Development of Analytical Method for Adsorption and Separation of Cadmium (II) By Magnetic Nanoparticles

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   Abstract: Cadmium is one of the toxic elements, used in many industries. It is an toxic heavy metal that affects living organism cadmium can be removed from water by adsorption, chemical precipitation, ion exchange, reverse osmosis, electrochemical treatments. Due to low cost-effective, high efficiency, adsorption technology is regarded as the most promising one to remove heavy metal ion from other techniques nanoscale iron oxides have become raw material for treating the waste waters and soils. Fe_2O_3 magnetic nanoparticles adsorbs Cadmium (II) this experiment was studied by Batch adsorption method

   Percentage adsorption decrease as pH of solution increases. The adsorption is maximum at 5 pH and then it is decreases. Percentage adsorption decrease as metal ion concentration increases. The adsorption is maximum up to 200 µg/ml and then it is decreases. Percentage adsorption decrease as metal ion concentration increases. The adsorption is maximum at 50 µg/ml. The 10 min. contact time is sufficient for maximum adsorption of Cd (II) particles

      The present study shows MNP's can be used as an inexpensive sorbent for the sorption of Cd^{+2} from aqueous solution. Thus, this work provides an alternative adsorbent for cadmium removal from aqueous solution

Index Terms - **Cadmium adsorption, toxic heavy metal, metal oxides, Nano scale iron oxide**

I. INTRODUCTION

Extensive, industrialization and improper disposal are attributed to be a prime factor responsible for the release of heavy metals into the ecosystems. Once released, the heavy metals tend to bio accumulate in higher trophic levels of the food chain. Almost all heavy metals are toxic to living beings and excessive levels are known to cause both acute and chronic toxicity. Heavy metals cannot be degraded or destroyed, moreover, the natural process of metal mineralization is very slow Hence, removal of heavy metals from water and waste water is best accomplished by immobilization and concentration on suitable sorbents. The sorbed metals can be removed and reused as raw materials. Cadmium is one of the toxic elements. Cadmium is mainly used in industries involved in electroplating, NiCd battery manufacturing, pigment manufacturing, galvanizing, plastic manufacture, alloy manufacture, etc. For quite a long time cadmium has been recognized only due its potential toxicity, but after the incident of "ltai Itai" disease in Japan due to poisoning concemrn regarding cadmium in the environment is on the increase [1].Cadmium is an extremely toxic heavy metal that can affect humans, animals, plants, and microbes [2]. In humans it is associated with

renal damage, bone pain and porosity, hypertension, anemia, and cancer (3) Nickel cadmium battery is one of the major rechargeable batteries in use today in a wide variety of consumer and industrial applications. To minimize any risk which might arise from the the disposal of the spent NiCd batteries, it is necessary to recycle all NiCd batteries by separating nickel and cadmium. Thus there is an analytical requirement to separate and determine traces of cadmium in various types of samples ranging from geological to industrial effluents, Cadmium as a minor component of zinc ores is a toxic heavy metal of environmental concern and is classified as Bl carcinogen by US Environmental Protection Agency [4-5] Exposure to cadmium released in food and drinking water will lead to cardiovascular and cerebrovascular diseases,calcareous bone and kidney dysfunction There are many types of nanomaterials with these characteristics ,but magnetic iron oxide nanoparticles are an efficient adsorbent, which couples magnetic separation with ion exchange capacity for removal of heavy metals pollutants. Nano iron oxides,such as magnetic (Fe_3O_4) and maghemite (y-Fe_2O_3), and also different ferrite compounds are known as materials used in different biological and industrial application. These materials have unique magnetic and electronic properties. Due to their chemical stability, biocompatibility and heating ability, ferrofluids of maghemite nanoparticles can be used for ferrofluids hyperthermia in tumor treatment [21]

1.1 Nanomaterial's as Sorbents to Remove Heavy Metal Ions

Heavy metal ions could be eliminated by several traditional techniques [22], including chemical precipitation [23], reverse osmosis [24]. electrochemical treatment techniques [25], ion exchange [26], membrane filtration [27], coagulation [28], extraction [29], irradiation [30], and adsorption [31]. Due to its low cost-effective, high efficiency, and simple to operate for removing trace levels of heavy metal ions, adsorption technology [32] is regarded as the most promising one to remove heavy metal ions from effluents among these techniques mentioned above. Several types of materials, such as activated carbons [33], clay minerals [34], chelating materials [35], and chitosan/natural zeolites [36] have been researched to adsorb metal ions from aqueous solutions. Although traditional sorbents could remove heavy metal ions from wastewater, the low sorption capacities and efficiencies limit their application deeply.

