

Sorption of Lead(II) ions from Aqueous Solution by Fabricated Magneto responsive CNT-IPSF/Fe₃O₄Nanocomposites

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Abstract: Rapid industrial development associated with production of toxic wastes, especially heavy metals, has led to an urgent need of creating new sorption materials to remove these wastes from water supplies. This study aimed at determining the effectiveness of as-prepared CNT-IPSF/Fe₃O₄ nanocomposites in removal of lead(II) ions from contaminated water. Carbon nanotubes prepared by CVD exhibited fine threads with average internal diameters of 40-50 nm while magnetite silica NPs had cubic spinel structure; due to the strongest reflection from the (311) plane. The silica coated magnetite had magnetization value of 2.5 emu/g while the polysulfone contributed towards well packed and uniform structure depicting higher surface area suitable in adsorption studies. The magnetite silica NPs had very intense peaks, indicating the ultra-fine nature and small crystallite size of the particles. The peaks indexed as planes (220), (311), (400), (422), (511) and (440) corresponded to a cubic unit cell, characteristic of a cubic spinel structure while crystallite size measurements were determined as 22.4 nm from the strongest reflection of the (311) peak, using the Scherrer approximation. Optimization of parameters for Pb(II) ions removal gave optimum conditions of adsorbent dose (0.05 g), contact time (60 mins) and pH 5 which were set constant in further analysis. Kinetics for adsorption of Pb(II) ions fitted well with pseudo second order model with highest correlation coefficient values of >0.9 while the adsorption process gave best fit with Freundlich isotherms. Desorption efficiencies (%) for Pb(II) ions of above 50% confirms the reliability of the desorption test in the reusability of the magneto responsive CNT-IPSF/Fe₃O₄ nanocomposite fabricated. Desorption of the Pb(II) ions using HNO₃ made the developed adsorbent a viable alternative to the common adsorbents available for treatment of wastewater with heavy metal ions. The nanocomposites showed 69 % for Pb(II) ions removal from wastewater compared to 54% Pb(II) ions removal for activated carbon used as standard adsorbent.

Keywords: adsorption, desorption, carbon nanotubes, magneto responsive, nanoparticles, nanocomposites, reliability, solubility

I. Introduction

Heavy metals represent a large class of pollutants responsible for the pollution of many potential drinking water sources around the world [1]. The removal of heavy metals from wastewater is important for the environmental protection and human health [2]. Several processes such as chemical precipitation, reverse osmosis, electrolytic recovery, ion exchange or adsorption have been developed and used over the years to remove metal ions [3]. Nanoparticles are fast emerging as potent candidates for water treatment in place of conventional technologies which, notwithstanding their efficacy, are often very expensive and time consuming [4]. Low cost of adsorbents, simplicity and high removal efficiency are few advantages of the adsorption method [5]. In order to make this method more environment friendly and economical, regeneration of adsorbent is very important aspect.

The need of recovery and regeneration depends on cost of the adsorbent and its regeneration [6]. The aim of this study was to investigate the effects of different factors on the adsorption properties of lead(II) ions by as-prepared CNT-IPSF/Fe₃O₄ nanocomposites, which will help to understand adsorption mechanism for other heavy metals. Lead is chosen as a model metal ion, which has been identified as one of the most toxic heavy metals and is included on the US Environmental Protection Agency (USEPA) list of priority pollutants. In this paper, adsorption features of as-prepared CNT-IPSF/Fe₃O₄ nanocomposites were investigated as a function of pH, adsorbent dose, initial Pb(II) concentrations and co-existing ions. The reliability of the nanocomposite was investigated using desorption test on removal of the adsorbed Pb(II) ions from the nanocomposites.

II. Experimental Stage

2.1 Fabrication and characterization of CNT-IPSF/Fe₃O₄ nanocomposites

A continuous chemical vapour deposition (CVD) of acetylene was used to produce CNTs at temperatures of 600 °C as outlined in previous studies [7] and were characterized using SEM, EDAX and TEM. Magnetic Fe₃O₄ particles were prepared via solvothermal reaction according to the method previously reported [8] and characterized using UV-Vis and SEM techniques. Magnetite microspheres were coated with

silica by sol-gel approach [9] by slow addition of 50 μL tetraethyl orthosilicate (TEOS). Structural and particle size were determined by X-ray diffractometer (Shimadzu, XRD-6000) equipped with $\text{CuK}\alpha$ radiation source using Ni as filter at setting of 30 kV/30 mA in the angular range $10 \leq 2\theta \leq 90^\circ$ with a scanning speed of $0.02^\circ/\text{s}$ and a step time of 3s. The magnetic properties of the prepared magnetite-silica NPs were determined by SQUID magnetometer. About 0.3g of magnetite-silica NPs were added to CNT-IPSF polymer solutions, ultrasonicated for 1 hour and the CNT-IPSF/ Fe_3O_4 solutions were immediately cast onto a glass plate with the aid of a casting blade to form CNT-IPSF/ Fe_3O_4 nanocomposites.

2.2. Removal of Pb(II) ions by fabricated CNT-IPSF/ Fe_3O_4 nanocomposites

2.2.1 Chemicals

All chemicals used in this study were of analytical grade obtained from Aldrich sigma Analytical Instruments Co. Ltd. Pb(II) ions solutions of different concentrations were obtained by diluting the stock solution. To adjust the pH, 0.1 mol/L HNO_3 and NaOH solutions were used. The effect of cationic ions (Zn^{2+} , Cu^{2+} , Cd^{2+}) and anion/ligands (NO_3^- , NH_3 and EDTA) on adsorption was studied. The regeneration studies of nanocomposites were also done using varying concentrations of Pb(II) ions.

