

Vibrational Spectral Magnetic Studies On The Removal Of Pb(II) And Ni(II) Ions Using Synthetic Nano Adsorbent Fe₃O₄

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Abstract: Adsorption of Pb(II) and Ni(II) from aqueous solutions on synthetic nano Fe₃O₄ has been studied. The effect of experimental parameters such as initial concentration of the metal ions, adsorbent dosage, contact time and pH has been investigated. Optimum removal efficiency of Pb(II) ion was found to be 99.7% with the dose rate of 1.07g/L in 60 minutes at pH = 6-6.5 and for Ni(II) ion, it was found to be 98.8% with the dose rate of 2.57g/L in 10 minutes at pH =6-6.5. The removal of Ni(II) ions require only 10 minutes with the efficient removal of 98.8%, whereas Pb(II) ions require 60 minutes with the maximum removal of 99.7%. In order to understand the effective removal of Pb(II) and Ni (II) ions on Fe₃O₄, room temperature magnetic measurement were carried out using Vibrational Spectrum Magnetometer (VSM), before and after adsorption with a maximum applied magnetic field of 20000 G.

Keywords: Adsorption, Pb(II), Ni(II) ions.

INTRODUCTION

Heavy metals' toxicity has been raised as a result of an interaction between the free metal ion and the susceptible target. Cells and tissues, such as gastro-intestinal, liver and renal, which are involved in transport of essential metal ions, are particularly susceptible to toxicity. And also, the toxicity arises owing to their binding affinity for the sulphhydryl (-SH) group of enzymes / protein, thus inhibiting the enzymatic activities and/ or disrupting the cellular structures which may vary from one metal to another. The binding or displacement of metal will lead to change in specific activity of biomolecules and may cause interruption to normal metabolism. Ochiai 1997 has framed the following three major categories of general toxicity mechanism for metal ions:

- Blocking the essential biological functional groups of biomolecules especially proteins and enzymes
- Displacing the essential metal ions in biomolecules and
- Modifying the active conformation of biomolecules resulting in the loss of specific activity.

The toxicity of Pb, Cd, Hg, Cu, Cr, Zn and Ni is due to their bio accumulation through food chain, which produces detrimental effects on human health². Generally, heavy metals cause irritation, nerve tissue injuries, cardiac strain, heart diseases, disturbed metabolism, kidney malfunction, and hypertension, destruction of central nervous, renal systems, brain damage and cancer. Lead is a dangerous and insidiously deceptive poison. Lead poison is called plumbism. It leads to Haematological damage, gastro-intestinal and hematological disturbances, attack central nervous system³. WHO suggests a provisional tolerance of lead (II) ion is 7mg kg⁻¹ body weight per day for adults. But, their presence in most of the industrial and mining effluents, soil of

industrial area, water and sewage system is beyond the tolerance limit. Nickel is a costly metal and industrially important one. The compounds of nickel are highly toxic to human beings as well as animals. According to Environmental Protection Agency (EPA), USA, the permissible limits of Ni(II) in waste water is 1.0 ppm and according to Bureau of Indian Standards, it is 3.0 ppm in India, acceptable limits of nickel in drinking water⁴ is 0.01 ppm. Nickel is a potent carcinogen. The contactness of nickel with skin results in painful disease, nickel itch, which is followed by sudden death⁵. Acute poisoning of nickel causes chest pain, tightness of the chest, headache, dizziness, nausea and vomiting, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness⁶ and gastrointestinal irritation and lung cancer^{6,7,8,9}. Nickel(II) ions in the effluent when disposed off into lakes and rivers produce ill-effects to living beings and vegetation¹⁰. Children are worst affected due to nickel toxicity present in sweets and other food items. Potential sources of nickel bearing waste include ceramics, nuclear power plants, cryogenic containers, electroplating and storage battery industries and silver refineries¹¹.

