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School of Basic Science

Chemistry Department



**IRON OXIDE NANOPARTICLES ASSISTED
ARSENIC, MERCURY, AND CADMIUM REMOVAL FROM
AQUEOUS SOLUTION.**

M. Sc. Thesis Submitted in Partial Fulfillment
of the Requirements for Master's Degree
of Science in Chemistry

Submitted by

Layla Abd Hamid Ammer
B. S and E g Tripoli University
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Supervised by

Dr. Abd Enaser Eturky

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿يرفع الله الذين آمنوا منكم والذين أوتوا العلم درجات

والله بما تعملون خبير﴾

طَبَرَاتِ الدِّينِ الْعَظِيمِ
صَلَّى اللَّهُ عَلَيْهِ وَسَلَّمَ

سورة المجادلة

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الإهداء

إلى من جرع الكأس فامرغاً ليسقيني قطر حب إلى من كلت أنامله ليقدّم لنا لحظة السعادة إلى من حصد الأشواق عن

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LIST OF ABBREVIATION

Nanoparticlas	NPs
X-ray diffraction	XRD
Fourier transform infrared	FTIR
Graphite furnace atomic absorption	GFAA
Oil dispersion in water	O/W
Water dispersion in oil	W/O
Atomic absorption spectrometry	AAS
Double de-ionized distilled water	D.IW
Inductively coupled plasma.	ICP
Poly vinyl alcohol	PVA
Iso electronic point	IEP
The standard treatment	S ₁ ,S ₂ ,S ₃
Scanning Electron Microscope	SEM
Transmission Electrone Microscope	TEM
Cloud point extraction	CPE
Solid phase extraction	SPE

Abstract

Iron oxide nanoparticles (IONPs) can play a significant role in the removal of heavy metal from contaminated solution. Arsenite, As(III), highly toxic, mobile and predominant species in arsenic contaminated water. IONPs have been synthesized, characterized and tested for the removal of As(III) from arsenic contaminated water. In this work, we synthesized IONPs using a chemical method involving dispersion of Fe^{3+} ions through polymer molecules of poly vinyl alcohol (PVA) in aqueous medium. X-ray diffraction (XRD) analysis confirmed the formation of a single phase rhombohedral crystal structure, the size of nanoparticles was 50-100 nm. Transmission electron microscopic images corroborate the result of IONPs (50-100 nm). The adsorption of As(III), Hg(II) and Cd(II) on (IONPs) was studied using four parameters: contact time, concentration, dose of IONPs and pH. Adsorption equilibrium was achieved in 100 min and maximum removal of As(III) was obtained at pH (6-6.5). The isotherm analysis indicated that the adsorption data better fitted to the Langmuir isotherm model. The maximum adsorption capacities were 101.2, 73.10 and 60.05 mg g^{-1} for As(III), Hg(II) and Cd(II), respectively.

الخلاصة

تم استخدام جزيئات ألفا أكسيد الحديد النانومترية المحضرة مسبقاً في المعمل لإزالة أيونات As(III) من المحاليل المائية الملوثة من العنصر.

حيث تم في البداية تحضير جزيئات ألفا أكسيد الحديد النانومترية بإتباع طريقة (Sol-gel).

حيث تم توصيف الجزيئات النانومترية المحضرة باستخدام أجهزة (XRD)، (SEM)، (TEM) وذلك لتعيين قطر هذه الجزيئات حيث وجد أن متوسط قطر هذه الجزيئات هو (50-100nm) وكان هناك توافق في النتائج بين (XRD)، (TEM) من حيث وصف هذه الجزيئات وهي $\alpha - Fe_2O_3$.

ثم دراسة ادمصاص أيونات الزرنيخ (III) والزنابق (II) والكاديوم (II) من المحاليل المائية على سطح جزيئات α أكسيد الحديد النانومترية.

وتم دراسة عدة عوامل تؤثر على عملية الادمصاص وهي pH، الزمن، تركيز الأيون وكمية المادة المدمصة، وتم الحصول على كمية الادمصاص القصوى في زمن 100 دقيقة لأيون الزرنيخ (III) عند $pH = (6.5-6)$ وتم تحليل النتائج المتحصل عليها من الادمصاص مع معادلة Langmuir الرياضية لتحديد سعة الادمصاص القصوى وثابت Langmuir وسعة الادمصاص القصوى المتحصل عليها هي (60.05 ، 73.10 ، 101.2) $mg\ g^{-1}$ لأيونات الزرنيخ (III)، الزنابق (II)، والكاديوم (II)، على التوالي.

Introduction:

Nanoparticles are defined as any particle with a size less than 100 nm, but like most things in particle technology, a more thorough discussion is required to achieve an unambiguous and complete response. The current agreement among the standard group is that the scale from 1-100 nm defines the size range of nanoparticles. Below 1nm may be excluded in order to avoid calling clusters of atoms a particle, but the literature contains references to particles < 1 nm. Since particles have three dimensions, the ASTM standard defines two or three dimensions must be between 1-100 nm. This applies for nanotubes with a diameter of 10 nm, but a length > 100 nm.

In nanotechnology, a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties. Particles are further classified according to diameter. Coarse particles cover a range between 2,500 and 10,000 nanometers. Fine particles are sized between 100 and 2,500 nanometers. Ultrafine particles, or nanoparticles, are between 1 and 100 nanometers in size. The reason for this double name of the same object is that during the 1970-80s, When the first thorough fundamental studies with “nanoparticles” were underway in the USA (by Grangvist and Buhrman) they were called “ultrafine particles”(UFP).

Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials.

Naturally occurring nanoparticles also include ultrafine sand grains of mineral origin (e.g. oxide, carbonates). In addition to commercial produced nanoparticles, many are unintentionally created by the noncombustion of diesel fuel ultrafine particles [1]. A large amount of sea salt aerosols are emitted from seas and oceans around the world [2]. These aerosols are formed by water evaporation and water produced water drops are ejected into the atmosphere. Their size range from 100 nm to several microns. An example of this phenomenon is Lake Michigan that rests in a limestone basin, the water containing high levels of calcium carbonate. During most of the year the calcium carbonate remains dissolved in the cold water, but at the end of summer the water temperature increases, lowering the solubility of calcium carbonate. As a result, the calcium carbonate may precipitate out of the water. Nanoparticles can also form in bodies of water through precipitation, as a result of temperature changes and evaporation [3]. As a combustion product, tobacco is composed of nanoparticles with size ranging from around 10 nm up to 700 nm, with a maximum located around 150 nm. The environmental tobacco smoke has a very complex composition, with more than

100,000 chemical components and compounds of the environmental tobacco smoke which is known to be toxic, both due to some of its gas phases as well as nanoparticles.

1- Nanoparticles

Links to articles describing the properties of various types of nano particles [4].

Table (1-1) types of nanoparticles

Gold Nannoparticles	Titanium Dioxide	Quantum Dots
Iron nanoparticles	Iron oxide nan particles	Silver nan particles
Platinum Nanoparticles	Silica nan particles	

1-1 Properties

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures .A bulk materials should have constant physical properties regard-less of its size but at the nana-scale size –dependent properties are often observed .Thus the properties of materials change as their size approaches the nana scale and as the percentage of atoms at the surface of a material becomes significant for bulk materials larger than one micrometer. Sometimes unexpected properties of Nanoparticles are therefore due to the large surface area of the material which dominates the contributions made by the small bulk of the material [5].

Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects for example gold nanoparticles appear deep red to black in solution.

Nanoparticles are usually yellow gold and gray silicon are red in color

Nanoparticles melt at much lower temperature (2.5nm size) than the gold slabs and absorption of solar radiation in photovoltaic cells is much higher in materials composed of nanoparticles than thin films of continuous sheets of material the smaller the particles the greater the solar absorption.

Other size-dependent property changes include quantum confinement in semiconductor particles, Surface Plasma Resonance in some metal particles and superparamagnetism in magnetic materials ironically the changes in physical properties are not always desirable ferromagnetic materials smaller than 10nm can switch their magnetization Direction using room temperature thermal energy thus making them unsuitable for memory storage [6].

Suspensions of nanoparticles are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid the high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures, sintering can take place at lower temperatures.

Over shorter time scales than for larger particles this theoretically does not affect the density of the final product though flow difficulties and the tendency of nanoparticles to agglomerate complicates matters moreover have been found to impart some extra properties to various day to day products for example the presence of titanium dioxide nanoparticles imparts when we call the self-cleaning effect and the size being nano-range the particles cannot be observed zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute this is one of the reasons why it is often used in the preparation of sunscreen lotions and is completely photo tubes.

Clay nanoparticles when incorporated into polymer matrices increase reinforcement leading to stronger plastics ,verifiable by a higher glass transition temperature and other mechanical property tests these Nan particles are hard and impart their properties to the polymer(plastic) Nan particles have also been attached to textile fibers in order to create smart and functional clothing.

Metal ,dielectric and semiconductor nanoparticles have been formed as well as hybrid structures (e.g. core shell nanoparticles) nanoparticles made of semiconducting material may also be labeled quantum dots if they are small enough (typically sub 10nm)that quantization of electronic energy levels occurs such nana scale particles are used in biomedical applications as drug carriers or imaging agents.

Semi-solid and soft nanoparticles have been manufactured a prototype
Nan particles of semi-solid nature is the liposome various types of
liposome Nan particles are currently used clinically as delivery systems
for anticancer drugs and vaccines [7].

1-2 Size of nanoparticles

Various nanostructure have been investigated to determine their properties and possible application those structures which include nanotube ,nanofibers, nanorods, nanowires.[8]

Table (1-2) The size of nanoparticles.

Nanomaterials	Size(approx)	Materials
Nanocrystals and clusters	Diameter 1-10	Metals, semiconductor
Other nanoparticles	Diameter 1-100	Ceramic oxides
Nanowires(NWS)	Diameter 1-100	Metals, semiconductors
Nano tubes	Diameter 1-100	Oxides,sulfides,nitrides Carbon. Layered metal Chalcogenised
Polymeric nanotubes	Diameter 2-200 nm	Poly pyrole, poly aniline
Nanocomposities	Diameter 20-200 nm	Poly pyroly,poly aniline Nanotubes; nanoparticals
2-dimensional arrays (of particals)	Several nm ₂ -ñm ₂	Metals, semiconductors
Surface and thin films	Thinkness1-1000 nm	Various mater
3-dimensional structures superlatices	Several nm in all three dimensions	Metals,semiconductors Magnetic materials

1-3 Iron Oxide nano structure

1-3-1 Structure

Magnetite Fe_3O_4 has an inverse spinel structure with oxygen forming a face-centered cubic crystal system. In magnetite, all tetrahedral sites are occupied by Fe^{3+} and octahedral sites are occupied by both Fe^{3+} and Fe^{2+} .

Maghemite Fe_2O_3 differs from magnetite in that all or most of the iron is in the trivalent state (Fe^{3+}) and by the presence of cation vacancies in the octahedral sites. Maghemite has a cubic unit cell in which each cell contains 32 O^{2-} ions, $21\frac{1}{3}$ Fe^{3+} ions and $2\frac{2}{3}$ vacancies. The cations are distributed randomly over the 8 tetrahedral and 16 octahedral sites. Fe_2O_3 can be obtained in various polymorphs. In the main ones, α and γ , iron adopts octahedral coordination geometry. That is, each Fe center is bound to six oxygen ligands.

1-3-2 Alpha phase Hematite: (α -Fe₂O₃):



Fig (1-3) Hematite α -Fe₂O₃ (blood ore) from Michigan

α -Fe₂O₃ has the rhombohedral, corundum(α -Al₂O₃) structure and is the most common form. It occurs naturally as the mineral hematite which is mined as the main ore of iron. It is antiferromagnetic below ~ 260 K (Morin transition temperature), and exhibits weak ferromagnetism between 260 K and the temperature, 950 K. It is easy to prepare using both thermal decomposition and precipitation in the liquid phase. Its magnetic properties are dependent on many factors, e.g. pressure, particle size, and magnetic field intensity.

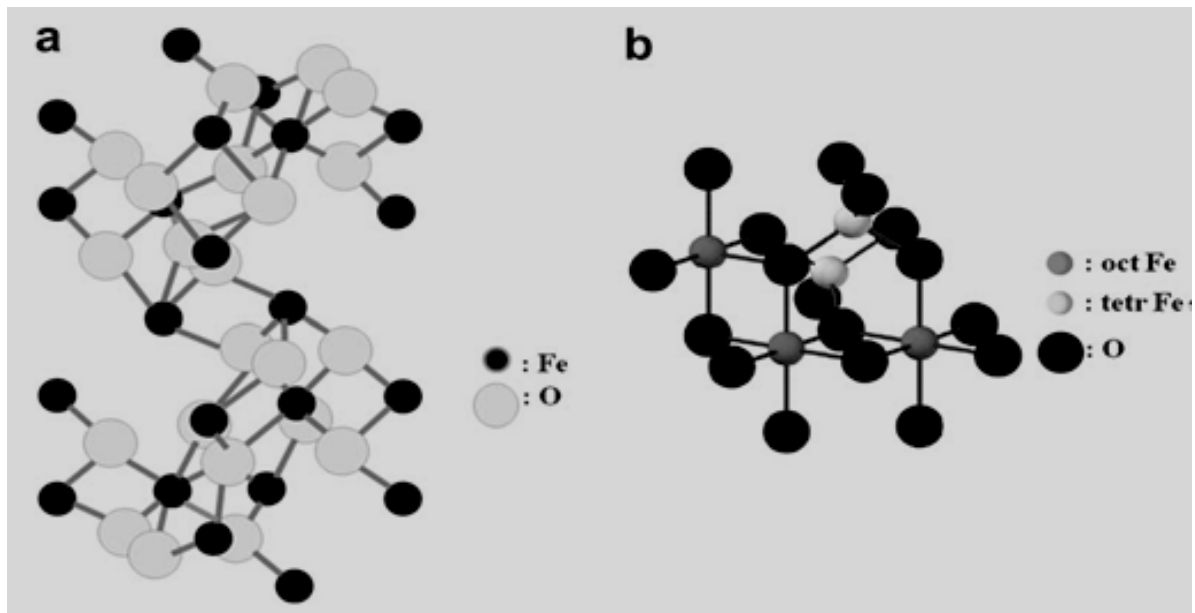


Figure (1-4) Crystal structures of (a) hematite(α -Fe₂O₃) and (b) magnetite(Fe₃O₄).

(Hematite.(α -Fe₂O₃)) Photograph of Kidney ore hematite(α -Fe₂O₃) from Michigan by DanielCD.

Fromcommons.wikimedia.org/wiki/File:Hematite.jpg.] b-c) Two views of the crystal structure of hematite(α -Fe₂O₃).

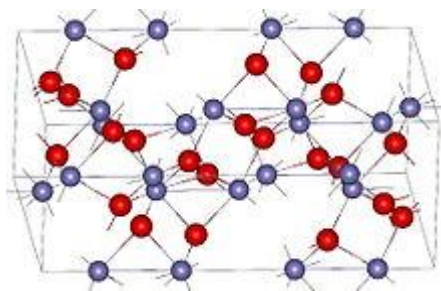


Fig (1-5) crystal structure of hematite(α -Fe₂O₃)

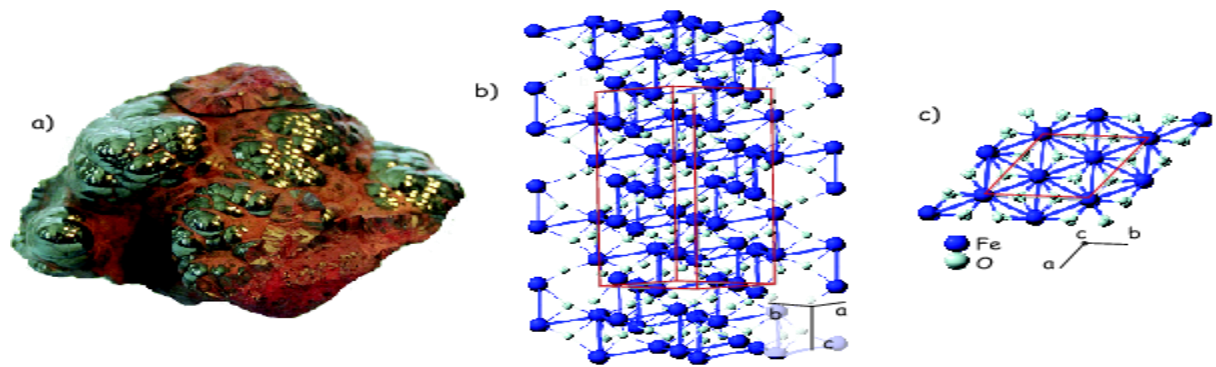


Figure (1-6) plane structure

Hematite, also spelled as **haematite**, is the mineral form of iron(III) oxide ($\alpha\text{-Fe}_2\text{O}_3$), one of several iron oxides. Hematite crystallizes in the rhombohedral system, and it has the same crystal structure as ilmenite and corundum. Hematite and ilmenite form a complete solid solution at temperatures above 950 °C.

