

FEASIBILITY OF MAGNETIC NANO ADSORBENT IMPREGNATED WITH PRAWN SHELLS ACTIVATED CARBON FOR HEAVY METAL (LEAD(II)) REMOVAL

Submitted in partial fulfillment of the requirements for the award of Bachelor of
Technology degree in Chemical Engineering

by

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**DEPARTMENT OF CHEMICAL ENGINEERING
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SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

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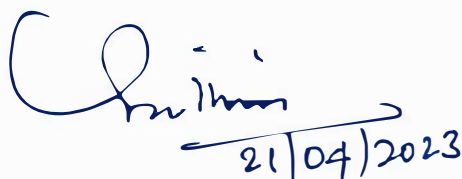
BONAFIDE CERTIFICATE

This is to certify that this Project Report is the Bonafide work of B.NIVYA(39190023), S.LALITHAMBEGAI (39190013) who carried out the project entitled "**Feasibility of Magnetic Nano Adsorbent Impregnated with Prawn Shell Activated Carbon for Heavy Metal (Lead(II)) Removal**" under my supervision from September 2022 to April 2023.



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We **B.NIVYA (39190023)** and **S.LALITHAMBEGAI (39190013)** hereby declare that the Project Report entitled “**Feasibility of Magnetic Nano Adsorbent Impregnated with Prawn Shells Activated Carbon for Heavy Metal (Lead(II)) Removal**” is done by us under the guidance of **Dr.D.PRABU MS (by Research), Ph.D.**, at Sathyabama Institute of Science and Technology is submitted in partial fulfillment of the requirements for the award of **BACHELOR OF TECHNOLOGY IN CHEMICAL ENGINEERING**.

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ABSTRACT

We are facing a serious issue of water pollution nowadays. It is caused due to various harmful pollutants like Heavy metals, Dyes, Oil spills etc. Treatment of this was found mandatory in order to reduce water pollution. Magnetic Nano Particle (MNP) was produced by the Co-precipitation process and is then impregnated with Prawn Shells (PS) to fabricate MNP-PS nanoparticles. The prepared adsorbent is studied for the removal of Pb(II). Pb(II) is extremely dangerous and can lead to tissue, kidney, brain, and lung diseases. In spite of all other removal techniques, Adsorption is preferred because of its less usage of chemicals and wide variety of Adsorbent Choices. Using of Magnetic Nano Adsorbent (MNP-PS) was found effective because of its super paramagnetic property and reusability. Prawn Shells which are of no economic value are implemented for an excellent sorbent to get rid of metal ions, dyes etc. Various Characterization methods including SEM with EDX, XRD, FTIR and VSM shows the property of Magnetic Nano Particle (MNP-PS). The Surface Morphology of 100-400nm was studied using SEM. EDX confirms that the prepared (MNP-PS) sample contains Iron (76.32%) and other compounds. Functional Groups were analyzed using FTIR. MNP-PS amount, initial Pb(II) ions concentration, contact time, and investigated have been the impacts of warmth on the phase sorption of Pb(II) by MNP-PS. The pseudo-second-order model and the Freundlich model, however, did an adequate job of characterizing the adsorption isotherms and dynamics, proposing a chemical and multi-layer adsorption of Pb(II) ions removal by MNP-PS. By just using Langmuir, Freundlich, as well as Temkin models, the sorption isotherms of Pb(II) ion elimination by MNP-PS have indeed been studied. A Freundlich as well as pseudo second order concepts offered the greatest fitting to the experimental data as from adsorbent dosage. Thermodynamic studies prove that the adsorption mechanism was exergonic, spontaneously, and practicable.

Keywords: Water Pollution, Adsorption, MNP-PS, Pb(II)

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LIST OF ABBREVIATIONS

ABBREVIATIONS	ACRONYMS
PS	Prawn Shells
MNP-PS	Magnetic Nanoparticle Impregnated with Prawn Shells
nZVI	Nano-Zero valent ion
MNP	Magnetic Nanoparticle
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-Ray Diffraction
VSM	Vibrating Sample Magnetometry

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CHAPTER-1 INTRODUCTION

Water (H_2O), which makes up more than 70% of the planet's surface, is the most precious resource and an endless substance. In nature, water may be found in three different states: Solid, liquid and gas. It has no flavor, no odor, and no color at room temperature with the exception of a very tiny blue tint. Every cell in our body uses water. The network in the share a variety nourishment, oxidant, and byproducts to and from various body's tissues and organs. Being a component of ourselves physiological temperature regulation mechanism, Fresh water serves to keep us hydrated. Particularly prone to contamination is water. Water has the ability to dissolve more substances than any other fluid on earth, giving it the title of "universal solvent". Because of it, Kool-Aid and vivid blue waterfalls exist. It also clarifies why water is so readily contaminated. It dissolves fast and contaminates the water by mixing with dangerous elements from nearby farms, towns, and businesses. There are numerous multiple kinds of effluent which are discharged through various firms, notably combined sewers, household effluent, hurricane flow effluent, farming sewage, and municipal waste. According to the AQUASTAT data, 3928 km² of freshwater are removed globally each year, of which 22% (865 km²) are utilized by industry. One of the main factors contributing to the ecosystem's irreparable harm is industrial effluents. Groundwater and other large water bodies ultimately become contaminated as a result of the improper handling and direct release of these hazardous effluents into sewer drains, which has an adverse effect on the health of both marine and terrestrial species. Vomiting, giardiasis, typhus, pneumonia, hepatitis, malaria, and cancer are some of the waterborne illnesses brought on by water pollution. Several nations are currently developing regulations to regulate water quality. Logic standards are being defined on the amounts of pollutants that might be safely ingested in certain water bodies, like rivers and lakes. Also being constructed are a variety of treatment facilities that use chemical, electrochemical, biological, and physical methods to produce drinking water. Numerous industrial planners and manufacturers are increasingly embracing technology to assure green economy, less water use, and less pollution, keeping in mind both economic expansion and the lack of clean water. Health and natural, sea life, and farming are all at threat from poisons discovered in effluent from several industries. These hazards typically comprise of pigments and heavy metals. The manufacture of the

industries of paints, dyes, pigments fabrics, drug products, newspaper, and explosives emit the majority of such metal pollutants. Phenol & phenolic compounds comprise two of the main carcinogens found in industrial waste water. Their primary function emitted by the resin from phenol-formaldehyde, massive pharmaceutical production, & also crude oil refineries sectors. Catalytic industry-produced resistant pollutants, which include petroleum-derived hydrocarbons, can be found in wastewater, sulphides, naphthalene acid, organochlorides, aniline, alkene, alkanes, nitrogen benzene and chlorine alkanes. There are now much more contaminants in the environment as a result of the recent, rapid industrialization. All sorts of biological forms have suffered harm by the improper dumping of some hazardous industrial waste into water bodies, either directly or indirectly. One of the most common types of chronic, non-recyclable water pollution is heavy metals. Aquatic fauna may introduce certain dangerous heavy metals into the food chain, which can negatively impact the health of other animals and eventually humans. They can be teratogenic, carcinogenic, and generate oxidative stress in addition to osmotic damage, organ dysfunction, neurological disabilities, and reduced growth and development. Sources of water from industrial plant are contaminated by the heavy metals that are carried by runoff water. Before disposing waste water, it is crucial to remove these hazardous heavy metals to prevent health risks. Due to their persistence and non-biodegradability, hazardous compounds that have been released in large amounts into the environment have caused a variety of environmental issues and may constitute very massive risk to human well-being because of inherent accumulation in environmental components like the food chain. Numerous traditional techniques, including chemical coagulation, liquid – liquid exchangers, ion exchanges, membrane filtration, electrical, chemical removal, coagulation, etc., Metals that are heavy are capable of being eliminated via aqueous medium. These methods, however, have several drawbacks, including insufficient removal, high energy needs, the availability of hazardous sludge, limited efficiency, delicate working conditions, and expensive disposal. Hence these types of hazardous and toxic effluents must be properly eradicated in order to make our environment pollution free.

1.1 HEAVY METALS AND ITS TYPES

1.1.1 Arsenic (As(III))



Fig.1.1 Arsenic (As(III))

The 20th most prevalent substance in the Earth's crust, the 14th in saltwater, and the 12th in the human body is As (III), a naturally occurring metalloid that is an element of more than 245 minerals. As(III) exposure at low levels may harm blood vessels and result in vomiting, nausea, stinging in the hands and legs, decreased erythrocyte and leukocyte production, and irregular heartbeats. When it is in its metallic phase, it is brittle, brilliant, and silver-grey in colour. Despite being heavily controlled, As(III) compounds are routinely used as rat poisons and insecticides.[1] Skin cancer is one of the drawbacks of As(III) heavy metal; prolonged exposure can also cause lung and bladder cancers. The International Agency for Research on Cancer (IARC) has classified As(III) compounds as carcinogenic to humans in addition to proving that arsenic in drinking water causes cancer in people. As(III) concentrations of metals in drinkable water are limited at 0.05 mg/L.

1.1.2 Lead (Pb(II))



Fig.1.2 Lead (Pb(II))

A harmful environmental toxin called Pb(II). It has highly toxic impacts in variety of living species. Exposure to Pb(II) may lead to neurology, pulmonary, urinary, and circulatory illnesses, alongside cellular antioxidant, swelling, and other toxic reactions.[2] Industrial wastewaters generally comprise Pb(II) ions at levels of 200–500 mg/L, which exceed the limits for water quality. The physical property of Pb(II) is among its characteristics are a lower melting point, dense population, limited ductility, simplicity in fabrication, chemical inertness, electrolytic responses with sulfuric acid, high stability in oxygen, liquid, and sediments, and also the ability to dampen mechanical stress, acoustic signals, and nuclear radiation. It is Bright, bluish. It is very flexible and brittle. Pb(II) in drinking purposes was usually obtained until 0.01 mg/L.

1.1.3 Mercury (Hg(II))



Fig.1.3 Mercury (Hg(II))

Hg(II) is a well-known dangerous element because of how frequently acute heavy metal poisoning is brought on by it. Hg(II) is a silvery white substance that slowly devalues in humid air and hardens into a soft substance. The kidneys, brain, and growing foetus might suffer harm if they are subjected to this metals, organic, and inorganic Hg(II). Anthropogenic comprises of farming, mines and disposing of trash from cities, industrial wastewater discharges and incineration are the major sources of Hg(II) pollution. It is a beautiful silver-white, odourless metal that occurs naturally. When heated, it changes into an odourless and colourless gas.[3] A maximum of 2,200 tons of Hg(II) are released in the environment each year, as according estimates. It might be difficult to diagnose organic Hg(II) poisoning because the symptoms are comparable to those of other illnesses, such as depression,

headaches, tremors, exhaustion, hair loss, and memory issues. Hg(II) levels in portable water must not exceed 0.001 mg/L.

1.1.4 Cadmium (Cd(II))



Fig.1.4 Cadmium (Cd(II))

Cd(II) emerged become a major metal used creating chargeable nickel- Cadmium (Ni-Cd) cells in addition to aluminum and metallic coating which acts as a barrier to prevent corrosion. Currently, it really is found in tobacco smoke along with rechargeable batteries, particular alloy production, and other products. Currently, common industrial uses for Cd(II) include pigments, plastic stabilizers, coatings (electroplating), solar cells, alloys, coatings, and batteries.[4] Cd(II) poisoning has been detected in rice, grains, and seafood. Commercial dust simply eliminates Cd(II) from the lungs. Acute or long-term exposure to Cd(II) in industrial settings can result in lung damage and renal tubular malfunction. Smokers have almost two times more of Cd(II) in their blood than non-smokers do. The authorized absolute maximum limit of Cd(II) in drinking water is 0.03 mg/L.[5]

1.1.5 Chromium (Cr(VI))



Fig.1.5 Chromium (Cr(VI))

Chromium (Cr(VI)), a found naturally heavy metal in use in industrial processes, is discovered in the crust of the earth and ocean. The name chromium, which derives from the Greek word *chromes*, which means "colour," refers to the intense and diverse colorations of contaminants. The metal Cr(VI) is hard, brittle, and bright. It possesses a silver-grey color and is highly polishable. [6]As Cr(VI) is fragile in oxygen, it rapidly creates a thin oxide film that protects the metal against oxygen. The growth of diverse abnormalities inside this pulmonary, laryngeal, liver, renal, ovaries, femur, and glands are one of the ailments which impair the epidermis, digestive, nerve systems and small intestine. Cr(VI) concentrations in drinking water are limited at 0.1 mg/L.

1.1.6 Copper (Cu(II))



Fig.1.6 Copper (Cu(II))

In its simplest form, Copper (Cu(II)) is a reddish-brown metalloid with a significant level of malleability. Cu(II) is primarily employed in industrial machinery, roofing, plumbing, and electrical wiring. Numerous human tissues are harmed either by detrimental impact that metal have, both in the immediate and distant futures[7]. Consequences caused by the toxic effect of heavy metal include cancer, birth defects, immune system dysfunction, cardiovascular disease, hyper-pigmentation, neurological number of weaknesses, renal and intestinal issues, lesions of the skin. Cu(II) levels in drinking water are limited to 1.3 mg/L.

1.1.7 Nickel (Ni(II))



Fig.1.7 Nickel (Ni(II))

Ni(II) is rigid, silver-white that solidifies into cubic shapes. It has superior strength and corrosion resistance, is malleable, and ductile. It has been shown that each cigarette contains around 1.1 and 3.1 g of Ni(II). In reality, several fruits and vegetables, including cocoa, chocolate, and almonds, as well as lettuce, asparagus, broccoli, carrots, and green beans, have high quantities of this dangerous metal. In addition, Ni(II) is accidentally consumed when food is processed on stainless steel equipment or when it comes into contact with the mouth.[8] Ni(II) can be found in the air, water, and food, which can expose the general public to it. People who are exposed to it may have a variety of harmful health effects, such as allergies, kidney, heart, and lung issues, fibrosis, and lung and nose cancer. Ni(II) concentrations in drinking water are restricted at 0.1 mg/L.

1.1.8 Zinc (Zn(II))



Fig.1.8 Zinc (Zn(II))

The metal Zn(II) is a bright bluish-white color. Becoming a component of several important proteins and regulating the regulation of a variety of immune-modulatory

functions, Zn(II), one of the most abundant toxic metal found in the Earth's crust, is considered to be an essential compound metal required for the development of living things. Its toxicity, which is carried on by a variety of anthropogenic sources, continuous exposure to polluted areas, and other natural phenomena, however, runs parallel to its essentiality. Certain vegetables, cattle, and dairy products have a high bioavailability of zinc, making them a useful source of the metal for human consumption.[9] Zn(II) metal is mainly used to preserve iron and steel against corrosion and to create brasses and alloys for die casting. Nausea, vomiting, and diarrhea are signs of heavy metal in Zn(II). Metallic oxide fever, stomach and intestinal problems, and/or liver malfunction can all be caused by excessive Zn(II) exposure. Zn(II) concentrations in drinking water are limited at 5.0 mg/L.

1.2 VARIOUS TREATMENT TECHNOLOGIES FOR HEAVY METALS

1.2.1 Adsorption

Successful techniques for removing very harmful chemical molecules from water are of great interest. to clean polluted water of organic contaminants. Coagulation/flocculation, filtration with coagulation, precipitation, oxidation, adsorption, ion exchange, reverse osmosis, and advanced oxidation processes are just a few of the techniques that have been used. Because to their extremely high initial investment and continuous operation cost, advanced oxidation techniques like reverse osmosis and ion exchange do not seem to be economical. Adsorption is the recommended way as compared to all of the other methods because of its favorable characteristic particles, ion, or nuclei out of a total soluble solid, vapor, or fluid stick the surfaces through the technique called as adsorption.[10] Adsorption is very beneficial form in treatment, particularly for industrial waste water. This technique coated the adsorbent's surface with an adsorbate layer. Adsorption has drawn a lot of attention in past years since it seems like a promising technique moreover typically long management and a practical method. Physical adsorption and Chemisorption's are the two kinds under which adsorption can be classified. If the interaction among the molecules that are adsorbed and the surface of the material is physical, the approach is called "physisorption." Adsorption is referred to as chemisorption when the forces of attraction between molecules that are absorbed and the surface of a solid are generated by chemical bonding. The adsorption

process (i.e., temperature, adsorbent quantity, pH value, adsorption period, and starting concentration of metal ions) is determined by the physiochemical characteristics of the adsorbent, heavy metals, and operating circumstances. According to reports; this method has a cost - effective system, a maximum removal capacity, simple implementation, and treatment. Due to their reversible character, the utilized adsorbents can perhaps be reconstituted using a proper decontamination methodology. Adsorption utilizing sorbents is one of the most often used treatments because it results in highly treated effluents when the adsorption process is designed properly.[11] The main benefit of the adsorption technique, which makes it cost-effective, is the recycle or regenerating of the adsorbent materials. The desorption or restoration ability of the adsorbent affects whether it can be reused. The following characteristics are adsorbent: area of surface, size of pore, volume of pores, and surface charge. Various materials, including biomaterials waste materials, have been utilized. To determine their potential for use in treating wastewater and their contribution to large-scale processes, it is essential to understand how different adsorbates interact with adsorbents in the laboratory scale. Adsorption, although, has several disadvantages as well, such as the inability to operate well at industrial scales due to a lack of suitable adsorbents with large adsorption capacities and the shortage of industrial scale columns. Secondly, a crucial step should be considered seriously while developing an efficient and suitable adsorbent. The development of nanotechnology has revealed an extraordinary potential for the development of novel adsorbents, and nano-materials have been used to achieve the goal of developing an optimal adsorbent that is effective and quick to remove pollution.

1.2.2 Chemical Precipitation

Chemical precipitation is a widely utilized industrial technique that is effective, affordable, controllable, and applicable across a wide temperature range. Chemical precipitation, also known as coagulation precipitation, is one of the most commonly used and developed processes in industry. Precipitation is the preferred technique to eliminate dissolved ions during conventional treatment. Chemical precipitation is widely used because it is comparatively cheap, straight-forward, and customizable.[12] The technique is determined by the pollutants to be removed size, density, and surface charge. Inorganic precipitants include limestone, caustic soda,

soda ash, sodium bicarbonate, sodium sulphide, and sodium hydrosulfide are among the most often used for the precipitation of heavy metals. Additionally, they have certain drawbacks including high lime and peroxide doses and pricey sludge fees. A highly prospective bidentate or tetradentate ligand with two cystamine groups and benzene as a backbone has been used to minimize metal contamination from acidic water coming directly from mines.

1.2.3 Ion Exchange

Ion exchange is a straightforward and cost-effective method for transferring soluble ions from the liquid phase to the solid phase. It has been demonstrated to be an effective approach for removing heavy metals from aqueous solutions, particularly in cases when the metal concentration is low. The elimination the metal ions to the solution, a specialized ion exchange with cations or anions (found naturally inorganic adsorbent or synthesized organic ion exchange materials) is used. By binding a heavy metal ion to an immovable solid particle and displacing it with the solid particle cation, a heavy metal ion is recovered from a wastewater solution.[13]The main advantages of ion-exchange are the eradicating of liquid problems Ion exchange polymers allow for the ability to eliminate substances such hard water, scale accumulation, nitrates, and arsenic. The biggest drawback of maintaining ion exchange technology is the high long-term expenses, ineffective at effectively purging water of germs. Typically, synthetic organic ion exchange resins are utilized as matrices. However, this method has some drawbacks, including membrane fouling, pH sensitivity, and non-selectivity of the membrane.

1.2.4 Flotation

Techniques for flotation are based on the various wet ability qualities of materials' surfaces property of density features with regard to the surface. To enhance separation, a centrifugal field may sometimes be used. With sulphide minerals, flotation, also known as froth flotation, is a gravity separation technique that is frequently used. It is unquestionably a byproduct of the processing of minerals. It is believed that its significance to the industrial economy at large must be enormous. In mineral processing, flotation is a technique for segregating and reducing ores by modifying their surfaces to a hydrophobic or hydrophilic state, indicating that the surfaces are either attractive to or repellent to water.[14] The froth flotation method

is used for more than a century and took a while to develop. It derives from the chemistry of the surface of micro-particles. Low sludge is obtained by the flotation process. Hence, this method is an ideal match to be integrated into the establishment of an effective and economic electrochemical treatment system. Wide application is one of flotation's key benefits. One of the most popular techniques, froth flotation method, holds a commanding position in many mineral processing technologies, High separation efficiency, thorough recovery that is good, reagent consumption, strict grinding size requirements, and numerous constraints.

1.2.5 Coagulation/ Flocculation

The destabilizing of colloidal particles known as coagulation is caused by the presence of a coagulant, a chemical reagent. Destabilized particle aggregation into micro-floc, followed by the formation of large floccules that can be settled, is known as flocculation. The chemical water purification procedure known as coagulation eliminates removing sediments from stagnant water altering the geostatic attraction molecules in river.[15]Coagulation is a method which, by encouraging the bond across the elements, renders the clumps much simpler to break apart. Coagulation distributes the pressure placed on the particulates whereas flocking lets the particles to join aggregate as well as grow wider to ensure that they can be evacuated from the liquid with greater ease. By eliminating the forces keeping colloids separate, coagulation leads colloids to be become instability, while flocculation causes destabilizing particles to cluster together. Both flocculation and coagulation are important techniques in the treatment of water and wastewater to separate and get rid of suspended materials. The operating costs of this technique are a major drawback. To obtain the appropriate level of flocculation, significant amounts of coagulant and flocculent may be required in some circumstances. The coagulant's effectiveness is determined by the coagulant's types, dosage, pH, temperature, alkalinity, and mixing conditions. To benefit from the financial, energy, and environmental benefits of coagulation, coagulation conditions and coagulant characteristics should be screened and analyzed to determine the best flocculation conditions.

1.3 VARIOUS ADSORBENTS

1.3.1 Prawn Shells



Fig.1.9 Prawn Shells

Shrimp shells are utilized as an adsorbent or biosorbent by converting to varied forms like chitin and chitosan. In many parts of the world, seafood is considered to be an important food source and plays an important role in the food chain system. There are several uses for chitosan in the healthcare, agricultural, biotech, cosmetics, pharmaceutical, culinary, paper, and textile industries. Epi-, exo-, and endocuticles are the three calcified outer layers of a shrimp shell, along with an inner membrane.[16]The epidermis' outermost and thinnest layer, the epicuticle, contains minerals in the form of islands of spherulitic calcite that are encased in a lipid-protein matrix. The basal layer of mineral-filled channels cuts through it at an angle, making it bilaminar. The executable, which lies underneath the epicuticle and is made up of layers of constantly shifting-orientation chitin-protein fibers embedded with mineral crystals. This continually changing orientation of chitin-protein stripes is also seen in the tip of the cuticle, which is the thickest & most calcified layer of the prawn shells under the carapace. Between 6 to millions of tons of waste crab, shrimp, and lobster shells are dispersed as waste every year on a global scale. These organic wastes, which include minerals, proteins, amino acids, arytenoids, and other fatty acids, can add significantly to the burden in landfills. It is essential to collect them and use them in a zero-waste way. Residual proteins found in waste shrimp shells can be considered of as the bacterial incubation medium. Moreover, the disposal of the

used shrimp shells would result in a high concentration of COD in the leachate, which would have a negative effect on the environment by causing oil and water pollution. Shrimp shell, which is typically eliminated as food waste and an industrial by-product, would be a good choice for environmentally friendly adsorbents shrimp weight is 40–66% shell waste. The technique of just using activated carbons as an adsorbent for organic pollutants is extensive, and there are still many challenges to overcome.[17] Chitosan and chitin are typically extracted from shrimp shells, and these materials are used for adsorption. Shrimp shells were chosen as a natural adsorbent for this research because of their availability, affordability, and ease of usage. The main difference between this study and others is the usage of raw shrimp shells without any chemical processing. Waste shrimp shell's economic advantages will be enhanced and environmental pollution will be reduced if they can be used successfully in production methods.

1.3.2 Fish Scales



Fig.1.10 Fish Scales

Fish scale bio sorbents have been reported to have excellent removal efficiency (50-100% for toxic metals and 78-90% for dyes) as well as extremely good adsorption capacities for heavy metals, dyes, and medicinal chemicals. The foundation of the scales comprises collagen fibers organized in a pattern akin to covered plywood. The bundles of collagen fiber are very tightly packed. Because of their hierarchically ordered structure, scales have a very high resistance to mechanical stress. Minerals (30-56%) and protein (40-60%) can both be found in fish scales.[18] Collagen makes

up 80–90% of the protein in scales. It's been revealed that using fish scales directly as food or indirectly to make feed additives is the optimal usage for them. Some have scales, whereas others don't. Many studies have been done on the usage of these scales to add value to life while limiting the ability to represent a nuisance when they are just dumped to the environment. Heavy metal removal from aqueous solutions is performed extremely successfully by bio-adsorbent made from fish scales, with most reported removal efficiencies above 50%.

1.3.3 Banana Peels



Fig.1.11 Banana Peels

One of the most popular fruits consumed worldwide is the banana (family Musaceae), which creates strong agro-waste issues. Cellulose, hemi cellulose, pectin, and some other low molecular weight species are the major components of banana peels. They also principally contain cellulose, pectin, and lignin. Utilizing a green method, naturally abundant plantain peels are used to produce Fe_3O_4 Magnetic nano-particle.[19]An eco-friendly, cost-effective replacement for chemical and physical processes has been proposed for nano-particle synthesis. Banana waste has been an important agricultural waste tested as an adsorbent due to the numerous pieces that can be utilized, such as shells, trunks, pseudo-stems, leaves, and core. These banana waste elements have received in-depth research as adsorbents for a wide range of contaminant. Banana waste (mostly peel) is the most common type of trash produced as a result of consumption fresh fruit, contributing for 29% of the total wastes generated in this category.

