PHYTOCHEMICAL MEDIATED SYNTHESIS OF NICKEL OXIDE NANOPARTICLES USING ANANAS COMOSUS AND ITS APPLICATION IN WATER TREATMENT

A PROJECT REPORT

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Submitted By:

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CANDIDATE'S DECLARATION

I, **Prachi Thukral**, **2K21/MSCCHE/55** student of M.Sc. (Department of Applied Chemistry), hereby declare that the project Dissertation titled **"Phytochemical Mediated Synthesis of Nickel Oxide Nanoparticles Using Ananas Comosus and its Application in Water Treatment"** which is submitted by me to the Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Science is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship, or other similar title or recognition.

Place: Delhi
Date: **(PRACHI THUKRAL)**

<u>CERTIFICATE</u>

I hereby certify that the Project Dissertation titled **"Phytochemical Mediated Synthesis of Nickel Oxide Nanoparticles Using Ananas Comosus and its Application in Water Treatment"** which is submitted by **Prachi Thukral**, **2K21/MSCCHE/55**, **Department of Applied Chemistry, Delhi Technological University, Delhi** in partial fulfillment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the student under my supervision. To the best of my knowledge, this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi   **DR. POONAM SINGH**

Date: **SUPERVISOR**

ACKNOWLEDGEMENT

ABSTRACT

In the present study, Nickel oxide nanoparticles (NiO NPs) were synthesized using *Ananas comosus* (pineapple) plant extract via a completely eco-friendly method where no toxic solvents or precursors were used. Various techniques were used to characterize the synthesized NiO NPs. The XRD analysis indicated that the average crystal size of NiO NPs was 20.31 nm. The FTIR analysis confirms the NiO formation with the Ni-O band's appearance at 465 cm^{-1}.

The synthesized NiO NPs were used to investigate the removal of different azo dyes such as Congo red, methylene blue, and crystal violet that may pose a threat to the environment in water. Among all the investigated dyes, NiO NPs have been demonstrated to be effective adsorbents for the removal of hazardous anionic dyes in polluted water, such as Congo Red (CR). Therefore, further studies such as effect of contact time, effect of different concentrations, and effect of adsorbent dosage were studied for the removal of CR dye. It was found that Langmuir's isotherm ($R^2 = 0.97629$) and pseudo-second-order ($R^2 = 0.99431$) provided the best fit for the isotherm and kinetic models, respectively. In addition, the sorbent's maximum adsorption capacity was calculated to be 46.92 mg/g. Hence, NiO NPs synthesized via a greener approach can be used as an efficient sorbent for the sequestration of toxic dyes from wastewater.

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LIST OF ABBREVIATIONS

Abbreviations	Full Form
NiO	Nickel Oxide
NPs	Nanoparticles
Fig.	Figure
FTIR	Fourier-transform infrared spectroscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
CR	Congo Red
MB	Methylene Blue
CV	Crystal Violet
MO	Metal Oxide
MONPs	Metal Oxide Nanoparticles

CHAPTER 1 INTRODUCTION

The deterioration of the natural environment has been brought about over time by human ambition and the desire for comfort. Because of this, the air quality has gotten worse, soils have been overused and turned barren due to improper management, and our natural waters are now seriously polluted, which is a problem that needs to be addressed [1].

Pollutants like heavy metals, radionuclides, phenolics, pesticides, and others contribute to environmental pollution. Despite this, dyes are a significant class of pollutants produced in significant quantities by the textile, dyeing, paper, pulp, tanneries, and paint industries. It is widely accepted that dyes reduce light penetration, significantly reducing photosynthetic activity. Many dyes' toxic and carcinogenic properties also threaten aquatic biota and human health.

After textiles are dyed, the leftover dye-concentrated wastewater is frequently released into the environment at high pH and temperatures without being treated. Ambient water bodies will be affected by these events as they can't transfer oxygen and are unable to self-purify [2]–[4]. The wastewater produced by the paint industry is a challenging effluent to treat due to high levels of suspended particles, and other dangerous compounds, as well as the aesthetic harm it does to the surrounding environment [5], [6]. There is generally a risk of cancer (bladder, kidney, and liver) as well as mutagenic effects and toxic effects from dyes. Furthermore, they can cause skin, eye, and mucous membrane allergies [7], [8]. Water contamination is a major issue on a global scale, and it is past time that we understood how serious it is. It is urgently necessary to remove contaminants from water, but finding an economical and environmentally safe way to do so is a difficult problem for researchers.

1.1 BACKGROUND OF PRESENT RESEARCH

Many industries, such as textile, leather, paper, printing, plastic, and so on, produce large amounts of wastewater with color [9]. The elimination of this type of pollution is crucial because dye pigments have a significant impact on the quality of water. The intricate chemical structures of dyes make them challenging to process through municipal waste

treatment systems[10]. The visible and undesirable qualities of dye are present even in little amounts. Additionally, the color that dyes in water produce makes it visually unattractive. Depending on the dye concentration and the length of exposure, they can have either acute or chronic impacts on exposed species. Additionally, a lot of colors are thought to be hazardous and potentially cancer-causing[9]–[12].

Due to the harm they cause and their widespread distribution in ecological environments, the separation and determination of these effluents have become an important study of environmental analysis. [13], [14].

1.2 RESEARCH OBJECTIVES

In order to remove dyes from industrial effluents, several physical, chemical, and biological decolorization techniques have reportedly been examined [15]–[18]. Since adsorption doesn't require a high temperature and allows the removal of multiple coloring components at once, this approach is found to be the most competitive among the ones that have been researched [9]. Adsorption's excellent efficiency, financial viability, and ease of design account for its adaptability [11]. For this investigation, two cationic dyes (Methylene Blue and Crystal Violet) and one anionic dye (Congo Red) were chosen as there are several factors that can affect the adsorption process. The usage of nano-based adsorbent for the adsorption of dyes is explored in this work. Among all of them, MO NPs are thought to be the best due to their biocompatibility, adaptable biosynthesis, and high stability. This has fueled the intense interest in the creation and synthesis of nanoparticles among scientists.

The Ananas comosus plant extract has been utilized in this study to produce NiO NPs. A tropical plant called the pineapple, *Ananas comosus* (L.) Merr produces a palatable fruit. The qualitative phytochemical examination of the *A. Comosus* plant extract also identified the presence of flavonoids, phenols, tannins, carbohydrates, glycosides, and proteins[19]. Also, the plant is easily available and is cost-effective. To the best of our understanding, this plant's potential has not yet been explored much.

Hence, in the current study, NiO nanoparticles are created in a novel, simple, and environmentally friendly manner and are used for dye adsorption properties that have received a lot of attention up to this point. The impact of the introduction of NiO NPs into the different dyes was investigated.

CHAPTER 2 LITERATURE REVIEW

2.1 NANOTECHNOLOGY

The field of nanotechnology has advanced significantly over the last few decades. The field focuses on the construction and use of nanoscale materials. It is the capacity to accurately construct objects, systems, and materials [20]. Nanotechnology is defined by the National Science Foundation of the United States as the study of systems and materials that exhibit the characteristics listed below: -

- At least one dimension must be in the range of 1 to 100 nm.
- demonstrate a fundamental ability to govern the physical and chemical properties of molecule configurations.
- The capacity to join with other building blocks to create larger buildings [21].

As materials at the nanoscale have properties that are very different from bulk materials, nanoscale science and technology are significant. When utilized in similar applications, nanoparticles exhibit improved performance characteristics when compared to bulk materials.

Due to its advantages over other conventional approaches, such as portable, quick, and sensitive detection, semiconducting metal oxide has received a lot of consideration. Because of their special qualities, engineered MONPs are among the most widely used produced nanomaterials. NPs also have peculiar adsorptive characteristics, quick diffusions, and are unstable under extreme circumstances [22].