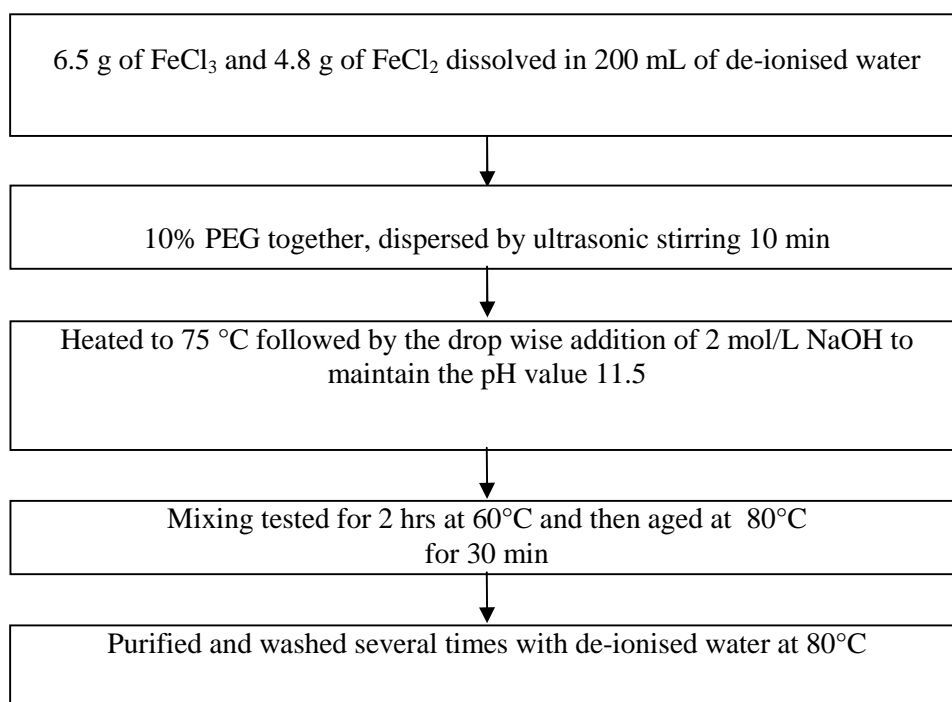
EXPERIMENTAL PROCEDURE

Preparation of Nano Fe₃O₄

Synthetic nano iron oxide (SNIO) was synthesized by acid - base hydrolysis of Ferrous and Ferric Chloride. All the chemicals were reagent grade (SD Fine) and were used without further purification. For the preparation of nano Fe₃O₄, 6.5 g of Ferric Chloride and 4.8 g of Ferrous Chloride were dissolved in 200 mL of distilled water and 10% Polyethylene glycol together and dispersed by ultra sonic stirring for 10 minutes. Then the mixture was heated to 75°C. The pH value of the mixture was adjusted to about 11.5 by using sodium hydroxide (1M). The mixing was continued for 2 hours at 60°C and then agitated at 80°C for 30 minutes, purified and washed several times with distilled water at 80°C until the silver nitrate test shows no chloride precipitation. The chemical reaction for the precipitation of Fe₃O₄ by alkalinizing aqueous mixture of ferric and ferrous salts with NaOH is expected as follows¹². The flow diagram and demonstration of the preparation of the nano iron oxide are given below.



Preparation of Nano Iron Oxide Particles



RESULTS AND DISCUSSION

X-ray analysis

Figure 1a and 1b shows the X-Ray diffraction pattern of the commercial micro Fe_3O_4 and chemically synthesized Fe_3O_4 particles by co-precipitation of Fe^{2+} and Fe^{3+} ions in aqueous medium. The curve shows all the diffraction peaks of the Fe_3O_4 (JCPDS-75-1609) and the broadening of the diffracted peaks of the chemically synthesized Fe_3O_4 shows a growth of nanocrystalline phase with an average size of 20 nm calculated from the Debye-Scherer formula.

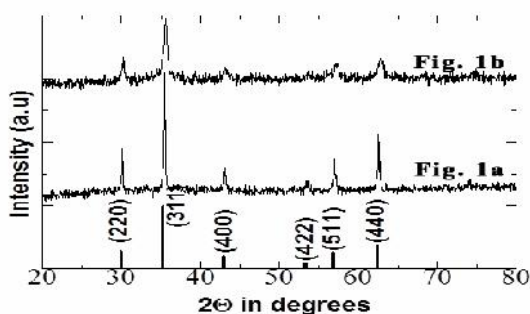


Figure 1. XRD pattern of Commercial micro and synthesized Nano Fe_3O_4

SEM analysis

Figure 2 shows the high resolution scanning electron microscope (HRSEM) image of Fe_3O_4 and shows the formation of mild agglomeration with particles in the range of 18-23 nms. A X-ray energy dispersion analysis (EDAX) of the lead and nickel solution treated Fe_3O_4 is depicted in **Figure 3a and 3b**. From the EDAX spectrum, it is observed that there is major component of Fe and O due to Fe_3O_4 and presence of lead and nickel adsorbed on it.