2.2.2 Optimization of adsorption parameters

2.2.2.1 Determination of pH_{pzc}

Molar solutions of HNO_3 and NaOH were mixed in six different vials at varied proportions to adjust the initial pH (pH_i) values to 2, 4, 6, 8, 10, and 12. 0.05 g of the adsorbent was added to each solution in the ratio of 1:5 w/v and shaken on an orbital platform shaker at 120 rpm for 24 h. The resulting solutions were left to settle for 5 min before the final pH (pH_f) was measured. From a plot of pH_f against pH_i , the pH_{pzc} was obtained as the plateau along the pH_i axis.

2.2.2.2 Effect of Adsorbent Dose

50 ml aliquot solutions having initial concentration of 2 mg/L and 4 mg/L of the Pb^{2+} ions solutions were placed in two sets of conical flasks. Each of the adsorbent masses (0.02 g, 0.04 g, 0.06 g, 0.08 g, 0.1 g, and 0.12 g) was added to each set of stoppered conical flasks and agitated (120 rpm) for 60 min using an orbital platform shaker, after which they were left to equilibrate for 2 h. This was followed by centrifugation to separate the bulk sorbent from the solution (before filtering) prior to subsequent analysis. At the end of the time, the mixtures were filtered and the Pb(II) ions concentrations in the filtrates were determined by an air acetylene flame atomic absorption spectrophotometer (UNICAM SOLAAR 32). Ten runs were conducted for each adsorbent dosage.

2.2.2.3 Effect of Contact Time

The effect of time on the interaction of the adsorbent with the Pb^{2+} ions was performed at optimum pH 5. The adsorption studies were carried out by adding 0.05 g of adsorbent into two sets of conical flasks each containing 50 ml of 2 mg/L and 4 mg/L Pb(II) ions solutions in water bath shaker. The contact time for adsorption was varied at 10, 20, 30, 60, 90, 120 and 240 mins of agitation and immediately centrifuged for 15 min. Then, the concentrations of the Pb(II) ions in the supernatants were measured by an air acetylene flame atomic absorption spectrophotometer (UNICAM SOLAAR 32). All the experiments were carried out on 10 samples.

2.2.2.4 Effect of pH on Pb(II) Adsorption

A series of experiments, with 50 ml aliquots standards of 2 mg/L and 4 mg/L Pb(II) solutions in two sets of conical flasks were conducted under different pH. The pH was first adjusted to a designed value, from 1.0 to 7.0 with 0.1 M HNO_3 or 0.1 M NaOH. Then it was adjusted hourly and maintained steadily throughout the experiment. This was to avoid the possible precipitation of target cations as hydroxides. About 0.05 g of the adsorbent was added to each flask (stoppered 100 mL flasks) and agitated using an orbital platform shaker (120 rpm) for 60 minutes (optimum contact time) at 25°C , after which they were left to equilibrate for 2 h. This was followed by centrifugation to separate the bulk sorbent from the solution (before filtering) prior to subsequent analysis. The suspensions were filtered and the concentration of Pb^{2+} ions in the filtrates was determined using an air acetylene atomic absorption spectrophotometer (UNICAM SOLAAR 32).

2.2.2.5 Determining Adsorption Kinetics Model for Pb(II) Adsorption onto Adsorbent

The adsorption studies were carried out by adding 0.05 g each of CNT-IPSF/ Fe_3O_4 nanocomposites and activated carbon adsorbent into two sets of conical flasks containing 50 ml of 2 mg/L Pb(II) ions solutions in water bath shaker. The contact time for adsorption was varied from 10 to 250 min and immediately centrifuged for 15 min. Then, the concentrations of the Pb(II) ions in the supernatants were measured after 10, 20, 30, 60, 90,

120, 180 and 250 mins of agitation by an air acetylene flame atomic absorption spectrophotometer at 248.3 nm. All of the adsorption experiments were conducted in triplicate, and the average results are reported.

2.2.2.6 Determining Adsorption Isotherms Model for Pb(II) Adsorption onto Adsorbent

The initial concentration of the metal ions was varied between 2 and 12 mg/L. A known weight (0.05 g) of the CNT-IPSF/Fe₃O₄nanocomposites was shaken with 50 ml of Pb(II) ion standards at pH 5 for 60 mins (optimized contact time) at 25 °C on a rotatory shaker to ensure removal equilibrium was reached. The adsorbent was removed after centrifugation (10 min) for easy filtration. Finally, the Pb²⁺ ions concentrations were determined by AAS. All of the adsorption experiments were conducted in triplicate, and the average results are reported. For control experiments, 0.05 g of standard adsorbent of activated carbon was put into plastic bottles with 50 ml of 2, 4, 6, 8, 10 and 12 mg/L of Pb(II) solutions at 25 °C and pH 5, and mixture shaken for 60 minutes of contact time. The mixtures were treated in similar way and residual Pb(II) determined by AAS. The adsorption data obtained were fitted to adsorption isotherms models.

2.2.2.7 Effect of Counter Ions on Pb(II) Adsorption

The effect of similar heavy metal ions and anionic ligands were studied by using 0.05 g CNT-IPSF/Fe₃O₄nanocomposites in 2 mg/L Pb(II) solution each spiked with respective cations (Zn²⁺, Cu²⁺ and Cd²⁺) and anion/ ligands (NO₃⁻, NH₃ and EDTA) of concentrations 1.0 mg/L. Blank samples without similar heavy metals and anionic ligands were used. Control experiment involved putting 0.05 g of activated carbon into plastic bottles with each 50 ml of 2 mg/L of Pb(II) ions solution spiked with Zn²⁺, Cu²⁺, Cd²⁺ cations and NO₃⁻, NH₃, EDTA at concentrations of 1 mg/L.