In nanotechnology, novel materials are studied and developed at a nanoscale and several synthetic methods were employed. There are generally two types of practices for creating nanomaterials and nanostructures when it comes to synthetic procedures [23]:

1. Bottom-up Approach
2. Top-down Approach

(I) A bottom-up strategy that involves downsizing material components to the atomic level and then allowing them to self-assemble into larger, more stable structures using nanoscale physical forces. This technique produces nanostructures. With this method, atomic or

molecular parts are arranged into hierarchical nano complexes; (II) In this paradigm (top down), macro-structures are controlled from the outside and nanostructures are produced from them. The top-down method, such as ball milling, mask etching, etc., adds or removes small layers of bulk materials [24], [25].

2.2 SYNTHESIS OF METAL OXIDE NANOPARTICLES

The synthesis of metal oxide nanoparticles has been carried out using a variety of physical and chemical techniques Figure 2.1 [26]–[36]
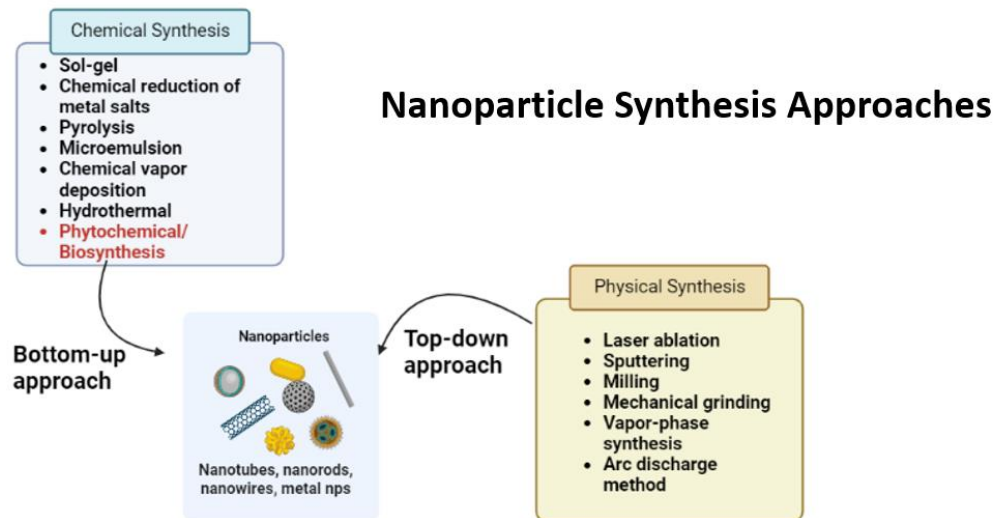
Fig.2.1 Synthetic methods and techniques used in nanotechnology that incorporate conventional procedures

There are several negative aspects to physical and chemical synthesis, such as high energy costs, environmental pollution, and health risks. These factors make them less than ideal-options [37].

2.2.1 Nickel Oxide Nanoparticles

Scientists around the world have recently become interested in nickel oxide (NiO) because of its potential for use in a variety of technological applications [38]–[41]. As a p-type semiconductor with a broadband gap (3.6–4.0 eV), it is widely used in many industries as adsorbents, photocatalytic agents, etc. [42], [43].

NiO NPs have recently been produced utilizing a variety of plant extracts, including those from *the Opuntia ficus indica* [44], *Calotropis gigantea* [34], *Callistemon viminalis* [35], *Gymnema Sylvestre* [45], and *Rhamnus virgate* [36].

Due to its excellent ferromagnetic characteristics, strong coercive forces, and chemical stability, NiO NPs production and its properties constitute an important area of research. NiO NPs are a crucial component of modern technology. Due to their natural abundance and capacity to catalyze reactions via several routes, they are utilized as inexpensive catalysts [46].

NiO NPs exhibit remarkable capacitance qualities outside of medicinal applications, serving as an energy storage device. Another application for NiO NPs is in the breakdown of wastewater dyes. NiO NPs have been observed to photo-catalytically degrade endocrine-disrupting chemicals such as 4-chlorophenol, p-nitrophenol dye, Congo red, and others[47]. NiO NPs are highly effective catalysts that are less expensive than other transition metals and noble metals[48].

2.3 METHODS INVOLVED IN THE SYNTHESIS OF NIO NPS

NiO NPs have been synthesized using a variety of physical, chemical, and biological techniques. Chemically, the sol-gel method is widely used to create NiO nanoparticles [49]-[50]. NiO NPs in basic solutions have been generated via the co-precipitation approach [51]. It's interesting to note that the combustion technique has also been used to create NiO NPs. One common technique for creating NiO NPs is laser ablation. In this technique, a laser is utilized as the energy source [52]. In addition to other methods, spray pyrolysis of aqueous solutions of Ni precursors, has also been used to create NiO NPs[53].

Chemical and physical approaches predominate in NP synthesis practices in the current technological landscape. However, there are a lot of drawbacks attached to them. In order to prepare NPs, physical approaches typically require expensive equipment. The difficult reaction conditions are another drawback of these approaches. Additionally, dangerous chemicals employed in their synthesis, low reaction yields, toxic by-products, and high energy needs make chemical and physical processes unfriendly to the environment[54]. As a result, there has been an increasing trend in recent years toward greener nano synthesis or methods that are bio-based.

Instead of employing conventional chemicals, biological synthesis methods often create NPs from plant extracts, bacteria, fungi, and the precursors. According to Nasrollahzadeh et al, the NPs created using this method are biodegradable, non-toxic, and have improved qualities for biomedical use and the procedures used to create the NPs are economical, secure, sustainable, and ecologically friendly [52].

2.3.1 Green Chemistry in Synthesis of Metal-based Nanoparticles

In order to create novel green synthesis methods, researchers employ the twelve green chemistry principles as a road map.

The main objectives of green synthesis methods are to be safer for human health and more effective than physical or chemical methods. Green synthesis is far more advantageous because it uses commonly available, affordable, and straightforward to obtain raw materials. Plant extracts might be the most efficient biosynthesis way for creating nanoparticles since they can be produced more quickly and cheaply in larger quantities. Plants are widely found in ecosystems and are very simple to collect. They contain enough phytochemicals to take the place of costly, environmentally hazardous, and extremely toxic chemical-reducing agents. Numerous studies have shown that plant extracts contain phytochemicals that can effectively reduce metal ions. In addition, these phytochemicals can perform a variety of capping, stabilizing, and chelating functions during the formation of nanoparticles. Plant-made nanoparticles are a significant advancement in several disciplines. They can catalyze processes that break down hazardous contaminants in water for water treatment.

Green chemistry and nanomaterials are working together to generate benign metal or metal oxide nanoparticles that are environmentally beneficial and use plants, microorganisms, and other natural resources to address toxicity issues [55].

2.3.2 Plant-mediated Synthesis of NiO NPs

In the past 30 years, the usage of plant extracts for the creation of NPs has engrossed a lot of interest. There have been reports of the production of NPs in a variety of plant species. The popularity of the plant-mediated technique is rising because it is easy, environmentally friendly, stable, quick, and economical.

Different plants have varying levels and compositions of organic reducing agents. A mixture of water-soluble metabolites and coenzymes are therefore utilized in the synthesis of NPs in plant-mediated biogenic reduction of metal ions[56].

$NiCl_2.6H_2O$ salt solution and *V. amygdalina* plant extract were used as precursors in the creation of NiO NPs [57]. Additionally, *Raphanus sativus* root-based extract was used to create NiO NPs [58]. Uddin and colleagues were able to provide NiO NPs by using the stem of the *Berberis vulgaris* plant [59]. In addition to leaf, root, and stem extracts, fruit juice-based production of NiO NPs has also been described. For instance, Kumar et al. produced NiO nanoparticles using a salt solution of Ni $(NO_3)_2$ and *Limonia acidissima* natural fruit extract[60].

2.3.3 Limitations of The Green Synthesis of Metal Oxide NPs

Although using plant extract in the synthesis of MONPs offers a very good cost-effective, clean technique, there are some drawbacks to this method. Sometimes, even minute amounts of phytochemicals found in plant extracts perform critical parts such as capping, chelating, and stabilizing agents. To get a good result in these circumstances, the experimental parameters including pH, extract concentration, and time should be maintained.

