University of Kerbala

College of Science

Department of Chemistry

Removal of some Metal Ions by Polysiloxane Immobilized polydonor Ligand System

A Thesis

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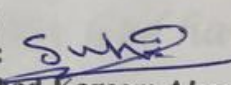
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Dedication

To the one whom God has crowned with awe and reverence and taught me to give without expectation and whose name I carry with all pride, my dear father, the dearest departeds to my heart and the most present absent person in my memory.

May God have mercy on you, my dear father.

to the one who stays awake nights and days,
for me to my dear mother

To those whom my Lord placed between him and me affection and mercy, to the highest symbols of sincerity and loyalty, a companion on the path, and to those who supported me and walked with me in my steps, my dear husband.

To those who accompanied me through thick and thin, and from them I draw strength and determination, my dear brothers and sisters.

To my adornment in this worldly life and the apple of my eye and those whose eyes I see optimism and happiness in their laughter, my daughter and sons, may God protect you for me.

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Summary

The world is moving towards using the best scientific methods to get rid of environmental pollution. Some metallic elements are natural and industrial pollutants like Cobalt, Copper, and Nickel. Also, Rice husks are one of the pollutants produced daily in all parts of the world. Therefore, rice husks were used to produce compounds to get rid of some polluting elements, thus eliminating two types of pollutants at the same time. Sodium silicate was prepared from rice husks, then reacted with ٣-aminopropyltriethoxysilane to produce RH-SiO$_٢$PrNH$_٢$ via the sol-gel method which was characterized by using the FTIR showed that the vibration NH$_٢$ and NH absorbed at ٣٢٨٣ and ٣١١٣ cm$^{-١}$, respectively. Then RH-SiO$_٢$PrNH$_٢$ reacted with ٢-amino-٣,٥-dibromobenzaldehyde to produce RH-SiO$_٢$PrADB which was characterized by using several techniques (FTIR, XRD, FESEM-EDX, CHN, AFM, TEM, and TGA/DTA):

The FT-IR spectrum displays azomethine group (C=N) is represented by the peak at ١٦٤٢ cm$^{-١}$. The XRD spectra were showed the amorphous nature of the prepared ligand. The elemental analysis of the RH-SiO$_٢$PrADB compound indicates that the percentage of carbon and nitrogen is ١٦.٦٣٪ and ٦.٤٪. FESEM images show an increase in the roughness of the outer surface of the sample with an increase in the rate of accumulation of nanoparticles as a result of the bonding of the RH-SiO$_٢$PrNH$_٢$ with ٢-amino-٣,٥-Dibromobenzaldehyde compound. Also, the images of AFM confirmed a clear increase in the roughness rate to reach ١٦.٢٤nm. This indicates the successful association of the RH-SiO$_٢$PrNH$_٢$ with the ٢-amino-٣,٥-Dibromobenzaldehyde compound. While TEM images were shown, the

I

presence of spherical clusters linked together. It was found that the average particle size is ٣٥ nm, and this value is consistent with the results of the FESEM and XRD analysis. The TGA analysis shows that the loss percentage reached (٥٣.٤٨٪) due to the evaporation of the adsorbed water molecules and the dissociation of the ٢-amino-٣,٥-Dibromobenzaldehyde compound, thus breaking the silanol bonds and the success of the synthesis process and the production of a compound with high stability. The specific area and pore diameter of the RH-SiO₂PrADB were using BET analysis, and it was determined to be equal to ٣.٨١٨ m²/g, and ١.٢١ nm, respectively.

In addition, sodium silicate was treated by adding Fe_3O_4 to produce magnetic nanosilicates. Following the same previous method, Fe_3O_4@RH-SiO₂PrADB was produced and characterized by several techniques (FTIR, XRD, FESEM-EDX, CHN, AFM, TEM, VSM and TGA/DTA):

The FT-IR spectrum showed an absorption band at ٦٣٦.٥ and ٥٧٠.٩ cm⁻¹ due to Fe-O bond in addition to bands same absorptions for compound RH-SiO₂PrADB. the XRD spectrum composite showed a clear displacement in the broad peak at (2θ =٢٢.٥ ° -٢٨.٨º) due to the RH-SiO₂PrABD compound and sharp peaks at (2θ =٢٩.٢º, ٣٥.٤º, ٣٩.١º, ٤٢.٤º, ٤٧.٩º, ٥٧.٠º, ٦٢.٨º, ٦٧.٠º) due to the cubic structure of Fe_3O_4. It was noted that the prepared composite is amorphous. The VSM showed that the prepared iron oxide (Fe_3O_4) has ferromagnetic behavior with a saturation magnetization up to ١٣.٣٩ emu g⁻¹. While the results of the saturation magnetization value for the Fe_3O_4@RH-SiO₂PrNH₂ and Fe_3O_4@RH-SiO₂ADB compounds showed a clear decrease in magnetism up to ٣.٨٨ and ٣.٨٧ emu g⁻¹, respectively.

The results showed that the specific surface area value of the RH-SiO٢ sample is ٣٩٠.١٢ m²/g and has a pore size distribution of ٣.٤٦٩ nm. While the specific surface area value of the RH-SiO٢PrNH٢ sample is ٠.٧٨٩ m²/g and has a pore size distribution of ١٥.٠٥٥ nm. In contrast, the surface area value in the Fe٣O٤@RH-SiO٢PrNH٢ sample decreased to up to ٠.٥٩٣ m²/g and has a pore size distribution of ٢١.٠٧٨ nm. whilst the Specific area of the RH-SiO٢PrADB was using BET analysis, to be equal to ٣.٨١٨ m²/g, and has a pore size distribution of ٣٦.٢١٦ nm. The specific surface area of Fe٣O٤@RH-SiO٢PrADB was (٣.٥٧٦ m²/g) and has a pore size distribution of ١٦.٥٨٦ nm which was decreased compared with the specific surface area of RH-SiO٢PrADB. This is due to the attachment of Fe٣O٤ particles to an RH-SiO٢PrADB surface, which reduces the surface area

The preparation of hybrid solid ligands was used to uptake the metal ions from its aqueous solution by using various conditions such as:- exposure time, pH, metal ion concentration, and ligand mass.

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List of Abbreviations

symbols	Name
%	Percentage
◦C	Degree Celsius
AFM	Atomic Force Microscope
APTES	٣-(aminopropyl)triethoxysilane
BET	Brunauer-Emmett-Teller
CHNS	Elemental analysis
DMSO	Dimethylsulfoxide
Fe_2O_4@RH-SiO$_2$ADB	magnetic mesoporous silica
Fe_2O_4@RH-SiO$_2$PrNH$_2$	magnetic mesoporous silica
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier-transform infrared spectroscopy
h	Hour
IUPAC	International Union of Pure and Applied Chemistry
L	Ligand
M	Molar
mol	Mole
RH-SiO$_2$PrADB	Rice Husk Silica –٢-amino-٣,٥-Dibromobenzaldehyde
RH-SiO$_2$PrNH$_2$	Rice Husk Silica- ٣-(Aminopropyl) Triethoxysilane
SEM	Scanning Electron Microscopy
TEM	Transmission electron microscopy
TGA	Thermo gravimetric Analysis
UV-Vis	Ultraviolet–visible spectroscopy
VSM	Vibrating Sample Magnetometry
XRD	X-ray diffraction

CHAPTER ONE
INTRODUCTION

١. Introduction

١.١ Rice husk

Rice is a kind of grass seed that originates from the species Oryza sativa, often known as Asian rice, or Oryza glaberrima, also known as African rice. Rice, which is frequently a staple food in many countries, is a widely produced food throughout the world. As a result, research has begun an extensive programme to increase rice output[١] The term "rice husk refers to the outer layer of rice. The rice grains and rice husk are normally separated during the milling process. ٢٠٪ of the weight of the paddy is hull. Rice Husk layers are of four types: structural, fibrous, sponge-like, or cellular as   Figure (١-١)[٢]. Typically, rice husks have been thought of as a waste product that is typically burned or dumped in landfills[٣]. But nowadays, rice husks are thought of as a product that can be sold[٤].

Paddy rice

RICE GRAIN
RICE HUSK   RICE BRAN
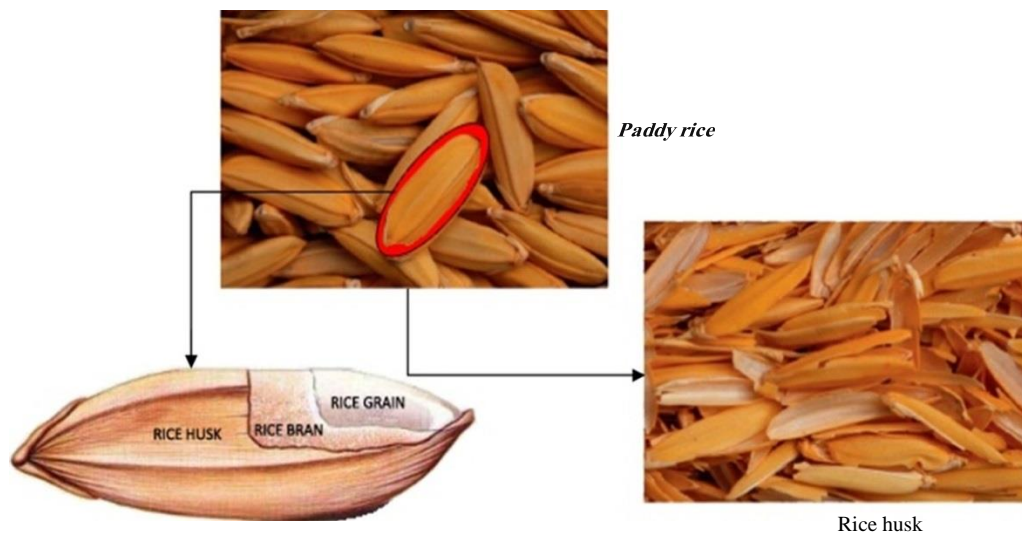
Rice husk

Figure ١-١ Rice grain and respective structures, and rice husk [٥]

The growing quantity of rice has led to an increase in the amount of rice husks, which are frequently seen as wastes[٦]. The UNEP (United Nations Environment Programme) has suggested that nations recover valuable materials from the waste stream to improve the conversion of waste into riches[٧]. Many governments and other organisations are making significant efforts to find ways to manage waste pollution caused by disposed rice husks in an effort to reduce the risk that these materials may represent to persons and regulate environmental pollution. By making such significant efforts, waste disposal expenses would be decreased, and profits from the sale of recovered materials (chemical compounds) and energy would be generated[٨].

The popularity of biopolymers and bioplastics in the modern world has drawn researchers' attention to biowaste [٩]. Functional materials that have found use in a variety of fields, including biotechnology and medicine, can be obtained from biowaste, which is a valuable resource. Rice husk (RH) is a type of agricultural biowaste that has a lot of silica, carbon structures, and other minor minerals that have lots of potential uses in both science and industry[١٠]. Rice husk has a low bulk density that ranges from ٩٠ to ١٥٠ kg/m^{٣}. The chemical analysis of rice husk shows the following components, SiO_2 is found to be ٢٠٪, the organic material and water content is ٧٥٪ and K_2O, CaO, MgO, MnO, $Al_٢O_٣$, $P_٢O_٥$, $Fe_٢O_٣$, $Na_٢O$ and $TiO_٢$ constitute about ٥٪. The organic part is composed of cellulose, lignin, and hemicellulose [١١].

١.٢ **Silica**

The generic term for the chemical silica is silicon dioxide. The chemical formula for this substance, SiO_2, is one silicon atom joined to two oxygen atoms. The crust and guts of the Earth are incredibly rich in silica, a compound of silicon and oxygen. Silica is the primary ingredient in more than ٩٥٪ of known rocks and accounts up ٥٩٪ of the mass of the Earth's crust. In nature, silica is present as quartz, tridymite, and cristobalite. These varieties of silicon dioxide are interchangeable at proper temperatures[١٢].

$$O = Si = O$$
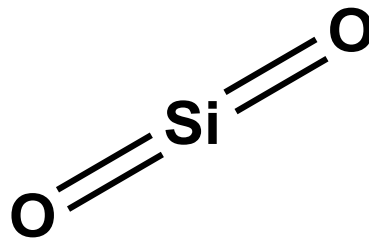
Figure ١-٢ The structure of silicon dioxide (SiO_2) is linear

Silicon dioxide is classified into two types. One is amorphous silica (a-silica), also known as non-crystalline silica. And the other is crystalline silica (c-silica). Covalent bonds are used to bind it. Each silicon atom in the three-dimensional structure of silicon dioxide is covalently bound to four oxygen atoms, and each oxygen atom to two silicon atoms. Tetrahedral oxygen atom geometry surrounds silicon as shown in Figure (١-٣)[١٣].
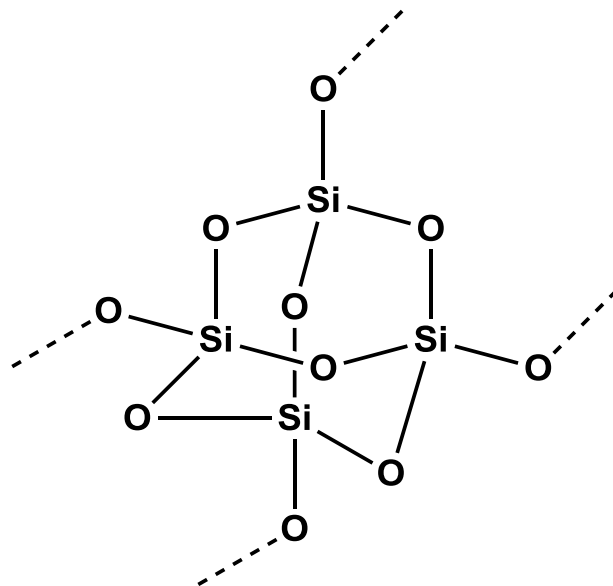
Figure ١-٣ Structure of Silicon Dioxide

Silicon dioxide is used in several industries such as pharmaceuticals, food, chemicals, electronics, construction, etc [١٤]. In the pharmaceutical sector, silicon dioxide is a component of drug additives. It takes up moisture and keeps the medications dry[١٥]. Silicon diovxide is used as an anti-caking agent in spices in the food sector. Additionally, it serves as a fining agent in beers, wines, and juices. Silicon dioxide is utilised in numerous production procedures in the chemical industry. Additionally, it is employed in the production of insecticides, anti-adhesives, adhesives, corrosion inhibitors, dyes, absorbents, sealants, porcelain, and ceramics. Additionally, silicon dioxide is employed as an absorbent in column chromatography. Interestingly Optical fibres used in the electronics sector are primarily made of silicon dioxide. Additionally, silicon dioxide and hydraulic fracturing are employed in the construction sector to create concrete. Recently, To increase the antibacterial and corrosion capabilities of biomaterials, silica, a biosafe ingredient, can be combined with silver nanoparticles[١٦]. Due to their vast surface area, when added to thermoplastic polymers, amorphous silica

nanoparticles from sources that are natural, such as fly ash and rice husk, can act as a nucleating agent[١٧].

١.٣   Surface of silica

The surface of silica comprises two kinds of functional groups, i.e. siloxane (Si–O–Si) and silanol (Si–OH) groups. It was discovered that the main modification pathway happens through the response of a specific molecule to the silica surface with the silanol groups[١٨].

Silanol groups are created by two primary procedures on the surface. First, such groups are created during silica synthesis, e.g. during condensation polymerization of Si(OH)٤. Secondly, surface groups may form as a consequence of rehydroxylation of dehydroxylated silica when treated with water or aqueous solutions [١٩] The silanol groups on silica surface can be classified into three types, Figure١.٤ [٢٠] :

١-isolated groups (or free silanols) where the surface silicone atom has three bonds in the bulk structure and the fourth bond is connected to a single –OH group.

٢-Vicinal silanols (or bridged silanols) where two single groups of silanols connected to distinct silicon atoms are near enough to the hydrogen bond.

٣-Geminal silanols consist of two hydroxyl groups that are connected to one silicon atom and that are too near to each other to form a hydrogen bond.

Germinal Silanol   Isolated Silanol   VicinalSilanol
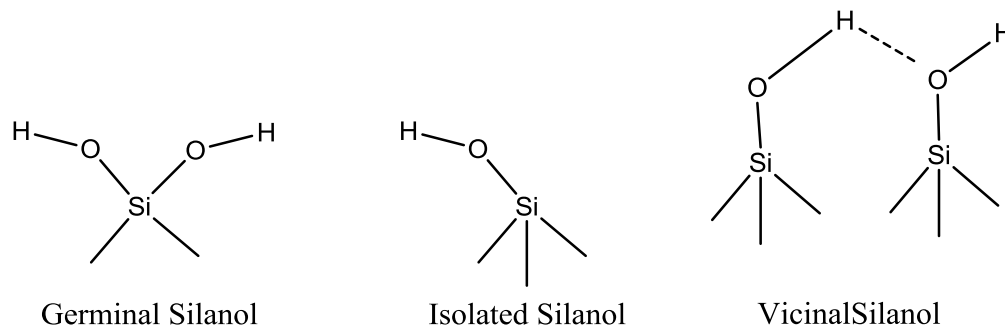
Figure 1-4: Different types of silanol group on the surface of silica [21]

On the other hand, silica shows three types of siloxane groups ($\equiv$Si–O–Si$\equiv$) Figure1.5 According to NMR study of the ^{29}Si nuclei [22]. these siloxane groups are represented as Q^n, where (n) indicates the number of bridging bonds (–O–Si) tied to the central Si atom, i.e.: Q^4 – four siloxane bonds to the silicon atom; Q^3 – three siloxane bonds to the silicon atom; and Q^2 – two siloxane bonds to the silicon atom. Generally, the number of siloxane groups can be determined from the following equation: $Q^n = Si\ (OSi)_n(OH)_{4-n}$ [23].

Germinal Silanol   Isolated Silanol   VicinalSilanol   surfaces siloxanes
Q^2 Q^3 Q^3 Q^4
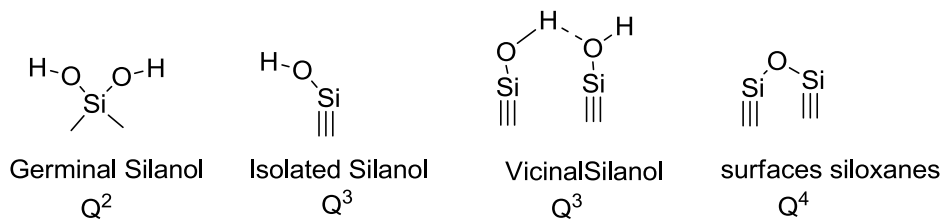
Figure 1-5 : Q^n nomenclature used to define the environment of the silicon atoms in silica [21]

١.٤   **Polysiloxanes**

polysiloxanes The most common type of polymers known as silicones, have a Si-O core with elevated bond energy (~٥٣٠ kJ.mol−١) with organic groups, usually methyl groups, attached to the Si atoms[٢٤]. Alkyl groups make up the side groups, whereas Si and O atoms make up the main chain (Figure ١-٦). When it comes to performance characteristics, polysiloxane occupies the top of the pyramid among the various kinds of speciality polymers[٢٥].

$$\left(\!\!\begin{array}{c} R_1 \\ | \\ \!-Si\!-\!O\!- \\ | \\ R_2 \end{array}\!\!\right)_n$$
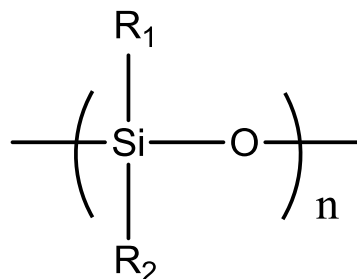
Figure ١-٦ Structure of a polysiloxane

There are several commercial and domestic uses for polysiloxanes (silicons), a significant class of inorganic polymers with great temperature and oxidative stability, exceptional low temperature flexibility, and strong resistance to weathering and many chemicals[٢٦]. Due to their inherent biological character, polysiloxanes were utilised in the medical industry. They are the fastest-growing group of polymers because to the enormous opportunities in the design, synthesis, and modification of their physical and chemical properties, and they have significant applications in cosmetology, medicine, and pharmacy[٢٧]. Organosilicon surfactants are extremely useful in a variety of uses, including transporters that improve corticosteroid drugs[٢٨]. Silicone materials exhibit also good biocompatibility, tolerance to sterilization, bio-durability and hemocompatibility[٢٩]. Functionalization of

polysiloxanes by chelating ligands has been widely employed to extract and preconcentrate trace metal ions from different media[٣٠]. In addition, because the inclusion of functional groups can alter the structure and properties of the original polysiloxanes, functionalized polysiloxanes play a significant role in organosilicon chemistry and have been used in a variety of industries[٣١]. Functional group can alter the structure and ownership of the original polysiloxanes. Notably, some functional groups are extremely reactive, therefore, functional polysiloxane could be expanded into multiplen organosilicon materials.

The polysiloxane-immobilized triamine ligand complexes (Figure ١.٧), which have applications in numerous fields of study, are extremely important in both science and business. Their preparation involves two steps: first, the chemical modification of the silica surface. The sol-gel method is the second technique [٣٢]
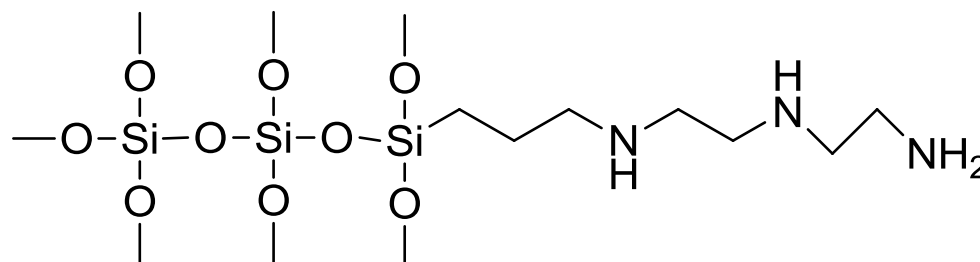
Figure ١-٧ Structure of the polysiloxane-immobilized triamine ligand

Applications in areas like the extraction procedure, regrowth, and removal of metal ions from aqueous solutions and organic solvents are expanding as a result of the incorporation of binding groups into polysiloxane matrices[٣٣].

Batch and dynamic approaches have frequently been used to extract and preconcentrate trace metal ions from different media using polysiloxanes functionalized with chelating ligands. Due to their strong potential for absorbing metal ions, functionalized polysiloxanes with suitable complexing agents are being developed with interest[٣٤].

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١.٥   Sol-Gel Technique

The term "sol-gel method" refers to the process of creating inorganic polymers or ceramics from solutions by converting liquid precursors into "sols" and then into network structures known as "gels" [٣٥]. It is thought that the sol-gel approach can be used to create materials at low temperatures that are entirely inorganic or contain both inorganic and organic components[٣٦]. It has been widely used as a way of preparing for single component oxides as well as multiple-component oxides since Dislich developed the sol-gel approaches to make optical coatings of glassy or crystalline systems in ١٩٧١[٣٧].

Sol-gel silica synthesis in polymer matrixes is a common practice. Alkoxysilane precursors are primarily hydrolyzed and polycondensed during this process[٣٨]. Precursors for a typical sol-gel process are typically metal alkoxides or inorganic metal salts that go through various hydrolysis and polycondensation processes[٣٩].

A bottom-up method called the sol-gel method entails connecting molecular building blocks like SiO_4 tetrahedra and TiO_6 octahedra with one another step by step[٤٠].

There are four main stages to the sol-gel process in general, however extra steps are sometimes incorporated to improve the gel's mechanical properties[٤١]. The framework of the gel is influenced by all synthesis processes, which also have an impact on the gel's properties and corresponding applications[٤٢].

I.   Sol preparation: A colloidal suspension is created by dispersing solid nanoparticles made from a precursor material in a solvent.

II.   Sol to gel transition (gelation) : An interconnected chain structure is created when an acid or a basic catalyst is added, creating cross-linked and branching particles.

III.   Ageing of the gel: The gel is matured in its original solution to strengthen the gel's structure and mechanical properties.

IV.   Drying of the gel: In order to prevent gel fracture, the solvent is removed from the pores of the gel[٤٣].

The equations for the sol-gel process given in Scheme ١-١ were proposed by Chen and Lin[٤٤]. These equations clarified the steps of polymerization and hydrolysis that could take place in sol-gel processes.

Initially, the hydrolysis of the precursor results in the formation of a sol of soluble hydroxylated monomer (equation ١-١). The phase separation and polymerization operations are then used to create a hydrated oxide hydrogel (equation ١-٢). The dry, porous xerogel is finally created by carefully extracting or drying the water from the wet gel (equation ١-٣)[٤٥].

$$\equiv SiOR \quad + \quad H_2O \quad \longrightarrow \quad \equiv Si\text{-}OH \quad + \quad ROH \qquad (1\text{-}1)$$

$$\equiv SiOH \quad + \quad \equiv SiOR \quad \longrightarrow \quad \equiv Si\text{-}O\text{-}Si\equiv \quad + \quad ROH \qquad (1\text{-}2)$$

$$\equiv SiOH \quad + \quad HOSi\equiv \quad \longrightarrow \quad \equiv Si\text{-}O\text{-}Si\equiv \quad + \quad H_2O \qquad (1\text{-}3)$$
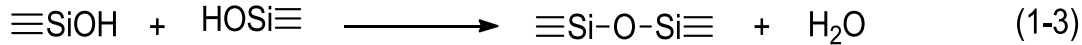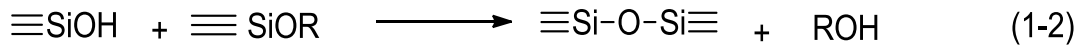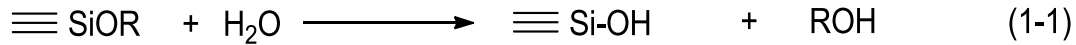
Scheme ١-١ : The suggested reactions for the hydrolysis and condensation processes that occur in the sol gel method

Compared to traditional ceramic preparation techniques, the sol-gel process has various benefits, including:

(١) reaction temperature is low; (٢) the products have high purity and homogeneity, (٣) new and various compositions, (٤) materials have a wide versatility in shapes; (٥) reaction systems are simple; (٦) the micro- and macrostructure of the host matrix may be controlled through the optimization of several parameters (e.g., water and/or alcohol content, temperature, pressure, type of catalyst, solvent); (٧) the presence of the silica network provides good mechanical resistance, extraordinary thermal stability, and amorphous character; and (٨) it is possible to graft organic groups into the inorganic backbone at low processing temperatures and to produce organic inorganic hybrid materials designated as ormosils (organically modified silicates), ormolytes (organically modified silicate electrolytes), or ormocers (organically modified ceramics), depending on the final application[٤٦].

١.٦   Modification of the surface of silica

The surface characteristics of silica materials, which are heavily influenced by the superficial functional groups added by various modification techniques, are crucial for their applications[٤٧].

Due to its potential to enable researchers to modify the chemical composition and technology traits of the composite material, modification of the silica surface has drawn a lot of attention. For the creation of vital substances with a variety of unique properties, such as liquid crystals, nanostructured silica materials, and selective heterogeneous catalysts, it is crucial to change the surface of silica[٤٨].

