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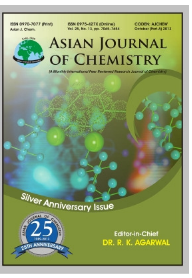

Adsorption of Lead from Aqueous Solution by Manganese Ferrite Nanoparticles

K.R. ASWIN SIDHAARTH[1,*] and J. JEYANTHI[2]

[1]Department of Civil Engineering, Anna University, Regional Centre, Coimbatore-641 047, India
[2]Department of Civil Engineering, Government College of Technology, Coimbatore-641 013, India

*Corresponding author: E-mail: aswincivil@gmail.com

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The adsorption of lead onto manganese ferrite nanoparticles was investigated. The adsorption characteristics and lead removal efficiency of the adsorbent have been determined by investigating the influence of operating variables such as contact time, dosage, pH, concentration of lead and agitation speed. The graphical correlation of various adsorption isotherm models like Langmuir, Freundlich and Tempkin have been used to evaluate the ongoing adsorption. The isotherm and kinetic studies suggest that the process follows Langmuir, pseudo first and second order kinetics. Column studies were also performed to test the ground efficiency of manganese ferrite nanoparticles by varying the depth and the results were subjected to Thomson and Yoon Nelson modeling. From both the modeling studies it was observed that the rate of removal of lead decreased from 3.350 to 1.525 and 18.53 to 9.19 mg/g as the filtering depth in the column increases.

Key Words: Manganese ferrite nanoparticles, Langmuir, Freundlich, Tempkin, Thomson, Yoon Nelson.

INTRODUCTION

The presence of heavy metals in wastewater and surface water is becoming a severe environmental and public health problem[1]. The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life[2]. They accumulate in living tissues throughout the food chain which has humans at its top[3]. These toxic metals can cause accumulative poisoning, cancer and brain damage when found above the tolerance levels[4]. Lead compounds are highly toxic to humans. The presence of lead in drinking water above the permissible limit (5 mg/mL) may cause adverse health effects such as anemia, encephalopathy, hepatitis and nephritic syndrome[5]. Hence it is important that lead should be removed from wastewater before being discharged into an aquatic environment. A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption. Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of the residual metal sludge[6].

Adsorption is a conventional but efficient technique to remove heavy metals or organics from aqueous solutions[7]. Many kinds of adsorbents for wastewater treatment have been commercialized or are being developed[8]. In most cases, these adsorbents are highly porous materials, providing adequate surface area for adsorption. However, the existence of intra-particle diffusion may lead to the decrease in the adsorption rate and available capacity, especially for macromolecules[9]. Thus, developing an adsorbent with large surface area and small diffusion resistance is of great significance in practical engineering application[10]. With the latest developments in nanotechnology, various types of magnetic nanoparticles have been successfully synthesized and have received considerable attention to solve environmental problems, such as accelerating the coagulation of sewage, removing radionuclides, adsorption of organic dyes and remediation of contaminated soils[1]. Apparently, the magnetic nanoparticles possess the advantages of large surface area, high number of surface active sites and high magnetic properties, which lead to high adsorption efficiency, high removal rate of contaminants and easy and rapid separation of adsorbent from solution *via* magnetic field[11-13]. In addition, it is possible that after magnetic separation by the external magnetic field, the harmful components can be removed from the magnetic particles, which can be reused[1]. The objective of the present work is to investigate the potential feasibility and field applicability of manganese ferrite nanoparticles for the adsorption of lead from the synthetic solution. The kinetic and equilibrium data were analyzed so that we can understand the adsorption mechanism. The Thomson and Yoon Nelson models were used to predict the performance of a fixed bed column for adsorption of lead on manganese ferrite.

EXPERIMENTAL

The concentration of lead was measured using atomic absorption spectrophotometer (Model-GBC 902). The adsorbent was prepared by selecting ferrous sulphate and manganese sulphate of analytical grade. Sodium hydroxide was used as a pH stabilizer. The surface morphology size presence of functional groups in the adsorbent was analyzed using FEG-SEM (JSM-7600F) and FTIR (MAGNA550) Spectroscopy.

Characterization of adsorbent: The formation of manganese ferrite nanoparticles was confirmed by doing the characterization studies by employing field emission Gun-Scanning electron microscope and Fourier transform Infrared spectrophotometer. The FEG-SEM analysis was employed to determine the surface morphology, size of the nanoparticle. FTIR analysis was used to determine the presence of functional groups present in the sample.

