contaminants from drinking water. Here, the Indian standard specification are given for drinking water in table 2.1 .

Table 2.1

**INDIAN STANDARD SPECIFICATIONS FOR DRINKING WATER
IS: 10500**

S.NO.	Parameter	Requirement desirable Limit	Remarks
1.	Colour	5	May be extended up to 50 if toxic substances are suspected
2.	Turbidity	10	May be relaxed up to 25 in the absence of alternate
3.	pH	6.5 to 8.5	May be relaxed up to 9.2 in the absence
4.	Total Hardness	300	May be extended up to 600
5.	Calcium as Ca	75	May be extended up to 200
6.	Magnesium as Mg	30	May be extended up to 100
7.	Copper as Cu	0.05	May be relaxed up to 1.5
8.	Iron	0.3	May be extended up to 1
9.	Manganese	0.1	May be extended up to 0.5
10.	Chlorides	250	May be extended up to 1000
11.	Sulphates	150	May be extended up to 400
12.	Nitrates	45	No relaxation
13.	Fluoride	0.6 to 1.2	If the limit is below 0.6 water should be rejected, Max. Limit is extended to 1.5
14.	Phenols	0.001	May be relaxed up to 0.002
15.	Mercury	0.001	No relaxation
16.	Cadmium	0.01	No relaxation
17.	Selenium	0.01	No relaxation
18.	Arsenic	0.05	No relaxation
19.	Cyanide	0.05	No relaxation
20.	Lead	0.1	No relaxation
21.	Zinc	5.0	May be extended up to 10.0
22.	Anionic detergents (MBAS)	0.2	May be relaxed up to 1
23.	Chromium as Cr ⁺⁶	0.05	No relaxation
24.	Poly nuclear aromatic Hydrocarbons	--	--
25.	Mineral Oil	0.01	May be relaxed up to 0.03
26.	Residual free Chlorine	0.2	Applicable only when water is chlorinated
27.	Pesticides	Absent	--
28.	Radio active	--	--

**DRINKING WATER SPECIFICATION: IS: 10500, 1992
(Reaffirmed 1993)**

TOLERANCE LIMITS

S.No	Parameter	IS: 10500 Requirement (Desirable limit)	Undesirable effect outside the desirable limit	IS: 10500 Permissible limit in the absence of alternate source
Essential Characteristics				
1.	pH	6.5 – 8.5	Beyond this range the water will effect the mucous membrane and / or water supply system	No relaxation
2.	Colour (Hazen Units), Maximum	5	Above 5, consumer acceptance decreases	25
3.	Odour	Unobjectionable	--	--
4.	Taste	Agreeable	--	--
5.	Turbidity, NTU, Max	5	Above 5, consumer acceptance decreases	10
Following Results are expressed in mg/l :				
6.	Total hardness as CaCO ₃ , Max	300	Encrustation in water supply structure and adverse effects on domestic use	600
7.	Iron as Fe, Max	0.30	Beyond this limit taste/appearance are affected, has adverse effect on domestic uses and water supply structures, and promotes iron bacteria.	1.0
8.	Chlorides as Cl, Max	250	Beyond this limit tast, corrosion and palatability are effected	1000
9.	Residual, Free Chlorine, Min	0.20	--	--
Desirable Characteristics				
10.	Dissolved solids, Max	500	Beyond this palatability decreases and may cause gastro intentional irritation	2000
11.	Calcium as Ca, Max	75	Encrustation in water supply structure and adverse effects on domestic use	200

12.	Magnesium as Mg, Max	30	--	100
13.	Copper as Cu, Max	0.05	Astringent taste, discoloration and corrosion of pipes, fitting and utensils will be caused beyond this	1.5
14.	Manganese as Mn, Max	0.1	Beyond this limit taste/appearance are affected, has adverse effect on domestic uses and water supply structures	0.3
15.	Sulphate as SO ₄ Max	200	Beyond this causes gastro intentional irritation when magnesium or sodium are present	400
16.	Nitrates as NO ₃	45	Beyond this methanemoglobinemia takes place	100
17.	Fluoride, Max	1.0	Fluoride may be kept as low as possible. High fluoride may cause fluorosis	1.5
18.	Phenolic compounds as C ₆ H ₅ OH, Max	0.001	Beyond this, it may cause objectionable taste and odour	0.002
19.	Mercury as Hg, Max	0.001	Beyond this, the water becomes toxic	No relaxation
20.	Cadmium as Cd, Max	0.01	Beyond this, the water becomes toxic	No relaxation
21.	Selenium as Se, Max	0.01	Beyond this, the water becomes toxic	No relaxation
22.	Arsenic as As, Max	0.05	Beyond this, the water becomes toxic	No relaxation
23.	Cyanide as CN, Max	0.05	Beyond this, the water becomes toxic	No relaxation
24.	Lead as Pb, Max	0.05	Beyond this, the water becomes toxic	No relaxation
25.	Zinc as Zn, Max	5	Beyond this limit it can cause astringent taste and an opalescence in water	15
26.	Anionic detergents as MBAS, Max	0.2	Beyond this limit it can cause a light froth in water	1.0
27.	Chromium as Cr ⁶⁺ , Max	0.05	May be carcinogenic above this limit	No relaxation
28.	Ploynuclear aromatic hydrocarbons as PAH, Max	--	May be carcinogenic	--

29.	Mineral Oil, Max	0.01	Beyond this limit undesirable taste and odour after chlorination take place	0.03
30.	Pesticides, Max	Absent	Toxic	0.001
31.	Radioactive materials	--	--	0.1
	a) α emitters Bq/l, Max	--	--	1
	b) β emitters Pci/l, Max			
32.	Alkalinity, Max	200	Beyond this limit taste becomes unpleasant	600
33.	Aluminum as Al, Max	0.03	Cumulative effect is reported to cause dementia	0.2
34.	Boron, Max	1	--	5

2.2 INTRODUCTION OF CHLORIDE

Chloride is a salt compound resulting from the combination of Chlorine gas and a metal. The common chloride salts include Sodium Chloride (NaCl), and Magnesium Chloride (MgCl₂). Industrial processes such as battery manufacturing, pulp mills, bullion refining, electroplating, pesticide manufacturing, a large number of small scale processing units etc are the main sources of chlorides in water. In majority of these industries, the main source of chlorides in the effluent is the use of Lime (Ca (OH) ₂) or Sodium Hydroxide (NaOH) for the neutralization of acidic effluents. At different instances, Acids like Hydrochloric Acid (HCl), or Sodium Hydroxide (NaOH) can be a major part of the industrial processes, where they are used for the initial de-coating of Oil film on the raw material. Naturally, they contribute substantially to the chlorides in wastewater. The major impact that chlorides impart on the receiving waters is the permanent hardness. They are also known to increase the rate of sedimentation and thereby decreasing the water column depth. When such effluents are disposed on land, chlorides tend to initially percolate some distance, but over a period of time, they cause surface salt formation, thereby causing increased alkalinity of the soil, thereby resulting in loss of soil.

2.2.1 CHEMICAL IDENTIFICATION:-

The chloride ion is the anion (negatively charged ion) Cl⁻. It is formed when the element chlorine (a halogen) gains an electron or when a compound such as hydrogen

chloride is dissolved in water or other polar solvents. Chlorides salts such as sodium chloride are often very soluble in water. It is an essential electrolyte located in all body fluids responsible for maintaining acid/base balance, transmitting nerve impulses and regulating fluid in and out of cells. The word chloride can also form part of the name of chemical compounds in which one or more chlorine atoms are covalently bonded. For example, methyl chloride, more commonly called chloromethane, (CH₃Cl) is an organic compound with a covalent C-Cl bond. It is not a source of chloride ion.

2.2.2 ELECTRONIC PROPERTIES:-

Chloride is much larger than a chlorine atom, 167 and 99 pm, respectively. The ion is colorless and diamagnetic. In aqueous solution, it is highly solvated, being bound by the protic end of the water molecules.

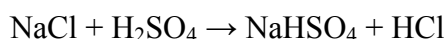
2.2.3 OCCURRENCE IN NATURE:-

Sea water contains a 1.94% chloride. Some chloride-containing minerals include the chlorides of sodium (halite or NaCl), potassium (sylvite or KCl), and magnesium (bischofite), hydrated MgCl₂. Called serum chloride, the concentration of chloride in the blood is regulated by the kidneys. A chloride ion is a structural component of some proteins, e.g., it is present in the amylase enzyme.

2.2.4 REACTIONS OF CHLORIDE:-

Chloride can be oxidized but not reduced. The first oxidation, as employed in the chlor-alkali process, is conversion to chlorine gas. Chlorine can be further oxidized to other oxides and oxyanions including hypochlorite (ClO⁻, the active ingredient in chlorine bleach), chlorine dioxide (ClO₂), chlorate (ClO₃⁻), and perchlorate (ClO₄⁻).

In terms of its acid-base properties, chloride is a very weak base as indicated by the negative value of the pK_a of hydrochloric acid. Chloride can be protonated by strong acids, such as sulfuric acid:



Ionic chloride salts reaction with other salts to exchange anions. The presence of chloride is often detected by its formation of an insoluble silver chloride upon treatment with silver ion:

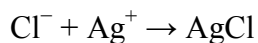


Fig 2.1



2.2.5 EXAMPLES OF CHLORIDES COMBINATIONS:-

An example is table salt, which is sodium chloride with the chemical formula NaCl . In water, it dissociates into Na^+ and Cl^- ions. Salts such as calcium chloride, magnesium chloride, potassium chloride have varied uses ranging from medical treatments to cement formation. Another example is calcium chloride with the chemical formula CaCl_2 . Calcium chloride is a salt that is marketed in pellet form for removing dampness from rooms. Calcium chloride is also used for maintaining unpaved roads and for fortifying road bases for new construction. In addition, Calcium chloride is widely used as a De-icer since it is effective in lowering the melting point when applied to ice. Examples of covalently bonded chlorides are phosphorus trichloride, phosphorus pentachloride, and thionyl chloride, all three of which reactive chlorinating reagents that have been used in a laboratory.

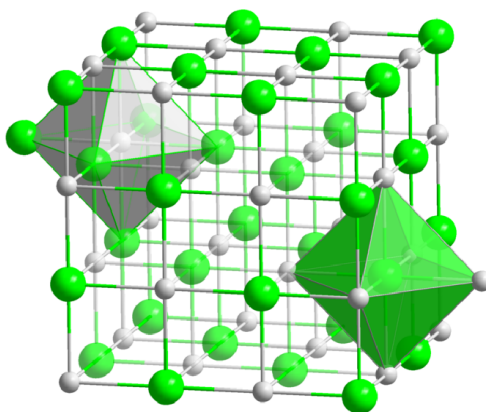







Fig 2.2

Chlorine can assume oxidation states of -1 , $+1$, $+3$, $+5$, or $+7$. Several neutral chlorine oxides are also known.

Table 2.2

Chlorine oxidation state	-1	$+1$	$+3$	$+5$	$+7$
Name	chloride	hypochlorite	chlorite	chlorate	perchlorate
Formula	Cl^-	ClO^-	ClO_2^-	ClO_3^-	ClO_4^-
Structure					

2.3 SOURCE

Almost all natural waters contain chloride and sulfate ions. Their concentrations vary considerably according to the mineral content of the earth in any given area. In small amounts they are not significant. In large concentrations they present problems. Usually chloride concentrations are low. Sulfates can be more troublesome because they generally occur in greater concentrations. Low to moderate concentrations of both chloride and sulfate ions add palatability to water. In fact, they are desirable for this reason. Excessive concentrations of either, of course, can make water unpleasant to drink. Chloride is commonly found in streams and wastewater. Chloride may get into surface water from several sources including:

Chlorides added into surface water of this village from several sources including:

- 1) rocks containing chlorides;
- 2) Agricultural runoff;
- 3) Wastewater from small scale industries; and
- 4) Effluent wastewater from wastewater treatment plants.
- 5) Produced water from gas and oil wells

2.4 EFFECTS OF CHLORIDES

Chloride in concentration above 600mg/l tends to give water a salty taste. The concentration of chloride content above 200mg/l is considered objectionable. Presence of high quantity of chloride content in water resources indicates pollution due to human and industrial wastes and also from the earthen rocks in the subsurface. High chloride concentrations in freshwater can harm aquatic organisms by interfering with osmo-regulation, the biological process by which they maintain the proper concentration of salt and other solutes in their bodily fluids. Difficulty with osmo-regulation can hinder survival, growth, and reproduction. Chlorides are not usually harmful to people; however, the sodium part of table salt has been linked to heart and kidney disease. Sodium chloride may impart a salty taste at 250 mg/L; however, calcium or magnesium chlorides are not usually detected by taste until levels of 600 mg/L are reached. Chlorides can corrode metals and affect the taste of food products. Therefore, water that is used in industry or processed for any use has a recommended maximum chloride level. Chlorides can contaminate fresh water streams and lakes. Fish and aquatic communities cannot survive in high levels of chlorides.

2.4.1 EFFECTS ON HUMAN BODY

A normal adult human body contains approximately 81.7 g chloride. On the basis of a total obligatory loss of chloride of approximately 530 mg/day, a dietary intake for adults of 9 mg of chloride per kg of body weight has been recommended (equivalent to slightly more than 1 g of table salt per person per day). For children up to 18 years of age, a daily dietary intake of 45 mg of chloride should be sufficient. A dose of 1 g of sodium chloride per kg of body weight was reported to have been lethal in a 9-week-old child.

Chloride toxicity has not been observed in humans except in the special case of impaired Sodium chloride metabolism, e.g. in congestive heart failure. Healthy individuals can tolerate the intake of large quantities of chloride provided that there is a associated intake of fresh water. Little is known about the effect of prolonged intake of large amounts of chloride in the diet. As in experimental animals, hypertension associated with sodium chloride intake appears to be related to the sodium rather than the chloride ion.

2.5 SCOPE OF THE PRESENT STUDY

The main objective of this study is to understand the availability of possible pollutants in the drinking water in Indian Villages & provide a low cost treatment method of drinking water in the Indian Villages by characterizing their need of specific removal. Different places

in the country have different type of impurity in their drinking water. A onsite check for different types of drinking parameters has been done in a Village Kharak Kalan, district Bhiwani, Haryana by taking sufficient samples from Pond Water as well as well water. The test results shows excess of chloride content and hardness in water. Other parameters found within the safe range as per BIS. Therefore, we will only deal the chloride removal.

Considering the merits and limitations of various techniques reported in literatures for the removal of chloride, adsorption is considered to be one of the effective methods. With proper control of the process, it is possible to meet the discharge limits and no harmful by products are generated like ion exchange and reverse osmosis. If low cost Bio adsorbents are available and regeneration of adsorbent is possible, adsorption technique becomes economical. Literature review highlighted the effectiveness of various Bio adsorbents for removals of chloride, Fluoride from wastewater. Easy and cheap availability made this an attractive option in industrial wastewater treatment Work.

CHAPTER 3

SOURCES OF WATER FOR WATERSUPPLY IN RURAL AREA

Water in rural area is being derives from different sources such as from surface water, spring, ground water or even rainwater catchments, local, or is developed from different methods, such as gravity schemes, wells, boreholes, the decentralized systems are usually the most cost-effective approach. In fact, the majority of people in the developing world gain access to groundwater either by means of a bucket and rope or by using a hand pump.

3.1 RAW WATER SOURCE

The various sources of water can be classified into two categories:

1. Surface sources, such as
 - a. Ponds and lakes;
 - b. Streams and rivers;
 - c. Storage reservoirs; and
 - d. Oceans, generally not used for water supplies, at present.
2. Sub-surface sources or underground sources, such as
 - a. Springs;
 - b. Infiltration wells ; and
 - c. Wells and Tube-wells.

Here the study is based on the Pond water and Well water only

3.2 WATER QUALITY

The raw or treated water is analyzed by testing their physical, chemical and bacteriological characteristics:

Physical Characteristics: Turbidity, Color, Taste, Odour & Temperature

Chemical Characteristics: pH, Acidity, Alkalinity, Hardness, Chlorides, Sulphates ,Iron Solids Nitrates

Bacteriological Characteristics: Bacterial examination of water is very important, since it indicates the degree of pollution. Water polluted by sewage contains one or more species of disease producing pathogenic bacteria. Pathogenic organisms cause water borne diseases, and

many non pathogenic bacteria such as *E.Coli*, a member of coliform group, also live in the intestinal tract of human beings. *Coliform* itself is not a harmful group but it has more resistance to adverse condition than any other group. So, if it is ensured to minimize the number of coliforms, the harmful species will be very less. So, coliform group serves as indicator of contamination of water with sewage and presence of pathogens. The methods to estimate the bacterial quality of water are:

- ❖ Standard Plate Count Test
- ❖ Most Probable Number
- ❖ Membrane Filter Technique

3.3 LAKES AND POND:-

Lakes and ponds are inland bodies of standing or slowly moving water. Although lakes and ponds cover only 2 percent of the world's land surface, they contain most of the world's fresh water. Individual lakes and ponds range in area from a few square meters to thousands of square kilometers. In general, ponds are smaller than lakes, though regional idiosyncrasies of naming abound—Henry David Thoreau's famous Walden Pond in Massachusetts has a surface area of 64 acres. Lakes and ponds are an important source of fresh water for human consumption and are inhabited by a diverse suite of organisms.

3.3.1:- FORMATION

Lakes and ponds are formed through a variety of events, including glacial, tectonic, and volcanic activity. Most lakes and ponds form as a result of glacial processes. As a glacier retreats, it may leave behind an uneven surface containing hollows that fill with water. Glacial activity at the end of the Pleistocene epoch (ten thousand to twenty thousand years ago) resulted in the formation of most of the lakes and ponds in the Northern Hemisphere, including the Great Lakes of North America. Some of the oldest lakes and ponds (more than three hundred thousand years old) were formed by tectonic activity related to movement of Earth's crust. For example, Lake Baikal in Siberia formed from the movement of **tectonic plates** and is the largest freshwater lake by volume in the world. Volcanic activity can also lead to lake and pond formation. For example, the collapse of a volcanic cone of Mount Mazama in Oregon led to the formation of Crater Lake, the seventh deepest lake in the world.

3.3.2 PHYSICAL AND CHEMICAL FEATURES:-

Light and temperature are two key physical features of lakes and ponds. Light from the sun is absorbed, scattered, and reflected as it passes through Earth's atmosphere, the water's surface, and the water. The quantity and quality of light reaching the surface of a lake or pond depends on a variety of factors, including time of day, season, latitude, and weather. The quality and quantity of light passing through lake or pond water is affected by properties of the water, including the amount of particulates (such as algae) and the concentration of dissolved compounds. (For example, dissolved **organic** carbon controls how far ultraviolet wavelengths of light penetrate into the water.)