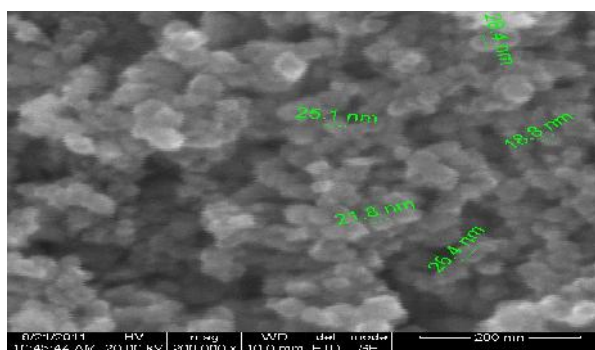


Figure 2. SEM image of synthetic nano Fe_3O_4

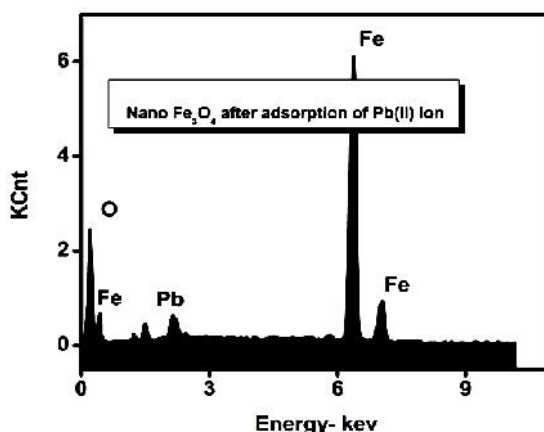


Figure 3a EDAX for nano Fe_3O_4 after adsorption of $\text{Pb}(\text{II})$ ions

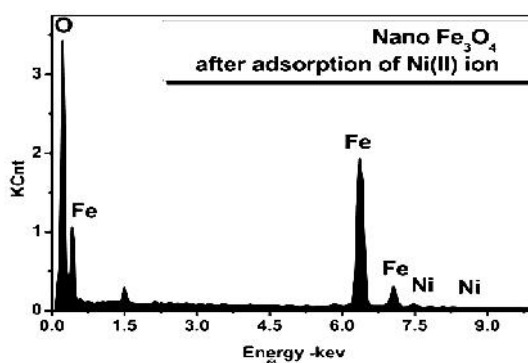


Figure 3b EDAX for nano Fe_3O_4 after adsorption of Ni(II) ions

Effect of Initial Concentration

The adsorption experiment was carried out varying the concentration of Pb(II) and Ni(II) ions (25, 50, 100, 150, 200, 250, 300, 350, 400 ppm) keeping the fixed dose of synthetic nano Fe_3O_4 (1.07 g/L for Pb(II) ion, and 2.57 g/L for Co(II) ion), contact time (60 min), pH (6-6.5) and temperature $28 \pm 1^\circ\text{C}$. The variation in the percentage removal of Cu(II) and Co(II) ions with their concentration are shown diagrammatically in Figure 4. It was observed that the percentage removal of Pb(II) and Ni(II) ions by nano Fe_3O_4 is low at higher concentration and gradually increases as the concentration decreases. This is due to the fact that after the formation of mono-ionic layer at lower concentration over the adsorbent surface, further formation of layer is highly hindered at higher concentration due to interaction between Pb(II) and Ni(II) surface and in the solution. In addition to that at low concentration of the Pb(II) and Ni(II) ions, the ratio of the initial number of moles of the Pb(II) and Ni(II) ions to the available surface area of the adsorbent is large and subsequently, the fraction of the adsorption becomes independent of the initial concentration of the metal ion. But at higher concentration, the adsorption sites available for adsorption become lesser, and hence, the percentage removal of the metal ions at higher concentration decreases¹³. The optimum concentration was found as 300 ppm for Pb(II) and 50 ppm for Ni(II) ion with the effective removal of 99.7% for Pb(II) and 98.8% for Ni(II) ions.

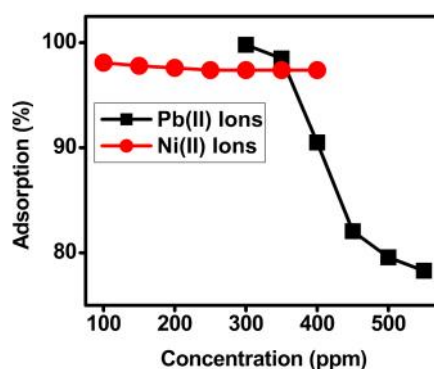


Figure 4 : Effect of initial concentration of Pb(II) and Ni(II) ions on synthetic nano Fe_3O_4