1.3.4 Orange Peels



Fig.1.12 Orange Peels

Orange peels are widely utilized as adsorbent in the process of treatment of wastewater due to their huge surface area and active functional groups; nevertheless, their expensive cost occasionally precludes their use. Orange residue, a by-product of the fruit industry that is mostly utilized as animal feed, is one of the citrus fruits that are easily obtainable in India. The majority of its component are low molecular weight components such cellulose, pectin, hemicelluloses, lignin, chlorophyll pigments, and limonene.[20]Orange peels have been utilized in adsorption studies and are recognized in the literature as an agriculture industrial residue having adsorptive characteristics.

1.3.5 Rice Husk



Fig.1.13 Rice Husk

As an effective adsorbent material for treating diverse pollutants from water and wastewater, husk is a kind of Coarse structure, becomes impermeable in water, is inorganic resistant, is indeed corrosion resistant. Rice husk, the amount of irrigated area, regional environmental factors, the use of fertilizers, climate variance, soil chemistry, and the efficiency of crop production and agronomic techniques all impact how quickly rice develops.[21]Due to the uneven surface of rice that enables for the adsorption of metals in various parts of this material the morphology of rice husk may facilitate the adsorption of metals and other toxins.

1.4 MAGNETIC NANOPARTICLE AND ITS TYPES

Heavy metal ion removal from aqueous solutions has been suggested for nanomaterials having magnetic characteristics. Magnetic nanomaterials may be created utilizing a variety of methods. It was discovered that magnetic nano-adsorbents are inexpensive, easy to use, ecologically friendly, and very effective in removing metals from vast amounts of water and waste quickly. New varieties of nanoparticles for remediation of polluted water have been developed as a result of the recent advancements in nanotechnology.[22]By combining magnetic separation with nanotechnology, nano-adsorbents may provide an effective method for removing harmful metal ions from aqueous solutions. Metal oxide nano-adsorbents has received a great deal of attention because they exhibit several desirable characteristics as compared to their bulk form, including a high adsorption capacity, improved catalytic activity, a high degree of dispersion, and super para-magnetism behavior.

TYPES OF MAGNETIC NANO PARTICLES

1.4.1 Carbon based nanoparticles

Carbon nanotubes, carbon black, graphene oxide, and biochar are just a few of the carbonaceous materials that have been the subject of intense investigation for their ability to absorb various environmental contaminant. A wide range of Activated Carbon sorbent materials may be produced for a wide range of environmental applications, including the removal of aqueous solutions containing heavy metals.[23]Due to the high production costs associated with this technique, a recent advancement in the area of adsorption of toxic metals involves the use of biochar as a less expensive substitute for coal-based activated carbon. Since the advent of

nanotechnology, several studies have been conducted on the potential applications of graphene-based substances for the elimination of toxic metals, like Carbon Nanotubes, reduced Graphene Oxide, and graphene Oxides.

1.4.2 Nano zero valent ion (nZVI)

Nanosized zero-valent nanoparticles have emerged as a new and highly successful remediation method for heavy metals considering its strong reduction capacity, considerable certain pore volume. Zero-valent ion at the nano-scale, a material that is harmless for the environment, has been utilized to successfully treat a number of metallic ions in aqueous solutions.[24]In terms of the reduction of heavy metal ions, nZVI has shown outstanding promise thanks to its strong reactivity, extraordinary reactive lifespan, and low toxicity. nZVI is a substance that is widely used to eradicate heavy metals from freshwater, it has exceptional capabilities for absorbing and decreasing various types of toxic metal ions.

1.4.3 Silica based nanoparticles

Over the past 10 years, silica-based using nanostructures studied is investigated. SiO₂ has long been recognized as the best material for water treatment because of its distinctive properties, which include affordability, non-toxicity, strong acid resistance, and simplicity of modification.[25]It needs to be emphasized that the specific amounts of complicated chemicals bound to those, as previously said, modified SiO₂ nanoparticles are unknown.

1.4.4 Nanocomposites

Nanostructured materials are used to remediate water. They have exceptional characteristics owing to its tiny dimensions, vast large region, and high "surface to volume" proportion. The characteristics increase the removal efficiency of the nanostructured materials. These materials differ from regular materials in that they have exceptional properties including large specific surface area, significant reactivity, and catalytic potential. Nanostructured particles have a very large number of active spots for interacting with various chemical species due to their massive surface area.[26]The extraordinary surface characteristics of nano-silica were used to make two novel composites utilizing a simple and eco-friendly chemical process. The nanocomposite was assessed using a variety of methods to confirm the

change. The nanocomposite was therefore used to adsorb or remove metals after being placed within a glass column.

1.4.5 Polymeric Nanoparticles

Over the past 10 years, metallic nanoparticles adsorption (MNP) has attracted a lot of interest due to its efficiency and broad application. It is because the procedure is simple to utilize. Surface polymeric MNPs, including such MNP polymer composites with core-shell MNP, have received a lot of interest lately since the polymer shell prevents the core portion of the Magnetite nanoparticles from collating into bulk materials and enhances the stability of dispersion of the core-shell nanoparticles in a suspension medium.[27] Polymeric nanoparticles are receiving a lot of interest due to their alluring functional groups and ease of modification. These polymeric nanoparticles may be distributed effectively by the organic and aqueous phases. Rapid synthesis of polymeric nanoparticles is possible with a simple precipitation method and low-cost starting materials.

1.4.6 Ceramic Nanoparticles

Ceramic membranes are being employed in more and more applications due to their wide chemical and temperature operating range. Ceramic membranes' exceptional antifouling capabilities and long operating life greatly minimize the high startup design complexity. More than 20 nations employ ceramic water filters as an alternative point-of-use water purification system.[28] Two locally sourced materials are utilized to produce Ceramic Water Filters: clay and sawdust. Ceramic composites membranes offer greater antifouling qualities with increased mechanical and chemical durability when compared to polymeric composite membranes.

1.4.7 Metal Oxide Nanoparticles

Magnetic nanoparticles made of iron offer unique properties such a larger surface - to-volume ratio, a lower demand for chemicals, and a lack of secondary pollutants. Fe_3O_4 nanoparticles (MNP's) are a new category of nanomaterials that are easy to recycle, can be enhanced through magnetic separation, have high stability, are bioactive, have a low toxic level, are less expensive, have a uniform size distribution, have a high magnetic permeability, and have a sizable surface area. Fe_3O_4 adsorbents have arrived at the perfect moment because of these exceptional

properties.[29] Fe_3O_4 magnetic nanoparticles are indeed an intriguing new category of nanometer-sized components because they will show a variety of distinctive and certain values like a huge area, possibility for precision, chemical sensitivity, catalyst potential, and an absence of internal diffusion resistance, which are promising to develop new or improve existing innovations in wastewater treatment.

1.5 METHODS FOR PREPARING MNP

1.5.1 Co-precipitation

Various methods have been used to manufacture nano-magnetite (Fe_3O_4), comprising sol-gel synthesis, thermal decomposition, co-precipitation and hydrothermal synthesis. The most popular techniques are thermal decomposition and co-precipitation. There are four various forms of co-precipitation processes: mechanical entrapment, mixed crystal, occlusion, and surface adsorption. Compared to other synthesis techniques, co-precipitation is simpler and more useful. Co-precipitation is one of the most successful and attractive procedure due to its simple experimental setup and efficient formation of tiny particulates at low testing temperature.[30]The chemical co-precipitation technique has a number of advantages, including a simple process, outstanding material quality with control over microscopic particle size, and a reasonably short reaction time at ambient temperature. Co-Precipitation is the drawing down of soluble substances by a precipitate under particular circumstances generally, a nucleation emerges out of thin air in solution when a component concentration reaches super saturation. Compared to different sources, Co-precipitation is vital in the synthesis of magnetic nano-particles. Fe_3O_4 nanoparticles can be synthesized easily via co-precipitation. Co-precipitation will be utilized to produce magnetite nanoparticles. The co-precipitation technique has a high yield, high product purity, no requirement for organic solvents, is easily repeatable, and is cheap. The usage of capping agents can modify the crystallite size and shape of the material created using this process.[31]However, the co-precipitation process has some major limitations, including the requirement for frequent washing, drying, and carbonization to produce a pure phase of phosphorous. An important method for separating and also from various samples is co-precipitation method.

1.5.2 Sol-Gel

The sol-gel process consists of two major steps: hydrolysis of the precursors in basic or acidic conditions and polycondensation of the hydrolyzed products. The size distribution of sol-gel alumina nanoparticles is between 10 and 20 nm, and they are more spherical and homogenous in structure. For production of various nanostructures, especially the sol-gel approach corresponds to the more scientific (moist chemicals) strategy producing nanoparticles made from oxides.[32] Due to the low heating rates that can be utilized to heat-treat the "green" coatings, sol-gel processing enables the synthesis of thin films with high adhesion property. The main advantages of sol-gel processing method were high purity and the capability of uniform nanostructures at low temperature. The remaining gel has eventually dehydrated, at which point its fluid is extracted out from gel's composition. The characteristics of both the cured gel are highly altered by the drying process. Phrasing it yet another way, the "removing solvent method" has determined by keeping its envisaged utilizing gel.

1.5.3 Thermal Decomposition

A novel technique for producing stable mono-dispersed nano-particles involves thermal decomposition. Decomposition reactions are available in three varieties thermolysis, electrolysis, photolysis. The process of decomposing by electricity is known as electrolysis. The term "photolysis" refers to the decomposition caused by light. There are two or more products, but only one reactant in a thermal decomposition reaction. Since warmth seems to be a substrate in all these interactions, most also thermodynamically favorable, it signifies that heat energy's needed to destroy the covalent bonds that link the molecules. Thermo-chemical decomposition is simple and affordable.[33]The rate of decomposition could be determined using a device called a thermo-gravimeter, while zeta potential was used to determine stability in biological applications. Recent studies, however, reveal that the magnetic magnetite/maghemite phases continue after the thermal decomposition processes actually start with the production of a nonmagnetic Wüstite phase due to oxidation when exposed to the ambient oxygen. The reaction can occur at a high reflux temperature due to the highly boiling point solvents utilized

in Thermal Decomposition procedures, especially dioctyether, whose boiling point is nearly to 300 °C.

1.5.4 Hydrothermal Synthesis

The most common technique for generating nanomaterials is hydrothermal synthesis. In hydrothermal synthesis, nanomaterials can be created at a variety of temperatures, including very high temperatures and room temperature. The word "hydrothermal synthesis" represents a temperatures and pressures that are beyond ambient, diverse reactions in water-based solutions are used to generate organic chemicals.[34] Magnetic nano-particles as well as a wide variety of other nano-materials may now be made using hydrothermal techniques. The hydrothermal process is often carried out in an "Autoclave," a pressurized vessel. Both pressure and temperature can be controlled by it. Graphene-ZnS nano-composites can be easily created by hydrothermally treating GO and ZnS precursor with water, a process known as hydrothermal synthesis. The hydrothermal synthesis strategy is cleaner and more efficient than the synthesis techniques outlined above, but there are still some major challenges, such as the yield and dispersion of Magnetic nano particles.

1.6 APPLICATIONS OF MNP

- ❖ Industrial applications
- ❖ Medical and Biomedical applications
- ❖ Sensors and Catalysis
- ❖ Environmental usage and Molecular Imaging

CHAPTER-2 LITERATURE SURVEY

- **Dr.D.Prabu *et al.* (2021)** has published a scientific article titled **“Feasibility of Magnetic Nano Adsorbent impregnated with activated carbon from animal bone waste”**. Chromium is a heavy metal that causes a lot of pain for the environmental elements when it is present in effluents. This MNA from animal wastes is used to remove heavy metals like chromium. The new MNA Fe_3O_4 -BAC was created, examined, and employed in the study as an effective sorbent for the elimination of chromium in liquid solution. The thermally treated BAC is co-precipitated onto the magnetic nano adsorbent under ultrasonic conditions. The Fe_3O_4 -BAC's enhanced shape is seen in the SEM imaging with a more favorable structure for 100-446nm, among the nanoparticle narrow size distribution comprised. At an acidic pH during a contact period of 60 minutes with an adsorbent concentration of 5g/L, optimal adsorption has been discovered. Nano adsorbent has an ideal binding of 27.86 mg/g. A procedure feasibility has been confirmed by thermodynamic and isotherm experiments. Additionally, the kinetic experiments demonstrate the examined Fe_3O_4 -BAC's propensity towards pseudo-first order models. As a result, Fe_3O_4 -BAC may have application to be an absorber to extract with aqueous media, chromium.
- **Christos Liosis *et al.* (2021)** has published an article titled **“Heavy Metal Adsorption Using Magnetic Nanoparticles for Water Purification: A Critical Review”**. With a focus on water quality and technique applicability, a framework for analyzing the key discoveries too earlier studies in ions elimination by MNP is offered. Numerous studies have been conducted with an emphasis on the synthesis, characterization, and capability of uptake of bare & modified iron nanoparticles, to the related desorption process of the approach the research techniques reveal effective sorption of impurities into marine conditions, according to the current review study likewise a yield of as much as 90 can be accomplished through reusing the nanoparticles to a maximum of five times. Moreover, it deserves to be acknowledged that nanoparticles have rarely endured up to 22 episodes of recovery.

- **Milton Manyangadze et al. (2020)** has published an article titled **“Adsorption of lead ions from wastewater using nano silica spheres synthesized on calcium carbonate templates”**. In this article, they looked into the method of purifying wastewater for use by plants, animals, or industrial processes by removing Pb(II) ions using adsorption. To eradicate lead metal from water, they created nano silica hollow spheres (NSHS) & employed them as adsorbents. Silica amorphous attribute is clear when they used X-Ray diffraction to analyze the NSHS; a representation for a typical crystalline was 39.5 nm. The structure of the adsorbent was studied using scanning electron microscopy, and it was discovered that the particles were spherical and ranged in size from 100 to 200 nm. The loss of weight of NSHS, which was found to be 2% at 800°C, was calculated by thermo-gravimetric analysis. At a maximum temperature of 60°C and a maximum starting metal concentration of 300 mg/L, the adsorption efficiency was 200 mg/g and 262 mg/g, respectively, and the adsorption rate was 99.6% & 87.4%, respectively. The equilibrium and thermodynamic data showed that the Langmuir adsorption isotherm ($q_{\max} = 266.89$ mg/g and $b = 0.89$ L/mg) provided a better description of the process. Both the endothermic and spontaneous adsorption processes were present. They draw the conclusion that NSHS were effectively synthesized, used to eliminate Pb(II) ions, and their production has a greater capacity than the majority of other adsorbents examined by other researchers.
- **Minh Trang Hoang et al. (2018)** has published an article titled **“Removal and recovery of lead from wastewater using an integrated system of adsorption and crystallization”**. Besides the interest of getting rid of and reclaim oceanic Pb environments, in this investigation investigates viability of like a trigeneration system that combines sorption in crystallisation in a particle furnace. With the use of citric acid-modified sugarcane bagasse (SCA), researchers looked into the preferential adsorption of Pb²⁺ over Ca²⁺ and Mg²⁺ in batch and column systems. With a 7 cm slope, a 1.5 ml/min flow rate, as well as an edge activator intensity of 0.482 mmol/L, led has indeed been preferentially immobilized on SCA in a chromatographic column up to an efficiency of 0.767 mmol/g. Selective separation of Pb²⁺ from the mixed solution was accomplished at a molar ratio $3.22 < 4.49$ in batch mode.

According to the dynamic analysis, the Thomas & Yoon-Nelson models and the experimental findings are very closely correlated. The dissolving examination of the perfect balance biosorbent SCA in a column system demonstrates that it is a possible desorption reagent with a dissolution capability of 80% Pb^{2+} . A quantitative recovery of Pb(II) was achieved under ideal circumstances of pH 10, superficial velocity of 9.55 m/h, and starting Pb(II) concentration of 2.43 mm. Overall, it was determined that the designed system, which combines adsorption utilising a briquette heater, is enough to eliminate they extract Pb form effluent via PbCO_3 .

- **Shijie Liu, Suping Cui et al. (2021)** has published an article titled **“Adsorption of Lead Ion from Wastewater Using Non-Crystal Hydrated Calcium Silicate Gel”**. In order to produce low-cost and effective adsorption materials, this study used calcium acetate and water glass as raw materials to synthesise calcium silicate hydrate silicate gel via precipitation process. By means of X-ray spectroscopy, FTIR, a particular surface area analyzer, & a SEM, functionality and composition of hydrated calcium silicate gel was methodically investigated. According to studies, non-crystal hydrated calcium silicate gel (CSH) was effectively created, and utilizing CSH, lead ions were removed at a rate of more than 90%. The adsorption process is consistent with both the pseudo-second-order kinetic model and the Langmuir adsorption isotherm model, with a maximum adsorption capacity of 263.17 mg/g. The lead ion adsorption capability employing CSH was demonstrated in the acid treatment experiment, and the adsorption rate persisted at >60% after 5 cycles. The study could provide an adsorbent with cheap cost, high efficiency, and great stability.
- **Ata UrRehman et al. (2021)** has published a journal titled **“Toxicity of heavy metals in plants and animals and their uptake by magnetic iron oxide nanoparticles”**. Heavy Metals are present in the environment naturally, but because of human activity and some natural processes, they have gotten into the air, the water, and the soil and have grown to be a significant worldwide problem. Most of them build up in the body for extended periods of time after entering it, causing a variety of issues, as in the case of plants it will harm vital parts like elements of organelles, bases, and foliage, and obstruct crucial

biochemical processes like photosynthesis and mineral absorption. Similar to how they may harm an animal's essential bodily organs like the kidney and liver, they can also lead to deadly illnesses like cancer. The dose, length of exposure, and concentration of these heavy metals all have a significant role in the illnesses they cause. Because of the toxicity, bioaccumulation, and non-biodegradability of heavy metals, this issue has become quite serious. Various sources have exposed living organisms to these heavy metals, but drinking water is one of the main ones. To eliminate these metals from water, a lot of work has been done. However, the traditional methods have a number of shortcomings, such as being uneconomical and having an effect on the environment. Numerous benefits include regeneration, surface alteration, economic effectiveness, ease of usage, and environmental friendliness.

- **Fahad Saleem Ahmed Khan *et al.* (2020)** has published scientific article titled **“Magnetic nano adsorbents potential route for heavy metals removal—a review”**. The dumping of local waste and the fast expansion of the heavy metal-based businesses have had serious negative effects on the ecosystem. Reverse osmosis and ion exchange methods were commonly used in the past to remove heavy metals, but these processes have significant drawbacks. Because of this, a lot of work has gone into developing improved techniques, especially for the elimination of heavy metals. The application of nanotechnology presents the opportunity to enhance currently employed approaches in order to more effectively address problems. Numerous novel materials, including magnetic nano-particles, have been discovered as a result of advancements in nanotechnology. These nanoparticles have good qualities such a high surface-to-volume ratio, less toxicity, and simple separation. Additionally, as compared to other conventional adsorbents, magnetic nanoparticles may be retrieved after adsorption quickly and effectively. The effectiveness in metal ions removal from fluid using magnetic nano-adsorbent is only major focus of this review. Additionally, a thorough examination of the methods used to create, characterize, and modify magnetic nanoparticles is provided in a methodical manner. Additionally, the potential benefits and drawbacks of utilizing

magnetic nanoparticles as an adsorbent to remove heavy metals are highlighted.

- **Fato Patrice Fato *et al.* (2019)** has published a journal titled “**Simultaneous Removal of Multiple Heavy Metal Ions from River Water Using Ultrafine Mesoporous Magnetite Nanoparticles**”. Numerous ions found in river water can have an impact on the adsorption process in an aquatic environment. Four heavy metal ions, Pb^{2+} , Cd^{2+} , Cu^{2+} , and Ni^{2+} , have been successfully removed simultaneously from river water using UFMNPs due to the attraction of these metal ions to the surface of the particles and their unique mesoporous structure, which facilitates the simple adsorption. Individual Pb^{2+} , Cd^{2+} , Cu^{2+} , and Ni^{2+} ion removal efficiencies from river water were 98, 87, 90, and 78%, whereas combined Pb^{2+} , Cd^{2+} , Cu^{2+} , & Ni^{2+} ion removal efficiencies on same flowing water were 86, 80, 84, and 54%, respectively. This work has shown that UFMNPs have a great deal of promise for use in treating wastewater, particularly simultaneous elimination of metal ions in environments.
- **Noraziah Abu Yazid *et al.* (2019)** has published a journal titled “**Co-precipitation synthesis of magnetic nanoparticles for efficient removal of heavy metal from synthetic wastewater**”. Magnetic nanoparticles (MNP) have emerged as a valuable tool or catalyst in a variety of commercial applications. MNP is smaller than bigger particles and as a result has a larger surface area, which renders it more responsive to particular chemicals. The main emphasis of this work is the application of MNP to the environmental problem associated with the heavy metal discharge from industrial effluents. Varied variables, including temperatures and prioritizes (KOH), sodium hydroxide & ammonium hydroxide) is appended to a mixture containing Fe(II) and Fe(III), were used synthesis the MNP in order to produce different sizes and morphologies. Atomic Adsorption Spectroscopy was used to assess the effectiveness of MNP removal on a solution containing Cr, Ni, and Cu before the results were examined (AAS). TEM, FTIR, and XRD were used to characterize the MNP. Based on the findings, it is determined that MNP produced with NH_4OH at 70°C is responsible for 90% of the Cr removal. The MNP has the shortest size (9 nm), which allows it to absorb more Cr ions. As

a result, the strong base produces MNP with the lowest dispersion, while the addition of surfactant results in less heavy metal adsorption but greater oxidation resistance. This research has shed light on the viability of using the MNP as a metal ion removal option.

- **Junhua You *et al.* (2021)** has published a journal titled “**A review of amino-functionalized magnetic nanoparticles for water treatment: Features and prospects**”. Due to their remarkable qualities and wide range of uses, such as the treatment of wastewater and/or water, increased curiosity in nanotechnology have emerged. Because of the negative consequences on both people and the environment, the release of toxic substances and other toxins into water supplies is a problem. Aminated or amino-functionalized MNP are produced by grafting amino functional groups onto magnetic nanoparticles. This work reviews the production, separation, and adsorption processes as well as the potential applications of amino-functionalized magnetic nanoparticles in water treatment. To elimination form groundwater of metallic, radioactive substances, organics, colors, and microorganisms, a number of significant works have also been mentioned. Additionally, the effects of variables like pH, contact duration, ion selectivity, and recycled content are discussed, as well as the dose of magnetic nanoparticles.
- **Mohamed A. Tahooun *et al.* (2020)** has published a journal titled “**Effective Heavy Metals Removal from Water Using Nanomaterials: A Review**”. High harm to the environment is posed by the release of heavy metals such as Zn, Ni, Pb, Cu, Cr, Cd in water over the allowed limits. Better clean-up methods have recently been made available employing nanotechnology and nanomaterials. The focus was on newly created, cost-effective nanomaterials for use in water and wastewater clean-up, including zeolite, carbonate, polymer-based, chitin, ferrous, metal oxide, bimetallic, and metallic materials. This review concentrated on the synthesis of different nano-adsorbent materials and their capacity to remove various hazardous ions. Also studied was the impact of many experimental physicochemical variables on the adsorption of heavy metals, including ionic strength, starting ionic strength, temperature, contact duration, adsorbent dosage, and pH.

- **Lakshmi Prasanna Lingamdinne *et al.* (2019)** has published a journal titled Green “**Synthesis of Iron Oxide Nanoparticles for Lead Removal from Aqueous Solutions**”. Because it is a carcinogen and a heavy metal, Pb(II) always poses a serious hazard to human kind. It is widely employed technique for removing metals because it is very efficient, simple to use, and economical. Size, large surface area, and magnetic properties, oxides of iron is discovered in appealing for heavy metal elimination from ocean. At an initial metal concentration of 10 ppm & room temperature of 25°C, it was discovered that 0.6 g/L of T-Fe₃O₄ was able to remove 99% of Pb(II) via adsorption. On the homogenous surface of the adsorbent, a monolayer adsorption isotherm was discovered. In order to provide clean and sanitary water for a healthy and sustainable existence, lead may be removed from water resources using green tangerine peel altered iron oxide nanoparticles.
- **K.Anbalagan *et al.* (2021)** has published scientific article titled “**Removal of heavy metal ions from industrial wastewater using magnetic nanoparticles**”. By the co-precipitation approach, maghemite (γ -Fe₂O₃) and MNP (Fe₃O₄), were created in this study, and they were characterised using EDS, XRD, SEM, and FTIR Spectroscopy. These particles, which ranged in size from 20 to 100 nm, were utilised as nano adsorbents to filter out toxic metals like copper and chromium from synthetic wastewater. Adsorption is dependent on factors including pH (2.5 & 6.5), contact duration (60 and 80 minutes), and doses at room temperature, which were shown to have a 92% removal effectiveness for chromium and copper. These particles demonstrated astounding metal removal effectiveness. Additionally, these particles were renewed for reuse; for the desorption of copper and chromium metals, respectively, HCl and NaOH effluent were used. The observed data clearly show that magnetic nanoparticles have improved pollution removal. The separation factor (*r*), which ranges from 0 to 1, shows that the Langmuir isotherm favours both the ions of copper and chromium.

CHAPTER-3 AIM AND SCOPE

3.1 AIM

- ❖ Synthesis of Prawn Shell impregnated Magnetic Nanoparticle (MNP-PS).
- ❖ Characterization of Prawn Shell impregnated Magnetic Nanoparticle (MNP-PS)
- ❖ To improve variables like pH, Temperature, Time, Dosage, and Concentration through batch adsorption experiments.
- ❖ To study isotherm models for Langmuir, Freundlich Temkin and Sips and to analyze experimental data using the Pseudo-First order and Pseudo-Second order Adsorption Kinetic Models.
- ❖ Removal of Pb(II) ions from Industrial Effluent using Prawn Shell impregnated Magnetic Nanoparticle (MNP-PS).

3.2 SCOPE

- ❖ The utmost scope of this work is to treat water contamination using eco-friendly Prawn Shells.
- ❖ Since Nanoscience is advancing day-by-day, these prawn shells are converted into Magnetic Nanoparticle for the removal of Pb(II) ions from Water.
- ❖ Pb(II) ions causes several serious damages to Human Life, Marine Life and to the whole ecosystem itself. So, treatment of them in a novel way is found mandatory.