TABLE-1
OPTIMIZATION OF PROCESS PARAMETERS

S. No.	Parameter	Experimental Range	Optimized value
1.	Contact time	0-120 minutes	20 min
2.	Dosage of adsorbent ($MnFe_2O_4$)	0.01-0.50g	0.04 g
3.	pH of the lead aqueous solution	2-12	8
4.	Initial ion concentration of lead in the solution	10-100 mg/L	80 mg/L
5	Agitation speed	50-250 rpm	100

TABLE-2
ISOTHERM CONSTANTS FOR MANGANESE FERRITE NANOPARTICLES

Isotherms	Constants		R^2	Range
Langmuir	b = 0.894 q_{max} = 7.14 mg/g	R_L = 0.021	0.811	0-1
Freundlich	n = 0.697	K_f = 0.015	0.473	1<n>10
Tempkin	A = 5.105	B = 34.63	0.259	B=1-50

Adsorption studies

Batch study: The conformity of formation of manganese ferrite nanoparticles for the removal of lead from aqueous solution was experimented by varying the adsorption design parameters such as contact time, dosage, pH of the lead synthetic solution, initial concentration of lead and agitation speed. The experiments were carried out by mechanical agitation (agitation speed of 150 rpm) at 30 ºC where predetermined quantities (50 mL) of desired concentration of lead synthetic solution were agitated continuously with known weight of the magnetic nanoparticles. The mixing arrangement was facilitated by incubator shaker. After agitation, all sample solutions were filtered through Whitman filter paper and the filtrate was tested for the presence of lead. The optimum values of all the design parameters were achieved from batch experiments in a similar manner. The experimental data was validated and analyzed by using the isotherm and kinetic models.

Adsorption isotherm study: Adsorption isotherms are prerequisites to understand the nature of interaction between adsorbate and the adsorbent used for the removal of pollutants. Successful application of the adsorption technique demands studies based on various adsorption isotherm models because adsorption isotherm models clearly depict the relationship of amount adsorbed by a unit weight of adsorbent with the concentration of adsorbate remaining in the medium at equilibrium. There are many equations for analyzing experimental adsorption equilibrium data. The equation parameters of the equilibrium models often provide some insight into the adsorption mechanism, the surface properties and affinity of the adsorbent for adsorbate.

TABLE-3
KINETIC CONSTANTS FOR MANGANESE FERRITE NANOPARTICLES

Kinetics	Constants
Pseudo first order	q_e = 5.457 mg/g k = 0.039 g/mg-min
Pseudo second order	q_e = 47.61 mg/g k = 0.0176 g/mg-min
Intra particle diffusion	kid = 1.052 min^{-1}, ci = 38.56

The parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity towards the adsorbate. Several isotherm equations have been developed and employed for such analysis and the three important isotherms are applied in this study.

TABLE-4
THOMAS MODEL PARAMETERS

Waste treated	Adsorbent	Bed depth (cm)	K_{Th} (mL/min mg)	q_e (mg/g)
Synthetic solution containing lead as adsorbate	Manganese ferrite	3	0.00068	3.35
		6	0.00056	1.855
		9	0.00062	1.519
		12	0.0006	1.525

Adsorption kinetics: One of the essential requirements for the proper interpretation of the experimental data obtained during kinetic studies is to identify the steps governing overall rate of removal during the adsorption process. The kinetics of adsorption indicates the factor control the efficiency of the process and the equilibrium time and show the rate of adsorbate uptake on manganese ferrite nanoparticles. To identify the potential rate involved in the process of adsorption three kinetic models were applied for fitting the experimental data of the lead adsorption including pseudo first order, second order and intraparticle diffusion models.

TABLE-5
YOON NELSON MODEL PARAMETERS

Waste treated	Adsorbent	Bed depth (cm)	K_{YN} (L/min)	τ (min)	q_e (mg/g)
Synthetic solution containing Lead as adsorbate	Manganese ferrite	3	0.006	482	18.53
		6	0.005	534.2	10.27
		9	0.006	607.83	7.79
		12	0.005	956.2	9.19

Column studies: A packed bed column made of glass with an internal diameter of 2 cm and a total height of 20 cm consisting of sampling ports at height of 3, 6, 9 and 12 cm in a single column was fabricated and it is used for the study. To enable a uniform inlet flow of the solution into the column glass beads of 1.5 mm diameter were placed for a height of 2 cm. It was followed by glass wool for a height of 1 cm was provided at the top and bottom of the column to support the packing. Manganese ferrite nanoparticles were loaded in the column. The adsorption of lead in the packed bed column is largely dependent on the bed height, which is directly proportional to the quantity of manganese ferrite nanoparticles in the column. The effect of bed height on breakthrough curve analysis was studied by varying the bed height to 3, 6, 9 and 12 cm, respectively. The adsorption breakthrough curves were obtained by varying the bed heights at a flow rate of 5 mL/min and an inlet lead ion concentration of 50 mg/L. The values were subjected to two types of modelling which includes Thomson and Yoon Nelson model.