When using alkyl silanes to modify the surface, superficial silanol groups are crucial[٤٩]. The silanol groups on the silica surface get dehydrated as the temperature rises, whereas a steady rise in temperature causes silanol groups to become dehydrated, which results in the production of siloxane bonds[٥٠].

According to the various methods of incorporating silica components into silica-based hybrid nanostructures, silica-based nanomaterial manufacturing can be broadly divided into two categories[٤٥]:

١) The first approach entails a heterogeneous reaction, as shown in Scheme ١-٢A, between the silylating agents and the ligand complex, followed by the immobilisation of the resultant ligand with the pre-formed silica.

٢) The second method entails using the complex group to treat the post-polysiloxane, as shown in Scheme ١-٢B.

A)   R-H + $(C_2H_5O)_3Si(CH_2)_3X$ $\xrightarrow{\text{heat}}$ $(C_2H_5O)_3Si(CH_2)_3R$ + HX

$(C_2H_5O)_3Si(CH_2)_3R$ $\xrightarrow{\text{heat / SiO}_2}$ [silica matrix]─O─O─O─Si─(CH$_2$)$_3$─R + $3C_2H_5OH$

B) SiO_2 + $(C_2H_5O)_3Si(CH_2)_3X$ $\xrightarrow{\text{heat}}$ [silica matrix]─O─O─O─Si─(CH$_2$)$_3$─X + $3C_2H_5OH$

[silica matrix]─O─O─O─Si─(CH$_2$)$_3$─X $\xrightarrow{\text{RH / heat}}$ [silica matrix]─O─O─O─Si─(CH$_2$)$_3$─R + HX
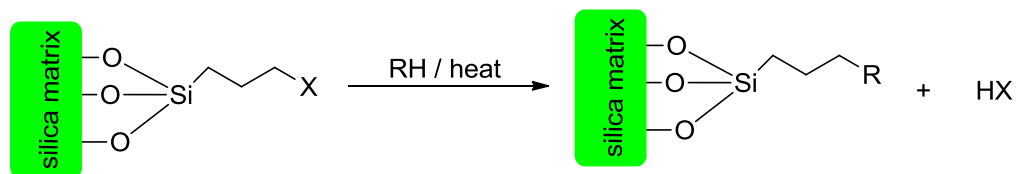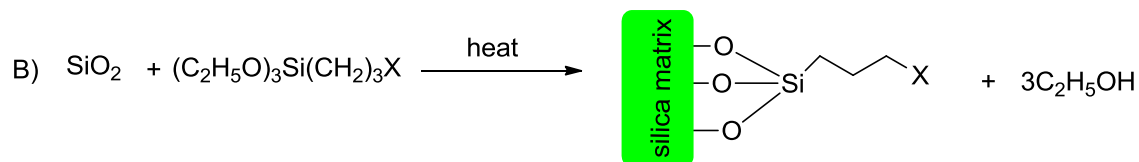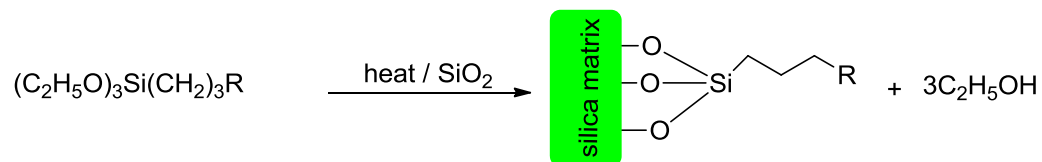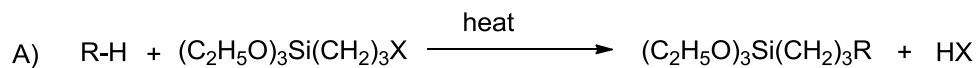
Scheme ١-٢: Modification of silica surface, (١) deposited to method (٢) growing from method

Specific organic processes can lengthen the organic chain when a given alkoxysilane is bound to an inorganic support in order to encourage the surface enhancement of additional basic centers[٥١].

١.٧   Iron Oxide Nonaparticales

Relative to the transitional elements in the same group, Iron is the most recent transitional mineral and the primary component of the earth's crust. Iron oxides are created chemically when the elements of oxygen and iron are combined to produce iron compounds. Applications involving biology and geology typically use these materials[٥٢]. Hematite (Fe_2O_3), magnetite (Fe_3O_4), and maghemite (Fe_2O_3) are three distinct forms of iron oxide that have crystalline structures and differing magnetic and structural properties. The crystal structures of oxide form tetrahedral and octahedral can be represented by close-packed planes of iron cations and oxygen anions[٥٣] .Oxygen ions are arranged hexagonally in the crystal structure of hematite, whereas iron ions (III) occupy the octahedral positions. The iron ions (III) are randomly distributed between the octahedral and tetrahedral regions, and the iron ions (II) occupy the octahedral positions, whereas the oxygen ions appear to be arranged in a cubic pattern in magnetite and maghemite. Consequently, the cubic inverted spinel arrangement is the ultimate form. High stability to oxidation, superparamagnetic characteristics, biocompatibility, and non-toxicity are all present in iron oxide nanoparticles[٥٤]. Its usefulness in numerous fields, including wastewater treatment, catalysts, high-density data storage, batteries made from lithium ion, modified anti-corrosive coatings, Ferro fluids and supercapacitors, materials for electrodes, and separating of biological products, attracted researchers' attention as a result. Additionally, due to iron oxide nanoparticles' low toxicity, they are useful in the medical field for a variety of medical applications, including drug delivery, thermal therapy, tissue-specific release of therapeutic agents, magnetic sensing probes for in-vitro diagnostics (IVD), and hyperthermia-based cancer treatments[٥٥] Mesoporous, silica-coated magnetite nanoparticles have been known since

٢٠٠٤, whenWu et al. [٥٦] reported the preparation of a novel material, comprised of magnetite nanocores and double silica shell (a dense shell closer to the core and mesoporous one next from the center). However, such particles were irregularly shaped and had a wide size distribution, from hundreds of nanometers up to few microns. A year later, Zhao et al. [٥٧], in a two-step process, obtained almost spherically shaped particles, with narrow size distribution, containing hematite core, the inner, dense silica shell with a tunable thickness, and an outer mesoporous shell that increased the total surface area of the material up to ٢٨٣ m^2g^{-1} which enabled surface functionalization, typical of pure mesoporous silica.

١.٨   Schiff bases

Aldehyde (or ketone) to Schiff base conversion is a reversible reaction that often occurs under acid (or base) catalysis or following heating. In most cases, the product is separated from the formation, the water is removed, or both are done. Aqueous acid or base has the ability to hydrolyze several Schiff bases back to their respective aldehydes, ketones, and amines. As depicted in Scheme ١.٣[٥٨].
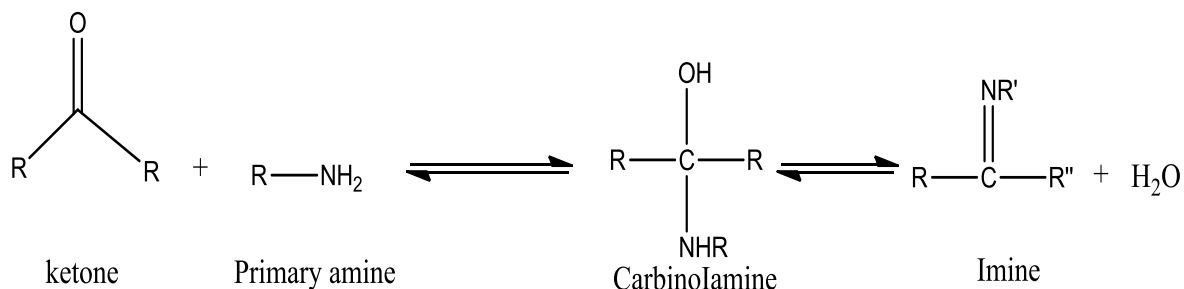
Scheme ١-٣: Formation and hydrolyze back of Schiff base

Because of their wide range of biological activities, schiff bases are frequently utilised as chelating ligands in coordination chemistry[٥٩] and are crucial in the pharmaceutical industry. The majority of them exhibit biological properties such herbicidal, antibacterial, antifungal, antidiabetic, antitumor, antiproliferative, and anticancer actions[٦٠].

For their intriguing and significant characteristics, such as their ability to reversibly bind oxygen, catalytic activity in olefins hydrogenation and amino group transfer, photochromic properties, and complexing capacity towards specific toxic metals, a large number of Schiff bases and their complexes have been studied[٦١]. Schiff bases provide a flexible and adaptable set of ligands that can bind to various metal ions to produce complexes with properties that are acceptable for theoretical or practical application[٦٢]. It has been demonstrated that an important chemical class in illuminating the transamination reaction mechanism in biological systems is the metal chelates from the Schiff bases derived from salicylaldehyde and amino acids[٦٣].

١.٩   Using silica as a solid support in metal ion extraction

Water metal contaminants have been removed using a variety of methods, including adsorption, precipitation, membrane filtration, and ion exchange. However, it has been demonstrated that adsorption is both affordable and efficient at removing heavy metals, organic pollutants, and colours from contaminated water. Activated carbon, silica, and graphene are just a few of the adsorbents that can be used to clean water[٢٢].

It has been demonstrated that modified mesoporous silica is an efficient adsorbent for trace metal ions. The mesoporous silica's capacity for adsorption has been improved by the application of several optimization techniques[٦٤].

The capture and removal of tiny amounts of metal from wastewater streams from different business operations is one of the most significant elements of today's study interest. As a result, there was great research potential for creating polysiloxane ligand systems (Figure ١. ٨), which can be used to preconcentrate and remove trace metal ions in a highly selective manner. Both hydrolytic polycondensation and silica modification were used to create these polysiloxane immobilised ligand complexes[٦٥].
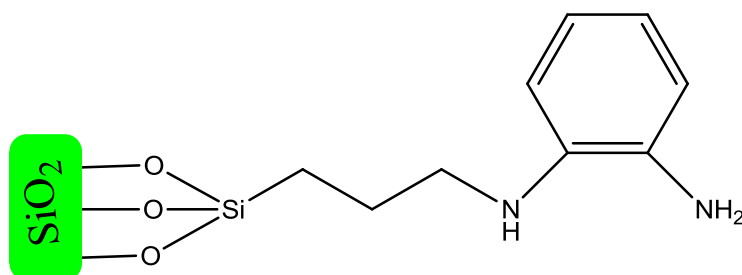
Figure ١-٨ : ٢-aminophenylaminopropylpolysiloxane ligand systeme

The removal of metal ions from aqueous solutions is one use for these polysiloxane immobilised ligand complexes. Compared to the more conventional organic resins and modified silica ligand architectures, these materials exhibit superior thermal and hydrolyte stability. Because they can chemisorb heavy metal ions consistently and selectively, chelating resins are frequently utilised to extract them from complex matrices[٦٦]. It is possible to directly create these immobilised ligand complexes via the sol-gel method or by chemically altering the polysiloxanes generated in Figure ١.٩[٣٤].
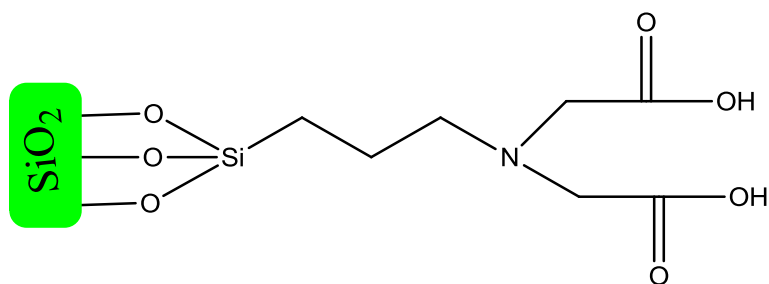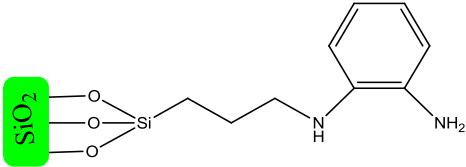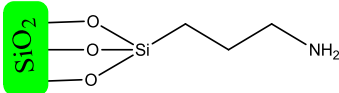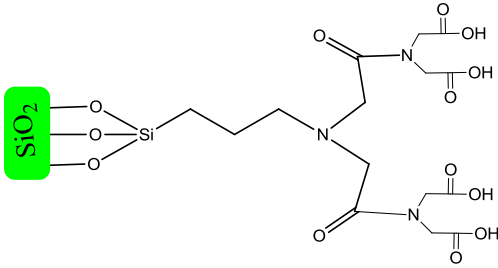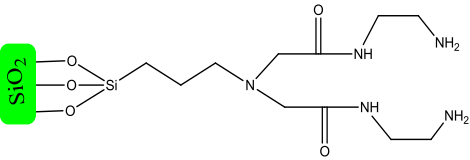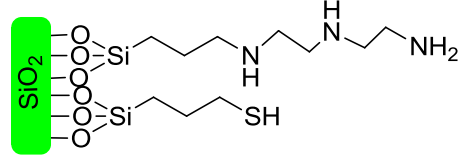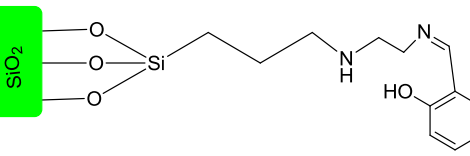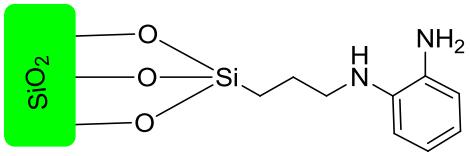
Figure ١-٩ The functionalized polysiloxane immobilized iminodiaacetic acid ligand system

In general, the presence of heavy metal ions in environmental samples has drawn more researchers' attention. A variety of ligands or functional groups are immobilised onto a sturdy support matrix as a solid phase extractant in order to extract and enrich trace metal ions from environmental specimens[٦٧]. Table ١.١ displays a list of silica support materials along with examples of their applications.

Table ١-١: list of silica support materials along with examples of their applications.

Compound	Applications	Structure	Reference
٢-aminophenylaminopolysiloxae	Extraction of Co, Ni, Cu, Zn and Cd ion using ٢-aminophenylaminopropylpolysiloxane		[٦٥].
٣-aminopropylpolysiloxane	Preconcentration and Separation of Copper(II) by ٣-aminopropylpolysiloxane Immobilized Ligand System		[٦٨]
Di(amidomethyl)aminetetr acetic Acid Polysiloxane	Extraction of divalent metal ions (Co(II), Ni(II), Cu(II), and Zn(II)) from aqueous solution		[٦٦]

N-٢-aminoethylacetamide	Metal uptake by porous iminobis (N-٢-aminoethylacetamide)-modified polysiloxane ligand system		[٦٩]
Polysiloxane immobilized triaminethiol and thiol-acetate ligand system	Uptake of divalent metal ions (Cu²⁺, Ni²⁺ and Co²⁺⁾ by polysiloxane immobilized triaminethiol and thiolacetate ligand system		[٧٠]
RHACSALEN ligand	Synthesis of Silica-Salen Derivative from Rice Husk Ash and its Use for Extraction of Divalent Metal Ions Co(II), Ni(II) and Cu(II)		[٧١]
Silica-o-Phenylenediamine	Uptake of Nickel(II) Ion by Silica-o-Phenylenediamine Derived from Rice Husk Ash		[٧٢]

١.١٠ Heavy metals pollution

In the environmental literature, the term "heavy metals" is frequently used to describe metals and metalloids linked to environmental pollution, toxicity, and negative effects on biota. The phrase has been defined in a variety of ways, primarily in relation to density, relative atomic mass, and atomic number.

Chemical definition: "a substance that conducts electricity, has a metallic lustre, is malleable and ductile, forms cations, and has basic oxides[٧٣].

Although heavy metals are naturally occurring elements of the environment, human indiscriminate consumption has changed the geological cycles and biological equilibrium of these elements. This leads to an excessive release of heavy metals into natural resources including the soil and aquatic ecosystems, including cadmium, copper, lead, nickel, and zinc sources of heavy metals in the environment[٧٤].

A Schiff base and its Ni(II) and Cu(II) complexes were synthesised by Leila Tahmasbia et al.[٧٥] and supported on mesoporous silica nanoparticles. These hybrid composites were made to offer an adequate surface for effective interaction with medicines and enzymes (Figure ١-١٠).
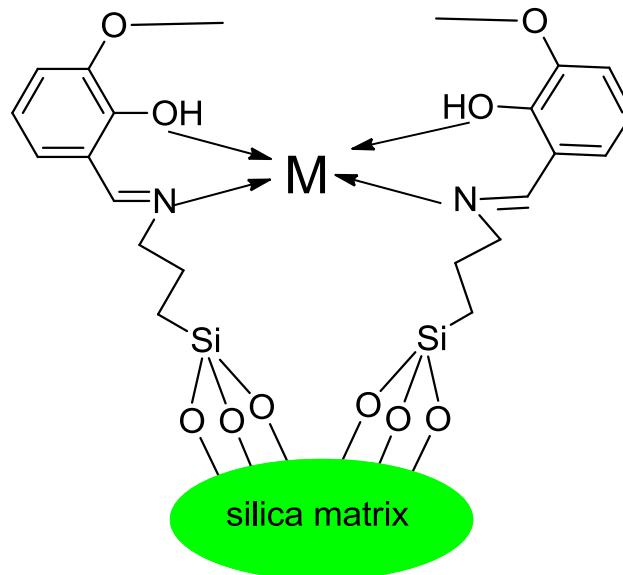
Figure ١-١٠ : Functionalized mesoporous silica nanoparticles

Anbarasu et al[٧٦]. synthesised an immobilised silica material based on copper(II) Schiff base complex and ٢-thio-phenecarboxaldehyde (Figure ١.١١).
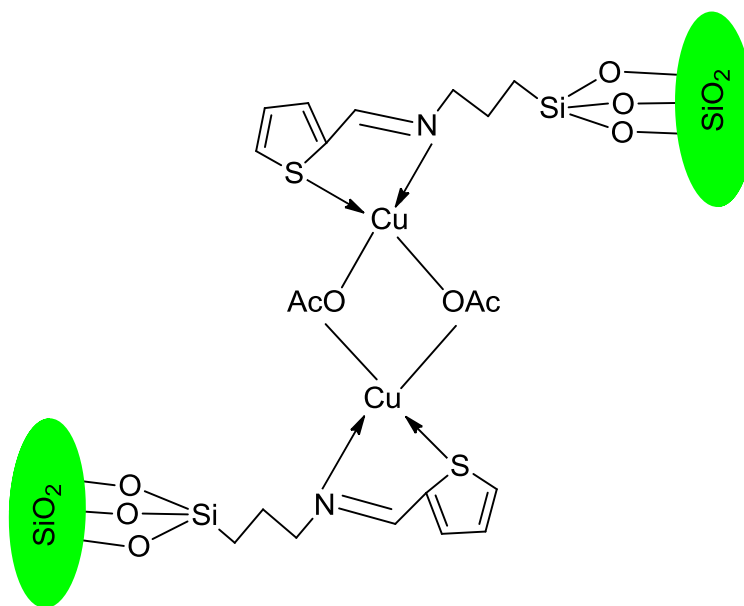
Figure ١-١١ : copper(II) Schiff base complex and ٢-thio-phenecarboxaldehyde

Sharma and Deepti Rawat[٧٧] Synthesized a covalently anchored nickel complex onto functionalized silica, depicted in Figure ١-١٢
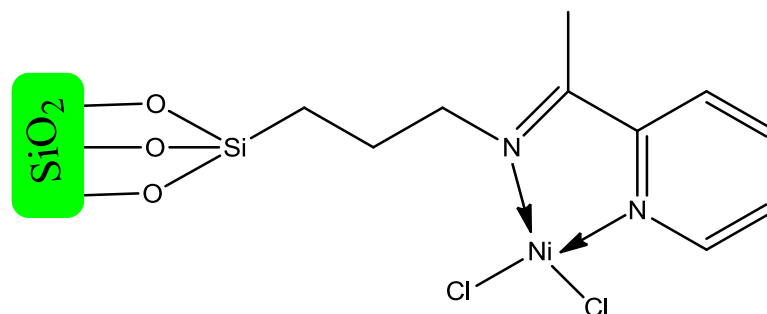
Figure ١-١٢ Ni(II) complex with functionalized silica

One of the most widely used cobalt compounds in laboratories is hexahydrate CoCl$_2$.٦H$_2$O, which is typically provided as cobalt (II) chloride[٧٨]. Cobalt and its many derivatives are widely used around the world and are thought to be potential environmental pollutants[٧٩].

Figure ١-١٣ Cobalt flakes

A cobalt (II) Schiff base complex supported by silica gel was created and utilised to oxidise alkyl aromatic compounds under atmospheric pressure

utilising molten oxygen as the oxidant. The synthesised catalyst demonstrated a high conversion of alkyl aromatics, was selective to benzylic ketones, and could be recycled at least five times without suffering any appreciable loss of catalytic activity[٨٠].
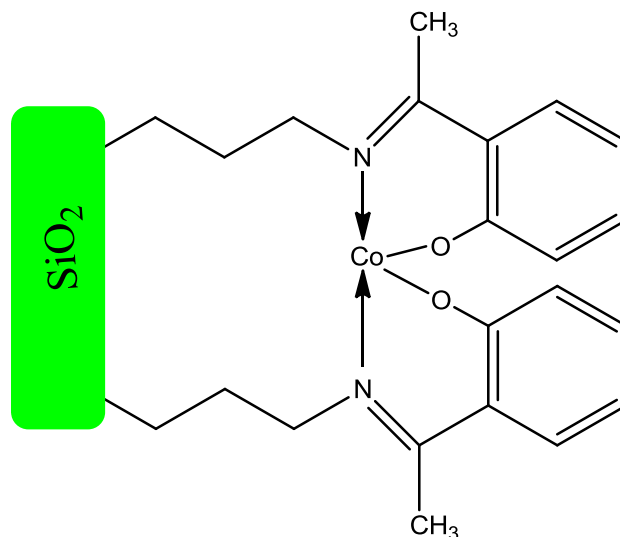
Figure ١-١٤ Cobalt (II) complex

The chemical atom of copper has the atomic symbol Cu which has an atomic mass of ٢٩. Since the Romans first got their hands on copper metal from Cyprus, the term copper and the symbol Cu are derived from "aes cyprium" (later Cuprum) [٧٨]

As a trace dietary mineral, copper is necessary for all living things since it is an important part of the respiratory enzyme complex cytochrome c oxidase. The blood pigment hemocyanin contains copper in molluscs and crustaceans, while iron-complexed haemoglobin is used instead in fish and other vertebrates. Copper is primarily found in the liver, muscle, and bone of humans[٨١]. The amount of copper in an adult's body, per kilogramme of body weight, ranges from ١.٤ to ٢.١ mg [٨٢].

Figure ١-١٥ Local Copper

Wen-Juan Zhou et al.[٨٣], Figure ١-١٦, had created a copper (II) Schiff base complex with the N-(salicylaldimine)-(Npropyltrimethoxysilane)-diethylenetriamine.

Figure ١-١٦ Copper complex

١.١١ The Aims
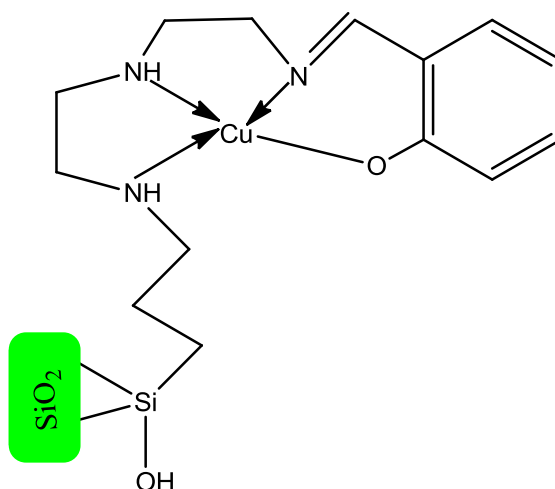
١-Preparing some porous material derived from plant wastes, and their characterization using suitable physical measurements.

٢- Addition of metallic nanoparticles MNPs to the prepared porous materials to obtain polymerically stable metallic nanoparticles PSMNPs and their characterization using suitable physical measurements. Such as: Fourier-transform infrared spectroscopy(FT-IR), CHNS Elemental analysis, Field Emission Scanning Electron Microscopy (FESEM), Scanning Electron Microscopy (SEM), Atomic Force Microscope(AFM), X-ray diffraction (XRD).

٣- Functionalization of prepared porous material with some organic molecules to prepare solid ligands. and their characterization using suitable physical measurements. Such as: Fourier-transform infrared spectroscopy(FT-IR), CHNS Elemental analysis, Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Atomic Force Microscope(AFM), Energy Dispersive Spectroscopy (EDS), BET analysis, the N_2 adsorption-desorption isotherms, Thermogravemetric analysis (TGA/DTA) , X-ray diffraction (XRD).

٤- Extraction of some metal ions from their aqueous solutions is suitable and optimize the physical and chemical parameters of the newly determined method, such as pH, concentration, and time of reaction etc.

CHAPTER TWO
EXPERIMENTAL PART

٢. Experimental Part

٢.١   Instruments:

Table ٢-١ List of instruments, supplier companies and place of measurement

Instrument	Manufacturer	Place of measurement
FTIR	Shimadzu ٨٤٠٠s	University of Kerbala / College of science – Iraq
UV-Vis	Shimadzu double beam ١٨٠٠ UV	University of Kerbala / College of science – Iraq
XRD	Shimadzu X-ray Diffractometer	Beam Gostar Taban Lab/Iran
SEM-EDX	FESEM MIRA III (TESCAN)	Beam Gostar Taban Lab/Iran
BET	BEL BELSORP MINI II	Beam Gostar Taban Lab/Iran
TGA/DTA	SDT Q٦٠٠ V٢٠.٩ Build ٢٠	Beam Gostar Taban Lab/Iran
CHNS	Eager ٣٠٠ for EA١١١٢	Beam Gostar Taban Lab/Iran
Water bath	Lab. Companion BS-١١ shaking water	University of Kerbala / College of science – Iraq
Oven	Model un ١١٠ plus	University of Kerbala / College of science – Iraq
Hot plate magnetic stirrer	LMS١٠٠٣, Labtech, Techco, LTD	University of Kerbala / College of science – Iraq
TEM	Philips CM١٢	Beam Gostar Taban Lab/Iran
AFM	CSPM-AA٣٠٠٠	Beam Gostar Taban Lab/Iran
VSM	Xiamen Dexing Magnet Tech. Co., Ltd	Beam Gostar Taban Lab/Iran

٢.٢   Materials

All chemicals were used directly without further purification. Rice husks were collected from a local factory for rice production in Najaf Governorate-Abbasiya city. Table ٢-٢ shows the chemicals used in this work.