2.2.3 Application of CNT-IPSF/Fe₃O₄Nanocomposite in Wastewater Treatment

2.2.3.1 Wastewater Sampling

Ten water samples containing industrial effluents of about one litre capacity were collected using a standard sampling technique [10]. Care was taken to avoid contamination of the sample during sampling, handling and transport to the laboratory by using polyethylene bags as leaching and adsorption are minimal. Sample containers were cleaned and where reagents were added during the preservation step, a sample of the added reagents was also submitted for analysis as a reagent blank. The samples were immediately cooled (on ice) before further analysis.

2.2.3.2 Application of CNT-IPSF/Fe₃O₄Nanocomposite to Pb(II) ions Removal from Wastewater

Prior to sorption and desorption experiments, the water samples were filtered and portions of it analyzed for initial concentrations of Pb(II) ions using AAS. The rest of water samples were stored at 4 °C in a refrigerator for further analysis. 50 mL each of the effluent samples whose pH had been adjusted to 5 was gently agitated with 0.05 g of as-prepared adsorbent on a rotatory shaker (120 rpm) for 1 h at 25 °C. Before AAS analysis, the mixtures were immediately filtered through No 1 paper filter. The adsorbent with adsorbed lead were washed three times using 0.1M HNO₃. All the experiments were carried out on 10 samples. Control experiments used 0.05 g standard adsorbent (activated carbon) on 50 ml effluent samples and agitated at fixed temperature 25°C for one hour and at 120 rpm. The standard adsorbent was also washed three in 0.1M HNO₃ before determining residual Pb(II) ions in the resultant filtrates. Comparison of their % removal efficiencies was done to establish if the prepared adsorbent was more efficient than the standard adsorbent employed.

2.2.4 Regeneration and Reusability Studies on Adsorbent Using Lead(II) ions

2.2.4.1 Adsorption-Desorption Experiments for Pb(II) ions

Desorption studies were carried out in order to determine the strength of the adsorption process and investigate the feasibility of its regeneration for reuse. Each of the 0.05 g adsorbent was continuously stirred with 50 ml of 2 mg/L Pb(II) solutions in plastic bottles to allow adsorption to take place. After filtration, each adsorbent with Pb(II) load was transferred to each conical flask containing 50 ml desorption solvents of H₂O, 0.1 M HNO₃, and 0.1 M EDTA. The mixtures were shaken at 120 rpm for 18 h followed by determination of the concentration of Pb(II) in the filtrates after desorption. The experiment was repeated using 0.05 g of standard activated carbon adsorbent into each of the plastic bottles (pools) containing 2 mg/L Pb(II) ions solution and treated in the same manner as for prepared adsorbent. Ten sample portions were run for this experiment and the Pb(II) ions in filtrates was determined by AAS.

2.2.4.2 Reusability of CNT-IPSF/Fe₃O₄Nanocomposite for Pb(II) Ions

To investigate the reusability of the adsorbent, desorption and regeneration of Pb-loaded CNT-IPSF/Fe₃O₄nanocomposites were also carried out. Adsorption desorption experiments were carried by agitating 0.05 g of prepared adsorbent in varying Pb²⁺ ions concentrations (1, 2, 4, 6, 8 and 10 mg/L). After adsorption

process, the adsorbent was separated magnetically and washed several times with deionized water to remove any unadsorbed Pb(II) ions and then desorption studies were performed by mixing resultant Pb-loaded adsorbent with 20 mL of 0.10 M HNO₃ in water shaker bath for 1h. Then the adsorbent was separated magnetically and the dried adsorbent was added to the solution of fresh Pb(II) ions solutions and after stirring with mechanical stirrer, the spent adsorbent was separated from the solution. Then Pb-loaded adsorbent was mixed with 20 mL of 0.10 M HNO₃, shaken and separated from the solution. The process was repeated three times to investigate reliability of the adsorption test for possible reuse of the adsorbent as per the equation (1):

$$\% \text{ Desorption Efficiency} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \dots\dots\dots 1$$

2.2.4.3 Solubility Studies on CNT-IPSF/Fe₃O₄Nanocomposite

Approximately 0.05 g of the adsorbent was added to 50 mL deionized water and conditioned at the pH values of 2, 4, 7, 9, and 12 [11] and thoroughly mixed on a vortex, followed by equilibration for 24 h at ambient temperature. The resulting mixture settled down, and with careful suctioning the remaining solid material obtained was then dried at 100 °C to a constant mass. Solubility was determined as the difference between the initial mass of the adsorbent (m_i) and that of the residue (m_f), as given by the equation (2):

$$\% \text{ Solubility} = \frac{m_i - m_f}{m_i} \times 100 \dots\dots\dots 2$$

III. Results

3.1 Fabrication of magnetic CNT-IPSF nanocomposites

The HRSEM of prepared CNTs contain thin-like strings characteristic of CNTs (Fig. 1a). However, the SEM image shown in Fig. 1b shows the formation of magnetite-silica nanoparticles which were monodispersed in the presence of TEOS. Other studies found that with the increase of silica layer thickness, silica-coated magnetite particles become more monodispersed as a result of the reduction in the relatively size distribution and uniform silica-coated magnetite particles were formed [12, 13]. The XRD diffraction pattern in Fig.1c shows a complete range of allowed electron transitions in our synthesized magnetite NPs with the most intense peak given by D-value of 311 from the Bragg's law: $n\lambda = 2d\sin \theta$. The sample show very intense peaks, indicating the ultra-fine nature and small crystallite size of the particles as shown by other studies [14]. Crystallite size measurements were determined as 22.4 nm from the strongest reflection of the (311) peak, using the Scherrer approximation, which assumed the small crystallite size to be the cause of line broadening [15, 16].