CHAPTER-4 MATERIALS AND METHODOLOGY

4.1 MATERIALS

The List of materials employed to synthesize MNP-PS nanoparticles are listed below:

4.1.1 Chemicals Required

- ❖ Hydrochloric Acid (HCl)
- ❖ Ferric Chloride (FeCl_3)
- ❖ Ferric Sulphate ($\text{Fe}_2(\text{SO}_4)_3$)
- ❖ Ammonium Hydroxide (NH_4OH)
- ❖ Ethanol ($\text{C}_2\text{H}_5\text{OH}$)
- ❖ Distilled Water
- ❖ Lead Nitrate ($\text{Pb}(\text{NO}_3)_2$)

4.1.2 Equipment Required

- ❖ Muffle Furnace
- ❖ Hot Air Oven
- ❖ Hot Plate Magnetic Stirrer
- ❖ Rotary Shaker

4.2 METHODOLOGY

4.2.1 Drying of Prawn Shells



Fig.4.1 Drying of Prawn Shells

Prawn shells are collected from Marina Beach and Local Markets in Chennai. To get rid of grime, dust, and traces of blood, prawn shells are properly cleaned with deionized water. Following that it is dried in the sun until it becomes crispy and fine.

4.2.2 Preparation of Activated Carbon of MNP-PS



Fig.4.2 Preparation of Activated Carbon of MNP-PS

Prawn Shells are kept in the Muffle Furnace for about 2 hours at 600°C. The powdered prawn shells are activated by immersing it in Hydrochloric Acid (HCl) for about 24 hours. The solution is then filtered and the solid powder is washed thoroughly with Distilled Water. It is then dried in the Muffle Oven for 1 hour at 200°C. The dried particle is the Prawn Shell Activated Carbon (PS).

4.2.3 Impregnation Process of MNP-PS



Fig.4.3 Impregnation Process of MNP-PS

The Activated Carbon is then impregnated with Ferric Chloride and Ferric Sulphate. Weighed 2g of Ferric Chloride (FeCl_3), 1g of Ferric Sulphate ($\text{Fe}_2(\text{SO}_4)_3$) and 1g of the PS. All the solid particles are added in the conical flask and kept in the Hot Plate Magnetic Stirrer. To it, added 50 ml of Distilled Water. The temperature is kept at 40°C and it is allowed to stir continuously for 15 mins.

4.2.4 Co-precipitation Process of MNP-PS



Fig.4.4 Co-precipitation Process of MNP-PS

Ammonium Hydroxide (NH_4OH) is added to the solution kept in the Magnetic Stirrer for co-precipitation process. 50ml of Ammonium Hydroxide is measured and added to the solution drop wise with constant stirring.

4.2.5 Magnetic Separation of MNP-PS

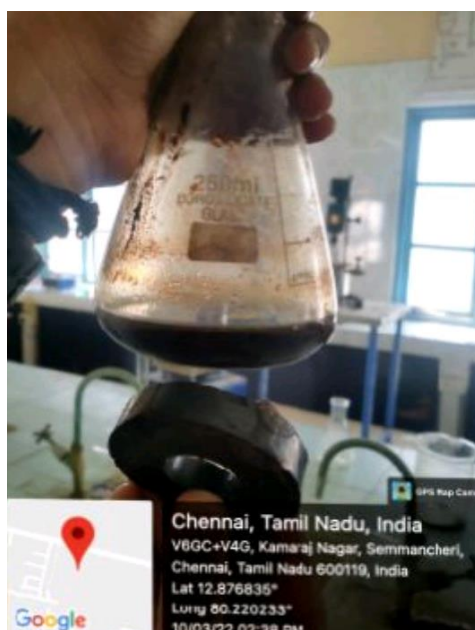


Fig.4.5 Magnetic Separation of MNP-PS

Magnetic Attraction is checked with the help of a Magnetic.

4.2.6 Filtration and Drying of MNP-PS



Fig.4.6 Filtration of MNP-PS



Fig.4.7 Drying of MNP-PS



Fig.4.8 MNP-PS

The solution is filtered and washed with ethanol to prevent rusting. The Filtrate is then dried in Muffle Oven at 150°C for 30mins. The powdered particle is the Magnetic Nanoparticle impregnated with Prawn Shells (MNP-PS).

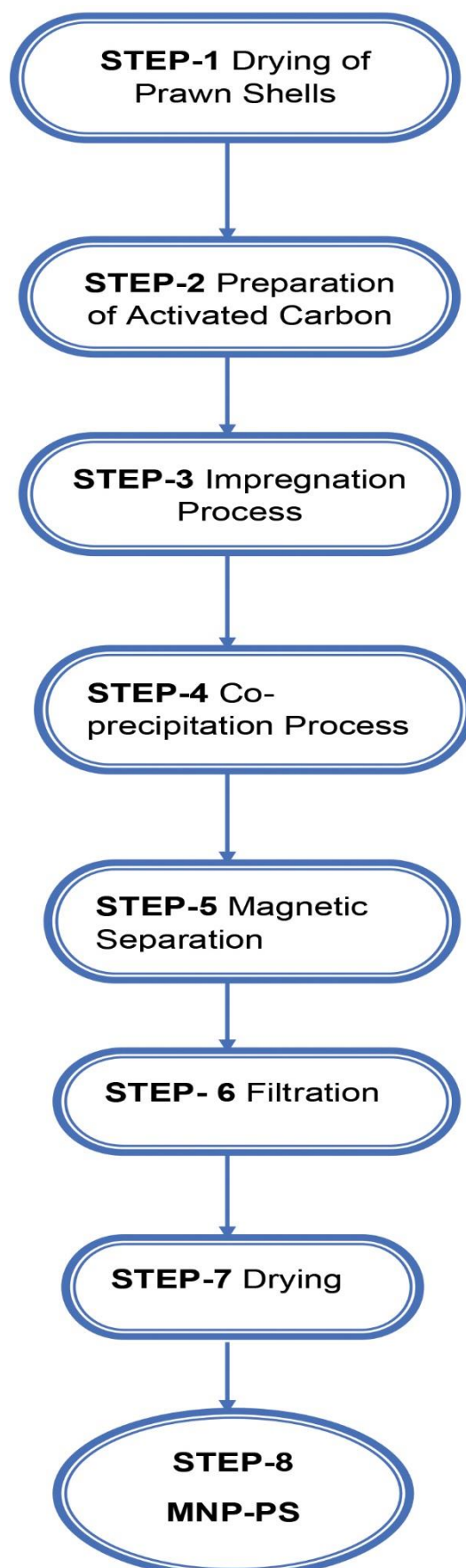


Fig.4.9 Schematic Representation of Preparation of MNP-PS

4.3 PREPARATION OF Pb(II) ION SOLUTION

Analytical Reagents Grades was indeed the criteria for all chemicals handled (AR). The measured quantity (1.6g) of lead nitrate (Pb(II)) adsorption was neutralized in the double water to produce a stock solution with such a Pb(II) levels of 1000mg/L. Pb(II) are generated again for required test concentrations(20-100mg/L) following diluting the stock solution mostly in right sequence. Have used 0.1M NaOH or 0.1M HCl, the pH of each standard solution was raised to the optimum consistency prior to actually introducing the adsorbent to an aqueous phase. Using a pH metre, the solution's pH was determined (Elico Model, India).

4.4 ADSORPTION EXPERIMENT

- ❖ Using MNP-PS as one method for increasing the adsorption of Pb(II) ions from aqueous media, batch adsorption experiments been performed to improve the processing parameters, like temperatures, preliminary Pb(II) ion amounts, solution pH, adsorbent dose and contact duration.
- ❖ Even during batch sorption studies, 100mL of Pb(II) ions treatment with variable starting Pb(II) levels (20-100mg/L), pH (2.0-8.0), and quantities of adsorbent (2.0-8.0g/L) all taken in 100mL flasks containing and then the combination was mixed in a Rotary shaker.
- ❖ These extracts is drawn out again in several time (0-60 minutes), when respective Pb(II) levels were evaluated.
- ❖ Adsorption Thermodynamics, Kinetics, Mechanism, and Isotherms were all employed systematically.
- ❖ The following process were employed in order to estimate the proportion of Pb(II) ion eliminated.
- ❖ Equation:

$$\% \text{ Removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100$$

Where C_o (mg/L) is starting and C_e (mg/L) are balancing levels of Pb(II) ions, as shown.

4.4.1 Adsorption Isotherm Experiments

Adsorption isotherm measurements is executed just putting 0.2 grams of without moisture MNP-PS samples into 100mL of a Pb(II) Ionized fluid and both the starting Pb(II) ion concentration varying between 20-100 mg/L at an optimal situation. The combination then was agitated in a Rotary Shaker till it reached a steady. The Pb(II)ion's sorption into aqueous phase was described by using two equations isotherm models consist of Langmuir, Freundlich, Temkin, and Sips isotherm models. The comparability of these model applicability coefficient of correlation (R^2) values and error values (SSE, sum of squared error and RMSE, root mean squared error). The two adsorption isotherm models using the following two parameters are as follows:

Langmuir Isotherm Model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

Equilibrium variable is:

$$R_L = \frac{1}{1 + K_L C_0} \quad (2)$$

Freundlich Isotherm Model:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Temkin Isotherm Model:

$$q_e = B \ln (A C_e) \quad (4)$$

Sips Isotherm Model:

$$q_e = \frac{K_s C_e^{\beta_s}}{1 + \alpha_s C_e^{1/\beta_s}} \quad (5)$$

where q_e is a proportion of absorbance in Pb(II) ions accumulated in MNP-PS (mg/g), q_m is very highest quantity of remaining coverage in Pb(II) ions consumed into MNP-PS(mg/g), K_L is the Langmuir constant relating in towards proximity Pb(II) ions to the adsorbent (L/mg), C_e represents the equilibrium state of Pb(II) ion solution

(mg/L)[35], K_F denotes the constant $((\text{mg/g})(\text{L/mg})^{1/n})$ adsorbent potential, n is a variable that correlates to the density of adsorption (g/L), $B=RT/b$ represents the constant associated with heat of adsorption, biosorbent warmth (kJ/mol), R denotes the gas constant (8.314 J/mol K), T denotes the temperature (K), A is greatest adherence energy correlated with optimum binds constant (L/mg), K_s as Sips system isotherm value (L/g) β_s , α_s is the Sips model constant $(\text{L/g})^{1/\beta_s}$ and β_s is often regarded as the heterogeneity factor, with values close to 1 indicating a homogeneous binding site and values greater than 1 indicating a heterogeneous adsorption system.

4.4.2 Adsorption Kinetics and Mechanism Experiments

By inserting 0.2g of MNP-PS in 100mL of Pb(II) ions solution (20-100mg/L) in a sequence of flasks containing, Pb(II) ions successfully removed employing MNP-PS. The samples were drawn out of the conical flasks at predetermined intervals while they were maintained in a shaking incubator (0-60min). The following expressions were used to determine the amount of Pb(II) ions adsorbed onto MNP-PS given time t , q_t (mg/g):[36]

$$q_t = \frac{(C_o - C_t)V}{m} \quad (6)$$

where, C_t is concentrated level of Pb(II) ions present with in mixture via period t (mg/L), V is density of Pb(II) ion solution (L) and m is Mass of MNP-PS (g). The statistics on kinetic model is utilized to examine equilibrium adsorption models that describe the adsorption characteristics, including such pseudo-first order, pseudo-second sequence, & Elovich Kinetic parameters.

The following are kinetic models:

Pseudo-first order Kinetic Model:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

Pseudo-second order Kinetic Model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Elovich Kinetic Model:

$$q_t = (1 + \beta_E) \ln(1 + \alpha_E \beta_E t) \quad (9)$$

Here q_e denotes the experimental equilibrium efficiency (mg/g), q_t denotes the capability to sorption anywhere at particular time. (mg/g), k_1 with fictitious initial kinetic order law (min^{-1}), t denotes the time (min), k_2 is fictional second kinematic reaction rate (g/mg.min) and $k_2.q_e^2=h$, it refers to first-order adhesion frequency (mg/g.min), β_E is there a connection between the re-sorption rate & adsorption and desorption activation energy (g/mg) and α_E is starting sorption qualities (mg/(g.min)).[37]

4.4.3 `Adsorption Thermodynamic Experiments

The sorption study was done with infusing 0.2g of MNP-PS to 100mL of Pb(II) solution inside a series of conical flasks having initial Pb(II) ion values ranged from 20 to 100mg/L. The adsorption equipment has been kept in an incubation shaker, which was effectively maintained at various climate extremes from 303 and 333 K. The set of equations were applied to be able to find values in terms of the enthalpy variable (ΔG°) (variation in surface energy), (ΔH°) (variation in enthalpy), and (ΔS°) (variation in entropy):

$$K_c = \frac{C_{Ae}}{C_e} \quad (10)$$

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

$$\log \left(\frac{C_{Ae}}{C_e} \right) = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (12)$$

now K_c is the equilibria value, C_{Ae} is number as for times Pb(II)ion particles got put on it by the MNP-PS each litre at optimal amount (mg/L), C_e is the accumulation of Pb(II) ions that are present (mg/L), R denotes the gas constant (8.314 J/mol/K) and T denotes the temperature (K).[38]

CHAPTER-5 RESULTS AND DISCUSSION

5.1 CHARACTERIZATION OF MNP-PS

5.1.1 Scanning Electron Microscopy (SEM)

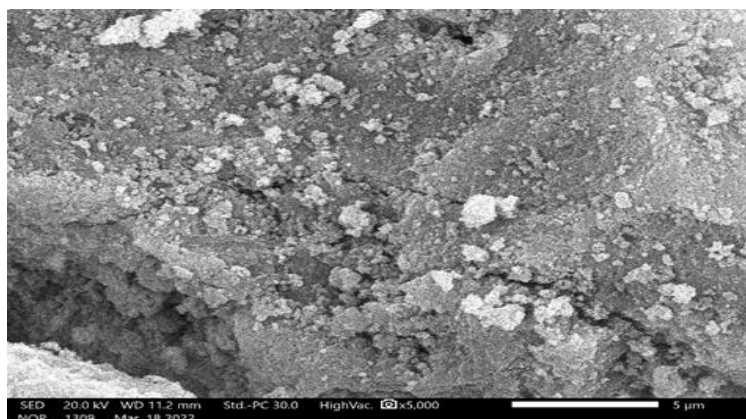


Fig.5.1 Sem Image (a)of MNP-PS

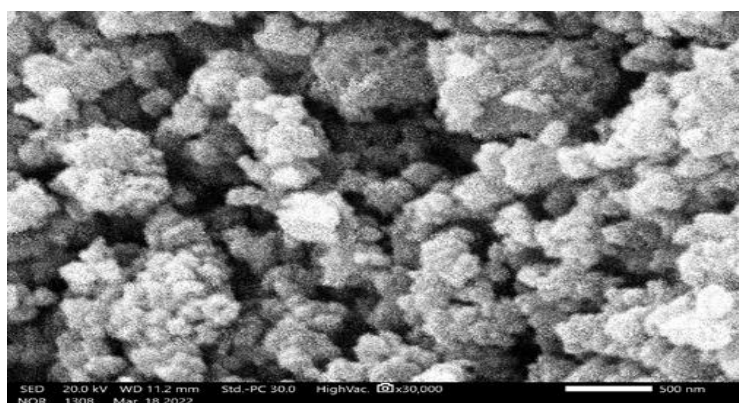


Fig.5.2 Sem Image (b) of MNP-PS

Fig.5.1 and **Fig.5.2** refers to the SEM image. The Scanning Electron Microscope (SEM) is one of the most widely used experimental methods for the research and analysis of micro and nanoparticle imaging characterisation of solid materials. SEM is utilised for particle size characterization primarily because of its 10nm resolution. SEM is used to examine the morphology of the powder before consolidation. The methods are simple: a two-sided carbon tape is applied to a SEM sample stub, then powder is sprinkled on top. SEM examinations were used to examine the produced MNP-PS sample's morphology. SEM pictures of the MNP-PS sample reveal a porous, uneven surface that lacks specific shape.

5.1.2 Energy Dispersive X-Ray (EDX)

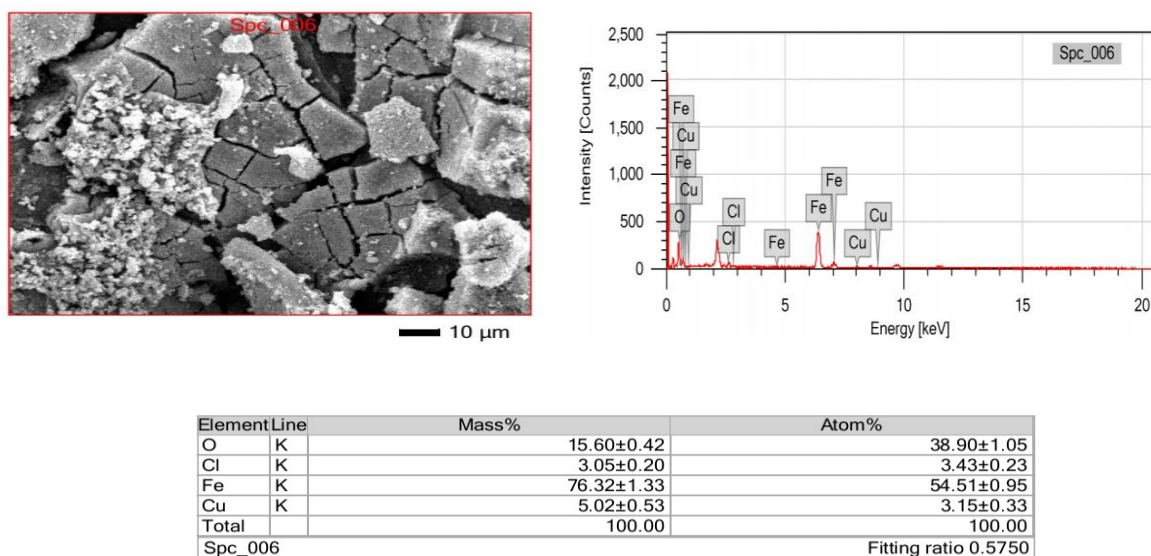


Fig.5.3 EDX Image of MNP-PS

Fig.5.3 represents the EDX pattern with weight percentage of MNP-PS. An X-Ray technique called Energy Dispersive X-Ray Analysis (EDX), often known as EDS or EDX, is used to determine the elemental composition of a substance. SEM is carried out paired with EDX to determine the types and amounts of elements present at the nanomaterial surface. Using EDX analysis, the MNP-PS sample's elemental composition was investigated. The synthesised MNP-PS sample principally comprises iron (76.32%), copper (5.02%), oxygen (15.60%), and chlorine (3.05%), according to the EDX pattern.

5.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

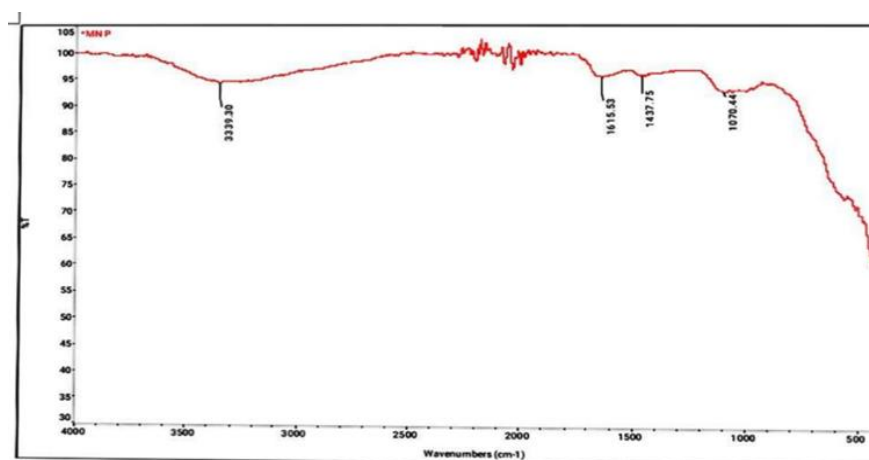


Fig.5.4 FTIR Image of MNP-PS

FTIR analysis was used to analyse the functional groups responsible for the production and characterization of iron oxide impregnated activated carbon generated from prawn shell waste (Fe₃O₄-PS-MNP) adsorbents. **Fig.5.4** depicts MNP-PS Adsorbents. Additionally at 3339.30 cm⁻¹ there is a small drop in the spectra which shows the presence of O-H stretch in the nano particle and the presence of atmospheric CO₂. At 1615.53 cm⁻¹, a medium adsorption band is seen indicating the C=C stretch aromatic vibrations in organic content of MNP-PS adsorbent. C-H methyl (-CH₃) is seen at 1437.75 cm⁻¹. The C-O stretch (secondary alcohol) is seen at 1070.44 cm⁻¹. The synthesis of Fe₃O₄-PS-MNP adsorbent is validated by comparing the FTIR spectrum.

5.1.4 X-Ray Diffraction (XRD)

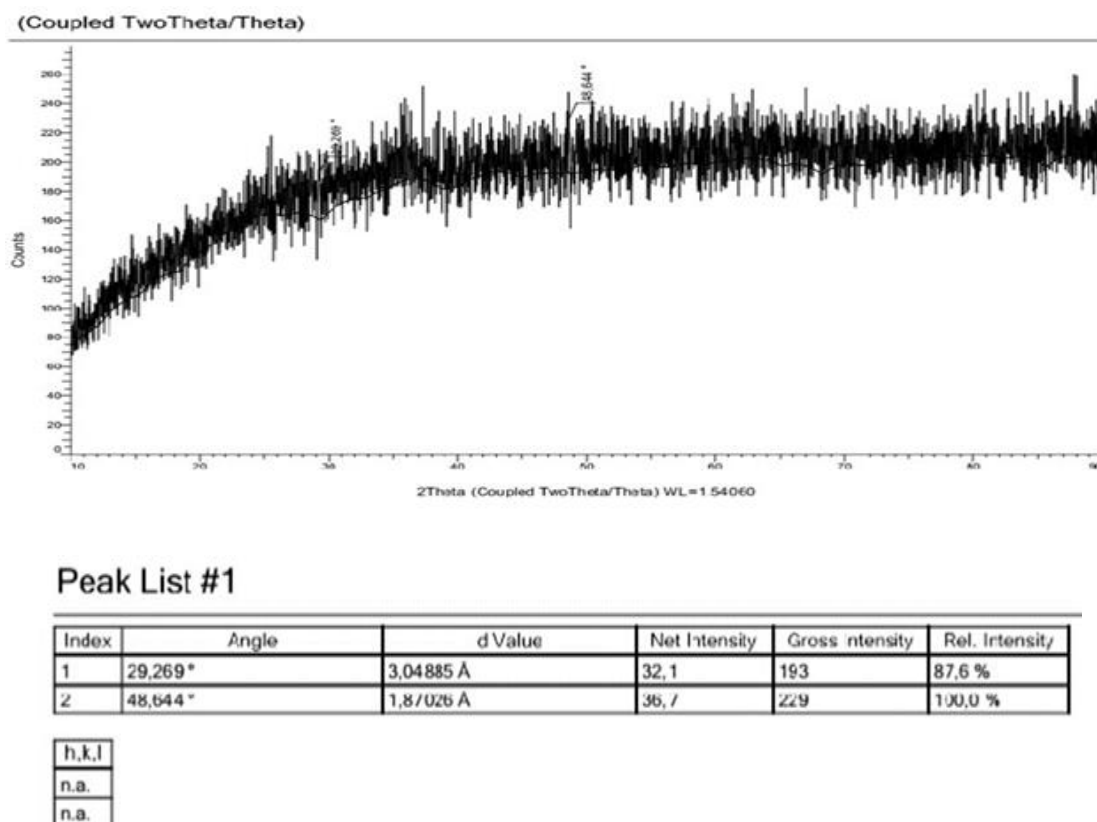


Fig.5.5 XRD Image of MNP-PS

Fig.5.5 depicts the X-Ray Diffraction (XRD) pattern of activated carbon impregnated with iron oxide and generated from prawn shell. The technique used for determining a material's underlying crystal structure is XRD. The fundamental idea behind X-ray diffraction is constructive interference between monochromatic X-rays and a crystalline material. These X-rays get generated by a cathode ray tube & are

collimated to concentrate them while being directed at the material. Two magnetic diffraction peaks with miller indices may be identified from the XRD pattern by matching two theta values, which are 29.269 and 48.644 degrees. The Peak list can be seen in **Fig.5.5**.