Light and wind combine to affect water temperature in lakes and ponds. Most lakes undergo a process called thermal stratification, which creates three distinct zones of water temperature. In summer, the water in the shallowest layer (called the epilimnion) is warm, whereas the water in the deepest layer (called the hypolimnion) is cold. The middle layer, the metalimnion, is a region of rapid temperature change. In winter, the pattern of thermal stratification is reversed such that the epilimnion is colder than the hypolimnion. In many lakes, thermal stratification breaks down each fall and spring when rapidly changing air temperatures and wind cause mixing. However, not all lakes follow this general pattern. Some lakes mix only once a year and others mix continuously. The chemistry of lakes and ponds is controlled by a combination of physical, geological, and biological processes. The key chemical characteristics of lakes and ponds are dissolved oxygen concentration, nutrient concentration, and pH. In lakes and ponds, sources of oxygen include diffusion at the water surface, mixing of oxygen-rich surface waters to deeper depths, and photosynthesis. Oxygen is lost from lakes and ponds during respiration by living organisms and because of chemical processes that bind oxygen. The two most important nutrients in lakes and ponds are nitrogen and phosphorus. The abundance of algae in most lakes and ponds is limited by phosphorus availability, whereas nitrogen and iron are the limiting nutrients in the ocean. The acidity of water, measured as pH, reflects the concentration of hydrogen ions. The pH value of most lakes and ponds falls between 4 and 9 (the pH value of distilled water is 7). Some aquatic organisms are adversely affected by low pH conditions caused by volcanic action, acid-releasing vegetation surrounding bog lakes, and acid rain.

3.3.3 HABITATS AND DIVERSITY

Lakes and ponds are characterized by three main habitats: the pelagic zone, the littoral zone, and the benthic zone. The pelagic zone is the open water area of lakes and ponds. In large lakes, the pelagic zone makes up most of the lake's volume. The littoral zone is the inshore area where light penetrates to the bottom. This zone often contains large, rooted plants called macrophytes. The areas of the lake or pond bottom that are not part of the littoral zone are referred to as the benthic zone. This zone contains fine sediment that is free of plant life because light levels are too low to support plant growth.

Lakes and ponds typically contain a diversity of organisms that perform different ecological functions. Many of the organisms in lakes and ponds are quite small and can only be seen with a microscope. Plankton is microscopic aquatic organisms, including bacteria, algae, and zooplankton, that have little or no means of locomotion. In addition, there are many larger vertebrate animals that inhabit lakes and ponds, including fish and amphibians. Other organisms that use lakes and ponds for some activities include birds such as ducks, mammals such as beavers, and reptiles such as snakes.

Larger lakes can support as many as four or five different trophic levels, or groups of organisms that get energy in the same way. For instance, the major trophic levels in the pelagic zone, or open water areas, are phytoplankton, zooplankton, planktivorous (plankton-eating) fish, and piscivorous (fish-eating) fish. Microbes such as bacteria and protists are also important in lakes and ponds due to their role in decomposition and nutrient recycling. The food web in the pelagic zone is connected to the inshore food web because many mobile organisms from the pelagic zone (especially fish) use the inshore areas for shelter and food.

3.4 WELL & TUBE WELL WATER:-

Ground water occurs almost everywhere beneath the land surface. The widespread occurrence of potable ground water is the reason that it is used as a source of water supply by about one-half the population of the India, including almost all of the population that is served by domestic water-supply systems.

Natural sources of freshwater that become ground water are (1) aerial recharge from precipitation that percolates through the unsaturated zone to the water table (Figure 3.1) and (2) losses of water from streams and other bodies of surface water such as lakes and wetlands. Aerial recharge ranges from a tiny fraction to about one-half of average annual

precipitation. Because areal recharge occurs over broad areas, even small average rates of recharge (for example, a few inches per year) represent significant volumes of inflow to ground water. Streams and other surface-water bodies may either gain water from ground water or lose (recharge) water to ground water. Streams commonly are a significant source of recharge to ground water downstream from mountain fronts and steep hill slopes in arid and semiarid areas and in karst terrains (areas underlain by limestone and other soluble rocks). (source is http://pubs.usgs.gov/circ/circ1186/html/gen_facts.html)

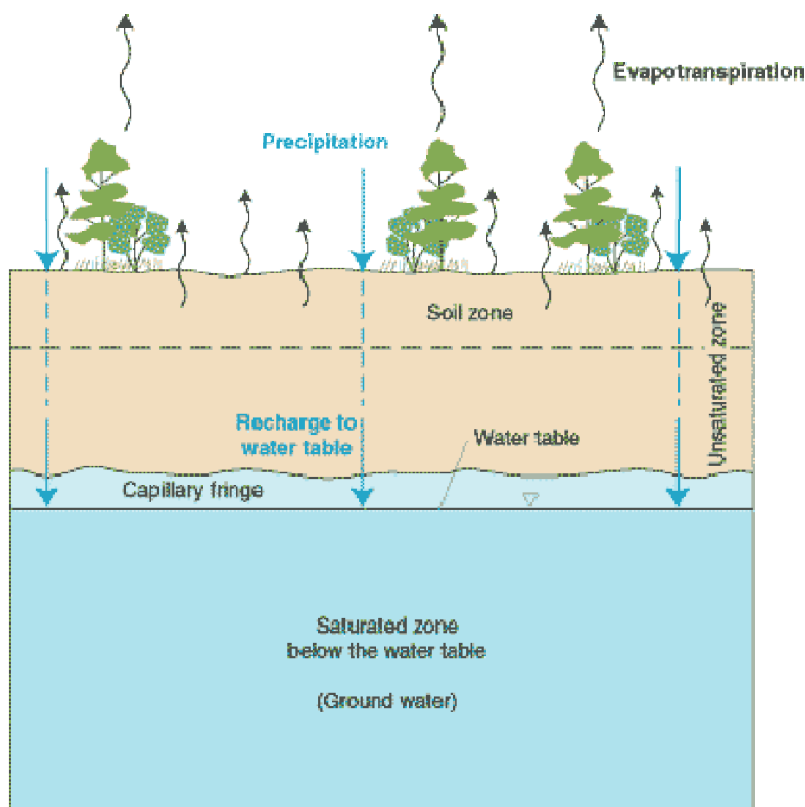


Fig 3.1

3.4.1 GERMS IN WELL WATERS:-

As water moves down through layers of soil, disease-causing germs such as bacteria and viruses are filtered out. For this reason, groundwater often produces drinking water that does not need to have chlorine added to kill germs.

Wells close to streams or lakes, however, might not produce germ-free water. These wells are said to be under the direct influence of surface water. Water from these wells might not pass through very much soil as it moves from surface water to the well. Without soil filtration, germs from the surface water might be present in the well water.

Additionally, some wells are not constructed properly and allow germs to enter groundwater from the well itself. This is not a natural characteristic of groundwater and is discussed in more detail in the wells section under protecting groundwater.

3.4.2 MINERALS:-

Common Minerals in Groundwater: Iron. Water turns orange, stains laundry and bathroom fixtures, may make the water taste like metal Calcium & Magnesium. Cause "hard water" and leave chalky white deposits.

While iron, calcium, and magnesium are common, minerals contained in groundwater vary greatly. These minerals are dissolved from the rocks of the aquifer. Generally, the longer water has been underground, the more natural minerals it contains. You can predict the type of rocks the groundwater flowed through during its time underground by the minerals in the water. A small amount of minerals in water gives it a pleasant taste In excess, natural minerals can be a nuisance, but most are not a health concern one exception is arsenic.

In a few parts, arsenic has been found in the groundwater above safe levels for drinking water. While arsenic can be a contaminant from human activity, the arsenic appears to be naturally dissolved from rocks in the aquifers.

3.4.3 TYPES OF WELL

★ **Dug wells:** - Until recent centuries, all artificial wells were pump less hand-dug wells of varying degrees of formality, and they remain a very important source of potable water in some rural developing areas where they are routinely dug and used today. Hand-dug wells are excavations with diameters large enough to accommodate one or more people with shovels digging down to below the water table. They can be lined with laid stones or brick; extending this lining upwards above the ground surface to form a wall around the well serves to reduce both contamination and injuries by falling into the well. A more modern method called caissoning uses reinforced concrete or plain concrete pre-cast well rings that are lowered into the hole. A well-digging team digs under a cutting ring and the well column slowly sinks into the aquifer, whilst protecting the team from collapse of the well bore. Hand dug wells provide a cheap and low-tech solution to accessing groundwater in rural locations in developing countries, and may be built with a high degree of community participation, or by local entrepreneurs who specialize in hand-dug wells. They have been successfully excavated to 60 meters (200 ft). Hand dug wells are inexpensive and low tech (compared to drilling) as they use mostly hand labour for construction. They have low operational and maintenance costs, in part because water can

be extracted by hand bailing, without a pump. The water is often coming from an aquifer or groundwater, and can be easily deepened, which may be necessary if the ground water level drops, by telescoping the lining further down into the aquifer. The yield of existing hand dug wells may be improved by deepening or introducing vertical tunnels or perforated pipes.

Drawbacks to hand-dug wells are numerous. It can be impractical to hand dig wells in areas where hard rock is present, and they can be time-consuming to dig and line even in favorable areas. Because they exploit shallow aquifers, the well may be susceptible to yield fluctuations and possible contamination from surface water, including sewage. Hand dug well construction generally requires the use of a well trained construction team, and the capital investment for equipment such as concrete ring moulds, heavy lifting equipment, well shaft formwork, motorized de-watering pumps, and fuel can be large for people in developing countries. Construction of hand dug wells can be dangerous due to collapse of the well bore, falling objects and asphyxiation, including from dewatering pump exhaust fumes.

★ **Driven wells:** - Driven wells may be very simply created in unconsolidated material with a *well hole structure*, which consists of a hardened drive point and a screen (perforated pipe). The point is simply hammered into the ground, usually with a tripod and *driver*, with pipe sections added as needed. A driver is a weighted pipe that slides over the pipe being driven and is repeatedly dropped on it. When groundwater is encountered, the well is washed of sediment and a pump installed

★ **Drilled wells:** - Drilled wells are typically created using either top-head rotary style, table rotary, or cable tool drilling machines, all of which use drilling stems that are turned to create a cutting action in the formation, hence the term *drilling*. Drilled wells can be excavated by simple hand drilling methods (auguring, sledging, jetting, driving, hand percussion) or machine drilling (rotary, percussion, down the hole hammer). Deep rock rotary drilling method is most common. Rotary can be used in 90% for formation types.

Drilled wells can get water from a much deeper level than dug wells can—often up to several hundred meters.

Drilled wells with electric pumps are used throughout the world, typically in rural or sparsely populated areas, though many urban areas are supplied partly by municipal wells. Most shallow well drilling machines are mounted on large trucks, trailers, or tracked vehicle carriages. Water wells typically range from 3 to 18 meters (9.8–59.1 ft) deep, but in some areas can go deeper than 900 meters (3,000 ft)

3.5 HARYANA AT A GLANCE

STATE PROFILE	LONGITUDE 74°27'00" TO 77°35'00" E
LOCATION	LATITUDE 27°39'00" TO 30°55'00" N
AREA	44,212 SQ. KM.
POPULATION	21,082,989 APPROX.
PHYSIOGRAPHY	(I) HILLY AREA - 682 SQ. KM. (II) ALLUVIAL AREA – 43,530 SQ. KM.
AVERAGE ANNUAL RAINFALL	573MM (RANGE FROM 325 MM IN THE SOUTH-WEST TO 988 MM IN THE NORTH-EAST)

★ GEOLOGY

Quaternary	Recent	Newer Alluvium	Aeolian deposits : windblown fine sand and silt, sand dunes, fluvial deposits, unconsolidated sand, silt, clay, kankars etc.
	Pleistocene	Older Alluvium	Fluvial deposits: Unconsolidated gravel, sands, silts, clays and kankar.
Tertiary	Middle Miocene to lower Pleistocene	Siwalik system	Sandstone, boulders, conglomerate, siltstone, claystone, clays and sand
	Oligocene	Kasauli beds	Sandstone, claystone, siltstone and purple shales
	Eocene	Subathu beds	Limestone, shales (Gypseous)
Pre-Cambrian	Delhi & Aravali systems		Phyllites, mica schist, quartzite.

**WATER AVAILABILITY FROM RAINFALL, HARYANA
(ON THE BASIS OF NORMAL RAINFALL)**

SL NO	DISTRICT	RAINFALL (mm)	AREA (SQ.KM)	TOTAL PRECIPITATION (BCM)
1	Ambala	1078	1574	1.697
2	Bhiwani	422	4778	2.016
3	Faridabad	603	2151	1.297
4	Fatehabad	344	2520	0.867
5	Gurgaon	626	2766	1.732
6	Hissar	416	3983	1.657
7	Jhajjar	431	1834	0.790
8	Jind	516	2702	1.394
9	Kaithal	481	2317	1.114
10	Karnal	724	2538	1.838
11	Kurukshetra	702	1530	1.074
12	Mohindergarh	499	1859	0.928
13	Panchkula	1029	898	0.924
14	Panipat	621	1268	0.787
15	Rewari	511	1582	0.808
16	Rohtak	594	1745	1.037
17	Sirsa	319	4277	1.364
18	Sonepat	624	2122	1.324
19	Yamunanagar	1108	1768	1.959
	TOTAL		44212	24.608

★ **SOIL**

1. Loamy Sand
2. Sandy Loam
3. Sandy Soils
4. Loamy Soils

★ **LAND USE (SQ. KM)**

1. Forest area	1,690
2. Land not available for cultivation	4,170
3. Other uncultivable land excluding Fallow land	480
4. Fallow land	1,690
5. Net area sown	35,750
6. Cultivable area	37,920
7. Area sown more than once	23,440

8. Total cropped area 59,190

★ GROUND WATER BALANCE

TOTAL REPLENISHABLE GROUND WATER RESOURCE (M.HAM/YR)	1.457111	
PROVISION FOR DOMESTIC , INDUSTRIAL AND OTHER USES (M.HAM./YR)	0.218567	
AVAILABLE GROUND WATER RESOURCES FOR IRRIGATION (M.HAM./YR)	1.238544	
UTILIZABLE GROUND WATER RESOURCES FOR IRRIGATION (M.HAM./YR)	1.11469	
GROSS DRAFT (M.HAM./YR) AS ON 31.3.02- PRORATA BASIS	1.17496	
NET DRAFT (M.HAM./YR) AS ON 31.3.02	0.822472	
BALANCE GROUND WATER RESOURCE FOR FUTURE USE (M.HAM./YR)	0.416072	
	PRESENT	66.40637
	AFTER 5 YEARS	71.89162

★ RIVER BASINS

S. No.	Basin	Sub Basins	Area (Sq. Km.)
1.	Ganga	Yamuna	11,271
2.	Ganga	Internal	18,262
3.	Indus	Ghaggar	14,679

★ CROPPING PATTERN

Sr.No.	Crops	Area (Sq. Km.)	Production (Thousand tones)
1	Food grains	40,790	9.559
2	Oil seeds	4,885	638
3	Cotton lint	4,906	1,155*
4	Sugarcane	1,478	780
5	Potatoes	105	165
6	Tobacco	**	0.1

* In thousand bales of 170 kg. each.

Less than 0.5 Sq. Km.

**

★ IN-STORAGE GROUND WATER RESOURCES (First Approx.)

a) Unconsolidated/semi-consolidated sediments (Up to 450 m)		
(i) Fresh	:	420.44 BCM
(ii) Brackish/Saline	:	36.57 BCM
b) Hard Rock (Up to 100 m)		
(i) Fresh	:	0.28 BCM
(ii) Brackish/Saline	:	0.76 BCM

★ GROUND WATER EXPLORATION

No. of Exploratory Wells Drilled	341
Observation Wells	233
Piezometers	141
Slim Holes	21

★ NO. OF HYDROGRAPH NET WORK STATIONS

a) Dug wells	308
b) Piezometers	206
c) Total	514

3.6 About Bhiwani District

Bhiwani District lies in South-Western part of Haryana state covering an area of 5140 sq.Km. There is no perennial river passing through the district. Physiographical the district consists of flat and level plain interrupted from place to place by cluster s of sand dunes, isolated hillocks and rocky ridges. A few isolated rocky ridges elevated sharply from the plain occur in the south central portion or the district. Dohan River is the only ephemeral al stream in the area and flows in direct response to precipitation. Bhiwani district ranks 3rd in Haryana with a population of 14,25,022. The density of population is 298 per Sq.Km. The literacy rate in the district is around 73%. About 67% of the population lives in Rural area and the remaining 33% of the population lives in Ur ban area. Out of 444 villages 437 are inhabited and 7 are less inhabited.

The climate of Bhiwani district can be classified as tropical steppe, semi-arid and hot which is mainly dry with very hot summer and cold winter except during monsoon season when moist air of oceanic origin penetrate into the district. There are four seasons in a year. The hot weather season starts from mid March to last week of the June followed by the south- west monsoon which lasts up to September. The transition period from

September to October forms the post-monsoon season. The winter season starts late in November and remains up to first week of March. The normal annual rainfall of the district is 420 mm which is unevenly distributed over the area. The south west monsoon, sets in from last week of June and withdraws in end of September, contributed about 85% of annual rainfall. July and August are the wettest months. Rest 15% rainfall is received during non-monsoon period in the wake of western disturbances and thunder storms. Generally rainfall in the district increases from southwest to northeast.

Normal Annual Rainfall	: 420 mm
Normal monsoon Rainfall	: 355 mm
Temperature	
Mean Maximum	: 41°C (May & June)
Normal Raindays	: 22

3.7 About Village Kharak Kalan

Kharak Kalan is a Village in Bhiwani Tehsil in Bhiwani District of Haryana State, India. It belongs to Hisar Division. It is located 19 KM towards East from District head quarters Bhiwani. 18 KM from Bhiwani. 255 KM from State capital Chandigarh. Kharak Kalan Pin code is 127114 and postal head office is Kharak Kalan. Malkosh (3 KM), Nimri (3 KM), Rankoli (5 KM), Bamla-1 (6 KM), Baund Kalan (6 KM) are the nearby Villages to Kharak Kalan. Kharak Kalan is surrounded by Bhiwani Tehsil towards west, Maham Tehsil towards North, Dadri-I Tehsil towards South, Dadri-II Tehsil towards South. Bhiwani, Charkhi Dadri, Rohtak, Jhajjar are the nearby Cities to Kharak Kalan.

Kharak Kalan is situated at 221.35 meters above from the mean sea level. Type of soil in this region is sandy and loamy. The climate in this region is hot and cold. Hot months of this region are May and June; these are the warmest months of this village. Hot air (known as loo) blows in the summer. Rainy months are July, August and September. Usually 443 mm. rainfall is measured in this region annually. This rainfall is very less as compare to the water requirement of this village for drinking as well as agriculture.