The hysteresis loop of our synthesized Fe₃O₄-SiO₂ NPs at room temperature is showed in Fig.1d. From the magnetization behavior, the magnetization curve is without hysteresis. It can also be seen that the saturation magnetization (M_s) of the Fe₃O₄-SiO₂ NPs increase from 1.50 to 2.0 emu/g. This confirms that the as-prepared magnetite-silica NPs are characteristic of superparamagnetic properties. These particles also have zero coercivity and have no hysteresis. This study shows an external field response which follows a sigmoidal curve, a characteristic property of superparamagnetic NPs [17].

From the SEM image of fabricated CNT-IPSF/Fe₃O₄nanocomposites in Fig.1eshows a well packed and uniform structure depicting higher surface area suitable adsorption studies. Also a large quantity of dispersive NPs having moderately uniform and cubic structure can be observed. Chemical analysis spectrum from EDAX (Fig. 1f) confirmed the presence of Fe and O elements, with a stoichiometry Fe₃O₄ phase C and S are candidates for CNTs and Infused polysulfone respectively.

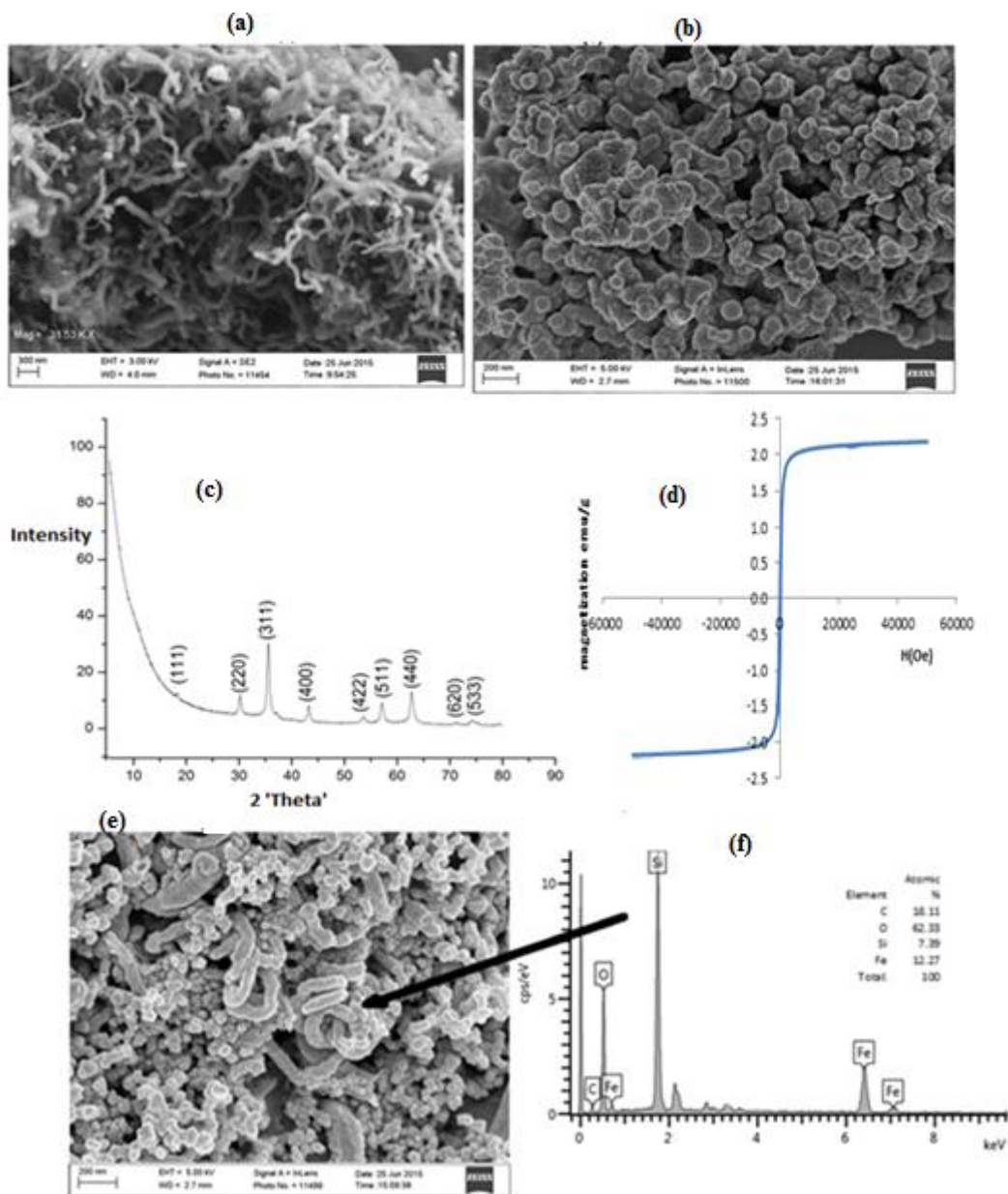


Figure (I) Characterization of products

2.3. Efficiency of Magnetic CNT-IPSF Nanocomposite in Removal of Lead (Ii) Ions from Wastewater

3.2.1 Optimization of Factors

The pH_{pzc} is used to investigate whether the surfaces of adsorbent are either positively or negatively charged depending on their interaction with the pH of the solution in contact. From the pH_{pzc} curve of the sample, the pH_{pzc} value was found to be around 4.5 (Fig. 2a). This result reveals the possible presence of acidic oxygen-bearing surface functionalities, such as -COOH and -OH groups. Essentially, at pH_{pzc} values 6–8, these groups would become negative via deprotonation, creating vacant sites for the binding of positively charged metal ions. Considering that the MWCNTs sample had already been functionalized with mineral acid HNO_3 during purification stage, exhibiting such groups in significant quantities could be more economical. It is therefore expected that the adsorbent would bind to the Pb^{2+} ions through electrostatic interaction or by cation exchange. Hence, a high removal capacity (for the metal ions) from the solution is expected at pH values higher than pH_{pzc} . Our results are in agreement with the reported point of zero charge of polysaccharide extract at 4.4 [11]. High removal capacity from the solution is expected at pH values greater than pH_{pzc} . Hence all the adsorption experiments were conducted at pH 5.