Effect of Dose Rate

The removal of the Pb(II) and Ni(II) ions was studied with different dose of synthetic nano Fe_3O_4 from (0.82 to 2.07 g/L) at the optimum concentration of 300 ppm for Pb(II) ions and 50 ppm for Ni(II) with fixed contact time (60 min), pH (6-6.5) and temperature of $28 \pm 1^\circ\text{C}$. The effect of the dose rate of synthetic nano Fe_3O_4 on the removal of Pb(II) and Ni(II) is pictured in Figure 5. It was noted that the percentage removal of the Pb(II) and Ni(II) ion increases as the concentration of nano Fe_3O_4 increases owing to the enhanced total surface area of the adsorbent. This means that the toxic ions can be removed effectively from the contaminated water with the proper amount of the adsorbent, which would possess more adsorption sites available for the metal ion uptake

from the solution¹³. The optimum dose rate was found to be 1.07g/L for Pb(II) ion and 2.57g/L for Ni(II) ion with the effective removal of 99.7% for Pb(II) and 98.8% for Ni(II) ions.

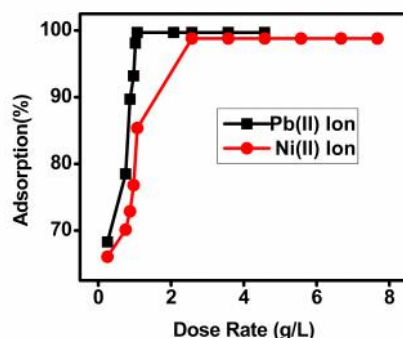


Figure 5. Effect of the dose rate in the percentage removal of the Pb(II) and Ni(II) ions by adsorption on synthetic nano Fe₃O₄

Effect of Contact time

In order to study the effect of contact time on the removal of Pb(II) and Ni(II) ions, experiment were conducted at different contact times (from 10 to 60 min) keeping the following conditions: optimum concentration (300ppm for Pb(II) and 50ppm for Ni(II) ions), fixed dose of synthetic nano Fe₃O₄ (1.07g/L for Pb(II) ions, 2.57g/L for Ni(II) ions), pH(6-6.5) and temperature of $28 \pm 1^\circ\text{C}$. The variation of the percentage removal of Pb(II) and Ni(II) ions by synthetic nano Fe₃O₄ with contact time was shown in Figure 6. The extent removal of Pb(II) and Ni(II) ion increases sharply initially and found to be constant after the optimum contact time. The optimum contact time was found to be 60 minutes for Pb(II) ions and 10 minutes for Ni(II) ions with the effective adsorption of 99.7% for Pb(II) and 98.8% for Ni(II) ions.

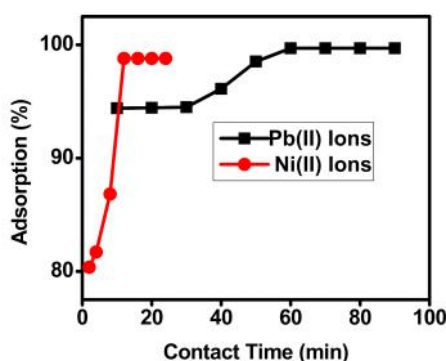


Figure 6 . Effect of Contact time in the percentage removal of the Pb(II) and Ni(II) ions by adsorption on synthetic nano Fe₃O₄

Effect of pH

The pH is one of the important parameter controlling the uptake of Pb(II) and Ni(II) ions from aqueous solution by the adsorbent. The adsorption potential of the synthetic nano Fe₃O₄ was found out at various pH values (1.8-6) keeping the system at the following conditions: optimum concentration (300ppm for Pb(II) and 50ppm for Ni(II) ions), fixed dose of synthetic nano Fe₃O₄ (1.07g/L for Pb(II) and 2.57g/L for Ni(II) ions), optimum contact time (60 min for Pb(II) ion and 10 min for Ni(II) ions) and temperature $28 \pm 1^\circ\text{C}$. The removal of the Pb(II) and Ni(II) ions by synthetic nano Fe₃O₄ was effective in acidic medium only and the effective pH range was found to be 6-6.5 for Pb(II) ions and 6.4 for Ni(II) ions. This observation reveals that the adsorption process is pH dependent. At low pH, because of the higher concentration of the H⁺ ion and its higher mobility due to smaller size, the H⁺ ions are preferentially adsorbed compared to the Pb(II) and Ni(II) ions, thus lowering the extent of the removal of the metal ions. At optimum pH, the concentration of the H⁺ ions is lowered which leads to the preferential adsorption of the Pb(II) and Ni(II) ions. At higher pH the hydroxide ion concentration is

increased and preferentially adsorbed on the adsorbent¹³. Moreover, at higher pH, the Pb(II) and Ni(II) ion forms various complex anion, hydroxide complexes, etc., which are retarded by the negatively charged surface of the adsorbent. The plots of the percentage removal of Pb(II) and Ni(II) ions with respect to pH change were shown in Figure 7.