Hematite is a mineral, colored black to steel or silver-gray, brown to reddish brown, or red. It is mined as the main ore of iron. Varieties include kidney ore, martite (pseudomorphs after magnetite), iron rose and specularite (specular hematite). While the forms of hematite vary, they all have a rust-red streak. Hematite is harder than pure iron, but much more brittle.

1-3-3 Maghemite Fe_2O_3), is a hematite- and magnetite-related oxide mineral

Huge deposits of hematite are found in banded iron formations. Gray hematite is typically found in places where there has been standing water or mineral hot springs, such as those in Yellowstone National Park in the United States. The mineral can precipitate out of water and collect in layers at the bottom of a lake, spring, or other standing water. Hematite can also occur without water, however, usually as the result of volcanic activity [9].

Clay-sized hematite crystals can also occur as a secondary mineral formed by weathering processes in soil, and along with other iron oxides or oxyhydroxides such as goethite, is responsible for the red color of many tropical, ancient, or otherwise highly weathered soils.

The name hematite is derived from the Greek word for blood because hematite can be red, as in rouge, a powdered form of hematite. The color of hematite lends it well in use as a pigment. The English name of the stone is derived from Middle French: *Hématite Pierre*, which was imported from Latin: *Lapis Hæmatites*, which originated from Ancient Greek: (*haimatitēs*lithos, “blood-red stone”) [10].

Ochre is a clay that is colored by varying amounts of hematite, varying between 20% and 70% Red ochre contains unhydrated hematite, whereas yellow ochre contains hydrated hematite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). The principal use of ochre is for tinting with a permanent color.

1-3-4 Gamma phase:maghemite. $\gamma\text{-Fe}_2\text{O}_3$

$\gamma\text{-Fe}_2\text{O}_3$ has a cubic structure. It is metastable and converts to the alpha phase at high temperatures. It occurs naturally as the mineral maghemite. It is ferromagnetic and finds application in recording tapes, although ultrafine particles smaller than 10 nanometers are superparamagnetic. It can be prepared by thermal dehydration of gamma iron (III) oxide – hydroxide careful oxidation of iron (II,III) oxide. Another method involves the careful oxidation of Fe_3O_4 . The ultrafine particles can be prepared by thermal decomposition of iron(III) oxalate .

1-3-5 Other phases

Several other phases have been identified or claimed. The beta-phase is cubic body centered (space group Ia3), metastable, and at temperatures above 500 °C (930 °F) converts to alpha phase. It can be prepared by reduction of hematite by carbon, pyrolysis of iron (III) chloride solution, or thermal decomposition of iron (III) sulfate. The epsilon phase is rhombic, and shows properties intermediate between alpha and gamma. So far has not been prepared in pure form; it is always mixed with the

alpha phase or gamma phases. Material with a high proportion of epsilon phase can be prepared by thermal transformation of the gamma phase.

This phase is also metastable, transforming to the alpha phase between 500 and 750 °C (930 and 1,380 °F). It can also be prepared by oxidation of iron in an electric arc by sol-gel precipitation from iron (III) nitrate. Additionally at high pressure an amorphous form is claimed.

1-3-6 Iron oxide-metal nanocomposites

They were obtained from ethanolic solution of ferric nitrate by slow addition of propylene oxide to occur rapid gelation. When other fine-grained metal powders (e.g., Al) were added to the stirred Fe(III)/epoxide solution just before gelation, rigid composite gel was obtained. Slow evaporation or supercritical extraction with CO₂ brought about xerogel. As shown in Fig. (1-8) the microstructure of the monolithic xerogel comprises interconnected clusters of hematite (3-10 nm) with well-dispersed Al particles of ca. 30 nm.

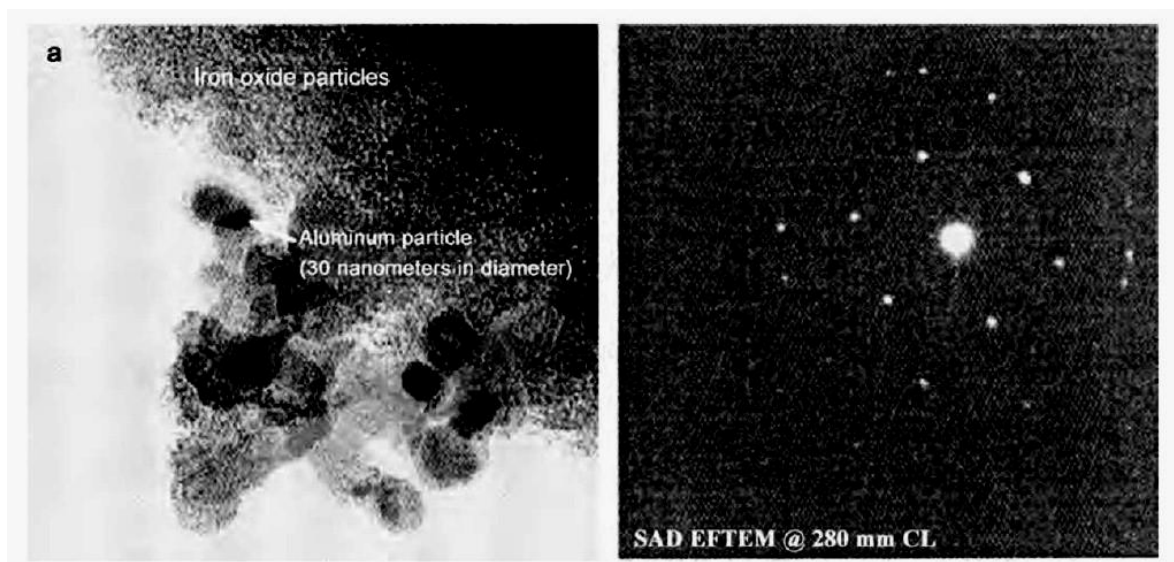
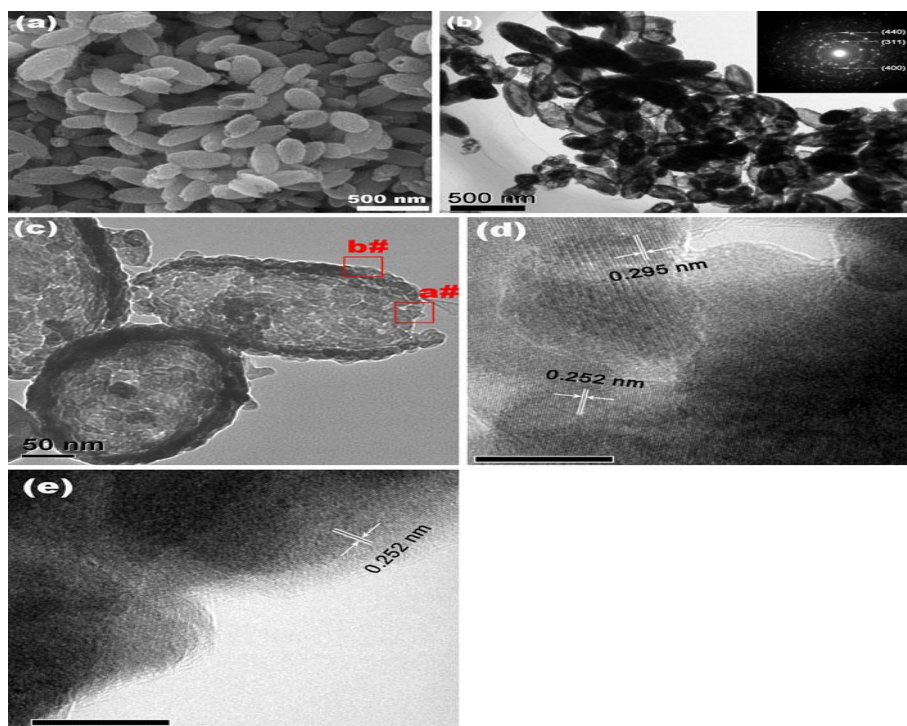


Fig.(1-7) HRTEM of Fe_2O_3 /ultrafine-grained Al powders xerogelnanocomposite and (b) SAED pattern of the labeled nanoparticle in (a).

We report in the abstract a rational synthesis of maghemite (Fe_2O_3) short-nanotubes (SNTs) by a convenient hydrothermal method and subsequent annealing process. The structure, shape, and magnetic properties of the SNTs were investigated. Room-temperature and low-temperature magnetic measurements show that the fabricated Fe_2O_3 SNTs are ferromagnetic, and its coercivity is nonzero when the temperature above blocking temperature (TB). The unique magnetic behaviors were interpreted by the competition of the demagnetization energy of quasi-one-dimensional nanostructures and the magnetocrystalline anisotropy energy of particles in SNTs.



Fig(1-8) SEM (a), TEM (b, c), and HRTEM (d, e , of Fe_2O_3 nanoparticles

1-4 IRON OXIDE NANOPARTICLES

The iron oxide nanoparticles and iron oxide nanoparticle coated with dextrin have been synthesized using aqueous solution of ferric and ferrous ions and mixtures of dextrin with sodium salt. The size of the iron-oxide nanoparticles is controlled by the concentration of sodium salt in the medium. An average size of iron oxide and iron coated with dextrin was found by transmission electron microscopy (TEM), the iron oxide nanoparticles are nearly spherical with an average diameter of about $8.0 \pm 1 \text{ nm}$. The iron oxide nanoparticles coated with dextrin appear as cluster-like aggregate. The average diameter of these nanoparticles is about 5.1 nm. The attachment of the dextrin on the particle surface was confirmed by FTIR spectroscopy and thermogravimetric analyses (TGA).

1-5 Synthesis of Iron Oxide NPs.

Many reports have been described efficient synthesis. These approaches produce the shape controlled stable biocompatible, and monodispersed iron oxide NPs. The most common methods including precipitation, thermal, decomposition, hydrothermal, synthesis, microemulsion, sonochemical synthesis and sonochemical synthetic route can all be directed to the synthesis of high quality of iron oxide NPs. In addition

these NPs can be prepared by other methods such as electro chemical synthesis laser pyrolysis techniques microorganism or bacteria synthesis especially the magnetotactic bacteria and iron reducing bacteria) we try to present typical and recent examples for the discussions of each synthetic pathway and the corresponding formation mechanism[11].

1-5-1 Co-Precipitation

The most conventional method for obtaining Fe_3O_4 , or $\alpha\text{-Fe}_2\text{O}_3$ is by co-precipitation this method consists of mixing ferric and ferrous ions in a 1;2 molar ratio in highly basic solutions at room temperature or elevated temperature the size and shape of the iron oxide NPs depends on the type of salt used (such as chlorides, sulfates, nitrates, perchlorates, etc) the ferric and ferrous ions ratio the reaction temperature the PH value ionic strength of the media and the other reaction parameters.

Recently we have reported the co-precipitation synthesis of Fe_3O_4 NPs and their corresponding morphology structure and magnetic properties at different reaction temperature are investigated .

This method would critically affect the physical and chemical properties of the nanosized iron oxide particles.

Generally the saturation magnetization values found in nanostructured materials are usually smaller than the corresponding bulk phase provided that no change in ionic configuration occurs Accordingly experimental

value for Sm in magnetic iron oxide NPs have been reported to span the 30-80 emug range ,lower than the bulk magnetic value of 100 emug in addition Fe_3O_4 NPs are not very stable under ambient conditions and are easily oxidized Fe_2O_3 or dissolved in an acidic medium in order to avoid the possible oxidation in the air the synthesis of Fe_3O_4 NPs must be done in an anaerobic conditions .

Based on this point , Fe_3O_4 NPs can also be utilized to prepare the Fe_2O_3 NPs by oxidation or anneal treatment under oxygen atmosphere .and oxidation is not the important influence factor for Fe_2O_3 NPs due to its own chemical stability in alkaline or acidic environment.

However this method generates particles with a wide particle size distribution ,which requires secondary size selection sometimes A wide particle size distribution will result in a wide range of blocking temperatures due to TB depends on particle size and therefore non-ideal magnetic behavior for many applications.

Reported a synthesis of monodispersed uniform and narrow size distributional Fe_3O_4 NPs (the diameter of NPs was 8.5 ± 1.3 nm) by- co precipitation without surfactants ,the reaction in an aqueous solution with a molar ratio of $\text{Fe(II)}/\text{Fe(III)}=0.5$ and a $\text{pH}=11-12$ and the colloidal suspensions of the magnetite can be then directly oxidized by reaction to form colloidal suspensions of $\alpha\text{-Fe}_2\text{O}_3$ In contrast many recent

publications have described efficient routes to obtain the monodispersed NPs surfactants such as dextran or polyvinyl alcohol (PVA) can be added in the reaction media or the particles can be coated in a subsequent step [17-18] surfactants act as protecting agent for controlling particle size and stabilizing the colloidal dispersions.

Additionally the disadvantage of these aqueous solution synthesis is that the high pH value of the reaction mixture has to be adjusted in both the synthesis and purification steps, and the process to obtain uniform and monodispersed NPs has only very limited success on the other hand waste water with very basic pH values are also generated in the experiment, which require subsequent treatment for protecting the environment [12].

1-5-2 Thermal Decomposition

An organic solution phase decomposition route has been widely used in iron oxide NPs synthesis and decomposition of $\text{Fe}(\text{cup})_3$ (cup=N-nitrosophenyl hydroxylamine) or $\text{Fe}(\text{CO})_5$ followed by oxidation can lead to high-quality nanodispersed iron oxide NPs which usually requires relatively higher temperatures and a complicated operation.

It was reported a general decomposition approach for the synthesis of size-controlled monodispersed magnetite NPs based on high temperature (265 °C) reaction of $\text{Fe}(\text{acac})_3$ in phenyl ether in the presence of alcohol oleic acid and oleylamine with the smaller magnetite NPs as seeds, larger

monodispersed magnetite NPs of up to 20 nm in diameter can be synthesized and dispersed into non polar solvent by seed mediated growth method the process does not require a size-selection procedure and readily sealed up for mass production as-synthesized Fe_3O_4 nanoparticle assemblies can be transformed easily into $\alpha\text{-Fe}_2\text{O}_3$ NPs by annealing at high temperature (250°C) and oxygen for 2h [13].

Generally direct decomposition of $\text{Fe}(\text{acac})_3$ single precursor can lead to monodispersed $\text{Fe}(\text{acac})_3$ NPs .

The thermal decomposition of $\text{Fe}(\text{CO})_5$ produces iron NPs and the following oxidation by a chemical reagent can also lead to monodispersed $\alpha\text{-Fe}_2\text{O}_3$ NPs for instance reported a synthesis of highly crystalline and monodispersed iron NPs without size selection process by the thermal decomposition of iron pent carbonyl in the presence of oleic acid at the resulting iron NPs were transformed to monodispersed $\alpha\text{-Fe}_2\text{O}_3$

Nanocrystallites by controlled oxidation using trimethylamine oxide as mild oxidant particle size can be varied from 15 nm to 16 nm by controlling the experimental parameters.

Although the thermal decomposition method has many advantages for producing highly monodispersed particles with a narrow size distribution it has a big disadvantage that the resulting NPs are generally only dissolved in nonpolar solvents.

1-5-3 Microemulsion

Microemulsion is a thermodynamically stable isotropic dispersion of two immiscible phases (water and oil) under the surfactant present the surfactant molecules may form a monolayer the interface between the oil and water with the hydrophobic tails of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the aqueous phase .As in the binary system (water/surfactant or oil/surfactant)self-assembled structures of different types can be formed ranging for example from (inverted) spherical and cylindrical micelles to lamellar phases and bicontinuous microemulsions which may coexist with predominantly oil or aqueous .