Table ٢-٢ Chemicals used in this work and their provider

Chemical	Formula	Purity (%)	Provider
Acetone	C_3H_6O	٩٨	ROML British
Dimethylsulfoxide	$(CH_3)_2SO$	٨٩	GCC, England
Ethanol	C_2H_5OH	٩٩	Sigma-Aldrich, Germany
Toluene	C_7H_8	٩٩	Merk, KGaA, Germany
٣-(aminoproply)-triethoxysilane	$H_2N(CH_2)_3Si(OC_2H_5)_3$	٩٩	Sigma-Aldrich, Germany
Nitric acid	HNO_3	٧٠	CDH, India
٢-amino-٣,٥-Dibromobenzaldehyde	$C_7H_5Br_2NO$	٩٩	CDH, India
Sodium hydroxide	NaOH	٩٦	BDH, England
Ferric(III) Chloride hexahydrate	$FeCl_3 . 6H_2O$	٩٨	HIMEDIA
Urea	$CO(NH_2)_2$	٩٨	HIMEDIA
Citric acid	$C_6H_8O_7$	٩٨	HIMEDIA
Copper(II)chloride dehydrate	$CuCl_2 . 2H_2O$	٩٦	BDH, England
Nickel(II)chloride hexahydrate	$NiCl_2 . 6H_2O$	٩٦	BDH, England
Cobalt(II)chloride hexahydrate	$CoCl_2 . 6H_2O$	٩٧	BDH, England

٢.٣   The preparation methods

٢.١.١. Preparation of sodium silicate solution and solid silica (RH-SiO₂) from rice husks

The rice husk (RH) was washed with distilled water for the first time to remove adhering materials. It was leached for about ٢٤ h at room temperature. A ٣٠.٠ g sample of dried RH was weighed and transferred into a glass container. ٥٠٠ mL of ١.٠ M HNO₃ was added into the container and stirred for ٢٤ h in order to remove unwanted metal. The acid treated RH-NO₃ was filtered and washed with distilled water until it reached a constant pH (٦ - ٧.٠) and dried in oven at ١١٠ °C overnight , The weight of the product is ٢٦.٦ g . The cleaned RH-NO₃ was stirred in ٢٠٠ mL of ١.٠ M NaOH for ٢٤ h. The mixture was suction filtered to obtain a dark brown filtrate (sodium silicate) which was kept in a covered plastic container, as for the weight of the remaining cellulose on the filter paper, it is ٢٢ grams.(i.e. the ratio of silica in used husk is ١٧٪).

The prepared sodium silicate was titrated slowly with ٣.٠ M HNO₃ until it reached pH ٩.٠. The yellowish gel obtained was aged in a covered container for ٢ days. The gel was recovered by centrifuge at ٤٠٠٠ r/minute and followed by washing with copious amount of distilled water. It was dried in an oven at ١١٠ °C for ٢٤ h. It was allowed to cool in a desiccator. Finally, the product (solid silica) was ground into fine powder labeled as RH-SiO₂. The weight of the product is ٥ g.

٢.١.٢. Preparation of Rice Husk Silica- ٣-(Aminopropyl) Triethoxysilane, RH-SiO₂PrNH₂

The prepared sodium silicate was add ٦ mL of ٣-(aminopropyl)triethoxysilane (APTES) and titrated with ٣.٠ M nitric acid until the value of pH reached to ٣. The formed gel was separated by centrifuge at ٤٠٠٠ r/min for ٥ min and washed with distilled water for five times and finally in acetone, then dried up to ٢٤ h at ١١٠°C in oven. The powder obtained was labeled as RH-SiO₂PrNH₂ The weight of the product was ٨.٤g.

٢.١.٣. Preparation of Rice Husk Silica –٢-amino-٣,٥-Dibromobenzaldehyde, RH-SiO₂PrADB

One gram of RH-SiO₂PrNH₂ was added to ٢-amino-٣,٥-dibromobenzaldehyde about ٠.٥ g and the mixture was refluxed in ٣٠ mL of toluene at ١١٠ °C for ٢٤ h. The yellow solid product was filtered and washed with an amount of ethanol, acetone and DMSO. Then dried at ١١٠°C for ٢٤ h. Finally, ١.١ g of powder obtained was labeled as RH-SiO₂PrADB.

stirred 24 h

Rice husk   +   NaOH ⟶ Sodium Silicate

RH

Sodium Silicate + $(CH_3CH_2O)_3SiCH_2CH_2CH_2NH_2$ ⟶ $\dfrac{3M\ HNO_3}{pH=3}$ ⟶ [SiO₂]—O,O,O—Si—propyl—NH_2

APTES

RH-SiO₂PrNH₂

[SiO₂]—O,O,O—Si—propyl—NH_2 + 2-amino-3,5-Dibromobenzaldehyde (Br, NH_2, Br, O) ⟶ $\dfrac{Toluene}{110\ ^oC\ /\ 24\ hrs}$ ⟶ [SiO₂]—O,O,O—Si—propyl—N=CH—(Br, H_2N, Br)

RH-SiO₂PrNH₂   2-amino-3,5-Dibromobenzaldehyde
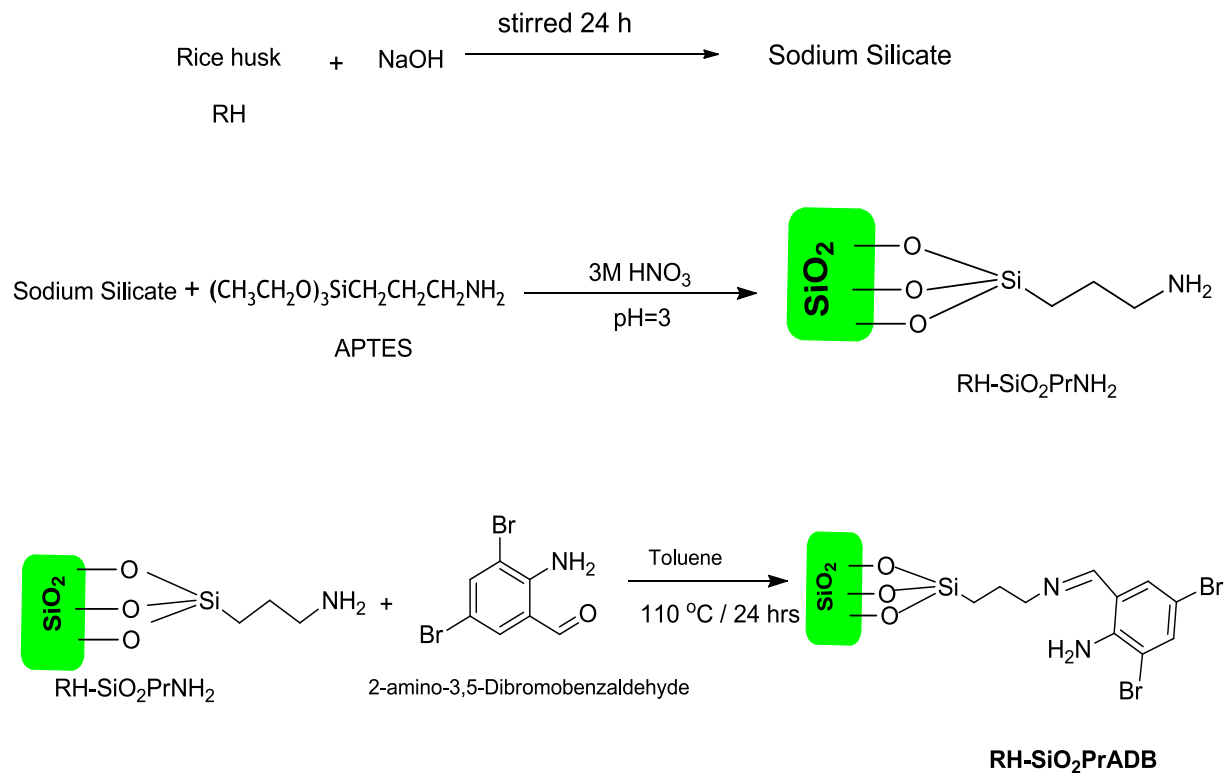
RH-SiO₂PrADB

Scheme ٢-١: The synthesis steps of RH-SiO٢PrADB

٢.١.٤. Synthesis of magnetic Fe٣O٤ nanoparticles

Fe٣O٤ nanoparticles method were synthesized through a solvothermal method . ٦ g (٠.٠٢٢١ mole) FeCl٣ .٦H٢O ,١٠ g (٠.١٦٥ mole) Urea and ١.٦ g (٠.٠٠٨٣ mole) Citric acid were loaded into a ١٠٠ ml Teflon-lined stainless steel autoclave, which was then fill ٦٠ mL absolute ethylene glycol (EG) heated to ٢٠٠ °C and maintained there for about ١٨ h . After cooling to room temperature naturally. The black products were filtered off, washed with distilled water and ethanol for several times and dried in vacuum at ٥٠ °C for ١٢ h.[٨٤]

٢.١.٥. Synthesis of magnetic mesoporous silica; Fe_3O_4 @ RH-SiO_2PrNH_2

One gram of Fe_3O_4 was add into sodium silicate for ٣٠ minutes in Ultrasound. The mixture was treated with ٦ ml APTES and titrated with ٣.٠ M nitric acid until the value of pH reached to ٣ , stirred for ٤٨ h. The formed was separated by centrifuge at ٤٠٠٠ r/min for ٥ min and washed with distilled water for five times and finally in ethanol, then dried up to ٢٤ h at ١١٠°C in oven obtained black powder (٥g) .

٢.١.٦. Synthesis of magnetic mesoporous silica Fe_3O_4 @ RH-SiO_2PrADB

Three grams of Fe_3O_4@RH-SiO_2PrNH_2 was added to ٢-amino-٣,٥-dibromobenzaldehyde (١.٥ g) and the mixture was refluxed in ٣٠ mL of toluene at ١١٠°C for ٢٤ h. The dark brown solid product was filtered and washed with an amount of ethanol, acetone and DMSO. Then dried at ١١٠°C for ٢٤ h. Finally, ٣.٦ g of powder obtained.
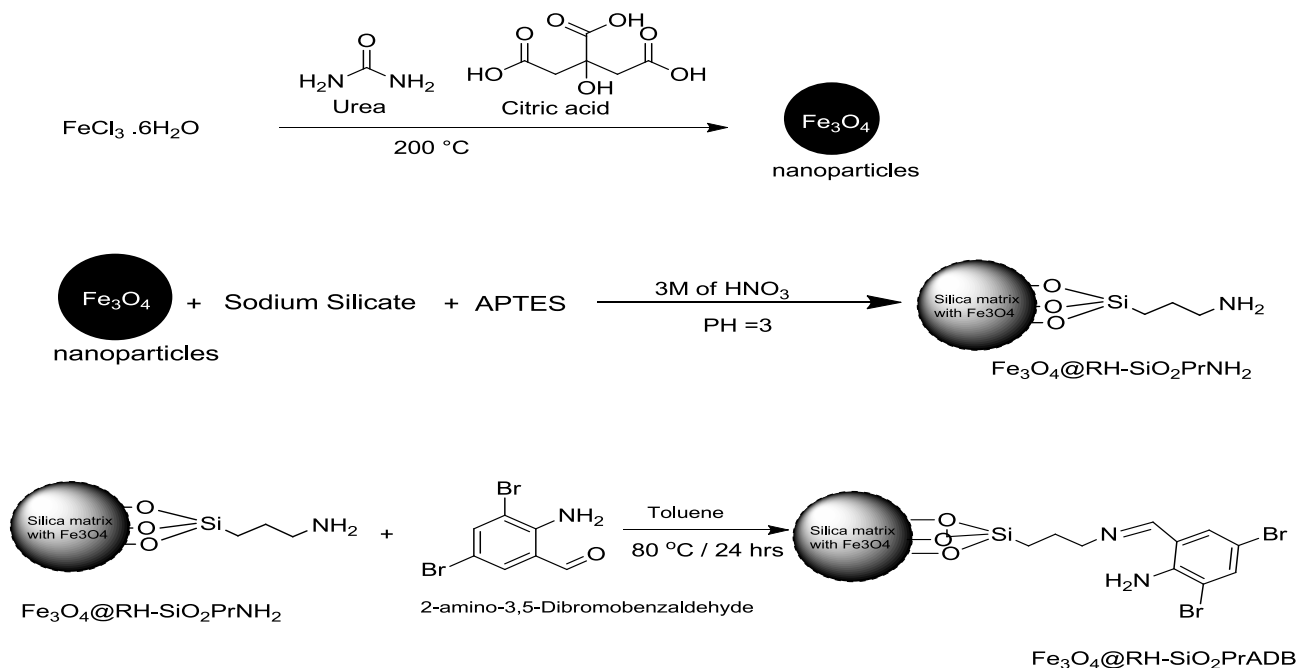
Scheme ٢-٢: The synthesis steps of Fe٣O٤@RH-SiO٢PrADB

٢.٤   Removal of metal ions from aqueous solution

٢.١.٧.   UV-Visible measurements for aqueous solutions of Ni(II), Co(II) and Cu(II)

UV-Visible spectroscopy of aqueous alternatives diluted Ni(II), Co(II) and Cu(II) was registered to explore λ max of each solution. The spectra acquired are shown in Figure٢.١. The spectra acquired shows that λ max of Ni(II), Co(II) and Cu(II) alternatives are ٣٩٤, ٥١١ and ٨٠٩ nm respectively. These wavelengths were used in these solutions ' calibration research.
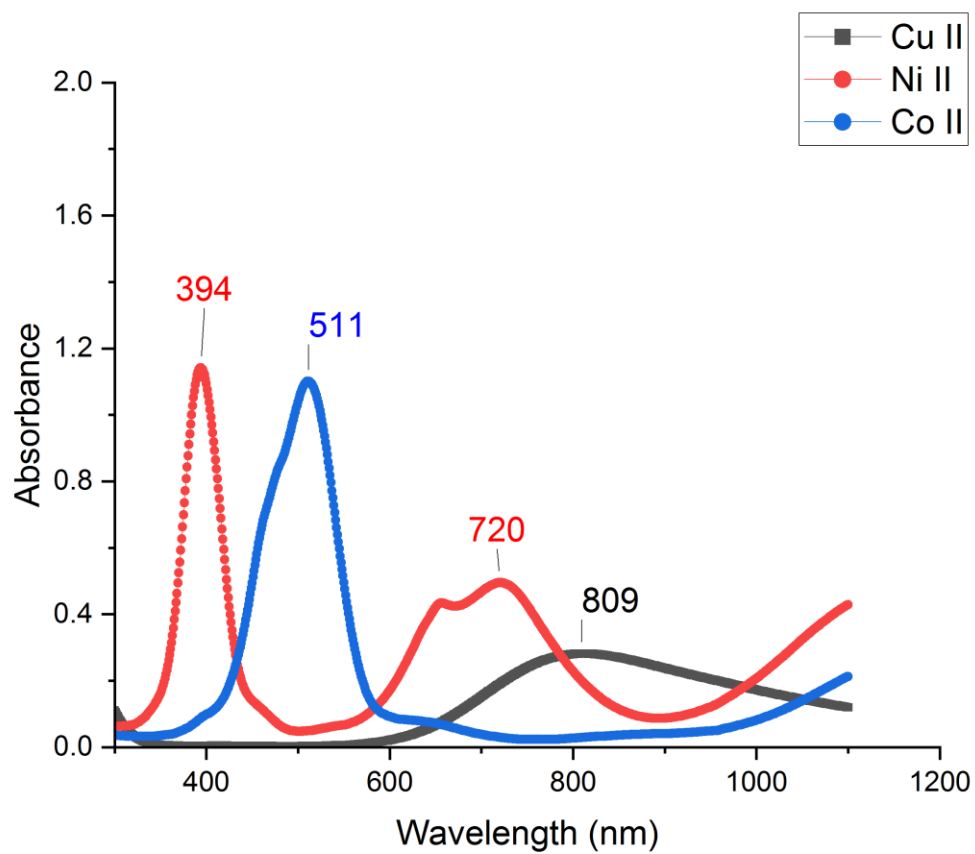
Figure ٢-١ UV-Visible spectra of Ni(II), Co(II) and Cu(II) aqueous solutions

٢.٢. Calibration curve

Figure ٢.٢ shows the calibration curve of Ni(II), Co(II) and Cu(II) that performed by calculating the absorption of known metal concentration.

Figure ٢-٢ Calibration curve of Ni(II), Co(II) and Cu(II)

٢.٣. Tests on the absorption of metal

Two types of ligands (RH-SiO٢PrADB &Fe٢O٤@RH-SiO٢PrADB) were used to remove a number of ions represented by cobalt, nickel and copper. The method was done using a volumetric vial containing ٥٠ mL of one of the ions such as cobalt with ٠.٠٢ g of one of the ligands such as of (RH-SiO٢PrADB), and it was shaken for ten minutes. After that, ٥ mL of the mixture was withdrawn and filtered. Through the needle of the syringe to remove the solid particles, then the residual concentration of the metal ion was measured by the solution absorption measurement every hour for ten hours. This method was used for nickel, and copper ions with one ligand at a time. The following equation was used to calculate the removal efficiency(E%) of copper, nickel and cobalt from aqueous solutions [٨٥] :

$$\% \, E = \frac{C_o - C_e}{C_o} \times 100$$

Where C_o and Ce are the initial concentration at zero and the adsorbed concentrations after contact time, respectively, The effects of trembling time, pH effect, ion concentration, and weight for (RH-SiO$_2$PrADB& Fe$_3$O$_4$@RH-SiO$_2$PrADB) were studied as optimization conditions.

٢.٤. Optimization conditions:-

٢.٤.١. Experience Time

The impact of reaction time on the absorption of metal ions by (RH-SiO$_2$PrADB, Fe$_3$O$_4$@RH-SiO$_2$PrADB) were explored. The response was performed with ٠.٠٢ g ligands and shaken for ١٠ h with an aqueous solution of divalent metal ions. The absorption was calculated every ١ h.

٢.٤.٢. Concentration of metal ion

The effect of metal ion concentration was studied using different concentrations (٠.٠١ M , ٠.٠٤ M , ٠.٠٦ M , and ٠.٠٩ M) for each metal in with ligands (RH-SiO$_2$PrADB , Fe$_3$O$_4$@RH-SiO$_2$PrADB)

٢.٤.٣. Weight of the ligand

The effect of the weight of the ligand was investigated using three different weights (٠.٠١, ٠.٠٢, ٠.٠٣, ٠.٠٤ g) of ligands (RH-SiO$_2$PrADB, Fe$_3$O$_4$@RH-SiO$_2$PrADB)

٢.٤.٤. Effect of pH

The effect of the pH function on the adsorption of ions by the prepared compounds was used pH (٢ , ٣ , ٤).

Diagram: This diagram briefly explains the method of preparing the compounds

RH-SiO₂PrNH₂ , Fe₃O₄@RH-SiO₂PrNH₂ , RH-SiO₂PrABD and Fe₃O₄@RH-SiO₂PrABD

Rice

Rice grinding

Washing with distilled water, treatment with HNO₃

remaining rice husks

RH-NO₃

The acid treated RH-NO₃ was filtered and washed with distilled water until it reached a constant pH (٦ - ٧.٠) and dried in oven at ١١٠

Rice husks free of metal oxides

NaOH

Sodium silicate

Fe₃O₄   APTE   APTE

Fe₃O₄@RH-SiO₂PrNH₂   RH-SiO₂PrNH₂

Characterized by   FTIR , BET , XRD , CHN , FESEM , AFM , TEM, TGA/DTA   Characterized by

٢-amino-٣,٥-dibromobenzaldehyde   ٢-amino-٣, ٥-dibromobenzaldehyde

Fe₃O₄@RH-SiO₂PrABD   RH-SiO₂PrABD

Characterized by   Characterized by

FTIR, N₂ adsorption-desorption, XRD, CHN, FESEM, AFM, TEM, TGA/DTA

Figure ٢-٣ : Research progress and results continuation

CHAPTER THREE

RESULTS AND

DISCUSSION

٣. Results and Discussion

٣.١. Introduction

The researchers is moving towards using the best scientific methods to eliminate environmental pollution. Some metallic elements are natural and industrial pollutants like Cobalt, Copper, and Nickel. Rice husks can produce silica-based porous materials with a large surface area developed to eliminate these elements.

The method for preparing two types of porous materials includes washing rice husks with distilled water and then treating them with nitric acid. RH-NO₃ was filtered and shaken in distilled water until it reached a stable pH (٦ - ٧). The product was dried at ١١٠ ^{o}C in an oven overnight. After that reacted with sodium hydroxide to produce sodium silicate, which was finally ground to get a fine powder called RH-SiO₂. Sodium silicate was added to ٣-(aminopropyl) triethoxysilane and calibrated with nitric acid (٣ M) until the pH value reached ٣, then the gel formed was separated by centrifuge after that washed away with distilled water and finally in ٢-propanone. Then dried in an oven to produce a powder of RH-SiO₂PrNH₂.

Toluene was refluxed with the mixture of ٢-amino-٣,٥-dibromobenzaldehyde and RH-SiO₂PrNH₂. The ethanol, acetone, and DMSO were used to filter and wash the yellow solid result. then ٢٤ hours of drying at ١١٠°C. Finally, the resulting powder was identified as RH-SiO₂PrADB.

Fe₂O₄ was add into sodium silicate for ٣٠ minutes in Ultrasound. The mixture was treated with APTES and titrated with ٣.٠ M nitric acid until the value of pH reached to ٣ , stirred for ٤٨ h. The formed was separated by

centrifuge and washed with distilled water for five times and finally in ethanol, then dried up to ٢٤ h at ١١٠ °C in oven obtained Fe₃O₄@RH-SiO₂PrNH₂ which was added to ٢-amino-٣,٥-dibromobenzaldehyde and the mixture was refluxed in of toluene at ١١٠ °C for ٢٤ h . The dark brown solid product was filtered and washed with an amount of ethanol, acetone and DMSO. Then dried at ١١٠ °C for ٢٤ h.

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٣.٢. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) is the measurement of the interaction of infrared radiation with matter by absorption, emission, or reflection. It is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms.. The technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) which produces an infrared spectrum. An IR spectrum can be visualized in a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency, wavenumber or wavelength on the horizontal axis. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer. In order for a vibrational mode in a sample to be "IR active", it must be associated with changes in the molecular dipole moment. A permanent dipole is not necessary, as the rule requires only a change in dipole moment. Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N₂, the band is not observed in the IR spectrum, but only in the Raman spectrum. Asymmetrical diatomic molecules, e.g. carbon monoxide (CO), absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more

complex, i.e. big molecules have many peaks in their IR spectra.[٨٦]. Figure (٣-١) shows FTIR for the compounds group was preparation.
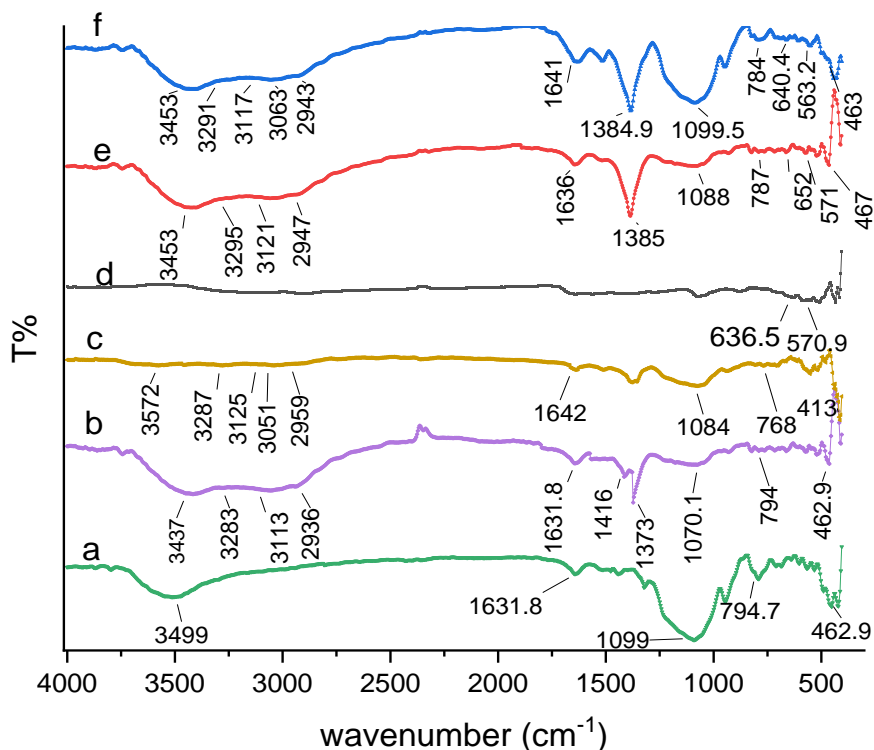
Figure ٣-١ FTIR for (a) RH-SiO₂ (b) RH-SiO₂PrNH₂ (C) RHSiO₂PrADB (d) Fe₃O₄ (e) Fe₃O₄@RH-SiO₂PrNH₂ (f) Fe₃O₄@RH-SiO₂PrADB

Figure٣-١ A displays the FTIR of the rice husk (RH-SiO₂) which contains a group of distinct bands at ٣٤٩٩ cm⁻¹ and a medium sharp band at ١٦٣١ cm⁻¹, due to surface hydroxyls on the silica surface and coordination water [٨٧].while the band at ١٠٩٩ , ٧٩٤.٧ and ٤٦٢ cm⁻¹ which hand over to siloxane to the expansion shaking of Si-O-Si bond[٨٨]. Whilst Figure٣-١B the FT-IR spectrum for RH-SiO₂PrNH₂ showed that the vibration NH₂ and NH absorbed at ٣٢٨٣ and ٣١١٣ cm⁻¹, respectively. The C–H group in propyl moiety of RH-SiO₂PrNH₂ absorbed at ٢٩٣٦ cm⁻¹. The C-H bending and CH₂

vibrations were assigned the bands at ١٤١٦ cm⁻¹ and ١٣٧٣ cm⁻¹, respectively[٢٣]. Figure٣-١ C also displays the FT-IR spectrum for RH-SiO٢PrADB gave bands as follows;. The C-H Aromatic peak is at ٣٠٥١ cm⁻¹. The CH٢ moiety is responsible for the peak at ٢٩٥٩ cm⁻¹[٨٩]. The azomethine group (C=N) is represented by the peak at ١٦٤٢ cm⁻¹[٩٠]. Figure٣-١d indicates that The FTIR spectrum of iron oxide (Fe٢O٤) showed an absorption band at ٦٣٦.٥ and ٥٧٠.٩ cm⁻¹ due to Fe-O bond[٩١]. As shown in Figure٣-١e the FT-IR spectrum for Fe٢O٤@RH-SiO٢PrNH٢ showed that the absorption bands same absorption for Fe٢O٤ and RH-SiO٢PrNH٢[٩٢]. Whilst Figure٣-١f shows the FTIR spectrum of Fe٢O٤@RH-SiO٢PrADB showed that the absorption bands same absorptions for compounds Fe٢O٤ and RH-SiO٢PrADB[٩٠].

٣.٣. Surface area analysis

Adsorption of gases onto porous particles is one of the key methods for defining the shapes of ceramic substances. The most important morphological parameters can be determined or inferred from analyses of the connection between the amount of material adsorbed and the pressure distribution of a physiologically adsorbing gas. These calculations and estimates are based on the pore representation assumptions and the equations connecting the pressure distribution to the gaseous physisorbed state[٩٣]. As a result, the Brunauer-Emmett-Teller (BET) gas adsorption approach has emerged as the most popular standard method for calculating the surface area of finely split and porous materials.. Using the Barrett- Joyner-Halenda (BJH) method, the materials pore diameter and pore size distribution were determined using the adsorption isotherms[٩٤].