5.1.5 Vibrating Sample Magnetometry (VSM)

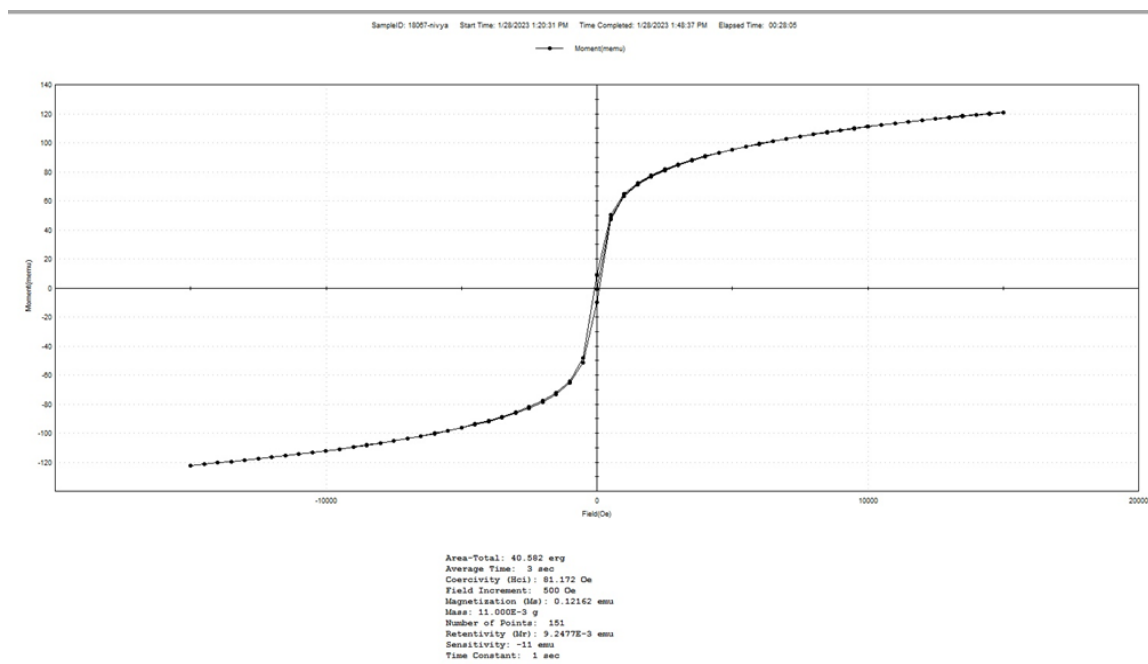


Fig.5.6 VSM Image of MNP-PS

A popular instrument to analyse the magnetic properties of a wide range of materials, comprising diamagnetic, paramagnetic, Ferromagnetic, ferromagnetic, and anti-ferromagnetic, involves a vibrating sample magnetometer. As a direct consequence of an applied magnetic field, the magnetometer observes magnetic moment. VSM functions by creating an electric field from a changing magnetic field, as per Faraday's Law of Induction. The adsorbent exhibits super paramagnetic properties, as discovered by VSM. The adsorbent exhibits super paramagnetic properties, as discovered by VSM. The results have demonstrated that the saturation magnetization rises over 40 emu.

5.2 OPTIMIZATION PARAMETERS

5.2.1 Effect of pH of MNP-PS

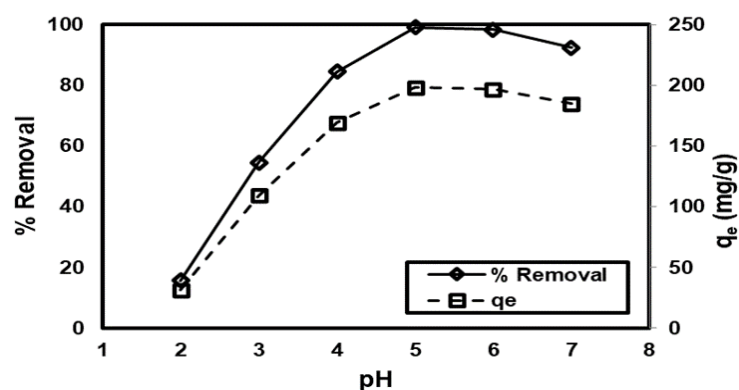


Fig.5.7 Effect of pH on Pb(II) ion removal by MNP-PS; (initial Pb(II)ion concentration= 20 mg/L, dose= 5 g/L, volume = 100 ml, time = 30 min, and temperature = 30°C)

An adsorption onto the PS-MNP over a pH range of 2-8 was studied. From the **Fig.5.7** we could observe Pb(II) ions decreases in rising pH. In lower pH values i.e. at pH 7 which is a neutral state, H⁺ ions occupies most of the adsorption sites on the MNP-PS surface and less Pb(II) ions adsorbed because of electrostatic repulsion with H⁺ ions on MNP-PS surface. From the graph, disposal percentage decreases in rise in pH range & optimum pH was found to be 5.0 for 99.134% removal.

5.2.2 Effect of Contact Time of MNP-PS

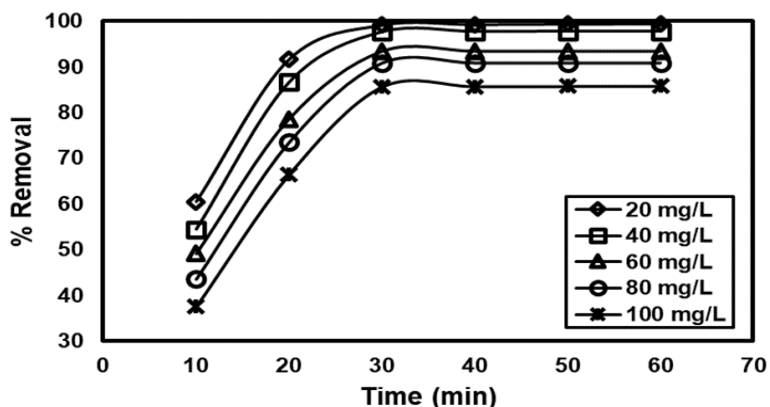


Fig.5.8 Effect of contact time on Pb(II) ion by MNP-PS (initial Pb(II) ion concentration = 20-100 mg/L, pH= 2.0, dose =3 g/L, volume =100 ml and temperature = 30°C).

An impact in operation time (0-60 minutes) on just elimination of Pb(II) through adsorptive PS-MNP displayed in the following **Fig.5.8**. From this graph, it's apparent proportion to Pb(II) ion eradicated rises with increasing time reaches at 30 min. Whenever the residential time for Pb(II) ion adsorption over onto adsorbent is long, the greatest percent of Pb(II) ion elimination could be seen. The result clearly shows that the percentage removal increases with increase in contact time and the balancing has indeed been achieved at 30 minutes for MNP-PS for 5 distinct starting Pb(II) ions accumulations. The adsorption curves were single, smooth and continuous leading to saturation and indicates the possible mono-layer coverage on the surface of adsorbent by the ion molecules. Since the difference between the adsorption values at 40 and 60 minutes is so minor, a steady-state approximation for the 40 minutes contact was used, along with the assumption of a quasi-equilibrium scenario.

5.2.3 Effect of Concentration of MNP-PS

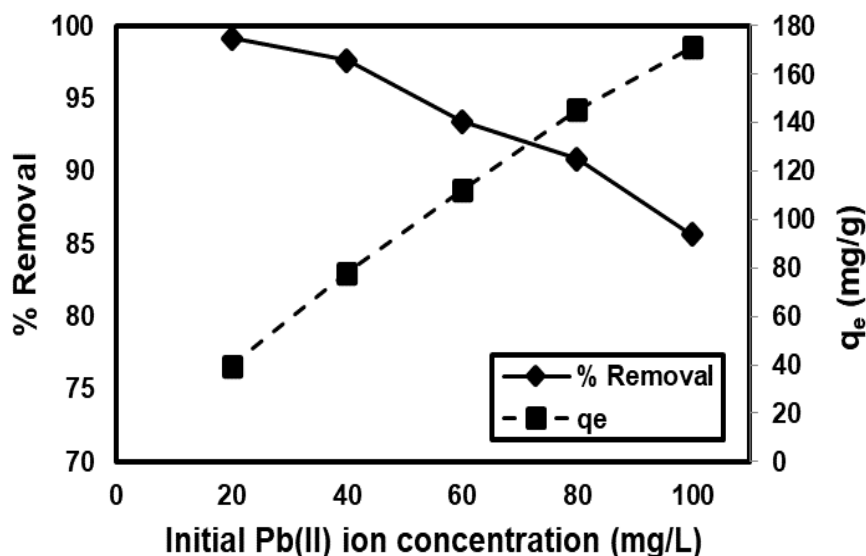


Fig.5.9 Effect of initial Pb(II) ion concentration for the adsorption of Pb(II) onto MNP-PS (pH = 5.0, dose = 5 g/L, volume =100 ml, time =30 min and temperature= 30°C).

The impact of an initial concentration of ions in the 20 to 100 mg/L range was examined, and the results are depicted in **Fig.5.9**. The picture makes it evident that as the starting ion concentration increased, the proportion of Pb(II) ions removed dropped. The driving force required to overcome the barrier to Pb(II) mass transfer

between the aqueous phase and solid phase is provided by the initial ion concentration. The effect of initial Pb(II) ion concentration (20-100 mg/L) was investigated at pH of 5.0 in the presence of the desired adsorbent. The plots revealed that an increase in the Pb(II) ion concentration from 20-100 mg/L resulted in decrease in percentage of Pb(II) ion removal from 99.134% to 85.634%. The depletion of viable catalytic activity here on MNP-PS more than a specific concentration of Pb(II) ion is indeed origin something like the lowering mostly in percent of Pb(II) ion clearance. It concluded that it's important velocity combined making use of every possible active sites for sorption at increased Pb(II) ion content may have been to responsibility for such rise in sorption.

5.2.4 Effect of Temperature of MNP-PS

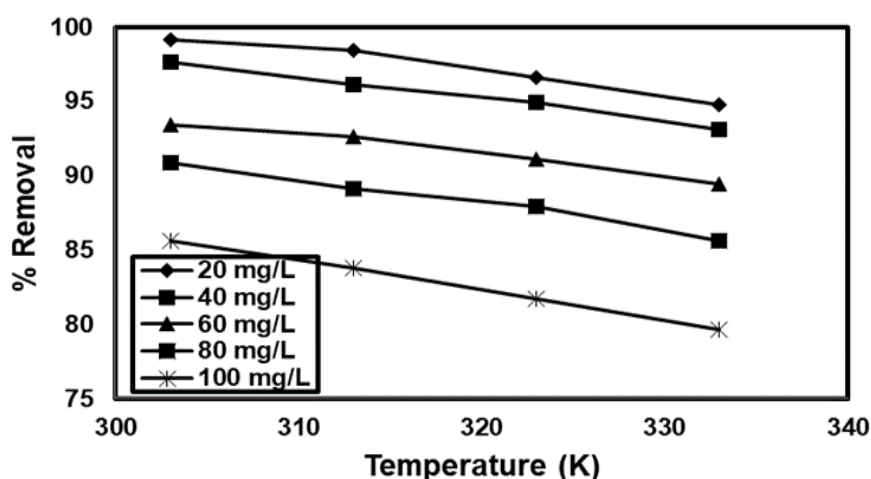


Fig.5.10 Effect of temperature on Pb(II) ion removal by MNP-PS (Initial Pb(II) ion concentration = 20 to 100 mg/L, pH = 5.0, dose = 5 g/L, volume = 100 mL and time= 30 min)

The above figure represents the optimized temperature conditions. Here the temperature range varies from 300K to 333K. The optimum temperature is 303K, where the % removal is maximum. This measurement is taken for sample at different dosages that is from 20 mg/L to 100 mg/L. As the temperature increases the value of % removal decreases gradually. This is mainly due to the decrease in surface activity suggesting that the adsorption between Pb(II) ion and the adsorbents is an exothermic process as shown in **Fig.5.10**.

5.2.5 Effect of Dosage of MNP-PS

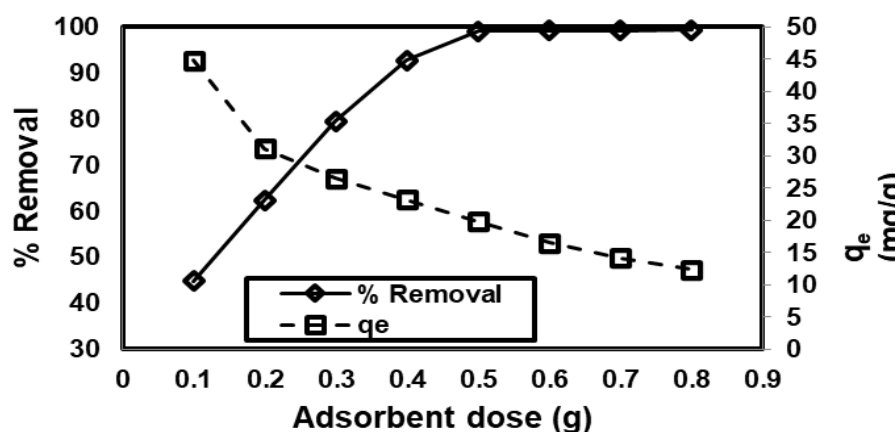


Fig.5.11 Effect of adsorbent dose on Pb(II) ions removal by MNP-PS (initial Pb(II) ion concentration = 50 mg/L, pH = 2.0, volume = 100 ml, time = 30 min, temperature = 30°C)

The PS dosage performs a major significant in determining adsorption potential of given initial concentration of Pb(II) ions. The above **Fig.5.11** represents the plot between adsorbent dose vs percentage removal (%). It demonstrates that the percentage of Pb(II) ions removed varies with changing adsorbent mass and rises with increasing adsorbent dose. For a rise in adsorbent dosage ranging from 2 to 8g/L, the removal percentage rises from 44.875% to 99.389%. The optimum dosage is 5 g/L as shown in **Fig.5.11**. When the MNP-PS to Pb(II) ion concentration ratio is smaller, a very fast superficial adsorption onto the MNP-PS surface occurs at higher MNP-PS to Pb(II) ion concentration ratios, which results in a lower Pb(II) ion concentration in the solution.

5.3 ADSORPTION ISOTHERMS

The correlation in between adsorbate on the adsorbent as well as the adsorbate in the fluid medium at an intermediate state is indicated by the adsorption isotherm. This has an essential relevance in assessing adsorption isotherm data through matching it to various adsorption isotherm models that can be utilised for adsorption design phase and enhancing the construction of an adsorption process for the absorption of adsorbate.

The adsorption equilibrium here between Pb(II) ions and MNP-PS as evaluated in this research to use the Langmuir, Freundlich, Temkin, and Sips models. By implementing MATLAB R2009a to apply the statistics on the adsorbent surface ($C_e V_{sqe}$), to all of these equation state of adsorption. The validity of these isotherm was examined. The answers are shown in **Fig.5.12**. The coefficient of determination and considering the importance of the adsorption isotherm variables (q_m , K_L , K_F , n , B , A , K_S , s , s), Errors data (SSE and RMSE) and (R^2) statistics were compiled within **Table5.1**. The Freundlich and Sips adsorption isotherm theory may accurately describe the equilibrium adsorption statistics in accordance with R^2 standard in accuracy these results from **Table 5.1**. Besides that, the Freundlich model fits the experimental data the best comparing to the Langmuir, Temkin, and Sips theories.[39] The Freundlich adsorption isotherm, which would have been appropriate to either a sole exposure adsorbed species each of one limited concentration scope, is in concept a functional application if an adsorb besides a highly incongruous high adsorption layer. The implications of the value of n , that supplies an indication of regarding pseudo-linearity's extent here among the intensity on the remedy with adsorption, to be as follows:

$n = 1$ (adsorption is linear);

$n < 1$ (adsorption is a chemical process); and

$n > 1$ (adsorption is a physical process).

Table 5.1 indicates that the n amount was calculated to be 3.964. This a n -value corresponds to existing adsorption structure anywhere around 1 and 10, implying believed adsorption was indeed a physical entity one. An MNP-PS was determined to have a highest monolayer adsorption capacity (q_{max}) for metal adsorption of 27.86 mg/g. The significance of the R_L value, which were employed to forecast the optimal design, is: $R_L = 0$ (irreversible); $0 < R_L < 1$ (favourable); $R_L = 1$ (linear); and $R_L > 1$ (unfavourable).[40] An existing adsorption mechanism calculated value of R_L were in the band of 0 and 1, which suggests that the adsorbed procedure worked effectively. Weak interaction here between Pb(II) ion and the MNP-PS is demonstrated by the current adsorbent state's heat of absorption(b) value having less than 8 kJ/mol. The above demonstrates that perhaps the current approach of adsorption had been an evolving method. Based on R^2 and error values, the

accompanying is really the finest combination for the algorithms for isotopes of adsorption examined for extraction Pb(II) particle in MNP-PS:

Freundlich >Sips> Langmuir > Temkin isotherms

It indicates that the experimental evidence and the Freundlich model complement well alongside one another. The applicability of this theory for the removal of Pb(II) ions by MNP-PS confirmed that, under the evaluated test conditions, multilayer adsorption was retained on the adsorbent surface.[41]

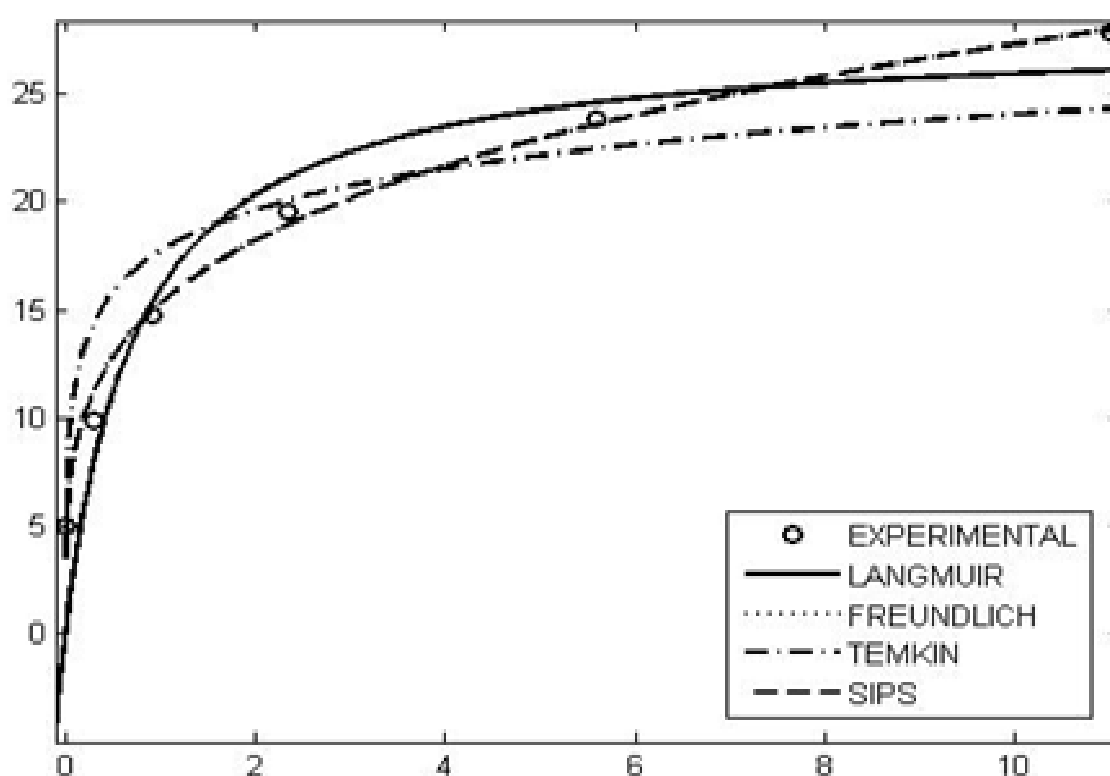


Fig.5.12 Adsorption isotherm studies for the removal of Pb (II) ions by MNP-PS

Table 5.1 Adsorption isotherm parameters for the removal of Pb(II) ions by MNP-PS

ADSORPTION ISOTHERM MODELS	DIMENSIONS	VALUES	R ²
Langmuir	q _m (mg/g)	27.86	0.9098
	K _L (L/mg)	1.345	
	SSE	33.26	
	RMSE	2.884	
Freundlich	K _F ((mg/g) (L/mg) ^(1/n))	15.28	0.9886
	n (g/L)	3.964	
	SSE	4.205	
	RMSE	1.025	
Temkin	A	631.3	0.8644
	B	1.193	
	b (kJ/mol)	2.111603	
	SSE	50	
	RMSE	3.556	
Sips	K _S (L/g) ^(β_s)	0.009892	0.9808
	α _s (L/mg) ^(β_s)	3.918	
	B _s	1560	
	SSE	4.255	
	RMSE	1.191	

5.4 ADSORPTION KINETICS AND MECHANISM

The equilibrium adsorption statistics then exploited to anticipate the ratio and method of sorption involving Pb(II) ions and MNP-PS. In this study three kinetic models are examined. They are pseudo first-order, pseudo second-order, and Elovich kinetic model is helped to know about sorption kinetics for elimination Pb (II) & the accurate answers are represented in **Fig.5.13**.

Table 5.1 lists predictions for a selection of configurations, including pseudo first-order kinetic constant (k₁), pseudo second-order kinetic constant (k₂), q_e, and Elovich kinetic model constant (αE) & βE. The observed adsorb rates have been

linked using (q_e , Cal), the experimental sorption capacity (q_e , exp). It is shown in **Table 5.2**. Both, comparing to pseudo second-order and Elovich kinetic models, the measurement of the coefficient of correlation (R^2) for the pseudo first-order kinetic was higher. The physical adsorption is the percentage phase, according to the constant fitting of sorption kinetic proof for elimination of Pb(II) to MNP-PS with a pseudo first-order kinetic model. To grasp the adsorption mechanism, it is essential to figure out the rate-limiting phase.

Table 5.2 Adsorption Kinetic value for elimination of Pb(II) ions by MNP-PS

Kinetic Model	Parameters	Concentration of Pb(II) ion solution (mg/L)				
		20	40	60	80	100
Pseudo- first-order equation	$K_{ad} \text{ (min}^{-1}\text{)}$	0.0028	0.0011	0.00064	0.0004	0.0002
	$q_{e,cal} \text{ (mg/g)}$	46.8	95.22	140.3	188.6	231.2
	R^2	0.8829	0.8924	0.9049	0.8763	0.8971
Pseudo-second-order Equation	$k \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	0.1001	0.0880	0.0796	0.0715	0.0645
	$q_e, cal \text{ (mg/g)}$	40.59	80.54	116.3	152.6	182.5
	$q_e, exp \text{ (mg/g)}$	39.653	78.108	112.11	145.37	171.258
	R^2	0.957	0.963	0.963	0.953	0.943

Table 5.2 shows that perhaps the Arrhenius equation quantities "k" decline during growth Pb(II) ion concentrations; this could be due to fewer competition for complex formation in concentrations. Due to enhanced putative binding rivalry at elevated

At lower doses, slower sorption speeds be reached. The observations showed considerable agreement here between q_e estimated to use the pseudo-first-order kinetic parameters and thus the q_e experimental result, validating the practicality.

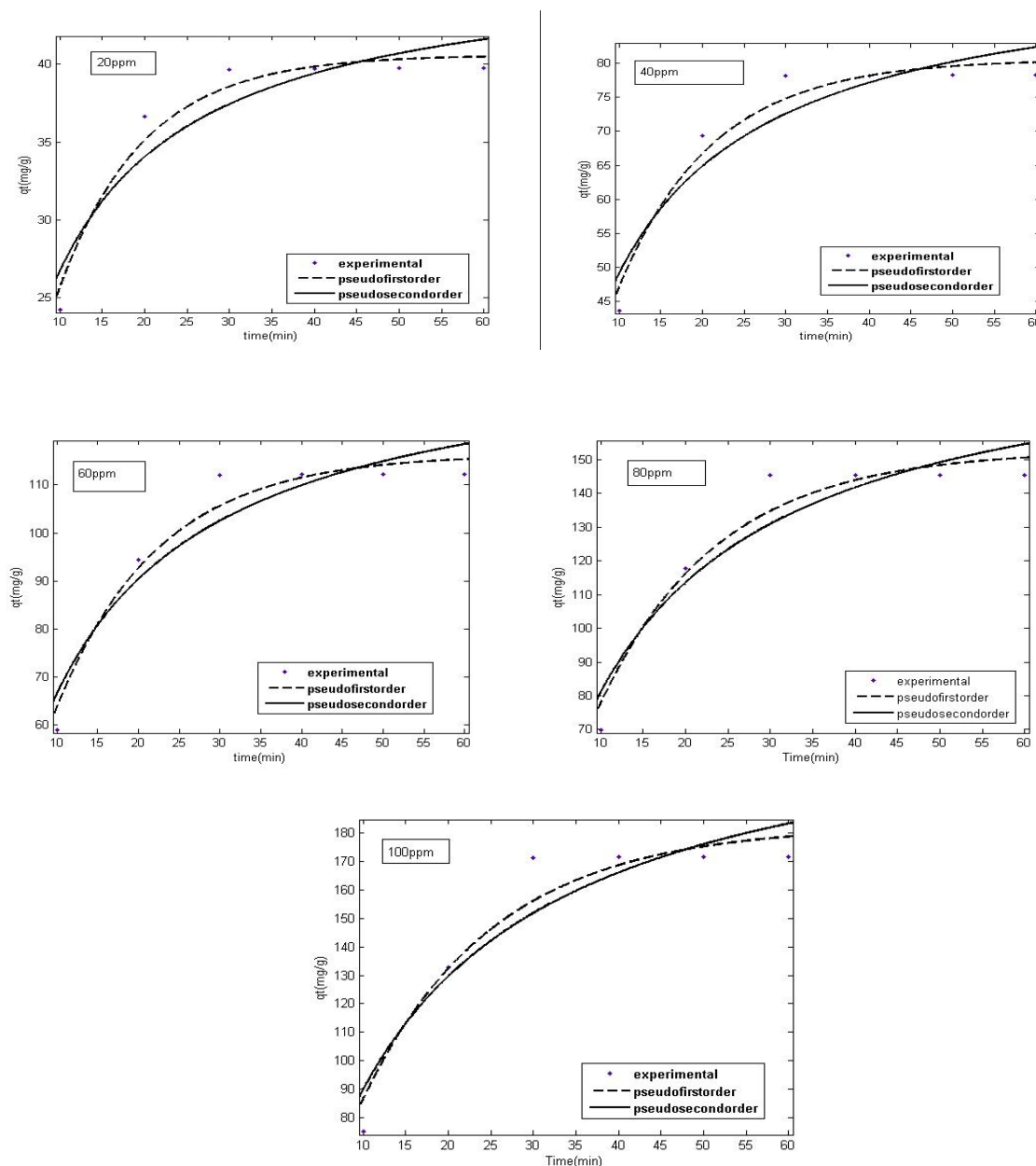


Fig.5.13 Adsorption kinetic for the eradicating Pb (II) ions by MNP-PS (Lead metal concentration = 20-100 mg/L, solution pH = 3.0, adsorbent dose = 5g/L, volume of sample= 100mL, temperature = 30°C)

5.5 EVALUATION OF THERMODYNAMIC PARAMETERS

An aspect of thermodynamics gives structure to the underlying enthalpy change connected to the adsorption process. Instead of focusing on MNP-PS, the thermodynamic parameters change in free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were utilised to define the process. The values of ΔH° and ΔS° were determined based on that the intercept and gradient, correspondingly, straight curve generated per retelling the tale $\log K_c$ vs. $1/T$ (**Fig.5.14**). **Table 5.3** shows the calculated thermodynamic parameter values. The negative value of ΔG° at different temperature, as shown in **Table 5.3**, indicated the durability of the adsorbate and the spontaneous aspect of the reactions. Also, the fact that the negative value of ΔG° increases as the temperature drops shows process of adsorption is advantageous at limited temperature. It is really feasible to the rise in temperature facilitated its mobility in previously adsorbed Pb(II) ions, which led structure desorption of Pb(II) ions from both the exterior ions of MNP-PS. A size ΔG° could additionally shed the mystery of the adsorption process. The preceding is claimed as the essence of ΔG° . Chemical adsorption extends between 80 to 400 kJ/mol, while physical adsorption extends between 20 to 0. The existing adsorption system was however confirmed as an actual physical process. Due to the poor association here between Pb(II) ions and MNP-PS, the values for ΔH° were revealed to be negative, implying that the sorption capacity was naturally exothermic. Furthermore, it was learned from **Table 5.3** that the negative sign of ΔS° indicate a decline in unpredictability at the surface or interface in the adsorption system because of adsorption.[42] This realism now is case of the former particles lose at most of freedom motion as they are adsorbed onto the adsorbent could be the cause of the fall in ΔS° in all instances. At any and at beginning temperature changes with copper concentration levels it was discovered the values of ΔH° were higher $T\Delta S^\circ$. This indicates that enthalpy changes rather than enthalpy change had a bigger influence on the adsorption studies.

