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Research Article

Adsorption Studies on Ni(II), Fe(II), ions from Aqueous Solution Using Poly(Azomethineamide)s: Equilibrium and Kinetic Approach

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Abstract

Toxic heavy metals of particular concern in treatment of industrial wastewater include Nickel, Iron, Zinc, Copper, Mercury, Cadmium, Lead and Chromium. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants, and human beings. In this study we mainly focused on two heavy metals, Ni(II) and Fe(II). Nickel ions represent a serious environmental problem, since they are widely used in many industries for general applications. Ni(II) containing wastewater are common as nickel is used in a number of industries including electroplating, batteries manufacturing, mining, metal finishing and forging. The higher concentration of Ni(II) in ingested water may cause severe damage to lungs, kidneys, vomiting, diarrhea, pulmonary fibrosis, renal edema and skin dermatitis. Iron is essential for human health and necessary for proper functioning of the biological system. Deficiency of iron causes anemia. However, excess of iron is toxic to human. Excessive iron intake leads to haemochromatosis resulting in tissue damage due to iron accumulation. Initial symptoms of iron toxicity on human are vomiting, diarrhea, and damage to the intestine. Recently, the adsorption process with strong affinity and high loading capacity for targeted metal ions has developed much attention which has paid to modification of super adsorbent. Super adsorbent (Polymers) that can absorb heavy metals in aqueous solutions but adsorption of heavy metals by the composites is very important for selection of adsorbent to metal removal from aqueous solutions.

Polymers are useful materials in fabrication, flexibility, chemical inertness as well as being light in weights. Polymers with highly conjugated chains have attracted much attention in the last few years because they are materials of academic interest and also they are investigated as the materials of electronics and photonics. Since many years this polymer family have been of interested for their good thermal stability and interesting optoelectronics properties. Some poly(azom ethines)have been prepared by solvent based polymerization and their thin films have been deposited by spin-on technique. The main aim of this study to prepare Poly(azomethineamide)'s, for removal of toxic heavy metal ions such as Ni(II) ions and Fe(II) ions. In addition, the optimum parameters affecting the metal ions uptake such as time dependence, pH profile, and dosage will be investigated. Finally the equilibrium removal performance of the composites will also be analyzed according to the Langmuir and Freundlich adsorption isotherm model.

Keywords: Nickel (II), Iron (II), Adsorption, Poly(azomethineamide)'s, Polymer.

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Introduction

Heavy metals in present era are the most important pollutants in treated water, and are becoming a severe public health problem, can be toxic to aquatic life and cause natural water to be unsuitable as potable water sources. In order to reduce heavy metal pollution problems, heavy metals in the environment removed by processes such as Oxidation-Reduction process, filtration, electro-chemical treatment, evaporation, ion exchange, or reverse osmosis, and adsorption. Recently, the adsorption process with strong affinity and high loading capacity for targeted metal ions has developed much attention which has paid to modification of super adsorbent. Super adsorbent (Polymers) that can absorb heavy metals in aqueous solutions but adsorption of heavy metals by the composites is very important for selection of adsorbent to metal removal from aqueous solutions.

Polymers are useful materials in fabrication, flexibility, chemical inertness as well as being light in weights [1]. Polymers with highly conjugated chains have attracted much attention in the last few years because they are materials of academic interest and also they are investigated as the materials of electronics [2], optoelectronics [3], and photonics [4]. Since many years this polymer family have been of interested for their good thermal stability and interesting optoelectronics properties. Some poly(azomethines)have been prepared by solvent based polymerization and their thin films have been deposited by spin-on technique [5]. The main aim of this study to prepare Poly(azomethineamide)'s, for removal of toxic heavy metal ions such as Ni(II) ions and Fe(II) ions. In addition, the optimum parameters affecting the metal ions uptake such as time dependence,pH profile, and dosage will be investigated. Finally the equilibrium removal performance of the composites will also be analyzed according to the Langmuir and Freundlich adsorption isotherm model.

Materials and Methods

2-aminoterephthalic acid (Aldrich, Japan), p-chlorobenzaldehyde (Himedia, India), 4,4'Diaminodiphenylsulphone (Merck,India), and recrystallised from ethanol. Ammoniumthiocyanate (Merck, India), Hydrochloric acid (Qualigens, India), Sulphuric acid (Qualigens, India), Lithium chloride (Fulka, Switzerland) were used to prepare polymer.