1.2 Criteria of Nanomaterials for Adsorption

Used as sorbents for removing heavy metal ions in wastewater, nanomaterials should satisfy the following criterions.

1) The Nano sorbents themselves should be nontoxic.

2) The sorbents present relatively high sorption capacities and selectivity to the low concentration of pollutants.

3) The adsorbed pollutant could be removed from the surface of the nano adsorbent easily.

4) The sorbents could be infinitely recycled. So far, a variety of nanomaterials such as carbon nanotubes, carbon based material composites, graphene, nano metal or metal oxides, polymeric sorbents have been studied in the removal of heavy metal ion from aqueous solutions and result indicate that these nanomaterials show high adsorption capacity.

1.3 Various Nanomaterials used for adsorption

a. Carbon based nanomaterials

As one of the inorganic materials, carbon based nanomaterials are used widely in the field of removal heavy metals in recent decades, due to its nontoxicity and high sorption capacities. Activated carbon is used firstly as sorbents, but it is difficult to remove heavy metals at ppb levels. Then, with the development of nanotechnology, carbon nanotubes, fullerene, and graphene are synthesized and used as Nano sorbents.

b. Nanoparticles from metal or metal oxides

Nanoparticles formed by metal or metal oxides are other inorganic nanomaterials, which are used broadly to remove heavy metal ions in wastewater treatment. Nano sized metals or metal oxides include Nano sized silver nanoparticles, ferric oxides, manganese oxides, titanium oxides, magnesium oxides, copper oxides, cerium oxides, and so on, all these provide high surface area and specific affinity. Besides, metal oxides possess minimal environmental impact and low solubility and no secondary pollution; have been adopted as sorbents to remove heavy metals.

c. Polymer supported Nano sorbents

More recently, the development of hybrid sorbents has opened up the new opportunities of their application in deep removal of heavy metals from water. Polymer-layered silicate nanocomposites have attracted both academic and industrial attention because they exhibit dramatic improvement in properties at very low filler contents

1.4 Adsorption Isotherm

Adsorption is the process in which heavy metals are adsorbed on the solid surface, and the equilibrium is established when the concentrations of heavy metal adsorbed and in water become constant. At equilibrium, the relationship between amounts of heavy metal ions adsorbed and in water is called an adsorption isotherm [37]. From these isotherms, several adsorption parameters could be calculated. The most widely used adsorption isotherms are Langmuir model and Freundlich model.

a. Langmuir model

In this model, adsorption occurs uniformly on the active sites of the adsorbent, and once the active sites are occupied by adsorbates, the adsorption is naturally terminated at this site. The non-linear Langmuir equation is

$q = q_{max} . K_L C / 1 + K_L C$

where K_L is the equilibrium constant (L mg^{-1})

q_{max} is the maximum adsorption capacity (mg g^{-1}) of adsorbent is the equilibrium concentration

(mg L^{-1}), q is the amount of metals adsorbed at equilibrium (mg g^{-1}) The linear

Langmuir model is given by following equation

$C_e/q_e = C_e/q_m + 1/bq_m$

Where qm and b are the saturated monolayer adsorption capacity and the adsorption equilibrium constant. A plot of C_e/q_e versus C_e would result in a straight line. From the slope and intercept, the maximum adsorption capacity and bond energy of adsorbates can be calculated.

b. Freundlich adsorption isotherm

The Freundlich equation is an empirical model allowing for multilayer adsorption on sorbent. The non-linear form of Freundlich model is

$q_e = K_F C_e^n$

The linear form of Freundlich model can be expressed as:

Log q_e=log K_F + log C_e/n

where q_e is loading of adsorbate on adsorbent at equilibrium (mg g^{-1}), KF is indicator of sorption capacity (mg^{1-n} L^n g^{-1}) n is adsorption energetics and Ce is aqueous concentration of adsorbate at equilibrium (mg L^{-1}).