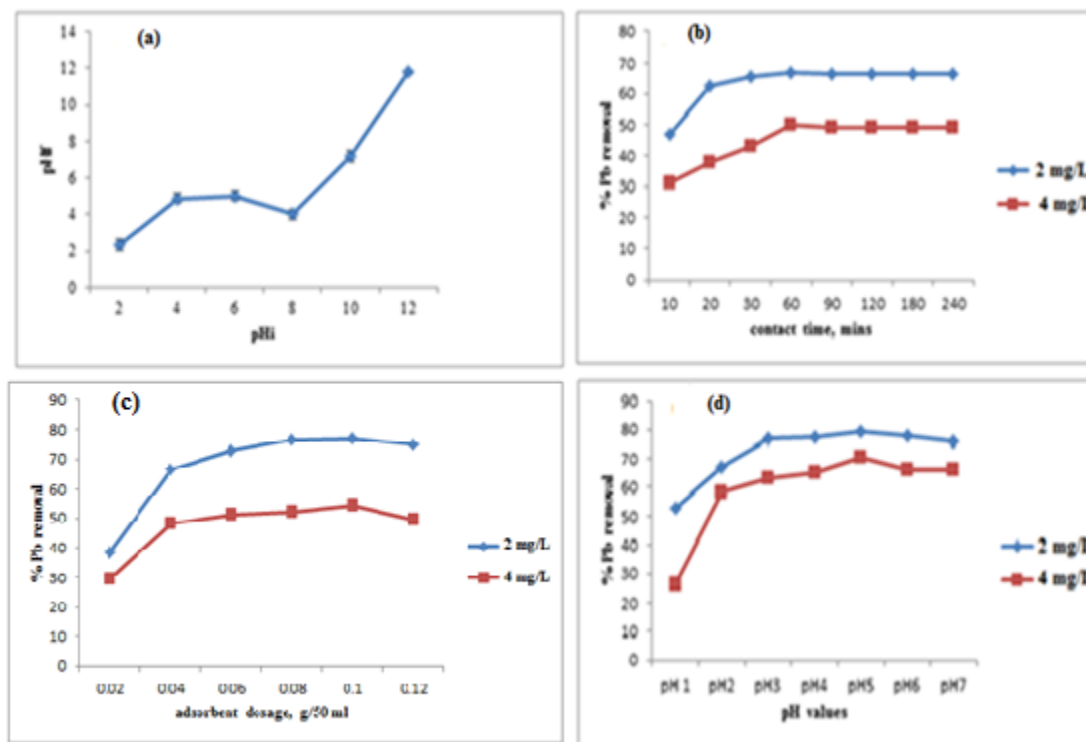


Figure (1) Optimization of Factors

The adsorption of lead ion on adsorbent was studied by varying the adsorbent dosage from 0.02–0.12 g at lead ion concentration (2 mg /L and 4 mg/L) while keeping other operational parameters constant: pH 5, shaking speed 120 rpm and temperature 25 °C (Fig. 2b). The initial rapid increase observed could be due to the increased availability of binding sites and surface area for easy adsorption of Pb(II) ions until equilibrium was reached [18]. The results showed an exponential increase in the removal of Pb²⁺ as the dosage was increased at constant Pb²⁺ ions concentrations (2 and 4 mg/L). This is because increasing the amount of the sorbent provides a larger surface area (more sorption sites) for binding metal ions.

This study investigated the removal efficiency of Pb²⁺ ions as a function of contact time between 10 and 240 min (Fig. 2c). There was maximum removal of Pb²⁺ ions of 67 % (2 mg/L) and 50 % (4 mg/L) at 60 mins of contact time indicating that equilibrium condition had been reached. This shows that the remaining empty sites on the adsorbent had been occupied leading to repulsive forces between adsorbed lead(II) ion on the adsorbent and those in the aqueous phase [19].

The effects of solution pH on lead(II) removal by the adsorbent was studied in the pH range 1 – 7 at contact time of 60 mins and all measurements were made at room temperature for initial Pb(II) concentrations of 2 and 4 mg/L (Fig.2d). The increase in the removal of Pb²⁺ ions with the pH could be due to the fact that as the pH increases, the H⁺ ions are desorbed from the functional groups. Hence, the adsorbent's surface becomes more negative, thereby increasing the attraction of metal ions to the free sites of the adsorbent, resulting in high removal efficiencies. The adsorbent's adsorption efficiencies toward Pb²⁺ ions were optimized by 79 % and 70 % at pH 5 for 2 and 4 mg/L Pb²⁺ ions concentrations respectively.

3.2.2 Adsorption Kinetics Modeling for Pb(II) Adsorption onto Adsorbent

The experimental values for adsorption of lead ion involved agitating 0.05 g/50 mL prepared (CNT-IPSF/Fe₃O₄) and standard (activated carbon) adsorbents at the Pb(II) ion concentrations of 2 mg/L and contact times of 10-250 mins, and pH5. In this study, two kinetic models were studied to describe the kinetics of adsorption. These include Pseudo First Order (equation 3) and Pseudo Second order (equation 4) [20].

$$\log(Q_e - Qt) = \log Q_e - \frac{K_{1p}}{2.303} t \dots\dots\dots (3)$$

$$\frac{t}{Q_t} = \frac{1}{K_{2p} Q_e^2} + \frac{1}{Q_e} t \dots\dots\dots (4)$$

The kinetic parameters are shown in Table (1):

Table (1) Pseudo first and second order adsorption constants

Kinetics	Parameters	Samples	
		Prepared (CNT-IPSF)	Standard (activated carbon)
Pseudo 1 st order	q _e	0.34	0.24
	K _{1p}	0.0046	0.005
	R ²	0.7348	0.1992
Pseudo 2 nd Order	q _e	0.38	0.43
	K _{2p}	0.308	0.28
	R ²	0.9982	0.999

From the above results, the kinetics of adsorption followed the pseudo-second-order model. This model gives the best-fit to experimental data for Pb(II) for the prepared and standard adsorbents studied in this study, which have highest correlation coefficient values of 0.9982 and 0.999 respectively for same initial Pb(II) ions concentration of 2 mg/L. That means that the rate of occupation of adsorption sites is proportional to the square number of unoccupied sites, because the pseudo-second order model is based on a second order mechanism [21].