RESULTS AND DISCUSSION

Preparation of manganese ferrite nanoparticles ($MnFe_2O_4$): The chemical co-precipitation method was used for the preparation of $MnFe_2O_4$ nanoparticles. 500 mL solution containing 0.51 mol $FeSO_4$ $7H_2O$ and 500 mL solution containing 0.24 mol $MnSO_4.H_2O$ were prepared and these solution were mixed in a glass beaker. The glass beaker was placed above the magnetic stirrer. 6 M NaOH solution was added to it drop wise until pH14 and the reactants were vigorously stirred for 1 h. Finally a green precipitate was formed which was made to settle quickly by applying external magnetic field by placing a permanent magnet below the beaker and the supernatant was decanted. The obtained precipitate was washed with distilled water until pH was reduced to 7 the impurities were removed with ethanol. The ferrofluid was then evaporated in oven at 100 ºC for 10 h. The $MnFe_2O_4$ nanoparticles thus formed was weighed and stored in air tight container.

Determination of the zero point charge (pH_{ZPC}): The pH corresponding to the point of zero charge pH_{ZPC} for this new solid phase was determined by the solid addition method. The pH_0 values were adjusted between 2-10 by adding either 0.1 N HCl or 0.1 N NaOH to the 45 mL of KNO_3 solution. 1 g of adsorbent ($MnFe_2O_4$) was added to each flask and securely capped. The suspension was then manually agitated. By plotting the curve between pH = [pH_0 - pH_0 - pH_f] *versus* pH_0 the pH_{ZPC} of manganese ferrite nanoparticle was found out to be 6.8 (Fig. 1).

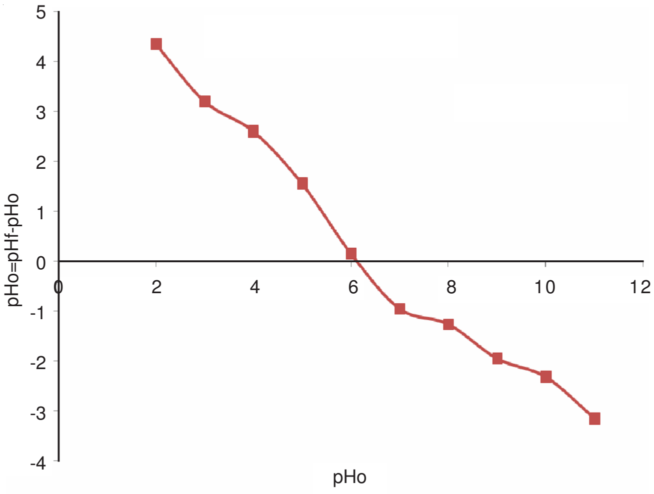

Fig. 1. Zero point of charge of manganese ferrite nanoparticle

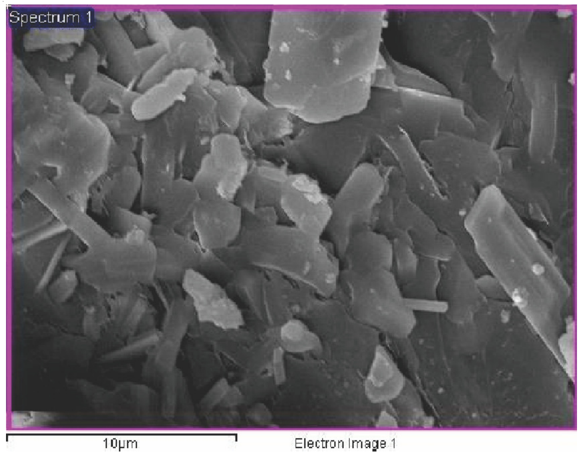

Fig. 2. SEM and EDAX image of manganese ferrite nanoparticles

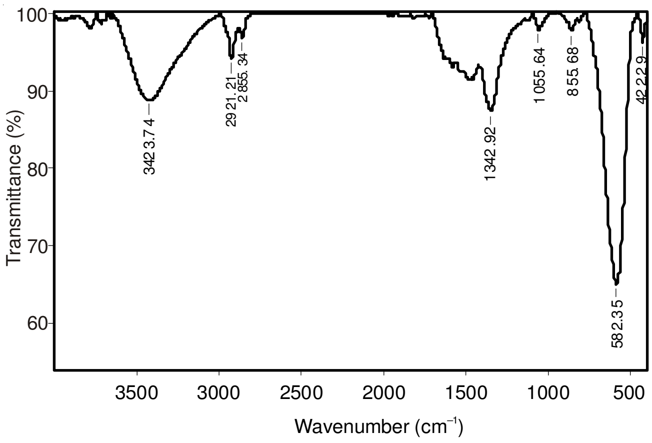

Fig. 3. FTIR image of manganese ferrite nanoparticles

Characterization of adsorbent: The SEM and FTIR images of the prepared nanoparticles were obtained as shown in Figs. 2 and 3. Manganese ferrite surface morphology analysis demonstrated the agglomeration of many ultrafine particles with diameter of range 80-100 nm. The vibrational spectra of the absorption bands of $MnFe_2O_4$ nanoparticles were observed at 582 and 422 cm^{-1}. There were still traces of broadband absorption peaks at 1342, 2855, 2921 and 3423 cm^{-1} due to traces of adsorbed or atmospheric CO_2 and O-H stretching vibration, respectively[14].