2.4 DEGRADATION OF DYES USING NiO NPs

Today, wastewater treatment is a major environmental issue. The traditional methods for treating dye-contaminated cost a lot of money. On the other hand, NPs like NiO NPs have great photocatalytic qualities and cause dyes to degrade and are cost effective.

2.5 DYES

Dyestuffs are tinted organic chemical composites that are hydro- or oil-soluble and bind to surfaces or fabrics to give textiles their color. The bulk of dyes is intricate organic compounds that must be resistant to a variety of environmental influences in order to form a strong bond with the polymer molecules that make up the textile fiber [61]–[63].

The majority of the colors are unsaturated and aromatic organic substances. Their naturally occurring color is primarily caused by the existence of chromophores, which are unsaturated chemical groups [64]. The substance to be colored must allow the dyes to penetrate and be permanently attached. Some compounds that lack color can get color by adding an autochrome group. The majority of naturally occurring red dyes, including madder, is based on anthraquinone chromogens as opposed to azo dyes, which have no natural counterparts [65].

Due to their chemical stability, simplicity of synthesis, and wide range of colors, dyes are frequently employed in the textile industry [66]. However, dyes pollute once they are released, and the discharge results in additional issues such as energy use, emissions into the atmosphere, solid waste, and odors. As a result of the discharge, other sources of potential risk are created, including persistence, bioaccumulation, and cancer from chlorination products (SPC), all of which must be handled before being released into the sewerage system. 12% of dyes, regrettably, are examined before being released into the receiving networking, where they remain stable and resistant to deterioration because of their unique characteristics[67], [68].

However, a number of dyes are hazardous, resistant to degradation, and carcinogenic, seriously endangering human safety and health [69]. Light, heat, and natural oxidants can

cause dyes to oxidize, so dye removal from wastewater is imperative to prevent their oxidative destruction. Many dyes have excellent chemical and thermal stability, which means they are resistant to oxidative degradation [70].

More than one million different colors are visible to human sight, all of which are present in our natural surroundings. These stunning and distinctive hues draw people's attention away from their surroundings, and commonplace objects have been designed to imitate them. Archaeological research demonstrates that the practice of dying has existed since the dawn of human society.

2.5.1 CLASSIFICATION OF DYES

It has become necessary to classify dyes as a result of the growth in both their variety and quantity throughout history. On the basis of their structure, source, color, solubility, and application techniques, there are numerous different classes. In essence, the most typical classification is based on their chemical makeup and use [71]. They are categorized as reactive, direct, and acid (anionic dyes), basic (cationic dyes), or disperse and vat (non-ionic dyes) depending on the application method [72].

2.5.2 DYES USED IN THIS STUDY

Table 2.1 depicts the information regarding dyes that are investigated in this study.

Dye	Molecular Formula	Molecular mass (g/mol)	λ_{max} (nm)	Appearance
Congo Red	$C_{32}H_{22}N_6Na_2O_6S_2$	696.7	498	Red to red-brown solid
Methylene Blue	$C_{16}H_{18}ClN_3S$	319.9	664	Dark green crystals or powder
Crystal Violet	$C_{25}N_3H_{30}Cl$	408	590	Dark green powder with metallic shine

Table 2.1 Information of different dyes used in the study

The following figures (2.2, 2.3, and 2.4) depict the structure of investigated dyes.
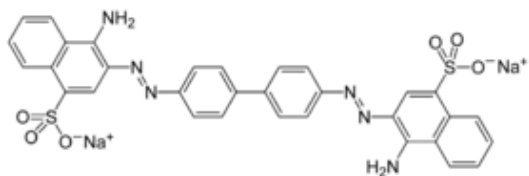
Fig.2.2 Structure of Congo Red Dye
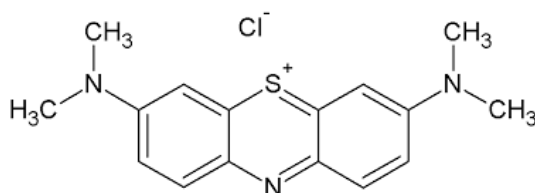
Fig.2.3 Structure of Methylene Blue Dye
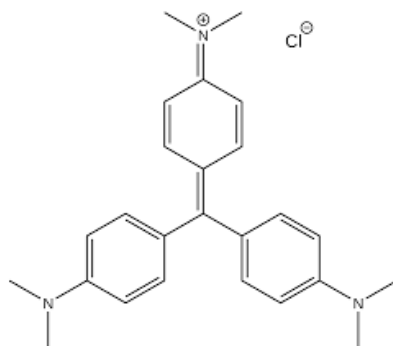
Fig.2.4 Structure of Crystal Violet Dye

2.5.3 DYE REMOVING METHODS, TECHNOLOGIES

Reverse osmosis[73], coagulation/flocculation [74], electrocoagulation [75], biological treatment [76], ion exchange and advanced oxidation [77], adsorption on activated carbon [78], and biosorption using natural materials [79] are a few of the technologies that have been used to remove dyes. In this situation, nanotechnology can be quite effective for the adsorption of colors from aqueous solutions [80]. This procedure is regarded as one of the most effective options to take into consideration for the treatment of toxic and/or refractory

effluents because of the physicochemical properties of the nanoparticles [81]. While these methods are effective, they are also inefficient and costly, produce a large number of hazardous byproducts, and are difficult to dispose of toxic sludge. Many studies have been conducted on the adsorption process since it is widely applicable, low-cost, and adsorbent materials are readily available [82].

Adsorption techniques have gained popularity because they are effective at eliminating contaminants that are too stable for other techniques [83]. The procedure can also be used singly (mostly to remove dye from synthetic or simulated wastewater) or in combination with other cleaning techniques to completely clean wastewater [83].

2.6 GENERAL ASPECTS OF THE ADSORPTION PROCESS

2.6.1 ADSORPTION

Adsorption is a technique by which an adsorbate is attracted to the surface of an adsorbent and held there until equilibrium in the amount of the adsorbate is reached and no additional adsorption proceeds. It might alternatively be described as the development of an adsorbate layer caused by the attraction of Van der Waals forces on the surface of an adsorbent. According to Ademiluyi and Nze [84], One of the finest techniques for eliminating contaminants from solutions is adsorption.

2.6.1.1 Factors Affecting the Adsorption Process

The efficiency of liquid phase adsorption and, consequently, the efficiency of the method used to treat water are influenced by a number of variables. The features of the utilized adsorbent, the type of pollutant (in this study, the dyes), and its chemical structure all have an effect on how well sorption works. These physicochemical parameters include, but are not limited to, the adsorbent/adsorptive interaction, the surface of the adsorbent's reactivity and structure of pores, the dimension of the particles, the adsorbent's nature, the presence or absence of other ions in the solution, pH, pressure, temperature, and contact time. It is

also important to consider the adsorbate's characteristics, including its polarity, size, molecular weight, and molecular structure [85].

When constructing an adsorption process, the effects of each of these characteristics should be taken into attention. The improvement of such surroundings will be very helpful for the advancement of large-scale dye removal technologies.

2.6.2 Adsorbents for Dyes Removal

Recent publications of several works have as their main objective the investigation of the removal of various contaminants utilizing adsorbent materials [86]–[88].

Adsorption efficiency will depend on the porosity, surface area, and pore size of the adsorbent. Numerous conventional adsorbents, including activated carbon, zeolites, limestone, natural clay, and industrial and agricultural waste, have been employed over time to remove colors from wastewater [89]. To increase the performance of these traditional adsorbents, however, surface functionalization is required, and this requires expensive and difficult multistep synthesis techniques that are not suitable for large-scale manufacturing [90].

Nano adsorbents have been developed to overcome the limitations of conventional adsorbents [91]. These materials have exceptional physical and chemical properties that make them superior adsorbents to their corresponding bulk materials [92], [93]. These have a high adsorption ability to remove toxins [94], have great potential to remove pollutants from air and wastewater, and provide new opportunities for environmental applications [95].

2.6.3 EQUILIBRIUM ISOTHERM AND KINETICS MODELING

In order to set up experiments for optimal dye adsorption, equilibrium isotherms, and kinetic modeling are essential in adsorption investigations.