In this sense microemulsion and inverse micelles route can be employed for obtaining the shape and size controlled iron oxide NPs [14].

Particularly water-in-oil (w/o)microemulsions are formed by well-defined nanodroplets of the aqueous phase,dispersed by the assembly of surfactant molecules in a continuous oil phase which have been reported the synthesis of monodisperse maghemite NPs by the onepotmicro emulsion method the spherical shaped particles capped with a monolayer coating of oleylamine (or oleic acid)show a narrow size distribution of 3.5 ± 0.6 nm are well crystallized and have high saturation magnetization values (76.3 Am/kg for uncoated NPs 35.2Am/kg for oleic acid coated

NPs and 33.2 Am/kg for oleylamine coated NPs) moreover the results show that oleylamine act as precipitating and capping agent .

However, cyclohexylamine acts only as precipitating agent and does not avoid particle aggregation chin and yaacob reported the synthesis of magnetic iron oxide NPs (less than 10 nm) via w/o micro emulsion Furthermore in comparison to the particles produced by Massarts procedure particles produced by microemulsion technique were smaller in size and were higher in saturation magnetization .

However, despite the presence of surfactants the aggregation of the produced NPs usually need several washing processes and further stabilization treatments

1-5-4 Hydrothermal Synthesis

Iron oxide NPs with controlled size and shape are technologically important due to strong correlation between these parameters and magnetic properties the microemulsion and thermal decomposition methods usually lead to complicated process or require relatively high temperatures .As an alternative ,hydrothermal synthesis includes various wet chemical technologies of crystallizing substance in a sealed container from the high temperature aqueous solution (generally in the range from 130 to 250C⁰)at high vapor pressure(generally in the range from 0.3 to a MPa)this technique has also been used to grow dislocation free single crystal particles and grains formed in this process could have a better

crystalline than those from other processes so hydrothermal synthesis is prone to obtain the highly crystalline iron oxide NPs.

Several authors have reported the synthesis of iron oxide NPs by hydrothermal method .there are two major methods according to whether or not use the specific surfactants for example have reported a one-step hydrothermal process to prepare highly crystalline Fe_3O_4 powder (40 nm)obtained at 140 °C for 6h possessed a saturation magnetization of 85.8 emu. g a little lower than that of the correspondent bulk Fe_3O_4 (92 emug) it is suggested that the well-crystallized Fe_3O_4 grains formed under appropriate hydrothermal conditions should be responsible for the increased saturation magnetization in nanosized Fe_3O_4 [15].

Reported a hydrothermal route for preparing Fe_3O_4 NPs with diameter of ca 27 nm in the presence of a surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT).

The magnetic properties of the NPs exhibited a super-paramagnetic behavior at room temperature [16].

Moreover ,recently hydrothermal treatment is one of the successful ways of growing crystals for iron oxide NPs by Daou et al .It was reported that the magnetite particles with an average size of 39nm and good monodispersity have been synthesized by co-precipitation at 70 °C from ferrous and ferric ions by a $\text{N}(\text{CH}_3)_4\text{OH}$ solution followed by

hydrothermal treatment at 250⁰C the magnetite NPs before the hydrothermal step display an average size of 12 nm and are highly oxidized when they are in contact with air. Additionally hydrothermal synthesis is conducive to prepare the unusual iron oxide nanostructures such as iron oxide nanocubes.

1-6 Characterization of nanoparticles

Nanoparticles are generally characterized by the following techniques;

1-Transmission Electron Microscopy (TEM)

2-Aerosol Mass Spectroscopy (Aerosol MS)

3-X-ray Diffraction (XRD)

4-Fourier Transform Infrared (FTIR)

5- High Resolutions Scanning Microscopy (HRSEM)

There are several other techniques used to characterize and illustrate the physical and chemical properties of nanoparticles. Some of these techniques are quantitative and some are qualitative but a combination of these techniques can always give a clear picture of the shape, size and morphology of materials. Some of the techniques are used in the research [17].

1-7 X-Ray- Diffraction

XRD is essential for the identification of the purity of the product, In addition phase identification ,XRD provides information about crystal size and crystal perfection .X-ray diffractions (XRD) is based on the interference effect from the scattered radiation by the different location of atoms in the material .X-ray diffraction method is one of key techniques for the investigation of structures properties of various materials. **XRD** is essential in the determination of the crystal structures and crystal grain size according to the Scherrer equation.

$$T = \frac{K\lambda}{B \cos \theta}$$

Where K is dimensionless constant, θ is the diffraction angle, λ is the wave length of the X-ray radiation ,and B is the width at half maximum (FWHM) of the diffraction peak. Crystallite size is determined by measuring the broadening of a particulate peak in a diffraction pattern associated with a particular planar reflection within the crystal unit cell [18].

1-8 Fourier Transform Infrared

FTIR stands for Fourier transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample and some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis [19].

1-9 Mercury Analyzer (Hg Analyzer)

levated mercury (Hg) levels in marine and freshwater ecosystems are a growing concern to both environmentalists and consumers. The combustion mercury analyzers described here in provide crucial testing by employing some or all of the following techniques:

Hermaide composition, catalytic conversion, and (gold) amalgamation. Mercury or containing compounds are separated through multiple steps involving several combinations of these processes. Detection is then achieved by atomic absorption spectrophotometry. A mercury analyzer can achieve combustion temperatures of 1000°C or more to provide results in five minutes or less. Mercury analyzer offers high linearity of 2000 ng or more. Because of the toxic nature of mercury, Hg analyzer will have extensive safety features that ensure proper evacuation or containment of gases[20].

1-10 Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

Graphite furnace atomic absorption (GFAA) spectrometry is a highly sensitive spectroscopic technique that provides excellent detection limits for measuring concentrations of metals in aqueous and solid sample. GFAA has been used primarily in the field for the analysis of metals in water .GFAA could be used to determine metals in soil, but the sample preparation for metal in soil is extensive and is not practical for field application.

GFAA cannot be described as a truly field portable instrument. GFAA instruments are extremely sensitive and therefore, must be operated in a clean, climate controlled environment. This can be difficult but not impossible to achieve in a field environment. In addition ,the 220-volt Felectrical power requirement often precludes remote operation. .However, GFAA is an example of” taking the laboratory to the field”. Miniaturization of electronics has significantly reduced instrument size and weight, making it easier to use the instrument in a field laboratory.

1-10-1 System Components

GFAA spectrometry instruments have the following features:

- source of light (lamp) that emits resonance line radiation.
- atomization chamber (graphite tube)in which the sample is vaporized.
- monochromator for selecting only one of the characteristic wavelengths visible or ultraviolet of the element of interest.
- detector, generally a photomultiplier tube (light detectors that are useful in low intensity applications),that measures the amount of absorption .
- signal processor-computer system(strip chart recorder, digitaldisplay, meter, or printer).

1-10-2 Mode of operation

Most currently available GFAs are fully controlled from a personal computer that has Windows-compatible software. Aqueous samples should be acidified (typically with nitric acid)to a pH of 2.0 or less. Discoloration in a sample may indicate that metals are present in the sample. For example ,a greenish color may indicate a high nickel content, or a bluish color may indicate a high copper content. A good rule to follow is to analyze clear samples first, and then analyzer colored

samples. It may be necessary to dilute highly colored samples before they are analyzed [21].

After the instrument has warmed up and been calibrated ,a small aliquot (usually less than 100 microliters (ml)and typically 20ml) is placed, either manually or through an automated sampler,into the opening in the graphite tube. Click to see a cross-sectional view of a graphite tube The sample is vaporized in the heated graphite tube: the amount of light energy absorbed in the vapor is proportional to atomic concentrations. A nalysis of each sample takes from 1 to 5 minutes, and the resulte for a sample is the average of triplicate analysis.

1-10-3 Analytical applications

Within the group, GFAAs has been applied to the determination of trace metals in a wide range of sample types, in various field:

Clinical and biological materials blood,urine synovial Fluid	Environmental samples:naturalwaters,s ediments,plant materials	Industrial materials:steels,petroleu m products
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1-10-4 Interferences

the GFAA technique is subject to chemical, spectral, and ionization interferences. The composition of the sample matrix typically has the largest effect on the results of the analysis.

Chemical interference occurs when the atoms are not completely free or in their ground state. Spectral interferences occur when atomic or molecular species other than the element being analyzed absorb energy at the wavelength of interest. Ionization interferences occur when the furnace causes complete removal of electrons from an atom, thereby lowering the concentration of ground-state atoms available to absorb light [22].

A serial dilution technique may be used to help verify the absence of chemical and spectral interference. In cases in which interference is suspected, samples should be treated in one or more of the following ways: (1) samples should be diluted and reanalyzed successively to determine whether the interference can be eliminated, (2) matrix modifiers should be added, or (3) the sample should be analyzed by method of standard additions. It is common practice to add matrix modifiers to all samples to compensate for potential chemical and spectral interferences [23].

1-10-5 Detection Limits

Numerous metals can be analyzed by GFAA, as long as their atoms can be vaporized in the graphite furnace. Such elements include aluminum, arsenic, barium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, Manganese, mercury, molybdenum, nickel, potassium, selenium, silicon, silver, sodium, titanium, terbium, vanadium, ytterbium, and zinc. Click to view a table showing the typical detection limits for some of the metals listed above. Detection limits can be very low with GFAA analyses (below most of maximum contaminant levels [MCL] for drinking water established by the U.S. Environmental Protection Agency (EPA) and usually are 10 to 100 times lower than the detection limits for analyses by flame AA or ICP for the same element [24].

Table (1-3) Detection Limit of trace element/mg/l using (GFAAS).

Element	Al	As	Cd	Cr	Ni	Pb	Se	Ti	Tl	V
Detection	0.2	0.04	0.01	0.075	0.5	0.2	0.3	0.75	0.35	0.5

1-11 Applications of Nanoparticles:

1-11-1 Application of nanoparticles in Environment

Researchers are using gold nanoparticles embedded in a porous manganese oxide as a room temperature catalyst to breakdown volatile organic pollutants in air [25].

Nanoparticles exhibit unique physical properties (such as particle aggregation and photoemission, and electrical and heat conductivities and chemical properties (such as catalytic activity).and hence have received much attention from scientists and research in different areas of biological sciences.

In this review, we briefly summarize the major types of nanoparticles the have been used so far and discuss the possible applications of these nanoparticles in biological and environmental research , and the potential environmental and health impacts associated with use of these nanoparticles [26] .

1-12 Arsenic in water

Arsenic can be found in seawater (2 to 4 ppb) ,and in rivers (0.5 ppb). Half of the arsenic present is bound to particles .freshwater and seas algae contain about 1-250 ppm of arsenic ,freshwater mycrophytes contain 2-1450 ppm, marine molluscs contain 1-70 ppm ,marine crustaceans 0.5-69 ppm ,and fishes 0.2-320 ppm (all values are based on dry mass). In some marine organisms ,such as algae and shrimp, arsenic can be found in organic compounds.

The legal limit for arsenic in water applied by the world Health organization (WHO) is 10 ppb.

Arsenic compounds are abundant in the earth crust. Particles are released during mining ,and spread throughout the environment .

Arsenic from weathered rocks and soils dissolves in groundwater.

Arsenic concentrations in groundwater are particularly high in areas with geothermal activity .

1-12-1 Sources in water.

Elementary arsenic is fairly insoluble, whereas arsenic compounds may readily dissolve .Arsenic is mainly present in watery solutions as

HAsO_4^- (aq) and H_2AsO_4^- (aq), and most likely partially as H_3AsO_4 (aq), AsO_4 (aq) or H_2AsO_3 (aq).

Examples of solubility of arsenic compounds: arsenic (III) hydride 700mg/L, arsenic (III) oxide 20g/L, arsenic acid($\text{H}_3\text{AsO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$) 170 g/L and arsenic (III) sulfide 0.5 mg/L [27].

1-12-2 Toxicity of Arsenic

Arsenic toxicity is another important characteristic. The boundary concentration of arsenic is 2-46 ppm for freshwater algae.

Arsenic related illness is usually caused by consumption of contaminated drinking water. In the old days it was applied as a poison, because symptoms of arsenic poisoning resemble cholera symptoms, and therefore the intentional factor was shaded [28].

Arsenic appears to be essential for some plant and animal species. A possible safe dose for humans was calculated. If arsenic is a dietary mineral, this dose would be 15-25 mg. This amount could be absorbed from food without any trouble. The total amount of arsenic in a human body is about 0.5-15 mg. Many arsenic compounds are absorbed 60-90 %, but they are also easily excreted. Humans can develop resistance to certain arsenic concentrations. Shortly after absorption arsenic can be

found in liver, spleen, lung and digestive tract. Most arsenic is excreted, and residues may be found in skin, hair, nails, legs and teeth.

Under conditions of prolonged exposure, many organs may be damaged, skin pigmentation may occur, hair may fall out and nail growth may stop.

Toxicity differs between various arsenic compounds, for example, monomethyl arsenic acid and inorganic arsenic have a higher toxicity level than arsenic choline. Acute toxicity is generally higher for inorganic arsenic compounds than for organic arsenic compounds. Oral intake of more than 100 mg is lethal. The lethal dose of arsenic trioxide is 10-180 mg, and for arsenide this is 70-210 mg. The mechanism of toxicity is binding and blocking sulphurenzymes. Symptoms of acute arsenic poisoning are nausea, vomiting, diarrhea, cyanosis, cardiac arrhythmia, confusion and hallucinations. Symptoms of chronic arsenic poisoning are less specific. These include depression, numbness, sleeping disorders and headaches [29].

Arsenic related health effects are usually not acute, but mostly encompass cancer, mainly skin cancer. Arsenic may cause low birth weight and spontaneous abortion.

Arsenic in drinking water is an issue of global importance, therefore the legal limit was decreased to 10 l. This legal limit is not met in

countries such as Vietnam and Bangladesh, where millions of people consume drinking water with an arsenic content of over 50 μ /L. This problem results in long-term chronic health effects, such as skin disease, skin cancer, and tumours in lung, bladder, kidneys and liver.

1-13 Hg in Water

Mercury is one of the very serious pollutants it is found naturally in the environment and is transported by natural processes and human activity.

Mercury is a toxic environment of pollutants which could turn into Metal mercury, a compound highly toxic, which has the ability to assemble objects in saluting the focus on the length of the string food private aquaculture (fish and marine).

There are several methods for the analysis of mercury in the environment is cold vapor technique of the most important devices for measuring mercury concentrations with high sensitivity and very small quantity.

In this context we note that the consumption of fresh or canned fish is the main road to mercury exposure, where many of the study showed a positive relationship between increased consumption of fresh fish and mercury exposure [30].

1-13-1 Sources of mercury

1-13-1-1 Natural

Natural sources of mercury include volcanoes, forest fires, cinnabar (ore) and fossil fuels such as coal and petroleum.

1-13-1-2 Anthropogenic

Levels of mercury in the environment are increasing due to discharge from hydroelectric, mining, pulp, and medical waste and emissions from coal-using power plants contribute to high levels of mercury.

Mercury released from ongoing human activity into four broad categories. The first category is “area sources” Landfills, dental preparations, and laboratory use are defined as area source. The second category is combustion processes. These include coal-fired power generation, medical waste incinerators, and municipal waste combustors. The third category is the manufacture of metals, alkali and cement. Other industrial processes fall into the fourth category. Processes, refining, lubrication, and dental amalgams [31].

1-13-2 The toxicity of mercury.

Like many environmental contaminants, mercury undergoes bioaccumulation. Bioaccumulation is the process by which organisms (including humans) can take up contaminants more mercury in their body accumulates over time. If for a period of time an organism does not ingest mercury, its body burden of mercury will decline. If, however, an organism continually ingests mercury, its body burden can reach toxic levels. The rate of increase or decline in body burden is specific to each organism for humans, about half the body burden of mercury can be eliminated in 70 days if no mercury is ingested during that time. Biomagnification is the incremental increase in concentration of a contaminant at each level of a food chain.