Effect of contact time: Equilibrium time is one of the most important parameters in the design of economical wastewater treatment system. 0.05 g of manganese ferrite nanoparticles was added into a 50 mL of lead solution with a concentration of 50 mg/L. The residual lead concentration in the solution was determined from atomic absorption spectrophotometer. The contact time was varied from 10 to 120 min at interval of 10 min. Rapid uptake and quick establishment of equilibrium time imply the efficiency of particular adsorbent in terms of usage in wastewater treatment. Fig. 4 shows the effects of contact time on adsorption of lead by $MnFe_2O_4$ nanoparticle and it was observed that the adsorption rate was rapid at the initial stages and then gradually decreased with

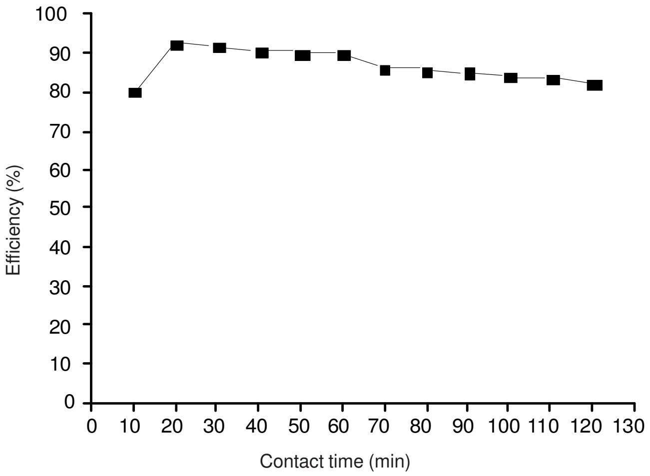

Fig. 4. Optimization of contact time

the progress of adsorption. The maximum removal efficiency was found to be 92.8 % at contact time of 20 min. Further batch studies were carried out at this optimum contact time.

Effect of adsorbent dosage: One of the most critical parameter for rapid and efficient metal removal is size and amount of adsorbent which must be optimized. The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of lead solution. The effect of adsorbent dose on the lead removal is shown in Fig. 5. It was observed that there was subtle changes throughout the range 0.01-0.50 g. The optimum dosage was found to be 0.04 g.

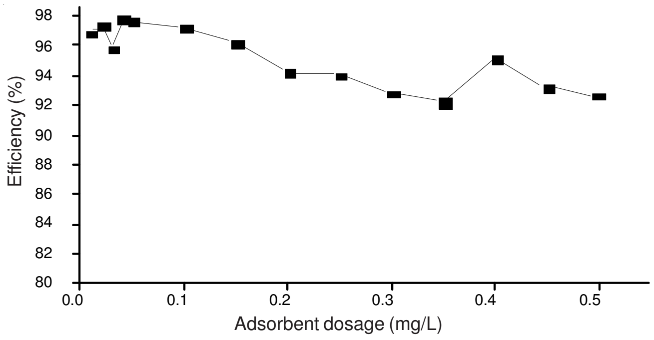

Fig. 5. Optimization of manganese ferrite nanoparticles dosage

Effect of pH and initial lead concentration: The wastewater from plating industries usually has a wide range of pH values. Thus pH of the system plays an important role in the plating waste treatment. The value of pH affects both aqueous chemistry and surface bonding sites of the adsorbents. Similar to pH the effluents coming out from the industries have concentration variation. The above two important design parameters have to be optimized. The optimum concentration was obtained by varying the concentration from 10 to 100 mg/L. The experiment was carried out for a optimized contact time of 20 min with a dosage of 0.04 g. Sample was kept under agitation of 150 rpm. It was seen that the lead adsorption efficiency increases with increase in its concentration and tends to attain saturation at higher concentrations. It was also observed that as the pH was increased from 2 to 8 the removal efficiency gradually increased from 20 to 80 % and then gradually decreased from 80 to 70 % from pH 8 to 12. This phenomenon can be explained from the fact that the surface charge is neutral at pH_{ZPC} which is 6.8 for $MnFe_2O_4$ nanoparticles. Below the pH_{ZPC} manganese ferrite surface is positively charged and Pb^{2+} would result in electrostatic repulsion. At pH higher than pH_{ZPC} the adsorbent surface is negatively charged which would have increased the adsorption with positively charged Pb(II) species. From the experimental observation the optimum pH was found to be 8 and initial concentration of 80 mg/L (Fig. 6).