The efficacy of sorption is significantly influenced by kinetics. Adsorption kinetics essentially describes the rate of solute absorption and the residence duration of adsorbates at the solid-liquid interface. Adsorption isotherms are helpful in defining how adsorbate and

adsorbent interact. They are crucial in defining the ideal adsorption capacity of an adsorbent, showing how well it can adsorb, and enabling an evaluation of the applicability of an adsorbent. Isotherms are crucial components in the design of an adsorption system because they show how much adsorbate binds to the surface of an adsorbent depending on the material present in the solution[96].

2.6.3.1 Adsorption Kinetics

The rate at which a sorbate is retained or released at the solid-phase contact is described by adsorption kinetics. Adsorption uses kinetics analysis, either linear or non-linear. The model that best captures the process is chosen using the goodness of fit index[97].

(i)   Pseudo-first order (Largergren model)

According to the model, the difference between the concentration and rate at which the adsorbate is removed over time closely correlates to the rate of change that occurs in the absorption of adsorbate at a specific reaction time. In the equation (2.1) below, the model also referred to as the Largergren model is depicted[98]:

$$ln(q_e - q_t) = ln q_e - k_1 t \qquad (2.1)$$

Where q_e and q_t are adsorption loading at equilibrium and time t (min) in mg g^{-1} respectively; k_1(min^{-1}) is the rate constant of pseudo first order adsorption.

The linear relationship between kt and qe can be inferred from the slope and intercept of the plot of log (qe - qt) vs t.

(ii)   Pseudo Second Order

The adsorption kinetics rate equation for pseudo-second-order is given as follows by equation (2.2) [99]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_t^2} + \frac{t}{q_e} \qquad (2.2)$$

According to Edet and Ifelebuegu (2020), the linear relationship formed by the plot of (t/qt) and t in equation (7) can be utilized to calculate qe and k$_2$.

Where q_e and q_t are adsorption loading at equilibrium and time t (min) in mg g^{-1} respectively; k_2 (mg (g min)$^{-1}$) is the rate constant of pseudo-second order adsorption.

2.6.3.2 Adsorption Isotherms

Adsorption isotherms have significance for optimizing the utilization of any adsorbent because they define the relationship between the adsorbate and the adsorbent. An isotherm's shape can reveal details about the adsorption affinity of molecules as well as the stability of the contacts between adsorbent and adsorbate. Adsorption isotherms can be expressed mathematically in a variety of ways. Some of these mathematical representations are based on a simplified physical description of adsorption, whilst others are empirical and require the correlation of experimental data[100].

(i)   Langmuir Adsorption Isotherm

The Langmuir theory's fundamental premise is that adsorption takes place at particular homogenous sites inside an adsorbent and that once an adsorbate inhabits a site, no more adsorption may take place there.

The model is helpful in forecasting how various adsorbents will function. According to Sampanpiboon et al., a K_L value (related to the energy of sorption) that is signaling high adsorption affinity and q_m reflecting maximal adsorption capacity (i.e. monolayer saturation) declines with increasing temperature[101].

Langmuir developed what is now known as the Langmuir adsorption isotherm, a link between the amount of gas adsorbed onto a surface and gas pressure, based on his discovery of surface chemistry. In his model, he used the following assumptions: Each adsorbent has set adsorption sites on its surface, and at a specific temperature and pressure, a portion of these sites may be filled by adsorbates; One entry can fit in each adsorption site on the surface of the adsorbent.

As adsorbates occupying multiple adsorption sites have the same heat of adsorption, there is no interaction between adsorbates occupying various adsorption sites. The equation (2.3) for Langmuir isotherm is depicted as;

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad \textbf{(2.3)}$$

C_e is the dye concentration at the concluding stage (in mg/L), and q_e and q_{max} are the equilibrium and maximum adsorption capabilities (in mg/g), respectively. The Langmuir equilibrium constant is indicated by K_L (L/mg).

The plot of $\frac{C_e}{q_e}$ against C_e would give a straight line.

The equilibrium parameter, R_L, a dimensionless constant separation factor, can also be used to express the Langmuir isotherm and is given as equation (2.4).

$$R_L = \frac{1}{1+K_L C_0} \qquad \textbf{(2.4)}$$

According to Table 2.2, the parameter R_L specifies the type of isotherm shape.

R_L Value	Isotherm Type
$0 < R_L < 1$	Favorable
$R = 0$	Irreversible
$R = 1$	Linear
$R > 1$	Unfavorable

Table 2.2 R_L Parameter

(ii)   Freundlich Adsorption Isotherm

According to Sampranpiboone et.al, in order to assess the equilibrium relationship between the adsorbate concentration and the amount of adsorbate removed per unit weight of carbon, Freundlich adsorption isotherm is generally used. The Freundlich adsorption isotherm is written as follows equation (2.5)[101]:

$$\ln q_e = \ln K_F + \frac{1}{n} ln C_e \qquad \textbf{(2.5)}$$

Where; Freundlich adsorption intensity is constant n, and a value of n > 1 indicates that the conditions are favorable for adsorption. The Freundlich equilibrium constant is indicated by K_F (mg/g).

Although the Freundlich equation is mostly empirical, it is occasionally employed as a tool for data description. This is because the equation accurately describes the non-linear adsorption process across a wide range of adsorbate concentrations.

Its capacity to depict the adsorption process on energetically heterogeneous surface adsorption sites is made possible by the mathematical simplicity of the model. A straight line with 1/n and log K_f as the slope and intercept results from the plot of log q_e vs log C_e.

CHAPTER 3 MATERIALS AND METHODS

The objectives of this chapter are to provide information regarding the acquisition of research material (chemicals used), the methodology used for executing the experiments, and the experimental procedures employed in the investigation of the adsorption activity of different dyes.

3.1 GLASSWARE AND APPARATUS USED

All glassware, including pipettes, measuring cylinders, beakers, and conical flasks, were designed by Borosil/Rankem. The following is a list of every piece of equipment and machinery utilized in the experiment:

Table 3.1 List of All Instruments Used

INSTRUMENT	FUNCTION
Electronic weight balance	To measure weight
pH meter	To measure and maintain the pH
Oven	To dry the samples / to maintain the temperature
Magnetic Stirrer	To stir the solutions
Spectrophotometer (UV/ Vis)	Absorbance
Thermo Gravimetric Analyzer (TGA)	Thermal analysis
X-Ray Diffraction (XRD)	examining a material's atomic or molecular structure
Fourier-transform infrared spectroscopy (FTIR)	to get the infrared spectrum of a solid, liquid, or gas's absorption or emission

3.2. MATERIALS

Ananas comosus leaves (obtained from the local market), deionized water, $NiCl_2.6H_2O$ salt, and different dyes solution (Congo red, methylene blue, and crystal violet).

3.3. PLANT EXTRACT PREPARATION

The plant's (Ananas comosus) leaves were washed with deionized water and dried for over a month in the sunlight. The dried leaves were crushed into a fine powder, and a leaf broth solution was made by blending 20 g of the powdered leaves with 200 mL of deionized water in a 250 mL conical flask, which was then heated at 80°C for 30 minutes. The mixture was filtered after cooling, and the filtrate (extract) was stored at room temperature for further investigation. A visual representation is shown in figure 3.1.
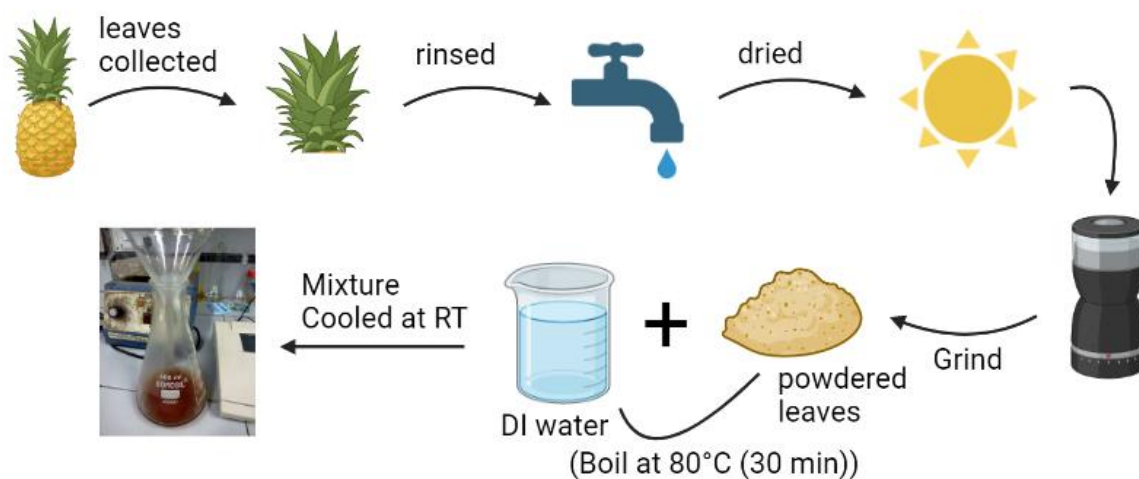
Fig. 3.1 Visual Representation of Plant Extract Preparation