This phenomenon occurs because the food source for organisms higher on the food chain is progressively more concentrated in mercury and other contaminants, thus magnifying bioaccumulation rates at the top of the food chain. The bioaccumulation effect is generally compounded the longer an organism lives, so that larger predatory game fish will likely have the highest mercury levels. Adding to this problem is the

fact that mercury concentrates in the muscle tissue of fish. So, unlike organic contaminants (for example PCBs and dioxins) which concentrate in the skin and fat, mercury cannot be filleted or cooked out of consumable game fish.

Humans generally uptake mercury in two ways;(1) as methyl mercury (CH_3Hg)⁺ from fish consumption ,or (2) by breathing vaporous mercury (Hg) emitted from various sources such as metallic mercury ,dental amalgams, and ambient air. Our bodies are much more adapted for reducing the potential toxicity effects from vapor ous mercury ,so health effects from this source are relatively rare. Methylmercury, on the other hand ,affects the central nervous system, and in severe cases irreversibly damages areas of the brain .The most well documented cases of severe methyl mercury poisoning from Minamata Bay ,Japan in 1956 (industrial release of methyl-mercury) and in Iraq in 1971 (wheat treated with a methyl mercury fungicide) In each case ,hundreds of people died, and thousands were affected ,many with permanent damage. In milder cases of mercury poisoning, adults complain of reductions in motor skills and dulled senses of touch taste and sight. These milder effects are generally reversible if exposure to mercury is halted. unborn children are greatest risk from low-level exposure to

methylmercury. Recent research suggests that prenatal effect occur at intake levels 5- 10 times lower than that of adults. If these results are confirmed a substantial fraction of unborn children would be at risk [32].

1-14 Cadmium in water

Cadmium (Cd) is a naturally occurring metal used in batteries and in electroplating to protect other metals from corrosion. Cadmium can be released directly to water from human activities like production of pulp and paper and processing of metals, and from wastewater treatment plants.

Cadmium is used primarily for metal plating and coating operations, including transportation equipment, machinery and baking enamels, photography, and television phosphors. It is also used in nickel-cadmium solar batteries and pigments[33].

1-14-1 Sources of Cadmium

Water, sewage and other systems were responsible for 50% (1356 Kg) of the total Cd released (2739Kg) to water.

The second-largest proportion of the national release came from pulp, paper and paperboard mills, representing 28%(766Kg) of the total. The non-ferrous production and processing (excluding aluminum) industry ranked third, with 12% (321 kg) of total Cd releases [34].

1-14-2 The Toxicity of Cadmium

Cadmium is an extremely toxic metal which metal has no known necessary function in the body. Cadmium toxicity contributes to a large number of health conditions, including the major killer diseases such as heart disease, cancer and diabetes.

Cadmium toxicity is increasing in incidence today for several reasons. One of the primary reasons is a zinc deficiency in many commonly eaten foods. Zinc, which is protective against cadmium, is becoming increasingly deficient in the soil and consequently in foods. Food processing and eating of refined foods further reduces zinc intake.

The most common sources of cadmium toxicity are foods such as rice and wheat which are grown in soil contaminated by sewage sludge, super phosphate fertilizers and irrigation water.

Large ocean fish such as tuna, codfish and haddock concentrate within their tissues relatively large amounts of cadmium. Oysters, although containing large amounts of cadmium also contain large amounts of zinc which serves to protect against cadmium toxicity [35].

Besides contaminated product and organ meats such as liver and kidneys, a significant source of cadmium toxicity is a diet high in refined foods.

Zinc, which normally protects against the toxic effects of cadmium, is largely removed during the milling process, leaving cadmium.

1-15 Preconcentration methods.

The direct determination of extremely low concentration of trace elements was done by modern atomic spectroscopic methods. Such as atomic absorption spectrometry (**AAS**) ,(**GFAAS**) and inductively coupled plasma atomic emission spectrometry (**ICP-MS**) is often difficult. Limitations arise from the insufficient sensitivity of these techniques as well as the matrix interferences. For this reason the preliminary separation and preconcentration of trace elements from matrix is often required .The most widely used techniques for the separation and preconcentration of trace elements[36] are;

1-Solid Phase extraction (**SPE**).

2-Co precipitation.

3-Cloud point extraction.

4-Liquid-liquid extraction.

1-15-1 Solid Phase extraction (SPE).

Solid phase extraction (SPE) using nanometersized metal oxide as a solid sorbent can be utilized for the separation and preconcentration of trace amounts of aluminum in various samples[37].

(SPE)has several major advantages, which include simple operation ,safety with respect to hazardous samples, high selectively, low cost and short analysis time and possibility to be combined with different modern detection techniques. (MONPs) are a promising solid phase extractant because of its large specific surface area, high adsorption capacity and possibility of low temperature modification[38].

1-15-2 Co precipitation

Co precipitation is a phenomenon where a solute that would normally remain dissolved in solution precipitation out on a carrier that forces it to bind together, rather than remaining dispersed. This can occur in nature.In environmental remediation in particular co precipitation can be on extremely useful tool for samples, purifying solutions and cleaning up environmental hazards [39].

1-15-3 Cloud point extraction(CPE)

The technique is based on the property of most nonionic surfactant in aqueous solution to form micelles and to separate into a surfactant-rich phase of small volume and diluted aqueous phase when heated to a temperature known as the cloud point temperature. The advantage of simple, cheap, high efficient, speed and lower toxicity to environment than those extraction that use organic solvents [40].

1-15-4 Liquid-liquid extraction.

Also known as solvent extraction and partitioning is method to separate compounds based on their relative solubility in two different immiscible liquid, usually water and an organic solvent[41].

1-16 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or liquid (adsorbent), forming a molecular or atomic film (the adsorbent). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Adsorption is operation in natural physical, biological, and chemical system, and is widely used in industrial applications such as activated carbon, synthetic resins and water purification.

1-16-1 Type of adsorption.

1-16-1-1 Physisorption or physical adsorption

Is a type of adsorption in which the adsorbate adheres to the surface only through van der Waals (weak intermolecular).

1-16-1-2 Chemisorption:

Chemisorption is a type of adsorption where by a molecular adhere to a surface through the formation of a chemical bond, as opposed to the van der Waals forces which causes physisorption. Adsorption is usually described through isotherm, that is function which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). In this work use Langmuir isotherm because based on four hypotheses: The surface of the adsorbent is uniform, that is, all the adsorption sites are equal. Adsorbed molecules don't interact. All adsorption occurs through the same mechanism. At the maximum adsorption only a mono layer formed. Oxide materials can present ionic or mixed ionic or electronic conductivity and it is experimentally well established that both can be influenced by the nanostructure of the solid. The number of electronic charge carriers in a metal oxide is a function of the band gap energy. The number of free electron or

holes of an oxide can be enhanced by introducing non stoichiometry and in case are balanced by the much less mobile oxygen cation vacancies. In an analogous manner of hopping type conduction ,ionic conduction take place when ions can hop from site to site within a crystal lattice as a result of thermal activation the metal oxide such as ZnO,TiO₂,CuO,Cr₂O₃[42].

1-17 Objectives

Because As (III),Hg(II),Cd(II) is widely used in industry, result from some gaseous, these gaseous falling acid rain, which mobilize and release As(III),Hg(II),Cd(II),into soil solution underground and surface water.

However, lead to increase elevated levels of As(III),Hg(II),Cd(II)

Concentration, with (WHO) world health organization comparable.

1- Prepare the $\alpha - Fe_2O_3$ nanoparticles study of preconcentration of As (III), Hg(II), Cd(II),using Fe_2O_3 nanoparticles.

2- Characterization of Fe_2O_3 nanoparticles using HRSEM,TEM and XRD.

3- Study the effect of different parameters such as contact time,pH concentration of As(III),Hg(II),Cd(II) by preconcentration method.

Removal of As(III),Hg(II),Cd(II) from contaminated water solutions

Compare the results with (WHO).

4- Removal of As(III),Hg(II) and Cd(II) from contaminated water samples.

5- Fit the experimental data to adsorption model Langmuir or Freundlich mathematical equation .

6-Determination of As(III),Hg(II) and Cd(II) in near water samples.

7-Compare the nesults with (WHO)standards.

2-1 Literature Review

-We:etal reported that surface functionalized magnetic iron oxide nanopartical (NPs) are a kind of novel functional materials, which have been widely used in the biotechnology and catalysis. This review focuese on the recent development and various strategies in preparation,structure and magnetic properties of naked and surface functionalized iron oxide NPs and their corresponding application briefly.In order to implement the practical application, the particles must have combined properties of high magnetic saturation,stability, biocompatibility, and interactive functions at the surface. Moreover, the surface of iron oxide NPs could be modified by organic materials or inorganic materials, such as polymers ,biomolecule ,silica, metals, etc. The problems and major challenges, along with the directions for the synthesis and surface fictionalization of iron oxide NPs, areconsidered. Finally, some future trends and prospective in these research areas are also discussed [43] .

-Daniel, L, etal reported that the fied of molecular imaging has recently seen rapid advances in the development of novel contrast agents and the implementation of insightful approaches to monitor biological processes non-invasively. Inparticular, superaramagnetic iron oxide nanoparticles (SPIO) have demonstrated their utility as an important tool for enhancing

magnetic resonance contrast, allowing researchers to monitor not only anatomical changes, but physiological and molecular changes as well [44]

-Predoi, et al., the application of iron oxide nanoparticles coated with dextrin using aqueous solution of ferric and ferrous ions and mixtures of dextrin with sodium salt. The size of the iron-oxide nanoparticles was controlled by the concentration of sodium salt in the medium. An average size of iron oxide and iron oxide coated with dextrin was found by transmission electron microscopy (TEM). The iron oxide nanoparticles were nearly spherical with an average diameter of about 8.0 ± 1 nm. The iron oxide nanoparticles coated with dextrin appear as cluster-like aggregates. The average diameter of these nanoparticles is about 5.1 nm. The attachment of dextrin on the particle surface was confirmed by FTIR spectroscopy and thermogravimetric analyses (TGA) [45].

-Gengiz et al. reported the degradation of toxic monochlorophos (MCP) was comparatively studied by electrochemical method such direct electro oxidation indirect electro oxidation electro coagulation and electro fenton processes. In the direct electro oxidation process using Ti electrodes in electrolyte solutions (16 g/L NaCl) at two different current densities of 50 and 100 A/m² degradation of MCP from aqueous solution in different initial concentration (50-100-200-300 mg/L) was investigated to evaluate

MPC degradation it was determined that increases in the initial MPC concentration and current density lead to increase MPC degradation in this process considering the effects of different electrolyte concentrations of NaCl (1.3.6 g/L) and different electrolyte (6 g/L Na₂SO₄), it was observed that high NaCl concentration increases the MCP degradation and decreases the energy consumption the degradation and removal of 300 mg/L MPC solution by electro coagulation using Fe electrodes (pH) 8.5.6.g/L Na Cl 93A/m₃) was investigated and 78/removal was achieved. The degradation and mineralization of 300mg/L MPC solution (6g/L NaCl 50) by the indirect electro oxidation processes using Ti electrodes by adding 2 mmol H₂O/min was also investigated 100/MPC degradation and 20/TOC removal was obtained. finally, the degradation and mineralization of 300 mg/L MPC solution (6g/L Na Cl.93) by the electro-fenton process using Fe electrodes by adding 2 mmol H₂O₂/min was performed it was observed that MCP was degraded completely in less than 10 min and was mineralized up to the yields of 66/efficiency for 90 min [46].

-Karbasihadietal, reported that multielement simultaneous determination of 35 trace elements in environmental samples by inductively coupled plasma emission spectrometry (ICP-OES) after preconcentration with octadecyl. silicagel modified with aurintricarboxylic acid (Aluminon)

optimal experimental conditions including Ph sample solution. sample volume, sample and eluent flow rate, type, concentration and volume of eluent and foreign ions effect were investigated and established.

Trace element ions in aqueous solution were quantitatively adsorbed onto octadecylsilicagel modified with aurintricarboxylic acid at pH 8.0 with a flow rate of 11.0 ml min. The adsorbed element ions were eluted with 3-5 ml of 0.5 mol HNO_3 at a flow rate of 10.0 ml min and analyzed by ICP-OES simultaneously [47].

-Abu Ghalwa et al reported that modified electrode, which can be used as an anode for electro catalytic oxidation processes of dyestuff in aqueous solutions and, was fabricated by electro position of a lead oxide layer on a titanium substrate. The modified electrode was used for the electrochemical degradation of an acid green dye. the results of the electro catalytic oxidation process of the dyestuff solution were expressed in terms of the remaining dye concentration and chemical oxygen demand(COD) values the different operating condition of the treatment process were studied the optimum operating conditions for the dye and modified electrode were determined good results for complete removal of the dye and COD were achieved the optimum conditions were applied to the treatment of a sulfur black dye in true wastewater solutions [48].

Dahui Chen et al. reported that a simple and sensitive method using micro column packed with 3-(2-aminoethylamino) propyltrimethoxysilane (AAPT)s modified ordered mesoporous silica combined with inductively coupled plasma optical emission spectrometry (ICP-OES) for the speciation of inorganic arsenic (As(III) and As(V)) [49].

Total inorganic arsenic was extracted after the oxidation of As(III) to As(V) with 50.0 mol KMO₄. The assay of As(III) was based on subtracting As(V) from total As. The effect of various parameters on the separation/preconcentration of As(III) and As(V) have been investigated and the optimal experimental conditions were established. The adsorption capacity of AAPTs modified ordered mesoporous silica for As(V) was found to be 10.3 mg/g. The detection limit of the method for As(V) was 0.05 with an enrichment factor of 100 and the relative standard deviation (R.S.D) was 5.7% (n=7, C=1.0). In order to validate the developed method a certified reference material GSBZ50004-88 environmental water sample was analyzed and the determined values were in good agreement with the certified values. The proposed method was successfully applied to the speciation analysis of inorganic arsenic in natural water sample [50].

Chazhang Huang et al. reported that a novel absorbent prepared by dimercaptosuccinic acid chemically modifying mesoporous titanium dioxide and was employed as the micro-column packing

material for simultaneous separation /preconcentration of inorganic arsenic and antimony species. it was found that both trivalent and pentavalent of inorganic As and Sb species could be adsorbed quantitatively on dimercaptosuccinic acid modified TiO_2 within pH range of 4-7 and only As(III) and Sb(III) could be quantitatively retained on the micro-column within pH range of 10-11 while As(V) and Sb(V) were passed through the micro-column without the retention. Based on this fact a new method of flow injection on-line micro-column separation /preconcentration coupled to inductively coupled plasma optical emission spectrometry was developed for simultaneous speciation of trace inorganic arsenic and antimony in natural waters. Under the optimized conditions, an enrichment factor of 10 and sampling frequency of 10 h were obtained with on-line mode. The detection limits of As(III), As(V), Sb(V), and Sb(V) are 0.53, 0.49, 0.77 and 0.71 for on-line mode and as low as 0.11, 0.10, 0.15 and 0.13 for off-line mode due to its higher enrichment factor (50), respectively. The relative standard deviations of two modes are less than 6.7% ($c=20\text{ng}$). The concentration ratio of lower oxidation states /higher oxidation states changing from 1;10 to 10;1 has no obvious effect on the recoveries of As(III) and Sb(III). In order to validate the developed method two certified reference materials of GSBZ500-88 and GBW (E)080545 water sample were analyzed and

the determined values are good agreement with the certified values .the proposed method was successfully

appalled to the simultaneous speciation of inorganic arsenic and antimony in natural water [51].

3.1-Glasswares:

All glass ware,used for this research ,were washed with (D.I.W) and 10% HNO₃ many times.

Table (3-1) Glassware used in this study.

Equipment	Size
Graduated flasks	1000,500,250,100,50ml
Pipettes	2,5,25ml
Beakers	500,250,100,50ml
Erlemeyer flask with ground –plastic stoppers	100ml
Crucibles	different sizes

3.2-Instruments:

Table (3-2) Instruments used in this study.

Order	Instrument	Type
1	Shaker	Edmund Buhllr,k1-2 Germany
2	Digital pH meter	WTW525,Germany
3	Graphit furnace Atomic absorption Spectrometer Mercury analysis (Gf-AAS)	AA-6800,shimadzu,Japan
4	Furnace	Metller Toledo AB 104-s-Germany
5	Analytical balance	Memner 600-Germany-(0.00001/g
6	Furnace	Qallenhamb,Hotspot temperature (0-1000C)Germany
7	High Resolution Scanning Microscope	Hitatchi Namber 5400E
8	TEM	Oxford systems

3-3-Chemicals:

All chemical used in this study were of high purity as shown in table in (3-3).