3.2.3 Adsorption Isotherm Modeling for Pb(II) Adsorption onto Adsorbent

The initial metal ion concentration provides an important force to overcome all mass transfer resistances of the metal ions between aqueous and solid phase (Aksu&Akpınar, 2000). The subsequent removal of metal ions using a constant amount of adsorbent was examined at various concentrations in the range 2–12 mg/L. The adsorption isotherms data were fitted to both the Langmuir (equation 5) and Freundlich (equation 6) isotherm equations [22].

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot b} + \frac{C_e}{q_m} \dots\dots\dots (5)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots (6)$$

According to the R² for each sample in Table (2), both Langmuir and Freundlich models fitted the experimental data by linear analysis.

Table (2) Langmuir and Freundlich adsorption isotherm constant for adsorption of Pb(II) onto magnetic CNT-IPSF adsorbent and activated carbon adsorbents

Isotherms	Parameters	Samples	
		Prepared (CNT-IPSF)	Standard (activated carbon)
Langmuir	Q _m	20.62	20.33
	b	0.04	0.26
	R ²	0.9968	0.9942
Freundlich	K _f	1.13	2.09
	1/n	0.8286	0.85
	n	1.21	1.24
	R ²	0.9969	0.9984

The linear form of correlation coefficient value R² = 0.9968 (prepared) and R²=0.9942 (standard) for Langmuir isotherm and R² = 0.9969 (prepared) and R²=0.9984 (standard) for Freundlich can suggest that both isotherms provide a good result for the adsorption model of Pb(II) on the adsorbents. The Langmuir isotherm provides a good model for the adsorption process as indicated by the regression coefficient (R²) ranging from 0.9968 to 0.9942 for prepared and standard adsorbents respectively. This indicates that the surface of the CNT-IPSF/Fe₃O₄nanocomposite is uniform, all the adsorption sites are equivalent and the adsorbed lead molecules do not interact. At the maximum adsorption, only a monolayer is formed [23]. The values of n=1.21 for CNT-IPSF/Fe₃O₄nanocomposite were between 1 and 10 representing beneficial adsorption [24]. The obtained values of 1/n are less than unity (1/n=0.83) which is an indication that significant adsorption takes place at low metal ions concentrations.

3.2.4 Effect of Counter Ions

Industrial wastewater often contains other similar divalent cations such as Zn²⁺, Cu²⁺ and Cd²⁺, and NO₃⁻, NH₃ and EDTA [25], which may interfere with the uptake of Pb(II) ions by adsorbent. The effect of such cations and anion/ligands on adsorption was studied and the results are shown in Figure 3a and 3b respectively.

It can be seen that 1mg/L of Cu^{2+} greatly reduced Pb(II) removal by a significant drop of about 2.08 % on the standard adsorbent from when 1mg/L of Zn^{2+} was used on standard adsorbent. The as-prepared adsorbent was not affected by any of the counter cations. Comparison of Pb(II) removal by both activated carbon (standard) and CNT-IPSF/ Fe_3O_4 (prepared) adsorbents revealed similar trend with EDTA significantly reducing Pb(II) removal by almost the same margin.

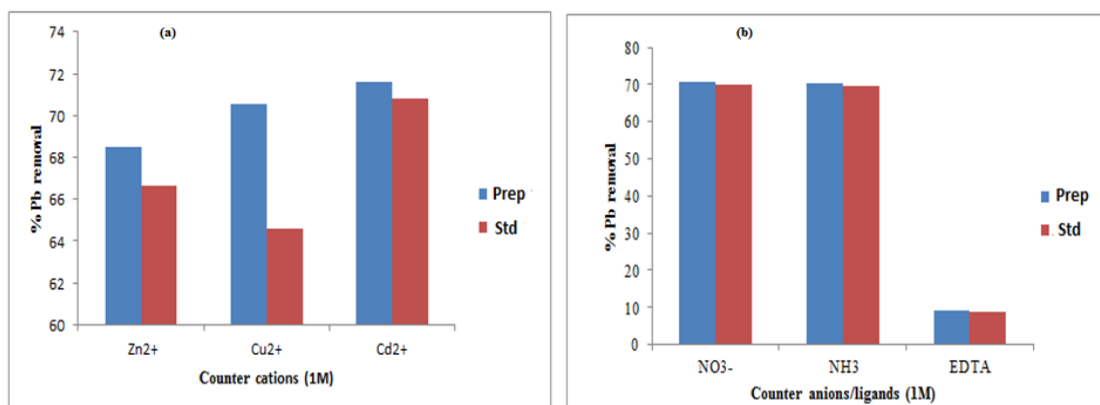


Figure (2) Application of CNT-IPSF/ Fe_3O_4 Nanocomposite in Wastewater Treatment

Application studies using polluted water samples with industrial effluent was carried out to determine the practicality of CNT-IPSF/ Fe_3O_4 nanocomposites at optimum batch condition as shown in Figure 4