3.4. GREEN SYNTHESIS OF NICKEL OXIDE NANOPARTICLES

The leaves of the plant (Ananas comosus) were cleaned with DI water and let to dry in the sun for 2 weeks. The dried leaves were ground into a fine powder, and 20 g of the powdered leaves were combined with 200 mL of DI water in a 250 mL conical flask, which was then heated at 80°C for 30 minutes, to create a leaf broth solution. After cooling, the mixture was filtered, and the filtrate (extract) was kept at room temperature for future research. A visual representation is shown in figure 3.2.
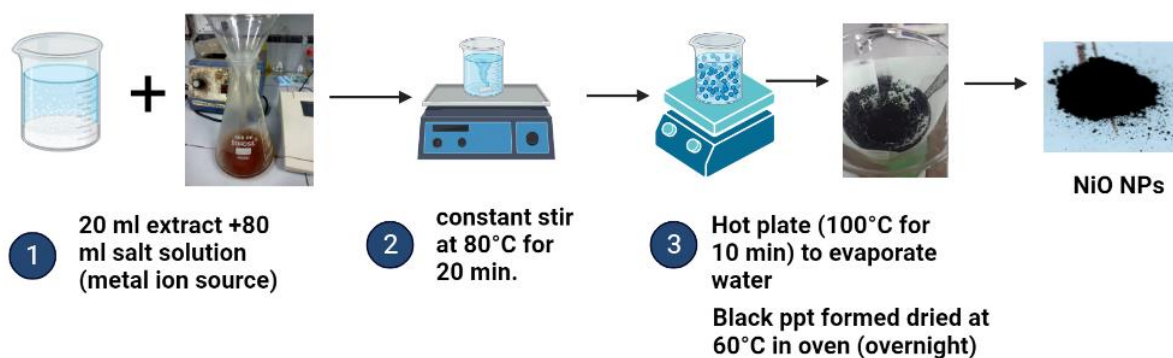
Fig. 3.2 Visual Representation of NiO NPs Preparation

3.5. PREPARATION OF DYE SOLUTIONS

The stock solution of dyes (Congo red, methylene blue, and crystal violet) was prepared by weighing 0.01g of dye and mixing it in 100 ml of distilled water in a conical flask and was kept for further use.

The stock solution was further diluted with deionized water to obtain the necessary concentration of dye solutions (10, 20, 40, 60, 80, and 100 mg/L).

3.6. METHODS

3.6.1 ADSORPTION WITH DIFFERENT DYES
(Comparison of Adsorption Efficiency for Azo Dyes)

Understanding the adsorbing properties of nickel oxide nanoparticles as an adsorbent for several dyes (Congo red, methylene blue, and crystal violet) was the main goal of the current study.

For the decolorization of dye, dye concentration (20 ppm) was optimized. The required volume of dye solution (MB, CV, CR) is taken from the prepared stock and 0.02g of NiO NPs were added respectively. The beaker was kept on a magnetic stirrer for 30 minutes and a small aliquot from the reaction mixture was taken out after every 5 minutes to check its absorbance using a UV-Visible spectrophotometer.

3.6.2 ADSORPTION STUDIES FOR CONGO RED

In a beaker, the Congo Red dye solution was added together with synthesized Ni-NPs. The beaker was placed on a magnetic stirrer for 90 minutes, and after every 15 minutes, a tiny aliquot of the reaction mixture was removed to be tested for absorbance using a UV-visible double-beam spectrophotometer. Congo red direct dye decolorization was optimized for dye concentration (10, 20, 40, 60, 80, and 100 mg/L), Ni-NPs concentration (0.05g, 0.1g,0.02g, and 0.15g), and contact time (5, 10, 20, 30, and 60 mins.) at 20 ppm. One parameter is changed at a time, with the other parameters remaining the same.

3.6.3 EQUILIBRIUM ISOTHERMS AND KINETIC MODELLING

Utilizing synthesized NiO (dose = 0.1 g) with an initial CR concentration of 20 ppm, magnetic stirring-assisted kinetic and isotherms investigations were carried out. In order to determine the concentration of CR dye in the samples, samples were taken periodically after their adsorption. The experimental data were fitted using two distinct kinetics and isotherms models respectively.

CHAPTER 4 RESULTS AND DISCUSSION

4. CHARACTERIZATIONS

The synthesized NiO NPs were characterized by X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR) techniques, and the adsorption activity was performed by a UV–Vis spectrophotometer.

4.1 XRD

XRD pattern of NiO NP crystalline structures is shown in Figure 4.1. The average crystalline size of NiO NPs was determined using Scherer's formula (equation 1) and the peak position of an XRD pattern and was found to be 20.31 nm. The XRD pattern represented in the figure 4.1 matches the literature reports validating the product.

$$D = \frac{k\lambda}{\beta cos\theta} \quad \text{(Equation 1)}$$
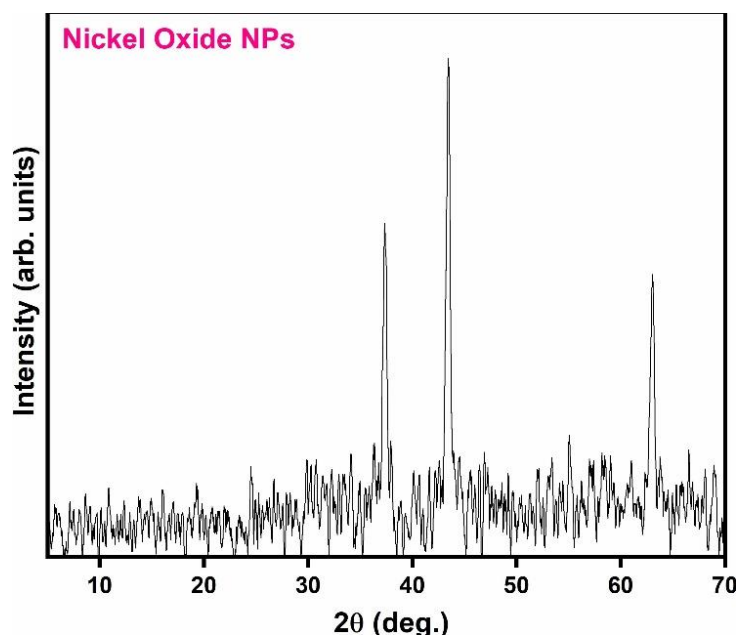
Fig.4.1 XRD Pattern of Synthesized NiO NPs