Table (3-3) Chemicals used in this study.

Order	Materials	Company	Purity
1	PVA(Poly vinyl alcohol)	BDH chemicals Ltd poole England	99.9%
2	Fe(NO ₃) ₂	Riedel-de-Haen	98.5%
3	(As ₂ O ₃)	Riedel-de-Haen	98.5%
4	Hg(NO ₃) ₂ H ₂ O	Riedel-de-Haen	98.5%
5	Cd(NO ₃) ₂ H ₂ O	Riedel-de-Haen	98.5%
5	Hydro chloric acid	Sigma-Aldrich USA	37%
6	Soduim hydroxide	Merck,Germany	Analytical grade

3-4 Preparation of metal Ion Solutions;

3-4-1: stock solutions:

Weighting process;

1- PVA(polyvenylalcohol) 30g/L

30g1L(1000 ml)

x 250

$$X = \frac{30 \times 250}{1000} = 7.5 \text{ g.}$$

1-was dissolved in 7.50g of PVA in a 200 ml of de-ionized distilled water(**D.I.W**) . the solution was transfer to a 250 ml volumetric flask and completed the volume to the mark .

$\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$: 10.1g of $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ was dissolved in 25 ml de-ionized distilled water.

2-30grams of sucrose was dissolved in a liter of (D.I.W) Preparation of 0.1M NaOH solution concentration .

$$\begin{aligned}\text{Wt}(\text{weight of NaOH}) &= M \times M.Wt \times V(L) \\ &= (0.1 \times 40 \times 0.25) = 1\text{g}\end{aligned}$$

3-1g of NaOH was dissolved in 200ml of distilled water .and transferd to 250 ml volumetric flask and completed the volume to the mark with (D.I.W).

4-preparation of 10.1 HCl solution with specific concentration:

$$(\text{weight of HCl}) = M \times M.Wt \times V(l)$$

$$0.1 \times 36.5 \times 0.25$$

$$M = \frac{1000 \times 37\% \times 1.86}{36.5} = 12.022 \text{ molar (mol/L)}$$

5-Dilution Factor;

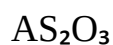
$$M_1 \times V_1 = M_2 \times V_2 = \text{number of moles}$$

$$12.022 \times V_1 = 0.1 \times 250$$

$$V_1 = \frac{0.1 \times 250}{12.022} = 2.07 \text{ ml}$$

2.07 ml of 0.1M HCl was transfer into 250ml volumetric flask and completed the volume to the mark with (D.I.W)

6-Preparation of 100ppm of As_2O_3 solution .



$$197.84 \quad 74.92 \times 2$$

$$\times \quad 1$$

$$X = \frac{197.84}{149.84} = 1.32\text{g}$$

$$\text{Wt of As}_2\text{O}_3 = 1.32\text{g}$$

Of As_2O_3 1.32g was dissolved in 100 ml of distilled water and Transferred to 1L volumetric flask and completed to the mark .(1000ppm As), Consequently , dilute the solution to 1ppm.

7-Preparation of Hg^{2+} solutions

$$X = (1 \times 342.62) / 207 = 1.655 \text{ g}$$

correction for purity: 99%

$$1.655 \quad 99$$

$$\times \quad 100$$

$$\text{Wt of Hg}^{2+} = \frac{100 \times 1.655}{99} = 1.672 \text{ grms}$$

Dissolved 1.672 g of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ was dissolved in 100 ml of distilled water and Transferred the solution to 1L volumetric flask and completed to the mark .(1000ppmHg).Consequently , dilute the solution to 1ppm.

8-Preparation 1000 of Cd^{2+} solution .

$$\text{Wt}(\text{Cd}) = (1 \times 308.47) / 114.41 = 2.696\text{g}$$

$$2.696 \quad 99$$

$$\times \quad 100$$

$$\text{Wt of Cd}^{2+} = \frac{100 \times 2.696}{99} = 2.723 \text{ g}$$

Required Wt of $\text{Cd}(\text{NO}_3)_2 = 2.723\text{g}$

1.672 g of $\text{Cd}(\text{NO}_3)_2$ was dissolved in 100 ml of distilled water and Transferred the solution to 1L volumetric flask and completed to the mark .(1000ppmCd). Consequently , dilute the solution to 1ppm.

3-4-10 Preparation of 1ppm solution of As .

$$100\text{ppm} \quad 1 \text{ ppm}$$

$$100 \times V_1 = 1 \times 1000$$

$$V = \frac{1000 \times 1}{100} = 10 \text{ ml (use 20 ml for 2L) .Required volume of 100ppm}$$

As₂O₃ solution=20 ml.

Transfer 20 ml of 100ppm As₂O₃ into a 2000ml volumetric flask and complete the volume to the mark (result 1ppm).

3-5 Preparation of Fe₂O₃ nanoparticles.[sol-gel] technique

In 250ml PVA(7.5g/L), in Erlenmeyer flask, 25 ml of Fe(NO₃)₂ was added and mixed then few drops of sucrose was added. The mixture was heated up to the boiling , on electrical heater, for about one hour. After that the mixture was put on magnetic stirrer for an hour. The precipitate was filtered and washed with distilled water then left to dry in air for 24 hours. The dry precipitate was further dried in drying oven, at 60-80 °C, for an hour .The resulted granular material was darkblack in color. Finally, the powder treated in burning furnace, at 300 and 400°C at diffemt times . The nano-material α- Fe₂O₃ is a powder and appears in different colors according to the burning heat as the following:

When the precipitate (sludge)was burned at 400 °C for two hours,the product was red in color,but when the precipitate (sludge)was burned at 300°C for three hours the color was gray.

When the weight ratio of the reactants used in the preparation of sludge was changed to 100ml(PVA)+25ml($\text{Fe}(\text{NO}_3)_2$)+200ml sucrose, the product (sludge) had never been formed.

3-6 The effect of Contact time:

To each of seven Erlenmeyer flasks contain 20 ml of 1ppm As(III) solutions, 0.1g Fe_2O_3 of nano-particle was added and shaken, using mechanical shaker (vibrator). These samples were taken at different intervals of contact time 0,20,40,60,80,120, min. The suspension was filtered. The concentration of As in solution C_t was directly determined by (GF-AAS) at the end of each time interval. The results were recorded in table (3-4).

Table (3-4) The effect of contact time on adsorption of As(III) on Fe_2O_3 nano-particles adsorption of wt=0.1g in $c_0=1000\text{ppb}$ pH=6, contact time=100min.

1ppmAs	S_1	S_2	S_3	S_4	S_5	S_6	S_7
Time(Min)	0	20	40	60	80	100	120

3-7 Effect of pH:

Eight Erlenmeyer flasks each one contain 20 ml of 1ppm As(III) solutions, 0.1g Fe_2O_3 of nano-particle added and to each flask the pH was adjusted to 2,3,4,5,6,7,8,9, using HCL or NaOH. The mixture was shaken, using mechanical shaker (vibrator) for one hour. The

concentration of As in solution C_t was directly determined by (GF-AAS) at different pH values. The mean of the results was recorded in table- (3-5) All replicated samples were (3) for each concentration.

Table (3-5) Effect of pH on adsorption of 1ppm As(III) on Fe_2O_3 nanoparticles surface adsorption of wt=0.1g in $c_0=1000$ ppb, pH=6, contact time=100min.

No.	pH	V=100ml	V=100ml	V=100ml
1	2	2.43	2.40	2.44
2	3	3.20	3.04	3.17
3	4	3.96	4.07	4.03
4	5	5.38	5.44	4.99
5	6	6.30	6.35	5.86
6	7	7.24	7.03	7.08
7	8	8.18	8.41	8.40
8	9	8.99	9.03	8.96

Table (3-6) Effect of pH on adsorption of 1ppm of As on Fe_2O_3 nanoparticles for different samples adsorption of wt=0.1g in $c_0=1000$ ppb, pH=6, contact time=100min.

No	pH	V=100ml	V=100ml	V=100ml
1	2	r_1	r_2	r_3
2	3	r_1	r_2	r_3
3	4	r_1	r_2	r_3
4	5	r_1	r_2	r_3
5	6	r_1	r_2	r_3
6	7	r_1	r_2	r_3
7	8	r_1	r_2	r_3
8	9	r_1	r_2	r_3

Table (3-7) Dilution sequence of 1 ppm (final volume 100 ml) adsorption of wt=0.1g in $c_0=1000\text{ppb}$, pH=6, contact time =100min.

NO	MI	Concentration ppm
1	1	0.01
2	5	0.05
3	8	0.08
4	10	0.1
5	20	0.2
6	40	0.4
7	50	0.5
8	60	0.6

To each of eight Erlenmeyer flask contain 20 ml of solutions of different concentrations C_0 (0.01 ,0.05,0.08,

,0.2,0.4,0.5,0.6), 0.1g Fe_2O_3 of nano-particle was added .the pH was adjusted to 6 .

and was shaken, using mechanical vibrator for one hour. The concentration of As in solution C_t was directly determined by (GF-AAS)for each concentration.The results was recorded in table (3-7) All the samples were tripled to get the accurate results.

Table (3-8) Effect As concentration on adsorption of As on Fe₂O₃ nanoparticles surface modified by oxine adsorption of wt=0.1g in c₀=1000ppb,pH=6,contact time =100min.

Concentration	pH20 ml	pH 20 ml	pH 20 ml
0.01 ppm	6.05	6.01	6.05
0.05 ppm	6.09	6.07	6.07
0.08 ppm	5.97	6.03	6.03
0.1 Ppm	6.01	6.01	6.03
0.2 ppm	5.98	5.96	6.09
0.4 ppm	5.93	5.93	5.60
0.5 ppm	5.88	5.74	5.72
0.6 ppm	5.70	5.68	5.78

The pH Of 6 samples (n=6) was measured with sludge.

$$1000 \times V = 100 \times 100 \text{ ml}$$

$$V = 10 \text{ ml}$$

Take 10 ml of liter 100ml

Of concentration(Hg) 100

Stoke concentration following.

Table (3-9) Dilution sequence of 100 ppm (final volume 100 ml) adsorption of wt=0.1g in c₀=1000ppb,pH=6,contact time=100min.

No	ml of 100ppm	Concentration of Hg
1	0.5	0.5
2	2.5	2.5
3	1	1
4	5	5
5	10	10
6	25	25

Table(3-10) Mixture of 10ml 0,5ppm As +10ml of Hg and pH of the solution: adsorption of wt=0.1g in $c_0=1000\text{ppb}$, pH=6, contact time=100min.

No	As ppm	Hg ppm	pH	pH
1	0.5	0.5	6.23	6.34
2	0.5	2.5	6.34	5.86
3	0.5	1	6.18	6.11
4	0.5	5	6.24	6.22
5	0.5	10	6.32	6.30
6	0.5	25	6.32	5.88

$$1000 \times V = 100 \times 100$$

$$V = 100 \times 100 / 1000 = 100 \text{ ML}$$

Table (3-11) Dilution sequence of 100 ppm (final volume 100ml): adsorption of wt=0.1g in $c_0=1000\text{ppb}$, pH=6, contact time=100min.

No	Ml of 100ppm	Concentration of Cd
1	0.5	0.5
2	2.5	2.5
3	1	1
4	5	5
5	10	10
6	25	25

Table (3-12) Mixture of 10ml o 0,5ppmf As +10ml ofCd and pH of the solution: adsorption of wt=0.1g in $c_0=1000\text{ppb}$, pH=6, contact time=100min.

No	As ppm	Cd ppm	pH	pH
1	0.5	0.5	6.17	6.29
2	0.5	2.5	6.30	6.25
3	0.5	1	6.16	5.96
4	0.5	5	5.87	5.98
5	0.5	10	6.29	6.05
6	0.5	25	6.19	5.96

Result and discussion

4-1 Characterization of prepared Fe₂O₃ nanoparticles.

XRD and TEM, SEM were used to characterize Fe₂O₃ nanoparticles for preparation of Fe₂O₃ nanoparticles that the powder was nanoscale. According to the experimental section (3-6-1) and (3-6-2).

4-1-1 XRD

XRD pattern were recorded on prepared and calcined samples using instrument as described in section (1-23). the 2θ scans were recorded at several resolution using Cuka radiation of wave length 1.54Å in the rang 20-80 with 0.05 step size. The recorded patterns were analyzed using jade soft ware to determine the peak position, width and intensity. Full width at half maxima (FWHM) data was analyzed by scherrer's formula.

$$T = \frac{0.9\lambda}{b \cos \theta}$$

Where λ is x-ray wave length, B is peak width and θ Braggs angle K.

Fig (4-1) shows the (XRD) pattern for Fe₂O₃ nano particles synthesized via this method .The prepared nanoparticles showed that (Fe₂O₃) has tetragonal symmetry (simple tetragonal) and belongs to D_{4h} .

-14/and space group with lattice constants of $a=0.348\text{nm}$, $C=0.952\text{nm}$ and $\frac{c}{a}=0.73\text{nm}$. The crystal structure of the obtained powder was indicated in figure (4-1). All the diffraction peaks can be indexed as the pure phase for Fe_2O_3 nanoparticles. The obtained powder has high purity of anatase phase. No characteristic peak impurity of impurities such as $\text{Fe}(\text{NO}_3)_2$ was detected. The average crystalline size of nanoparticles were determined to be (70 nm) utilizing Scherrer formula ($T=\frac{k\lambda}{b\cos\theta}$), where T is the mean crystallite size of the powder, λ is the wavelength of $\text{CuK}\alpha$, $\lambda=1.5405\text{\AA}$, B is the full width at half maximum (FWHM) intensity of the peak in radian. θ is Bragg's diffraction angle and K is a constant usually equal to 0.9. Thus peaks are in good agreement with rutile phase (JCPDS) card No-21-1267.

$$T = \frac{0.9 \times \lambda}{B \cos \theta} = \frac{0.9 \times 1.54056}{0.6469 \times 7.93 \times 10^{-3}}$$

$$= 700\text{\AA} \quad = 70\text{nm}$$

B_a measured breadth of bulk material about maximum intensity B_0 measured breadth of observed material in half maxima.

$$[B = (B^2 - B_0^2)^{1/2}]$$

1-The XRD data peak positions are the same for all the samples.

2-The phases formed are pure.

3-All the samples show marked peak broadening confirming that the samples are indeed nanostructures, the size analysis was done.