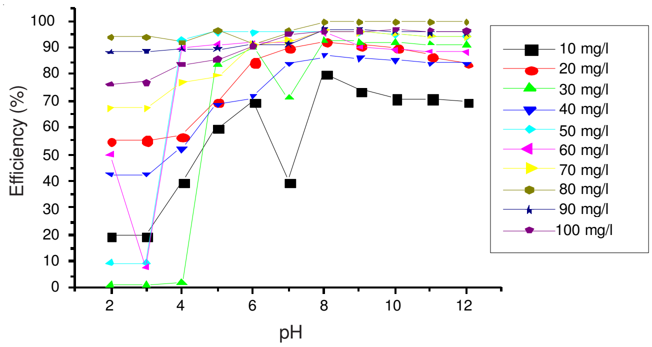

Fig. 6. Optimization of pH and initial lead concentration

Effect of agitation speed: The speed is one of the important design parameters for the design of adsorption system. The rate of contact between the adsorbent and the adsorbate is an important governing parameter for optimum removal. The experiment was carried out in the operating speed range of *ca.* 50-250 rpm. With other optimized parameter values of adsorbent dosage of 0.04 g contact time of 20 min, pH and initial lead concentration of 8 and 80 mg/L, respectively. From the experiment the optimum value of speed was found out to be 100 rpm (Fig. 7).

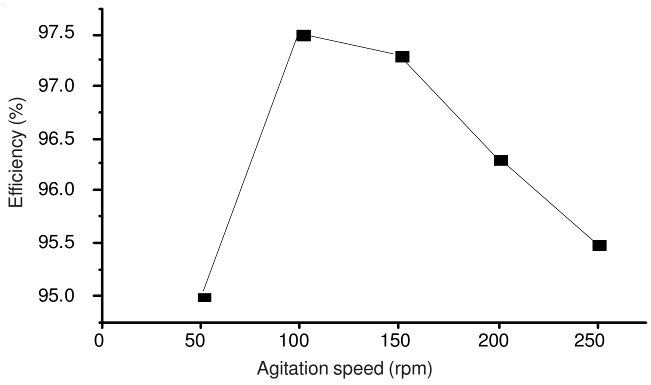

Fig. 7. Optimization of agitation speed

Langmuir isotherm: The Langmuir isotherm is based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a pollutant occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature. The Langmuir equation, which is valid for monolayer adsorption onto a completely homogeneous surface with a finite number of identical sites with negligible interaction between adsorbed molecules, is represented in the linear form as follows.

$$q_e = \frac{X}{M} = \frac{q_{max} bC_e}{1 + bC_E}$$

where b = constant that increases with increasing molecular size q_{max} = amount adsorbed to form a complete monolayer on the surface (mg/g).

The above equation can be represented in the linear form as follows:

$$\frac{C_e}{X/M} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} b}$$

The equilibrium parameter (R_L) can be calculated by the following equation

$$R_L = \frac{1}{1 + bC_o}$$

Here from the graph and calculations the isotherms of lead on manganese ferrite nanoparticles was found to be linear over the whole concentration range studies. Here the equilibrium parameter R_L= 0.021 which was found to lie between 0 and 1 (Fig. 8).

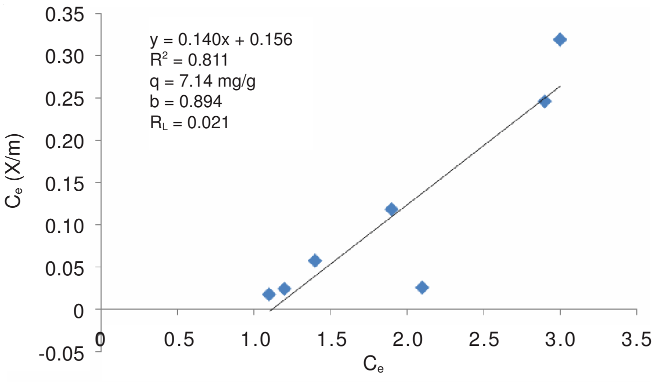

Fig. 8. Langmuir isotherm for lead adsorption using manganese ferrite nanoparticles

Freundlich isotherm: The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of sorption heat over the surface was presented in the linear form as follows:

$$\ln q_e = \frac{1}{n} \ln C + \ln K$$

where K [(mg g^{-1})/(mg L^{-1})$^{1/n}$] is the Freundlich constant related to the bonding energy and can be defined as the adsorption or distribution coefficient and represents the quantity of lead adsorbed onto adsorbent. The 1/n factor is heterogeneity factor and n is a measure of the deviation from linearity of adsorption, which its value indicates the degree of non-linearity between solution concentration and adsorbent as follows: if the value of n = 1 the adsorption is linear ; n < 1 the adsorption process is chemical if n > 1 the adsorption is a favourable physical process. Slope and intercept plot of ln q_e *versus* ln (X/M) indicate the value of K and n. As it can be seen Freundlich is unsuitable model for interpreting whole isotherm equation (Fig. 9).