The IUPAC in Figure(٣-٢) has given an empirical classification of hysteresis loops in which the shape of the hysteresis loops (types H١–H٤). The technique of a microporous adsorbent is often described by type I isotherm, which approaches a limit value. With weak and strong adsorbate and adsorbent interactions, respectively, Types II and III characterise the adsorption of macroporous adsorbents. Types IV and V consist of capillary condensation in addition to mono- and multi-layer adsorption. Adsorption isotherms may contain one or more steps, as demonstrated by Type VI, which wasn't included in the Gibbs classification.[٩٥]. Table (٣-١) and Figure (٣-٣) show information about the results obtained regarding the value of the specific surface area, pore diameter, and hysteresis loops for the prepared compounds.
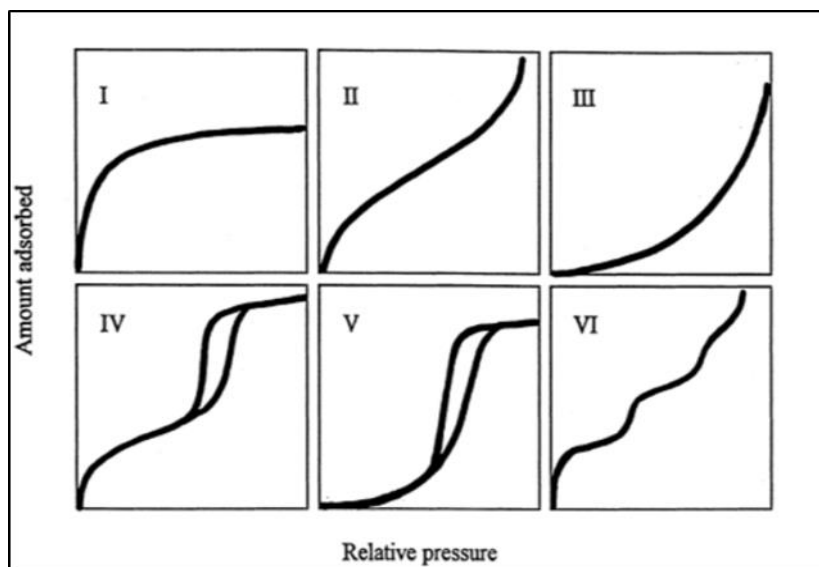
Figure ٣-٢ The IUPAC Classification of Adsorption Isotherms[٩٥]

Table ٣-١ Surface area analysis (BET, BJH) of RH-SiO₂PrNH₂, Fe₃O₄@RH-SiO₂PrNH₂, RH-SiO₂PrADB, and Fe₃O₄@RH-SiO₂PrADB

Sample	Specific surface area (m²/g)	Average pore volume	Mean pore diameter (nm)
RH-SiO₂	٣٩٠٫١٢	٠٫٣٠٧	٣٫٤٦٩٨
RH-SiO₂PrNH₂	٠٫٧٨٩	٠٫٠٠٣٠	١٥٫٥٥
Fe₃O₄@RH-SiO₂PrNH₂	٠٫٥٩٣	٠٫٠٠٣٥	٢١٫٠٧٨
RH-SiO₂PrADB	٣٫٨١٨	٠٫٠٣٥١	٣٦٫٢١٦
Fe₃O₄@RH-SiO₂PrADB	٣٫٥٧٦	٠٫٠١٦١	١٦٫٥٨٦

Figure ٣-٣: (a) Nitrogen adsorption-desorption isotherm, (b) pore size distribution for the RH-SiO٢ (C) Nitrogen adsorption-desorption isotherm (D)pore size distribution for RH-SiO٢PrNH٢ (E) Nitrogen adsorption-desorption isotherm, (F) pore size distribution for the Fe٢O٤@RH-SiO٢PrNH٢ (G) Nitrogen adsorption-desorption isotherm, (H) pore size distribution for the RH-SiO٢PrADB (I) Nitrogen adsorption-desorption isotherm, (J) pore size distribution for the Fe٢O٤@RH-SiO٢prADB

The results showed that the mean pore diameter of the RH-SiO٢ sample is ٣.٤٦٩٨ nm and has a pore size distribution which occur between (٢ and ٢٠ nm) which fall in the mesoporous range, as shown in Figure(٣-٢a and b) and Table (٣-١). The results showed that the adsorption and desorption isotherms follow type (IV) and show H٢ hysteresis loops based on the IUPAC classification. Hysteresis H٢ is often associated with a pore shape resembling a round-bottom flask[٩٦]. While the mean pore diameter value of the RH-SiO٢PrNH٢ sample is ١٥.٠٥٥ nm and has a pore size distribution which occur between (٢ and ١٠ nm) which fall in the mesoporous range , as shown in

Figure(Υ-Υ C and D) and Table (Υ-Υ). The adsorption-desorption isotherm follows the (IV) type and hysteresis loops HΥ, this indicates strong attractive interactions between the molecules. In contrast, the mean pore diameter value in the $Fe_\Upsilon O_\xi$@RH-$SiO_\Upsilon PrNH_\Upsilon$ sample decreased to up to $\Upsilon\Upsilon.\cdot\Upsilon\Lambda$ nm, and has a pore size distribution which occur between (Υ and $\Upsilon\Lambda$ nm) which falls in the mesoporous range as shown in Figure(Υ-Υ E and F) and Table (Υ-Υ). This refers to the immobilization of $Fe_\Upsilon O_\xi$ nanoparticles on the RH-$SiO_\Upsilon PrNH_\Upsilon$ surface. Adsorption-desorption isotherm belongs to type (IV) and the hysteresis loop is of type (HΥ). This indicates the presence of narrow interconnected pores with a complex network. whilst mean pore diameter of the RH-$SiO_\Upsilon PrADB$ were using BET analysis, to be equal to $\Upsilon\Upsilon.\Upsilon\Upsilon\Upsilon$ nm, and has a pore size distribution which occur between (Υ and $\Upsilon\circ$ nm) which falls in the mesoporous range as shown in Figure(Υ-Υ G and H) and Table (Υ-Υ). These isotherms exhibited a typical type IV curve and the hysteresis loop is of type (HΥ). It was noted that the reaction of RH-$SiO_\Upsilon PrNH_\Upsilon$ with the Υ-amino-Υ,$\circ$-Dibromobenzaldehyde compound increased the value of the surface area as a result of the presence of a carbon network that works to increase the effective sites, and this makes the surface highly effective towards adsorbed nitrogen gas. This type of isotherm shows that the particles are plate-like[$\Upsilon\circ$]. The mean pore diameter of $Fe_\Upsilon O_\xi$@RH-$SiO_\Upsilon PrADB$ was $\Upsilon\Upsilon.\circ\Lambda\Upsilon$ nm and has a pore size distribution which occur between (Υ and $\Upsilon\cdot$ nm) which falls in the mesoporous range, as shown in Figure(Υ-Υ I and J) and Table (Υ-Υ) which was decreased compared with the specific surface area of RH-$SiO_\Upsilon PrADB$. This is due to the attachment of $Fe_\Upsilon O_\xi$ particles to an RH-$SiO_\Upsilon prADB$ surface, which reduces the surface area. The adsorption-desorption isotherm follows the (III) type and hysteresis loops HΥ.

٣.٤. X-ray Diffraction analysis XRD

The innovation of X-rays paved the way for important developments in all branches of science as well as the invention of new technological applications. The investigation of X-ray diffraction (XRD) by crystals has given a new direction to the study of crystalline materials. These processes have now undergone predictive refinement into highly effective tools in the fields of engineering and materials science. Experimental X-ray processes have three basic categories that are used in materials science and engineering. X-ray spectroscopy is often used in quantitative and qualitative chemical study, particularly with electron microscopes. In X-ray radiography, the force flowing from a material is recorded using films or detectors, which, thanks to a local change in absorption, allow one to examine the internal structure of the item. One of the most important developments in this field over the past few decades is X-ray tomography. XRD techniques, which allow a comprehensive analysis of the structure of crystal phases, are based on the ability of the crystals to have X-ray diffraction. Several micro-sample components and the overall structure additionally contributed to the obtained diffraction patterns. The peak position can be used to study lattice properties, space groups, chemical composition, or qualitative phase analyses. The peak intensity can be used for crystal structure determination (atomic position, temperature factor, occupancy), quantitative phase analyses, and other information. Finally, the peak pattern reveals the sample magnification aids (microstrains and crystal size) That is, XRD analysis reveals whether the materials are crystalline or non-crystalline[٩٧]. The crystalline type, phase, and crystal size of solid nanomaterials can be ascertained quickly and accurately by XRD analysis[٩٨]. Figure (٣-٤) shows the XRD spectrum of compounds that were prepared.

**Figure ٣-٤ XRD spectrum for (A) RH-SiO٢ (B) RH-SiO٢PrNH٢ (C) RH-SiO٢PrADB
(D) Fe٣O٤ (E) Fe٣O٤@RH-SiO٢PrNH٢ (F) Fe٣O٤@RH-SiO٢PrADB**

The XRD spectrum of RH-SiO٢ in Figure٣-٤A the existence of a wide
diffraction peak at (٢θ= ٢٢.٢°) and the absence of sharp peaks in the other
regions of the spectrum indicates the amorphous nature of the prepared RH-
SiO٢ sample. While RH-SiO٢PrNH٢ can show in Figure٣-٤B. As the spectrum
showed the existence of a wide diffraction peak at (٢θ= ٢٢°) and the absence
of sharp peaks in the other regions of the spectrum indicates the amorphous
nature of the prepared RH-SiO٢PrNH٢ sample[٩٩]. Figure٣-٤C shows the
RH-SiO٢PrABD sample. As it was noticed that sharp peaks disappeared in the
spectrum with the existence of one broad peak at (٢θ= ٢٢.٥°). The spectrum

data confirmed that the material is of an amorphous nature and high purity because no additional peaks appeared in the spectrum [١٠٠] .

XRD patterns of Fe_rO_ξ NPs' are shown in Figure٣-٤D. The diffraction peaks of   ٢θ= ٣٠.٣٣, ٣٥.٦١, ٤٣.٠٣, ٥٣.١٧, ٥٧.٧٢, and ٦٢.٦٦ were visible in the XRD patterns of Fe_rO_ξ NPs. This illustrates Fe_rO_ξ's cubic spinel structure (JCPDS Card No. ١٩-٦٢٩). The exceptional purity of the Fe_rO_ξ NPs is indicated by the absence of other peaks in the spectrum [١٠١]. The crystalline size of all compounds was calculated according to the Scherrer equation as shown in Table (٣-٢).

$$D = \frac{K * \lambda}{\beta * Cos(\theta)}$$

Where (D) Crystallite size , (K) A dimensionless shape factor with a value without unity. The shape factor has a typical value of about ٠.٩, but varies with the actual shape of the crystallite, (λ) is the X-ray wavelength, (β) is the line broadening at half the maximum intensity (FWHM) and (θ) is the Bragg angle, While showed the **Figure ٣-٤E** XRD spectrum of the Fe_rO_ξ@RH-SiO_rPrNH_r composite showed diffraction peaks at (٢θ =٢٩.٦°, ٣٢.٣°, ٣٥.٧°, ٣٩.٢°, ٤٣.١°, ٤٨.٥°, ٥٦.٨°, ٦١.٣°, ٦٢.٧°) assigned to the cubic crystalline structure of Fe_rO_ξ, and the broad peak (٢θ =١٧.٨° -٢٨.٦°) due to the presence of carbon in the RH-SiO_rPrNH_r structure, as in the Figure٣-١٧. This indicates the success of the Fe_rO_ξ bonding with the RH-SiO_rPrNH_r, which has an amorphous nature (١٠٢). On the other hand, the XRD spectrum of the Fe_rO_ξ@RH-SiO_rPrABD in **Figure ٣-٤F** composite showed a clear displacement in the broad peak at (٢θ =١٨.٦° -٢٨.٨°) due to RH-SiO_rPrABD compound and sharp peaks at (٢θ =٢٩.٢°, ٣٥.٤°, ٣٩.١°, ٤٢.٤°, ٤٧.٩°, ٥٧.٠°,

٦٢.٨°, ٦٧.٠°) due to the cubic structure of Fe$_3$O$_4$. As it was noted that the prepared composite is of an amorphous nature.

Table ٣-٢ Crystallite size and Average crystallite size of Fe^{3}O^4 , Fe^{3}O^4@RH-SiO^{2}PrNH^2 and Fe^{3}O^4@ RH-SiO^{2}PrABD

Compounds	Pos. [°٢Th.]	FWHM [°٢Th.]	Rel. Int. [%]	crystallite size D (nm)	D(nm) Average)
Fe$_3$O$_4$	١٤.٨٦٧٧	٠.٢٧٧٣	٥١.٢٥	٢٨.٨٩٦	١٨.٦١٣
	٣٥.٧٩٢٦	٠.٥٢	١٠٠	١٦.٠٥٤	
	٥٤.٢٧٤	٠.٤٤٥٢	٣٠.٨٤	٢٠.٠٥٢	
	٦٢.٧٢٥٩	٠.٩٨٤	٤٣.٤١	٩.٤٥٥	
Fe$_3$O$_4$@RH-SiO$_2$PrNH$_2$	٣٠.١٥٢٣	٠.٥٧٦١	٧٤.٥١	١٤.٢٨١	٣٤.٥٦٦
	٣٥.٧٥	٠.٦١٦٥	١٠٠	١٣.٥٤٠	
	٦١.٢٩٩٥	٠.١٢١٧	٨٣.٠١	٧٥.٨٧٨	
Fe$_3$O$_4$@ RH-SiO$_2$PrABD	٢٩.٧٥	٠.٥٦٤١	٤٠.٣٧	١٤.٥٧١	٤١.١٤١
	٣٥.٤٩٦٧	٠.٤٨٤٢	١٠٠	١٧.٢٢٧	
	٣٩.٠٢٤٩	٠.٢٨٣٣	٥١.٠٢	٢٩.٧٥١	
	٦٢.٦٩٦٦	٠.٠٩٠٣	٤٦.٥١	١٠٣.٠١٥	

٣.٥. Elemental Analysis (CHN)

Determine the carbon (C), hydrogen (H), and nitrogen (N) contents of organic and inorganic samples using CHN elemental analysis. Can identify even minute amounts of elements and the technique is dependent on the sample being completely burned. Solid, liquid, volatile, and viscous materials can all be subjected to CHN measurements. The sample size can be quite small. Based on the conventional Pregl-Dumas method, this analysis is

conducted at a high temperature (about ١٠٠٠°C) in an oxygen-rich environment[١٠٢].
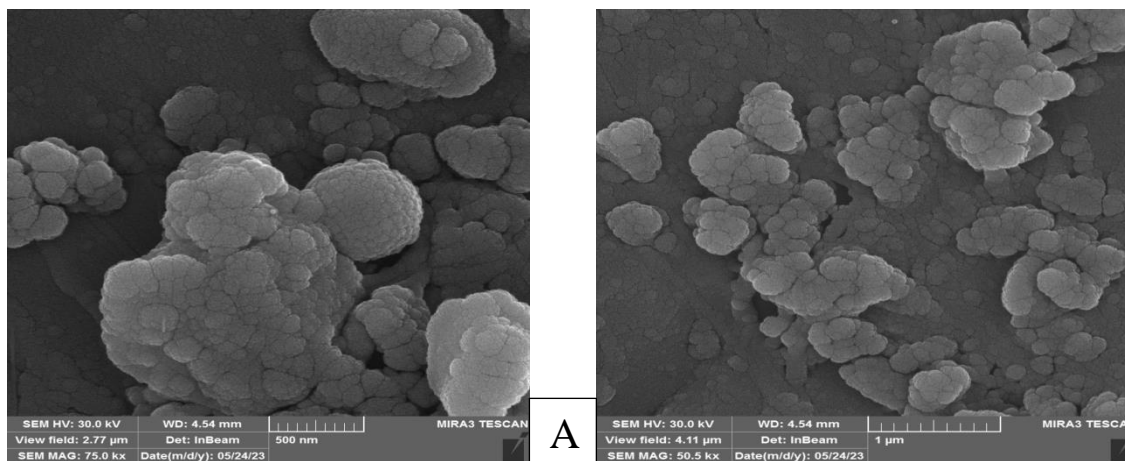
Table (٣-٣) shows the results obtained for the ratio of carbon and Nitrogen as it was for the compound RH-SiO₂ showing that the percentage of carbon and nitrogen reaches ٨.٦٠٪ and ٠.٥%. The RH-SiO₂PrNH₂ showed that the percentage of carbon and nitrogen reaches ١٤.٤٤٪ and ٨.٦٤٪, respectively. On the other hand, their percentage in the Fe₃O₄@RH-SiO₂PrNH₂ compound decreased slightly, which indicates the success of the ligand binding with Fe₃O₄. Also, the elemental analysis of the RH-SiO₂PrADB compound indicates that the percentage of carbon and nitrogen is ١٦.٦٣٪ and ٦.٤٪, as the high percentage of carbon is due to the association of the RH-SiO₂PrNH₂ with ٢-amino-٣,٥-Dibromobenzaldehyde. As it was observed that the association of the RH-SiO₂PrADB with Fe₃O₄ increases the percentage of carbon to about ١٨.٧٧٪ . The silica extraction process was carried out by base digestion and not by burning, and therefore there was a percentage of organic materials in the sodium silicate solution and thus appeared in the CHN analysis[١٠٣].
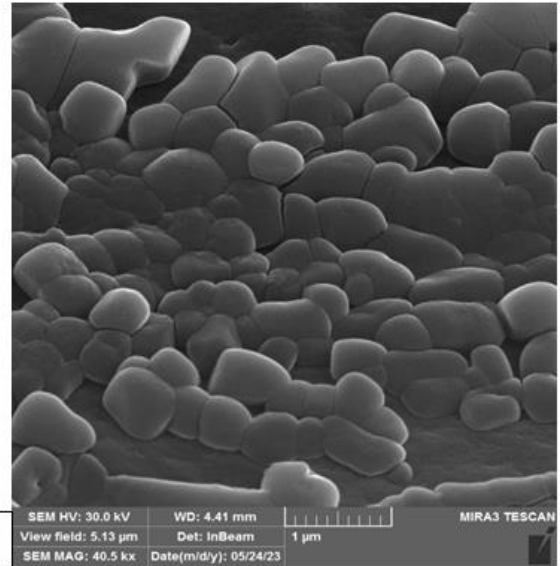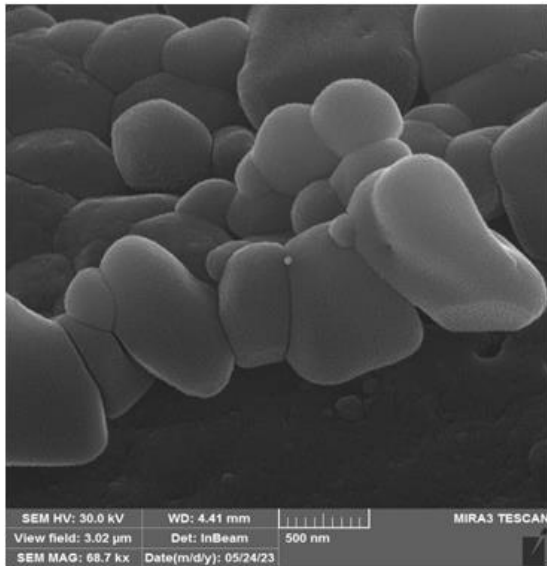
Table ٣-٣ : Chemical analysis of RH-SiO₂, RH-SiO₂PrNH₂, Fe₃O₄@RH-SiO₂PrNH₂, RH-SiO₂PrADB, and Fe₃O₄@RH-SiO₂PrADB using CHN

Sample	C (%)	H (%)	N (%)
RH-SiO₂	٨.٦٠	٢.٦٤	٠.٥
RH-SiO₂PrNH₂	١٤.٤٤	٢.٦٥	٨.٤٦
Fe₃O₄@RH-SiO₂PrNH₂	١٤.٤٣	٣.١٣	٨.٢
RH-SiO₂prADB	١٦.٦٣	٣.١٦	٦.٤
Fe₃O₄@RH-SiO₂PrADB	١٨.٧٧	٥.٩٠	٧.٠

٣.٦. Field emission scanning electron microscopy (FESEM)

FESEM is an important technique that reveals the morphology, size, and crystalline nature of the prepared compounds. Secondary electrons are released from the sample surface when it is exposed to a strong electron beam (also known as an electron probe). Surface morphology can be seen by performing a double-dimensional scan of the electron sample over the surface and acquiring an image from the secondary electrons found[١٠٤]. Figure (٣-٥) shows the FESEM images for the group of compounds that were prepared. while Figure (٣-٦) displays the EDX analysis for the group of compounds that were prepared.
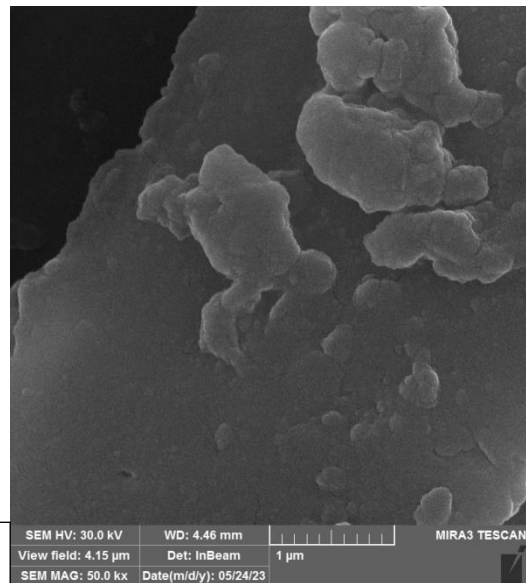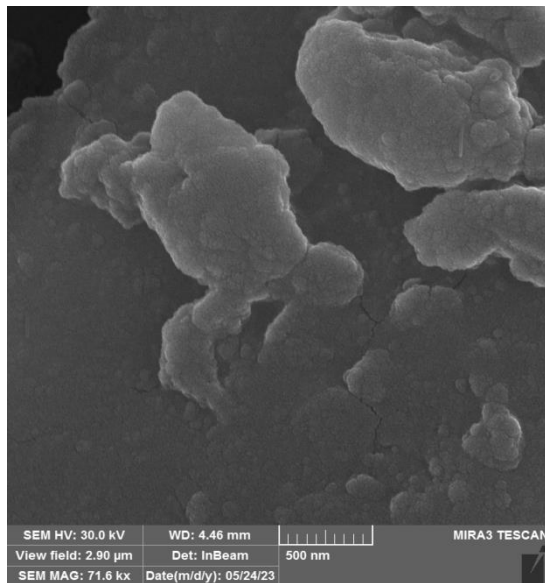
Figure ٣-٥ FESEM images for (A) RH-SiO٢ (B) RH-SiO٢PrNH٢ (C) RH-SiO٢PrADB (D) Fe٣O٤@ RH-SiO٢PrNH٢ (E) Fe٣O٤@ RH-SiO٢PrADB

Figure ٣-٦ EDX chart for (A) RH-SiO٢ (B) RH-SiO٢PrNH٢ (C) RH-SiO٢PrADB (D) Fe٣O٤@ RH-SiO٢PrNH٢ (E) Fe٣O٤@ RH-SiO٢PrADB