4.2. FTIR SPECTRA

The FTIR results are presented in Figure 4.2. The stretching vibration of the O-H groups of the water molecules present as moisture is what causes the broad absorption band at 3374 cm^{-1}. The Ni-OH stretching vibrations is responsible for the bands at 876 cm^{-1}. The existence of bands in the 400–600 cm^{-1} range can be used to establish the existence of metal–oxygen connections (M–O) in the synthesized nanoparticles. However, the extra bands at 1432 cm^{-1} are there because NiO-NPs have phytochemical carbonyl group linked to them.
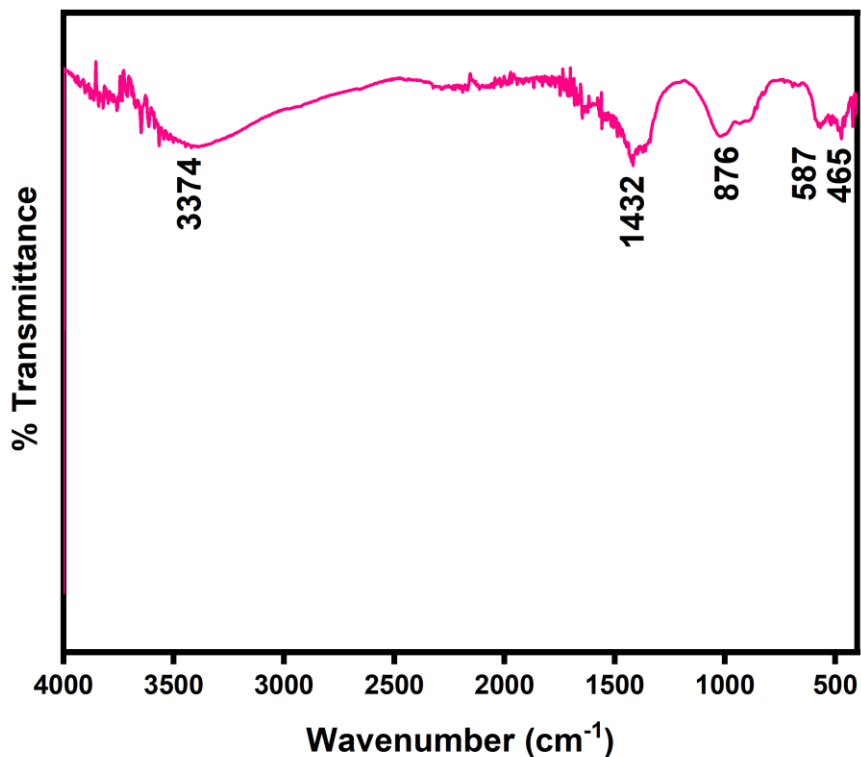
Fig.4.2 FTIR Spectra of synthesized NiO NPs

4.3 THERMO GRAVIMETRIC ANALYSIS (TGA)

Thermal stability studies were carried out to gather more information about the materials' stability.

Many substances are unstable and break down into different substances when heated. Thermo gravimetric analysis is used to characterize the prepared sample in order to determine its thermal stability.

TGA study from 25 to 800 °C in the presence of ambient gas was conducted to ascertain the impact of heat treatment of NiO. The TGA curve, which is shown in Figure 4.3, revealed three stages of weight loss. Half of the water molecules evaporate due to crystallization, which accounts for the initial weight loss of 1.8 wt.% in the temperature range of 25 -210 °C. The second weight loss, which was 3.3 weight percent, may have been caused by the thermal degradation of plant extract since it was caused by the elimination of water molecules between 210 and 500 °C. When the temperature rose over the calcining temperature of 400 °C, the third little weight loss was noticed, suggesting that NiO nanoparticle fabrication was almost complete. The NiO nanoparticles were calcined at 400 °C, according to the TGA study. There is no such significant weight loss above 400 °C.
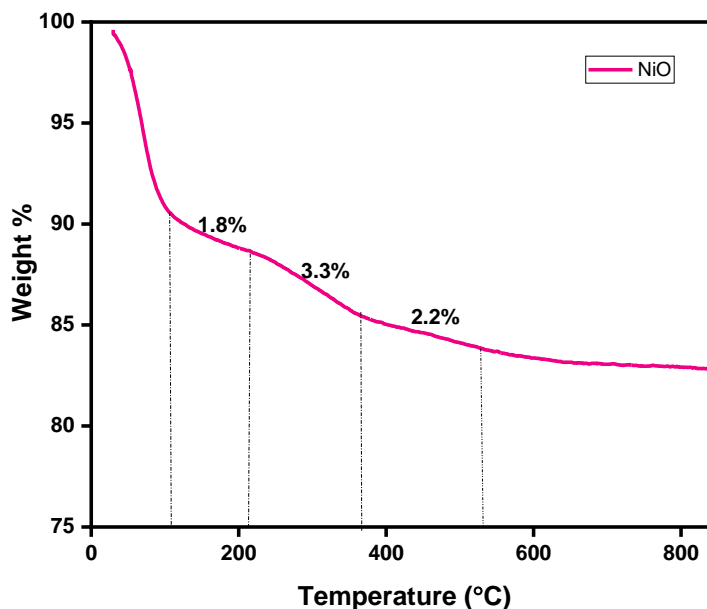
Fig.4.3 TGA of synthesized NiO NPs

4.4 COMPARISON OF ADSORPTION EFFICIENCY FOR AZO DYES

Figure 4.4 provides information regarding the percentage of azo dyes removed following sorption. Within 30 minutes of contact time, the adsorption efficiency follows the pattern CR (95.6%) > CV (49.9%) > MB (49.4%). The fabrication of NiO utilizing Ananas comosus plant extract can be used as an effective sorbent for the sequestration of anionic dyes, in this case, CR, according to the results of the aforementioned experiment.
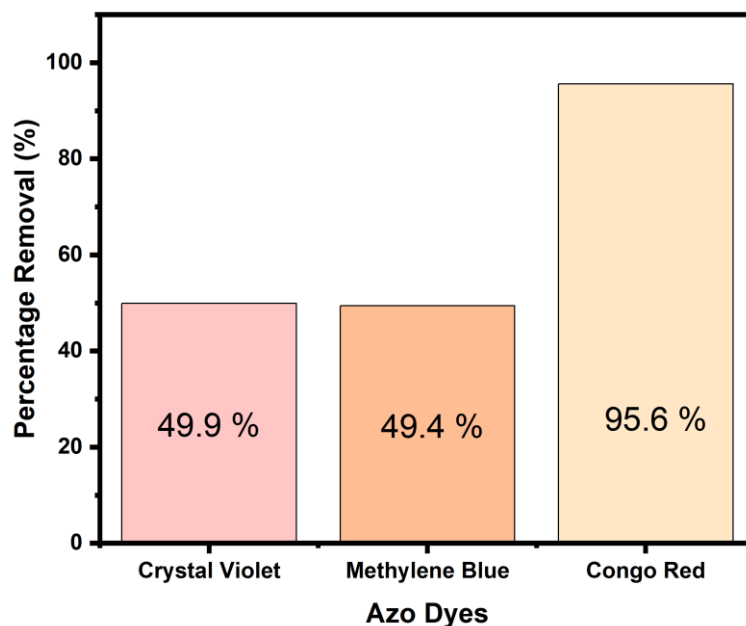
Fig.4.4 Plot of Percentage Removal

4.5 EFFECT OF CONTACT TIME

One of the vital elements in the adsorption process is contact time. As demonstrated, the adsorption rate grew quickly at first, and for any initial concentration, the ideal removal efficiency was attained in roughly 60 minutes. The uptake of metal ions happened in two stages, first with a quick uptake and then with a slower one. When there are many more

accessible sites than there are metal species to be adsorbed, the adsorption process seems to move along quickly. With more metal being adsorbed, more contact time was needed.