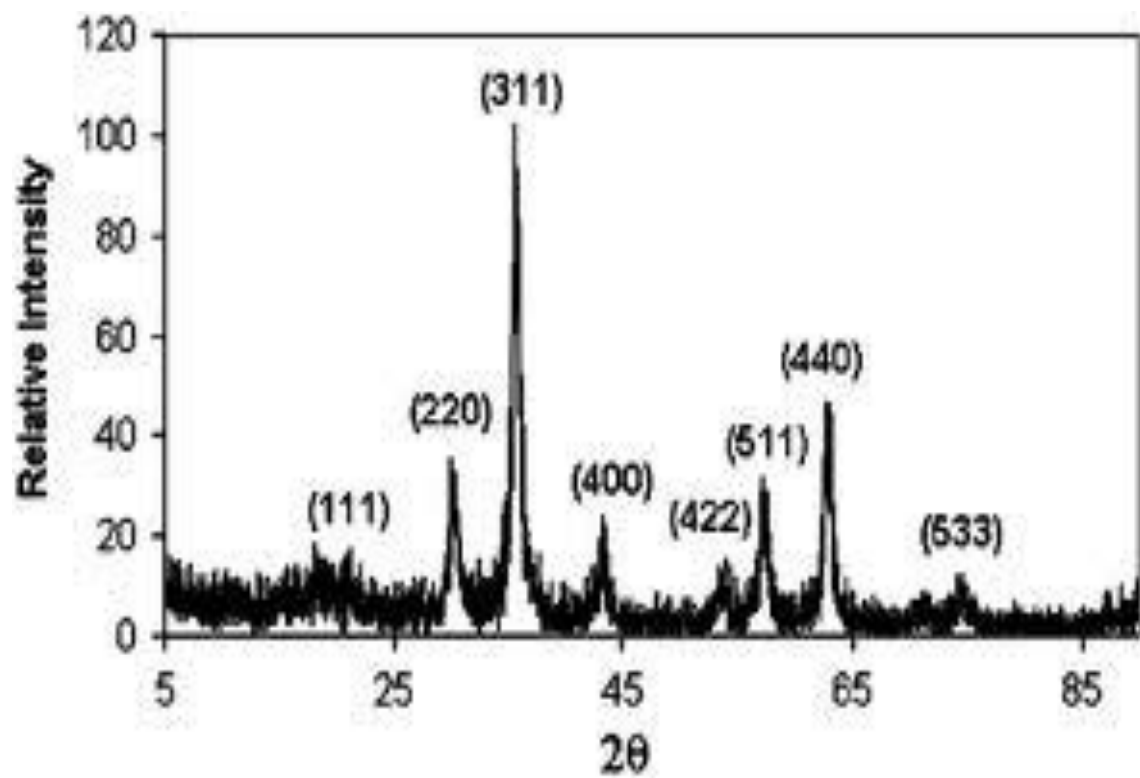


Fig (4-1) XRD of α Fe_2O_3 nano particles

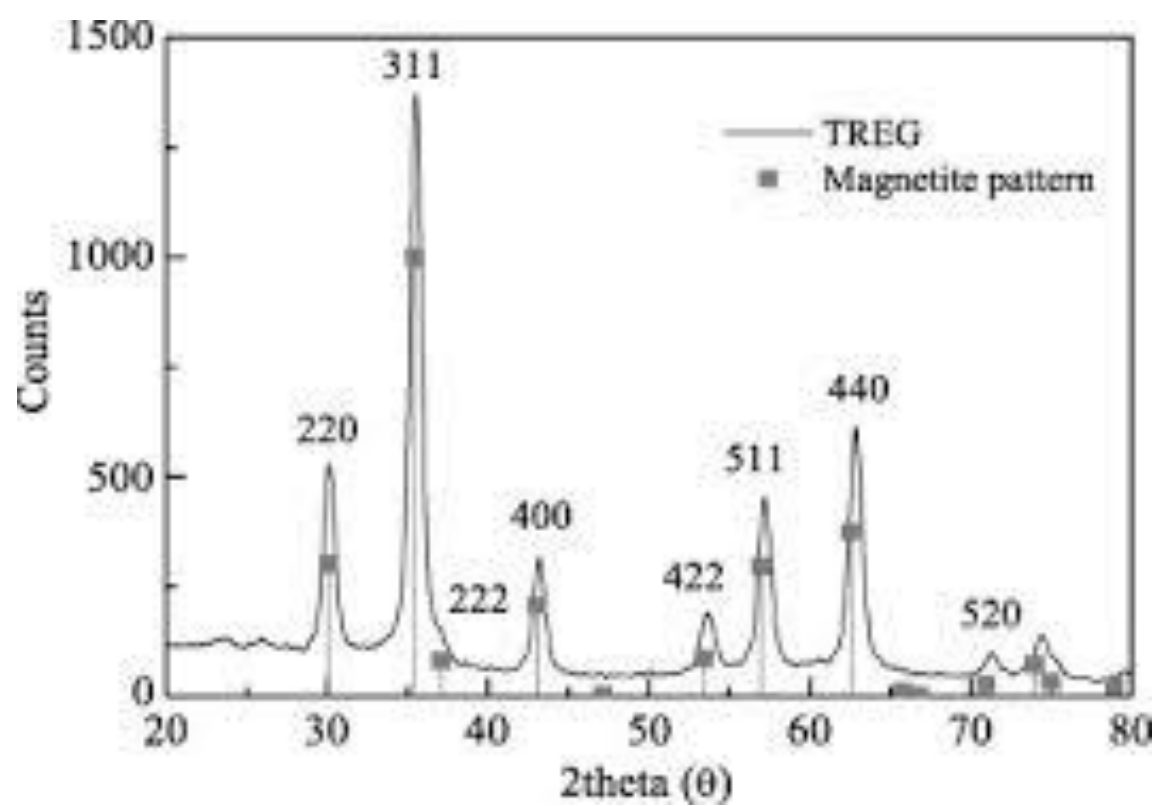


Fig (4-2) XRD of $\alpha\text{-Fe}_2\text{O}_3$ nano particles

4-1-2 SEM

Scanning electron microscope shows that the dimensions of the nanoparticles were between 30-70 nm Fig (4-3) and Fig(4-4) as shown in

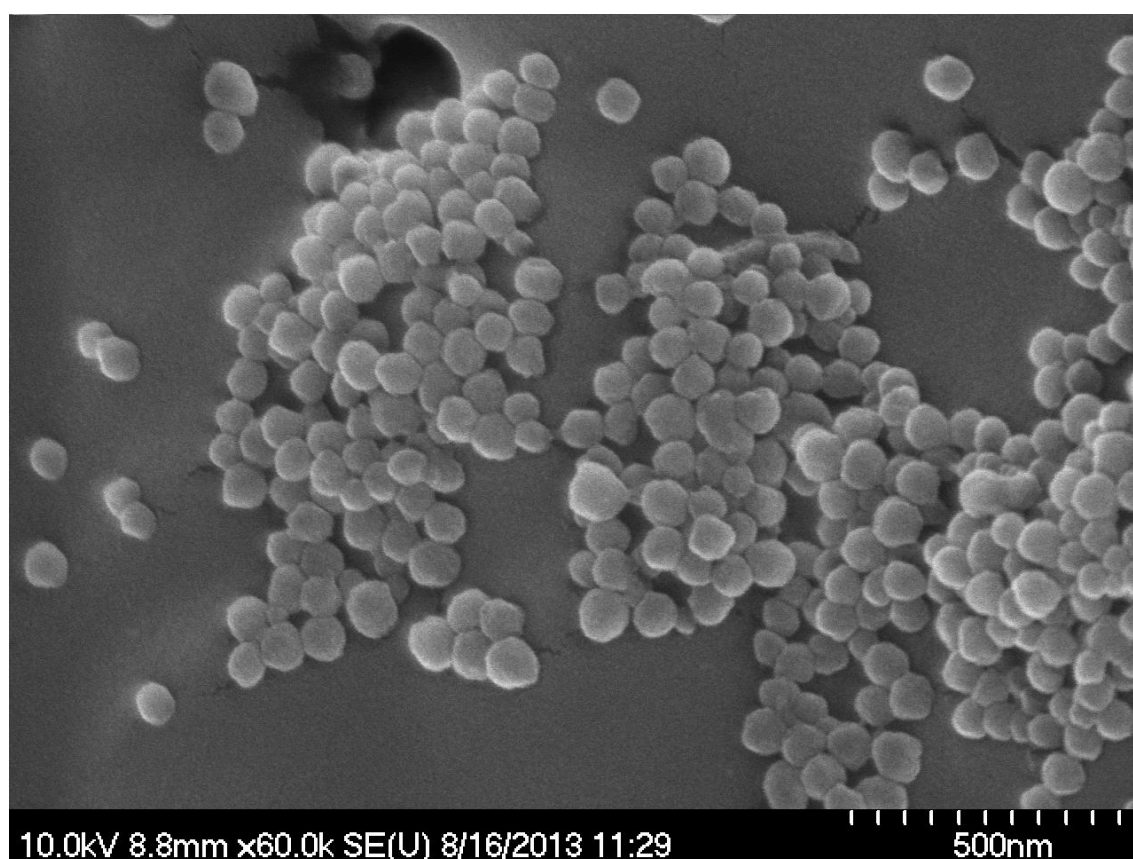


Figure (4-3) SEM Image of [α Fe_2O_3 nano particals]

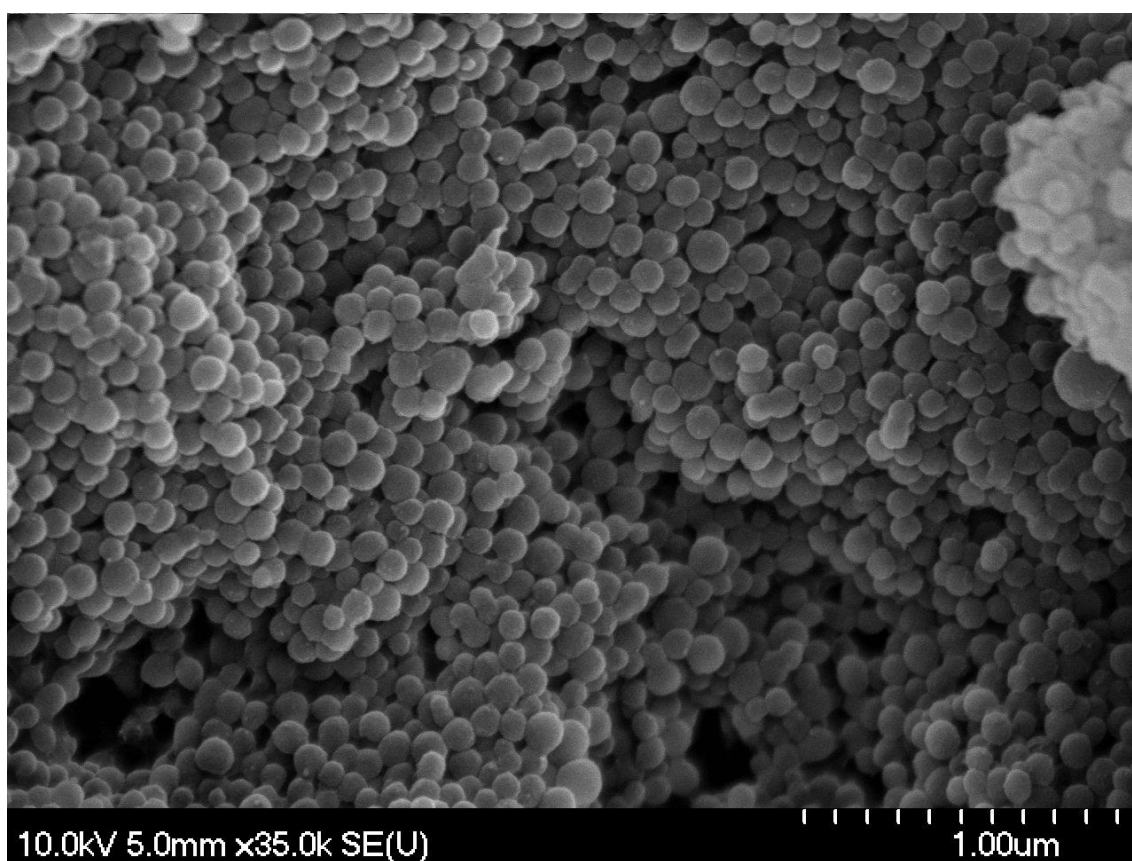


Figure (4-4) SEM Image of [α Fe_2O_3 nano particals]

4-1-3 TEM

TEM shows the dimensions of Fe_2O_3 nanoparticles were between 1-100 nm, as shown in figure (4-5).

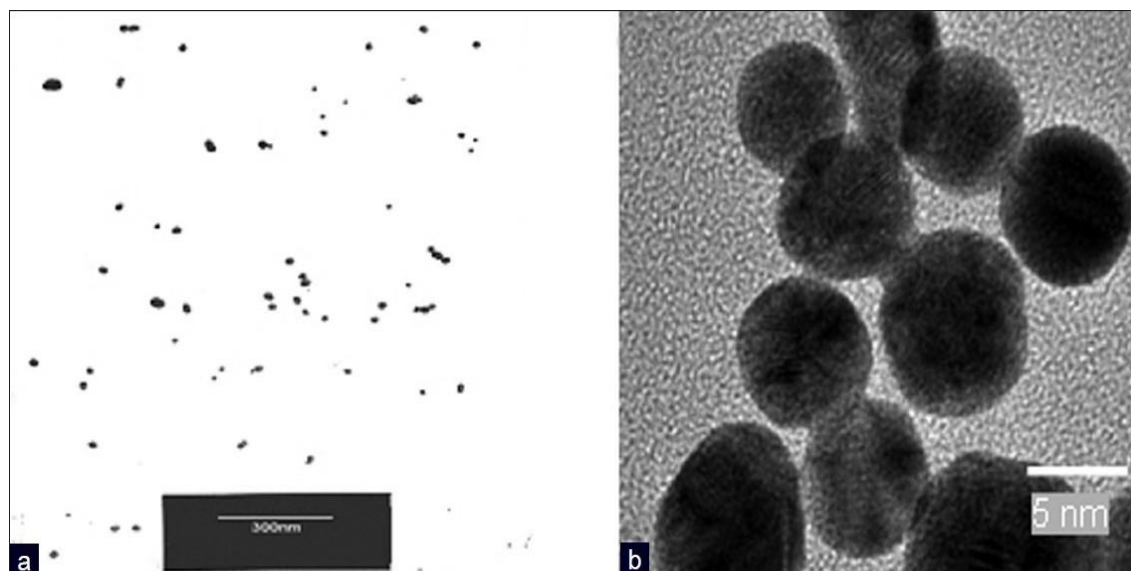


Fig (4-5) TEM Image of $\alpha\text{Fe}_2\text{O}_3$ nanoparticles

4-2 Adsorption Process

Contaminated aqueous solution were artificially prepared from stock solution of As(III) ,Hg(II) and Cd(II).The weight of Fe₂O₃ nanoparticles (0.10 g) was measured in erlenmeyer tubes.The contaminated aqueous solution were added to each tube.The time measuring at the moment the contaminated water is added.The adsorption behavior was studied under four different conditions of :

1-Contact time

2-Different pH Values

3-Different metal Ion concentrations

4-Different dosage of Fe₂O₃ nanoparticles.

4-2-1 The effect of contact time

The effect of contact time was examined to find suitable contact time at which the nanoparticles are saturated and the adsorption is at equilibrium

The artificially contaminated water (20 ml) were treated with 0.1 g of Fe_2O_3 nanoparticles in room temperature ($21.5 \pm 1^\circ\text{C}$) after different periods of contact times, the times of the treatments were: 20 min, 40 min, 60 min, 80 min, 100 min, 120 min. It was found that 100 min was the best period of time in which maximum percent removal was reached, so it was used during the study of other behaviours.

Table (4-1): Mean value of final concentration, C_f , of arsenic as a function of time, wt=0.1g, contact time 100 Min, pH =6.5, $C_0=1000\text{ppb}$

Time	As pbb	% Removal
20	174.295	82.57%
40	271.86	85.4%
60	117.265	88.27%
80	74.30	92.57%
100	18.64	98.14%
120	10.18	98.16%

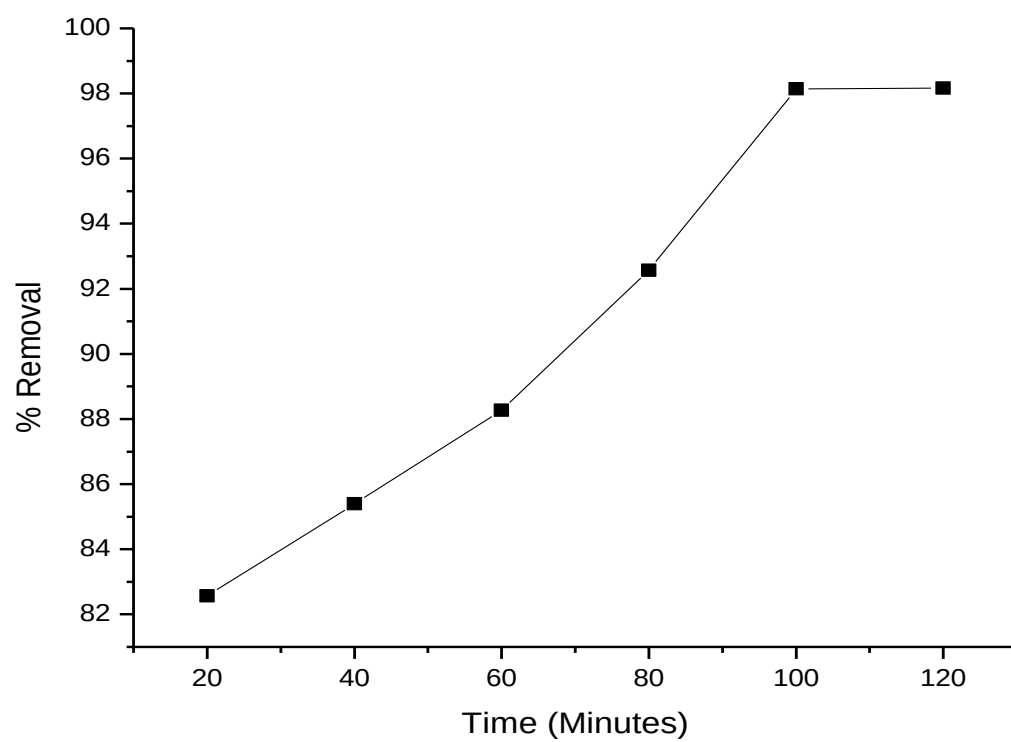


Fig (4-6) Adsorption of As on nano iron oxide surface

4-2-2 The effect of pH

The pH was adjusted by adding 0.1M HNO₃ and 0.1M NaOH Solutions into the ultra pure deionized water. Eight solutions of different pH (from pH 2 to pH9) were prepared. the solutions were treated for 100nm with 0.1 g of Fe₂O₃ nanoparticles in room Temperature and at pH 6.5.the concentration of metals was measured by(GFAAS) and ICP-MS before and after the treatment .the percent removal (%) of heavy metals was calculated Three trials for each PH conducted .