Table ٣-٤ : shows the EDX analysis the weight percentages of compound

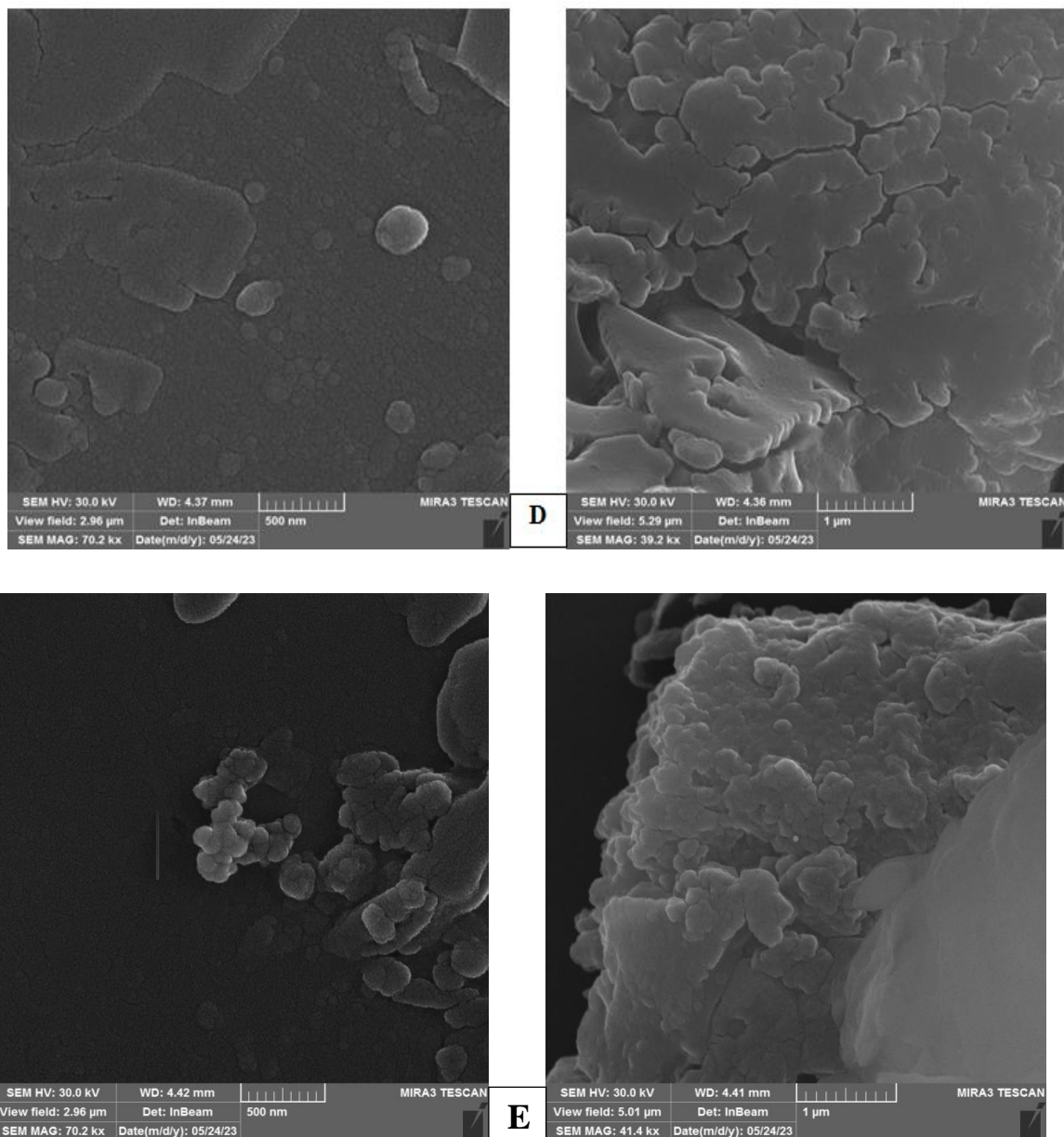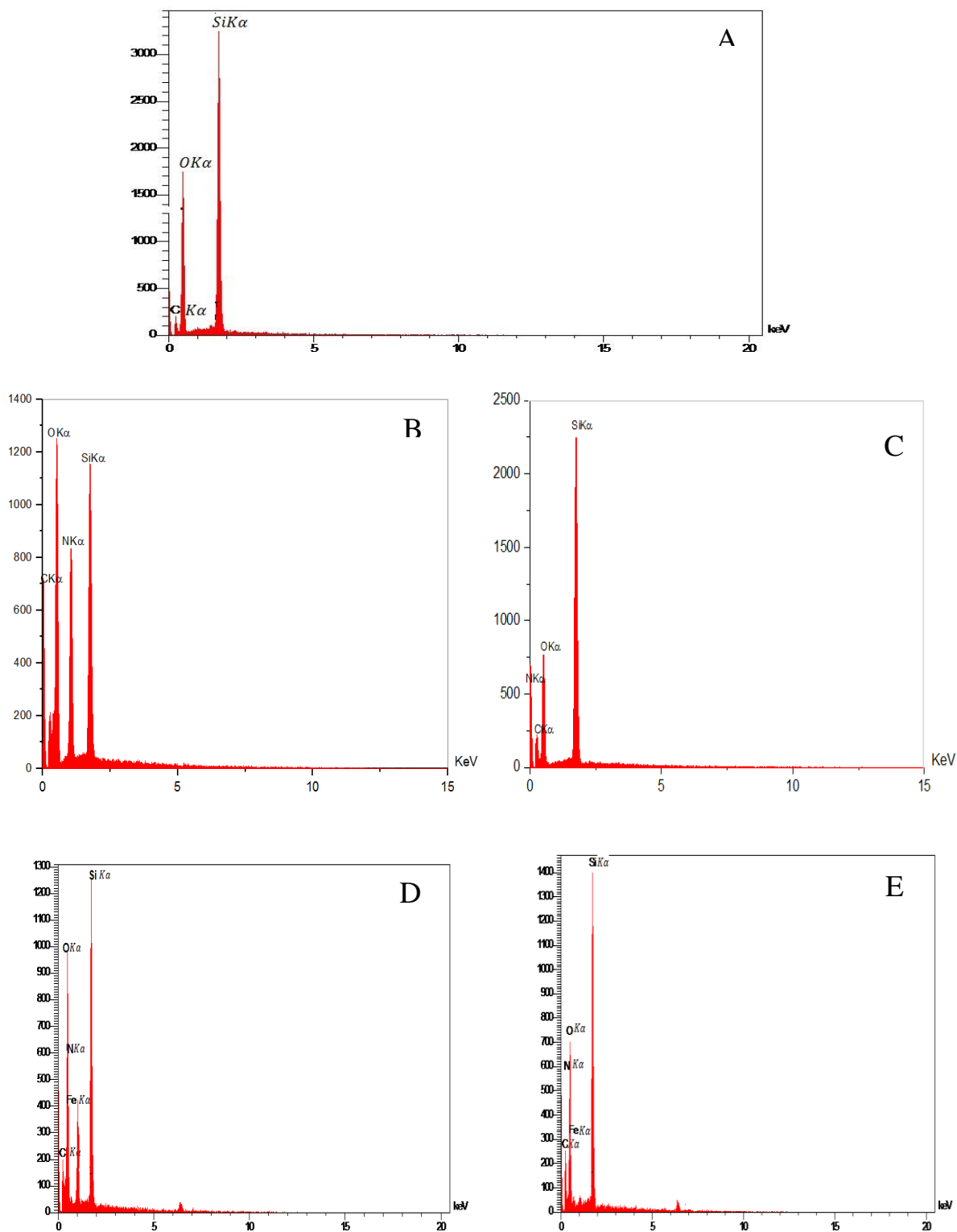| Compounds	carbon	nitrogen	oxygen	silicon	Iron
RH-SiO٢	٢١.٦٧%		٥٧.٣٨٪	٢٠.٩٥٪	
RH-SiO٢PrNH٢	١٣.٨٨٪	٢٠.٤٢٪	٥٧.١٣٪	٨.٥٧٪	
RH-SiO٢PrADB	٢٤.٦٣٪	١٢.٠١ %	٤٤.٣٦٪	١٨.٨٤٪	
Fe٢O٤@RH-SiO٢PrNH٢	١٤.٣٤٪	١٨.٢١٪	٥٤.١٤٪	١١.٣٢٪	١.٩٩٪
Fe٢O٤@RH-SiO٢PrADB	٢٣.١٥٪	١٣.٧٢٪	٤٦.٨٣٪	١٣.٧٩٪	٢.٣٣%

Figure (٣-٥A) shows the FESEM images of the RH-SiO٢. The images shows that the rice husk is composed mostly of amorphous silica. While the EDX analysis also showed as shown in **Figure (٣-٦a) shows** the weight percentages of RH-SiO٢ as follows: carbon (٢١.٦٧٪), oxygen (٥٧.٣٨٪), and silicon (٢٠.٩٥٪)(٩٦). **Figure٣-٥B** shows the FESEM images of the RH-SiO٢PrNH٢ compound, as it was observed that there are semi-spherical clusters with a smooth outer surface and irregularly distributed[١٠٥]. While **Figure(٣-٦B)** shows the EDX spectrum of RH-SiO٢PrNH٢. It explains the presence of the most important basic elements in the different intensities. According to the EDX analysis of RH-SiO٢PrNH٢, the weight percentage of an elements indicates the presence of carbon (١٣.٨٨٪), nitrogen (٢٠.٤٢٪), oxygen (٥٧.١٣٪), and silicon (٨.٥٧٪). This result is somewhat consistent with

the results of the elemental analysis of carbon and nitrogen in Table (٣-٥). FESEM images of the RH-SiO٢PrADB are shown in **Figure٣-٥C**. The images showed an increase in the roughness of the outer surface of the sample with an increase in the rate of accumulation of nanoparticles as a result of the bonding of the RH-SiO٢PrNH٢ with ٢-amino-٣,٥-Dibromobenzaldehyde compound[٧١]. This is highly consistent with previous studies[١٠٠]. While the EDX analysis also showed as shown in **Figure(٣-٦C)** the weight percentages of sample elements as follows: carbon (٢٤.٦٣٪), nitrogen (١٢.٠١ %), oxygen (٤٤.٣٦٪) and silicon (١٨.٨٤٪). The percentages shown confirm the success of the association of RH-SiO٢PrNH٢ with the ٢-amino-٣,٥-Dibromobenzaldehyde compound. FESEM images of the Fe٢O٤@RH-SiO٢PrNH٢ are shown in **Figure٣-٥D.** The FESEM analysis showed the presence of spherical shapes of different sizes and heterogeneities distributed on a rough and bumpy surface, and this confirms the successful attachment of iron oxide to the silica surface. In addition to increasing the surface area and pore diameter, this gives it a high efficiency in removing many pollutants[١٠٦]. While **Figure(٣-٦D)** showed the EDX analysis the weight percentages of sample elements as follows: carbon (١٤.٣٤٪), nitrogen (١٨.٢١٪) , oxygen (٥٤.١٤٪), silicon (١١.٣٢٪), and iron (١.٩٩٪). Finally, **Figure٣-٥E** shows the FESEM images of the Fe٢O٤@RH-SiO٢PrADB compound. As the images showed the presence of spherical clusters distributed on one side over a wrinkled surface with a dark black color, and this is similar to the above compound images and also confirms the increase in the rate of accumulation of particles due to the association of iron oxide with silica[١٠٧]. The EDX spectrum of Fe٢O٤@RH-SiO٢prADB sample is shown in **Figure(٣-٦E),** which clearly illustrates the presence of carbon (٢٣.١٥٪), nitrogen (١٣.٧٢٪), oxygen (٤٦.٨٣٪), silicon (١٣.٧٩٪), and iron (٢.٣٣%) [١٠٧].

٣.٧. Atomic Force Microscopy (AFM)

Almost any surface, including polymers, ceramics, composites, glass, and biological samples, can be imaged using the efficient AFM technique. AFM is used to quantify and localise a variety of forces, including mechanical properties, magnetic properties, and adhesion forces. With this kind of microscope, the electron force between a cantilever tip and the atoms on a specimen's surface is measured. High spatial resolution and extremely light surface forces are two of an AFM's primary benefits over other comparable techniques. Imaging non-conducting materials using AFM is achievable, which is necessary for research on the polymer/silica interface[١٠٨]. Figure (٣-٧) shows the AFM technique used to photograph the surface for the group of compounds that were prepared.
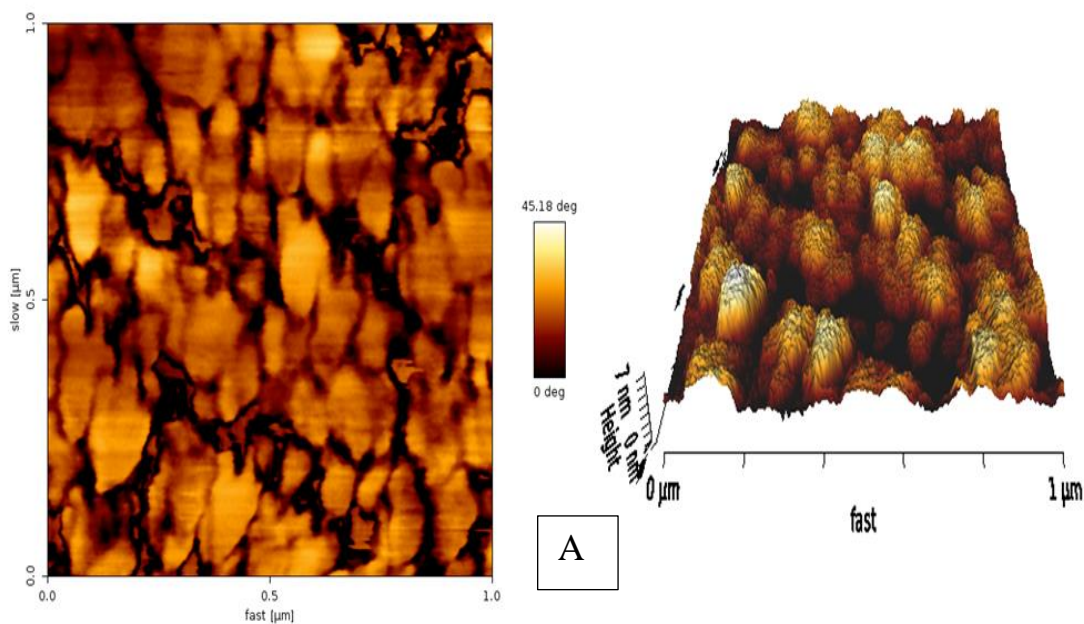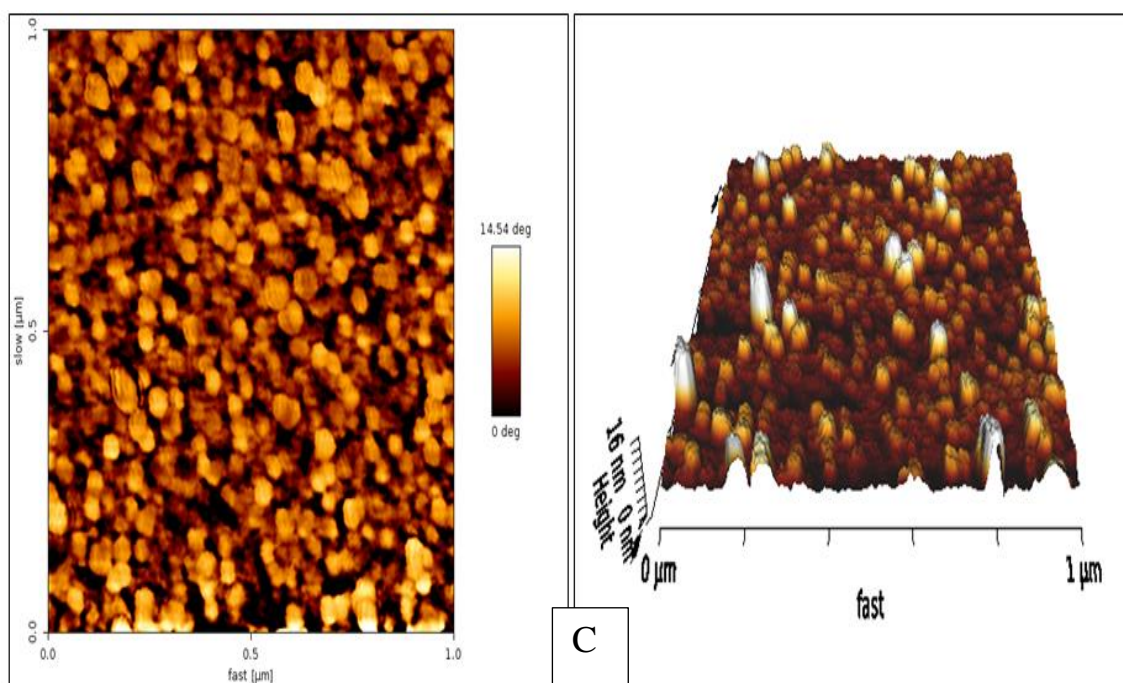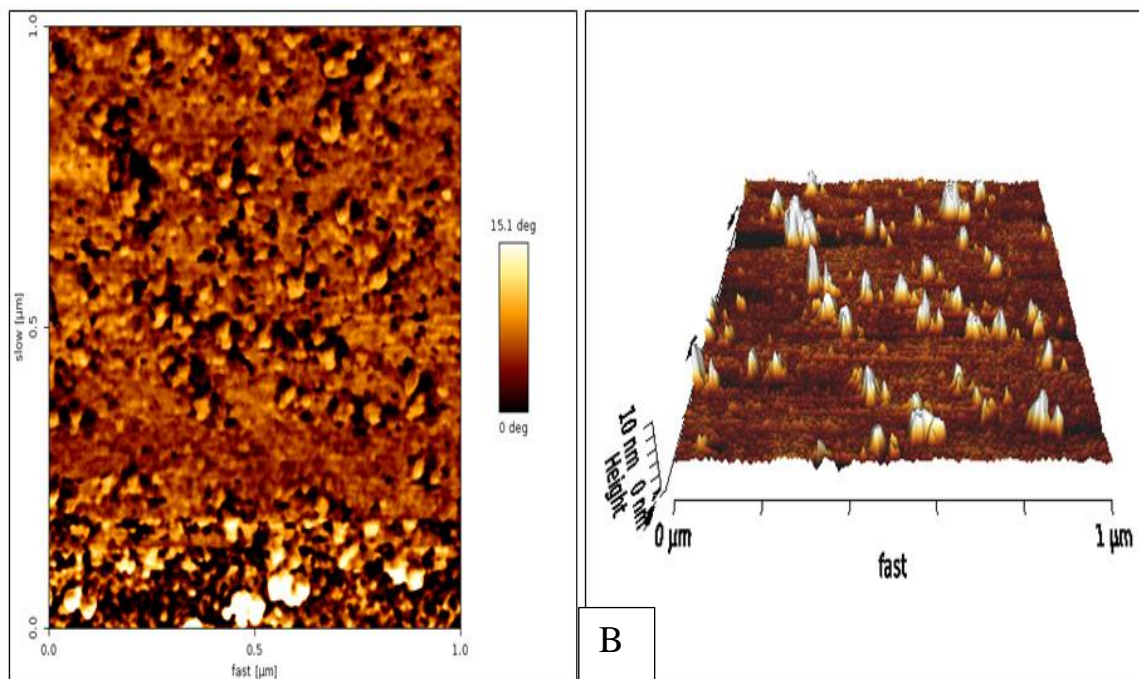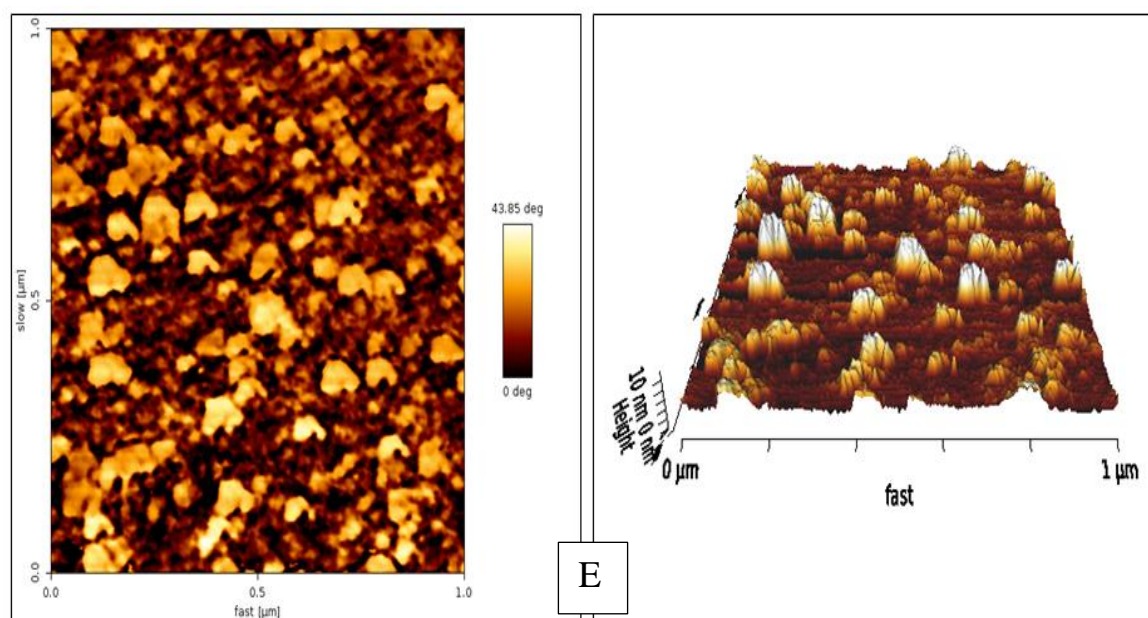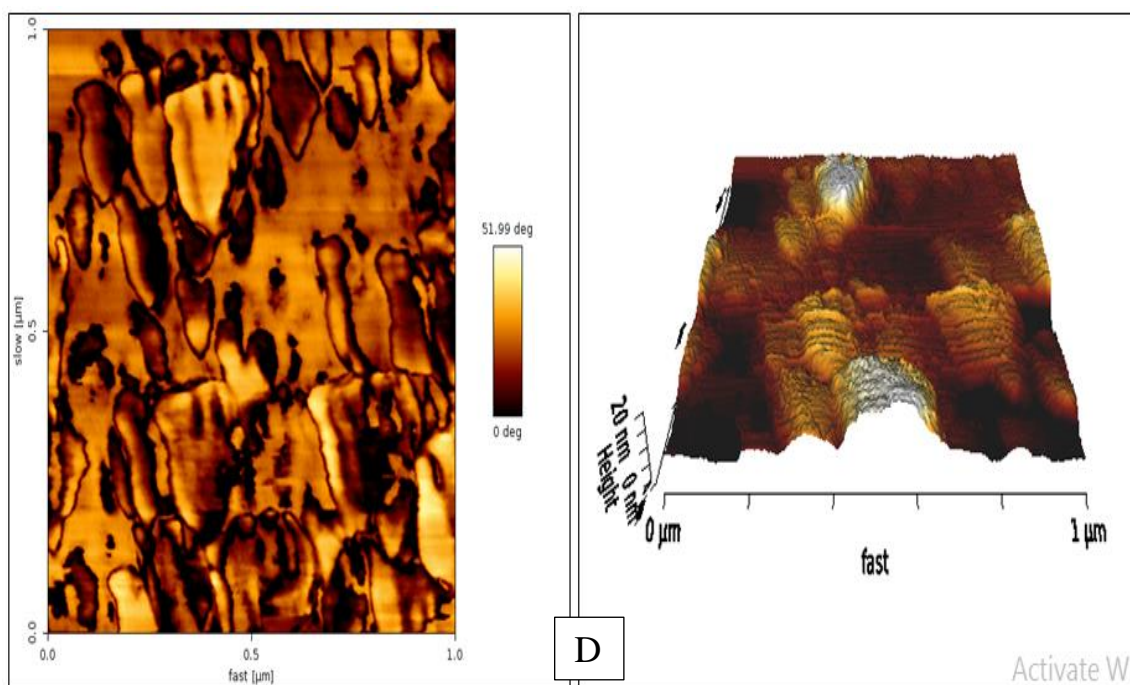
Figure ٣-٧ ٢D and ٣D AFM images of (A)RH-SiO٢ (B) RH-SiO٢PrNH٢ (C) RH-SiO٢PrADB (D) Fe٣O٤@RH-SiO٢PrNH٢ (E) Fe٣O٤@RH-SiO٢PrADB

Table ٣-٥ : shows the AFM analysis

Compounds	Average roughness Ra	RMS roughness Rq	peak-to-valley roughness Rt
RH-SiO٢	٩٩٣.٩ pm	١.٢٢٢ nm	٧.٣٥٦ nm
RH-SiO٢PrNH٢	٤٤٥.٢ pm	٨٠٧.١ pm	١٠.١٧ nm
RH-SiO٢PrADB	١.١١٤ nm	١.٦٦٣ nm	١٦.٢٤ nm
Fe٢O٤@RH-SiO٢PrNH٢	٢.٣٦٣nm	٣.٢٠٩ nm	٢٠.٣٦ nm
Fe٢O٤@RH-SiO٢PrADB	٩٥٨.٩ pm	١.٣٨٢ nm	١١.٨٥ nm

The results of RH-SiO٢ are shown in Figure (٣-٧A), where the images showed the presence of blocks of different shapes with a peak-to-valley roughness (Rt) value of ٧.٣٥ nm and RMS roughness (Rq) value of ١.٢٢nm.This is due to of agglomeration of nanoparticles. While photographing the surface of the RH-SiO٢PrNH٢, as shown in **Fig(.٣-٧B).** The images showed the presence of blocks of different a peak-to-valley roughness (Rt) value of ١٠.١٧ nm and RMS roughness (Rq) value of ١٠.٨٠٧ nm.. This is due to the increase in the rate of agglomeration of nanoparticles[١٠٩]. On the other hand, the images of the RH-SiO٢PrADB compound confirmed a clear increase in a peak-to-valley roughness (Rt) value of ١٦.٢٤ nm and as shows RMS roughness (Rq) value of ١.٦٦٣ nm as shown in **Figure(٣-٧C).** This indicates the successful association of the RH-SiO٢PrNH٢ with the ٢-amino-٣,٥-Dibromobenzaldehyde compound. **Figure٣-٧D** shows the images of the Fe٢O٤@RH-SiO٢PrNH٢ compound, as it was

found that the addition of Fe_3O_4 to the ligand changes the morphology of the prepared surface and significantly increases a peak-to-valley roughness (Rt) value of ٢٠.٣٦ nm and RMS roughness (Rq) value of ٣.٢٠٩ nm. The Fe_3O_4 acts as a barrier between the layers of ligand, which increases the thickness of the layer and makes the surface bumpy and wrinkled. Finally, the Fe_3O_4@RH-SiO_2PrADB compound showed a decrease in surface roughness, as shown in(**Figure٣-٧E).** It was observed that the bonding between Fe_3O_4 increased with the ligand, which leads to a decrease in the surface roughness and the disappearance of the nanoparticle clusters. It is found that the peak-to-valley roughness (Rt) value of ١١.٨٥ nm and an RMS roughness (Rq) value of ١.٣٨٢nm.[١١٠].

٣.٨. Transmission electron microscopy (TEM) analysis

Transmission electron microscopy (TEM) is the most useful technique for determining the morphology of NPs. An powerful electron beam is used in this sort of microscopy to travel through a sample, and the interaction between the electrons and the sample causes a picture to be created. After that, the image is magnified and focussed onto an imaging medium, such as a charge-coupled device, a screen made of fluorescent material, or a sheet of film for photography. When viewing TEM images at lower magnifications, contrast is produced by the material differential absorption of electrons as a result of variations in the material structure or thickness[١١١] , the prepared compounds were analyzed using TEM technology shown in Figure (٣-٨)