The elimination of CR gets stronger over time and reaches saturation in 60 minutes. The amount of CR removed in relation to the contact time is shown in Figure 4.5. During the first 60 min of the sorbate-sorbent contact, the CR dye exhibited a rapid rate of sorption; however, the rate of quantity removal quickly became negligible due to the rapid exhaustion of the adsorption sites.
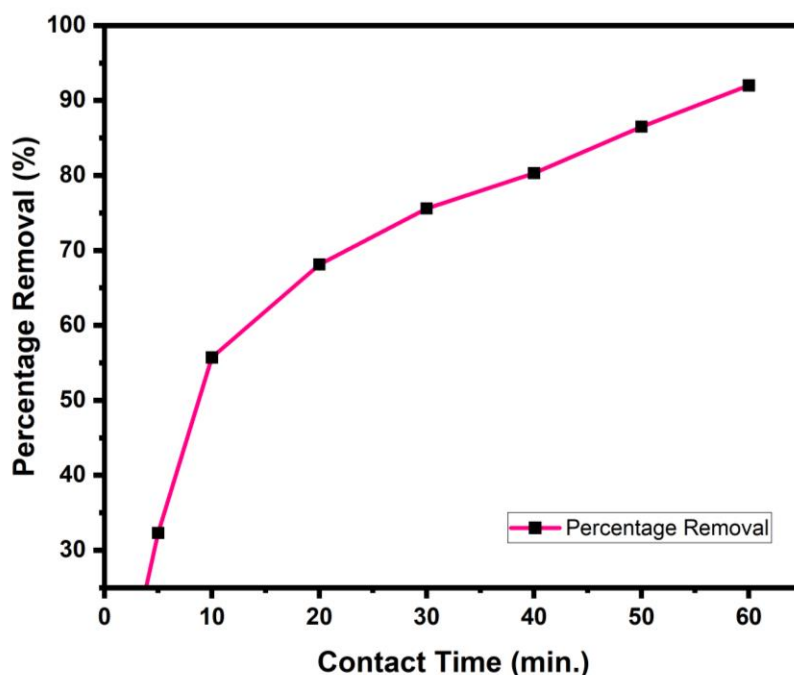
Fig.4.5 Plot of Percentage Removal w.r.t Contact Time

4.6 EFFECT OF ADSORBENT DOSAGE

The quantity of adsorbent is a significant factor that affects the adsorption process. The dosage of the adsorbent is a crucial parameter since it defines the adsorbent capacity for a specific starting concentration [187]. A constant starting concentration of adsorbent leads to a decrease in specific adsorbed volume according to Kroeker's rule [188]. Therefore, dye removal is more effective and performs better when the adsorbent dose is increased. By increasing the adsorbent dose, you increase the amount of active surface area available to

adsorb contaminants at constant concentrations [189]. The amount adsorbed per species, on the other hand, decreases as the biosorbent concentration rises. It is explained by the fact that the sorption isotherm changes shape as the concentration of the biosorbent increases. Specific adsorbed amounts are likely to decrease because part of it is possible that more concentrated solutions will not completely saturate the surface or surface groups [190-193]. At saturation, efficiency gradually declines, occasionally marginally, until it reaches a saturation state. Adding more adsorbent does not increase the number of bound and free ions, but achieves maximum adsorption if a certain amount of adsorbent is added.

NiO nanoparticles powder in amounts ranging from 0.02 to 0.15 g was used to evaluate adsorbent dosages for removing the CR from the aqueous solution. The outcomes are displayed in Figure 4.6.
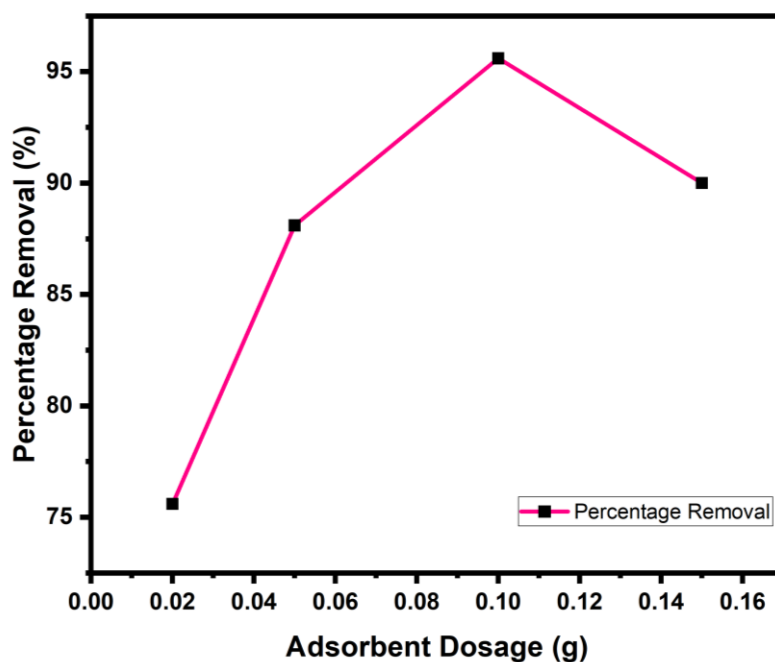
Fig.4.6 Plot of Percentage Removal w.r.t Adsorbent Dosage

4.7 EFFECT OF CONCENTRATION

The study was done on how initial dye concentration affected adsorption. The results of the experiment are shown in Figure 4.7. Adsorption was found to increase with a rise in the dye's concentration. The dye solution's adsorption ranged from 86.2 % at 10 ppm to 96.4 % at 60 ppm. This might be driven by an increase in the concentrate ion gradient's driving force, active sites that are available, or initial dye concentration.

Depending on the initial dye concentration, the adsorption process can be affected directly or indirectly by how many binding sites are available on the adsorbent surface, which reduces or increases dye removal. A strong correlation exists between the maximum quantity of dye bound in the equilibrium in similar water systems (q) equation (4.1) and the efficiency of dye removal (E) equation (4.2) [38,154].

$$q = \frac{(C_i - C_f) \times V}{m} \qquad \textbf{(4.1)}$$

$$E\ (\%) = \frac{C_i - C_f}{C_f} \times 100 \quad \textbf{(4.2)}$$

where: E (%)—efficiency; q (mg/g)—the amount of dye bound in equilibrium; C_i (mg/L)—initial dye concentration; C_f (mg/L)—final dye concentration; m (g)—the amount of adsorbent; and V (L)—volume of aqueous solution.

Looking at the influence of initial dye concentration, three patterns can be observed: (1) removal efficiency decreases with increasing initial concentrations, (2) removal efficiency increases with increasing initial concentrations, and (3) there is no discernible difference in removal efficiency.

Dye removal proportion decreases with increasing dye concentration. It is possible that this phenomenon is caused by the saturation of adsorption sites on the surface of the adsorbent. Since mass transfer is a significant driving force at high dye concentrations, in this scenario, adsorbent capacity increases with increasing dye concentration. Adsorption occurs as a result of mass transfer from the solution (which contains more dye) to the adsorbent's free surface due to the initial concentration of solutes [158,169].
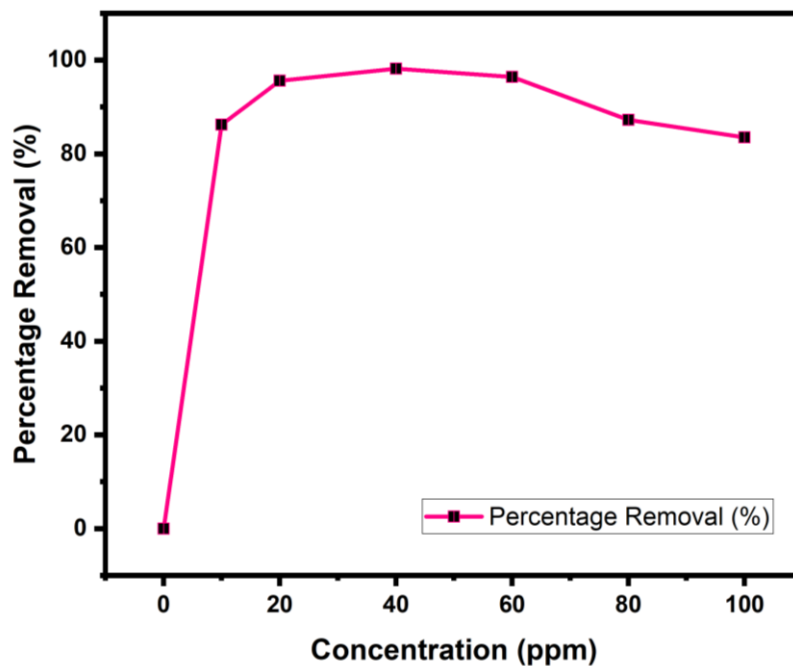
Fig.4.7 Plot of Percentage Removal w.r.t Different Concentrations

4.8 EQUILIBRIUM ISOTHERMS

Figure 4.8a and 4.8b shows the charts for the equilibrium isotherms that were used. Based on the linear fitting of experimental data, Table 4.1 shows the isotherm parameters and R^2 values. According to the Langmuir model, NiO nanoparticles were evenly adsorbed on their surfaces in a monolayer configuration, which is the maximum value of the determination coefficient (R^2).