Table (4-2) mean value of final concentration ,C_f of arsenic as a function of pH, wt=0.1g, contact time 100Min, Concentration =1000ppb

pH	Ppb of As (III)	% Removal
2	173.85	65%
3	202.51	71%
4	24.25	79%
5	5.995	97.57%
6	15.945	99.65%
7	3.545	99.40 %
8	16.125	98.38%
9	10.33	98.96%

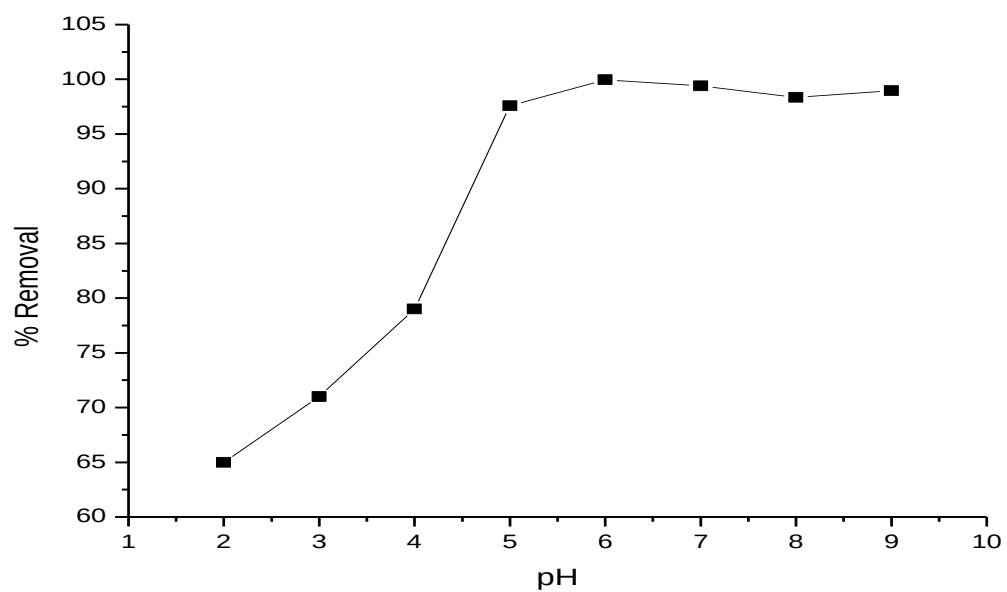


Fig (4-7) Adsorption of As on nano iron oxide surface

4-2-3 The effect of concentration of target metal ion

The effect of different concentrations of metal ions were prepared. All prepared solutions were treated for 100 min with 0.1g of Fe_2O_3 nanoparticles in room temperature and at pH 6. Three trials were made for each concentration.

Table (4-3) Mean value of final concentration, C_f of arsenic as a function of C_i , wt=0.1g, pH=6, contact time=100Min

C_i	C_f	Removal
10	1.8	82%
50	4.1	92%
80	1.54	98%
100	1.24	98.76%
200	1.16	99.42%
400	2.55	99.36%
500	0.62	99.98%
600	1.33	99.77%

C_i = Initial concentration

C_f = Final concentration

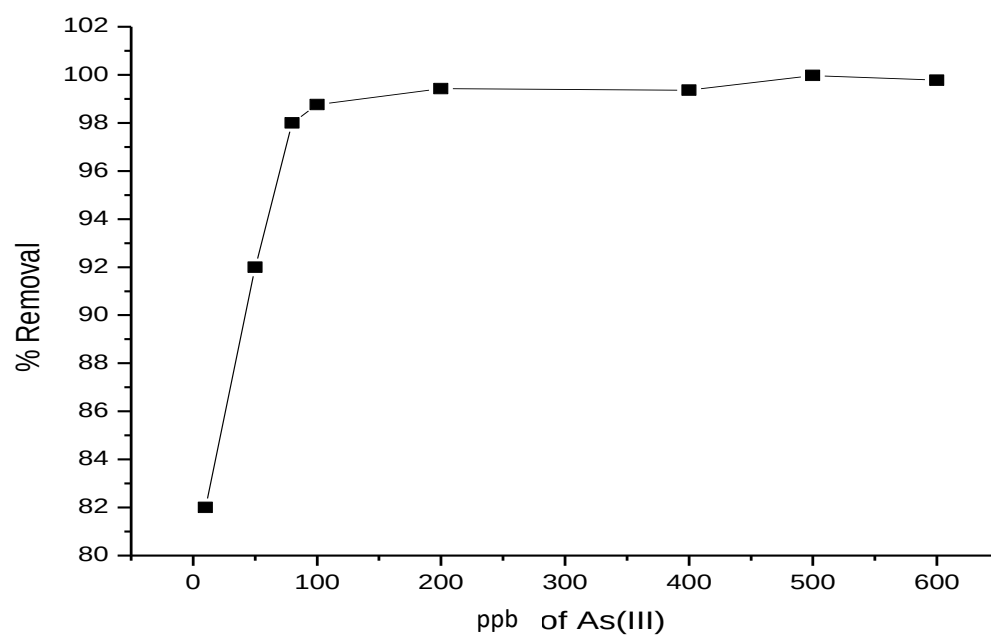


Fig (4-8) Adsorption of As on nano iron oxide surface

4-2-4 The effect of different dosage of Fe_2O_3 nanoparticles

Different masses of nanoparticles (0.1 g, 0.2 g, 0.5 g) were used to treat 20 ml of the metal ion solution. Three trials for each mass were conducted.

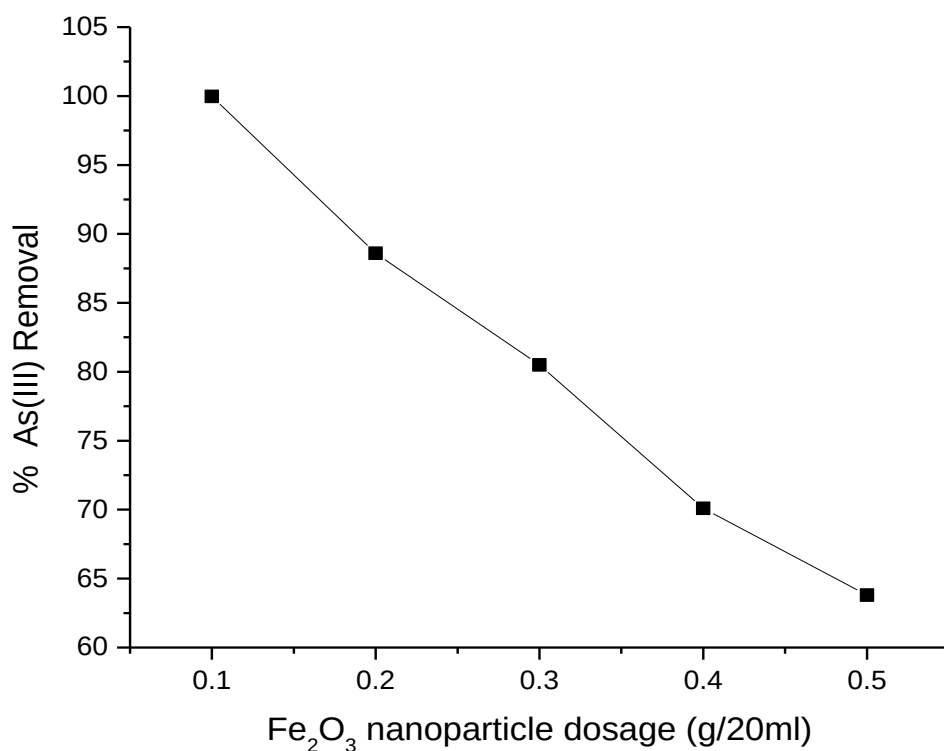


Fig (4-9) The effect of different dosage of Fe_2O_3 nanoparticles.

4-3 Effect of concentration of Hg

The results of adsorption of Hg on γ -Fe₂O₃ nanoparticles in the presence of 0.5 As shown in table (4-4) and figurer(4-9).

Table (4-4) Mean value of final concentration C_f of Hg a as a function of pH, wt= 0.1g, contact time 100 Min, Concentration =1000 ppb

C_i (Hg) ppm	C_f (Hg) ppm	% Removal
0.5	0.0650	87 %
1	0.0835	91.65 %
2.5	0.1580	93.76 %
5	0.3097	93.80 %
10	0.6350	93.65%
25	1.506	93.97 %

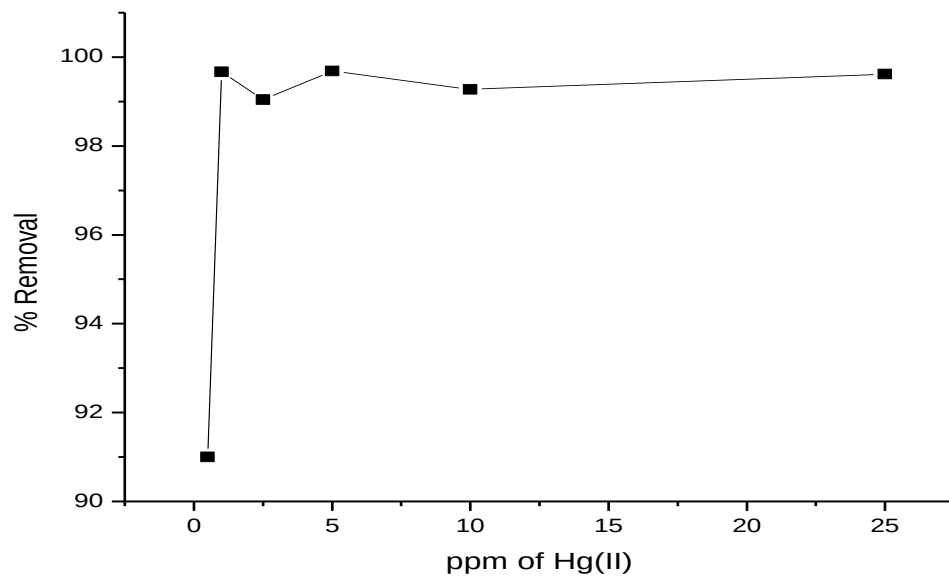


Fig (4-10) adsorption of Hg on-n $\propto Fe_2O_3$ the presence of (As, Hg).

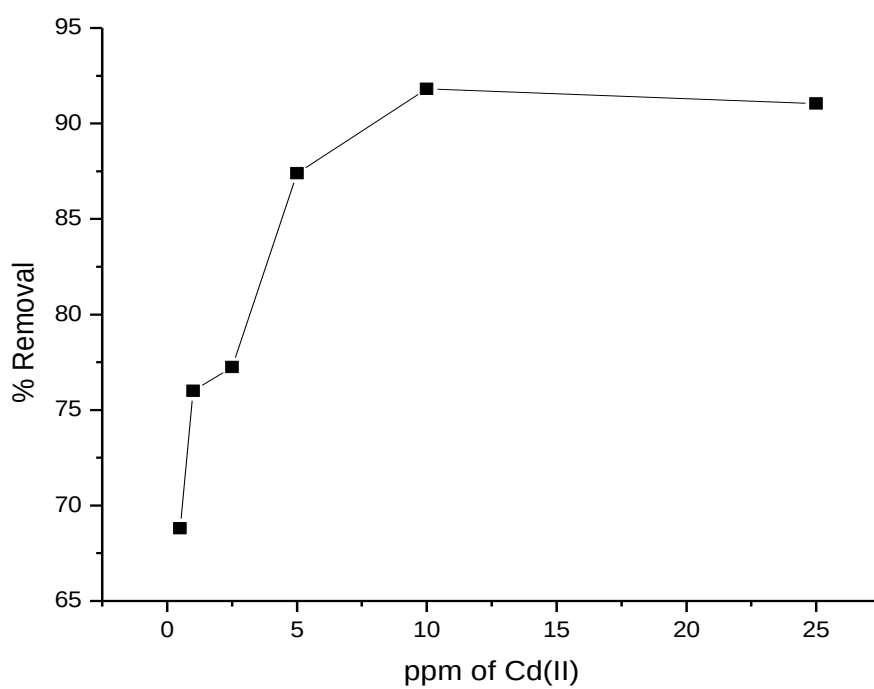
4-4 Effect of concentration of Cd

The results of effect of adsorption of Cd on n-Fe₂O₃ in the presence of 0.5

As shown in table (4-5) and figurer(4-10).

Table (4-5) Mean value of final concentration C_f of Cadium as a function of pH, wt=0.1g, contact time 100Min, Concentration =1000ppb

C_i	C_f	Removel
0.5	0.156	68.8 %
1	0.240	76 %
2.5	0.569	77.24 %
5	0.630	87.39 %
10	0.819	91.80 %
25	2.241	91.04 %



Fig(4-11) adsorption of Cd on $n \propto Fe_2O_3$ in the presence of (As, Cd).

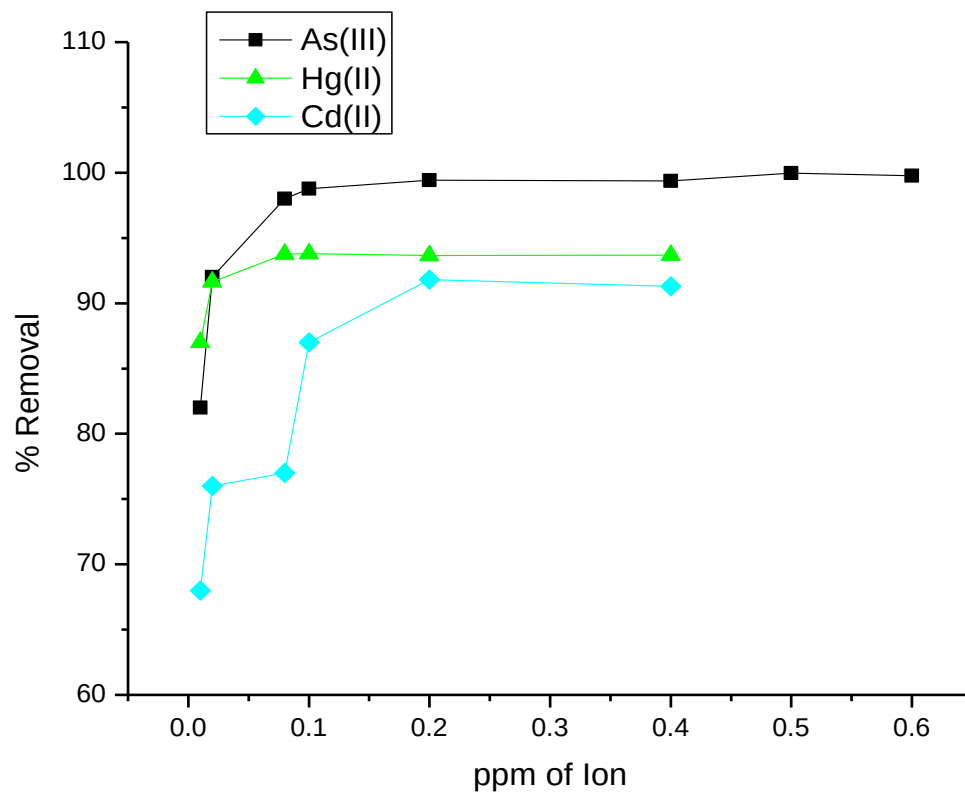


Fig (4-12) shows the relation between the concentration of metal ion (ppm) and % Removal for all the metal ions.