CHAPTER 4

REMOVAL TECHNIQUE OF CHLORIDE

4.1 NORCURE CONCRETE CHLORIDE REMOVAL SYSTEM:

Norcure technology is one of the most important techniques which were taken up in order to address the problem of corrosion of the concrete due to the entry of chlorides. The Norcure process is an electrochemical method of removing chloride ions and drawing them out of the concrete. Using this method, concrete could be rejuvenated without the inconvenience and disruption of conventional demolition and repair, resulting in significant savings. The corrosive nature of sodium chloride (salt) is well known. It can bring about rust on automobiles, and wreak havoc on concrete, where corrosive concentrations of chlorides are often found. The chloride ions percolate deep into the concrete structures due to the porous nature of concrete, eventually reaching the reinforced steel or rebar. Furthermore, after this, it begins to corrode the structure, and structures such as parking lots, highways and bridges become vulnerable due to its damaging effects. Once chlorides attack a structure, they quickly eat away at the reinforcing steel, causing cracks to appear. If left untreated, these chloride ions can cause concrete spalls, expose steel reinforcement bars and eventually reduce the structural integrity of the structure to dangerous levels.

4.2 CHLORIDE REMOVAL USING ION- EXCHANGE METHOD:

Ion exchange works on the basic principle of charge based transport of ions. In a lab scale study on pulp and paper mill, several resins were tested for chloride removal. The resins were either free base forms or hydroxide base forms. The study concluded that two hydroxide ion based resins named IRN78 and 4400OH achieved approximately 50% and 70% chloride removal at a dose of 10 g / L and were the potential resins that may be used in the reduction in chlorides in Pulp and paper mill effluent.

4.3 ULTRA- HIGH LIME WITH ALUMINUM (UHLA) PROCESS:

Lime softening serves as the favorite alternative for removing scale forming materials. However, the process does not remove silica, chloride or sulfates. A process named Ultra High Lime Softening was therefore devised, which successfully removed silica, but not sulfur and chlorides. Advanced methods are available for the removal of chlorides and sulfates, viz. Reverse osmosis, electro dialysis but lime softening is the cheapest alternative

available for recycled cooling water. Also, the process like reverse osmosis is not only expensive, but also difficult to maintain. Occurrence of problems like membrane fouling may require frequent cleaning and production of brine in the form of reject creates a problem of effluent disposal. The Ultra High Lime with Aluminum process is an innovative technology which operates in two stages. The high pH and Calcium content in the first stage allows for removal of sulfate by precipitation as Calcium Sulfo-aluminate ($\text{Ca}_6 \text{Al}_2 (\text{SO}_4)_3 (\text{OH})_{12}$). Also, these conditions of the first stage allow the precipitation of chlorides as Calcium chloraluminates ($\text{Ca}_4 \text{Al}_2 \text{Cl}_2 (\text{OH})_{12}$). The cost economics of the process depicted that the capital cost is equivalent to the conventional lime process due to the fact that the same equipment is usable. Operating cost of the UHLA system is slightly higher due to the constant requirement to add aluminum. The sludge that is obtained contains almost 39% aluminum by weight.

4.4 CALCINED LAYERED DOUBLE HYDROXIDES (CLDH) METHOD:

On the basis of an effect known as Memory Effect, it was said that CLDH, within a certain temperature range, has the capacity to regain its original form. Therefore, a study was conducted in order to observe the capacity of CLDH to assimilate chloride ions from aqueous solution. The study concluded that the assimilation of chloride ions by CLDH was consistent with Langmuir and Freundlich models.

4.5 ELECTROCHEMICAL METHOD FOR THE REMOVAL OF CHLORIDES:

Electrochemical Chloride Extraction (ECE) is essentially a simple electrochemical process which consists of the use of basic principle of ion migration towards oppositely Charged poles. The apparatus contained an anode which was inserted in an electrolyte media. The setup was then applied on the concrete surface. The anode and the reinforcing steel were connected to two terminals of a direct current (DC) power supply such that the anode was positively charged. Due to the charge on the anode, the migration of the Chloride ions from the concrete to the anode field occurred, thereby reducing the chloride content in the concrete, particularly on and around the reinforced steel end. At the termination of the process, chloride free, highly alkaline concrete is obtained, which results in strong repassivation of the embedded reinforced steel and halting of the corrosion of the same. A study was conducted in order to observe the free chloride content in a concrete block during electrochemical chloride removal. It showed that, due to the free chloride removal, bound chloride is dissolved in order to reestablish the

equilibrium between bound and free chloride. The above literature review clearly indicates the need for research on the application of the biological substances for the chloride removal process. These processes may prove effective solutions for cost economic chloride removal. Therefore, the present paper studies the compatibility of the bio-sorption phenomena for chloride reduction.

4.6 BIO-ADSORPTION:

Adsorption can be defined as a process in which atoms or molecules move from a bulk phase (that is, solid, liquid or gas) onto a solid or liquid surface. An example is purification of liquid/gases by adsorption where impurities are filtered by adsorption process onto the surface of a high-surface-area solid such as activated charcoal. Molecules that have been adsorbed onto solid surfaces are referred to as adsorbate, and the surface to which they are adsorbed as the adsorbent. The adsorption process can occur at interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid or liquid-solid interfaces. In the case of liquid-solid interfaces, three types of adsorption have been distinguished: (a) physical adsorption: due to Vander Waal's attraction, (b) chemical adsorption: due to formation of chemical bond and (c) exchange adsorption: due to electrical attraction of solute to the adsorbent. Chemical adsorption is characterized by high energies (> 40 kJ/mol) which are similar to those found between atoms within a molecule (for example, covalent bonds), strong localized bonds and is generally favored at higher temperatures. In physical sorption, the adsorbed molecule remains intact, but in chemisorptions the molecule can be broken into fragments on the surface, in which case the process is called dissociative chemisorptions. However adsorbed molecules are considered not to be free to move on the surface or within the interface and are referred to as "activated" adsorption (Weber, 1972) unlike physical adsorption. Most of the adsorption phenomena are coordination of the three forms of adsorption and are generally termed as sorption, which includes absorption too while desorption is the reverse process. The extent of adsorption depends on physical parameters such as temperature, pressure and concentration in the bulk phase, and the surface area of the adsorbent, as well as on chemical parameters such as the elemental nature of the adsorbate and the adsorbent. Low temperatures, high pressures, high surface areas, and highly reactive adsorbate or adsorbents generally favour adsorption.

Biomass used as adsorbent after necessary activation by different methods is referred as Bio adsorption.

CHAPTER 5

MATERIAL & METHODS

5.1 STUDY AREA

Samples of well water as well as pond water were collected and tested in Village Kharak Kalan, District Bhiwani, Haryana. Total Population of the village is 20,000. This village is located 100KM North West to Delhi. There are 10 water ponds and about 21 deep water wells. These are the only source of drinking water in this village.

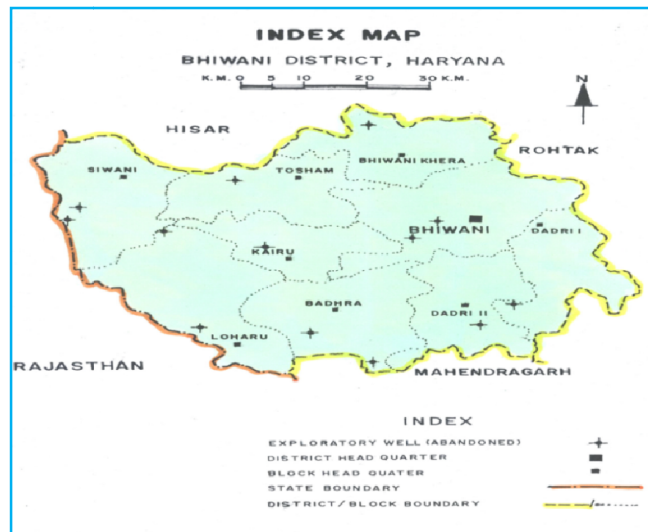


Fig 5.1

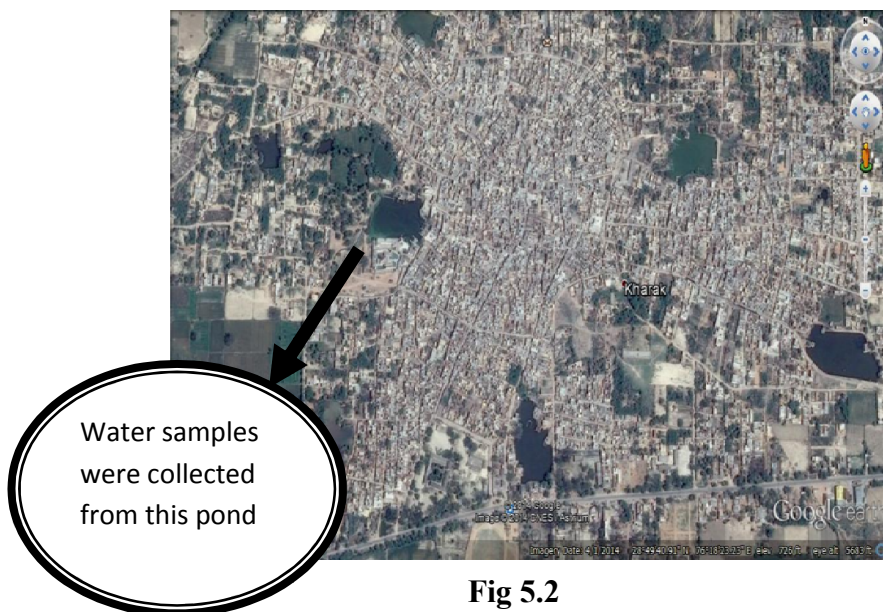


Fig 5.2

5.2 MATERIALS AND REAGENTS

The water was taken from the pond as well as from the well in the village. This water is being used by the villagers and the animals. The color of the water is green with high level of turbidity especially in the pond water. The onsite sampling and testing of the drinking water was done with the help of Jal Tara Water testing kit approved by Shriram Testing Lab, Delhi. This kit can test 14 parameters of drinking water quality. This kit contains all the required chemicals which are used for testing all 14 parameters. One parameter can be determined hundred times by one set of chemical in this kit.



Fig 5.3



Fig 5.4



Fig 5.5



Fig 5.6

List of parameter checked by Kit Table 5.1

SR. NO	PARAMETERS	STANDARD VALUE
1	PH	6.5-8
2	TEMPERATURE (°C)	-
3	COLI FORM	ABSCENT
4	FLUORIDE	1-1.5
5	DISSOLVE OXYGEN	>3 MG/L
6	RESIDUAL CHLORINE	0.2 MG/L
7	PHOSPHORUS	10-30 MICRO G/L
8	NITRATE	45
9	IRON	0.3-1
10	HARDNESS	300-600 PPM
11	CHLORIDE	250-1000
12	AMMONIA	<1.5 MG/L
13	TURBIDITY (NTU)	5-10 NTU
14	TDS	<400

5.2.1 USE OF CHLORIDE SAMPLE & GAJARGHAS (Parthenium) AS BIOADSORBENT

Natural Wastewater Sample with Chloride Concentration 1000 ppm was taken and the preliminary experiments were done with this sample. A plant known as grass / Gajarghas / Parthenium sps. / Congress (Belongs to the family asteraceae) was used as a bio-adsorbent. Before using, the Plant, it was dried & powdered (containing leaves and stem). The word 'Parthenium' has been derived from the Latin word 'Parthenice', meaning reputed medicinal merits. It has been speculated by scientists that the unique properties of this weed can be exploited for different purposes like activated carbon making, biomass generation, pesticide use etc.



Fig 5.7

Parthenium is considered to be one of the ten worst weeds in the world. Parthenium is an herbaceous annual or ephemeral member of the family Asteraceae. It can reach heights of up to 2 m in good soil, and attain flowering in less than 4– 6 weeks of germination. Seeds produced per plant can go up to 25000. Dispersion of the seeds occurs through various vectors like water, muddy surfaces, small animals, vehicles, machinery etc. Parthenium has a variety of vernacular names, like Congress grass, White top, Star Weed, Carrot Weed, Gajar Ghaas (Hindi), Ramphool, feverfew etc. The pollen and seeds of these plants are known to be a major cause of asthma, and bronchitis. The weed shows the presence of toxins known as Sesquiterpene lactones, parthenin, phenolic acids such as caffeic acid, vanillic acid, anisic acid, p-anisic acid, and parahydroxy benzoic acid which are known to be lethal to humans as well as animals.

5.2.2 METHOD OF ACTIVATION OF BIO-ADSORBENT:

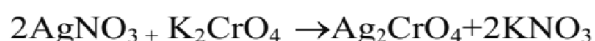
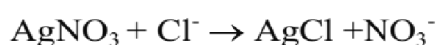
Sample collection was done on the basis of the health of the plant through visual observations. Young plants having a fresh green shoot and sizable stem thickness were selected. On collection, the specimens were washed with tap water and then distilled water. Further, for biomass collection, the specimens were subjected to drying in an oven at 100°C for three days. Drying was followed by careful crushing of the specimen, and then sieving the mixture through a 500 micron sieve. The obtained biomass was used for the study. The biomass was added to the test solutions in the ratio of 0.10 g: 100 ml test solution. The pH of the sample was maintained at 7, and the chloride concentration at 100% of the initial wastewater solution. The mixture was then incubated in a rotary shaker incubator at 150 rpm and 300 C for 60 minutes. On the termination of contact time, the solution was filtered using an ordinary filter paper. The sample was titrated for chloride content

using the Argentometric titration method specified in the APHA handbook for water and wastewater analysis. The tests were repeated by carrying out variations in pH, by using different chloride concentration levels, and with variable contact times.

5.2.3 DETERMINATION OF CHLORIDE ION:

Method used: Argentometric method

Principle: Chloride ion is determined by titration with standard silver nitrate solution in which silver chloride is precipitated first, due to the reaction of silver nitrate with chloride ions. The end of titration is indicated by formation of red silver chromate from excess AgNO_3 and potassium chromate used as an indicator in neutral to slightly alkaline solution.



Interference:

The substances found not interfering in potable water. Bromide, iodide and cyanide will titrate as chloride. Orthophosphate in excess of 25mg/l interfere. Sulphide, sulphite, thiosulphate and thiocyanate ions also interfere. However, these interferences can be eliminated the addition of hydrogen peroxide.

Apparatus required:

- Burette
- Pipettes
- Conical Flask

Reagents used:

- Chloride free distilled water.
- Standard Silver nitrate solution (0.0141N): Take 2.395g of silver nitrate and dilute to 1000ml with distilled water.
- Potassium Chromate indicator.
- Sodium chloride solution. (sample solution): Take suitable gram of NaCl salt and dilute to 1000 ml using distilled water to achieve required normality.

Procedure:

1. Take 50ml of the sample in a conical flask
2. Adjust its pH to be between 7 and 8 either with sulphuric acid or sodium hydroxide solution.

Otherwise, AgOH is formed at high pH levels or CrO_4^{2-} is converted to $\text{Cr}_2\text{O}_7^{2-}$ at low pH levels.

3. Add 1ml of potassium chromate indicator to get a light yellow color.
4. Titrate with standard silver nitrate solution till color change from yellow to brick red.
5. Note the volume of silver nitrate added. (A)
6. If more quantity of potassium chromate is added, Ag_2CrO_4 may form too soon.
7. For better accuracy, titrate distilled water in the same manner.
8. Note the volume of silver nitrate added for distilled water (B).

Calculations:

$$\text{Chloride content (mg/l)} = \frac{(A-B) \times \text{normality of AgNO}_3 \times 35.45 \times 1000}{\text{Volume of sample taken}}$$

Where:

A= ml titration for sample,

B= ml titration for blank.



Fig 5.8

5.3 BATCH MODE ADSORPTION EXPERIMENTS

Batch mode adsorption experiments were conducted at room temperature (23- 25 °C) except where mentioned. Predetermined quantities of adsorbent were added in the beaker and to achieve the degree of mixing and adsorption equilibrium, a magnetic stirrer was employed with speed adjusted at 100 rpm. A paddle stirrer was also employed with speed adjusted at 1000 rpm to check the difference in chloride removal due to different mode of physical mixing of bio-adsorbent ranging from pH 3- 11 which were well adjusted by using 0.1 N of

HCl and NaOH whereas extreme pH were adjusted using 1 N acid/base solution. Addition of acid/base solution to adjust the pH never exceeded 1% of the total volume of the reactor. The adsorption batch experiment is shown in Fig 5.8. The amount of Chloride adsorbed by adsorbent was calculated based on the difference of ion concentration in aqueous solution before and after adsorption according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where, q_t is the amount of chloride ions adsorbed per unit weight of adsorbent (mg/g) at time t , C_0 and C_t are the concentrations of chloride ions (mg/L) at initial time and at time t respectively, V is the initial volume of metal ions sample (L) and m is mass of adsorbent (g). When t is equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, then the amount of chloride ions adsorbed at equilibrium, q_e was calculated using equation as above.

5.4 ANALYTICAL TECHNIQUES

All analyses were carried out according to APHA (1998). Measurement of Chloride was carried out by **Argentometric method**. The calibration curve obtained and used for estimating the chloride concentration is shown in Fig 5.9. Drying and activation of bio adsorbent was done using a drying oven and a muffle furnace respectively. During adsorption experiment, degree of mixing was provided by employing magnetic stirrer or Jar test apparatus (Paddle Stirrer). Solution pH was measured by a digital pH meter. All weighing of reagents and adsorbents was carried out in an analytical weighing balance.