The study's computed R_L values, which vary from 0 to 1, indicate that dye adsorption is preferable to NiO NPs.

Table 4.1 Isotherm Parameters for CR dye absorption

Isotherm models	Plot	Slope	Intercept	Parameters	Values
Langmuir $$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}$$	$\frac{C_e}{q_e}$ vs C_e	$\frac{1}{q_{max}}$	$\frac{1}{q_{max}K_L}$	q_{max} K_L R^2	46.92633 mg/g 1.923285 L/mg 0.97629
Freundlich $$\ln q_e = \ln K_F + \frac{1}{n}lnC_e$$	lnq_e vs lnC_e	$\frac{1}{n}$	lnK_F	K_F $\frac{1}{n}$ R^2	33.414 mg/g 2.967183 0.57815
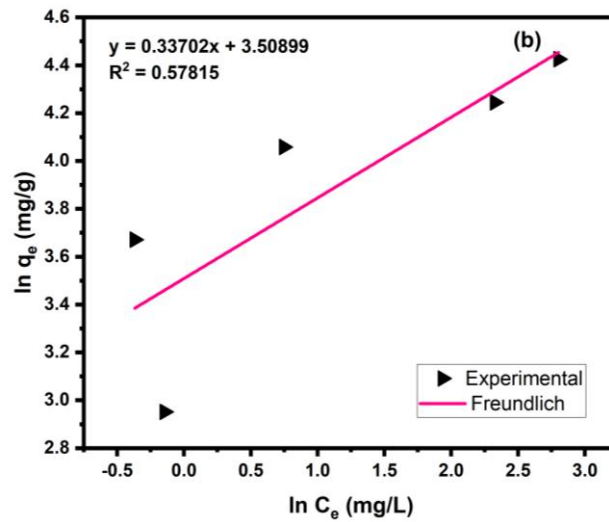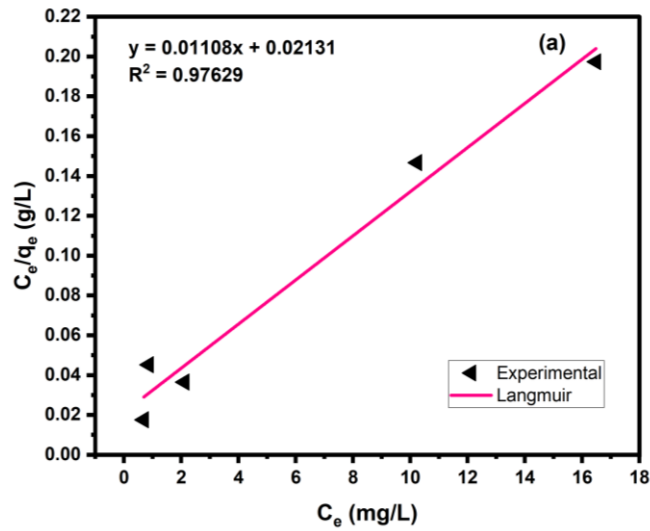
Fig.4.8 Linear Plot for (a) Langmuir and (b) Freundlich isotherms

4.9 KINETICS OF ADSORPTION

A visual representation of the investigated kinetic models is shown in Figure 4.9a and 4.9b. A determination coefficient value of 0.99 was obtained for the pseudo second order model, and according to the calculations, the adsorption capacity (21.24 mg/g) is similar to that measured experimentally of 19.13 mg/g. Despite this, a large variation in and can be observed for Pseudo First Order, indicating chemisorption of CR dye onto NiO nanoparticles and proving the suitability of the Pseudo Second Order model.

The linear regressions and kinetic parameters of the models used in the study are also summarized in Table 4.2.

Table 4.2 Kinetic Modelling Parameters for CR dye absorption

Kinetic Models	Plot	Slope	Intercept	Parameters	Values
Pseudo First Order $ln(q_e - q_t) = lnq_e - k_1t$	$ln(q_e - q_t)$ vs t	$-k_1$	lnq_e	k_1 q_e R^2	0.000761 min^{-1} 14.92 mg/g 0.95224
Pseudo Second Order $\dfrac{t}{q_t} = \dfrac{1}{k_2 q_t^2} + \dfrac{t}{q_e}$	$\dfrac{t}{q_t}$ vs t	$\dfrac{1}{q_e}$	$\dfrac{1}{k_2 q_t^2}$	k_2 q_e R^2	869.616 mg(gmin)$^{-1}$ 21.24495 mg/g 0.99431
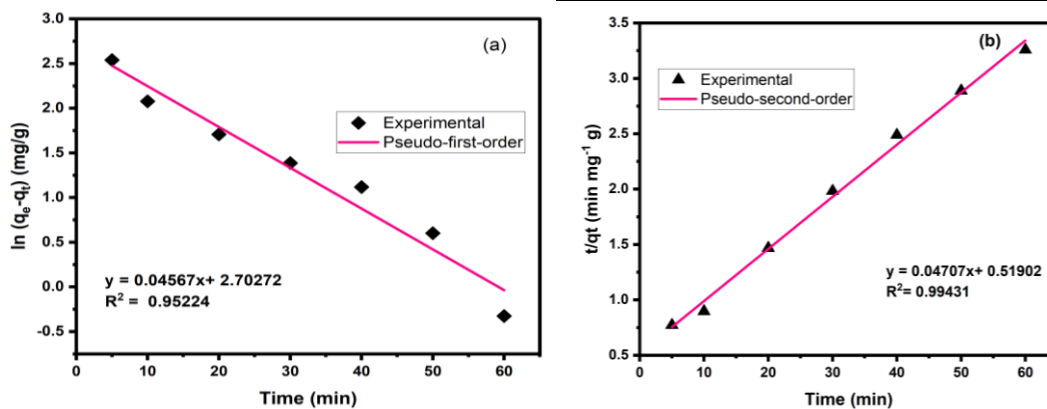
Fig.4.9 Linear Plot for (a) pseudo-first-order and (b) pseudo-second-order kinetics

CHAPTER 5 CONCLUSION AND FUTURE ASPECTS

5.1 CONCLUSION

In this study, NiO NPs are synthesized in a more environmentally friendly manner by using leftover pineapple leaves (*Ananas comosus*) as a plant extract. XRD and FTIR measurements qualitatively supported the production of NiO nanoparticles from plant extract. The crystallinity of these NiO nanoparticles was disclosed by the distinct peaks in the XRD pattern. The NiO nanoparticles have the functional groups of the plant extract integrated into them, according to the FTIR spectra.

The synthesized NiO NPs are used for dye adsorption properties. The impact of the introduction of NiO NPs into the different dyes (CR, MB and CV) was investigated. Among the investigated azo dyes, the maximum adsorption was observed in CR dye, thus for further investigations CR dye was used as adsorbate. The various factors like concentration of adsorbate, contact time, adsorbent dosage was evaluated. The equilibrium isotherms and kinetic modelling were too investigated.

There is a sincere need for the sustainable development of nanomaterials that can be used efficiently for waste water treatment; thus, a bio-based method for the synthesis of nanomaterials has been proposed as an eco-friendly alternative to chemical and physical processes.

5.2 FUTURE ASPECTS AND CHALLENGES

Even though there are an endless number of nanoparticles presently in existence, the need for innovative materials that are inexpensive, recyclable, and highly effective has not yet been met. Nanoparticle utilization has a lot of benefits, but there are also some downsides that cannot be ignored.

- Most researchers have not yet addressed the issue of scaling up nanoparticle production at the industrial level.

- Due to a number of factors, the study of metal oxide nanoparticles is still in the laboratory stage, and their commercial application is still far off.
- Nanoparticles may be released into the environment because of their small size and over time build up in nature.
- In addition, nanocomposites' potential hazards should be evaluated, and their effects on the environment and human health should be researched.

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