1.5 Adsorption Kinetics Model

In order to determine and interpret the mechanisms of metal adsorption processes and the main parameters governing sorption kinetics, several kinetic models are proposed.

a. Pseudo-first-order kinetics model

A simple kinetic model suggested for the sorption process in solid/liquid systems is Lasergren's pseudo-first-order expression, which is given as

$dq_t/dt = k_1 (q_e-q_t)$

Where k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}) q_e and q_t, are the amounts of metal ions adsorbed per gram of sorbents (mg g^{-1}) at equilibrium and at time t (min), respectively. After integration of this kinetic expression for the initial condition of qt equal to 0. when time (t) approaches 0, its linear form are obtained:

ln (q_e-q_t) =ln q_e - k_1t

b. Pseudo-second-order kinetics model

The kinetic data also can be analyzed by Ho's pseudo-second-order kinetics model. This model is based on the assumption the sorption follows second order chemisorptions, which can be represented in the linear expression as

$t/q_t=1/k_2q_e^2+t/q_e$

Where k_2 (g.mg^{-1}. min^{-1}) is the rate constant of the pseudo second order adsorption .

1.6 Measurement Techniques For Nanoparticles

There are various techniques for detecting, measuring and characterizing nanoparticles. There is not a method that can be selected that is the "best" method but rather a method is chosen to balance the restriction of the type of sample, the information required, time constraints and the cost of the analysis. A straight forward technique may simply detect the presence of nanoparticles, others may give the quantity, the sire distribution or the surface area of the nanoparticles. These measurement techniques differ from characterization techniques for assessing the chemical content of a nanoparticle sample, the reactions on the surface of the nanoparticles or for the interactions with other chemical species present. There is also a divide between techniques that give information on an amount of nanoparticulate material and those that can look at the individual nanoparticle within the sample. Sometimes measurement techniques will be combined to

provide more information from one sample. Different techniques will suit different types of sample. For example some techniques require the sample to be as an acrosol and others will use a suspension or liquid sample. There may be a sample protocol to be followed for collection of the sample for analysis by a certain technique. There are techniques for in situ measurements of samples and others that require treatment of the sample before analysis. Sometimes samples may not be able to withstand the required treatment and decompose or react. The amount of sample required can also vary and restrict choice of technique. Since different techniques provide different information and accuracy. efforts have and will be made to standardize the way nanoparticles are measured: to assess occupational exposure, health risks from products and environment risk. The most common techniques are shown in table 1. Small variations on a technique can generate a different name and abbreviation for a very similar technique. An example of this is in aerosol measurement where differential mobility analysers or electrical mobility analysers can be combined with other instruments or have minor adjustments to generate different measurement

2. AIM OF THE STUDY

To synthesize the Fe_3O_4 magnetic nanoparticles by using simple coprecipitation method and to develop analytical method for the adsorption of cadmium (II) from aqueous solution on these nanoparticles.

3. OBJECTIVES OF THE STUDY

There are many removal techniques such as adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis in order to diminish the pollution impact of these metals. Sorbents which have been for adsorption of metal ions include activated carbon, fly ash, crab shell, coconut shell, zeolite, manganese oxides, and rice husk. However, these adsorbents have poor removal efficiencies for low concentrations of metal ions. Moreover, the slow removal rates often fail to meet control requirements. To prevent deteriorating surface water quality, legislation governing the levels of heavy metals, such as cadmium, lead, nickel and zinc discharged from industries is becoming progressively more stringent. Thus, there is a need for exploring alternative adsorbents, with better metal removal efficiency for low aqueous concentrations. Also, due the development in nano technology, nanoscale iron oxides have became a raw material for treating the waste waters and soils, accelerating the coagulation of sewage, removing radionuclides, adsorbing organic dyes and cleaning up the contaminated soils.

So objectives of this study are to synthesize $Fe2O_3$ MNP'S and their use for the adsorption cadmium(II) by MNP'S. the adsorption experiment was studied by batch adsorption method.

Technique	Measure	Sample	Sensitivity	Notes
Transmission Electron Microscopy (TEM)	Particle size and characterization	< 1µg has to be prepared as a thin film and be stable under an electron beam and a high vacuum	down to 1 nm	additions to TEM can provide more information e.g. Scanning Transmission Electron Microscopy (STEM), High- Resolution TEM (HRTEM) or in-situ measurements as Environmental TEM
Scanning Electron Microscopy (SEM)	Particle size and characterization	sample must be conductive or sputter coated, easier to prepare than TEM sample	down to 1 nm	can be used in-situ as Environmental SEM
Atomic Force Microscopy (AFM)	Particle size and characterizaton	samples must adhere to a substrate and be rigid and dispersed on the substrate. The appropriate substrate must be chosen. Air or liquid samples.	1 nm – 8 µm	a form of Scanning Probe Microscopy (SPM). Requires less time and cost than SEM and TEM
Photon Correlation Spectroscopy (PCS)	average particle size and size distribution	sample must be a very dilute suspension	1 nm – 10 µm	based on Dynamic Light Scattering, an extension of the technique is Photon Cross Correlation Spectroscopy (PCCS) for high concentration opaque suspensions giving particle size and stability