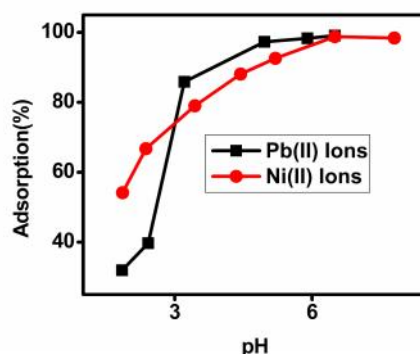


Figure 7. Variation in the percentage removal of the Pb(II) and Ni(II) ions by adsorption on synthetic nano Fe₃O₄

Vibrational Spectral Magnetic Studies (VSM)

It was observed that for the removal of Ni(II) ions by synthetic nano Fe₃O₄ require only 10 minutes for the maximum removal, whereas for Pb(II) ions it requires 60 minutes for the maximum removal. The less time required for Ni(II) ion is because nickel is Ferro magnetic in nature, hence it was easily attracted by synthetic nano Fe₃O₄. In the case of Pb(II) ions, which are Dia magnetic in nature, it does not experience magnetic force so it require 60 minutes for the maximum removal. It was further confirmed by Vibrational Spectral Studies and given in Table 1 and the results are shown in Figure 8a and 8b.

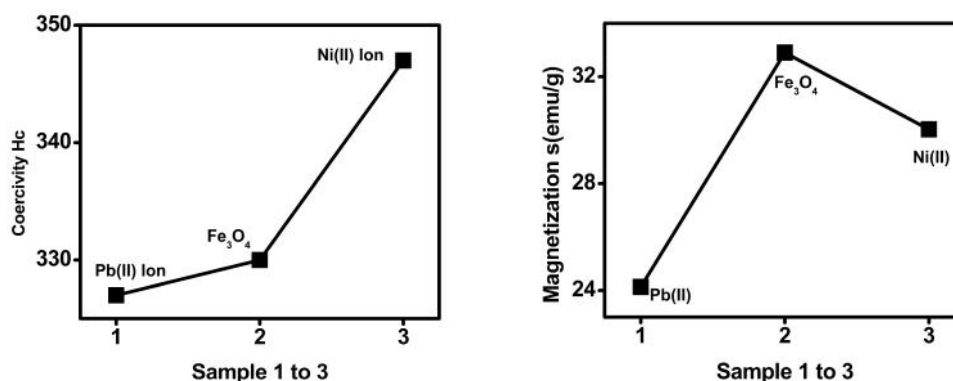


Figure 8a and 8b. Coercivity H_c and Magnetization M_s nature of synthetic nano Fe₃O₄ before and after adsorption of Pb(II) and Ni(II) ions

Table 1: Coercivity (H_c) and Magnetization values of synthetic nano Fe₃O₄ after adsorption of Cu(II) and Co(II) ions.

No	Element	Doping material	Coercivity H _c (G)	Magnetization _s (emu/g)
1	Fe ₃ O ₄	Pb(Dia)	327	24.13
2	Fe ₃ O ₄	--	330	32.90
3	Fe ₃ O ₄	Ni (Ferro)	347	30.03

Table 2 : Optimum Conditions for the removal of Cu(II) and Co(II) ion by using synthetic nano Fe₃O₄

Metal ion	Conc. (ppm)	DoseRate (g/L)	Time (min)	pH	% removal
Pb(II)	300	1.07	60	6-6.5	99.7
Co(II)	50	2.7	10	6.4	98.8

CONCLUSIONS

In the present study, the efficiency of the synthetic nano Fe₃O₄ towards the removal of the Pb(II) and Ni(II) ions was examined. Optimum conditions for the removal of Pb(II) and Ni(II) ions by using synthetic nano Fe₃O₄ was given in Table 2. Nickel is Ferro magnetic in nature, hence it shows optimum contact time of 10minutes only whereas lead is Diamagnetic in nature so it requires the optimum contact time of 60minutes. The results indicated that the synthetic nano Fe₃O₄ was found to be more suitable for the removal of Ni(II) ions than Pb(II) ions with the minimum contact time of 10min only.

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