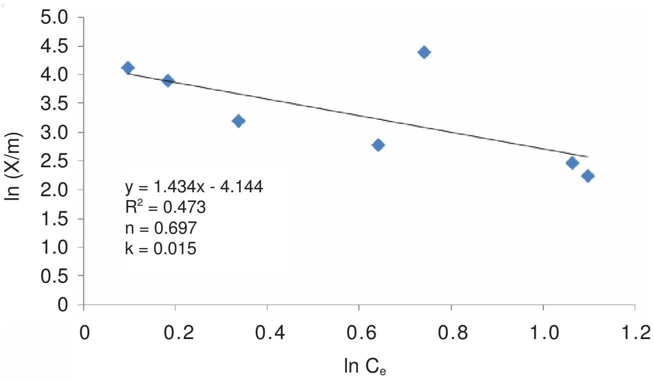

Fig. 9. Freundlich isotherm for lead adsorption using manganese ferrite nanoparticles

Tempkin isotherm: Heat of adsorption and the adsorbent-adsorbate interaction on adsorption isotherms were studied and analyzed by Tempkin and Pyzhev.The derivation of the tempkin isotherm indicates the multilayer adsorption on the adsorbent and its equation is given as:

$$\frac{X}{M} = B \ln A + B \ln C_e$$

where C = concentration of adsorbate in solution at equilibrium (mg/L), X = amount of metal adsorbed per unit weight of adsorbent (mg/g), M = weight of adsorbent (g), A and B = constants related to adsorption capacity and intensity of adsorption. Values of A and B were calculated from the plot ln C_e *versus* X/M. The graphical calculations indicate the suitability of Tempkin isotherm (Fig. 10).

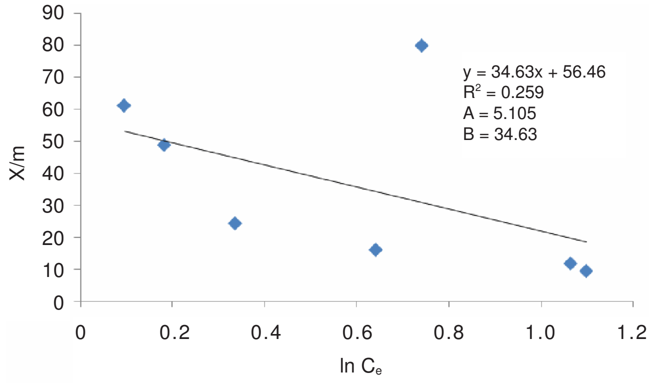

Fig. 10. Tempkin isotherm for lead adsorption using manganese ferrite nanoparticles

Pseudo first order kinetic model: The pseudo-first order kinetic model can be represented by the Lagergren rate equation.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k}{2.303t}\right)$$

where q_e and q_t are the amounts of adsorbed pollutant (mg/g) at equilibrium and at contact time t (min) respectively and K is the Pseudo first order rate constant (min^{-1}).

The values of q_e and K for the pseudo first order kinetic model were determined from the intercepts and slopes of the plots of log (q_e - q_t) *versus* t, respectively. Here the experimental q_e values were not close to the calculated ones, q_{ecal} obtained from the linear plots. It suggests that the kinetics of lead adsorption on manganese ferrite nanoparticle did not follow the pseudo first order kinetic model and hence are not diffusion controlled phenomena (Fig. 11).

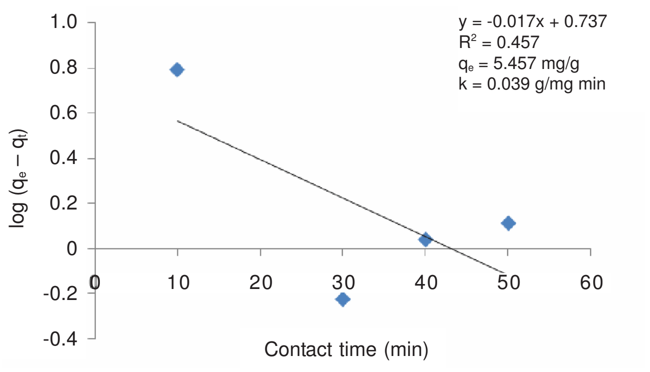

Fig. 11. Pseudo first order kinetics model for lead adsorption using manganese ferrite nanoparticles