				of nanoparticles
Nanoparticle Surface Area Monitor (NSAM)	human lung-deposited surface area of nanoparticles	aerosol, concentrations 0 to 10000 $\mu m^2/cm^3$, temps 10-35^0 C	down to 10 nm	similar to an Electrical Aerosol Detector (EAD)
Condensation Particle Counter (CPC)	number concentrations of particles	aerosol, concentrations 0 to 100,000 particles/ cm³, can be in a flow, higher temps to 200°C possible	2.5 to >3.000nm	can be used for a flow, hand held models available
Differential Mobility Analyzer	particle size distribution	aerosol	down to 3 nm	can be combined with other techniques to create Tandem DMA or DMPS
Scanning Mobility Particle Sizer (SMPS)	particle size distribution	aerosol, can be a concentrated sample of 1,000,000-2,400,000 particles/ cm³,	3- 1,000 nm	uses an electrostatic classifier and a CPC, can also add DMA
X Ray Diffraction (XRD)	average particle size for a bulk	larger crystalline samples (>1mg) required	down to 1 nm	Can identify individual crystals

4. Experimental

4.1 Materials

All metal solutions were prepared from their nitrate salts (AR). The standard sample was diluted using ultrapure water. Other chemicals (analytical grade) were all dissolved in distilled water. A atomic absorption spectrometer (Perkin-Elmer), a digital flame photometer (PI, Model no. 041, India), a digital Spectrophotometer Systronics 106, a digital pH meter (Model LI-120, ELICO, India) with glass and calomel electrodes and a wrist action orbital shaker with digital speed control were used.

4.2 Synthesis of Magnetic nanoparticles

The mixed ferric and ferrous salt solution (FeCl$_3$6H$_2$O 0.0227 mol FeCl$_2$.4H$_2$0 0.0151 mol, 100 mL of oxygen-free water) was stirred and heated to 50°C followed by addition of 10 mL of 13.38 mol/L ammonium hydroxide solution in a stepwise manner. It was noted that iron oxide black precipitation appeared rapidly. In order to precipitated the iron hydroxides, the pH value was raised and maintained to pH-3 for 30 min. The solution was rigorously stirred at a constant temperature during all the process. Then, the pH value was increased to 10. 1 g of the as precipitated nanoparticles was dispersed in 50 ml of a 2g/1 aqueous solution of SDS (Sodium Dodecyl Sulphate) followed by vigorous stirring for 2 hours. The pH was maintained at 10 to assure a stable suspension. The prepared suspension was washed with distilled water and magnetically separated for several times to remove the excess of SDS. Finally the NPs were dried and a suspension of 10g/1 aqueous solution of the SDS- modified nanoparticles was prepared.

4.3 Batch adsorption Experiment

The batch adsorption experiments were carried out in a orbital shaker the speed of 40 r/min at 25°C. The adsorbents were separated from aqueous solution by magnetic separation using a permanent magnet. All samples were prepared in duplicate. The analysis of cadmium content in the sample was determined by spectrophotometer with at PAR 520 nm [45]. The obtained results show good agreement with AAS results. The method is simple, rapid and selective with good reproducibility (approximately +2%).

To assess the effect of initial pH on adsorption capacity, the flasks cotaining 5 mL of 50 μg/ml Cd(II) solution and I mg MNP's adsorbent were shaken with the speed of 40 r/min at 25°C for 60 min. at different pH values from 2 to 10. Then, the magnetic adsorbent was separated and the residual metal concentrations in supernatant were determined.

Various amounts of Cd(II) solution were shaken at the speed of 40 r/min 25°C with 1 mg MNP's at pH 8.0 to determine the effect of it on adsorption capacity was determined. After 60 minutes, the magnetic adsorbent was separated and the residual cadmium ion concentration was analyzed by appropriate procedure. To assess the effect of contact time on adsorption capacity, the flasks containing 5 ml of 50 μg/ml Cd(II) solution and Img MNP's adsorbent were shaken at the speed of 40 r/min at 25°C by varying time from 5 to 60 minutes. Then, the magnetic adsorbent was separated and the residual metal concentrations in supernatant were determined.