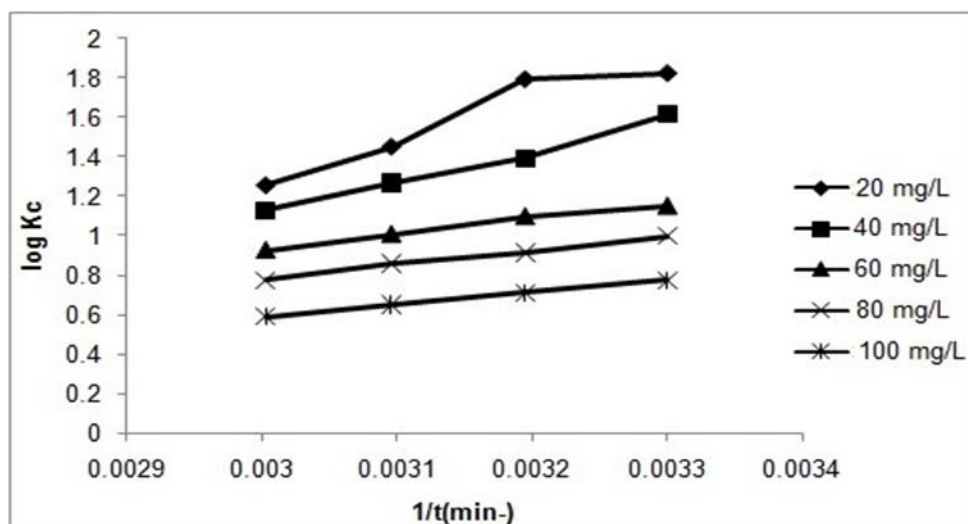


Fig 5.14: Thermodynamic analysis for the adsorption of Pb(II) by MNP-PS

Table 5.3 Thermodynamic parameters for the adsorption of Pb(II) ions onto MNP-PS

Initial Pb(II) ion Conc. (mg/L)	ΔH° (kJ mol ⁻¹)	ΔS° (Jmol ⁻¹ k ⁻¹)	ΔG° (kJ mol ⁻¹)			
			30°C	40°C	50°C	60°C
20	-53.152	-135.945	-11.943	-10.744	-8.978	-8.009
40	-30.558	-70.346	-9.374	-8.350	-7.850	-7.211
60	-14.703	-26.2316	-6.686	-6.589	-6.2422	-5.918
80	-13.866	-26.672	-5.785	-5.478	-5.325	-4.944
100	-11.785	-24.029	-4.498	-4.267	-4.0273	-3.775

SUMMARY AND CONCLUSION

Magnetic Nano particles are materials that are capable of removing pollutants from water. The new magnetic sorbent MNP-PS was identified in this work as an effective absorbent for the elimination of Pb(II) from effluent. The surface morphology was studied using SEM. The MNP-PS was characterized by FTIR and EDX, XRD and VSM. The Magnetic Property was studied by VSM. The use of Magnetic Nano based adsorbent will have a remarkable adsorption effectiveness since we understand that adsorption is the highly recommended technology for the removal of dye, heavy metals, and other toxic effluents. Water being an essential source for our environment, treating it with good process and good materials also matters. Considering all these things, it will be known that Prawn Shells when impregnated with Magnetic Particle will be a great adsorbent for the treatment process. The outcomes of the investigation therefore demonstrate the hypothesis of the quantity of MNP-PS particle have an important influence on the rate of reduction of Pb(II). It turned out that while the initial Pb(II) concentration risen, the percentage of adsorption of Pb(II) got smaller.[43] With rising initial pH & reducing initial Pb(II) concentration, the pH level of the resulting combination have an important effect on Pb(II) reduction effectiveness. A stability temperature were analysed introducing multiple adsorption process systems, together with Sips, Temkin, Freundlich, & Langmuir approaches.[44] Thermodynamic characteristics which including Gibbs free energy, enthalpy, as entropy estimates demonstrate that the adsorption process was exergonic, impulsive, and realistic. For the elimination of heavy metals from wastewater, the costlier adsorbents can be exchanged changed for the less expensive stuff. In order to effectively demonstrate the concept and consider different industrial effluents for affordable adsorbents, more research is required. Not only Prawn Shells there are many cost-effective adsorbents like Fish Scales, Vegetable Peels etc., Instead of using chemicals as adsorbents, these kinds of wastes which has no value can be turned into a wealth for treatment process. We draw the conclusion from our experiment that using is a viable substitute for expensive activated carbon and will prove successful in removing toxic pollutants from wastewater.

“WATER- NOT A LUXURY BUT A NECESSITY. TREASURE IT”

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CHAPTER-1 INTRODUCTION

Water (H₂O), which makes up more than 70% of the planet's surface, is the most precious resource and an endless substance. In nature, water may be found in three different states: Solid, liquid and gas. It has no flavor, no odor, and no color at room temperature with the exception of a very tiny blue tint. Every cell in our body uses water. The network in the share a variety nourishment, oxidant, and byproducts to and from various body's tissues and organs. Being a component of ourselves physiological temperature regulation mechanism, Freshwater serves to keep us hydrated. Particularly prone to contamination is water. ⁴³Water has the ability to dissolve more substances than any other fluid on earth, giving it the title of "universal solvent". Because of it, Kool-Aid and vivid blue waterfalls exist. It also clarifies why water is so readily contaminated. It dissolves fast and contaminates the water by mixing with dangerous elements from nearby farms, towns, and businesses. There are numerous multiple kinds of effluent which are discharged through various firms, notably combined sewers, household effluent, hurricane flow effluent, farming sewage, and municipal waste. According to the AQUASTAT data, 3928 km² of freshwater are removed globally each year, of which 22% (865 km²) are utilized by industry. One of the main factors contributing to the ecosystem's irreparable harm is industrial effluents. Groundwater and other large water bodies ultimately become contaminated as a result of the improper handling and direct release of these hazardous effluents into sewer drains, which ⁹has an adverse effect on the health of both marine and terrestrial species. Vomiting, giardiasis, typhus, pneumonia, hepatitis, malaria, and cancer are some of the waterborne illnesses brought on by water pollution. Several nations are currently developing regulations to regulate water quality. Logic standards are being defined on the amounts of pollutants that might be safely ingested in certain water bodies, like rivers and lakes. Also being constructed are a variety of treatment facilities that use chemical, electrochemical, biological, and physical methods to produce drinking water. Numerous industrial planners and manufacturers are increasingly embracing technology to assure green economy, less water use, and less pollution, keeping in mind both economic expansion and the lack of clean water.

Health and natural, sea life, and farming are all at threat from poisons discovered in effluent from several industries. These hazards typically comprise of pigments and heavy metals. The manufacture of the industries of paints, dyes, pigments fabrics, drug products, newspaper, and explosives emit the majority of such metal pollutants. Phenol & phenolic compounds comprise two of the main carcinogens found in industrial waste water. Their primary function emitted by the resin from phenol-formaldehyde, massive pharmaceutical production, & also crude oil refineries sectors. Catalytic industry-produced resistant pollutants, which include petroleum-derived hydrocarbons, can be found in wastewater, sulphides, naphthalene acid, organochlorides, aniline, alkene, alkanes, nitrogen benzene and chlorine alkanes. There are now much more contaminants ⁴⁵ in the environment as a result of the recent, rapid industrialization. All sorts of biological forms have suffered harm by the improper dumping of some hazardous industrial waste into water bodies, either directly or indirectly. One of the most common types of chronic, non-recyclable water pollution is heavy metals. Aquatic fauna may introduce certain dangerous heavy metals into the food chain, which can negatively impact the health of other animals and eventually humans. They can be teratogenic, carcinogenic, and generate oxidative stress in addition to osmotic damage, organ dysfunction, neurological disabilities, and reduced growth and development. Sources of water from industrial plant are contaminated by the heavy metals that are carried by runoff water. Before disposing waste water, it is crucial to remove these hazardous heavy metals to prevent health risks. Due to their persistence and non-biodegradability, hazardous compounds that have been released in large amounts into the environment have caused a variety of environmental issues and may constitute very massive risk to human well-being because of inherent accumulation in environmental components like the food chain. Numerous traditional techniques, including chemical coagulation, liquid – liquid exchangers, Ion exchanges, membrane filtration, electrical, chemical removal, coagulation, etc., Metals that are heavy are capable of being eliminated via aqueous medium. These methods, however, have several drawbacks, including insufficient removal, high energy needs, the availability of hazardous sludge, limited efficiency, delicate working conditions, and expensive disposal. Hence these types of hazardous and toxic effluents must be properly eradicated in order to make our environment pollution free.

1.1 HEAVY METALS AND ITS TYPES

1.1.1 ARSENIC (As)



Fig.1 Arsenic (As)

²⁹ The 20th most prevalent substance in the Earth's crust, the 14th in saltwater, and the 12th in the human body is arsenic (As), a naturally occurring metalloid that is an element of more than 245 minerals. Arsenic exposure at low levels may harm blood vessels and result in vomiting, nausea, stinging in the hands and legs, decreased erythrocyte and leukocyte production, and irregular heartbeats. When it is in its metallic phase, it is brittle, brilliant, and silver-grey in colour. Despite being heavily controlled, arsenic compounds are routinely used as rat poisons and insecticides.[1] Skin cancer is one of the drawbacks of arsenic heavy metals; prolonged exposure can also cause lung and bladder ²⁵ cancers. The International Agency for Research on Cancer (IARC) has classified arsenic and arsenic compounds as carcinogenic to humans in addition to proving that arsenic in drinking water causes cancer in people. Arsenic concentrations of metals in drinkable water are limited at 0.05 mg/L.

1.1.2 LEAD (Pb)

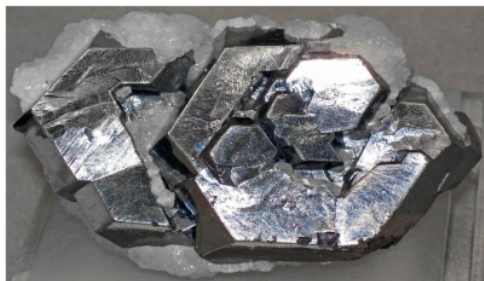


Fig.2 Lead (Pb)

A harmful environmental toxin called lead. It has highly toxic impacts in variety of living species. Exposure to lead may lead to neurology, pulmonary, urinary, and circulatory illnesses, alongside cellular antioxidant, swelling, and other toxic reactions.[2] Industrial wastewaters generally comprise lead ions at levels of 200–500 mg/L, which exceed the limits for water quality. The physical property of lead is among its characteristics are a lower melting point, dense population, limited ductility, simplicity in fabrication, chemical inertness, electrolytic responses with sulfuric acid, high stability in oxygen, liquid, and sediments, and also the ability to dampen mechanical stress, acoustic signals, and nuclear radiation. It is Bright, bluish. It is very flexible and brittle. Lead in drinking purposes was usually obtained until 0.01 mg/L.

1.1.3 MERCURY (Hg)



Fig.3 Mercury (Hg)

Mercury is a well-known dangerous element because of how frequently acute heavy metal poisoning is brought on by it. Mercury is a silvery white substance that slowly devalues in humid air and hardens into a soft substance. The kidneys, brain, and growing foetus might suffer harm if they are subjected to this metals, organic, and inorganic mercury. Anthropogenic comprises of farming, mines and disposing of trash from cities, industrial wastewater discharges and incineration are the major sources of mercury pollution. It is a beautiful silver-white, odourless metal that occurs naturally. When heated, it changes into an odourless and colourless gas.[3] A maximum of 2,200 tons of mercury are released in the environment each year, as according estimates. It might be difficult to diagnose

organic mercury poisoning because the symptoms are comparable to those of other illnesses, such as depression, headaches, tremors, exhaustion, hair loss, and memory issues. Mercury levels in portable water must not exceed 0.001 mg/L.

1.1.4 CADMIUM (Cd)



Fig.4 Cadmium (Cd)

Cadmium emerged become a major metal used creating chargeable nickel-Cadmium (Ni-Cd) cells in addition to aluminum and metallic coating which acts as a barrier to prevent corrosion. Currently, it really is found in tobacco smoke along with rechargeable batteries, particular alloy production, and other products. Currently, common industrial uses for cadmium include pigments, plastic stabilizers, coatings (electroplating), solar cells, alloys, coatings, and batteries.[4] Cadmium poisoning has been detected in rice, grains, and seafood. Commercial dust simply eliminates cadmium from the lungs. Acute or long-term exposure to Cadmium in industrial settings can result in lung damage and renal tubular malfunction. Smokers have almost two times more of cadmium in their blood than non-smokers do. The authorized absolute maximum limit in drinking water is 0.03 mg/L.[5]

1.1.5 CHROMIUM (Cr)



Fig.5 Chromium (Cr)

Chromium (Cr), a found naturally heavy metal in use in industrial processes, is discovered in the crust of the earth and ocean. The name chromium, which derives from the Greek word chromes, which means "colour," refers to the intense and diverse colorations of contaminants. The metal Cr is hard, brittle, and bright. It possesses a silver-grey color and is highly polishable.[6] As chromium is fragile in oxygen, it rapidly creates a thin oxide film that protects the metal against oxygen. The growth of diverse abnormalities inside this pulmonary, laryngeal, liver, renal, ovaries, femur, and glands are one of the ailments which impair the epidermis, digestive, nerve systems and small intestine. Chromium concentrations in drinking water are limited at 0.1 mg/L.

1.1.6 COPPER (Cu)



Fig.6 Copper (Cu)

In its simplest form, Copper (Cu) is a reddish-brown metalloid with a significant level of malleability. Copper is primarily employed in industrial machinery, roofing, plumbing, and electrical wiring. Numerous human tissues are harmed either by detrimental impact that metal have, both in the immediate and distant futures[7]. Consequences caused by the toxic effects of heavy metals include cancer, birth defects, immune system dysfunction, cardiovascular disease, hyper-pigmentation, neurological number of weaknesses, renal and intestinal issues, lesions of the skin. Copper levels in drinking water are limited to 1.3 mg/L.

1.1.7 NICKEL (Ni)



Fig.7 Nickel (Ni)

Nickel is rigid, silver-white that solidifies into cubic shapes. It has superior strength and corrosion resistance, is malleable, and ductile. It has been shown that each cigarette contains around 1.1 and 3.1 g of nickel. In reality, several fruits and vegetables, including cocoa, chocolate, and almonds, as well as lettuce, asparagus, broccoli, carrots, and green beans, have high quantities of this dangerous metal. In addition, nickel is accidentally consumed when food is processed on stainless steel equipment or when it comes into contact with the mouth.[8] Nickel can be found in the air, water, and food, which can expose the general public to it. People who are exposed to nickel may have a variety of harmful health effects, such as allergies, kidney, heart, and lung issues, fibrosis, and lung and nose cancer. Nickel concentrations in drinking water are restricted at 0.1 mg/L.

1.1.8 ZINC (Zn)



Fig.8 Zinc (Zn)

The metal zinc is a bright bluish-white color. Becoming a component of several important proteins and regulating the regulation of a variety of immune-modulatory functions, zinc (Zn), one of the most abundant toxic metal found in the Earth's crust, is considered to be an essential compound metal required for the development of living things. Its toxicity, which is carried on by a variety of anthropogenic sources, continuous exposure to polluted areas, and other natural phenomena, however, runs parallel to its essentiality. Certain vegetables, cattle, and dairy products have a high bioavailability of zinc, making them a useful source of the metal for human consumption.[9] Zinc metal is mainly used to preserve iron and steel against corrosion and to create brasses and alloys for die casting. Nausea, vomiting, and diarrhea are signs of heavy metal in zinc. Metallic oxide fever, stomach and intestinal problems, and/or liver malfunction can all be caused by excessive zinc exposure. Zinc concentrations in drinking water are limited at 5.0 mg/L.

1.2 VARIOUS TREATMENT TECHNOLOGIES FOR HEAVY METALS

1.2.1 ADSORPTION:

Successful techniques for removing very harmful chemical molecules from water are of great interest. to clean polluted water of organic contaminants. Coagulation/flocculation, filtration with coagulation, precipitation, oxidation, adsorption, ion exchange, reverse osmosis, and advanced oxidation processes are just a few of the techniques that have been used. Because to their extremely high initial investment and continuous operation cost, advanced oxidation techniques like reverse osmosis and ion exchange do not seem to be economical. Adsorption is the recommended way as compared to all of the other methods because of its favorable characteristic particles, ion, or nuclei out of a total soluble solid, vapor, or fluid stick the surfaces through the technique called as adsorption.[10] Adsorption is very beneficial form in treatment, particularly for industrial waste water. This technique coated the adsorbent's surface with an adsorbate layer. Adsorption has drawn a lot of attention in past years since it seems like a promising technique moreover typically long management and a practical method. Physical adsorption and Chemi-sorption's are the two kinds under which adsorption can be classified. If the interaction among the molecules

that are adsorbed and the surface of the material is physical, the approach is called "physisorption." Adsorption is referred to as chemisorption when the forces of attraction between molecules that are absorbed and the surface of a solid are generated by chemical bonding. The adsorption process (i.e., temperature, adsorbent quantity, pH value, adsorption period, and starting concentration of metal ions) is determined by the physiochemical characteristics of the adsorbent, heavy metals, and operating circumstances. According to reports; this method has a cost - effective system, a maximum removal capacity, simple implementation, and treatment. Due to their reversible character, the utilized adsorbents can perhaps be reconstituted using a proper decontamination methodology. Adsorption utilizing sorbents is one of the most often used treatments because it results in highly treated effluents when the adsorption process is designed properly.[11] The main benefit of the adsorption technique, which makes it cost-effective, is the recycle or regenerating of the adsorbent materials. The desorption or restoration ability of the adsorbent affects whether it can be reused. The following characteristics are adsorbent: area of surface, size of pore, volume of pores, and surface charge. Various materials, including biomaterials waste materials, have been utilized. To determine their potential for use in treating wastewater and their contribution to large-scale processes, it is essential to understand how different adsorbates interact with adsorbents in the laboratory scale. Adsorption, although, has several disadvantages as well, such as the inability to operate well at industrial scales due to a lack of suitable adsorbents with large adsorption capacities and the shortage of industrial scale columns. Secondly, a crucial step should be considered seriously while developing an efficient and suitable adsorbent. The development of nanotechnology has revealed an extraordinary potential for the development of novel adsorbents, and nanomaterials have been used to achieve the goal of developing an optimal adsorbent that is effective and quick to remove pollution.

1.2.2 CHEMICAL PRECIPITATION

Chemical precipitation is a widely utilized industrial technique that is effective, affordable, controllable, and applicable across a wide temperature range. Chemical precipitation, also known as coagulation precipitation, is one of the most commonly used and developed processes in industry. Precipitation is the preferred

technique to eliminate dissolved ions during conventional treatment. Chemical precipitation is widely used because it is comparatively cheap, straight-forward, and customizable.[12] The technique is determined by the pollutants to be removed size, density, and surface charge. Inorganic precipitants include limestone, caustic soda, soda ash, sodium bicarbonate, sodium sulphide, and sodium hydrosulfide are among the most often used for the precipitation of heavy metals. Additionally, they have certain drawbacks including high lime and peroxide doses and pricey sludge fees. A highly prospective bidentate or tetradentate ligand with two cystamine groups and benzene as a backbone has been used to minimize metal contamination from acidic water coming directly from mines.

1.2.3 ION-EXCHANGE

Ion exchange is a straightforward and cost-effective method for transferring soluble ions from the liquid phase to the solid phase. It has been demonstrated to be an effective approach for removing heavy metals from aqueous solutions, particularly in cases when the metal concentration is low. The elimination the metal ions to the solution, a specialized ion exchange with cations or anions (found naturally inorganic adsorbent or synthesized organic ion exchange materials) is used. By binding a heavy metal ion to an immovable solid particle and displacing it with the solid particle cation, a heavy metal ion is recovered from a wastewater solution.[13] The main advantages of ion-exchange are the eradicating of liquid problems Ion exchange polymers allow for the ability to eliminate substances such hard water, scale accumulation, nitrates, and arsenic. The biggest drawback of maintaining ion exchange technology is the high long-term expenses, ineffective at effectively purging water of germs. Typically, synthetic organic ion exchange resins are utilized as matrices. However, this method has some drawbacks, including membrane fouling, pH sensitivity, and non-selectivity of the membrane.

1.2.4 FLOTATION

Techniques for flotation are based on the various wet ability qualities of materials' surfaces property of density features with regard to the surface. To enhance separation, a centrifugal field may sometimes be used. With sulphide minerals, flotation, also known as froth flotation, is a gravity separation technique that is

frequently used. It is unquestionably a byproduct of the processing of minerals. It is believed²³ that its significance to the industrial economy at large must be enormous. In mineral processing, flotation is a technique for segregating and reducing ores by modifying their surfaces to a hydrophobic or hydrophilic state, indicating that the surfaces are either attractive to or repellent to water.[14] The froth flotation method is used for more than a century and took a while to develop. It derives from the chemistry of the surface of micro-particles. Low sludge is obtained by the flotation process. Hence, this method is an ideal match to be integrated into the establishment of an effective and economic electrochemical treatment system. Wide application is one of flotation's key benefits. One of the most popular techniques, froth flotation method, holds a commanding position in many mineral processing technologies, High separation efficiency, thorough recovery that is good, reagent consumption, strict grinding size requirements, and numerous constraints.

1.2.5 COAGULATION / FLOCCULATION

The destabilizing of colloidal particles known as coagulation is caused by the presence of a coagulant, a chemical reagent. Destabilized particle aggregation into micro-floc, followed by the formation of large floccules that can be settled, is known as flocculation. The chemical water purification procedure known as coagulation eliminates removing sediments from stagnant water altering the geostatic attraction molecules in river.[15] Coagulation is a method which, by encouraging the bond across the elements, renders the clumps much simpler to break apart. Coagulation distributes the pressure placed on the particulates whereas flocking lets the particles to join aggregate as well as grow wider to ensure that they can be evacuated from the liquid with greater ease. By eliminating the forces keeping colloids separate, coagulation leads colloids to be become instability, while flocculation causes destabilizing particles to cluster together. Both flocculation and coagulation are important techniques in the treatment of water and wastewater to separate and get rid of suspended materials. The operating costs²⁰ of this technique are a major drawback. To obtain the appropriate level of flocculation, significant amounts of coagulant and flocculent may be required in some circumstances. The coagulant's effectiveness is determined by the coagulant's types, dosage, pH, temperature, alkalinity, and

mixing conditions. To benefit from the financial, energy, and environmental benefits of coagulation, coagulation conditions and coagulant characteristics should be screened and analyzed to determine the best flocculation conditions.

1.3 VARIOUS ADSORBENTS

1.3.1 PRAWN SHELLS



Fig.9 Prawn Shells

Shrimp shells are utilized as an adsorbent or biosorbent by converting to varied forms like chitin and chitosan. In many parts of the world, seafood is considered to be an important food source and plays an important role in the food chain system. There are several uses for chitosan in the healthcare, agricultural, biotech, cosmetics, pharmaceutical, culinary, paper, and textile industries. Epi-, exo-, and endocuticles are the three calcified outer layers of a shrimp shell, along with an inner membrane.[16] The epidermis' outermost and thinnest layer, the epicuticle, contains minerals in the form of islands of spherulitic calcite that are encased in a lipid-protein matrix. The basal layer of mineral-filled channels cuts through it at an angle, making it bilaminar. The executable, which lies underneath the epicuticle and is made up of layers of constantly shifting-orientation chitin-protein fibers

embedded with mineral crystals. This continually changing orientation of chitin-protein stripes is also seen in the tip of the cuticle, which is the thickest & most calcified layer of the prawn shells under the carapace. Between 6 to millions of tons of waste crab, shrimp, and lobster shells are dispersed as waste every year on a global scale. These organic wastes, which include minerals, proteins, amino acids, aryltenoids, and other fatty acids, can add significantly to the burden in landfills. It is essential to collect them and use them in a zero-waste way. Residual proteins found in waste shrimp shells can be considered of as the bacterial incubation medium. Moreover, the disposal of the used shrimp shells would result in a high concentration of COD in the leachate, which would ⁶⁵have a negative effect on the environment by causing oil and water pollution. Shrimp shell, which is typically eliminated as food waste and an industrial by-product, would be a good choice for environmentally friendly adsorbents shrimp weight is 40–66% shell waste. The technique of just using activated carbons as an adsorbent for organic pollutants is extensive, and there are still many challenges to overcome.[17] Chitosan and chitin are typically extracted from shrimp shells, and these materials are used for adsorption. Shrimp shells were chosen as a natural adsorbent for this research because of their availability, affordability, and ease of usage. The main difference between this study and others is the usage of raw shrimp shells without any chemical processing. Waste shrimp shell's economic advantages will be enhanced and environmental pollution will be reduced if they can be used successfully in production methods.