Pseudo second order kinetic model: The pseudo second order kinetic model can be represented in the following form:

$$\frac{t}{q_t} = \left(\frac{1}{K_2} q_e^2\right) + \left(\frac{1}{q_e}\right) t$$

The plot of t/q_t *versus* t is a straight line and K_2 and q_e values determined from the slopes and intercepts of the plots. This procedure is more likely to predict the behavior over the whole range of adsorption. The linear plot shows good agreement between experimental and calculated q_e values. Besides the corresponding correlation coefficients (R^2) for the pseudo second order kinetic model to describe the adsorption process of lead on manganese ferrite adsorbents. The pseudo-second-order kinetic parameters obtained could be used to determine the equilibrium adsorption capacity (percentage of the removal of lead) rate constants and initial sorption rate for a reactor design (Fig. 12).

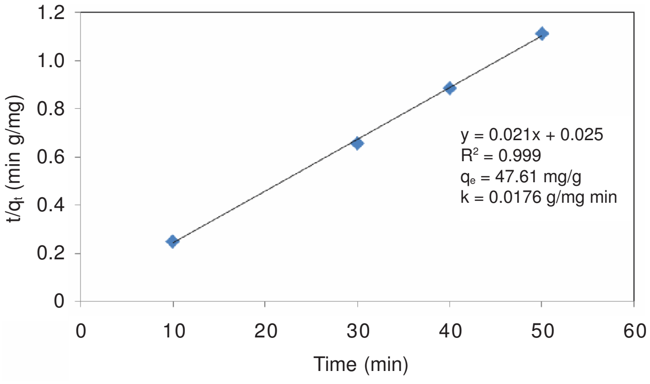

Fig. 12. Pseudo second order kinetics model for lead adsorption using manganese ferrite nanoparticles

Intraparticle diffusion model: Generally intraparticle diffusion model is one of the efficient models for evaluation of adsorption kinetics for most processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time. According to this theory, the intraparticle diffusion equation is expressed as follows:

$$q_t = K_{diff} t^{1/2} + C$$

where K_{diff} is the intraparticle diffusion rate constant (mg/g $min^{1/2}$) and C is the intercept. If the mechanism of adsorption process follows the intraparticle diffusion, the plot of q_t *versus* $t^{1/2}$ would be a straight line and K_{diff} and C can be calculated from the slope of the plot. Values of C give an idea about the thickness of boundary layer *i.e.*, the larger the intercept the greater the contribution of the surface sorption in the rate controlling step (Fig. 13). The breakthrough curves are plotted in Fig. 14.

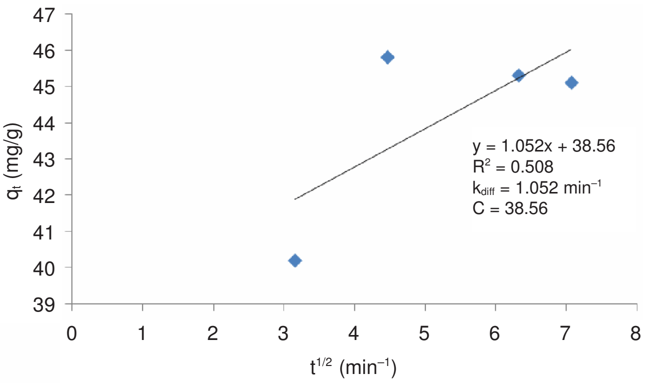

Fig. 13. Intra particle diffusion kinetics model for lead adsorption-manganese ferrite nanoparticles

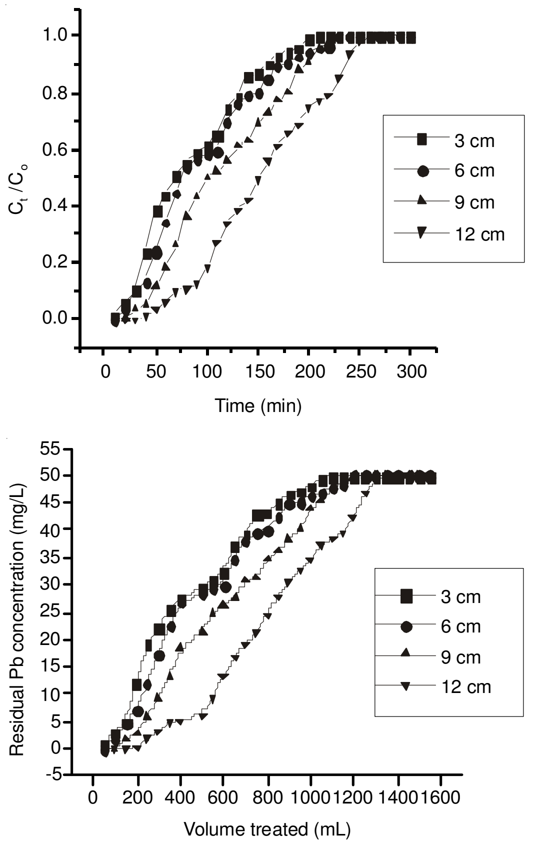

Fig. 14. Breakthrough curves for manganese ferrite nanoparticles

Column modelling

Thomas model: Thomas developed a model for adsorption processes in which external and internal diffusion limitations are not present. The linearized form of the Thomas model can be expressed as