Table 5.2: Experimental design for batch studies with chloride and Bio-adsorbent

Experimental Set	Variable parameters	Control parameters	Purpose
1	pH	Concentration and Dose	Effect on absorption of chloride due to variation in pH
2	Time	Concentration and Dose	Optimization of time for removal of chloride
3	Dose (1,2,3,4,5,6 7g)	Initial Concentration of chloride: 100 to 1000 mg/L	Adsorbent dose test

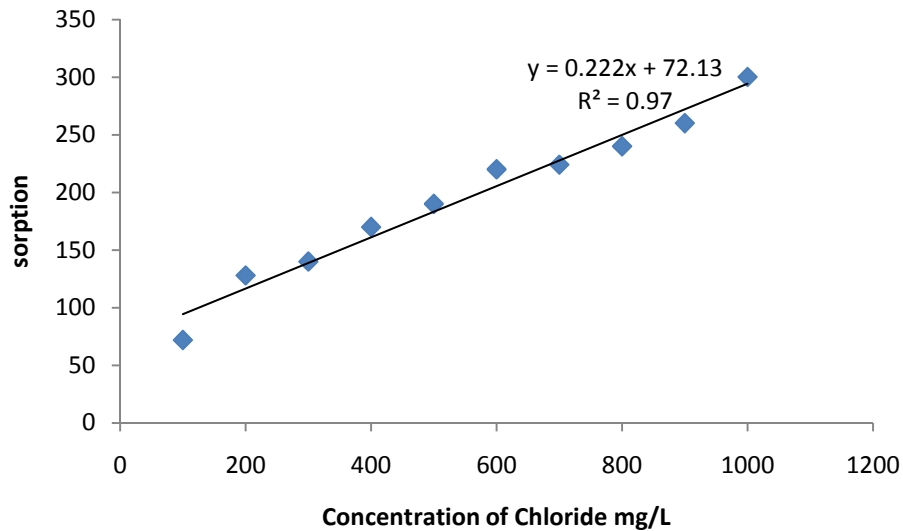


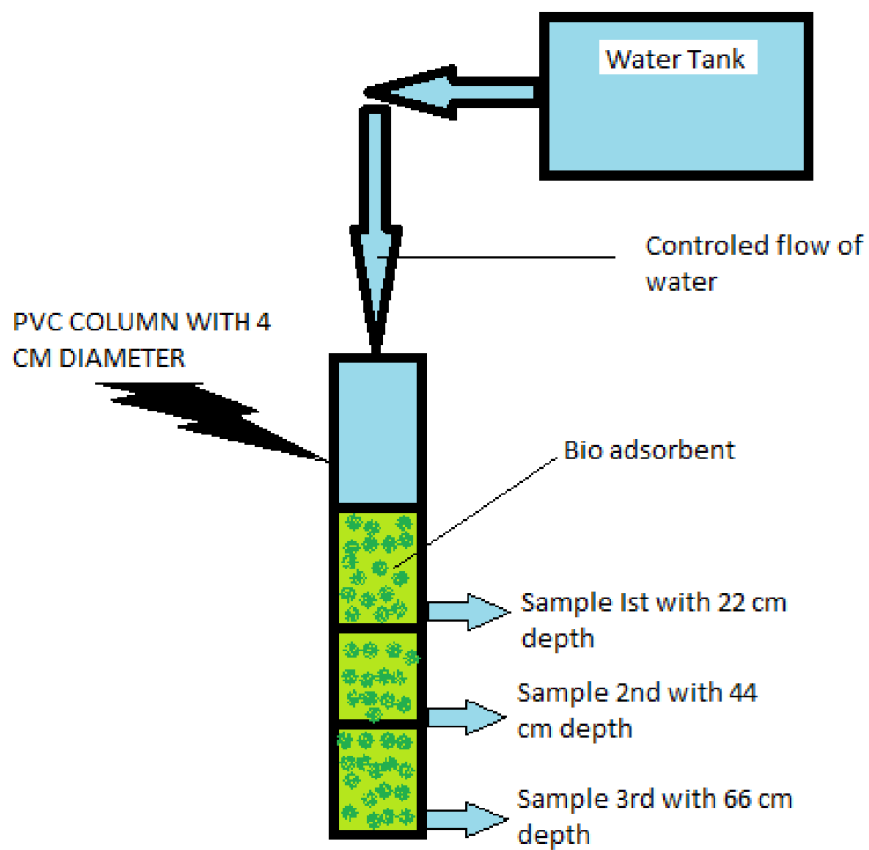
Fig 5.9

5.5 COLUMN STUDIES

Fixed bed column studies were conducted using PVC columns of 4 cm diameter and 66 cm length. The column was packed with adsorbent between two supporting layers of filters screens. The schematic diagram of the column study is shown in Fig.5.10. The particle size was 300–600 μm with a bed depth of 22 cm each and filling weight of 500 g. The packed density or bulk density of the adsorbent in the column was approximately 0.60 g cm^{-3} . The chloride solution was fed through the fixed-bed column in the down flow mode. Before operation, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particles with no void, channels, or cracks. The effluent samples were collected at specified time intervals and measured for the chloride concentration by Titration with Silver nitrate and indicator potassium chromate. The flow to the column was continued until the effluent concentration (C) approached the influent concentration (C_0).

The effects of the following parameters, on column adsorption system were investigated.

- Effect of bed height: bed height was varied between 22, 44 & 66 cm, keeping flow rate and initial Cl^- concentration constant
- Effect of flow rate: flow rate was varied between 5, 10 and 15 mL/min, while bed height and initial Cl^- concentration were held constant



Continuous flow column analysis

Fig 5.10

CHAPTER 6

RESULTS AND DISCUSSION

6.1 RESULT SYNOPSIS OF ONSITE TESTING OF WATER

As the onsite water testing were done in the village Kharak kalan, District. Bhiwani, Haryana by using Jal Tara Water testing Kit. The sample was taken twice in a month and this study was carried out for the water sample from January 2014 to June 2014 i.e. for six months. During this study the atmospheric temperature varied from 16⁰c to 41⁰c but it was seen that there was a very little temperature variation in the water. The color of the well water was transparent but the color of the pond water was greenish. In the pond water there was no aquatic life seen. Only bacterial presence was seen through the bacteria test. A high pH was noticed in the pond water. The first reason may be. When the water is allowed to sit in the open air, a considerable amount of the dissolved carbon dioxide dissipates. Correspondingly, the water's pH rises. The second cause of pH rise in ponds is algae. This pond water is green and will be more after period of time. That green coloring is plank tonic algae. Algae, like all green plants, converts sunlight to food via photosynthesis. As part of that process, the algae remove carbon dioxide from the water and produce oxygen. Again, removing carbon dioxide from the water produces a rise in pH. The pH of the deep well was also high but was less than pH range of pond water.

The coliform bacteria was present in the pond water but the same was absent in the well water. Coliform bacteria are a commonly used bacterial indicator of sanitary quality of foods and water. They are defined as rod-shaped Gram-negative non-spore forming bacteria which can ferment lactose with the production of acid and gas when incubated at 35–37°C. Coliform can be found in the aquatic environment, in soil and on vegetation; they are universally present in large numbers in the feces of warm-blooded animals. While coliforms themselves are not normally causes of serious illness, they are easy to culture and their presence is used to indicate that other pathogenic organisms of fecal origin may be present. Such pathogens include bacteria, viruses, or protozoa and many multi-cellular parasites. Coliform procedures are performed in aerobic or reduced oxygen conditions.

Typical genera include:

- Citrobacter,
- Enterobacter
- Hafnia
- Klebsiella

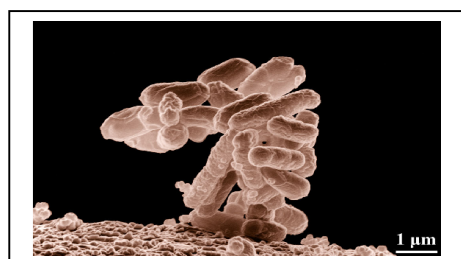


Fig 6.1

- Fecal coliform:
- Escherichia

The fluoride, nitrate, residual chlorine, iron and ammonia were found satisfactory. But the concentration of DO, phosphorus chloride and hardness were found on higher side. Chloride details has already studied in introduction chapter, let's take the details of effects of phosphorus and Hardness as below.

PHOSPHORUS: - Phosphorus is a common constituent of agricultural fertilizers, manure, and organic wastes in sewage and industrial effluent. It is an essential element for plant life, but when there is too much of it in water, it can speed up eutrophication (a reduction in dissolved oxygen in water bodies caused by an increase of mineral and organic nutrients) of rivers and lakes. Soil erosion is a major contributor of phosphorus to streams. Bank erosion occurring during floods can transport a lot of phosphorous from the river banks and adjacent land into a stream. Phosphorus gets into water in both urban and agricultural settings. Phosphorus tends to attach to soil particles and, thus, moves into surface-water bodies from runoff. A USGS study on Cape Cod, Massachusetts showed that phosphorus can also migrate with ground-water flows. Since groundwater often discharges into surface water, such as through stream banks into rivers, there is a concern about phosphorus concentrations in groundwater affecting the water quality of surface water. Phosphorus is an essential element for plant life, but when there is too much of it in water, it can speed up **eutrophication** (a reduction in dissolved oxygen in water bodies caused by an increase of mineral and organic nutrients) of rivers and lakes.

HARDNESS: - Hard water is water that has high mineral content (in contrast with "soft water"). Hard water is formed when water percolates through deposits of calcium and magnesium-containing minerals such as limestone, chalk and dolomite. Hard drinking water is generally not harmful to one's health, but can pose serious problems in industrial settings, where water hardness is monitored to avoid costly breakdowns in boilers, cooling towers, and other equipment that handles water. In domestic settings, hard water is often indicated by a lack of suds formation when soap is agitated in water, and by the formation of lime scale in kettles and water heaters. Wherever water hardness is a concern, water softening is commonly used to reduce hard water's adverse effects.

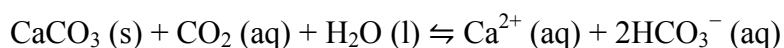
There is no known health risks associated with the consumption of hard water. In fact, studies have shown that people who regularly consume hard water throughout their lifetime have a lower rate of cardiovascular disease.

There are some problems associated with hard water. These include:

- gray staining of washed clothes
- scum on wash and bath water following use of soap or detergent
- reduced lathering of soaps
- buildup of scale on electric heating elements and boilers
- reduced water flow in hot water distribution pipes due to scale buildup
- accumulation of whitish-gray scale in tea kettles and other containers used to boil water

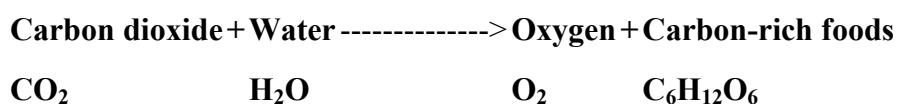
Water's hardness is determined by the concentration of multivalent cations in the water. Multivalent cations are cations (positively charged metal complexes) with a charge greater than 1+. Usually, the cations have the charge of 2+. Common cations found in hard water include Ca^{2+} and Mg^{2+} . These ions enter a water supply by leaching from minerals within an aquifer. Common calcium-containing minerals are calcite and gypsum. A common magnesium mineral is dolomite (which also contains calcium). Rainwater and distilled water are soft, because they contain few ions.

The following equilibrium reaction describes the dissolving and formation of calcium carbonate :



The reaction can go in either direction. Rain containing dissolved carbon dioxide can react with calcium carbonate and carry calcium ions away with it. The calcium carbonate may be re-deposited as calcite as the carbon dioxide is lost to atmosphere, sometimes forming stalactites and stalagmites. Calcium and magnesium ions can sometimes be removed by water softeners.

DISSOLVE OXYGEN:- The dissolved oxygen (DO) is oxygen that is dissolved in water. The oxygen dissolves by diffusion from the surrounding air; aeration of water that has tumbled over falls and rapids; and as a waste product of photosynthesis. A simplified formula is given below: Photosynthesis (in the presence of light and chlorophyll):



Fish and aquatic animals cannot split oxygen from water (H_2O) or other oxygen-containing compounds. Only green plants and some bacteria can do that through photosynthesis and similar processes. Virtually all the oxygen we breathe is manufactured by green plants. A

total of three-fourths of the earth's oxygen supply is produced by phytoplankton in the oceans.

The temperature effect

If water is too warm, there may not be enough oxygen in it. When there are too many bacteria or aquatic animal in the area, they may overpopulate, using DO in great amounts.

Oxygen levels also can be reduced through over fertilization of water plants by run-off from farm fields containing phosphates and nitrates (the ingredients in fertilizers). Under these conditions, the numbers and size of water plants increase. Then, if the weather becomes cloudy for several days, respiring plants will use much of the available DO. When these plants die, they become food for bacteria, which in turn multiply and use large amounts of oxygen. and this depleting all the oxygen.

How much DO an aquatic organism needs depends upon its species, its physical state, water temperature, pollutants present, and more. Consequently, it's impossible to accurately predict minimum DO levels for specific fish and aquatic animals. For example, at 5 °C (41 °F), trout use about 50-60 milligrams (mg) of oxygen per hour; at 25 °C (77 °F), they may need five or six times that amount. Fish are cold-blooded animals. They use more oxygen at higher temperatures because their metabolic rates increase.

Numerous scientific studies suggest that 4-5 parts per million (ppm) of DO is the minimum amount that will support a large, diverse fish population. The DO level in good fishing waters generally averages about 9.0 parts per million (ppm).

In the present work “characterization of rural drinking water quality and removal of excess chloride” was studied along with removal of chloride using low cost Bio-adsorbent. Chloride adsorption studies were conducted in batch mode as well its comparison with column study. The experimental studies for batch mode were conducted in three sets. Set 1 was carried out for investigation of effects of reaction pH towards adsorption and identification of the binding mechanism of chloride over Bio-adsorbent. Set 2. Was carried out to evaluate the effects of initial chloride concentration on adsorption. From the data obtained, adsorption isotherms study was also carried out. Effect of bio-adsorbent dose on chloride adsorption was studied by conducting Set 3 experiments. During the whole experiments the temperature variation was constant from 30⁰C to 35⁰ C. The Bio-adsorbent was first activated as per the details given earlier in the 2nd chapter. All these experiments were done in the DTU water and wastewater lab. The column continuous flow study was also done to compare the result with

batch process results. Column study was conducted on with a PVC conduit of 4 cm diameter and 66 cm length. To prepare this column, three nos. of PVC water purifiers taps are used. The height of each tap from each other is kept 22 cm. This experiment was done by varying the flow rate of water sample and by using different bed depth.

The tabulated and graphical results are as follows.

6.2 Test Results of Onsite tests using Jal Tara Kit.

OBSERVATION TABLE FOR DEEP WELL WATER Table 6.1

SR. NO	PARAMETERS	STANDARD VALUE	OBSERVED VALUE											
			JANUARY 2014		FEBRUARY 2014		MARCH 2014		APRIL 2014		MAY 2014		JUNE 2014	
			SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7	SAMPLE 8	SAMPLE 9	SAMPLE 10	SAMPLE 11	SAMPLE 12
1	PH	6.5-8	8	8	8	8.5	8.5	8.5	8	8	8	8	8	8
2	TEMPERATURE (°C)	-	21	21	21	21	21.5	22	22	23	23	22	22	22
3	COLI FORM	ABSCENT	A	A	A	A	A	A	A	A	A	A	A	A
4	FLUORIDE	1-1.5	1.6	1.5	1.2	1.2	1.2	1.2	1	1	.9	.9	1	1
5	DISSOLVE OXYGEN	>3 MG/L	10	9	11	10	10	10	10	11	11	11	10	10
6	RESIDUAL CHLORINE	0.2 MG/L	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
7	PHOSPHORUS	10-30 MICRO G/L	100	100	108	114	109	115	116	100	102	105	112	108
8	NITRATE	45	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
9	IRON	0.3-1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
10	HARDNESS	300-600 PPM	1100	1100	1130	1135	1147	1178	1127	1105	1173	1158	1155	1160
11	CHLORIDE	250-1000	1129	1140	1140	1204	1140	1148	1185	1168	1287	1297	1150	1174
12	AMMONIA	<1.5 MG/L	1	1	1	1	1	1	1	1	1	1	1	1
13	TURBIDITY (NTU)	5-10 NTU	CLEAR	CLEAR	CLEAR	CLEAR	CLEAR	CLEAR	CLEAR	CLEAR	CLEAR	CLEAR	CLEAR	CLEAR
14	TDS	<400	260	280	220	220	220	230	220	200	230	260	250	230

OBSERVATION TABLE FOR POND WATER Table 6.2

SR. NO	PARAMETERS	STANDARD VALUE	OBSERVED VALUE											
			JANUARY 2014		FEBRUARY 2014		MARCH 2014		APRIL 2014		MAY 2014		JUNE 2014	
			SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7	SAMPLE 8	SAMPLE 9	SAMPLE 10	SAMPLE 11	SAMPLE 12
1	PH	6.5-8	10	9	9	9	9	9	9	9	9	10	10	9
2	TEMPERATURE (°C)	-	22	23	22	22	23	23	25	25	25	25	26	26
3	COLI FORM	ABSCENT	P	P	P	P	P	P	P	P	P	P	P	P
4	FLUORIDE	1-1.5	1.6	1.5	1.2	1.2	1.2	1.2	1	1	.9	.9	1	1
5	DISSOLVE OXYGEN	>3 MG/L	0.4	0.3	0.5	0.5	0.8	0.6	0.6	0.8	0.8	0.6	0.6	0.6
6	RESIDUAL CHLORINE	0.2 MG/L	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
7	PHOSPHORUS	10-30 MICRO G/L	100	104	105	120	120	120	110	100	105	105	110	110
8	NITRATE	45	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
9	IRON	0.3-1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
10	HARDNESS	300-600 PPM	1120	1100	1170	1185	1247	1168	1147	1205	1153	1148	1135	1230
11	CHLORIDE	250-1000	1120	1100	1150	1200	1240	1248	1285	1268	1287	1297	1250	1274
12	AMMONIA	<1.5 MG/L	3	1	2	1	3	2	3	2	2	2	1	1
13	TURBIDITY (NTU)	5-10 NTU	60	60	65	65	60	60	65	60	60	55	55	60
14	TDS	<400	460	480	390	420	420	430	420	430	430	460	450	450