1.3.2 FISH SCALES



Fig.10 Fish Scales

Fish scale bio sorbents have been reported to have excellent removal efficiency (50-100% for toxic metals and 78-90% for dyes) as well as extremely good adsorption capacities for heavy metals, dyes, and medicinal chemicals. The foundation of the scales comprises collagen fibers organized in a pattern akin to covered plywood. The bundles of collagen fiber are very tightly packed. Because of their hierarchically ordered structure, scales have a very high resistance to mechanical stress. Minerals (30-56%) and protein (40-60%) can both be found in fish scales.[18] Collagen makes up 80–90% of the protein in scales. It's been revealed that using fish scales directly as food or indirectly to make feed additives is the optimal usage for them. Some have scales, whereas others don't. Many studies have been done on the usage of these scales to add value to life while limiting the ability to represent a nuisance when they are just dumped to the environment. Heavy metal removal from aqueous solutions is performed extremely successfully by bio-adsorbent made from fish scales, with most reported removal efficiencies above 50%.

1.3.3 BANANA PEELS



Fig.11 Banana Peels

One of the most popular fruits consumed worldwide is the banana (family Musaceae), which creates strong agro-waste issues. Cellulose, hemi cellulose, pectin, and some other low molecular weight species are the major components of banana peels. They also principally contain cellulose, pectin, and lignin. Utilizing a

green method, naturally abundant plantain peels are used to produce Fe_3O_4 Magnetic nano-particle.[19] An eco-friendly, cost-effective replacement for chemical and physical processes has been proposed for nano-particle synthesis. Banana waste has been an important agricultural waste tested as an adsorbent due to the numerous pieces that can be utilized, such as shells, trunks, pseudo-stems, leaves, and core. These banana waste elements have received in-depth research as adsorbents for a wide range of contaminant. Banana waste (mostly peel) is the most common type of trash produced as a result of consumption fresh fruit, contributing for 29% of the total wastes generated in this category.

1.3.4 ORANGE PEELS



Fig.12 Orange Peels

Orange peels are widely utilized as adsorbent in the process of treatment of wastewater due to their huge surface area and active functional groups; nevertheless, their expensive cost occasionally precludes their use. Orange residue, a by-product of the fruit industry that is mostly utilized as animal feed, is one of the citrus fruits that are easily obtainable in India. The majority of its component are low molecular weight components such cellulose, pectin, hemicelluloses, lignin, chlorophyll pigments, and limonene.[20] Orange peels have been utilized in adsorption studies and are recognized in the literature as an agriculture industrial residue having adsorptive characteristics.

1.3.5 RICE HUSK



Fig.13 Rice Husk

As an effective adsorbent material for treating diverse pollutants from water and wastewater, husk is a kind of Coarse structure, becomes impermeable in water, is inorganic resistant, is indeed corrosion resistant. Rice husk, the amount of irrigated area, regional environmental factors, the use of fertilizers, climate variance, soil chemistry, and the efficiency of crop production and agronomic techniques all impact how quickly rice develops.[21] Due to the uneven surface of rice that enables for the adsorption of metals in various parts of this material the morphology of rice husk may facilitate the adsorption of metals and other toxins.

1.4 MAGNETIC NANOPARTICLE AND ITS TYPES

Heavy metal ion removal from aqueous solutions has been suggested for nanomaterials having magnetic characteristics. Magnetic nanomaterials may be created utilizing a variety of methods. It was discovered that magnetic nano-adsorbents are inexpensive, easy to use, ecologically friendly, and very effective in removing metals from vast amounts of water and waste quickly. New varieties of nanoparticles for remediation of polluted water have been developed as a result of the recent advancements in nanotechnology.[22] By combining magnetic separation with nanotechnology, nano-adsorbents may provide an effective method for removing harmful metal ions from aqueous solutions. Metal oxide nano-adsorbents ⁶⁰has received a great deal of attention because they exhibit several desirable characteristics as compared to their bulk form, including a high adsorption capacity, improved catalytic activity, a high degree of dispersion, and super para-magnetism behavior.

TYPES OF MAGNETIC NANO PARTICLES

1.4.1 Carbon based nanoparticles

Carbon nanotubes, carbon black, graphene oxide, and biochar are just a few of the carbonaceous materials that have been the subject of intense investigation for their ability to absorb various environmental contaminant. A wide range of Activated Carbon sorbent materials may be produced for a wide range of environmental applications, including the removal of aqueous solutions containing heavy metals.[23] Due to the high production costs associated with this technique, a recent advancement in the area of adsorption of toxic metals involves the use of biochar as a less expensive substitute for coal-based activated carbon. Since the advent of nanotechnology, several studies have been conducted on the potential applications of graphene-based substances for the elimination of toxic metals, like Carbon Nanotubes, reduced Graphene Oxide, and graphene Oxides.

1.4.2 Nano zero valent ion (nZVI)

Nanosized zero-valent nanoparticles have emerged as a new and highly successful remediation method for heavy metals considering its strong reduction capacity, considerable certain pore volume. Zero-valent ion at the nano-scale, a material that is harmless for the environment, has been utilized to successfully treat a number of metallic ions in aqueous solutions. [24] In terms of the reduction of heavy metal ions, nZVI has shown outstanding promise thanks to its strong reactivity, extraordinary reactive lifespan, and low toxicity. nZVI is a substance that is widely used to eradicate heavy metals from freshwater, it has exceptional capabilities for absorbing and decreasing various types of toxic metal ions.

1.4.3 Silica based nanoparticles

Over the past 10 years, silica-based using nanostructures studied is investigated. SiO₂ has long been recognized as the best material for water treatment because of its distinctive properties, which include affordability, non-toxicity, strong acid resistance, and simplicity of modification.[25] It needs to be emphasized that the specific amounts of complicated chemicals bound to those, as previously said, modified SiO₂ nanoparticles are unknown.

1.4.4 Nanocomposites

Nanostructured materials are used to remediate water. They have exceptional characteristics owing to its tiny dimensions, vast large region, and high "surface to volume" proportion. The characteristics increase the removal efficiency of the nanostructured materials. These materials differ from regular materials in that they have exceptional properties including large specific surface area, significant reactivity, and catalytic potential. Nanostructured particles have a very large number of active spots for interacting with various chemical species due to their massive surface area.[26] The extraordinary surface characteristics of nano-silica were used to make two novel composites utilizing a simple and eco-friendly chemical process. The nanocomposite was assessed using a variety of methods to confirm the change. The nanocomposite was therefore used to adsorb or remove metals after being placed within a glass column.

1.4.5 Polymeric Nanoparticles

Over the past 10 years, metallic nanoparticles adsorption (MNP) has attracted a lot of interest due to its efficiency and broad application. It is because the procedure is simple to utilize. Surface polymeric MNPs, including such MNP polymer composites with core-shell MNP, have received a lot of interest lately since the polymer shell prevents the core portion of the Magnetite nanoparticles from collating into bulk materials and enhances the stability of dispersion of the core-shell nanoparticles in a suspension medium.[27] Polymeric nanoparticles are receiving a lot of interest due to their alluring functional groups and ease of modification. These polymeric nanoparticles may be distributed effectively by the organic and aqueous phases. Rapid synthesis of polymeric nanoparticles is possible with a simple precipitation method and low-cost starting materials.

1.4.6 Ceramic Nanoparticles

Ceramic membranes are being employed in more and more applications due to their wide chemical and temperature operating range. Ceramic membranes' exceptional antifouling capabilities and long operating life greatly minimize the high startup design complexity. More than 20 nations employ ceramic water filters as an alternative point-of-use water purification system.[28] Two locally sourced materials are utilized to produce Ceramic Water Filters: clay and sawdust.

Ceramic composites membranes offer greater antifouling qualities with increased mechanical and chemical durability when compared to polymeric composite membranes.

1.4.7 Metal Oxide Nanoparticles

Magnetic nanoparticles made of iron offer unique properties such a larger surface-to-volume ratio, a lower demand for chemicals, and a lack of secondary pollutants. Fe_3O_4 nanoparticles (MNP's) are a new category of nanomaterials that are easy to recycle, can be enhanced through magnetic separation, have high stability, are bioactive, have a low toxic level, are less expensive, have a uniform size distribution, have a high magnetic permeability, and have a sizable surface area. Fe_3O_4 adsorbents have arrived at the perfect moment because of these exceptional properties.[29] Fe_3O_4 magnetic nanoparticles are indeed an intriguing new category of nanometer-sized components because they will show a variety of distinctive and certain values like a huge area, possibility for precision, chemical sensitivity, catalyst ²⁷ potential, and an absence of internal diffusion resistance, which are promising to develop new or improve existing innovations in wastewater treatment.

1.5 METHODS FOR PREPARING MNP

1.5.1 CO-PRECIPIATION

Various methods have been used to manufacture nano-magnetite (Fe_3O_4), comprising sol-gel synthesis, thermal decomposition, co-precipitation and hydrothermal synthesis. The most popular techniques are thermal decomposition and co-precipitation. There are four various forms of co-precipitation processes: mechanical entrapment, mixed crystal, occlusion, and surface adsorption. Compared to other synthesis techniques, co-precipitation is simpler and more useful. Co-precipitation is one of the most successful and attractive procedure due to its simple experimental setup and efficient formation of tiny particulates at low testing temperature.[30] The chemical co-precipitation technique has a number of advantages, including a simple process, outstanding material quality with control over microscopic particle size, and a reasonably short reaction time at ambient temperature. Co-Precipitation is the drawing down of soluble substances by a precipitate under particular circumstances generally, a nucleation emerges out of

thin air in solution when a component concentration reaches super saturation. Compared to different sources, Co-precipitation is vital in the synthesis of magnetic nano-particles. Fe_3O_4 nanoparticles can be synthesized easily via co-precipitation. Co-precipitation will be utilized to produce magnetite nanoparticles. The co-precipitation technique has a high yield, high product purity, no requirement for organic solvents, is easily repeatable, and is cheap. The usage of capping agents can modify the crystallite size and shape of the material created using this process.[31] However, the co-precipitation process has some major limitations, including the requirement for frequent washing, drying, and carbonization to produce a pure phase of phosphorous. An important method for separating and also from various samples is co-precipitation method.

1.5.2 SOL-GEL

The sol-gel process consists of two major steps: hydrolysis of the precursors in basic or acidic conditions and polycondensation of the hydrolyzed products. The size distribution of sol-gel alumina nanoparticles is between 10 and 20 nm, and they are more spherical and homogenous in structure. For production of various nanostructures, especially the sol-gel approach corresponds to the more scientific (moist chemicals) strategy producing nanoparticles made from oxides.[32] Due to the low heating rates that can be utilized to heat-treat the "green" coatings, sol-gel processing enables the synthesis of thin films with high adhesion property. The main advantages of sol-gel processing method were high purity and the capability of uniform nanostructures at low temperature. The remaining gel has eventually dehydrated, at which point its fluid is extracted out from gel's composition. The characteristics of both the cured gel are highly altered by the drying process. Phrasing it yet another way, the "removing solvent method" has determined by keeping its envisaged utilizing gel.

1.5.3 THERMAL DECOMPOSITION

A novel technique for producing stable mono-dispersed nano-particles involves thermal decomposition. Decomposition reactions are available in three varieties thermolysis, electrolysis, photolysis. The process of decomposing by electricity is known as electrolysis. The term "photolysis" refers to the decomposition caused by light. There are two or more products, but only one reactant in a thermal

decomposition reaction. Since warmth seems to be a substrate in all these interactions, most also thermodynamically favorable, it signifies that heat energy's needed to destroy the covalent bonds that link the molecules. Thermo-chemical decomposition is simple and affordable.[33] The rate of decomposition could be determined using a device called a thermo-gravimeter, while zeta potential was used to determine stability in biological applications. Recent studies, however, reveal that the magnetic magnetite/maghemite phases continue after the thermal decomposition processes actually start with the production of a nonmagnetic Wüstite phase due to oxidation when exposed to the ambient oxygen. The reaction can occur at a high reflux temperature due to the highly boiling point solvents utilized in Thermal Decomposition procedures, especially dioctyether, whose boiling point is nearly to 300 °C.

1.5.4 HYDROTHERMAL SYNTHESIS

The most common technique for generating nanomaterials is hydrothermal synthesis. In hydrothermal synthesis, nanomaterials can be created at a variety of temperatures, including very high temperatures and room temperature. The word "hydrothermal synthesis" represents a temperatures and pressures that are beyond ambient, diverse reactions in water-based solutions are used to generate organic chemicals.[34] Magnetic nano-particles as well as a wide variety of other nano-materials may now be made using hydrothermal techniques. The hydrothermal process is often carried out in an "Autoclave," a pressurized vessel. Both pressure and temperature can be controlled by it. Graphene-ZnS nano-composites can be easily created by hydrothermally treating GO and ZnS precursor with water, a process known as hydrothermal synthesis. The hydrothermal synthesis strategy is cleaner and more efficient than the synthesis techniques outlined above, but there are still some major challenges, such as the yield and dispersion of Magnetic nano particles.

1.6 APPLICATIONS OF MNP

- ❖ Industrial applications
- ❖ Medical and Biomedical applications
- ❖ Sensors and Catalysis
- ❖ Environmental usage and Molecular Imaging

CHAPTER-2 LITERATURE SURVEY

- **Dr.D.Prabu *et al.* (2021)** has published a scientific article titled “**Feasibility of Magnetic Nano Adsorbent impregnated with activated carbon from animal bone waste**”. Chromium is a heavy metal that causes a lot of pain for the environmental elements when it is present in effluents. This MNA from animal wastes is used to remove heavy metals like chromium. The new MNA Fe_3O_4 -BAC was created, examined, and employed in the study as an effective sorbent for the elimination of chromium in liquid solution. The thermally treated BAC is co-precipitated onto the magnetic nano adsorbent under ultrasonic conditions. The Fe_3O_4 -BAC's enhanced shape is seen in the SEM imaging with a more favorable structure for 100-446nm, among the nanoparticle narrow size distribution comprised. At an acidic pH during a contact period of 60 minutes with an adsorbent concentration of 5g/L, optimal adsorption has been discovered. Nano adsorbent has an ideal binding of 27.86 mg/g. A procedure feasibility has been confirmed by thermodynamic and isotherm experiments. Additionally, the kinetic

experiments demonstrate the examined Fe_3O_4 -BAC's propensity towards pseudo-first order models. As a result, Fe_3O_4 -BAC may have application to be an absorber to extract with aqueous media, chromium.

- **Christos Liosis et al. (2021)** has published an article titled “**Heavy Metal Adsorption Using Magnetic Nanoparticles for Water Purification: A Critical Review**”. With a focus on water quality and technique applicability, a framework for analyzing the key discoveries too earlier studies in ions elimination by MNP is offered. Numerous studies have been conducted with an emphasis on the synthesis, characterization, and capability of uptake of bare & modified iron nanoparticles, to the related desorption process of the approach the research techniques reveal effective sorption of impurities into marine conditions, according to the current review study likewise a yield of as much as 90 can be accomplished through reusing the nanoparticles to a maximum of five times. Moreover, it deserves to be acknowledged that nanoparticles have rarely endured up to 22 episodes of recovery.

- **Milton Manyangadze et al. (2020)** has published an article titled “**Adsorption of lead ions from wastewater using nano silica spheres synthesized on calcium carbonate templates**”. In this article, they looked into the method of purifying wastewater for use by plants, animals, or industrial processes by removing Pb(II) ions using adsorption. To eradicate lead metal from water, they created nano silica hollow spheres (NSHS) & employed them as adsorbents. Silica amorphous attribute is clear when they used X-Ray diffraction to analyze the NSHS; a representation for a typical crystalline was 39.5 nm. The structure of the adsorbent was studied using scanning electron microscopy, and it was discovered that the particles were spherical and ranged in size from 100 to 200 nm. The loss of weight of NSHS, which was found to be 2% at 800°C, was calculated by thermo-gravimetric analysis. At a maximum temperature of 60°C and a maximum starting metal concentration of 300 mg/L, the adsorption efficiency was 200 mg/g and 262 mg/g, respectively, and the adsorption rate was 99.6% & 87.4%, respectively. The equilibrium and thermodynamic data showed that the Langmuir adsorption isotherm ($q_{\text{max}} = 266.89 \text{ mg/g}$ and

$b = 0.89 \text{ L/mg}$) provided a better description of the process. Both the endothermic and spontaneous adsorption processes were present. They draw the conclusion that NSHS were effectively synthesized, used to eliminate Pb(II) ions, and their production has a greater capacity than the majority of other adsorbents examined by other researchers.

- **Minh Trang Hoang *et al.* (2018)** has published an article titled “**Removal and recovery of lead from wastewater using an integrated system of adsorption and crystallization**”. Besides the interest of getting rid of and reclaim oceanic Pb environments, in this investigation investigates viability of like a trigeneration system that combines sorption in crystallisation in a particle furnace. With the use of citric acid-modified sugarcane bagasse (SCA), researchers looked into the preferential adsorption of Pb^{2+} over Ca^{2+} and Mg^{2+} in batch and column systems. With a 7 cm slope, a 1.5 ml/min flow rate, as well as an edge activator intensity of 0.482mmol/L, led has indeed been preferentially immobilized on SCA in a chromatographic column up to an efficiency of 0.767 mmol/g. Selective separation of Pb^{2+} from the mixed solution was accomplished at a molar ratio $3.22 < 4.49$ in batch mode. According to the dynamic analysis, the Thomas & Yoon-Nelson models and the experimental findings are very closely correlated. The dissolving examination of the perfect balance biosorbent SCA in a column system demonstrates that it is a possible desorption reagent with a dissolution capability of 80% Pb^{2+} . A quantitative recovery of Pb(II) was achieved under ideal circumstances of pH 10, superficial velocity of 9.55 m/h, and starting Pb(II) concentration of 2.43 mm. Overall, it was determined that the designed system, which combines adsorption utilising a briquette heater, is enough to eliminate they extract Pb form effluent via PbCO_3 .
- **Shijie Liu, Suping Cui *et al.* (2021)** has published an article titled “**Adsorption of Lead Ion from Wastewater Using Non-Crystal Hydrated Calcium Silicate Gel**”. In order to produce low-cost and effective adsorption materials, this study used calcium acetate and water glass as raw materials to synthesise calcium silicate hydrate silicate gel via precipitation process. By means of X-ray spectroscopy, FTIR, a particular surface area analyzer, & a SEM, functionality and composition of hydrated

calcium silicate gel was methodically investigated. According to studies, non-crystal hydrated calcium silicate gel (CSH) was effectively created, and utilizing CSH, lead ions were removed at a rate of more than 90%. The adsorption process is consistent with both the pseudo-second-order kinetic model and the Langmuir adsorption isotherm model, with a maximum adsorption capacity of 263.17 mg/g. The lead ion adsorption capability employing CSH was demonstrated in the acid treatment experiment, and the adsorption rate persisted at >60% after 5 cycles. The study could provide an adsorbent with cheap cost, high efficiency, and great stability.

- **Ata UrRehman et al. (2021)** has published a journal titled “**Toxicity of heavy metals in plants and animals and their uptake by magnetic iron oxide nanoparticles**”. Heavy Metals are present in the environment naturally, but because of human activity and some natural processes, they have gotten into the air, the water, and the soil and have grown to be a significant worldwide problem. Most of them build up in the body for extended periods of time after entering it, causing a variety of issues, as in the case of plants it will harm vital parts like elements of organelles, bases, and foliage, and obstruct crucial biochemical processes like photosynthesis and mineral absorption. Similar to how they may harm an animal's essential bodily organs like the kidney and liver, they can also lead to deadly illnesses like cancer. The dose, length of exposure, and concentration of these heavy metals all have a significant role in the illnesses they cause. Because of the toxicity, bioaccumulation, and non-biodegradability of heavy metals, this issue has become quite serious. Various sources have exposed living organisms to these heavy metals, but drinking water is one of the main ones. To eliminate these metals from water, a lot of work has been done. However, the traditional methods have a number of shortcomings, such as being uneconomical and having an effect on the environment. Numerous benefits include regeneration, surface alteration, economic effectiveness, ease of usage, and environmental friendliness.
- **Fahad Saleem Ahmed Khan et al. (2020)** has published scientific article titled “**Magnetic nano adsorbents potential route for heavy metals removal—a review**”. The dumping of local waste and the fast expansion of the heavy metal-based businesses have had serious negative effects on

the ecosystem. Reverse osmosis and ion exchange methods were commonly used in the past to remove heavy metals, but these processes have significant drawbacks. Because of this, a lot of work has gone into developing improved techniques, especially for the elimination of heavy metals. The application of nanotechnology presents the opportunity to enhance currently employed approaches in order to more effectively address problems. Numerous novel materials, including magnetic nanoparticles, have been discovered as a result of advancements in nanotechnology. These nanoparticles have good qualities such a high surface-to-volume ratio, less toxicity, and simple separation. Additionally, as compared to other conventional adsorbents, magnetic nanoparticles may be retrieved after adsorption quickly and effectively. The effectiveness in metal ions removal from fluid using magnetic nano-adsorbent is only major focus of this review. Additionally, a thorough examination of the methods used to create, characterize, and modify magnetic nanoparticles is provided in a methodical manner. Additionally, the potential benefits and drawbacks of utilizing magnetic nanoparticles as an adsorbent to remove heavy metals are highlighted.

- **Fato Patrice Fato et al. (2019)** has published a journal titled “**Simultaneous Removal of Multiple Heavy Metal Ions from River Water Using Ultrafine Mesoporous Magnetite Nanoparticles**”. Numerous ions found in river water can have an impact on the adsorption process in an aquatic environment. Four heavy metal ions, Pb^{2+} , Cd^{2+} , Cu^{2+} , and Ni^{2+} , have been successfully removed simultaneously from river water using UFMNPs due to the attraction of these metal ions to the surface of the particles and their unique mesoporous structure, which facilitates the simple adsorption. Individual Pb^{2+} , Cd^{2+} , Cu^{2+} , and Ni^{2+} ion removal efficiencies from river water were 98, 87, 90, and 78%, whereas combined Pb^{2+} , Cd^{2+} , Cu^{2+} , & Ni^{2+} ion removal efficiencies on same flowing water were 86, 80, 84, and 54%, respectively. This work has shown that UFMNPs have a great deal of promise for use in treating wastewater, particularly simultaneous elimination of metal ions in environments.
- **Noraziah Abu Yazid et al. (2019)** has published a journal titled “**Co-precipitation synthesis of magnetic nanoparticles for efficient removal**

of heavy metal from synthetic wastewater". Magnetic nanoparticles (MNP) have emerged as a valuable tool or catalyst in a variety of commercial applications. MNP is smaller than bigger particles and as a result has a larger surface area, which renders it more responsive to particular chemicals. The main emphasis of this work is the application of MNP to the environmental problem associated with the heavy metal discharge from industrial effluents. Varied variables, including temperatures and prioritizes (KOH), sodium hydroxide& ammonium hydroxide) is appended to a mixture containing Fe(II) and Fe(III), were used synthesis the MNP in order to produce different sizes and morphologies. Atomic Adsorption Spectroscopy was used to assess the effectiveness of MNP removal on a solution containing Cr, Ni, and Cu before the results were examined (AAS). TEM, FTIR, and XRD were used to characterize the MNP. Based on the findings, it is determined that MNP produced with NH_4OH at 70°C is responsible for 90% of the Cr removal. The MNP has the shortest size (9 nm), which allows it to absorb more Cr ions. As a result, the strong base produces MNP with the lowest dispersion, while the addition of surfactant results in less heavy metal adsorption but greater oxidation resistance. This research has shed light on the viability of using the MNP as a metal ion removal option.

- **Junhua You et al. (2021)** has published a journal titled **"A review of amino-functionalized magnetic nanoparticles for water treatment: Features and prospects"**. Due to their remarkable qualities and wide range of uses, such as the treatment of wastewater and/or water, Increased curiosity in nanotechnology have emerged. Because of the negative consequences on both people and the environment, the release of toxic substances and other toxins into water supplies is a problem. Aminated or amino-functionalized MNP are produced by grafting amino functional groups onto magnetic nanoparticles. This work reviews the production, separation, and adsorption processes as well as the potential applications of amino-functionalized magnetic nanoparticles in water treatment. To elimination form groundwater of metallic, radioactive substances, organics, colors, and microorganisms, a number of significant works have also been mentioned. Additionally, the effects of variables like pH, contact duration,

ion selectivity, and recycled content are discussed, as well as the dose of magnetic nanoparticles.