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{KThq_eW}{Q}-KThC_0(t)$$

where KTh is the Thomas rate constant (mL/min mg), q_e is the equilibrium of metal uptake (mg/g), C_o is the inlet metal concentration (mg/L), C_t is the effluent metal concentration at time t (mg/L), W is the mass of adsorbent (g), Q is the inlet flow rate (mL/min) and t is the flow time (min). The value of C_0/C_t is the ratio of inlet to outlet metal concentrations (Fig. 15). A linear plot of ln [(C_o/C_t) - 1] against time (t) was drawn to determine the values of q_e and from the interception point and slope of the plot, respectively. From the Thomas model it was observed that as the bed depth increases the adsorption capacity decreases from 3.350 to 1.525 mg/g. This is because the upper layer of the manganese ferrite nanoparticle having sufficient surface area have been fully utilized for the adsorption of lead.

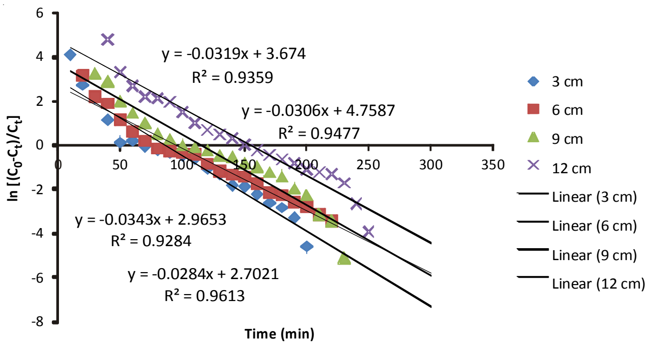

Fig. 15. Thomas model breakthrough curves for lead removal using manganese ferrite nanoparticles

Yoon-Nelson model: Yoon and Nelson developed a model to describe the adsorption behavior in the continuous column adsorption. The linearized form of the Yoon-Nelson model is,

$$\ln\frac{C_t}{C_0-C_T}=k_{YN}(t)-k_{YN}\tau$$

where, k_{YN} is the rate velocity constant (L/min) and is the time in (min) required for 50 % adsorbate breakthrough. A linear plot of ln [$C_t/(C_0 - C_t)$] against sampling time (t) was used to determine the values of k_{YN} and τ from the slope and intercept of the plot (Fig. 16). From the Yoon Nelson model it was observed that as the bed depth increases the adsorption capacity decreases from 18.53 to 9.19 mg/g. This is because the upper layer of the manganese ferrite nanoparticle having sufficient surface area have been fully utilized for the adsorption of lead.

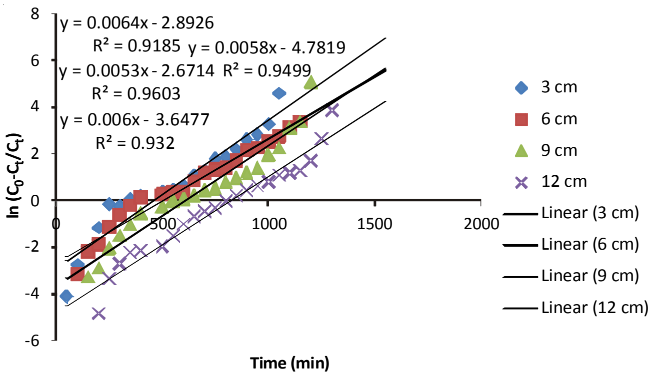

Fig. 16. Yoon Nelson model predicted breakthrough curves for lead removal using manganese ferrite nanoparticles

Conclusion

Manganese ferrite nanoparticle were synthesized and it was well confirmed by the FEG-SEM and FTIR analysis. The prepared manganese ferrite nanoparticle were subjected to batch studies for the removal of lead. Favourable results were obtained in the alkaline condition with a contact time of 20 min, adsorbent dosage of 0.04 g, lead concentration of 80 mg/L and an agitation speed of 100 rpm. Freundlich and Tempkin isotherms favoured the study. Pseudo second order kinetics fitted and was suitable. From the column studies faster breakthrough curves were observed at a shorter filtering depth of 3 cm. As the filtering bed height is directly influenced by the accommodative capacity of the filtering media, breakthrough curves were obtained at the shortest duration of time and space. Thomson and Yoon Nelson models showed that as the column depth increases the adsorption capacity decreases.

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