6.3 GRAPHICAL PRESENTATION OF POLLUTANTS CONCENTRATION.

CHLORIDE CONCENTRATION VARIATION CHART

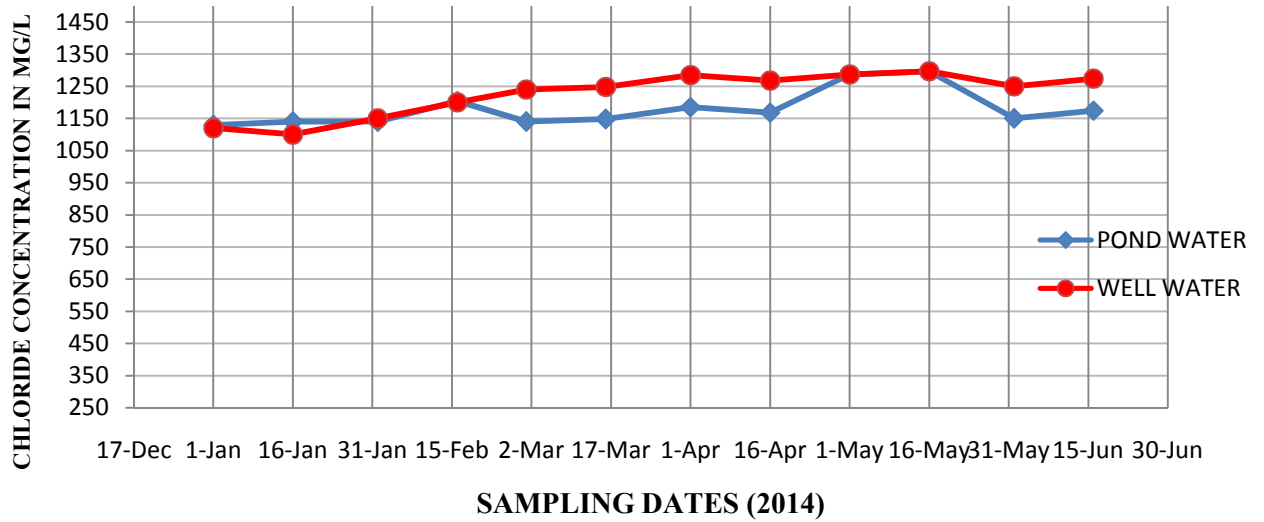


Fig 6.2

TDS CONCENTRATION IN WELL AND POND WATER

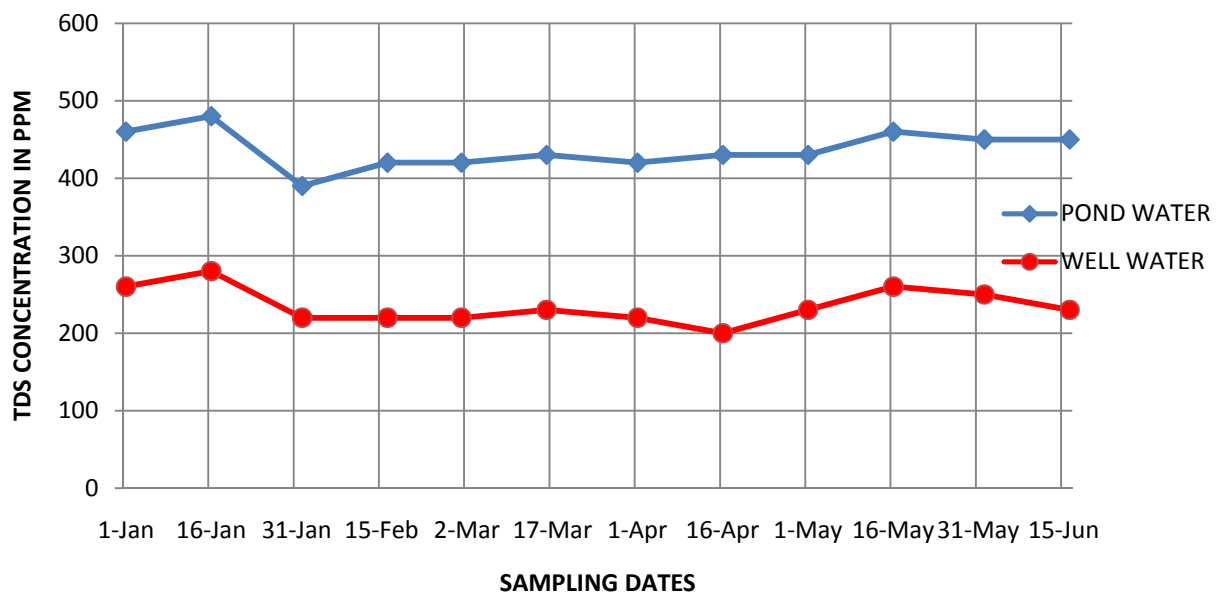


Fig 6.3

PHOSPHATE CONCENTRATION

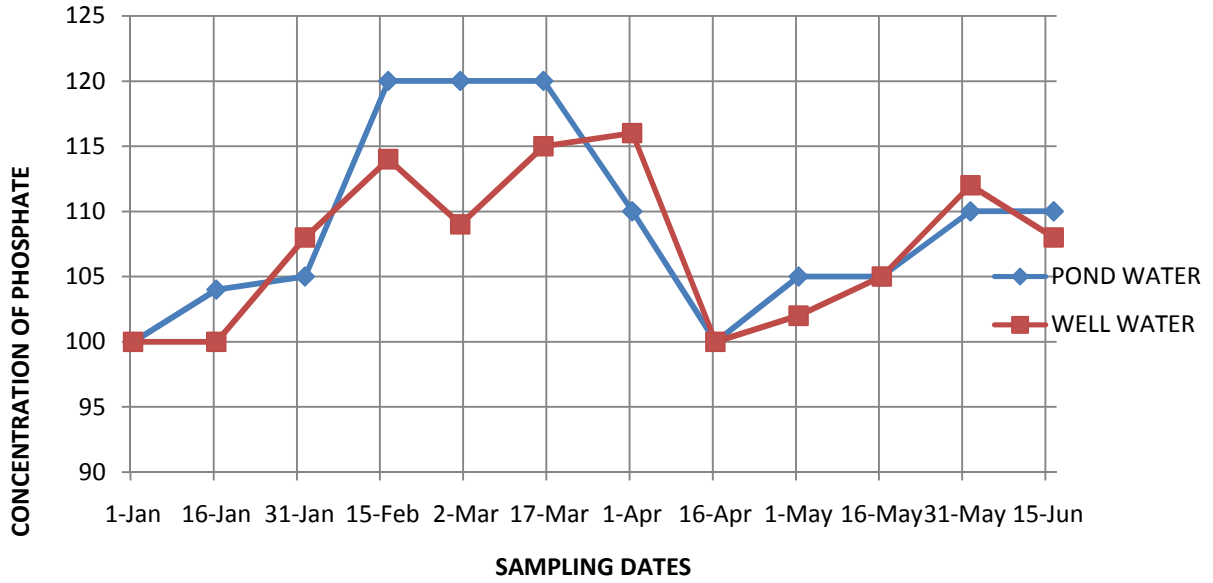


Fig 6.4

DISSOLVE OXYGEN CONCENTRATION

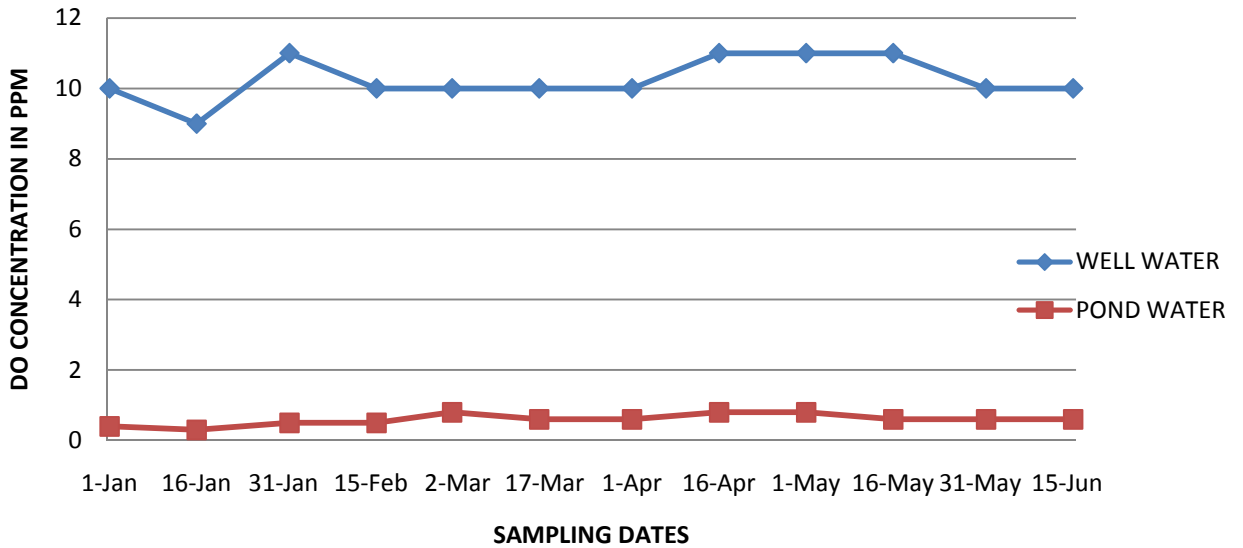


Fig 6.5

6.4 EFFECT OF REACTION pH IN BATCH STUDY

Solution pH is one of the most important parameter to reveal the mechanism of adsorption. The effect of solution pH effect is firstly studied by conducting control experiment without any adsorbents. it's clear that the solubility of chloride is consistent from pH range of 2- 12. Secondly, various pH range of chloride solution was contacted with Parthenium bio-adsorbent and the result is shown in Fig 6.6.

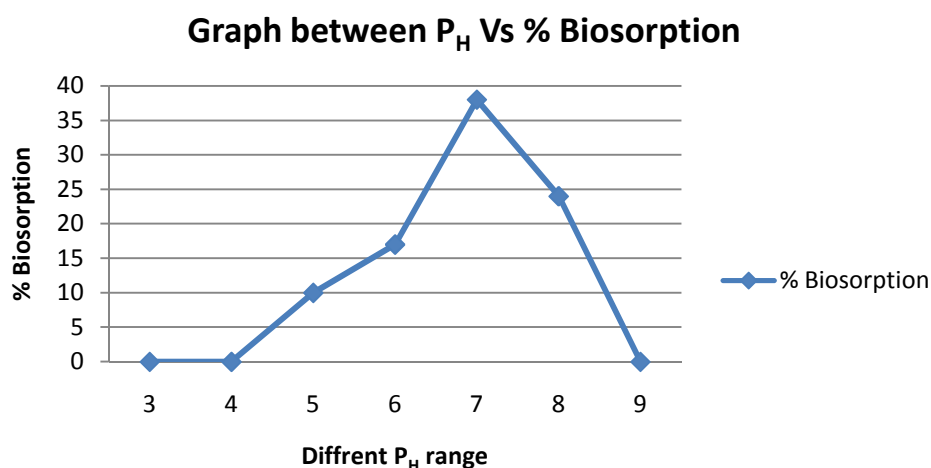


Figure: 6.6 Effect of reaction pH on adsorption of chloride by Parthenium at various reaction pH (Initial Chloride: 100 mg/L; dose: 0.10g/100ml of solution)

The best level of pH was found as pH 7, where the maximum absorption was observed by Parthenium.

6.5 EFFECT OF ADSORPTION TIME IN BATCH STUDY

The effect of initial chloride concentration on the adsorption was investigated varying initial chloride concentration in the range of 100–1000 mg/L. Batch experiments were performed at solution pH of 7.0 with 1 g/L bio- adsorbent. Removals of chloride ions (%) with time at a fixed initial chloride concentrations and amounts of chloride adsorbed are shown in Fig 6.7. and 6.8 respectively. The equilibrium between chloride and bio-adsorbent was attained within 5 minutes at initial chloride concentration of 100 mg/L and 20 minutes for all higher chloride concentrations. Equilibrium time increased to 90 minutes for almost all chloride concentration to 1000 mg/L and was constant beyond that. The chloride adsorption yield decreased with increase in initial concentration of chloride. At chloride concentration of 100 mg/L, 88% removal was achieved. When initial chloride concentration was increased to 1000 mg/L, chloride removal decreased to 40%. However, chloride uptake increased with increase in initial chloride ion concentration Fig 6.7. At initial chloride concentrations of 100 mg/L, chloride uptake was 84 mg/g and increased to 400 mg/g at

initial chloride concentration of 1000 mg/L. The reason was probably with increase in concentration, the number of Chloride ions increased and so chances of contact between chloride ions and adsorption sites also increased. This was responsible for higher chloride uptake by unit amount of adsorbent.

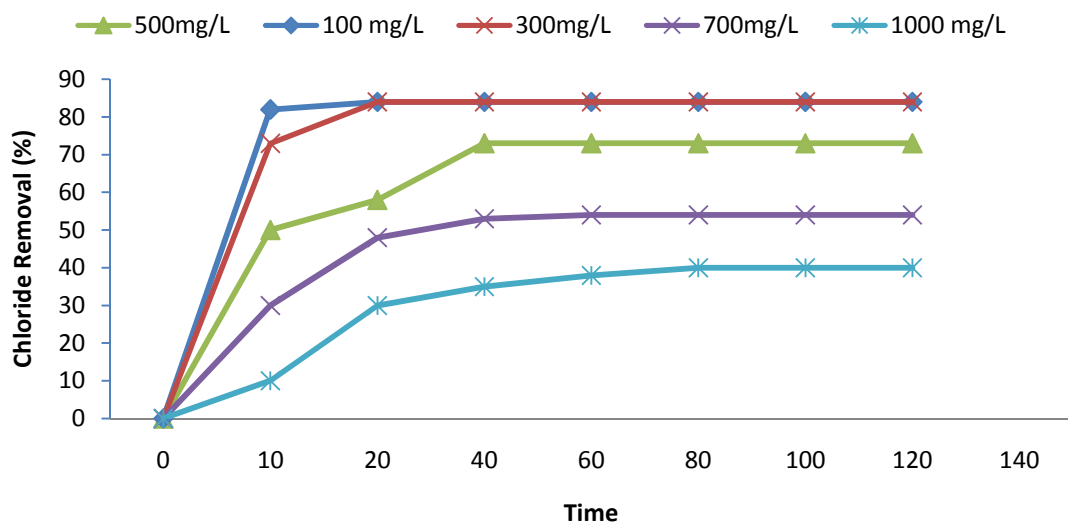


Figure: 6.7 Effect of reaction time on adsorption (%) of chloride by bio-adsorbent at various initial concentration of chloride (Reaction pH: 7; dose: 1 g/L)

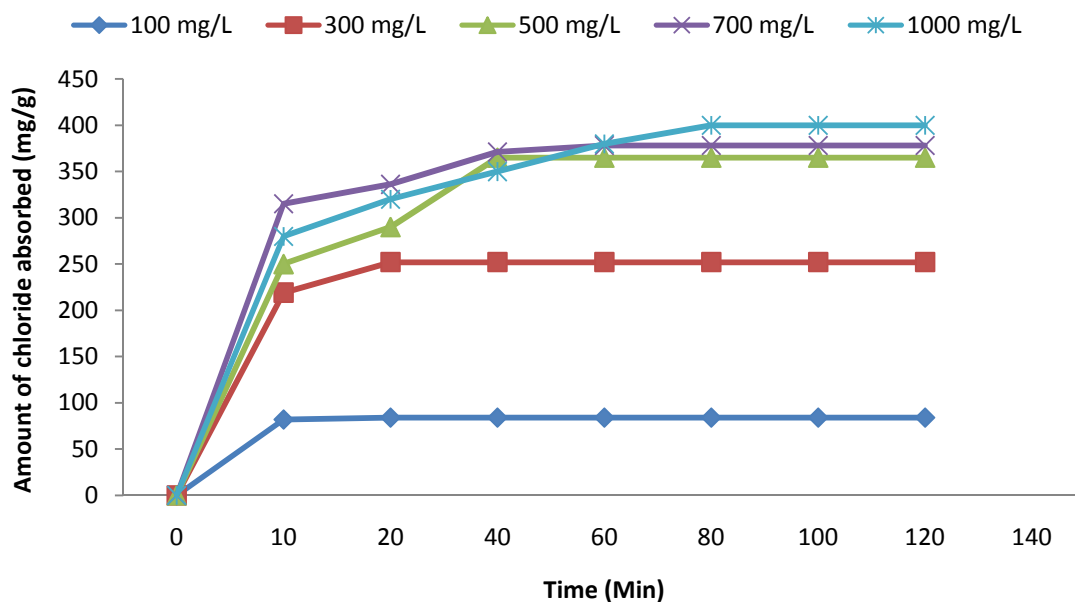


Figure: 6.8 Effect of reaction time on adsorption of chloride (mg/g) by Parthenium bio Adsorbent at various initial concentration of chloride (Reaction pH: 7; dose: 1 g/L)

This process of chloride adsorption was also conducted with a fixed concentration of chloride to 1000 mg/L as per the actual water sample concentration. The adsorbent dose was kept to 2 g. with a

fixed pH of 7. The performance of the adsorbent is as shown in the graph below. The contact time was kept to 10 min. to 240 min. with 500 rpm rotating system. This graph shows increased % of bio-adsorption with increased contact time.

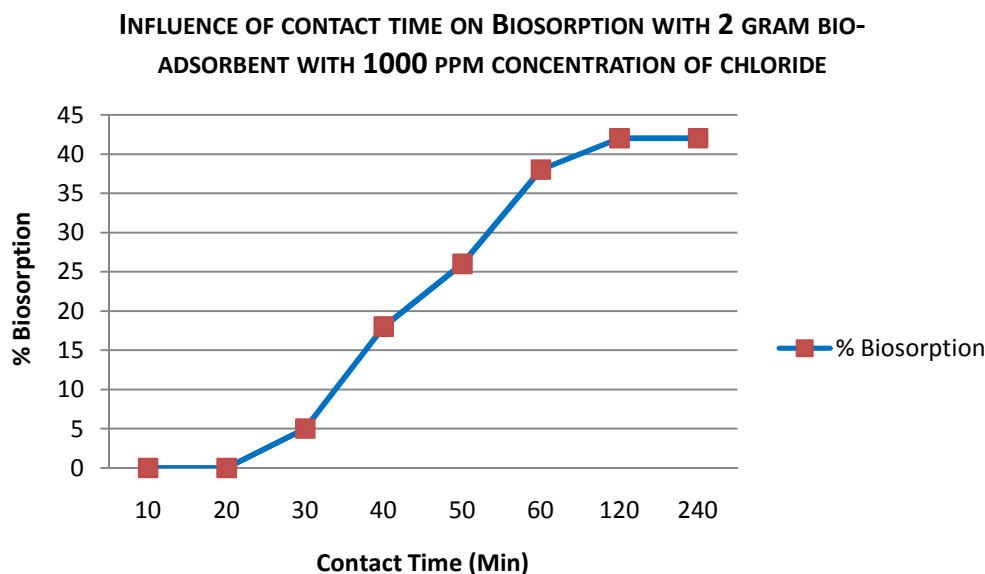


Figure: 6.9 Effect of reaction time on adsorption (%) of chloride by bio-adsorbent at 1000 mg/L initial concentration of chloride (Reaction pH: 7; dose: 2 g/L)

6.6 EFFECT OF ADSORBENT DOSE

Effect of adsorbent dose on chloride uptake was studied by varying the adsorbent dose from 1 g/L to 7 g/L for only one fixed initial chloride concentration of 1000 mg/L. Initial pH was adjusted to 7. Chloride removal (%) and uptake with adsorbent dose for fixed chloride concentrations are shown in Fig.6.10. It was observed that chloride removal (%) for fixed concentrations increased from 20% to 60% with increase in the adsorbent dose. The number of Chloride ions of adsorption sites or surface area increases with the weight of the adsorbent and hence results in a higher percent of metal removal at a high dose.