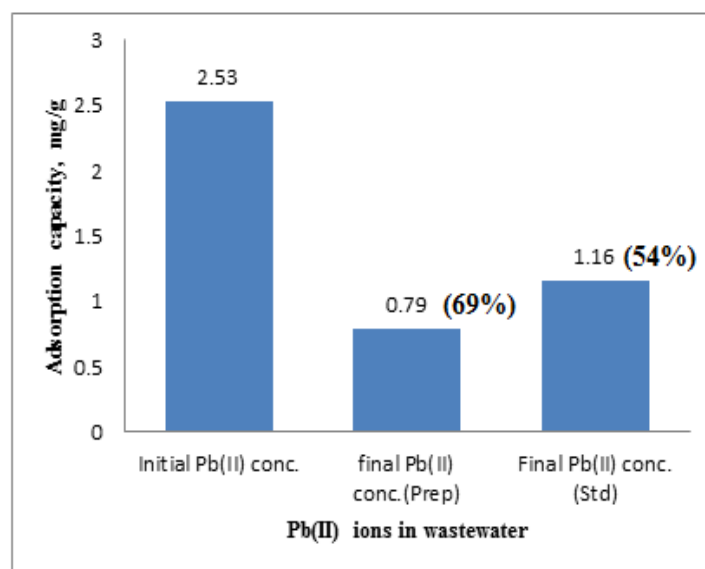


Figure (3) Industrial wastewater treatment

The prepared magnetic CNT-IPSF/ Fe_3O_4 nanocomposites and activated carbon adsorbent reduced initial concentration of Pb(II) ions from 2.53 mg/g to 0.79 and 1.16 mg/g which translated into 69 % and 54 % respectively after three washing times with HNO_3 . This implies that the CNT-IPSF/ Fe_3O_4 nanocomposite has adsorbent particles with higher affinity for Pb^{2+} ions than those in activated carbon [26]. The ability of CNT-IPSF/ Fe_3O_4 nanocomposite to remove Pb(II) ions from aqueous solutions could be attributed to its high magnetic response from single- and multi-core magnetic, and its tunable morphologies [27]. The prepared adsorbent was therefore more effective in the removal of Pb(II) ions from industry wastewater.

3.3 Regeneration and Reusability of Magnetoresponseive CNT-IPSF/ Fe_3O_4 Nanocomposite

3.3.1 Adsorption-Desorption Studies for Pb(II) ions

This study was carried out to assess the most suitable desorbing agent [28] for eluting adsorbed lead(II) ion from the surface of prepared CNT-IPSF/ Fe_3O_4 nanocomposites and standard activated carbon adsorbent. The effects of de-ionized water, 0.1M HNO_3 and 0.1M EDTA solutions were tested for their ability to remove the adsorbed lead(II) ion from the surface of the adsorbents (Figure 5). From the results, it can be seen that 0.1M

HNO₃ (78 % and 81 %) and 0.1M EDTA (77 % and 76 %) were equally more efficient than H₂O (9.09 % and 9.12 %) solvent. The high desorption ability of EDTA in desorption studies could be due to the high value of the conditional formation constant of the complex Pb(II)-EDTA ($K'_f = 3.55 \times 10^{11}$) at pH 5.0, which favors the desorption of Pb(II) from the sorbent [29]. However, HNO₃ acid desorption solvent was chosen for adsorption-desorption studies during reusability test since Pb-EDTA complexes has shown limited adsorption at various pH values.

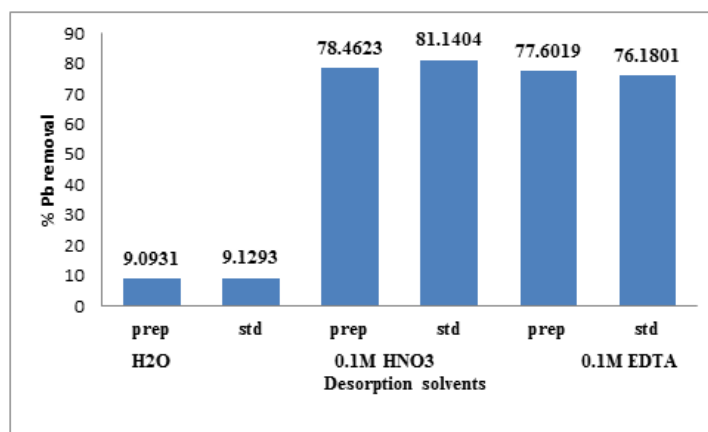


Figure (5) Comparing desorption abilities using different desorption solvents

3.3.2 Reusability of CNT-IPSF/Fe₃O₄Nanocomposite for Pb(II) Ions

Desorption efficiencies (%) were then carried out as a function of varying concentrations for Pb²⁺ ions solution (1, 2, 4, 6, 8 and 10 mg/L) on the prepared adsorbent using HNO₃ as desorption solvent (Figure 6a). This desorption test, if reliable, could positively impact the subsequent utilization of sorbents, thus providing high chances of its reusability. Herein, the concentrations of Pb²⁺ ions were measured after equilibrium had been reached. The desorption efficiency (% DE) was derived as the amount of adsorbed metal ions released from the sorbent's surface relative to the initially adsorbed on the adsorbent material before desorption using HNO₃ (Figure 6b).

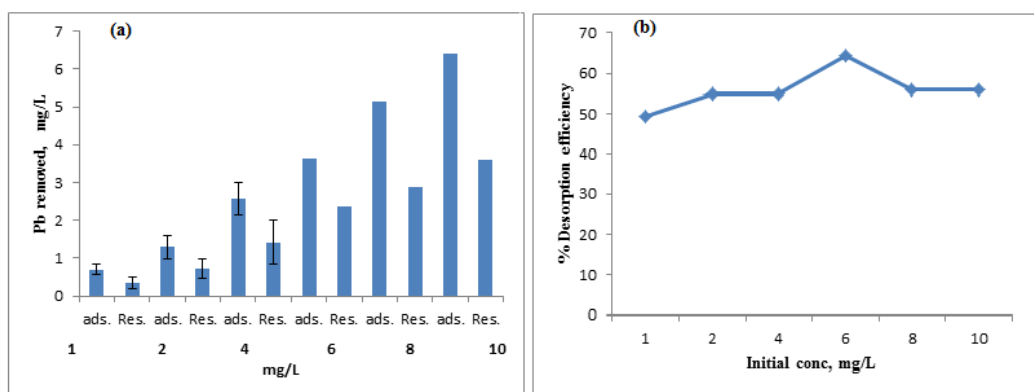


Figure (6) Investigating the reliability of the desorption test for Pb(II) ions.