5. RESULTS AND DISCUSSION

5. 1 Characterization of synthesized MNP's

The effect of temperature at the beginning of synthesis on particle size of Fe_3O_4 MNIS was investigated from 30 to 90 °C, and the results indicated that all the nanoparticles were in spinel structure with face-centered cubic phase. The result showed that the intensity of the Bragg peaks increase by increasing the temperature. According to the estimated size from Scherrer equation, the crystallite sizes of Fe_3O_4 MNPs are reduced with the increase of reaction temperature from 30 to 50°C and the crystallite size was increased from 8.3 nm to 13.2 nm when the temperature increased from 50 to 90°C, implying there was greater polydispersity in reactions at higher temperatures. Increasing the reaction temperature would reduce the extent of aggregation of Fe_3O_4 nucleus and reduce sizes of Fe_3O_4 nanoparticles. However, the growth of Fe_3O_4 nucleus is easier to happen when the temperature is higher than 50 C, resulting in larger size nanoparticles when the temperature is higher than 50 °C at the beginning synthesis of nanoparticles. On the other hand, a plausible explanation for this is that by increasing the reaction temperature there is more energy within the solution, this would increase mobility and cause a greater number of collisions between the particles. Therefore, the initial temperature of 50 °C will be used for this experiment.

5.2 Effect of pH on adsorption

The effect of pH on adsorption of cadmium(II) on magnetic nanoparticles is studied by shaking the flasks containing 5 ml of 50 µg/ml Cd(II) solution and Img MNP's adsorbent were shaken with the speed of 40 r/min at 25°C for 60 min at different pH values from 2 to 10. From the results it was observed that as p^H of solution increases the percentage adsorption increase from pH 2 to 5 and then it was decreases. So for the further studies pH 5 is maintained. The effect of pH on adsorption is summarized in following Table 1. The pH of solution is maintained by appropriate buffer solutions.

Table 1. Effect of pH on adsorption

pH	Percentage adsorption
2	55
4	82
5	**90**
6	85
7	82
8	80
9	74
10	65
11	62

5.3 Effect of Cd(II) ion concentration on adsorption

The effect of Cd(11) on adsorption of cadmium(II) on magnetic nanoparticles is studied by shaking the flasks containing 5 ml of Cd(II) solution containing 50 µg/ml to 1000 ug/ml of Cd(11) and Img MNP's adsorbent were shaken with the speed of 40 r/min at 25°C for 60 min. at pH=5

Table 2. Effect of Cd(II) ion concentration on adsorption

Concentration of Cd(II), µg/ml	Percentage adsorption
50	**91**
200	90
300.	84
400	79
500	75
600	52
700	47
800	45
900	41
1000	34

From the results it was observed that the percentage adsorption decrease as metal ion concentration increases. The adsorption is maximum up to 200 µg/ml and then it is decreases. The results are are summarized in Table 2 For the further studies 5 ml of Cd(II) solution containing 50 µg/ml was used.

5.4 Effect of contact time on adsorption

The effect of contact time on abopil capoty was we flasks containing 5 th of 50 µg/ml CoT) solutie pnd tog NN adsorbent were shaken at the speed of 40 min at 25°C by saring time I 5 to 60 minutes Then, the magnetic absorbent was separated and metal concentrations in supernatant were determined The results are summarized in the Table 3. From the s observed that the 10 mmutes time is sufficint for the maximum adsorption of Cd(II) so for further adsorption experiments 10 minutes shaking is maintained

Table 3.Effect of time on adsorption

Time , min	Percentage adsorption
5	84
10	**90**
20	91
30	92
40	92
50	92
60	92

6. Conclusions

Iron oxide nanoparticle was synthesized and was used as an effective magnetic nanoparticle adsorbent for cadmium removal from aqueous solution. Though the maximum adsorption capacity was not very high, there was much room to improve such as optimizing the adsorption condition and separation of Cd(ll) from matrix materials. The present study shows MNP's can be used as an inexpensive sorbent for the sorption of Cd^{+2} from aqueous solution. Thus, this work provides an alternative adsorbent for cadmium removal from aqueous solution. The following conclusions can be obtained in this study. The obtained data represents only the preliminary result obtained for achieving a systematic study regarding the removal of heavy metals from waste waters using as adsorbents the nanoparticles with high capacity of adsorption due theirs high surface area

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