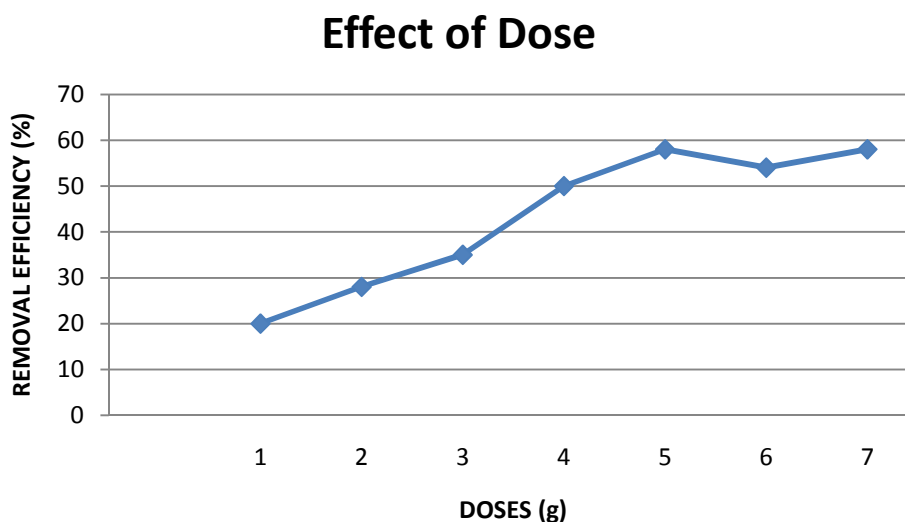


Figure: 6.10 Removal (%) of chloride with varied dose of bio-adsorbent

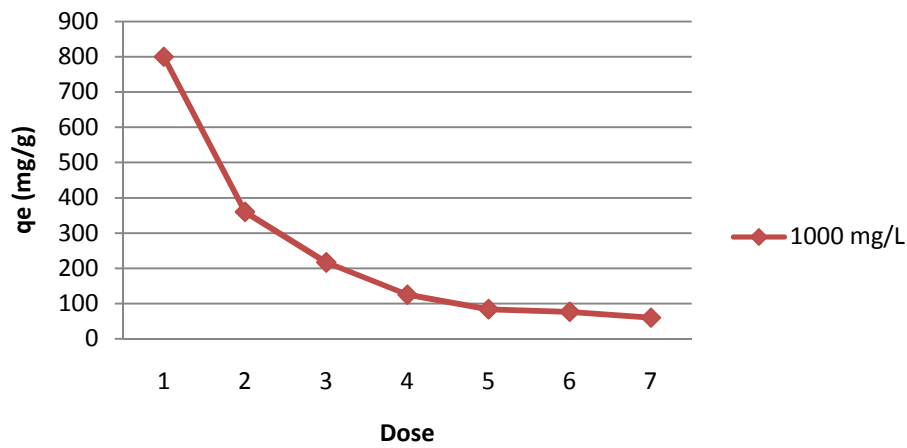


Figure: 6.11 Plot of Removal (q_e) for chloride Vs dose of Parthenium

6.7 ADSORPTION ISOTHERM

Adsorption isotherm is a mathematical model or functional expression to depict the distribution of solute between the solid and liquid phase at equilibrium at a constant fixed temperatures. The isotherm model relates the amount of solute adsorbed per weight of adsorbent (q_e), with amount of solute retain in solvent (C_e) at equilibrium. Commonly, the amount q_e increase with increase in C_e value, but not in direct proportion. Several mathematical model or isotherms were developed based on certain assumptions. Langmuir isotherm, Freundlich isotherm, Langmuir-Freundlich isotherm, BET isotherm, Temkin, Redlich–Peterson etc. are some of the well known models out of which Langmuir and Freundlich isotherm are the commonly and mostly applied models in chloride adsorption from aqueous solution.

6.7.1 LANGMUIR ISOTHERM

Langmuir isotherm is based on the following assumptions: (a) each surface site can be singly occupied, (b) there are no lateral interactions between adsorbed species, (c) the enthalpy of adsorption is independent of surface coverage and (d) energy of adsorption is constant thus creating homogeneity of energy on the surface (there is dynamic equilibrium between the adsorption and desorption processes).

$$K_d \theta = K_a C_e (1 - \theta)$$

$$\text{or, } \theta = \frac{K_a C_e}{K_d + K_a C_e} = \frac{b C_e}{1 + b C_e} \quad (\text{A})$$

The adsorption coefficient $b = \frac{K_a}{K_d}$, is related to the enthalpy of adsorption (ΔH) by

$$b = b_0 \exp^{-\Delta H / RT}$$

where b_0 is constant related to entropy, R is the universal gas constant, T is the temperature ($^{\circ}\text{K}$) (Voice and Weber 1983).

As q_e is proportional to θ , therefore, equation (A) can be written as,

$$q_e = \frac{bQ_m C_e}{1 + bC_e} \quad (\text{B})$$

where q_m is the maximum adsorption for a complete monolayer coverage. Equation (B) can be rearranged in variety of linear forms.

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (\text{C})$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \quad (\text{D})$$

$$q_e = Q_m - \frac{q_e}{bC_e} \quad (\text{E})$$

6.7.2 FREUNDLICH ISOTHERM

Freundlich model or van Bemmelen equation has been developed for adsorption system with emphasis on two factors, namely the lateral interaction between the adsorbed molecules and the energetic surface heterogeneity. The equation has the general form (Freundlich 1906)

$$q_e = K_f C_e^{\frac{1}{n}}$$

but it is well cited in logarithmic form as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (\text{F})$$

where K_f and n are empirical constant. Here, $K_f \propto RT \text{ nb } \exp(\Delta H/RT)$. Equation (F) suggests that with increase in C_e , adsorption capacity (q_e) would increase without restriction, which is practically impossible. The model may simulate concentrations far outside the range of the defining batch experiment. Extrapolating equation (F) into such concentration regions hence may give results of

unknown, but potentially very large error. However in practical situation, adsorption process are sufficiently dilute and one never encounters the region where Freundlich equation breaks down for this region and Freundlich isotherm equation implies that the energy distribution of adsorption site is of exponential (Cooney 1999).

In order to identify the best fit isotherm model, Chi square test was done by the following equation G. (Ho et al, 2005)

$$\chi^2 = \sum \frac{(q_e - q_{em})^2}{q_{em}} \quad (G)$$

Where, q_e is the experimental data of the equilibrium chloride uptake (mg/g) and q_{em} is the equilibrium uptake calculated from isotherm models (mg/g).

The linear plots of Langmuir isotherm is shown in Fig. 6.12 with $1/C_e$ Vs $1/q_e$. Also the linear plot of Freundlich isotherm with $\ln(C_e)$ Vs $\ln(q_e)$ is plotted in Fig. 6.13. The correlation coefficients and the coefficients are shown in Table 6.3. It shows that Langmuir isotherm fitted experimental data better than the Freundlich model as it showed larger R^2 value as compared to the Freundlich model. The Langmuir curves had good linearity (Correlation coefficient > 0.99) for Bio adsorbent doses indicating strong binding of chloride ions to the surface of Parthenium during adsorption. The Langmuir monolayer capacity (a) or maximum adsorption capacity is observed to be 24.39 mg/g. The adsorption equilibrium parameter b, which reflects quantitatively the affinity between the adsorbent and the adsorbate, is 0.0149 L/g. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L), which is defined by the following relation.

$$R_L = \frac{1}{1 + bC_0} \quad (H)$$

Where b is the Langmuir constant C_0 is the initial liquid phase chloride ion concentration and for favorable adsorption $0 < R_L < 1$. Separation factor R_L indicates the isotherm shape accordingly.

$R_L > 1$, Unfavorable

$R_L = 1$, Linear

R_L lies between 0 and 1, Favorable

$R_L = 0$, Irreversible.

Further the plot of comparison of q_e value of experimental and predicted through both Langmuir and Freundlich isotherms is shown in Fig. 6.14.

Table 6.3: Coefficients of Langmuir and Freundlich's isotherm

Langmuir				Freundlich			
R^2	a (mg/g)	b (L/mg)	λ^2	R^2	K_f	N	λ^2
0.9901	24.39	0.0149	0.64	0.9364	2.7604	2.9913	1.16

Table 6.4.Observation table during batch study

Co (mg/L)	Ce (mg/L)	1/Ce	LogCe	InCe	Qe	1/Qe	logQe	InQe	Ce/Qe g/L	qe(exp)	Qe (Lang)	Qe (Fre)
100	28	0.035714	1.447158	3.332205	7.2	0.138889	0.857332	1.974081	3.888889	7.2	7.1888668	8.409449
200	72	0.013889	1.857332	4.276666	12.8	0.078125	1.10721	2.549445	5.625	12.8	12.633952	11.53158
300	138	0.007246	2.139879	4.927254	16.2	0.061728	1.209515	2.785011	8.518519	16.2	16.418883	14.33323
400	232	0.00431	2.365488	5.446737	16.8	0.059524	1.225309	2.821379	13.80952	16.8	18.924879	17.0516
500	302	0.003311	2.480007	5.710427	19.8	0.050505	1.296665	2.985682	15.25253	19.8	19.961632	18.62297
600	380	0.002632	2.579784	5.940171	22	0.045455	1.342423	3.091042	17.27273	22	20.734372	20.10964
700	490	0.002041	2.690196	6.194405	21	0.047619	1.322219	3.044522	23.33333	21	21.456314	21.8935
800	579	0.001727	2.762679	6.361302	22.1	0.045249	1.344392	3.095578	26.1991	22.1	21.860492	23.14974
900	681	0.001468	2.833147	6.523562	21.9	0.045662	1.340444	3.086487	31.09589	21.9	22.205427	24.44014
1000	750	0.001333	2.875061	6.620073	25	0.04	1.39794	3.218876	30	25	22.389926	25.24153
		χ^2 of Lengmuir	χ^2 of Freundlich	a	b	Kf	n	R _L				
		1.72149E-05	0.203162104	24.39	0.014926	2.760467	2.991325	0.401186				
		0.002154067	0.125694191	24.39	0.014926	2.760467	2.991325	0.250928				
		0.002957397	0.215112022	24.39	0.014926	2.760467	2.991325	0.182554				
		0.268756607	0.003768144	24.39	0.014926	2.760467	2.991325	0.143463				
		0.001319433	0.069969707	24.39	0.014926	2.760467	2.991325	0.118161				
		0.072809692	0.162430223	24.39	0.014926	2.760467	2.991325	0.100446				
		0.009915341	0.038016173	24.39	0.014926	2.760467	2.991325	0.08735				
		0.002595655	0.049861887	24.39	0.014926	2.760467	2.991325	0.077275				
		0.004259605	0.294626176	24.39	0.014926	2.760467	2.991325	0.069283				
		0.272499434	0.002333381	24.39	0.014926	2.760467	2.991325	0.06279				
		0.637284446	1.164974007									

Langmuir Adsorption Isotherms

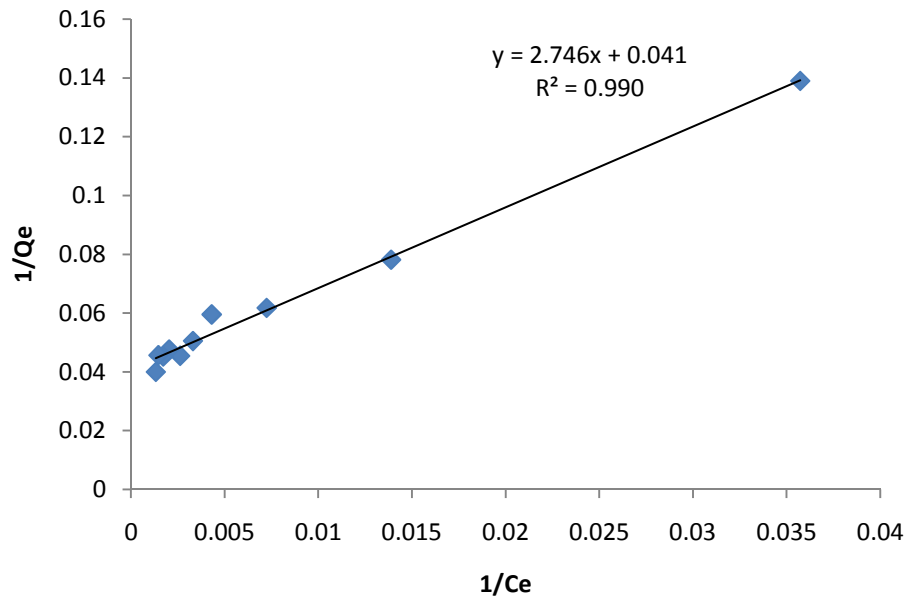


Fig 6.12

Freundlich adsorption Isotherm

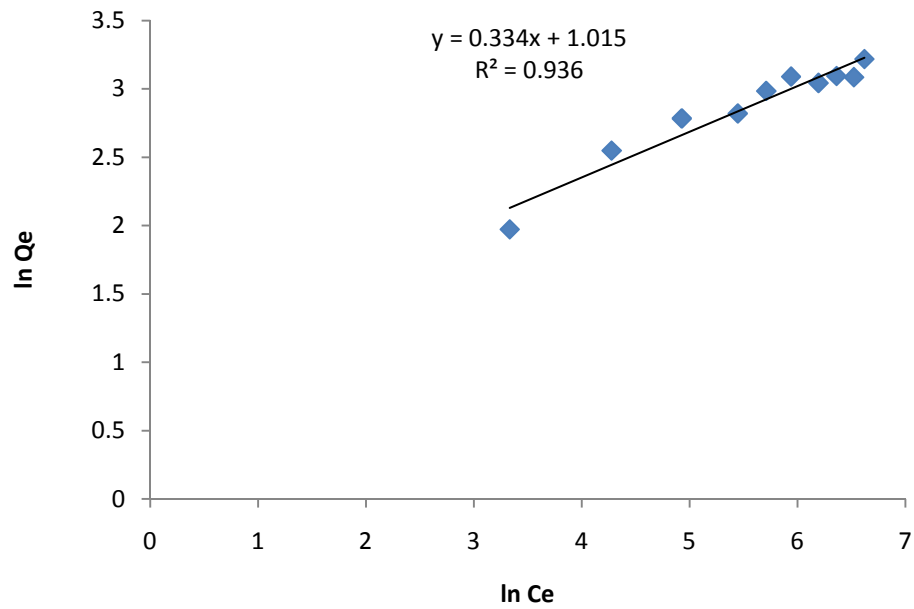


Fig 6.13

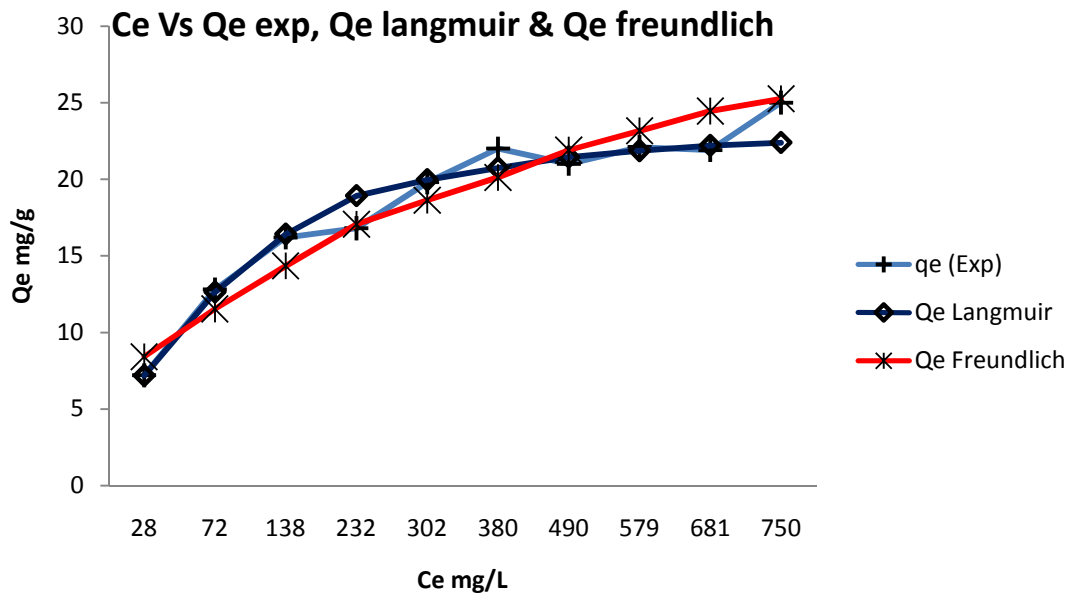


Figure 6.14: Comparison between experimental q_e and predicted q_e value of Langmuir & Freundlich's isotherm

6.7.3 TEMPKIN ISOTHERM

This isotherm contains a factor that explicitly taking into the account of adsorbent – adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against $\ln C_e$ and the constants were determined from the slope and intercept. The model is given by the following equation

$$q_e = \frac{RT}{b} \ln(A_T C_e)$$

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b} \right) \ln C_e$$

$$B = \frac{RT}{b_T}$$

$$q_e = B \ln A_T + B \ln C_e \dots\dots\dots(11)$$

A_T = Temkin isotherm equilibrium binding constant (L/g)

b_T = Temkin isotherm constant

R = universal gas constant (8.314J/mol/K)

T = Temperature at 298K.

B = Constant related to heat of sorption(J/mol)

Tempkin Isotherms

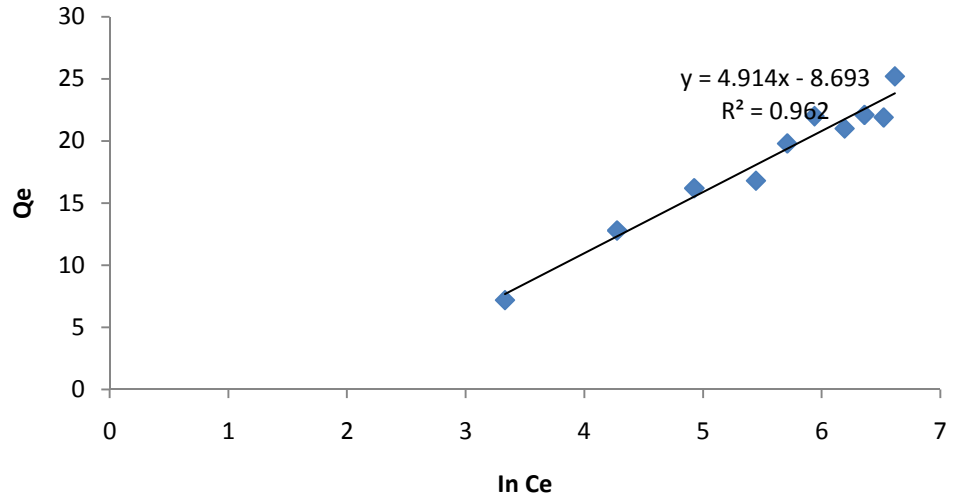


Fig 6.15

Table 6.5

Tempkin			
AT(L/mg)	bT	B	R2
5.863	504.11	4.9147	0.962

Table 6.6: Comparison of chloride adsorption capacities of various adsorbent

S. no	Adsorbent	chloride adsorption capacity
1	Activated Parthenium	medium
2	Crassipes (Water Hyacinth Plant)	medium
3	Silica Gel	average
4	Alumina	low
5	Amberlite	medium
6	Activated carbon	high
7	Cotton stalk	medium
8	Phosphoric Acid treated Parthenium	medium
9	Sulphuric acid treated Parthenium	medium
10	Garlic peel	high
11	Saw Dust	high

6.8 Adsorption kinetics

Adsorption kinetics is the rate of adsorption of adsorbate towards adsorbent. Slow kinetics will require more time to remove adsorbate effectively. Therefore to achieve large amount of adsorbate removal in short time, reactor volume needs to be increased. Chemical adsorption however displayed rapid kinetics due to formation of chemical bond. The adsorption kinetics of metal can be well treated and explained by Lagergren's first and second order kinetic models (Ho 2006). In order to examine the kinetics of chloride ion removal, the first order and second order kinetic models were tested with experimental data obtained from batch chloride removal experiments.