At all the initial concentrations for Pb²⁺, there was a positive trend in the removal of Pb²⁺ from the adsorbent using HNO₃. The % desorption efficiency of Pb²⁺ ions was found to be above 50%, which could imply that the active binding sites have higher affinity toward Pb²⁺ ions forming a stable structure with the coordination of oxygen atoms. This observation could also indicate that the attraction between the Pb²⁺ and the adsorbent is a weak physisorption (van der Waals force) and not of a true covalent or complexation interaction.

3.3.3 Solubility Studies on CNT-IPSF/Fe₃O₄Nanocomposites

The effect of pH on solubility of the adsorbent samples at pH values of 2, 4, 7, 9 and 12 was found to be 0.013%, 0.013%, 0.007%, 0.007%, and 0.01%, respectively (Figure 7). This is attributed to the amorphous nature of the adsorbent, which allow them to be insoluble in water [30]. This property meets environmental concern for synthetic processes which would not affect the safety of the drinking water [31].

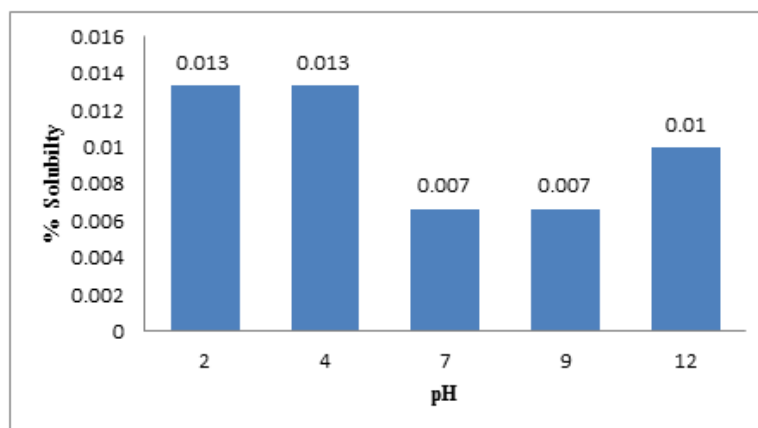


Figure (7) Investigating the solubility of prepared adsorbent

IV. Conclusions

The CNT-IPSF/Fe₃O₄ nanocomposites were successfully fabricated from CNT-IPSF polymer and SiO₂-Fe₃O₄ nanoparticles based on various characterization procedures. The SEM images for CNTs showed abundant threadlike entities for CNTs with lengths ranging from nanometers to micrometer. The SEM image revealed that the formation of magnetite-silica nanoparticles which were monodispersed. The XRD analysis revealed magnetite silica NPs with very intense peaks, indicating the ultra-fine nature and small crystallite size of the particles. The peaks indexed as planes (220), (311), (400), (422), (511) and (440) corresponded to a cubic unit cell, characteristic of a cubic spinel structure. Crystallite size measurements were determined as 22.4 nm from the strongest reflection of the (311) peak, using the Scherrer approximation, which assumes the small crystallite size to be the cause of line broadening. From the magnetization behavior, the magnetization curve did display very narrow hysteresis loop and zero coercivity was detected from the curve characteristic of superparamagnetic material with saturation magnetization of 2.5 emu g⁻¹. The SEM for as-prepared PSF-CNT/Fe₃O₄ nanocomposite further revealed well packed and uniform structure while EDAX confirmed the presence of Fe, Si and O elements, with a stoichiometry Fe₃O₄ phase.

The CNT-IPSF/Fe₃O₄ nanocomposites had been applied in the removal of Pb²⁺ ions from synthetic aqueous solutions, and wastewater. The nanocomposites showed 69 % for Pb(II) ions removal from wastewater compared to 54% Pb(II) ions removal for activated carbon used as standard adsorbent. Optimization of parameters for Pb(II) ions removal gave optimum conditions of adsorbent dose (0.05 g), contact time (60 mins) and pH5 which were set constant in further analysis. Kinetics for adsorption of Pb(II) ions fitted well with pseudo second order model with highest correlation coefficient values of >0.9 while the adsorption process gave best fit with Freundlich isotherms.

Desorption efficiencies (%) for Pb(II) ions of above 50% and gradual increase in desorption efficiency after three desorption cycles gives the reliability of the desorption test for the reusability of the magneto-responsive CNT-IPSF/Fe₃O₄ nanocomposite fabricated. Desorption of the Pb(II) ions using HNO₃ made the developed adsorbent a viable alternative to the common adsorbents available for treatment of wastewater with heavy metal ions.

V. Recommendations And Further Work

The fabricated CNT-IPSF/Fe₃O₄ nanocomposites material has capability for use in water treatment due to their good adsorption capacity, as well as ease of synthesis at relatively low cost.

Given the positive results found in this study, further investigations should be done on the use of this nanocomposite material on adsorption of other heavy metals and PAHs. More adsorption investigations for the material should be done at pH 7-8 based on results obtained on determination of pH at the point of zero charge (pH_{pzc}). There will be need to carry out further investigations into the environmental side effects that may emanate from disposal of these nanomaterials since both health and environmental effects are not yet well researched areas.

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