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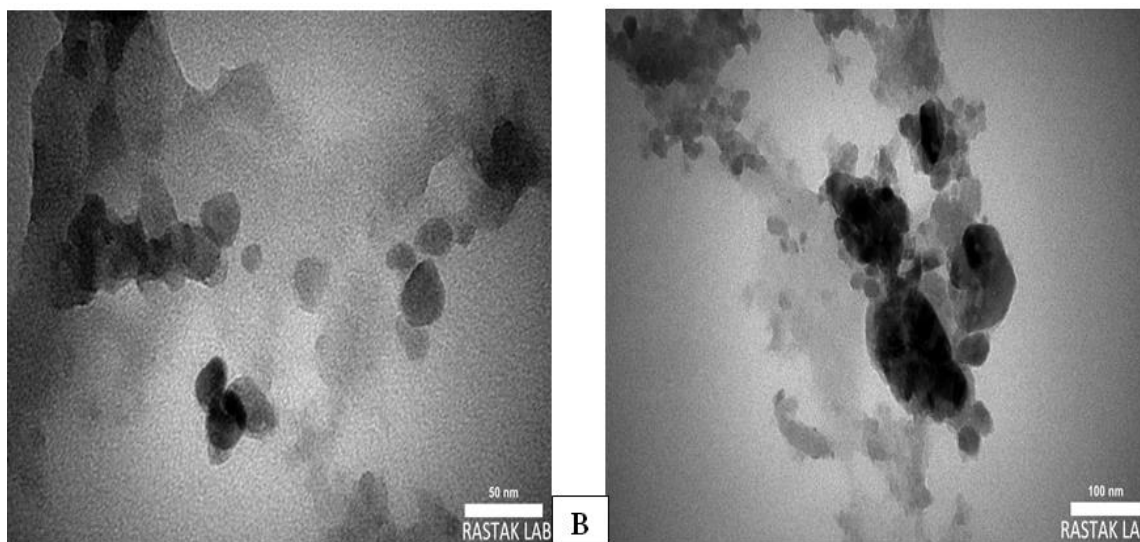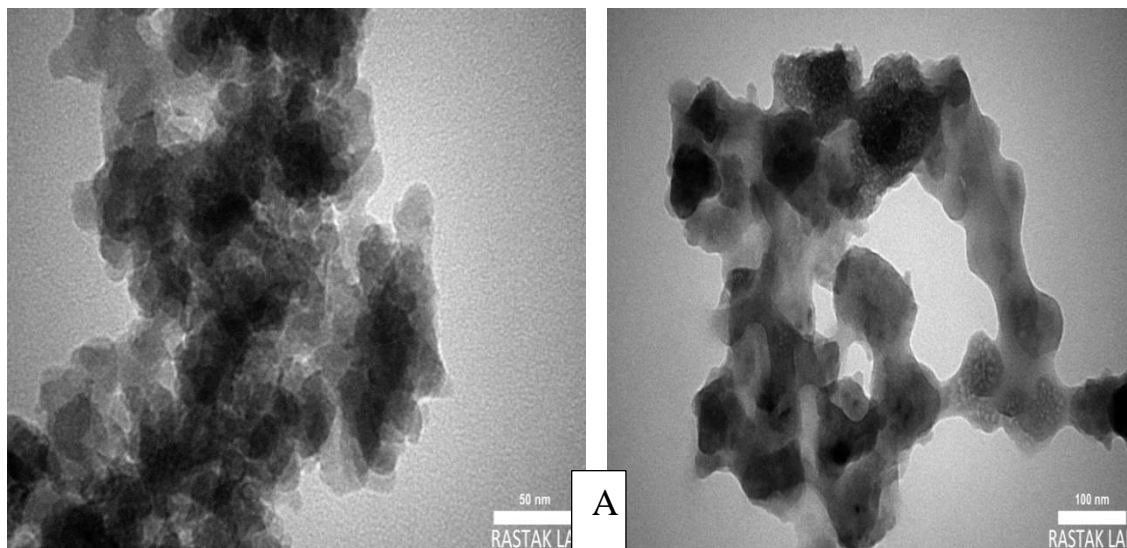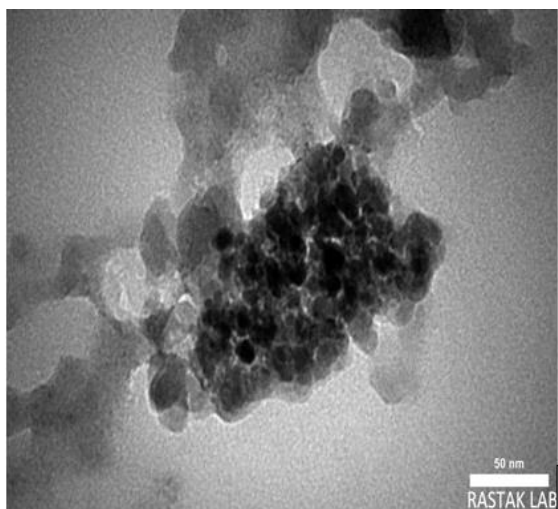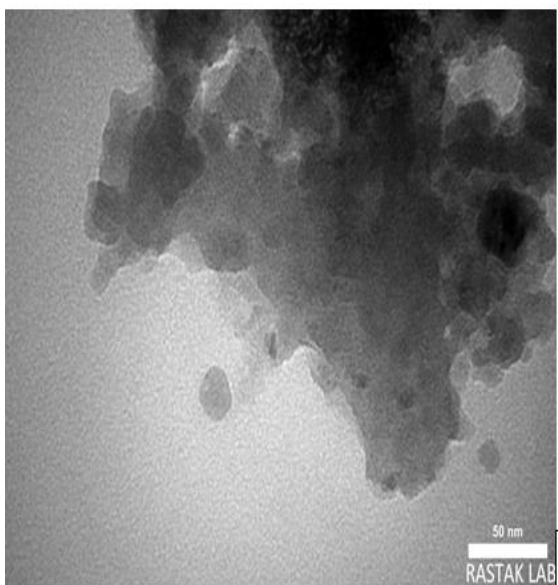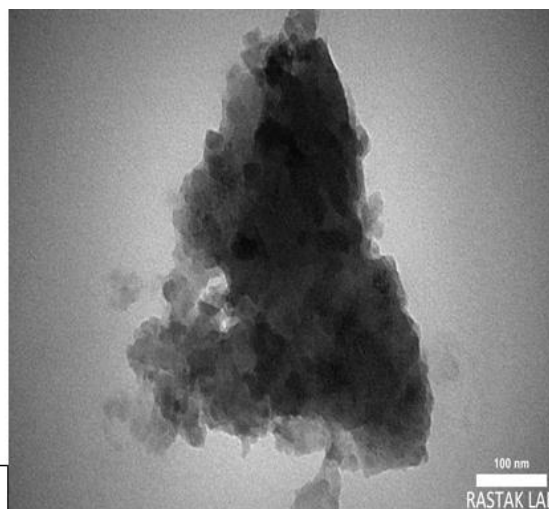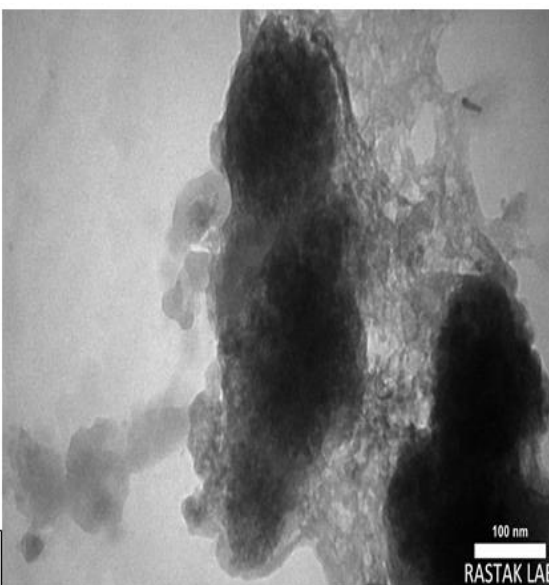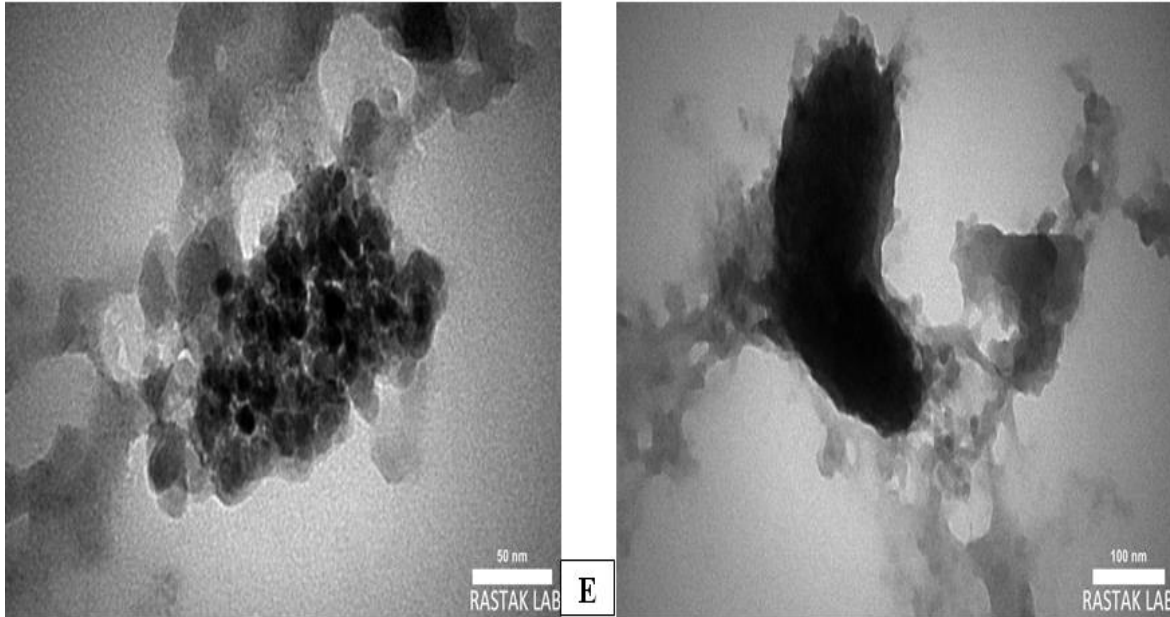
Figure ٣-٨ TEM images for (A) RH-SiO٢ (B) RH-SiO٢PrNH٢ (C) RH-SiO٢PrADB (D) Fe٣O٤@RH-SiO٢PrNH٢ (E) Fe٣O٤@RH-SiO٢PrADB

Through the images shown in Figure(٣-٨A) of the RH-SiO٢, it was found that there were irregularly agglomerated aggregates, which indicates that the shape of the particles is amorphous[١١٢] **Figure (٣-٨B)** shows the RH-SiO٢PrNH٢ sample, as it was observed that a transparent cloud appeared, with irregular and lumpy oval clusters in the middle, and this indicates that the silica coatings obtained from the rice husks are of an amorphous nature [١١٣]. While The RH-SiO٢PrADB was shown in **Figure (٣-٨C)**, the presence of spherical clusters linked together. It was found that the average particle size is ٣٥ nm, and this value is consistent with the results of the FESEM and XRD analysis. The Fe٢O٤@RH-SiO٢PrNH٢ compound is shown in **Figure(٣-٨D)** the Fe٢O٤ showed heterogeneous spherical shapes distributed on transparent Nano layers representing the RH-SiO٢PrNH٢ compound. This confirms the success of iron oxide grafting on the surface of the RH-SiO٢PrNH٢. In

addition, the rate of agglomeration of particles decreased as a result of the penetration of Fe_3O_4 particles between the nanoscale layers. Finally, the Fe_3O_4@RH-SiO$_2$PrADB compound is shown in the **Figure(٣-٨E)**. The images confirmed the success of Fe_3O_4 bonding on the RH-SiO$_2$PrADB surface, through the presence of black clusters spread on a wavy transparent surface. It was found that the average particle size was about ٥٠ nm.

٣.٩. Vibrating Sample Magnetometry (VSM)

VSM is a flexible method for determining a sample magnetic moment when it is vibrated perpendicular to a uniform magnetizing field. This approach can identify changes as tiny as $١٠^{-٥}$ to $١٠^{-٦}$ emu. Using Faraday law of magnetic induction as a foundation, the VSM approach can be used to determine a sample magnetic moment information where included the magnetic hysteresis curves of the Fe_3O_4, Fe_3O_4@RH-SiO$_2$PrNH$_2$, and Fe_3O_4@RH-SiO$_2$ADB nanocomposites are shown in **Figures (٣-٩ A ,B, and C)**
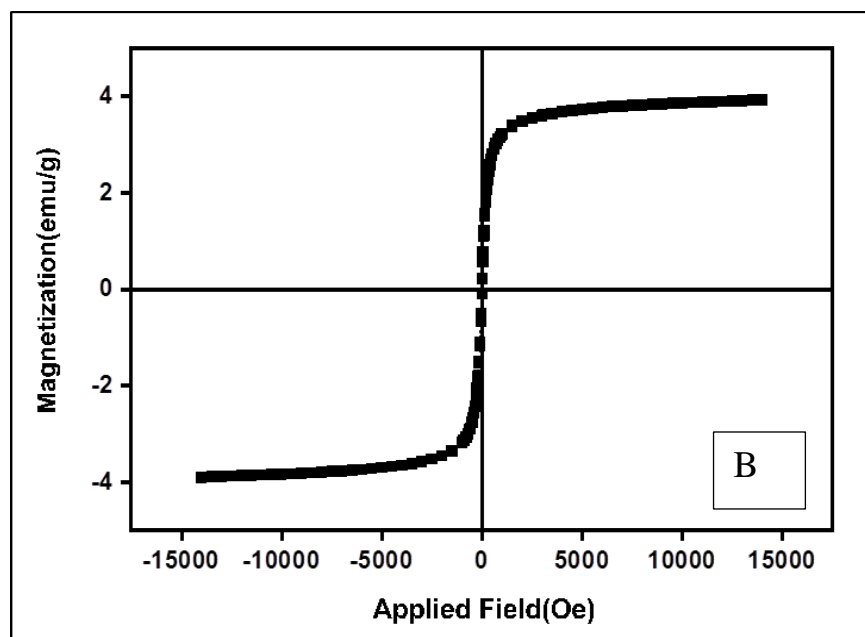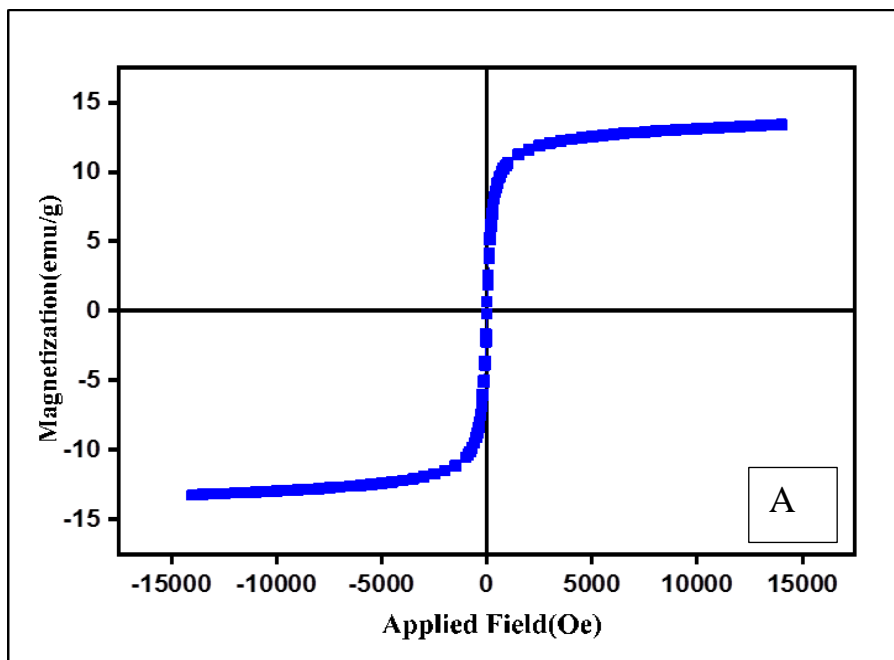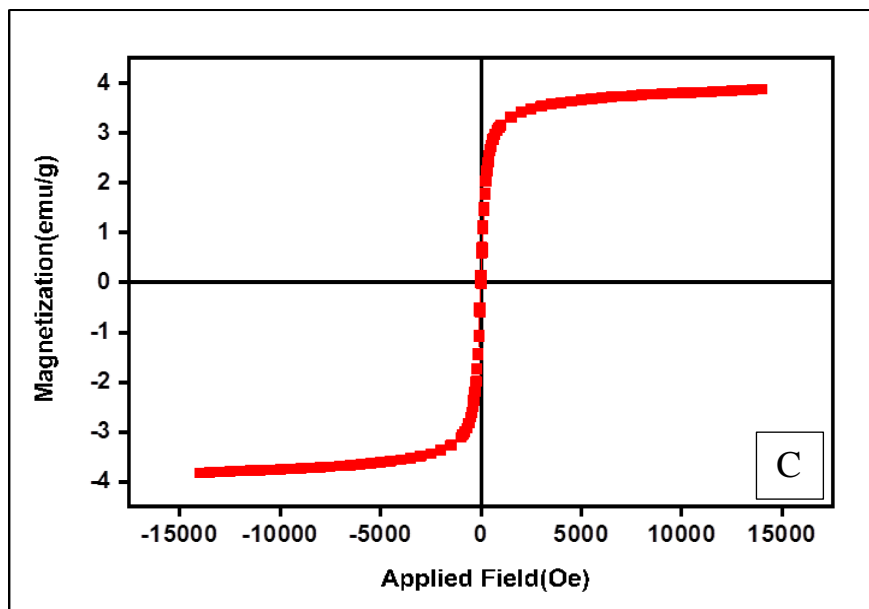
Figure ٣-٩ VSM spectra of (A) Fe٣O٤ (B) Fe٣O٤@RH-SiO٢PrNH٢ (C) Fe٣O٤@RH-SiO٢PrADB

The hysteresis loop showed that the prepared iron oxide (Fe₂O₄) has ferromagnetic behavior with a saturation magnetization up to ١٣.٣٩ emu g⁻¹[١١٤]. While the results of the saturation magnetization value for the Fe₂O₄@RH-SiO₂PrNH₂ and Fe₂O₄@RH-SiO₂ADB compounds showed a clear decrease in magnetism up to ٣.٨٨ and ٣.٨٧ emu g⁻¹, respectively. This is due to the addition of non-magnetic materials to the iron oxide that reduces the magnet moment of the compound. The addition of these materials with iron oxide leads to a complete coverage of the iron, and thus the attraction with the applied magnetic field decreases.

٣.١٠.Thermo gravimetric Analysis (TGA)

The main purpose of a TGA is to assess the thermal stability of various substances up to temperatures of about ١٠٠٠ °C. To detect variations in weight as an effect of rising temperature, TGA features a weight balance that

is incredibly sensitive. The instrument has a temperature limit of ١٥٠٠ °C and a sensitivity of ٠.١ g. To make sure thermal equilibrium was reached inside the sample, a heating rate of ١°C/min was used. To guarantee that the sample is not adversely affected by contaminants, the TGA is housed inside an inert gas glove box. The thermogravimetric analysis has been shown to be useful in the analytical technique of evaluating the kinetic parameters of different materials, which in turn provides valuable quantitative information on the stability of the material, as the thermogravimetric decomposition of the samples prepared in the temperature range of ١٠-٩٠٠°C is shown in Figure (٣-١٠).
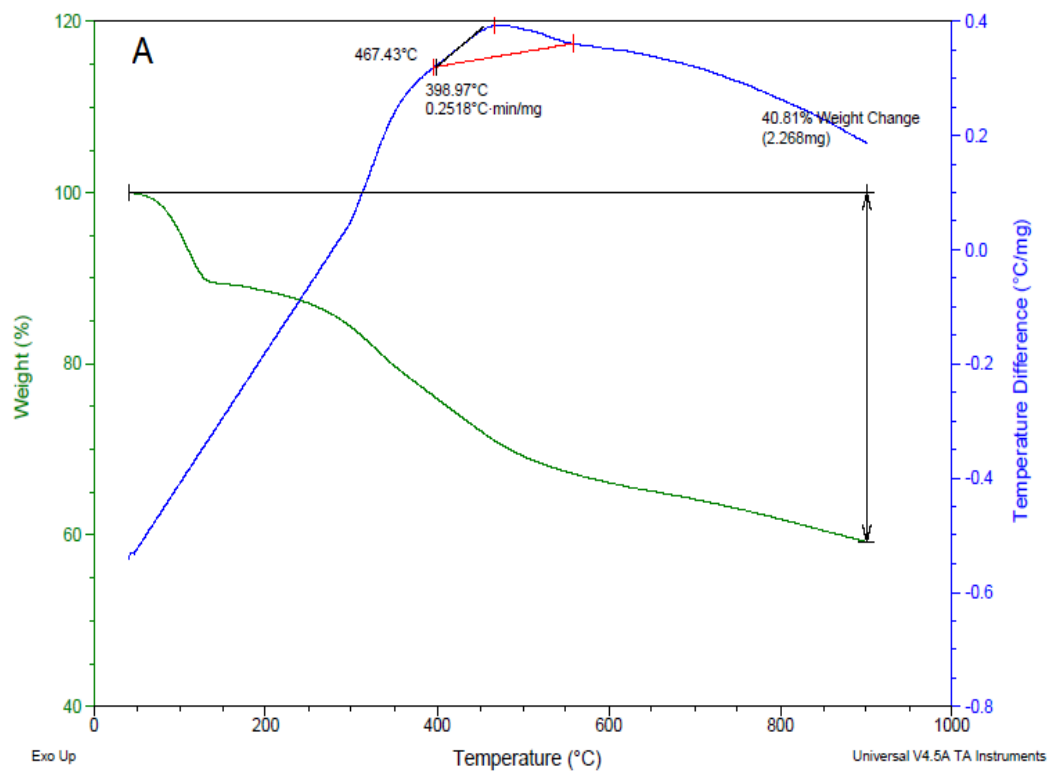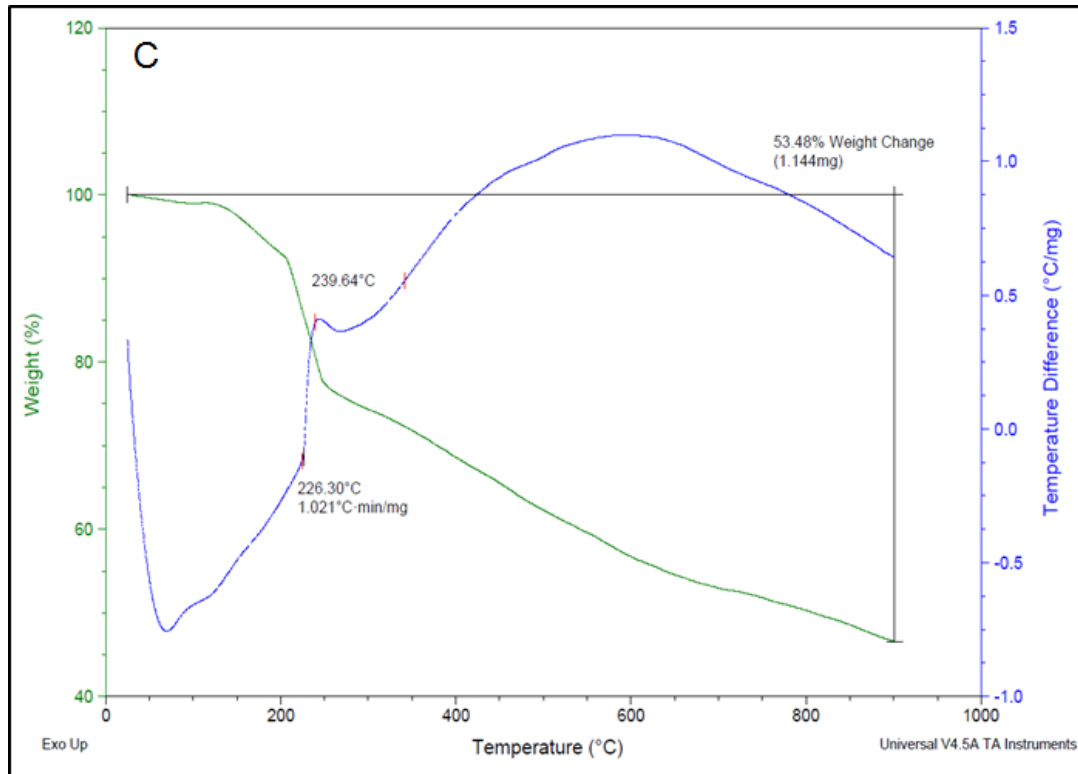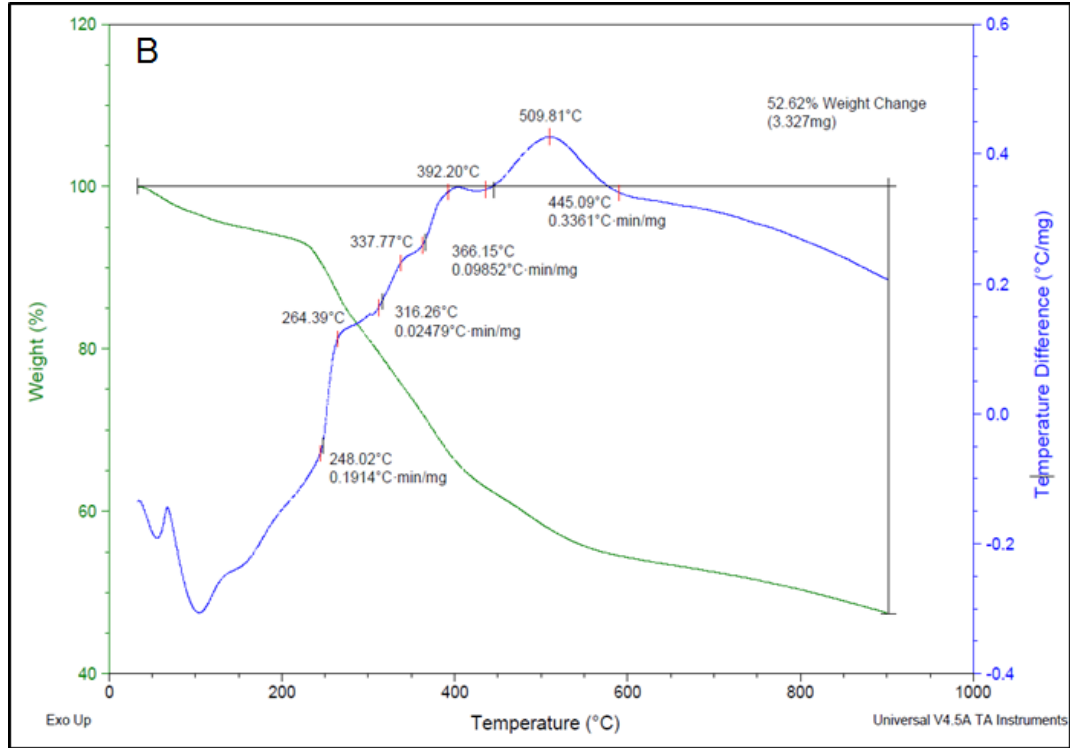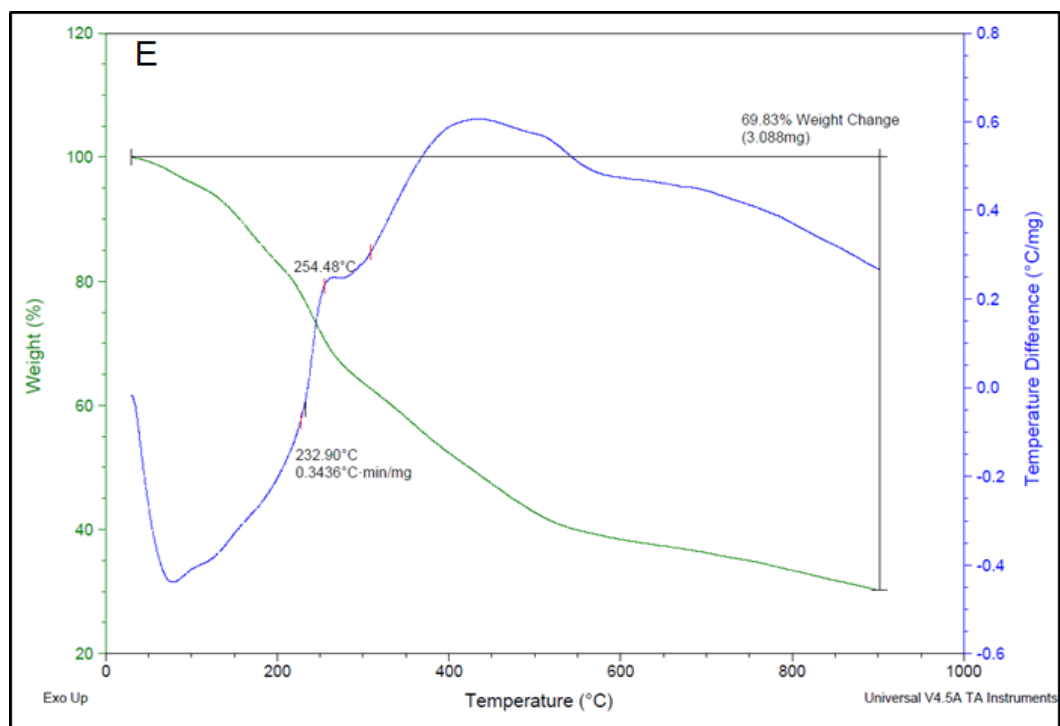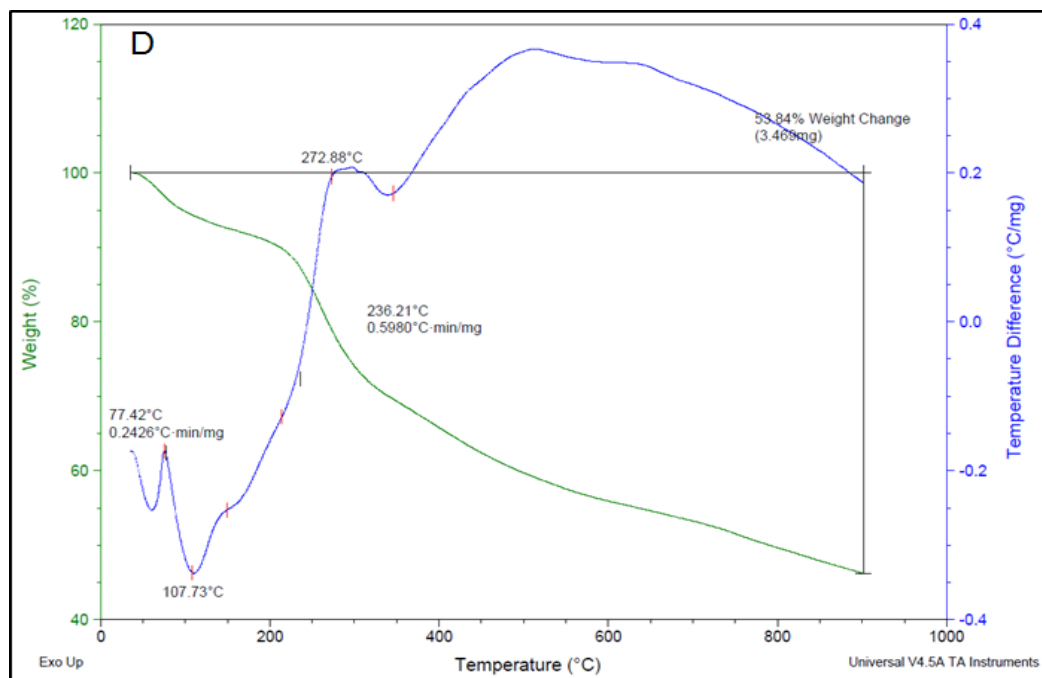
Figure ٣-١٠ TGA/DTA analysis of (A) RH-SiO₂ (B) RH-SiO₂PrNH₂ (C) RH-SiO₂PrADB (D) Fe₃O₄@RH-SiO₂PrNH₂ (E) Fe₃O₄@RH-SiO₂PrADB