6.8.1 First Order Adsorption Model

The first order kinetic model was suggested by Lagergren for the sorption of solid/liquid systems. First order kinetic model for removal of metal ion was observed by various researchers during removal of chloride by Parthenium (M.Shanmugasundaram Dr.K.Sudalaimani, 2012). The first order adsorption kinetic rate equation is given as

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (\text{A})$$

where, q_e and q_t are the amounts of chloride ions adsorbed on adsorbent (mg/g) at equilibrium and at time t , respectively, and k_1 is the rate constant of first order adsorption $(\text{min})^{-1}$.

After integrating eq. (A) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (\text{B})$$

Thus, chloride uptake can be expressed as a function of time, for first order model by eq. derived from eq. (B).

$$q_t = q_e (1 - e^{-k_1 t}) \quad (\text{C})$$

where, $\exp q_e$ is the experimental chloride uptake value and $\text{cal } q_e$ is the chloride uptake value calculated from the theoretical adsorption kinetic models.

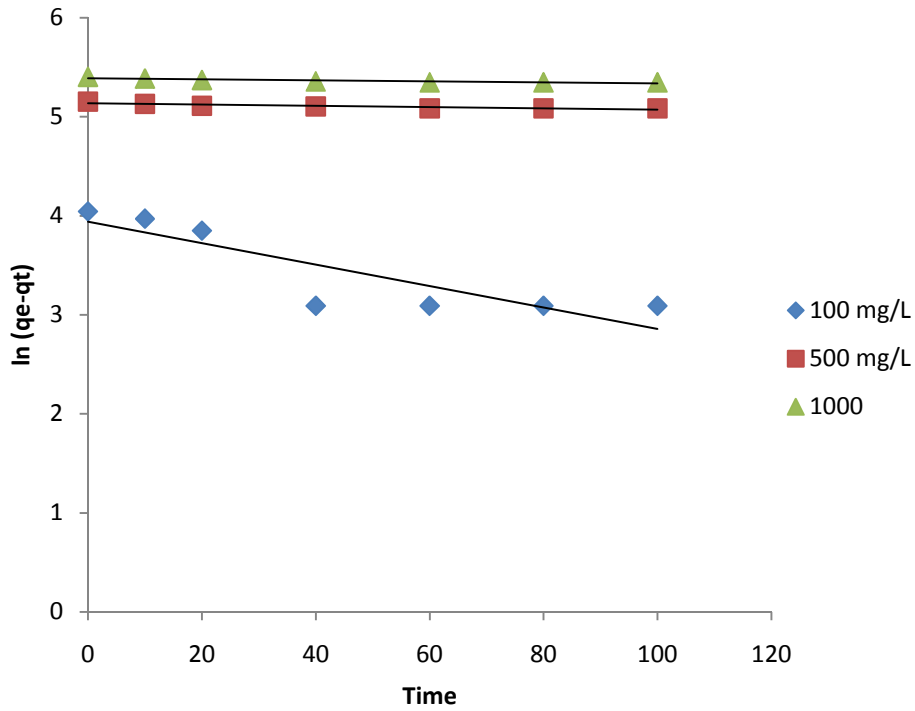


Figure 6.16: Plot of time vs $\ln(q_e - q_t)$ for First Order kinetic model

Table 6.7: Coefficients of first order model for chloride adsorption by Parthenium

Initial chloride concentration (mg/L)	k_1	q_e (Exp)	q_e (Predicted)	Correlation Coefficient (R^2)
100	0.010	72	51.47	0.758
500	0.001	198	169	0.808
1000	0.001	250	218	0.791

6.8.2 Second Order Adsorption Model

The second order adsorption kinetic rate equation was used by various authors (Chiron et al., 2003) and given as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (\text{A})$$

where, q_e and q_t are the amounts of chloride ions adsorbed on adsorbent (mg/g) at equilibrium and at time t , and k_2 (g/mg.min) is the rate constant of the second order adsorption.

Integrating (eq A) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, leads to

$$\frac{1}{q_e - q_t} - \frac{1}{q_e} = k_2 t \quad (B)$$

$$\text{or, } q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \quad (C)$$

$$\text{or, } \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (D)$$

The straight line plots of t/q_t against t (eq. D) for various chloride concentrations are shown in Figure

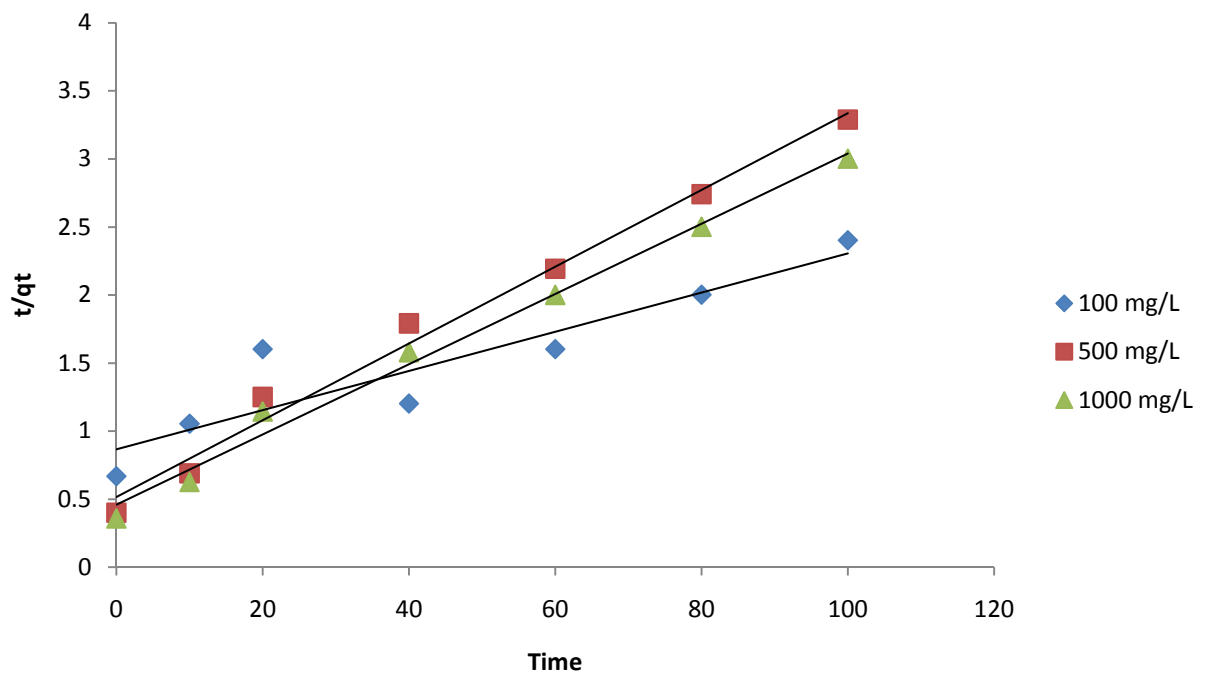


Figure 6.17: Plot of time Vs t/q_t for Second order kinetic model

Table 6.8: Coefficients of second order model for chloride adsorption by Parthenium

Initial chloride concentration (mg/L)	k_2	q_e (Exp)	q_e (Predicted)	Correlation Coefficient (R^2)
100	0.0002	72	71.42	0.842
500	0.0012	198	35.71	0.988
1000	0.0013	250	40	0.989

6.9 LIMITATION OF BATCH PROCESS

Batch process data has several limitation to predict the performance in practical situation such as actual industrial wastewater treatment plant where continuous reactor replaced batch operation. Beside in batch mode adsorption process adsorption equilibrium is achieved and the adsorption characteristics were analyzed by the Isotherms. However in fixed bed column, the adsorption zone or mass transfer zone keeps moving through the bed and the fluid and solid phase in that zone are never able to achieve equilibrium. Adsorption efficiency by column mode depend on flow rate, bed height and influent adsorbate initial concentration.(Deepa et al. 2008) generally the performance of the continuous column mode operation is usually described through the concept of breakthrough curve which is the typical 'S' shape profile of exit concentration (C) as a function of lapse time (t) or throughput volume (V_t) reacted . Throughput volume was calculated using equation.

$$V_t = Q \cdot t$$

Where Q is volumetric flow rate (mL/min)

Usually breakthrough is defined as phenomenon when concentration of adsorbate from column is about 3-5% (chen et al. 2003, Malkoc et al. 2006) . However breakthrough at 1 % was also considered and reported on basis of effluent discharge limit for specific metal adsorbate (Vijayaraghavan et al. 2005). Employment of breakthrough of 50% was also reported for removal of Pb (II) using treated granular activated carbon (Goel et al. 2005).

6.10 MODEL ON COLUMN PERFORMANCE

Optimization of parameters in the continuous adsorption process by experimental methods is an expensive and time consuming. It would be much cheaper and faster to use mathematical modeling to predict the duration of the column before regeneration become necessary (Warchol and Petrus 2006). Moreover, it is hard to generalized operational design parameters, therefore, theoretical models taking in to account of chemical and physical conditions become important (chen et al. 2003). Some of the well known mathematical models applied for column mode operation are Bed Depth Service Time (BDST) model, Thomas Model, Theoretical breakthrough curve etc.

6.10.1 BED DEPTH SERVICE TIME (BDST) MODEL

The Bohart-Adams equation can be represented as (Bohart and Adams 1920):

$$\ln\left(\frac{C_o}{C_b} - 1\right) = \ln(e^{k_{ads}N_0(z/u)} - 1) - k_{ads}C_0t_s$$

Further, Hutchins (1973) modified the Bohart Adams equation and presented a linear relationship between the bed depth and service time which required only three fixed bed tests to collect the necessary data.

$$t_s = \frac{N_0 Z}{C_0 u} - \frac{1}{K_{ads} C_0} \ln \left(\frac{C_0}{C_b} - 1 \right)$$

Where, t_s is the service time at breakthrough point (h), N_0 the dynamic bed capacity (mg L^{-1}), Z the packed- bed column depth (cm), u the linear flow rate (cm/h) defined as the ration of volumetric flow rate $Q(\text{cm}^3/\text{h})$ to the cross section area of the bed $A (\text{cm}^2)$, C_0 and C_b are respectively the influent and the breakthrough adsorbate concentration (mg/L) and K_{ads} the adsorption rate constant (L/mg.h). Plotting service time (t_s) versus bed depth (Z) will generate a straight line equation having slope of $(N_0/C_0.u)$ and the intercept of $(-)\frac{1}{K_{ads}C_0} \ln \left(\frac{C_0}{C_b} - 1 \right)$. Critical bed depth (Z_0) represents the theoretical minimum depth of column that would be able to prevent the adsorbate concentration from exceeding C_b . It is obtained when breakthrough is immediate and it can be calculated by substituting $t_s = 0$ in equation as below

$$Z_0 = \frac{u}{K_{ads} N} \left(\frac{C_0}{C_b} - 1 \right)$$

According to BDST model equation, the data collected from one flow rate experiment can predict the system with different flow rate. When an experiment conducted at flow rate Q_1 , yields an equation of the form

$$t_s = a_1 z + b_1$$

the predicted equation for new flow rate Q_2 is given by :

$$t_s = a_2 z + b_1$$

$$\text{and } a_2 = a_1 \left(\frac{Q_1}{Q_2} \right)$$

where a_1 and a_2 are the slop at flow rate Q_1 and Q_2 respectively. However the intercept b_1 remained same since it is independent of flow rate in linearized BDST equation. BDST equation can also be used to design system for treating other influent solute concentration using the data of a previous laboratory experiment of one influent solute concentration. When an experiment conducted at initial concentration C_1 , yield an equation of the form

$$t = r_1 X + S_1$$

The predicted equation for new flow rate Q_2 , is given by:

$$t = r_2 X + S_2 \text{ and}$$

The new slop and intercept values can be determined as :

$$r_2 = r_1 \left(\frac{C_1}{C_2} \right)$$

$$s_2 = s_1 \frac{C_1}{C_2} \left(\frac{\text{Ln} \left[\frac{C_2}{C_F} - 1 \right]}{\text{Ln} \left[\frac{C_1}{C_b} - 1 \right]} \right)$$

Where, r_1 and r_2 is slopes at influent concentration C_1 and C_2 respectively, S_1 and S_2 are intercept at influent concentration C_1 and C_2 respectively, C_F is effluent concentration at influent concentration C_2 and C_b is effluent concentration at influent concentration C_1 .

6.10.2 COLUMN ADSORPTION EXPERIMENTS

Continuous flow adsorption experiments were conducted in PVC columns of 4.0 cm inside diameter. At the top of the column, the influent fluoride solution (1000 mg /L) was pumped through the packed column (22, 44 and 66 cm), at flow rates of 5, 10 and 15 mL/min, using a peristaltic pump. Samples were collected from the exit of the column at regular time intervals and analyzed for residual fluoride concentration at pH 7. The parthenium first activated and then it was used as bio adsorbent .The saturation capacity for the Parthenium in these column studies was calculated from the following equation where q_e is the fluoride adsorbed (mg/g), C_0 is the influent fluoride concentration (mg/L), C is the effluent fluoride concentration (mg/L), VE is the volume of solution required to reach the exhaustion point (L), and m is the mass of adsorbent (g).

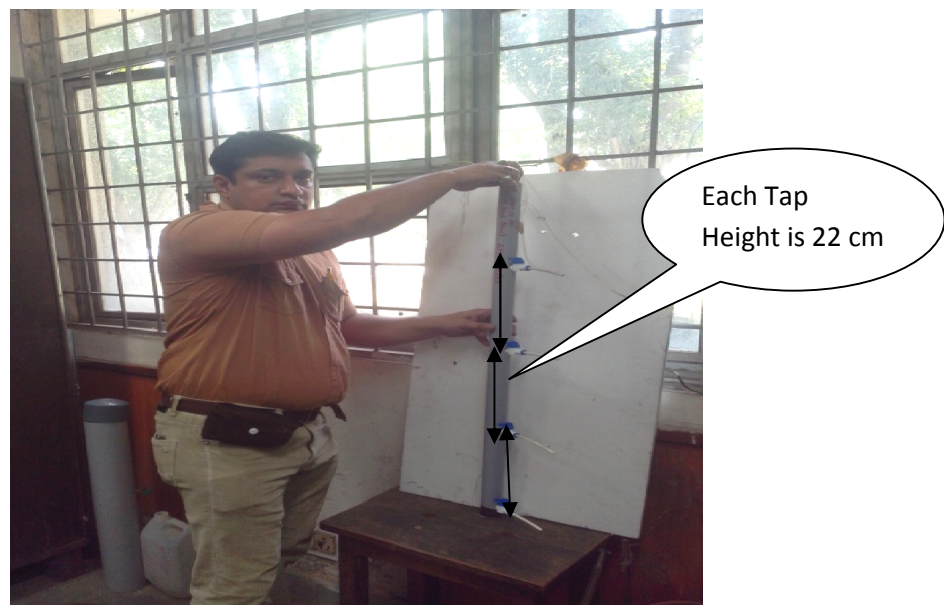


Fig 6.18



Fig 6.19

6.10.3 EFFECT OF FLOW RATE

The adsorption columns were operated with different flow rates (5, 10, and 15 mL/min) until no further chloride removal was observed. The breakthrough curve for a column was determined by plotting the ratio of the C_e/C_0 (C_e and C_0 are the chloride concentration of effluent and influent, respectively) against time, as shown in Fig6.20. The column performed well at the lowest flow rate (5 mL/min). Earlier breakthrough and exhaustion times were achieved, when the flow rate was increased from 5 to 10 mL/min. The column breakthrough time ($C_e/C_0=0.05$) was reduced from 65 to 35 min, with an increase in flow rate from 5 to 10 mL/min. This was due to a decrease in the residence time, which restricted the contact of chloride solution to the Parthenium. At higher flow rates the chloride ions did not have enough time to diffuse into the pores of the Parthenium and they exited the column before equilibrium occurred.

Successful design of a column chloride adsorption process requires a description of the dynamic behavior of chloride in a fixed bed. Various simple mathematical models have been developed to describe and possibly predict the dynamic behavior of the bed in column performance. One model used for continuous flow conditions is the Thomas model, which can be written as:

$$C_e/C_0 = 1/1 + \exp((k_{th}/Q)(q_0M - C_0V_{eff}))$$

Eq. can be expressed in linear form as:

$$\ln[C_0/C_e - 1] = k_{th}q_0M/Q - k_{th}C_0t$$

where V_{eff} is the volume of effluent (L), k_{th} is the Thomas model constant (L/mg h), q_0 is the adsorption capacity (mg/g), Q is the volumetric flow rate through column (L/h), M is the

mass of adsorbent in the column (g), C_0 is the initial chloride concentration (mg/L) and C_e is the effluent chloride concentration (mg/L) at any time t (h). The Thomas model constants k_{th} and q_0 were determined from a plot of $\ln [C_0/C_e - 1]$ versus t at a given flow rate. The model parameters are given in Table 6.10. The Thomas model gave a good fit of the experimental data, at all the flow rates examined, with correlation coefficients greater than 0.97, which would indicate the external and internal diffusions were not the rate limiting step. The rate constant (k_{th}) increased with increasing flow rate which indicates that the mass transport resistance decreases. The reason is that the driving force for adsorption is the chloride concentration difference between Parthenon and solution.