4-5 Adsorption capacities

The adsorption capacity is an important factor because it determines how much adsorbent is required to quantitatively concentrate the analyses a given solution. Study the adsorption capacity was mentioned in the paper recommended by Maguierira et al.

$$Q_e = \frac{C_0 - C_e V m}{W t(g) \times 1000}$$

Table (4-6) shows the relation between concentration of As(III) (ppb) and adsorption capacity Q_e (mg/g). Table (4-6) shows the mathematical Langmuir adsorption isotherm for adsorption of As(III) onto Fe_2O_3 nanoparticles modified oxine and figure (4-13). Table (4-6) shows the mathematical Langmuir adsorption isotherm for adsorption of As(III) onto Fe_2O_3 nanoparticles modified oxime. It was found that the maximum adsorption capacity of Fe_2O_3 nanoparticles modified oxine for As (III) up to .

Slop=1.136, intercept=0.0145.

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e}$$

$$\frac{1}{b Q_e} = \text{slop}$$

$$B = \frac{\text{Intercept}}{\text{slop}} = \frac{4.68 \times 10^{-4}}{0.1997} = 2.34 \times 10^{-3}$$

$$0.199 = \frac{1}{4.68 \times 10^{-4} \times Q_e}$$

$$Q_0 \times 0.000468 = 0.199$$

$$Q_0 = 427.136 \text{ (mg/g)}$$

Table (4-6) The relation between concentration of As^{+3} (mg/L) and adsorption capacity (Q_e) (mg/g). as a function of pH, wt=0.1g, contact time 100Min, Concentration =1000ppb.

C(ppm)	Ce (ppm)	(C₀-Ce) x 20	$\frac{(C - Ce) \times 20}{0.1 \times 10.0}$
0.01	0.0018	0.164	0.00164
0.05	0.004	0.920	0.0092
0.08	0.0016	1.568	0.0156
0.1	0.00124	1.975	0.0197
0.2	0.0016	3.968	0.0396
0.4	0.00256	7.948	0.0794
0.5	0.0001	9.998	0.0999
0.6	0.00138	11.972	0.1197

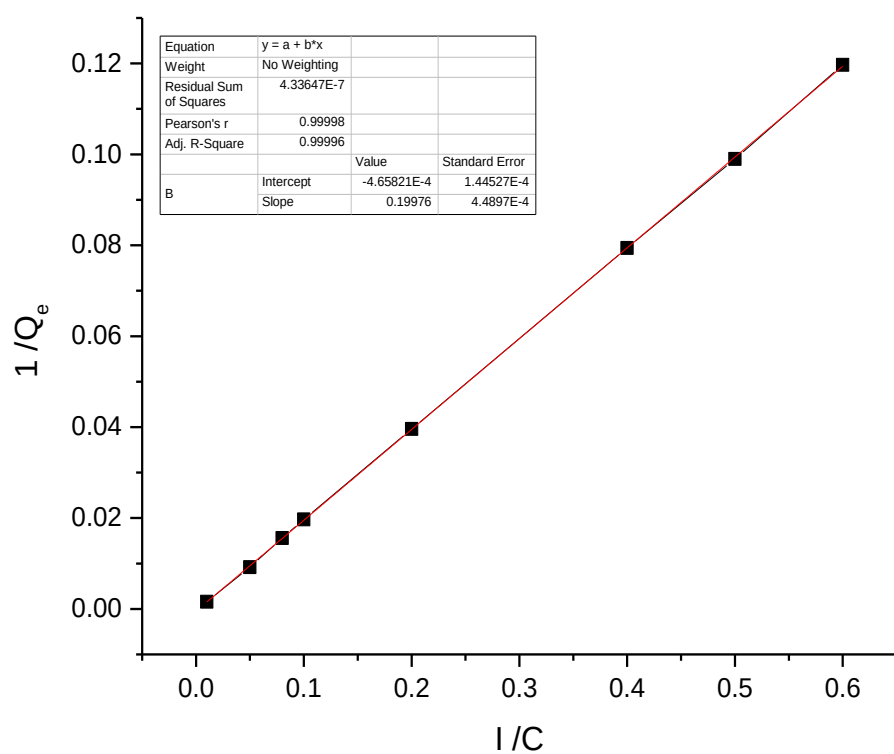


Fig (4-13) Langmuir adsorption isotherm for adsorption of As^{3+} onto $\alpha\text{Fe}_2\text{O}_3$ nanoparticles.

4-6 Analysis of As(III) in real samples.

20 ml of samples was transferred into a 100ml erlemeyer flask and pH was adjusted to the desired value pH with diluted HNO_3 and NH_4OH .

Then 100mg of Fe_2O_3 nanoparticles were added and the mixture was shaken vigorously for 6h to facilitate adsorption of As(III) Ions onto its surface. After the solution were centrifuge, concentration of As(III).Ions in the solution were directly determined by ICP-MS and GFAAS using EPA3005A1992.And EPA6010C2007.Nte every samples was repeated three times (n=3) .

Table(4-7) the results of As in real water samples (n=2)

Sample	Concentration of As (III) mg/l	Sd(yE)
1	0.94	0.97
2	1.64	0.14
3	1.535	0.24
4	1.24	1.03
5	1.16	0.11
6	2.545	1.59
7	0.615	0.19
8	1.33	0.43

-Elution;

0.5M HNO_3 was used for sufficient complete elution .Therefore the volume of 20 ml elute was added to filter paper after filtration the concentration the solution was measured using and GFAAS.

4-7 Stability and reproducibility tests;

To test stability and reproducibility,the new sorbent was subjected to several loading and elution bath operation.The sorption conditions are referenced according to the above experiments.The elution were carried out by shaking the sorbent with 20 ml of 0.5M HNO_3 together for 1h so as to ensure complete equilbation .The sorbent showed better stability and reproducibility As(III).

Conclusion

This study showed that the prepared α - Fe_2O_3 nanoparticles could be used as an alternate to the conventional adsorbents for the removal of metal ions from wastewater with high removal efficiency within a very short time. The removal of As, Hg and Cd as a typical metal ion commonly present in wastewater, by adsorption onto α - Fe_2O_3 nanoparticles was successfully accomplished. Adsorption was very rapid and equilibrium was achieved within As, Hg and Cd. It also showed that adsorption was highly dependent on the initial concentration of As, Hg, Cd and initial pH value. Maximum removal efficiency was achieved at pH 5.5 at room temperature. The adsorption isotherms were also determined and were appropriately described by both Langmuir and Freundlich models, with a better fitting to the Langmuir model than the Freundlich model. Therefore, α - Fe_2O_3 nanoparticles were recommended as fast, effective, and inexpensive nano adsorbents for rapid removal and recovery of metal ions from contaminated water.

Recommendations

There are different areas in which the project of this study can be further investigated. These include:

1-Research also needs to be undertaken to determine regeneration mechanism for Fe_2O_3 - nanoparticles.

2Study the kinetic of adsorption of As^{+3} onto Fe_2O_3 nanoparticles.

3-Apply this method solid phase extraction (SPE) to other real samples waste water.

4-Apply other nanoparticles such as Al_2O_3 , ZnO , Fe_2O_3 and Fe_3O_4 to other metal ions such as Pb^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , $\text{As}(\text{v})$.

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Final concentration, C_f , of arsenic as a function of time, t

Number	Experiment number	Time	As ppb
1	T_1	20	128.11
2	T_1	20	220.48
3	T_2	40	349.24
4	T_2	40	149.48
5	T_3	60	205.0
6	T_3	60	29.53
7	T_5	100	0.020
8	T_4	80	74.30
9	T_5	100	37.26
10	T_6	120	197.66
11	T_6	120	43.34

Final Concentration ,C_f of arsenic a function of pH.

Number	Experiment number	PH	As ppb
14	RPH ₂	2	163.57
15	RPH ₂	2	184.13
16	RPH ₃	3	207.29
17	RPH ₃	3	179.73
18	RPH ₄	4	12.06
19	RPH ₄	4	36.44
20	RPH ₅	5	7.23
21	RPH ₅	5	4.76
22	RPH ₆	6	27.48
23	RPH ₆	6	4.41
24	RPH ₇	7	3.77
25	RPH ₇	7	3.32
26	RPH ₈	8	27.39
27	RPH ₈	8	4.86
28	RPH ₉	9	4.9
29	RPH ₉	9	15.7

Final Concentration ,C_f of arsenic a function of pH.

Number	PH	As ppb (Ce)
14	2	163.57
15	2	184.13
16	3	207.29
17	3	179.73
18	4	12.06
19	4	36.44
20	5	7.23
21	5	4.76
22	6	27.48
23	6	4.41
24	7	3.77
25	7	3.32
26	8	27.39
27	8	4.86
28	9	4.9
29	9	15.7

final of concentration C_f of cadmium as a function

Number	C_i (Cd)	C_f(Cd)
1	0.5 ppm	0.04
2	0.5 ppm	0.131
3	1 ppm	0.031
4	1 ppm	0.03
5	2.5 ppm	0.036
6	2.5 ppm	0.02
7	5 ppm	0.112
8	5 ppm	0.349
9	10 ppm	0.2042
10	10 ppm	0.234
11	25 ppm	0.475
12	25 ppm	0.618

final of concentration C_f of Hg afunction

No	Ci (Hg)	Cf(Hg)
1	0.5 ppm	0.0374
2	0.5 ppm	0.0536
3	1 ppm	0.0055
4	1 ppm	0.0012
5	2.5 ppm	0.1090
6	2.5 ppm	0.0589
7	5 ppm	0.0302
8	5 ppm	0.0009
9	10 ppm	0.0118
10	10 ppm	0.1332
11	25ppm	0.0514
12	25 ppm	0.139

4-10 Statistical Analysis:

Statistical analysis were carried out all results using Orgin 7.5 program (2008),The results of all sample are shown in tables.

The statistical analysis of results (water sample n=3)

Row(x)	Mean(y)	Sd(y Er)	Se(y Er)	Min(y)	Max(y)	Range(y)	Sum(y)	N
1	0.94	0.97581	0.69	0.25	1.63	1.38	1.88	3
2	1.64	0.14142	0.1	1.54	1.74	0.2	3.28	3
3	1.535	0.24749	0.175	1.36	1.71	0.35	3.07	3
4	1.24	1.03238	0.73	0.51	1.97	1.46	2.48	3
5	1.16	0.11314	0.08	1.08	1.24	0.16	2.32	3
6	2.545	1.59099	1.125	1.42	3.67	2.25	5.09	3
7	0.615	0.19092	0.135	0.48	0.75	0.27	1.23	3
8	1.33	0.43841	0.31	1.02	1.64	0.62	2.66	3

The results of Hg in real samples(n=3)

pH	Concentration of Hg	Sd(yE)
6	0.0952	0.061
6	0.01555	0.020
6	0.00335	0.0030
6	0.0725	0.085
6	0.0455	0.011
6	0.08395	0.035

The statistical analysis of results (water sampes n=3)

Row(x)	Mean(y)	Sd(y Er)	Se(y Er)	Min(y)	Max(y)	Range(y)	Sum(y)	N
1	0.0952	0.06194	0.0438	0.0514	0.139	0.0876	0.1904	3
2	0.01555	0.02072	0.01465	9E-4	0.0302	0.0293	0.0311	3
3	0.00335	0.00304	0.00215	0.0012	0.0055	0.0043	0.0067	3
4	0.0725	0.08584	0.0607	0.0118	0.1332	0.1214	0.145	3
5	0.0455	0.01146	0.0081	0.0374	0.0536	0.0162	0.091	3
6	0.08395	0.03543	0.02505	0.0589	0.109	0.0501	0.1679	3

The results of Cd in real samples(n=2)

pH	Concentration of Cd	Sd(YE)
6	0.0855	0.064
6	0.0305	7.07
6	0.028	0.011
6	0.2305	0.16
6	0.2191	0.021
6	0.5465	6.10

The statistical analysis of results (water samples n=3)

Row(x)	Mean(y)	Sd(yEr)	Se(yEr)	Min(y)	Max(y)	Range(y)	Sum(y)	N
1	0.0855	0.06435	0.0455	0.04	0.131	0.091	0.171	3
2	0.0305	7.07107E-4	5E-4	0.03	0.031	1E-3	0.061	3
3	0.028	0.01131	0.008	0.02	0.036	0.016	0.056	3
4	0.2305	0.16758	0.1185	0.112	0.349	0.237	0.461	3
5	0.2191	0.02107	0.0149	0.2042	0.234	0.0298	0.4382	2
6	0.5465	0.10112	0.0715	0.475	0.618	0.143	1.093	3



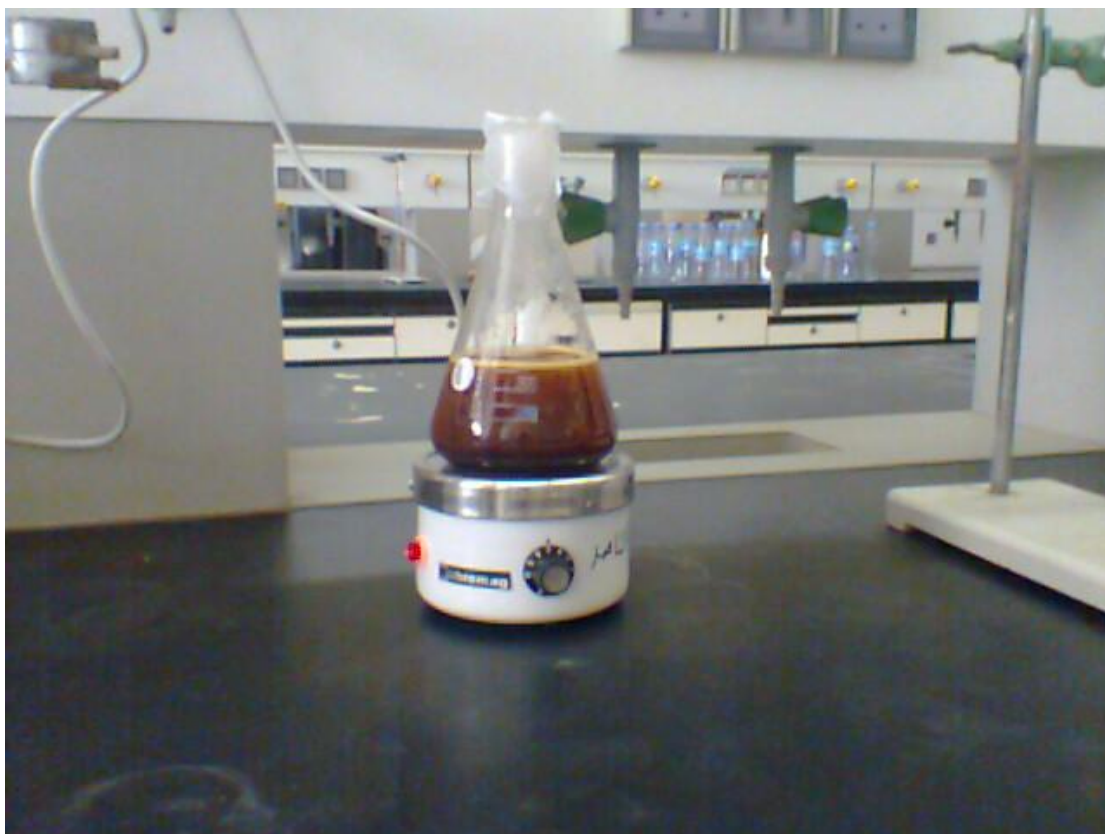
Chemicals used in this Study



α Fe_2O_3 Preparation



α Fe_2O_3 Preparation



α Fe_2O_3 Preparation



Shakers used in this study



α Fe_2O_3 Preparation



$\propto Fe_2O_3$ – *before (ignation)*



$\propto Fe_2O_3$ – *before (ignation)*



$\propto Fe_2O_3$ – *before (ignation)*