Figure (٣-١٠A) shows of the RH-SiO₂ sample, as it was noted that the total loss percentage of ٤٠.٨١٪ was attributed to the loss of ١٠% of water molecules at ١٠٠°C, The second weight loss was ١٧٪ which was assigned to the decomposition of the salen moiety that happened between ٢٥٠ and ٦٠٠°C, and also ١٣٪ due to the condensation of silanol groups and the breaking of all bonds at ٦٠٠°C. The TGA spectrum showed that the compound has good thermal stability due to the fact that the percentage of loss by weight of the material is low at high temperatures[١١٥]. **Figure(٣-١٠B)** shows a decomposition of the RH-SiO₂PrNH₂ sample, as it was noted that the total loss percentage of ٥٢.٦٢٪ at temperatures between ١٠ and ٩٠٠ °C has included the loss of ١٢٪ of water molecules, ٢٦٪ of weight loss belong to the aminopropyl group, and finally about ١٤٪ attributed to the breakdown of the silanol bonds[١٠٣]. The TGA spectrum showed that the compound has good thermal stability due to the fact that the percentage of loss by weight of the material is low at high temperatures [١١٦] In contrast, the RH-SiO₂PrADB compound is shown in **Figure (٣-١٠C)**. The results indicated that the loss percentage reached (٥٣.٤٨٪) included the evaporation of ١٢٪ of water molecules, the dissociation of ٢٧% which was assigned to the decomposition of the ٢-amino-٣,٥-Dibromobenzaldehyde compound, And ١٤% weight loss due to the breaking of silanol bonds and the success of the synthesis process and the production of a compound with high stability [١١٧]. The Fe₂O₄@RH-SiO₂prNH₂ sample is shown in **Figure (٣-١٠D).** displays the results of the TGA analysis of the Fe₂O₄@RH-SiO₂PrNH₂ sample. The weight change was (٥٣.٨٤٪) at temperatures between ١٠ and ٩٠٠ °C, and this was attributed to; about ١١ % of mass loss of the physically absorbed water molecules, ٣٢ % of mass loss belong to the aminopropyl group, and finally about ١٣٪ attributed to the breakdown of the silanol bonds[١٠٣][١١٨]. While the thermogravimetric

analysis of Fe_2O_4@RH-SiO$_2$PrADB material was illustrated in **Figure (٣-١٠E).**, revealing three distinct stages of decomposition. The initial loss, about ١٤٪ of the sample mass, occurred at a temperature of ٧٥ °C and was attributed to the physical adsorption of water[١١٩]. The second mass loss, comprising approximately ٣٤٪ of the total sample mass, was observed within the temperature range of ٢٠٠–٦٠٠ ∘C and can be attributed to the loss of organic compounds onto the silica matrix, specifically aminopropyl group and ٢-amino-٣,٥-dibromobenzaldehyde, and finally about ٢١٪ attributed to the breakdown of the silanol bonds and transform to silicon oxide[٣٦]. The outcomes show that the synthesis procedure was successful and that a high-stability material was produced.

CHAPTER FOUR
METAL UPTAKE

٤. Metal Uptake

٤.١ Introduction

Numerous potentially harmful compounds have been introduced to the environment as a result of accelerated development and human activity activity [١٢٠]. Toxic heavy metal pollution of the environment resulting from numerous industrial activity is a global phenomenon[١٢١]. Because heavy metal contamination has a direct impact on public health[١٢٢], it is crucial to address this issue. Wastewater from contemporary chemical industries are the main sources of heavy metals.

The capture and removing of tiny amounts of metal from wastewater streams coming from diverse industrial processes is one of the most important aspects of the study under consideration today. Therefore, there was a lot of room for study into creating polysiloxane ligand systems that could preconcentrate and extract trace metal ions in a very selective manner[١٢٣].

In the scientific community, a number of common methods to remove tiny amounts of metal from wastewater were listed, such oxidation, membrane filtration, adsorption, ion exchange, and others. The most popular adsorbents, such as silica gel, activated carbon, and aluminium oxide, are employed frequently as an effective physical separation method to remove or reduce the concentration of contaminants (organic and inorganic) in contaminated waters[٧٦].

٤.٢   Experimental of Metal Uptake

Two types of ligands (RH-SiO$_2$PrADB &Fe$_2$O$_4$@RH-SiO$_2$PrADB) were used to remove a number of ions represented by cobalt, nickel and copper. The method was done using a volumetric vial containing ٥٠ ml of one of the ions such as cobalt with ٠.٠٢ g of one of the ligands such as of (RH-SiO$_2$PrADB), and it was shaken for ten minutes. After that, ٥ ml of the mixture was withdrawn and filtered. Through the needle of the syringe to remove the solid particles, then the residual concentration of the metal ion was measured by the solution absorption measurement every hour for ten hours. This method was used for nickel, and copper ions with one ligand at a time. The following equation was used to calculate the removal efficiency(E%) of copper, nickel and cobalt from aqueous solutions [٨٥]:

$$E \% = \frac{C_o - C_e}{C_o} \times 100$$

Where C$_o$ and C$_e$ are the initial concentration at zero and the adsorbed concentrations after contact time, respectively, The effects of trembling time, pH effect, ion concentration, and solid ligand mass (RH-SiO$_2$PrADB& Fe$_2$O$_4$@RH-SiO$_2$PrADB) were studied as optimization conditions.

٤.٣   Metal Uptake by RH-SiO$_2$PrADB

٢.٤.٥.   Effect of vibration time on Removal of metal ions from aqueous solution

The impact of reaction time on the removal of metal ions by (RH-SiO$_2$PrADB) was explored. The response was performed with ٠.٠٢ g ligands and shaken for ١٠ h with an aqueous solution of divalent metal ions at a

concentration of ٠.٠٦ M. Calculation of the ion concentration removed by ligand every ١ h. The amount of time spent stirring is a crucial component of process the removal of metal ion since it demonstrates how quickly metal ions bind entirely to the surface. The impact of contact time on the adsorption process is depicted in Figure (٤-١). An excellent heavy metal removal (of cobalt, nickel, and copper) requires a minimum contract duration of ١ h, as can be seen from the fact that metals removal increases with increasing time in the first five hours and then becomes negligible beyond that , where it was the following results have been obtained at five o'clock (Co(II) ٧٨٪, Ni(II) ٨٢٪, and Cu(II) ٨٦٪). This suggests that heavy metal removal reaches its maximum within five hours, at which point the concentration of metals in the solution stabilizes. This may be attributed to the initial availability of many unoccupied sides for adsorption, which finally slowed down as a result of the solute molecule's attraction to the bulk phase and the exhaustion of the remaining surface sites[٩٩]. The optimal stirring time for the following studies has been determined to be ٥ hours based on the results.
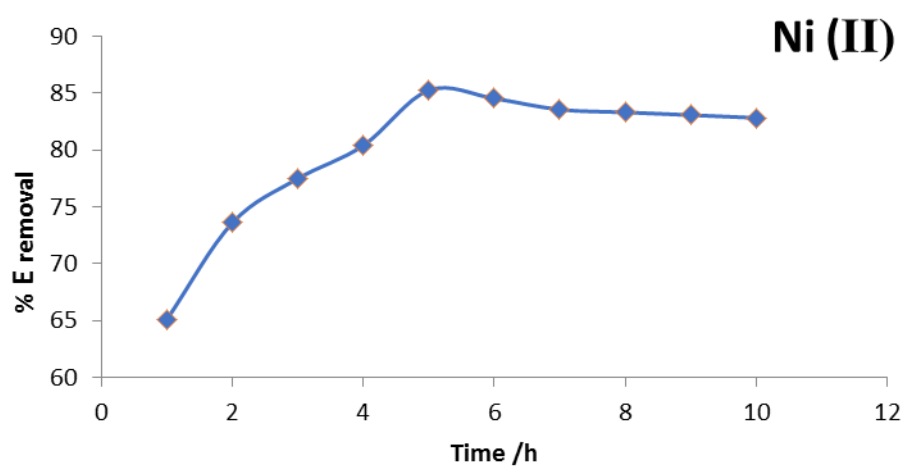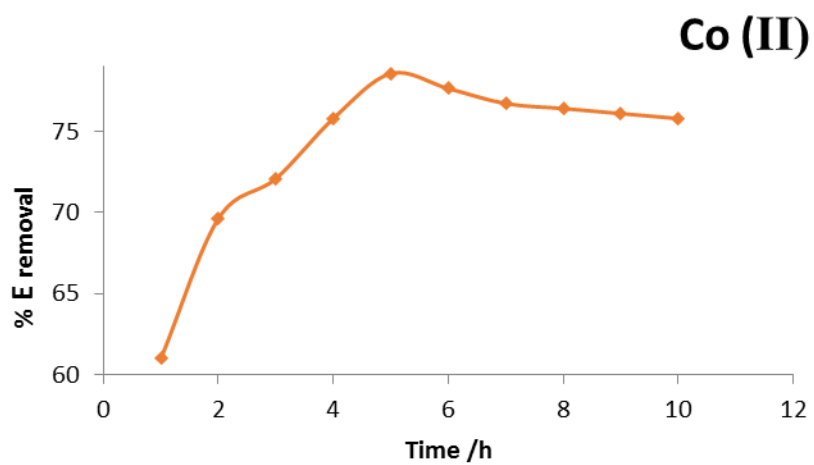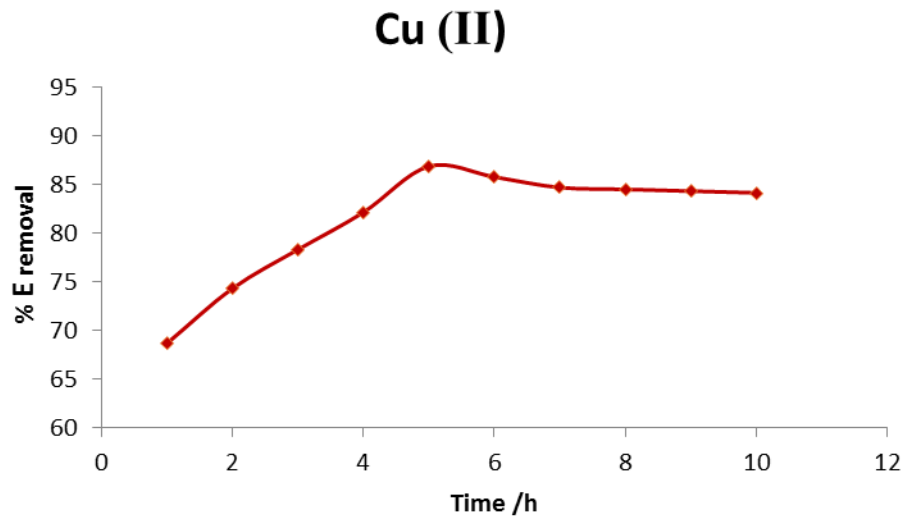
Co (II)

Ni (II)

Figure ٤-١ Effect of vibration time on removal of metal ions(Co(II), Ni(II) and Cu(II) (concentration ٠.٠٦M) by the ligand RH-SiO٢PrADB (dose = ٠.٠٢ g)

٢.٤.٦. Effects of concentration metal ions on the removal by the ligand RH-SiO٢PrADB

The impact of metal ion concentration was studied at different concentrations (٠.٠١, ٠.٠٤, ٠.٠٦, and ٠.٠٩ M) for each metal ion. Which was removed by the ligand RH-SiO٢PrADB (٠.٠٢ g). The results shown in Figure (٤-٢) show that the removal rate of ions increases with the increase in the concentration used, where the removal rate is (Co ٦٨٪, Ni ٦٣٪, and Cu ٧٨٪) when using ٠.٠١ M, while it rises to (Co ٨٢ %, Ni ٩٢٪, and Cu ٩٥٪) when using ٠.٠٩ M. This can also be explained by the fact that as the ion concentration increases, more adsorption sites are being covered. The reason for this is due to the availability of a greater number of ions in the solution with an increase in the concentration used, which gives a greater opportunity to occupy most of the ligand site. It should be noted that the removal rate decreases after five hours[١٢٤].
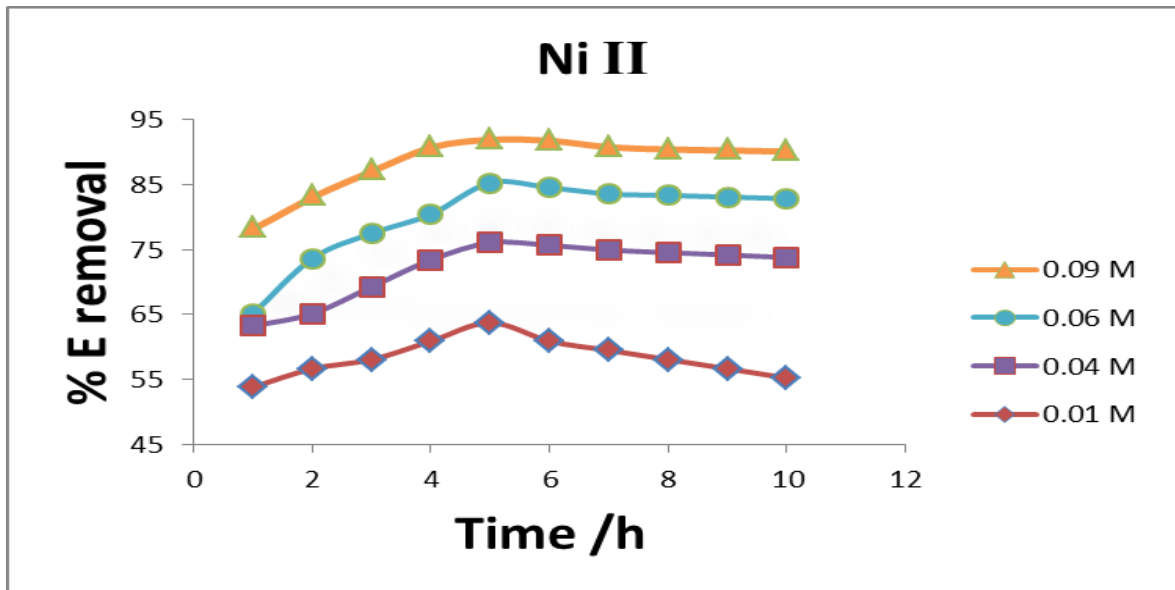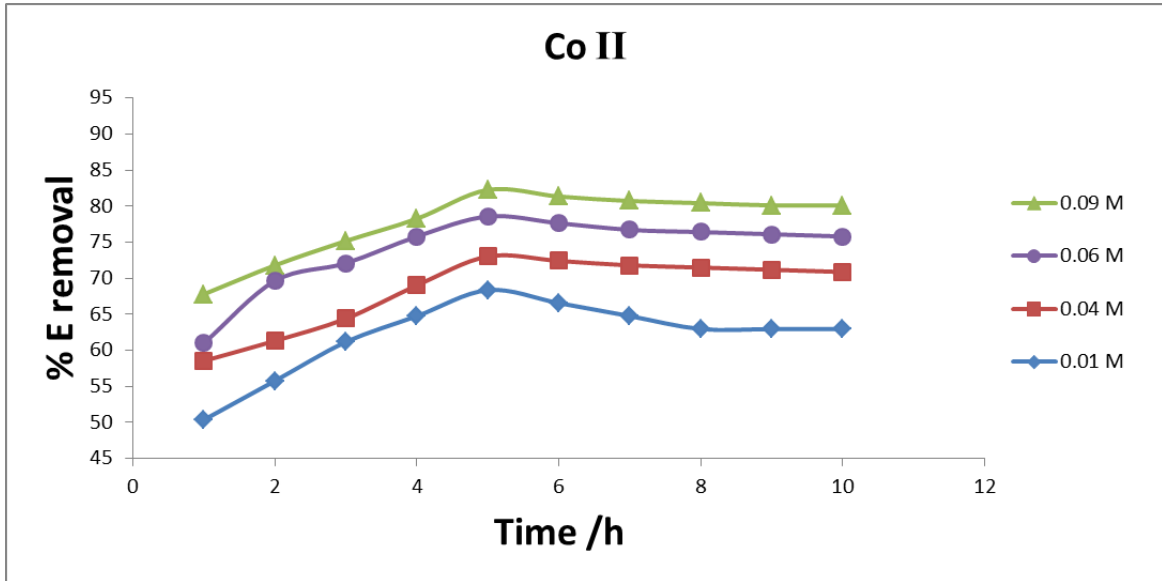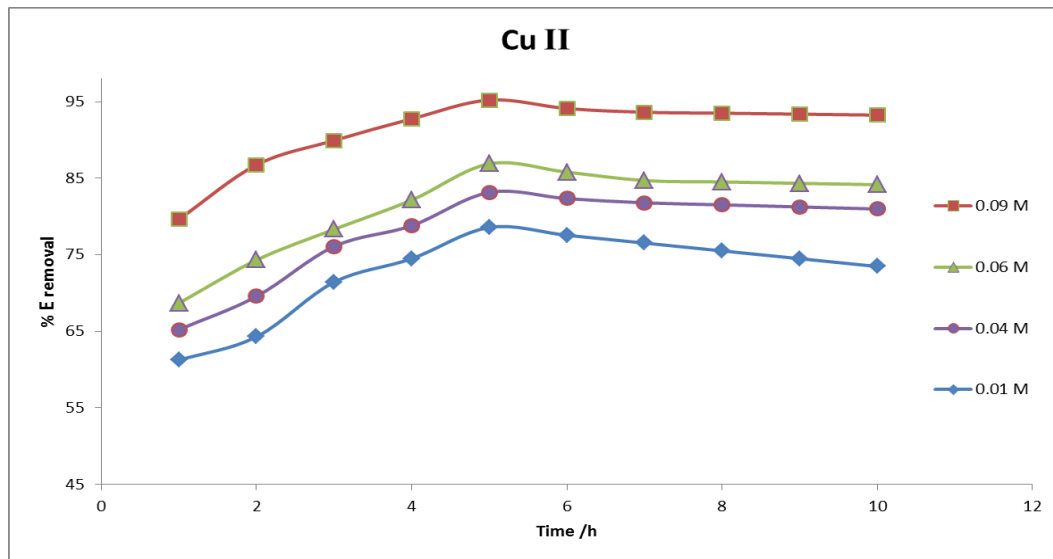
Co II

Ni II

Figure ٤-٢ Effects of concentration metal ions on the removal by the ligand RH-SiO٢PrADB (dose= ٠.٠٢ g)

٢.٤.٧. Effect of the weight of the RH-SiO٢PrADB

Different weights of the ligand were used, which are (٠.٠١, ٠.٠٢, ٠.٠٣, ٠.٠٤ g) in solution of metal ions at a concentration of ٠.٠٩ M. It was observed through the results as shown in Figure (٤-٣) that the removal rate of ions is as high as possible when using ٠.٠٢ g of the weight of the ligand, where the rates of removal of ions were (cobalt ٨٢٪, nickel ٩٢٪, and copper ٩٥٪), then the percentage decreased slightly when the weight of the ligand increased. This decrease in the removal value is explained by the agglomeration of the ligand at The use of weights higher than ٠.٠٢ g in the same volume used in the study, which causes agglomeration, closure of some active sites on the surface of the ligand, and this leads to a decrease in the surface area of the adsorbent surface[١٢٥].

Co II

Ni II

Figure ٤-٣ Effect of the weight of the RH-SiO٢PrADB on the removal of metal ions (Co(II), Ni(II) and Cu(II) (concentration ٠.٠٩M) by the ligand RH-SiO٢PrADB (dose= ٠.٠٢ g)

٢.٤.٨. Effect of pH on E removal of metal ions by the ligand RH-SiO٢PrADB

The effect of pH on the removal of metal ions was studied at a concentration of ٠.٠٩ M of ion with use ٠.٠٢ g of the ligand RH-SiO٢PrADB. The results shown in Figure (٤-٤) showed that the removal percentage of cobalt and nickel was as high as possible at pH= ٢ (Co ٩٥.٨٪ and Ni ٩٥.٥٪), while copper ions had the highest removal percentage at The pH= ٥ (Cu ٩٥.٢٪). The reason for this is due to the fact that cobalt and nickel ions in aqueous solutions are surrounded by water molecules in the form of hexagons, In highly acidic environments, the hydrogen ion will react with water molecules to form the hydronium ion, thus making the metal ions more free in solution and therefore the removal rate is higher. As for the copper molecules, they take either a tetrahedral shape or an angular shape with the water molecules. Therefore, the copper particles in the high acid medium pH٢ tend to interact with the negative ions in the solution, so they return again to CuCl٢,

but in the weak acid medium their effect is almost non-existent, so the removal rate is high[٣٠].
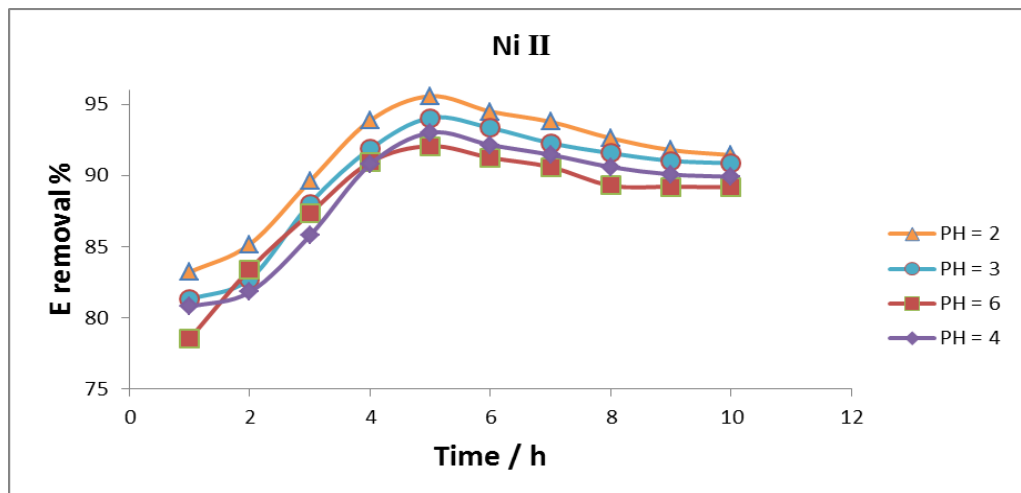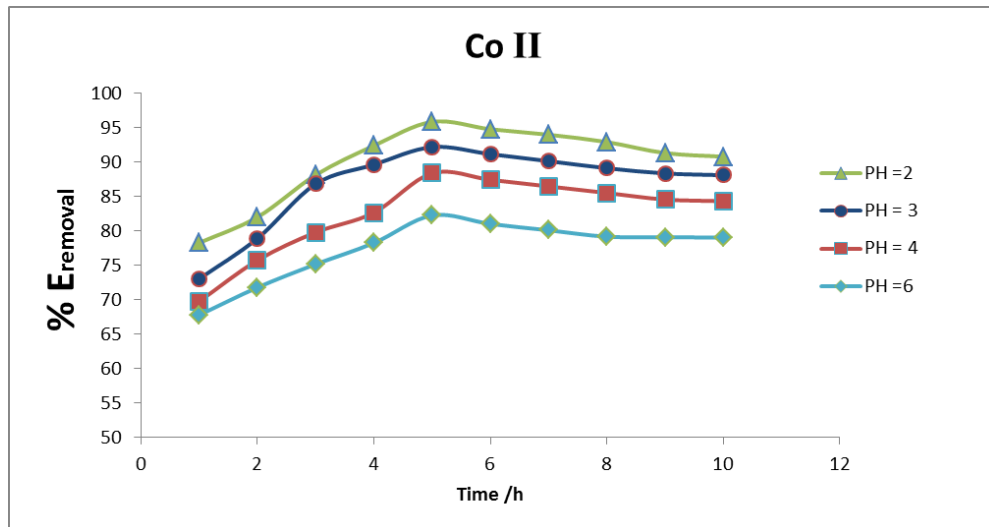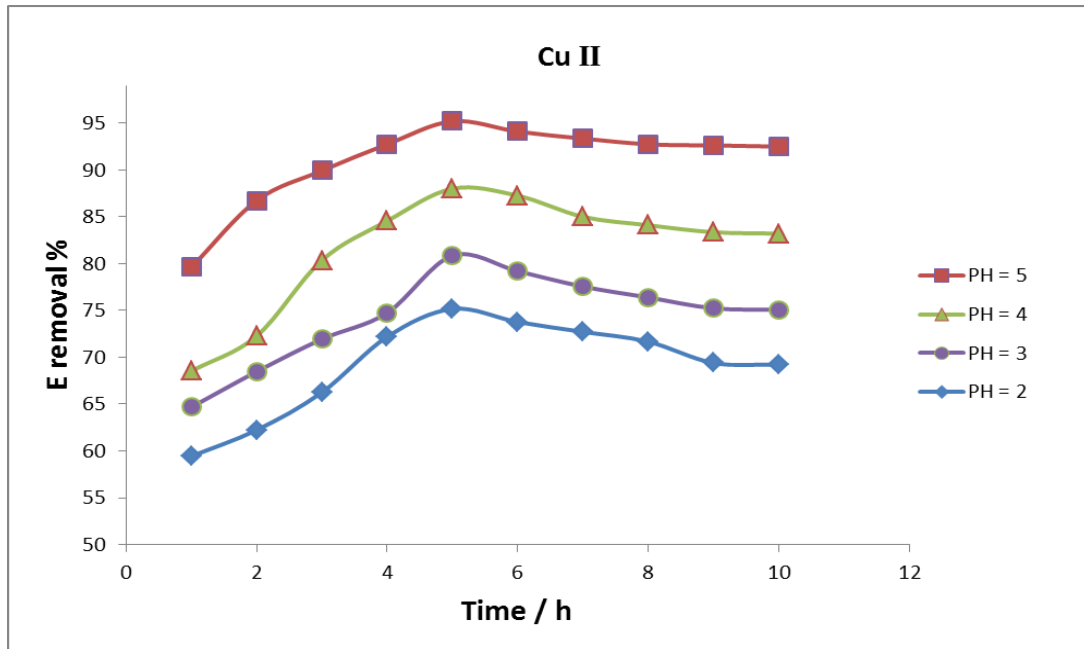
Figure ٤-٤ Effect of pH on the removal of metal ions (Co(II), Ni(II), and Cu(II) (concentration ٠.٠٩M) by the RH-SiO٢PrADB(dose= ٠.٠٢ g)