- **Mohamed A. Tahooun et al. (2020)** has published a journal titled “**Effective Heavy Metals Removal from Water Using Nanomaterials: A Review**”. High harm to the environment is posed by the release of heavy metals such as Zn, Ni, Pb, Cu, Cr, Cd in water over the allowed limits. Better clean-up methods have recently been made available employing nanotechnology and nanomaterials. The focus was on newly created, cost-effective nanomaterials for use in water and wastewater clean-up, including zeolite, carbonate, polymer-based, chitin, ferrous, metal oxide, bimetallic, and metallic materials. This review concentrated on the synthesis of different nano-adsorbent materials and their capacity to remove various hazardous ions. Also studied was the impact of many experimental physicochemical variables on the adsorption of heavy metals, including ionic strength, starting ionic strength, temperature, contact duration, adsorbent dosage, and pH.
- **Lakshmi Prasanna Lingamdinne et al. (2019)** has published a journal titled Green “**Synthesis of Iron Oxide Nanoparticles for Lead Removal from Aqueous Solutions**”. Because it is a carcinogen and a heavy metal, Pb(II) always poses a serious hazard to human kind. It is widely employed technique for removing metals because it is very efficient, simple to use, and economical. Size, large surface area, and magnetic properties, oxides of iron is discovered in appealing for heavy metal elimination from ocean. At an initial metal concentration of 10 ppm & room temperature of 25°C, it was discovered that 0.6 g/L of T-Fe₃O₄ was able to remove 99% of Pb(II) via adsorption. On the homogenous surface of the adsorbent, a monolayer adsorption isotherm was discovered. In order to provide clean and sanitary water for a healthy and sustainable existence, lead may be removed from water resources using green tangerine peel altered iron oxide nanoparticles.
- **K.Anbalagan et al. (2021)** has published scientific article titled “**Removal of heavy metal ions from industrial wastewater using magnetic nanoparticles**”. By the co-precipitation approach, maghemite (γ -Fe₂O₃) and MNP (Fe₃O₄), were created in this study, and they were characterised

using EDS, XRD, SEM, and FTIR Spectroscopy. These particles, which ranged in size from 20 to 100 nm, were utilised as nano adsorbents to filter out toxic metals like copper and chromium from synthetic wastewater. Adsorption is dependent on factors including pH (2.5 & 6.5), contact duration (60 and 80 minutes), and doses at room temperature, which were shown to have a 92% removal effectiveness for chromium and copper. These particles demonstrated astounding metal removal effectiveness. Additionally, these particles were renewed for reuse; for the desorption of copper and chromium metals, respectively, HCl and NaOH effluent were used. The observed data clearly show that magnetic nanoparticles have improved pollution removal. The separation factor (r), which ranges from 0 to 1, shows that the Langmuir isotherm favours both the ions of copper and chromium.

CHAPTER-3 AIM AND SCOPE

3.1 AIM

- ❖ Synthesis of Prawn Shell impregnated Magnetic Nanoparticle (MNP-PS).
- ❖ Characterization of Prawn Shell impregnated Magnetic Nanoparticle (MNP-PS)
- ❖ To improve variables like pH, Temperature, Time, Dosage, and Concentration through batch adsorption experiments.
- ❖ To study isotherm models for Langmuir, Freundlich Temkin and Sips and to analyze experimental data using the Pseudo-First order and Pseudo-Second order Adsorption Kinetic Models.

- ❖ ⁷ Removal of Pb(II) ions from Industrial Effluent using Prawn Shell impregnated Magnetic Nanoparticle (MNP-PS).

3.2 SCOPE

- ❖ The utmost scope of this work is to treat water contamination using eco-friendly Prawn Shells.
- ❖ Since Nanoscience is advancing day-by-day, these prawn shells are converted into Magnetic Nanoparticle for ⁴⁷ the removal of Pb(II) ions from Water.
- ❖ Pb(II) ions causes several serious damages to Human Life, Marine Life and to the whole ecosystem itself. So, treatment of them in a novel way is found mandatory.

CHAPTER-4 MATERIALS AND METHODOLOGY

4.1 MATERIALS

The List of materials employed to synthesize MNP-PS nanoparticles are listed below:

4.1.1 CHEMICALS REQUIRED

- ❖ Hydrochloric Acid (HCl)
- ❖ Ferric Chloride (FeCl_3)
- ❖ Ferric Sulphate ($\text{Fe}_2(\text{SO}_4)_3$)
- ❖ Ammonium Hydroxide (NH_4OH)
- ❖ Ethanol ($\text{C}_2\text{H}_5\text{OH}$)

- ❖ Distilled Water
- ❖ Lead Nitrate ($\text{Pb}(\text{NO}_3)_2$)

4.1.2 EQUIPMENTS REQUIRED

- ❖ ⁵⁴ Muffle Furnace
- ❖ Hot Air Oven
- ❖ Hot Plate Magnetic Stirrer
- ❖ Rotary Shaker

4.2 METHODOLOGY

4.2.1 Drying of Prawn Shells



Fig.14 Drying

Prawn shells are collected from Marina Beach and Local Markets in Chennai. To get rid of grime, dust, and traces of blood, prawn shells are properly cleaned with deionized water. Following that it is dried in the sun until it becomes crispy and fine.

4.2.2 Preparation of Activated Carbon



Fig.15 Preparation of Activated Carbon

Prawn Shells are kept in the Muffle Furnace for about 2 hours at 600°C. The powdered prawn shells are activated by immersing it in Hydrochloric Acid (HCl) for about 24 hours. The solution is then filtered and the solid powder is washed thoroughly with Distilled Water. It is then dried in the Muffle Oven for 1 hour at 200°C. The dried particle is the Prawn Shell Activated Carbon (PS).

4.2.3 Impregnation Process

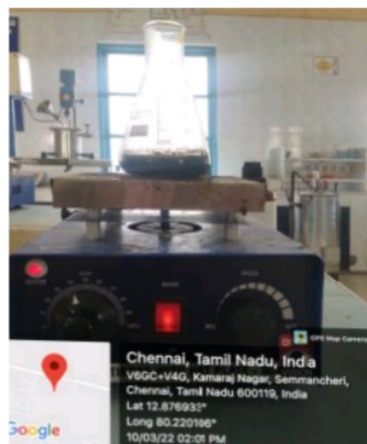


Fig.16 Impregnation Process

The Activated Carbon is then impregnated with Ferric Chloride and Ferric Sulphate. Weighed 2g of Ferric Chloride (FeCl_3), 1g of Ferric Sulphate ($\text{Fe}_2(\text{SO}_4)_3$) and 1g of the PS. All the solid particles are added in the conical flask and kept in the Hot Plate Magnetic Stirrer. To it, added 50ml of Distilled Water. The temperature is kept at 40°C and it is allowed to stir continuously for 15mins.

4.2.4 Co-precipitation Process

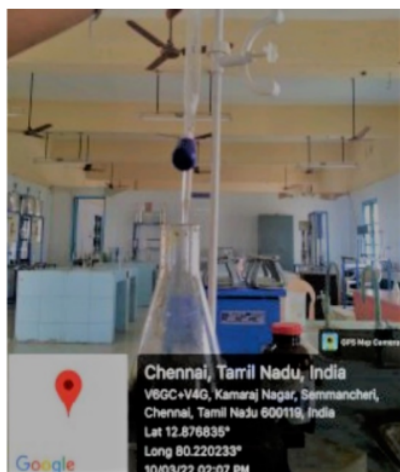


Fig.17 Co-precipitation Process

Ammonium Hydroxide (NH_4OH) is added to the solution kept in the Magnetic Stirrer for co-precipitation process. 50ml of Ammonium Hydroxide is measured and added to the solution drop wise with constant stirring.

4.2.5 Magnetic Separation

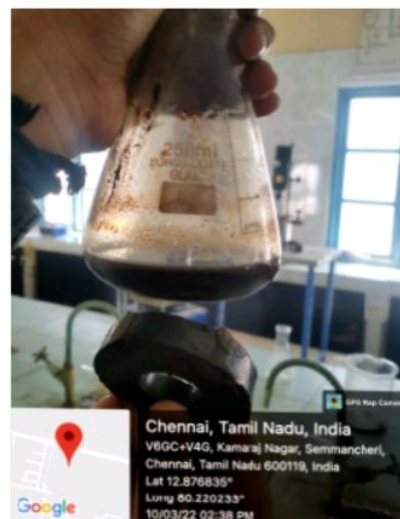


Fig.18 Magnetic Separation

Magnetic Attraction is checked with the help of a Magnetic.

4.2.6 Filtration and Drying

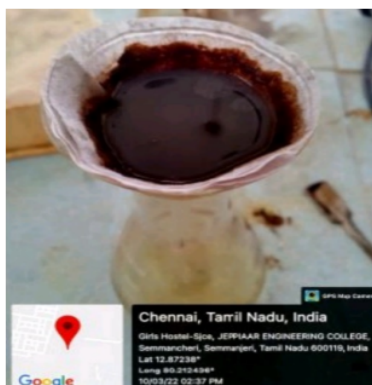


Fig.19 Filtration



Fig.20 Drying

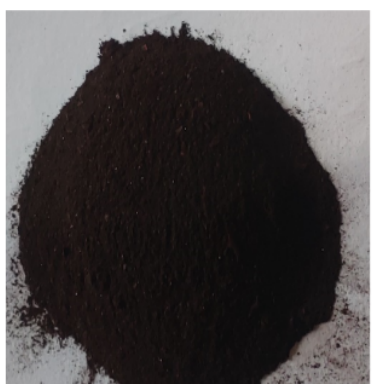


Fig.21 MNP-PS

The solution is filtered and washed with ethanol to prevent rusting. The Filtrate is then dried in Muffle Oven at 150°C for 30mins. The powdered particle is the Magnetic Nanoparticle impregnated with Prawn Shells (MNP-PS).

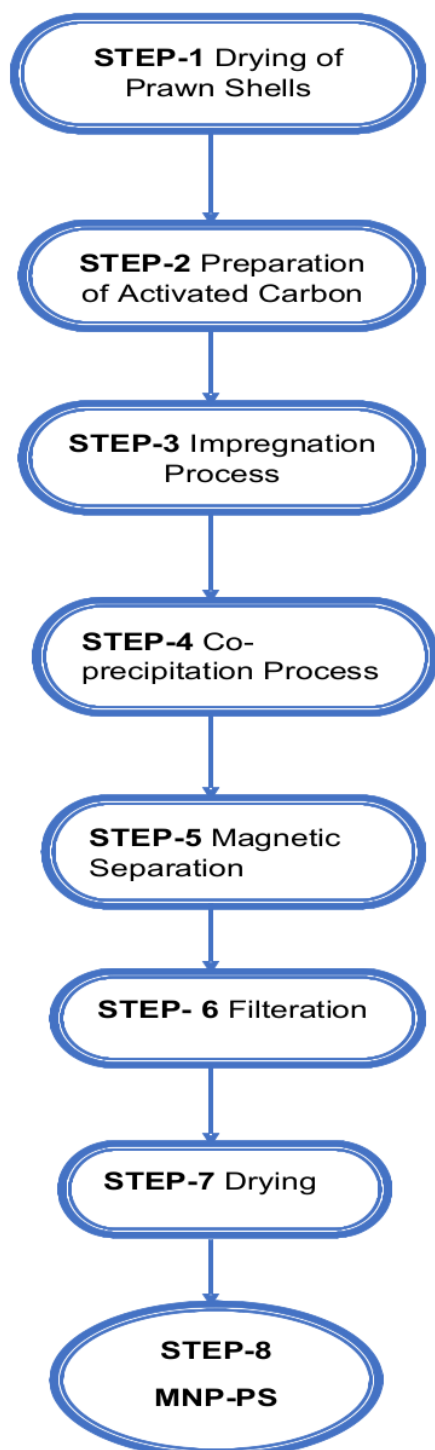


Fig.22 Schematic Representation of Preparation of MNP-PS

4.3 PREPARATION OF Pb(II) ION SOLUTION

Analytical Reagents Grades was indeed the criteria for all chemicals handled (AR). The measured quantity (1.6g) of lead nitrate (Pb(II)) adsorption was neutralized in the double water to produce a stock solution with such a Pb(II) levels of 1000mg/L. Pb(II) are generated again for required test concentrations (20-100mg/L) following diluting the stock solution mostly in right sequence. Have used 0.1M NaOH or 0.1M HCl, the pH of each standard solution was raised to the optimum consistency prior to actually introducing the adsorbent to an aqueous phase. Using a pH metre, the solution's pH was determined (Elico Model, India).

4.4 ADSORPTION EXPERIMENT

- ❖ Using MNP-PS as one method for increasing the adsorption of Pb(II) ions from aqueous media, batch adsorption experiments been performed to improve the processing parameters, like temperatures, preliminary Pb(II) ion amounts, solution pH, adsorbent dose and contact duration.
- ❖ Even during batch sorption studies, 100mL of Pb(II) ions treatment with variable starting Pb(II) levels (20-100mg/L), pH (2.0-8.0), and quantities of adsorbent (2.0-8.0g/L) all taken in 100mL flasks containing and then the combination was mixed in a Rotary shaker.
- ❖ These extracts is drawn out again in several time (0-60 minutes), when respective Pb(II) levels were evaluated.
- ❖ Adsorption Thermodynamics, Kinetics, Mechanism, and Isotherms were all employed systematically.
- ❖ The following process were employed in order to estimate the proportion of Pb(II) ion eliminated.
- ❖ Equation:

$$\% \text{ Removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100$$

Where C_o (mg/L) is starting and C_e (mg/L) are balancing levels of Pb(II) ions, as shown.

4.4.1 Adsorption Isotherm Experiments

Adsorption isotherm measurements is executed just putting 0.2 grams of without moisture MNP-PS samples into 100mL of a Pb(II) Ionized fluid and both the starting Pb(II) ion concentration varying between 20-100 mg/L at an optimal situation. The combination then was agitated in a Rotary Shaker till it reached a steady. The Pb(II) ion's sorption into aqueous phase was described by using two equations isotherm models consist of Langmuir, Freundlich, Temkin, and Sips isotherm models. The comparability of these model applicability coefficient of correlation (R^2) values and error values (SSE, sum of squared error and RMSE, root mean squared error). The two adsorption isotherm models using the following two parameters are as follows:

Langmuir Isotherm Model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

Equilibrium variable is:

$$R_L = \frac{1}{1 + K_L C_0} \quad (2)$$

Freundlich Isotherm Model:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Temkin Isotherm Model:

$$q_e = B \ln (A C_e) \quad (4)$$

Sips Isotherm Model:

$$q_e = \frac{K_s C_e^{\beta_s}}{1 + \alpha_s C_e^{1/\beta_s}} \quad (5)$$

where q_e is a proportion of absorbance in Pb(II) ions accumulated in MNP-PS (mg/g), q_m is very highest quantity of remaining coverage in Pb(II) ions consumed into MNP-PS(mg/g), K_L is the Langmuir constant relating in towards proximity

Pb(II) ions to the adsorbent (L/mg), C_e represents the equilibrium state of Pb(II) ion solution (mg/L)[35], K_F denotes the constant $((\text{mg/g})(\text{L/mg})^{1/n})$ adsorbent potential, n is a variable that correlates to the density of adsorption (g/L), $B=RT/b$ represents the constant associated with heat of adsorption, biosorbent warmth(kJ/mol), R denotes the gas constant (8.314 J/mol K), T denotes the temperature (K), A is greatest adherence energy correlated with optimum binds constant (L/mg), K_s as Sips system isotherm value (L/g) β_s , α_s is the Sips model constant (L/g) $1/\beta_s$ and β_s is often regarded as the heterogeneity factor, with values close to 1 indicating a homogeneous binding site and values greater than 1 indicating a heterogeneous adsorption system.

4.4.2 Adsorption Kinetics and Mechanism Experiments

By inserting 0.2g of MNP-PS in 100mL of Pb(II) ions solution (20-100mg/L) in a sequence of flasks containing, Pb(II) ions successfully removed employing MNP-PS. The samples were drawn out of the conical flasks at predetermined intervals while they were maintained in a shaking incubator (0-60min). The following expressions were used to determine the amount of Pb(II) ions absorbed onto MNP-PS given time t , q_t (mg/g):[36]

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (6)$$

where, C_t is concentrated level of Pb(II) ions present with in mixture via period t (mg/L), V is density of Pb(II) ion solution (L) and m is Mass of MNP-PS (g). The statistics on kinetic model is utilized to examine equilibrium adsorption models that describe the adsorption characteristics, including such pseudo-first order, pseudo-second sequence, & Elovich Kinetic parameters.

The following are kinetic models:

Pseudo-first order Kinetic Model:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

Pseudo-second order Kinetic Model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Elovich Kinetic Model:

$$q_t = (1 + \beta_E) \ln(1 + \alpha_E \beta_E t) \quad (9)$$

here q_e denotes the experimental equilibrium efficiency (mg/g), q_t denotes the capability to sorption anywhere at particular time. (mg/g), k_1 with fictitious initial kinetic order law (min^{-1}), t denotes the time (min), k_2 is fictional second kinematic reaction rate (g/mg.min) and $k_2 \cdot q_e^2 = h$, it refers to first-order adhesion frequency (mg/g.min), β_E is there a connection between the re-sorption rate & adsorption and desorption activation energy (g/mg) and α_E is starting sorption qualities (mg/(g.min)).[37]

4.4.3 `Adsorption Thermodynamic Experiments

The sorption study was done with infusing 0.2g of MNP-PS to 100mL of Pb(II) solution inside a series of conical flasks having initial Pb(II) ion values ranged from 20 to 100mg/L. The adsorption equipment has been kept in an incubation shaker, that was effectively maintained at various climate extremes from 303 and 333 K. The set of equations were applied to be able to find values in terms of the enthalpy variable (ΔG°) (variation in surface energy), (ΔH°) (variation in enthalpy), and (ΔS°) (variation in entropy):

$$K_c = \frac{C_{Ae}}{C_e} \quad (10)$$

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

$$\log \left(\frac{C_{Ae}}{C_e} \right) = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (12)$$

now K_c is the equilibria value, C_{Ae} is number as for times Pb(II) ion particles got put on it by the MNP-PS each litre at optimal amount (mg/L), C_e is the accumulation of Pb(II) ions that are present (mg/L), R denotes the gas constant (8.314 J/mol/K) and T denotes the temperature (K).[38]

CHAPTER-5 RESULTS AND DISCUSSION

5.1 CHARACTERIZATION OF MNP-PS

5.1.1 SCANNING ELECTRON MICROSCOPY (SEM)

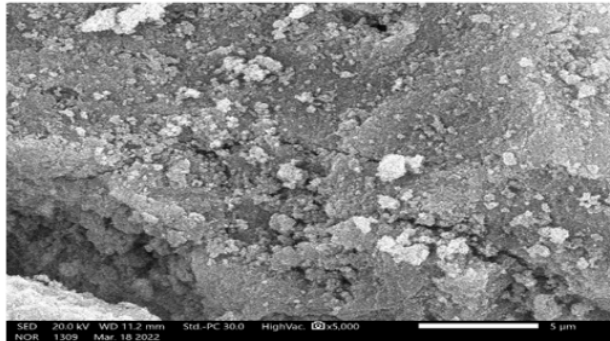


Fig.23 SEM IMAGE (a) Of MNP-PS

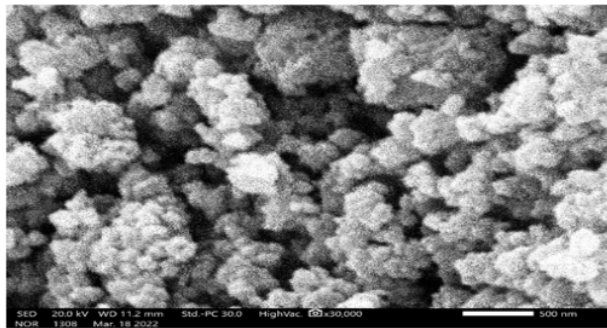


Fig.24 SEM IMAGE (b) Of MNP-PS

Fig.23 and **Fig.24** refers to the SEM image. The ⁴⁴Scanning Electron Microscope (SEM) is one of the most widely used experimental methods for the research and analysis of micro and nanoparticle imaging characterisation of solid materials. SEM is utilised for particle size characterization primarily because of its 10nm resolution. SEM is used to examine the morphology of the powder before consolidation. The methods are simple: a two-sided carbon tape is applied to a SEM sample stub, then powder is sprinkled on top. SEM examinations were used to examine the produced MNP-PS sample's morphology. SEM pictures of the MNP-PS sample reveal a porous, uneven surface that lacks specific shape.

7 5.1.2 ENERGY DISPERSIVE X-RAY (EDX)

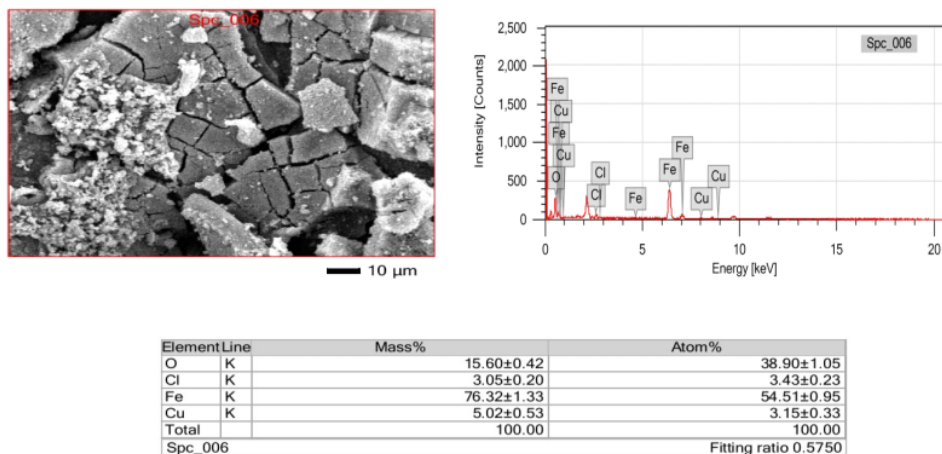


Fig.25 EDX Image Of MNP-PS

Fig.25 represents the EDX pattern with weight percentage of MNP-PS. An x-ray technique called Energy Dispersive X-Ray Analysis (EDX), often known as EDS or EDX, is used to determine the elemental composition of a substance. SEM is carried out paired with EDX to determine the types and amounts of elements present at the nanomaterial surface. Using EDX analysis, the MNP-PS sample's elemental composition was investigated. The synthesised MNP-PS sample principally comprises iron (76.32%), copper (5.02%), oxygen (15.60%), and chlorine (3.05%), according to the EDX pattern.

7 5.1.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

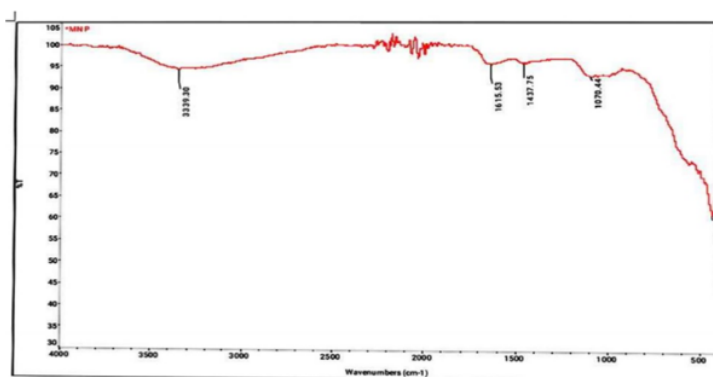


Fig.26 FTIR Image Of MNP-PS

FTIR analysis was used to analyse the functional groups responsible for the production and characterization of iron oxide impregnated activated carbon generated from prawn shell waste (Fe₃O₄-PS-MNP) adsorbents. Fig.26 depicts MNP-PS Adsorbents. Additionally at 3339.30 cm⁻¹ there is a small drop in the spectra which shows the presence of O-H stretch in the nano particle and the presence of atmospheric CO₂. At 1615.53 cm⁻¹, a medium adsorption band is seen indicating the C=C stretch aromatic vibrations in organic content of MNP-PS adsorbent. C-H methyl (-CH₃) is seen at 1437.75 cm⁻¹. The C-O stretch (secondary alcohol) is seen at 1070.44 cm⁻¹. The synthesis of Fe₃O₄-PS-MNP adsorbent is validated by comparing the FTIR spectrum.

5.1.4 X-RAY DIFFRACTION (XRD)

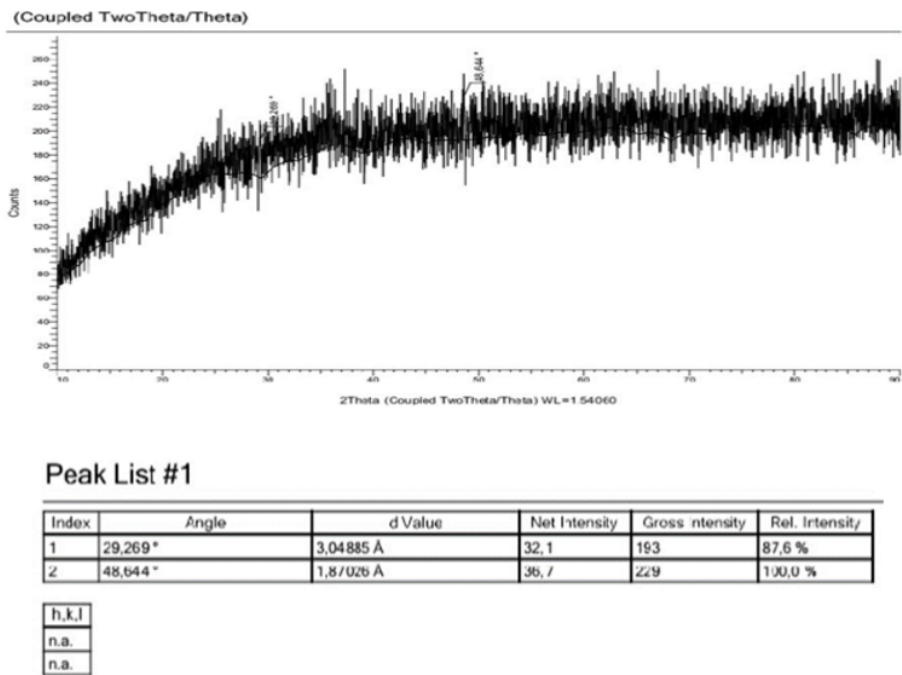


Fig.27 XRD Image Of MNP-PS

Fig.27 depicts the X-Ray Diffraction (XRD) pattern of activated carbon impregnated with iron oxide and generated from prawn shell. The technique used for determining a material's underlying crystal structure is XRD. The fundamental

idea behind X-ray diffraction is constructive interference between monochromatic X-rays and a crystalline material. These X-rays get generated by a cathode ray tube & are collimated to concentrate them while being directed at the material. Two magnetic diffraction peaks with miller indices may be identified from the XRD pattern by matching two theta values, which are 29.269 and 48.644 degrees. The Peak list can be seen in **Fig.27**.