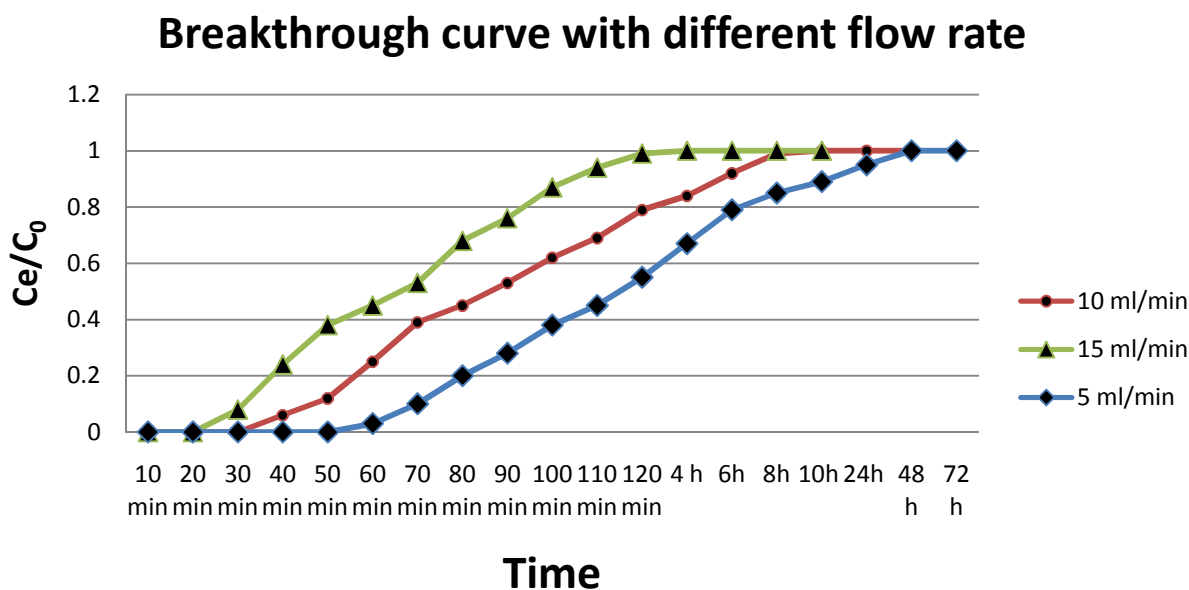


Fig 6.20 Breakthrough curves expressed as C_e/C_0 versus time at different flow rates (initial chloride Concentration 1000 mg/L, initial pH 7, bed depth 66 cm and temperature $30 \pm 1^\circ\text{C}$)

6.10.4 EFFECT OF BED HEIGHT

The accumulation of chloride in a fixed-bed column is dependent on the quantity of adsorbent inside the column. In order to study the effect of bed height on chloride retention dry activated parthenium of three different bed heights, viz. 22, 44, and 66 cm, were used. A chloride solution of fixed concentration (1000 mg/L) was passed through the fixed-bed column at a constant flow rate of 5 mL/min. As depicted by Fig. 6.21 the breakthrough time varied with bed height. Steeper breakthrough curves were achieved with a decrease in bed depth. The breakthrough time decreased with a decreasing bed depth from 44 to 22 cm, as binding sites were restricted at low bed depths. At low bed depth, the chloride ions do not have enough time to diffuse into the surface of the Parthenium and a reduction in breakthrough time occurs. Conversely, with an increase in bed depth, the residence time of

chloride solution inside the column was increased, allowing the chloride ions to diffuse deeper into the Parthenium. The breakthrough service time (BDST) model is based on physically measuring the capacity of the bed at various percentage breakthrough values. The BDST model constants can be helpful to scale up the process for other flow rates and concentrations without further experimentation. It is used to predict the column performance for any bed length, if data for some depths are known. It states that the bed depth, Z and service time, t of a column bears a linear relationship. The rate of adsorption is controlled by the surface reaction between adsorbate and the unused capacity of the adsorbent. The BDST equation can be expressed as follows

$$t_s = \frac{N_0 Z}{C_0 u} - \frac{1}{k_{ads} C_0} \ln \left(\frac{C_0}{C_b} - 1 \right)$$

where C_b is the breakthrough chloride concentration (mg/L), N_0 is the adsorption capacity of bed (mg/L), Z is depth of column bed (cm), u is the linear flow velocity of chloride solution through the bed (mL/cm²h), K_a is the rate constant (L/mg h). The column service time was selected as the time when the normalized concentration, C_e/C_0 reached 0.05. A plot of service time versus bed depth, at a flow rate of 5 mL/min was linear. The high correlation coefficient value ($R^2 = 0.988$) indicated the validity of the BDST model for the present system. The values of N and K_a were evaluated from the slope ($N/C_0 u$) and intercept ($(1/K_a C_0) \ln[(C_0/C_b) - 1]$) of the BDST plot. The values of BDST model parameters are presented in Table 6.9. The value of K_a characterizes the rate of transfer from the fluid phase to the solid phase. If K_a is large, even a short bed will avoid breakthrough, but as K_a decreases a progressively deeper bed is required to avoid breakthrough

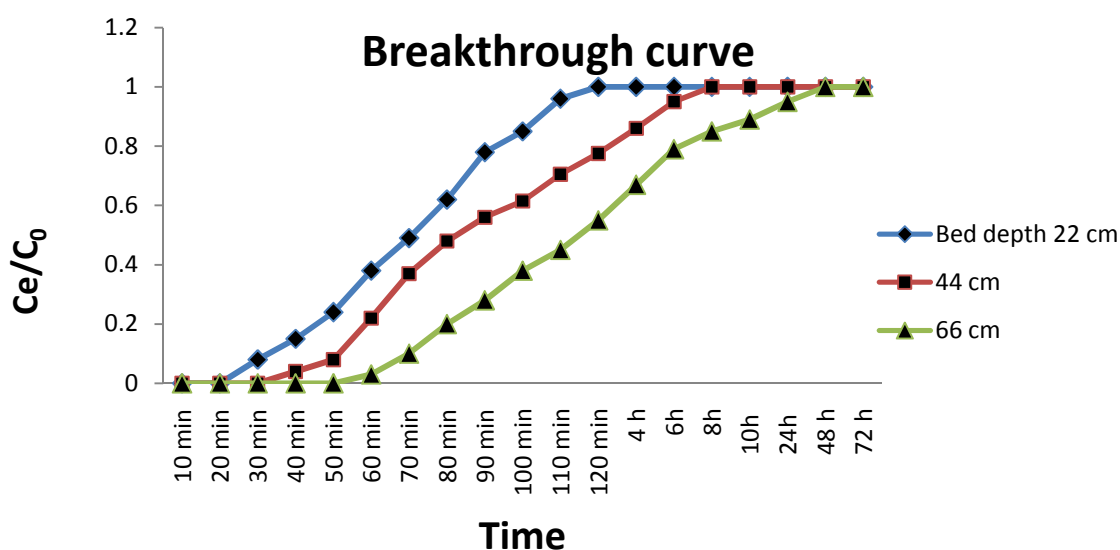


Fig 6.21 Breakthrough curves expressed as C_e/C_0 versus time at different bed depth (initial chloride Concentration 1000 mg/L, initial pH 7, flow rate 5 mL/min and temperature $30 \pm 1^\circ\text{C}$)

6.10.5 Thomas model and BDST model parameters for the adsorption of chloride on Parthenium

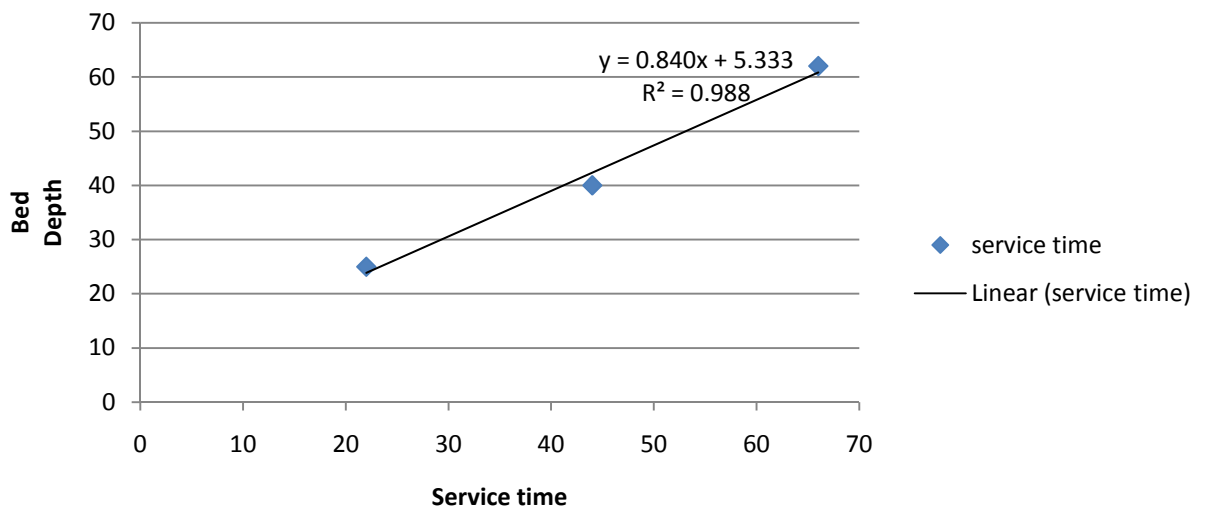


Fig 6.22 Parameters for BDST Models

Table 6.9 BDST MODEL COEFFICIENT

N (mg/L)	Ka (L/mg h)	R ²
20063	5.52X 10 ⁻⁴	0.998

PARAMETERS FOR THOMAS MODEL

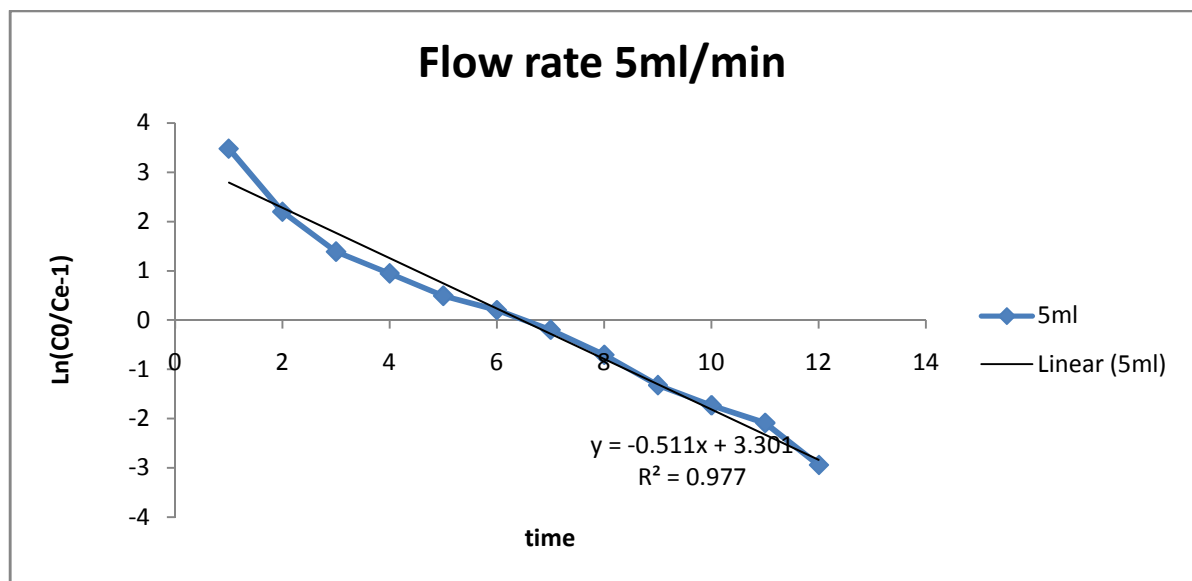


Fig 6.23

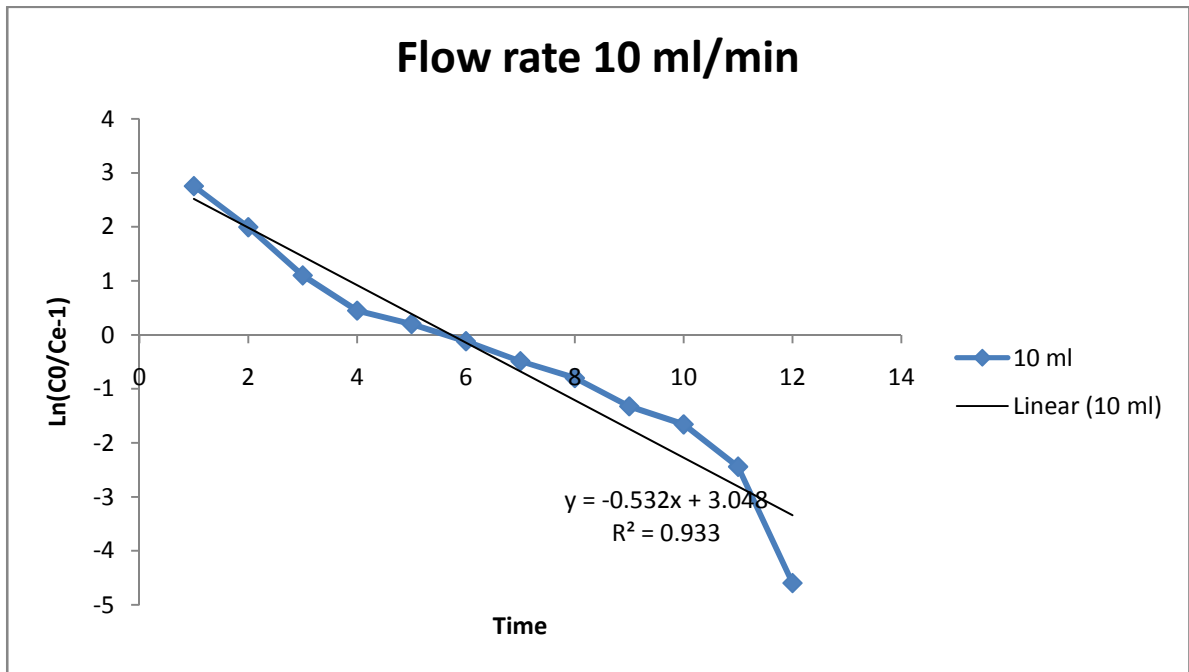


Fig 6.24

Table 6.10 THOMAS MODEL COEFFICIENT

Flow Rate (ml/min)	q_0 (mg/g)	K_{th} (L/mg h)	R^2
5	3.87	0.000511	0.977
10	6.85	0.000532	0.933
15	7.95	0.00065	0.945

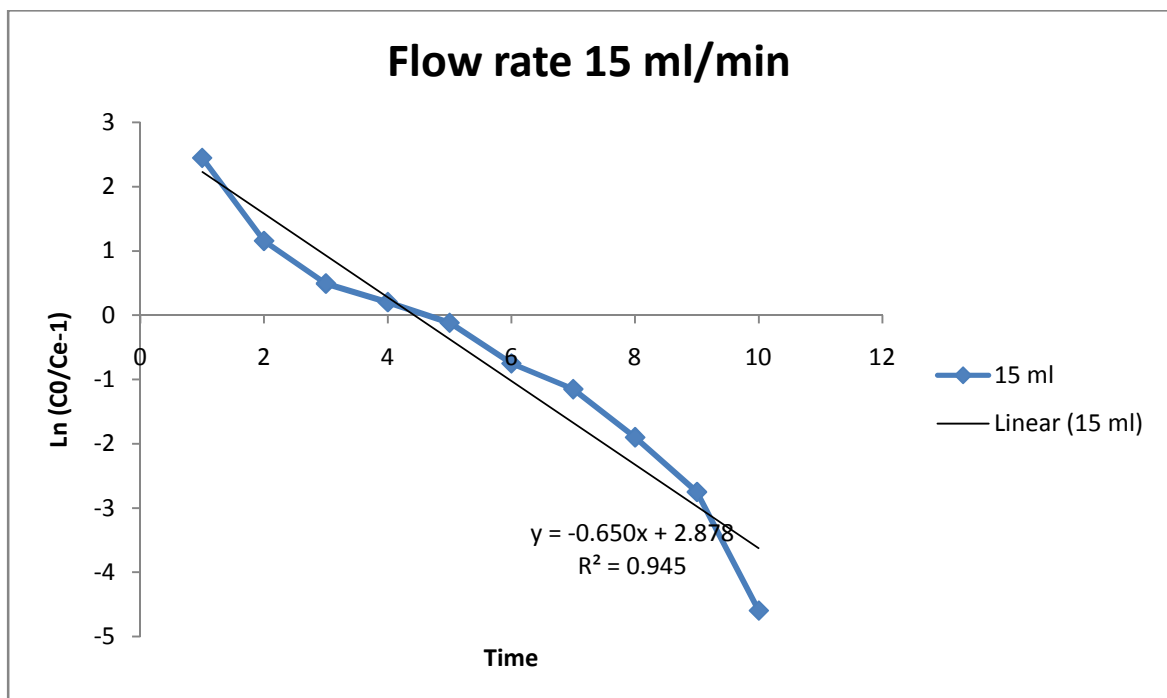


Fig 6.25

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

From the present study, major conclusions were drawn and are listed below.

1. Pond and the deep well are the sources of water supply for the rural area where water supply scheme do not exist.
2. Characteristic of pond water is done. The DO level in the pond water is found very low comparing to well water. This may be due to the presence of green algae in the water. The DO concentration also varies with Temperature. Low temperature shows high DO level in water.
3. Due to very low DO level, there is no aquatic life surviving in the pond of this village.
4. Phosphate level is fluctuating up and down with time. There is no major change. High phosphate level is creating eutrophication problem in some area.
5. TDS concentration is also fluctuating up and down with time and has no major change with time as the outflow and in flow of water is maintaining the concentration of TDS.
6. The Parthenium is showing maximum absorbance at pH 7.
7. During the variation in the adsorbent dose, corresponding increase in the adsorption was noted with increase in the dose in the solution.
8. The batch process results were best suited in to the Langmuir Isotherm instead of Freundlich Isotherm. R^2 of Langmuir is 0.99 and Freundlich is 0.93.
9. Freundlich isotherm 'n' value of 2.99 which is less than 10 and greater than 0 suggest the favorable adsorption of chloride by Parthenium.
10. The performance of Parthenium when subjected to actual water decrease by 15-25% due to the presence of other co-ions.
11. BDST model is best suited to the observation and adsorbent performance compare to Thomas model. The high correlation coefficient value ($R^2= 0.998$) indicated the validity of the BDST model for the present system.

7.2 RECOMMENDATION:-

Following recommendations are made from the study:

1. One of the solutions is maintaining continuous artificial aerations in the pond to increase the current DO level. This can be achieved by providing electrical pump and fountain system.

2. The rain water can also be diverted by constructing little drains from catchment areas and other nearby sources and by means of small tributaries. Another best way of receiving water is by means of ground water discharge. Special attention should be given for replenishment through ground water recharge. Programs should be needed to collect flood water for recharging ground water and filling water bodies.
3. There should be control on the discharge of untreated waste of high organic content from the village streets and residences. Treated water must not be mixed with untreated water. Additional low cost ETP's should be constructed nearby and obstruct to contribute pollutant load.
4. Provision of conveying storm water to the pond also helps in recharging of pond. Storm Water can be collected or directly allowing it to enter drains can be a feasible option.
5. Encroachment on pond bank need to be removed so that recharging of pond can take Place. A slow sand filter can also be installed for the periodic purification of pond water.

7.3 FUTURE SCOPE OF THE STUDY:-

This study can be extended for future research with other Bio adsorbing materials. These materials may be easily available. Broad study on column can be done with variation in flow rate and different bed depth of the bio adsorbent. Batch study can also be done with different adsorbent dose and different contact time. pH variation with different adsorbent dose & pollutant concentration study may also be carried out in batch process. There are many parameters which when alter may give stunning results for Bio-adsorption. As chloride is less harmful to human body therefore the study may also be carried out for removal of other harmful heavy metals (Arsenic, lead, fluoride etc.) from contaminated water.

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