٤.٤   Metal Uptake by Fe٢O٤ @ RH-SiO٢PrADB

٢.٤.٩. Effect of vibration time on Removal of metal ions from aqueous solution by the ligand Fe٢O٤@ RH-SiO٢PrADB

The effect of the reaction time of the ligand (Fe٢O٤@ RH-SiO٢PrADB ٠.٠٢g) with a solution of ions was studied in paragraph ٤.٣.١. It was noted through the results that the removal of all metal ions increases over time during the first four hours to reach a peak at the fourth hour, after which the concentration of ions reaches equilibrium. Where the removal percentage was (Co ٩٠٪, Ni ٩٣٪, and Cu ٩٤٪), which is shown in Figure (٤-٥). The reason for the increase in the removal of ions during a shorter period of time than the previous ligand (RH-SiO٢PrADB) is the presence of magnetic iron oxide, which gives the surface magnetic characteristics, which changes the surface charge and increases the withdrawal of positive ions [١٢٦][١٢٧].
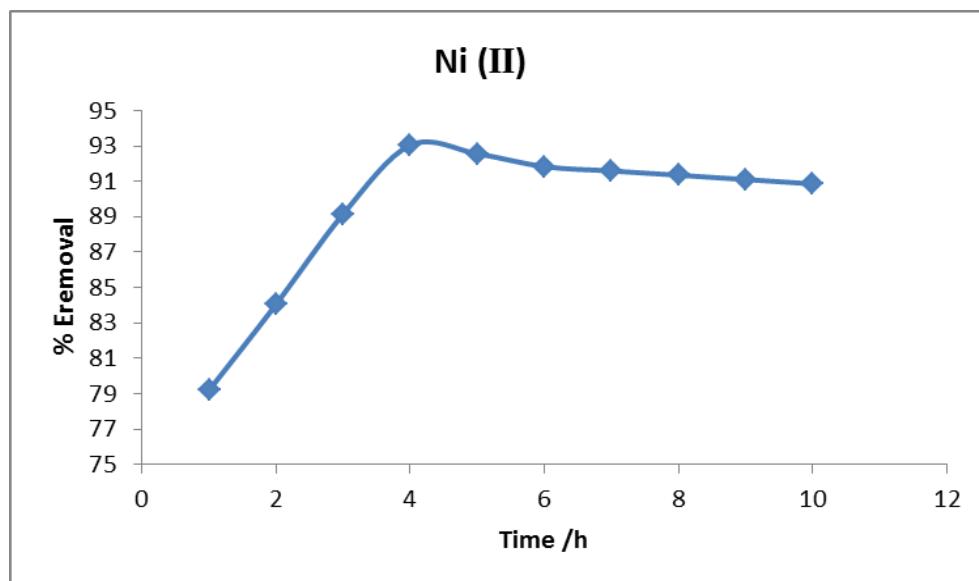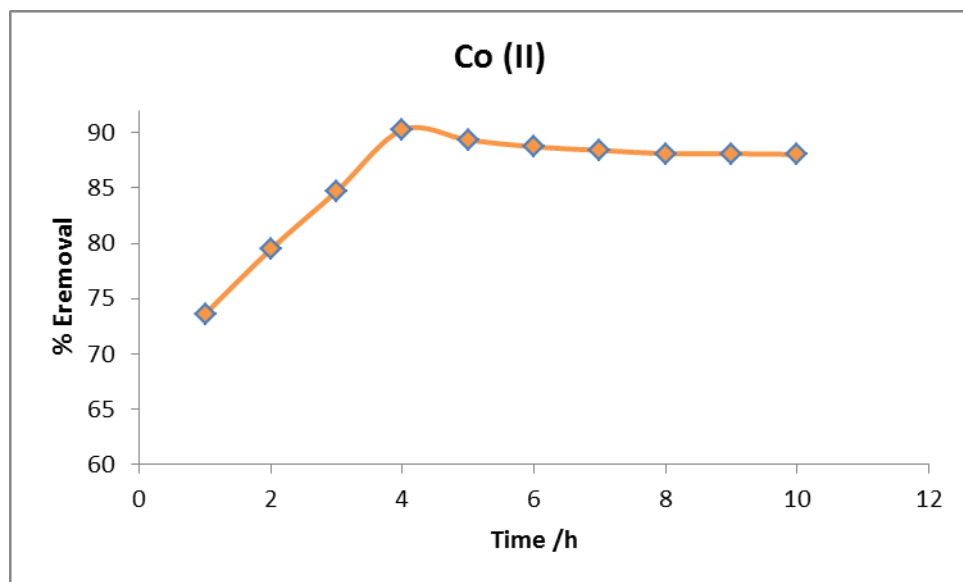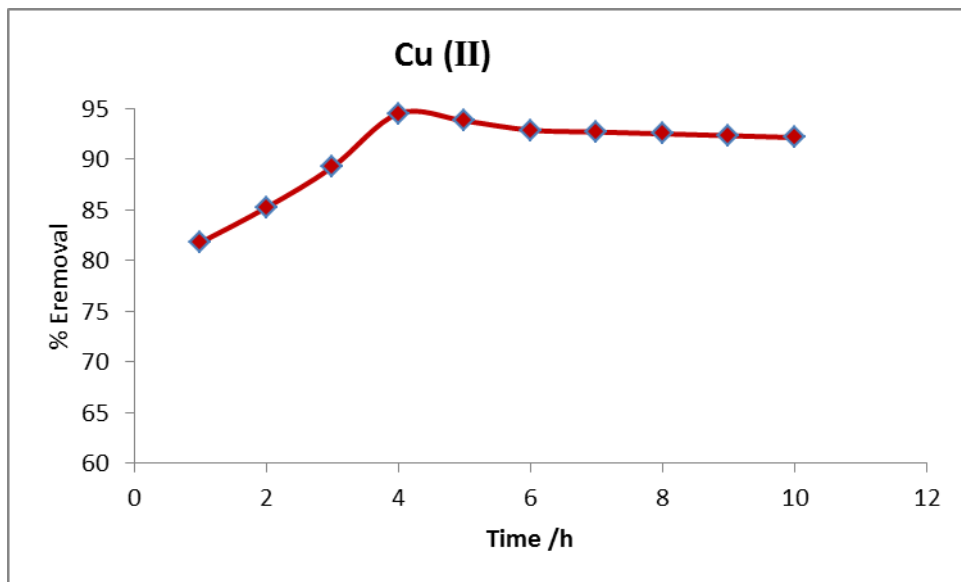
Co (II)

Ni (II)

Figure ٤-٥ Effect of vibration time on removal of metal ions Co(II), Ni(II) and Cu(II)

٢.٤.١٠.Effects of concentration metal ions on the removal by the ligand Fe₃O₄@ RH-SiO₂PrADB

The effect of metal ion concentration was studied at different concentrations (٠.٠١, ٠.٠٤, ٠.٠٦, ٠.٠٩ M) for each metal ion. which was removed by the Fe₃O₄@RH-SiO₂PrADB ligand (٠.٠٢ g). The results shown in Figure (٤-٦) show that the percentage of removal of ions increases with the increase of the concentration used, where the percentage of removal after four hours (Co ٦٤%, Ni ٦٦%, Cu ٨٦%) when used. ٠.٠١ M, while it rises to (Co ٩٣٪, Ni ٩٥٪, Cu ٩٧٪) when ٠.٠٩ M is used after the same period of time has passed at the same time. This can be explained by the fact that as the concentration of ions increases, more adsorption sites are covered[١٢٨].
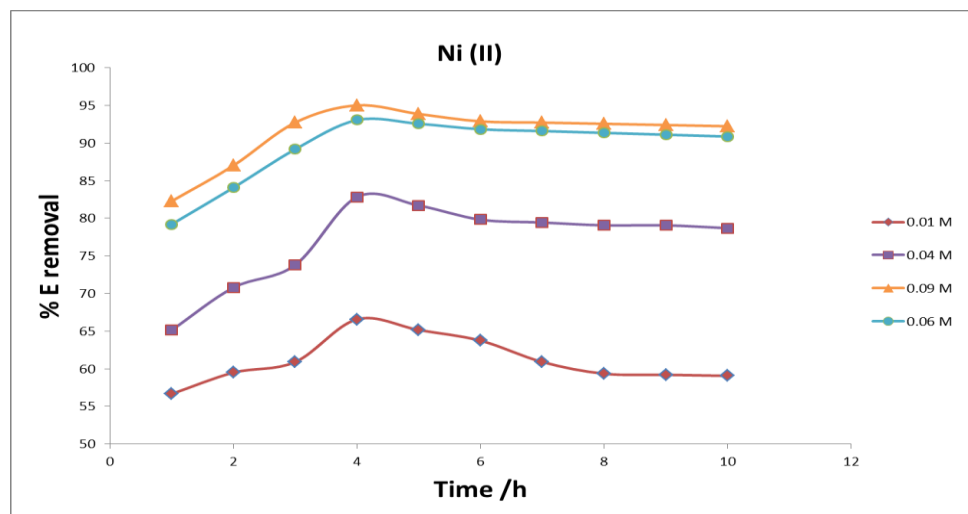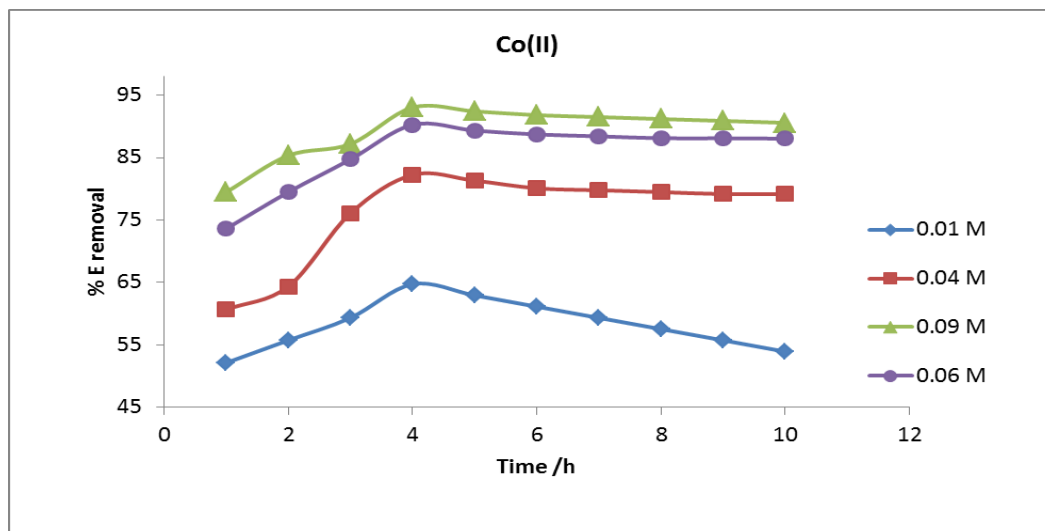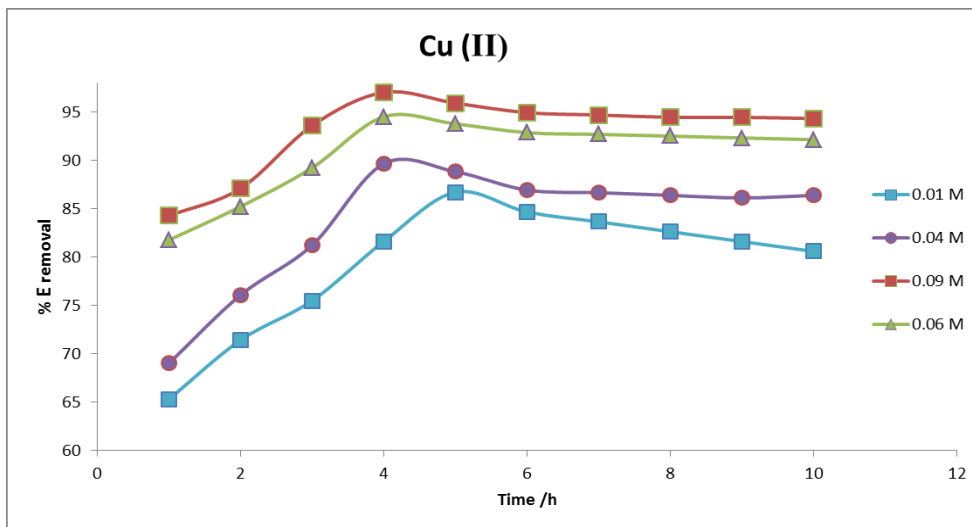
Figure ٤-٦ Effect of concentration of metal ions (Co(II), Ni II and Cu(II)) on the removal by the ligand Fe٣O٤@RH-SiO٢PrADB (dose= ٠.٠٢ g)

٢.٤.١١.Effect of the weight of the Fe₃O₄@ RH-SiO₂PrADB

Different weights of the ligand were used, which are (٠.٠١, ٠.٠٢, ٠.٠٣, ٠.٠٤ g) in a solution of metal ions at a concentration of ٠.٠٩ M. It was observed through the results as shown in Figure (٤-٧) that the removal rate of ions is as high as possible when using ٠.٠٢ g of the weight of the ligand Fe₃O₄@ RH-SiO₂PrADB, where the rates of removal of ions were (cobalt ٩٣٪, nickel ٩٥٪, and copper ٩٧٪), then the percentage decreased slightly when the weight of the ligand increased. This decrease in the removal value is explained by the agglomeration of the ligand at The use of weights higher than ٠.٠٢ g in the same volume used in the study, which causes agglomeration, closure of some active sites on the surface of the ligand, and this leads to a decrease in the surface area of the adsorbent surface[١٢٩].

Co (II)

Ni (II)

Figure ٤-٧ Effect of the weight of the Fe٣O٤ @ RH-SiO٢PrADB on the removal of metal ions (Co(II), Ni(II) and Cu(II) at a concentration ٠.٠٩ M

٢.٤.١٢. Effect of pH on E removal of metal ions

The effect of pH on the removal of metal ions from pH ٦ to ٢ was studied by the Fe٣O٤@RH-SiO٢PrADB ligand. The pH value of metal ions before the change (pH ٦, ٦, and ٥ for Co^{+2} , Ni^{+2} and Cu^{+2} respectively). The results showed as in Figure (٤-٨), that the percentage of metal ions removal decreased in acidic media when the pH is low, the concentration of H^+ ions is very high in the solution, and therefore a competitive reaction will occur between them and the ions that carry a positive charge on the sites. In addition, the surface of the overlay contains hydroxyl groups in the silica, where the amount of H^+ is low, and thus hydrogen bonding will occur between the chains on the surface. Thus, the surface is in a state of shrinking, which increases the difficulty of the diffusion of metal ions into the surface of the overlay. In addition, the Fe٣O٤ particles will react with the HCl which was used to adjust the pH and dissolve as FeCl٢ and FeCl٣[١٢٩].
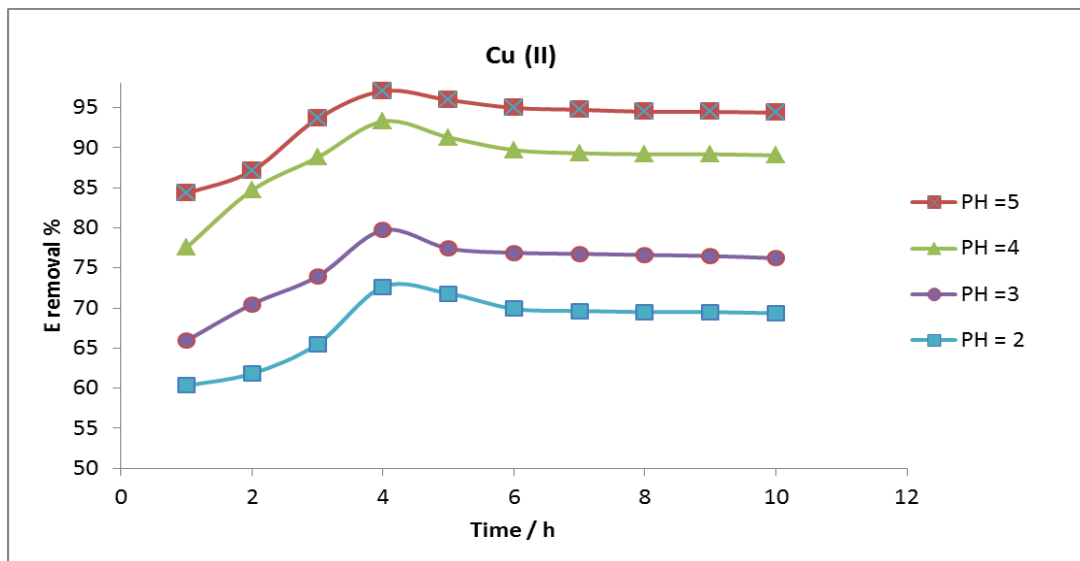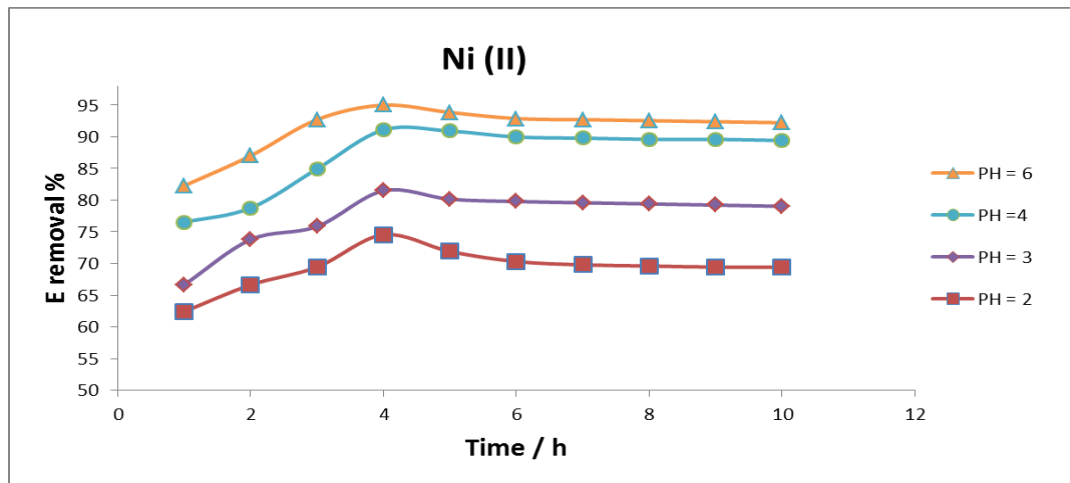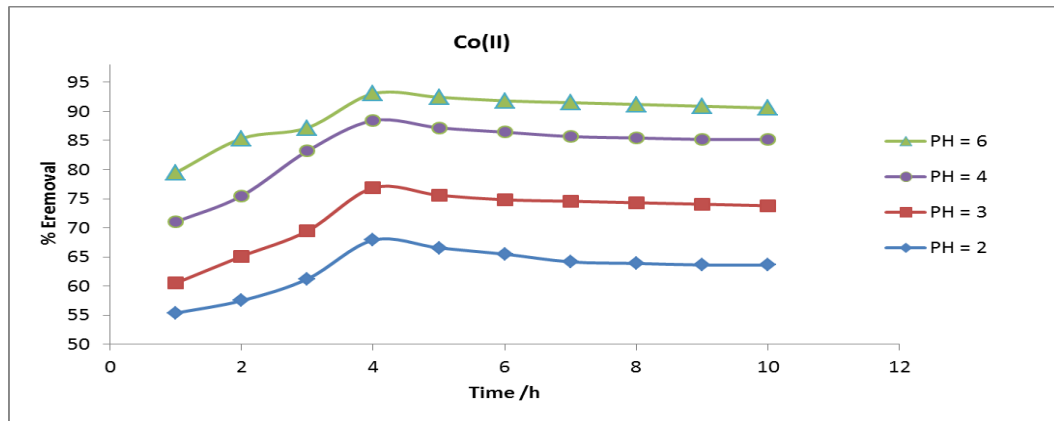
Figure ٤-٨ Effect of pH on the removal of metal ions (Co(II), Ni(II) at a concentration ٠.٠٩ M, and Cu(II) by the Fe٣O٤ @ RH-SiO٢PrADB(٠.٠٢ g)

٥. Conclusions

١- This study was based on the preparation of hybrid solid organosilicon ligand systems and was used in the uptake some of metal ions from an aqueous solution.

٢- Extracted silica was prepared from Iraqi rice husks to be used to remove pollutants and get rid of pollution resulting from rice husks.

٣ - The hybrid solid ligands (RH-SiO٢PrADB &Fe٣O٤@RH-SiO٢PrADB) were applied in the removal of metal ions (Ni(II), Co(II), and Cu(II)) from aqueous solution. From this application can be concluded:

a- The removal of metal ions as a function of exposure time was shown to be enhanced in a nonlinear fashion and the increase in the removal of metal ions over time is due to diffusion factors.

b- That removal increases when the acidity of the solution increases

c- The ability to remove heavy metal has been increased with an increase in the concentration of metal ions, which may be due to the increased driving power of the concentration of metal ions.

d- The obtained results showed that the maximum removal increased as the mass of the ligand decreased for (Ni (II), Co (II), and Cu(II)) ions. This can be due to a block of donor sites of solid ligands by the ligand itself.

Future studies

To further pursue this area of study, the investigator would like to suggest the following as a future project:

١. It would be intriguing to take into account several sources for the synthesis of amorphous silica.

٢. It is of interest to study the functionalization of silica with various organic group types.

٣. creation of novel organosilica compounds appropriate for applications in the steel, cement, and insulation industries.

٤. Use additional parameters, like temperature, in uptake applications.

٥. Use other elements, in removal applications to help in little pollution.

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الملخص

يتجه العالم نحو استخدام أفضل الطرق العلمية للتخلص من التلوث البيئي. بعض العناصر المعدنية هي ملوثات طبيعية وصناعية مثل الكوبالت والنحاس والنيكل. كما تعتبر قشور الأرز من الملوثات التي تنتج يومياً في جميع أنحاء العالم. ولذلك تم استخدام قشور الأرز لإنتاج مركبات للتخلص من بعض العناصر الملوثة، وبالتالي القضاء على نوعين من الملوثات في نفس الوقت. تم تحضير سيليكات الصوديوم من قشور الأرز، ثم تفاعل مع ٣-أمينوبروبيل ثلاثي إيثوكسيسيلان لإنتاج RH-SiO₂PrNH₂عبر طريقة sol-gel التي تم تشخيصها باستخدام FTIR وأظهرت أن الاهتزازات NH₂ و NH تم امتصاصها عند ٣٢٨٣ و٣١١٣ سم-١ على التوالي. ثم تفاعل RH-SiO₂PrNH₂مع 2-amino-٣,٥-dibromobenzaldehyde لينتج RH-SiO₂PrADB والذي تم تمييزه باستخدام عدة تقنيات N۲ Adsorption–Desorption Analysis (FTIR, XRD, FESEM-EDX, CHN, AFM, TEM, TGA/DTA :

يعرض طيف FT-IR مجموعة الآزوميثين (C=N) ممثلة بالذروة عند ١٦٤٢ سم⁻¹. أظهر أطياف XRD الطبيعة غير المتبلورة للمركب المحضر. يشير التحليل العنصري لمركب-RH SiO₂PrADB إلى أن نسبة الكربون والنيتروجين هي ١٦.٦٣% و٦.٤%. تظهر صور FESEM زيادة في خشونة السطح الخارجي للعينة مع زيادة في معدل تراكم الجسيمات النانوية نتيجة ترابط RH-SiO₂PrNH₂مع مركب ۲ -amino-٣,٥-Dibromobenzaldehyde. كما أكدت صور FAMزيادة واضحة في معدل الخشونة لتصل إلى ١٦.٢٤ نانومتر. يشير هذا إلى الارتباط الناجح لـ RH-SiO₂PrNH₂مع مركب ۲ -amino-٣,٥-Dibromobenzaldehyde. بينما أظهرت صور TEM، وجود مجموعات كروية مرتبطة ببعضها البعض. وقد وجد أن متوسط حجم الجسيمات هو ٣٥ نانومتر، وهذه القيمة تتفق مع نتائج تحليل FESEM و XRD. ويبين تحليل TGA أن نسبة الفقد وصلت إلى (٥٣.٤٨%) بسبب تبخر جزيئات الماء الممتزة وتفكك مركب ۲-أمينو-٣,٥-ثنائي بروموبنزالديهيد، وبالتالي كسر روابط السيلانول ونجاح عملية التخليق. وإنتاج مركب ذو ثباتية عالية. كانت المساحة المحددة وقطر المسام لـ RH-SiO₂PrADB تستخدم تحليلBET ، وتم تحديدها لتكون مساوية لـ ٣.٨١٨ م٢/جم، و١.٢١ نانومتر، على التوالي .

بالإضافة إلى ذلك، تمت معالجة سيليكات الصوديوم بإضافة Fe_3O_4 لإنتاج سلكيات نانوية مغناطيسية. باتباع نفس الطريقة السابقة، تم إنتاج $Fe_3O_4@RH\text{-}SiO_2PrADB$ ويتميز بعدة تقنيات (FTIR ، XRD، FESEM-EDX، CHN، AFM، TEM، TGA/DTA)

أظهر طيف FT-IR نطاق امتصاص عند ٦٣٦.٥ و٥٧٠.٩ سم$^{-1}$ بسبب رابطة Fe-O بالإضافة إلى نطاقات نفس الامتصاص للمركب RH-SiO_2PrADB. أظهر مركب طيف XRD إزاحة واضحة في الذروة العريضة عند (2θ=٢٢.٥° -٢٨.٨°) بسبب مركب RH-SiO_2PrABD والقمم الحادة عند (2θ= ٢٩.٢°, ٣٥.٤°, ٣٩.١°, ٤٢.٤°, ٤٧.٩°, ٥٧.٠°, ٦٢.٨°, ٦٧.٠°) بسبب التركيب المكعب لـ Fe_3O_4 وقد لوحظ أن المركب المحضر غير متبلور.

تم تحضير ليكاندات صلبة هجينة لامتصاص أيونات المعدن من محلولها المائي باستخدام ظروف مختلفة مثل:- زمن التعرض، الرقم الهيدروجيني، تركيز أيون المعدن، وكتلة الليكاند.

جامعة كربلاء

كلية العلوم

قسم الكيمياء

إزالة بعض الأيونات الفلزية بواسطة ليكاند متعدد المنح مثبت على البولي سيلوكسان

رسالة

مقدمة لكلية العلوم / جامعة كربلاء وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

كتب بواسطة

أيام طارق عبد الكاظم

بكالوريوس. كيمياء (٢٠١٣) / جامعة واسط

يشرف عليها

الأستاذ الدكتور. حيدر حميد محسن

و

الاستاذ المساعد. شيماء ابراهيم سعيد