5.1.5 VIBRATING MAGNETIC SPECTROSCOPY (VSM)

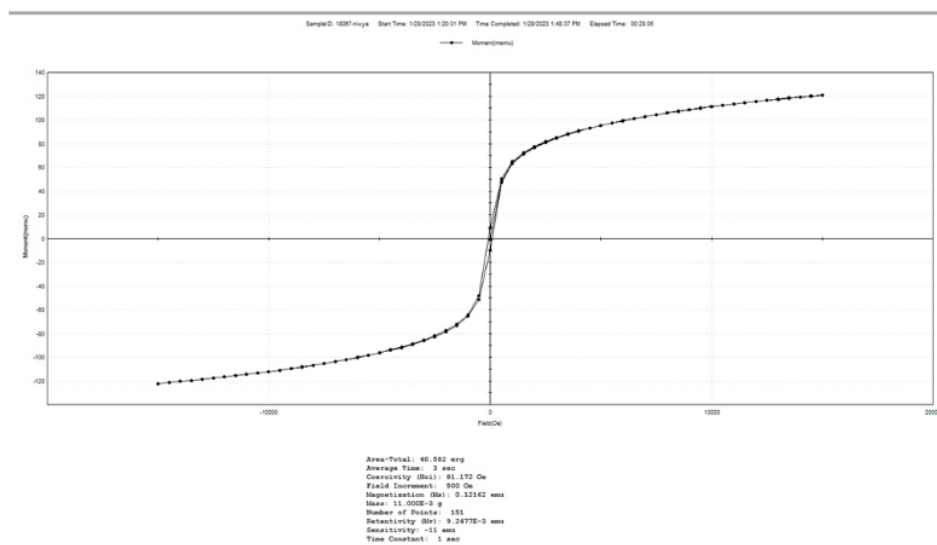


Fig.28 VSM Image of MNP-PS

A popular instrument to analyse the magnetic properties of a wide range of materials, comprising diamagnetic, paramagnetic, Ferromagnetic, ferromagnetic, and anti-ferromagnetic, involves a vibrating sample magnetometer. As a direct consequence of an applied magnetic field, the magnetometer observes magnetic moment. VSM functions by creating an electric field from a changing magnetic field, as per Faraday's Law of Induction. The adsorbent exhibits super paramagnetic properties, as discovered by VSM. The adsorbent exhibits super paramagnetic properties, as discovered by VSM. The results have demonstrated that the saturation magnetization rises over 40 emu.

5.2 OPTIMIZATION PARAMETERS

5.2.1 Effect of pH

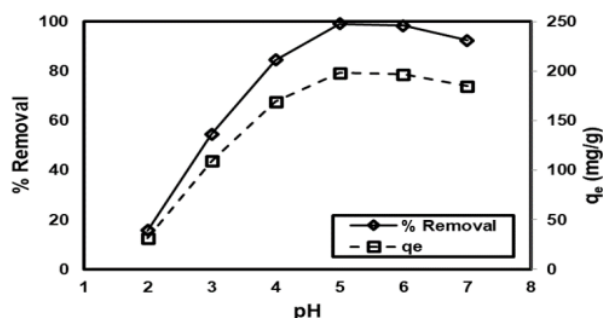


Fig.29 Effect of pH on Pb(II) ion removal by MNP-PS; (initial Pb(II) ion concentration= 20 mg/L, dose= 5 g/L, volume = 100 ml, time = 30 min, and temperature = 30°C)

A sorption onto the PS-MNP over a pH range of 2-8 was studied. From the **Fig.29** we could observe uptake Pb(II) ions decreases in rise pH. In lower pH values i.e. at pH 7 which is a neutral state, H^+ ions occupies most of the adsorption sites on the MNP-PS surface and less Pb(II) ions adsorbed because of electrostatic repulsion with H^+ ions on MNP-PS surface. From the graph, disposal percentage decreases in rise in pH range & optimum pH was found to be 5.0 for 99.134% removal.

5.2.2 Effect of Contact Time

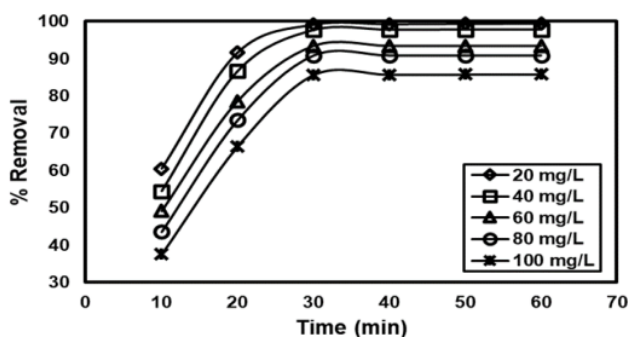


Fig.30 Effect of contact time on Pb(II) ion by MNP-PS (initial Pb(II) ion concentration = 20-100 mg/L, pH= 2.0, dose =3 g/L, volume =100 ml and temperature = 30°C).

An impact in operation time (0-60 minutes) on just elimination of Pb(II) through adsorptive PS-MNP displayed in the following **Fig.30**. From this graph, it's apparent proportion to Pb(II) ion eradicated rises with increasing time reaches at 30 min. Whenever the residential time for Pb(II) ion adsorption over onto adsorbent is long, the greatest percent of Pb(II) ion elimination could be seen. The result clearly shows that the percentage removal increases with increase in contact time and the balancing has indeed been achieved at 30 minutes for MNP-PS for 5 distinct starting Pb(II) ions accumulations. The adsorption curves were single, smooth and continuous leading to saturation and indicates the possible mono-layer coverage on the surface of adsorbent by the ion molecules. Since the difference between the adsorption values at 40 and 60 minutes is so minor, a steady-state approximation for the 40-minute contact was used, along with the assumption of a quasi-equilibrium scenario.

5.2.3 Effect of Concentration

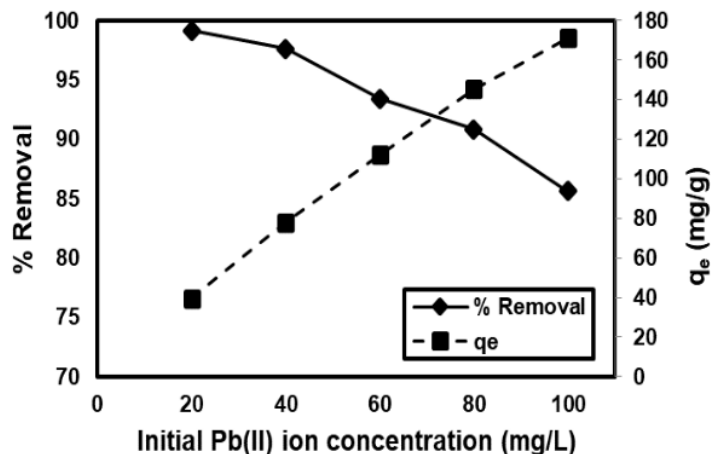


Fig.31 Effect of initial Pb(II) ion concentration for the adsorption of Pb(II) onto MNP-PS (pH = 5.0, dose = 5 g/L, volume =100 ml, time =30 min and temperature= 30°C).

The impact of an initial concentration of ions in the 20 to 100 mg/L range was examined, and the results are depicted in Fig. 31. The picture makes it evident that as the starting ion concentration increased, the proportion of Pb(II) ions removed dropped. The driving force required to overcome the barrier to Pb(II) mass transfer between the aqueous phase and solid phase is provided by the initial ion concentration. The effect of initial Pb(II) ion concentration (20-100 mg/L) was investigated at pH of 5.0 in the presence of the desired adsorbent. The plots revealed that an increase in the Pb(II) ion concentration from 20-100 mg/L resulted in decrease in percentage of Pb(II) ion removal from 99.134% to 85.634%. The depletion of viable catalytic activity here on MNP-PS more than a specific concentration of Pb(II) ion is indeed origin something like the lowering mostly in percent of Pb(II) ion clearance. It concluded that it's important velocity combined making use of every possible active sites for sorption at increased Pb(II) ion content may have been to responsibility for such rise in sorption.

5.2.4 Effect of Temperature

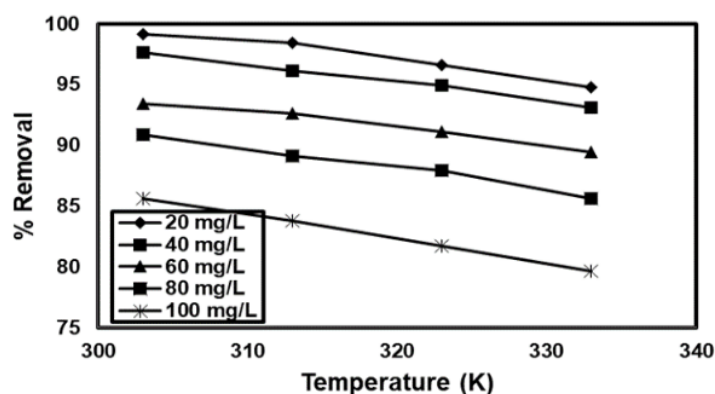


Fig.32 Effect of temperature on Pb(II) ion removal by MNP-PS (Initial Pb(II) ion concentration = 20 to 100 mg/L, pH = 5.0, dose = 5 g/L, volume = 100 mL and time= 30 min)

The above figure represents the optimized temperature conditions. Here the temperature range varies from 300K to 333K. The optimum temperature is 303K, where the % removal is maximum. This measurement is taken for sample at different dosages that is from 20 mg/L to 100 mg/L. As the temperature increases the value of % removal decreases gradually. This is mainly due to the decrease in

surface activity suggesting that the adsorption between Pb(II) ion and the adsorbents is an exothermic process as shown in Fig.32.

5.2.5 Effect of Dosage

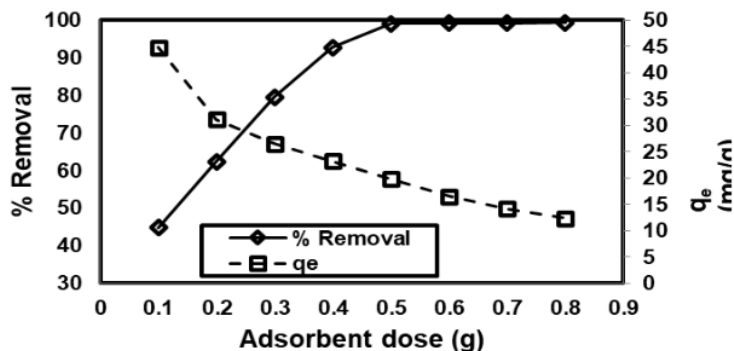


Fig.3.3 Effect of adsorbent dose on Pb(II) ions removal by MNP-PS (initial Pb(II) ion concentration = 50 mg/L, pH = 2.0, volume = 100 ml, time = 30 min, temperature = 30°C)

The PS dosage performs a major significant in determining adsorption potential of given initial concentration of Pb(II) ions. The above Fig.3.3 represents the plot between adsorbent dose vs percentage removal (%). It demonstrates that the percentage of Pb(II) ions removed varies with changing adsorbent mass and rises with increasing adsorbent dose. For a rise in adsorbent dosage ranging from 2 to 8g/L, the removal percentage rises from 44.875% to 99.389%. The optimum dosage is 5 g/L as shown in Fig 3.3. When the MNP-PS to Pb(II) ion concentration ratio is smaller, a very fast superficial adsorption onto the MNP-PS surface occurs at higher MNP-PS to Pb(II) ion concentration ratios, which results in a lower Pb(II) ion concentration in the solution.

5.3 ADSORPTION ISOTHERMS

The correlation in between adsorbate on the adsorbent as well as the adsorbate in the fluid medium at an intermediate state is indicated by the adsorption isotherm. This has an essential relevance in assessing adsorption isotherm data through matching it to various adsorption isotherm models that can be utilised for

adsorption design phase and enhancing the construction of an adsorption process for the absorption of adsorbate.

The adsorption equilibrium here between Pb(II) ions and MNP-PS as evaluated in this research to use the Langmuir, Freundlich, Temkin, and Sips models. By implementing MATLAB R2009a to apply the statistics on the adsorbent surface (C_e , v_{sqe}), to all of these equation state of adsorption. The validity of these isotherm was examined. The answers are shown in **Fig.34**. The coefficient of determination and considering the importance of the adsorption isotherm variables (q_m , K_L , K_F , n , B , A , K_S , s , s), Errors data (SSE and RMSE) and (R^2) statistics were compiled within **Table 5.1**. The Freundlich and Sips adsorption isotherm theory may accurately describe the equilibrium adsorption statistics in accordance with R^2 standard in accuracy these results from **Table 5.1**. Besides that, the Freundlich model fits the experimental data the best comparing to the Langmuir, Temkin, and Sips theories.[39] The Freundlich adsorption isotherm, which would have been appropriate to either a sole exposure adsorbed species each of one limited concentration scope, is in concept a functional application if an adsorb besides a highly in congruous high adsorption layer. The implications of the value of n , that supplies an indication of regarding pseudo-linearity's extent here among the intensity on the remedy with adsorption, to be as follows:

$n = 1$ (adsorption is linear);

$n < 1$ (adsorption is a chemical process); and

$n > 1$ (adsorption is a physical process).

Table 5.1 indicates that the n amount was calculated to be 3.964. This a n -value corresponds to existing adsorption structure anywhere around 1 and 10, implying believed adsorption was indeed a physical entity one. An MNP-PS was determined to have a highest monolayer adsorption capacity (q_{max}) for metal adsorption of 27.86 mg/g. The significance of the R_L value, which were employed to forecast the optimal design, is: $R_L = 0$ (irreversible); $0 < R_L < 1$ (favourable); $R_L = 1$

(linear); and $R_L > 1$ (unfavourable).[40] An existing adsorption mechanism calculated value of R_L were in the band of 0 and 1, which suggests that the adsorbed procedure worked effectively. Weak interaction here between Pb(II) ion and the MNP-PS is demonstrated by the current adsorbent state's heat of absorption(b) value having less than 8 kJ/mol. The above demonstrates that perhaps the current approach of adsorption had been an evolving method. Based on R^2 and error values, the accompanying is really the finest combination for the algorithms for isotopes of adsorption examined for extraction Pb(II) particle in MNP-PS:

Freundlich > Sips > Langmuir > Temkin isotherms

It indicates that the experimental evidence and the Freundlich model complement well alongside one another. The applicability of this theory for the removal of Pb(II) ions by MNP-PS confirmed that, under the evaluated test conditions, multilayer adsorption was retained on the adsorbent surface.[41]

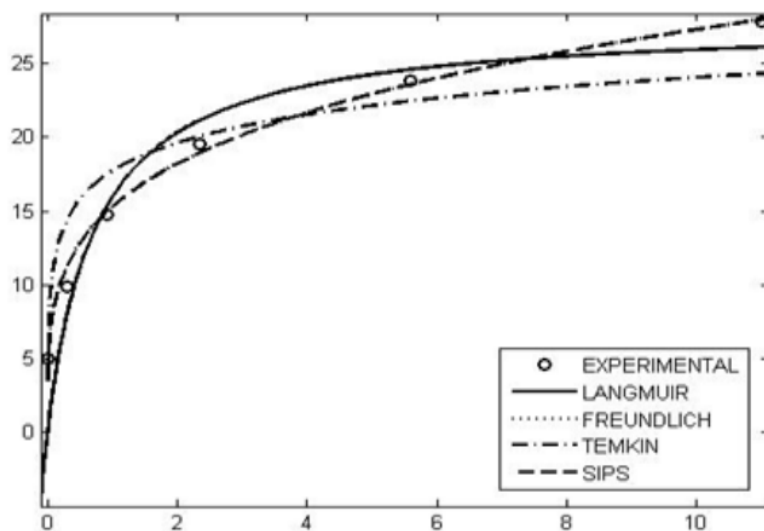


Fig.3.4 Adsorption isotherm studies for the removal of Pb (II) ions by MNP-PS

5.4 ADSORPTION KINETICS AND MECHANISM

The equilibrium adsorption statistics then exploited to anticipate the ratio and method of sorption involving Pb(II) ions and MNP-PS. In this study three kinetic models are examined. They are pseudo first-order, pseudo second-order, and Elovich kinetic model is helped to know about sorption kinetics for elimination Pb (II) & the accurate answers are represented in **Fig.35**.

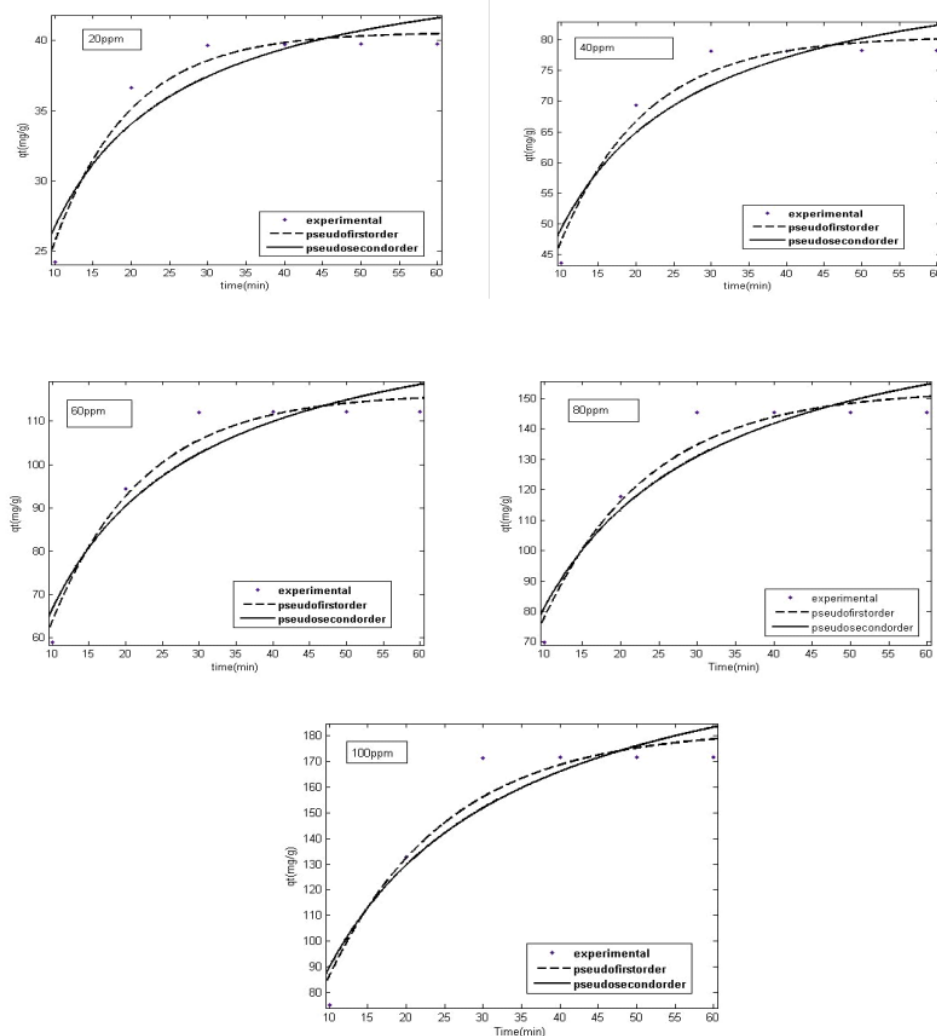


Fig.35 Adsorption kinetic for the eradicating **Pb (II)** ions by **MNP-PS** (Lead metal concentration = 20-100 mg/L, solution pH = 3.0, adsorbent dose = 5g/L, volume of sample= 100mL, temperature = 30°C)

Table 5.1 lists predictions for a selection of configurations, including pseudo first-order kinetic constant (k_1), pseudo second-order kinetic constant (k_2), q_e , and Elovich kinetic model constant (αE) & βE . The observed adsorb rates have been linked using (q_e , Cal), the experimental sorption capacity (q_e , exp). It is shown in **Table 5.2**. Both, comparing to pseudo second-order and Elovich kinetic models,

the measurement of the coefficient of correlation (R^2) for the pseudo first-order kinetic was higher. The physical adsorption is the percentage phase, according to the constant fitting of sorption kinetic proof for elimination of Pb(II) to MNP-PS with a pseudo first-order kinetic model. To grasp the adsorption mechanism, it is essential to figure out the rate-limiting phase. Table 5.2 shows that perhaps the Arrhenius equation quantities "k" decline during growth Pb(II) ion concentrations; this could be due to fewer competition for complex formation in concentrations. Due to enhanced putative binding rivalry at elevated doses, slower sorption speeds be reached. The observations showed considerable agreement here between q_e estimated to use the pseudo-first-order kinetic parameters and thus the q_e experimental result, validating the practicality.

5.5 EVALUATION OF THERMODYNAMIC PARAMETERS

An aspect of thermodynamics gives structure to the underlying enthalpy change connected to the adsorption process. Instead of focusing on MNP-PS, the thermodynamic parameters change in free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were utilised to define the process. The values of ΔH° and ΔS° were determined based on that the intercept and gradient, correspondingly, straight curve generated per retelling the tale $\log K_c$ vs. $1/T$ (Fig36). Table 5.3 shows the calculated thermodynamic parameter values. The negative value of ΔG° at different temperature, as shown in Table 5.3, indicated the durability of the adsorbate and the spontaneous aspect of the reactions. Also, the fact that the negative value of ΔG° increases as the temperature drops shows process of adsorption is advantageous at limited temperature. It is really feasible to the rise in temperature facilitated its mobility in previously adsorbed Pb(II) ions, which led structure desorption of Pb(II) ions from both the exterior ions of MNP-PS. A size ΔG° could additionally shed the mystery of the adsorption process. The preceding is claimed as the essence of ΔG° . Chemical adsorption extends between 80 to 400 kJ/mol, while physical adsorption extends between 20 to 0. The existing adsorption system was however confirmed as an actual physical process. Due to the poor association here between Pb(II) ions and MNP-PS, the values for ΔH° were revealed to be negative, implying that the sorption capacity was naturally exothermic. Furthermore, it was learned from Table 5.3 that the negative sign of ΔS° indicate a decline in unpredictability at the surface or interface in the adsorption system because of adsorption.[42] This realism now is case of the former particles lose at most of freedom motion as they are adsorbed onto the adsorbent could be the cause of the fall in ΔS° in all instances. At any and at beginning temperature changes with copper concentration levels it was discovered the values of ΔH° were higher $T\Delta S^\circ$. This indicates that enthalpy changes rather than enthalpy change had a bigger influence on the adsorption studies.

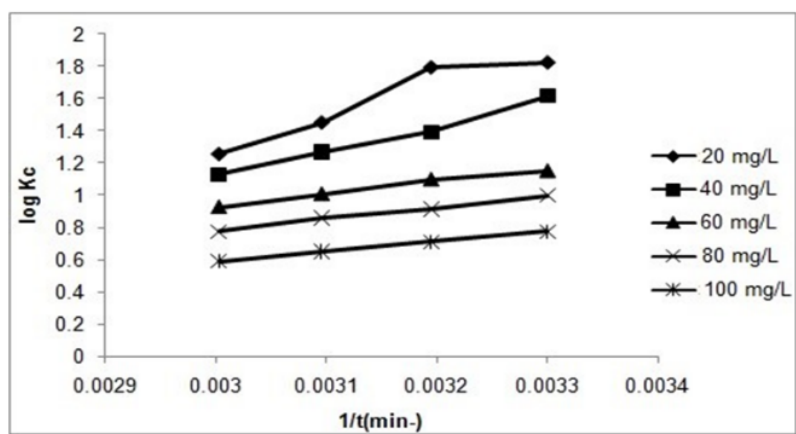


Fig 36: Thermodynamic analysis for the adsorption of Pb(II) by MNP-PS

SUMMARY AND CONCLUSION

Magnetic Nano particles are materials that are capable of removing pollutants from water. The new magnetic sorbent MNP-PS was identified in this work as an effective absorbent for the elimination of Pb(II) from effluent. The surface morphology was studied using SEM. The MNP-PS was characterized by FTIR and EDX, XRD and VSM. The Magnetic Property was studied by VSM. The use of Magnetic Nano based adsorbent will have a remarkable adsorption effectiveness since we understand that adsorption is the highly recommended technology for the removal of dye, heavy metals, and other toxic effluents. Water being an essential source for our environment, treating it with good process and good materials also matters. Considering all these things, it will be known that Prawn Shells when impregnated with Magnetic Particle will be a great adsorbent for the treatment process. The outcomes of the investigation therefore demonstrate the hypothesis of the quantity of MNP-PS particle have an important influence on the rate of reduction of Pb(II). It turned out that while the initial Pb(II) concentration risen, the percentage of adsorption of Pb(II) got smaller.[43] With rising initial pH & reducing initial Pb(II) concentration, the pH level of the resulting combination have an important effect on Pb(II) reduction effectiveness. A stability temperature were analysed introducing multiple adsorption process systems, together with Sips, Temkin, Freundlich, & Langmuir approaches.[44] Thermodynamic characteristics which including Gibbs free energy, enthalpy, as entropy estimates demonstrate that the adsorption process was exergonic, impulsive, and realistic. For the elimination of heavy metals from wastewater, the costlier adsorbents can be exchanged changed for the less expensive stuff. In order to effectively demonstrate the concept and consider different industrial effluents for affordable adsorbents, more research is required. Not only Prawn Shells there are many cost-effective adsorbents like Fish Scales, Vegetable Peels etc., Instead of using chemicals as adsorbents, these kinds of wastes which has no value can be turned into a wealth for treatment process. We draw the conclusion from our experiment that using is a viable substitute for expensive activated carbon and will prove successful in removing toxic pollutants from wastewater.

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