Solvents

N-N'dimethylformamide (Himedia,sugars, India), Pyridine (Qualigens, India), Triphenylphosphene (Rambacks, India), Triethylammine hydrochloride (Merck, India), were distilled once before use. Purification of solvents Ethanol N-methylpyrolidine (Himedia,India), Ethanol (Sakthi sugars) was refluxed with quick lime with an efficient condenser and a guard tube for 6 hours and allowed to stand overnight. It was then distilled and the middle fraction boiling at 78º C was collected and stored.

DMF

N-N'Dimethylformamide (Himedia, India) was mixed with potassium hydroxide and kept for 20 hours, filtered and distilled under reduced pressure. The middle fraction was collected and used.

Pyridine

Pyridine was refluxed with potassium hydroxide in a round bottomed flask fitted with an efficient condenser and a guard tube and refluxed for 30 minutes then distilled and distillate was stored in black container.

NMP

N-methyl pyrrolidine was refluxed with potassium hydroxide in a round bottomed flask fitted with an efficient condenser and a guard tube and refluxed for 30 minutes then distilled under reduced pressure.

Preparation of Azomethine dicarboxylic acid monomer

4-Chloro benzalaniline-2,5dicarboxylic acid [ADA]: The aromatic dicarboxylic acid monomer (ADA) was synthesized by condensing one mole of 2-aminoterephthalic acid with 2 moles of p-Chlorobenzaldehyde in DMF under nitrogen atmosphere at 100-110ºC for 4 hours. After cooling to room temperature, the contents were poured into water with stirring. It was allowed to settle and carefully filtered. The precipitate was washed with ethanol and then dried under vacuum pump at 90ºC.

Synthesis of polymers

Polythioamide was synthesized according to our earlier reports. In the typical procedure one equivalent of the monomer, two equivalent of the 4,4'bis(thiourea)biphenylsulphone, four equivalents of triphenylphosphite, four equivalents of TEA.HCl , 200 millimoles of pyridine were mixed and kept at temperature around 140ºC in DMF solvent for 6 hours. The reaction mixture was cooled to room temperature and poured into ethanol to precipitate the polymer. It was then filtered, washed with dilute HCl, dilute $NaHCO_3$. It was dried under vaccum pump at 100° C.

Experimental methods

Adsorption Studies

Batch mode adsorption experiments were carried out by shaking the flask at 180 rpm for a constant period of time using a mechanical shaker (Orbitek).Following a systematic process, the removal of heavy metal ions from aqueous solutions by the use of poly(azomethineamide)s [PAMA] in batch adsorption process.

In the present study, the data obtained in batch studies were used to calculate the percentage removal of heavy metal ions by using the following balance relationship:

$$\%\mathbf{removal} = \frac{\mathbf{C_o - C_e}}{\mathbf{C_o}} \mathbf{x}100$$

Where C_o and C_e is the initial and equilibrium concentration (mg/L) of the metal solutions respectively.

Effect of solution pH on adsorption

The effect of pH on the adsorption of PAMA was investigated using a 20 ml of 50 mg/L metal ion solution in the pH range between 3.0 to 8.0.The samples were then agitated in a mechanical shaker at 180 rpm at a different solution pH for 120 min and then filtered through Whatman 42 filter paper. The filtrate was analyzed using Atomic Adsorption Spectrometer (AA6300). Each determination was repeated thrice and the result obtained was their average values.

Effect of adsorbent dosage

Batch adsorption experiments were carried out with different adsorbent dosage of PAMA from 10 to 50 mg for a 20 ml of 50 ppm of Nickel solution at 6.0 pH, and Iron solution pH 7.0 for contact time of 120 min at a room temperature of 30°C. The samples were filtered and solutions to the filtrates were analyzed as mentioned above.

Effect of contact time

Batch adsorption experiments were carried out with different contact time (40 to 240 min) for an initial concentration of 50 mg/L of metal ion solution at pH 6.0 for Ni(II) and pH 7.0 for Fe (II), the PAMA dose concentration is 20 mg in 20 ml of metal ion solution in 250 ml conical flask at 30°C.Flasks were agitated for 160 min to ensure that the equilibrium is attained. The mixture was then filtered and the concentration of metal ion in the filtrates was measured using AAS.

Effect of metal ion concentration

Batch adsorption experiments were carried out by contacting 20 mg of PAMA with 20 mL of metal ion solution of different initial concentration (50 to 250 mg/L) at a pH value of 6.0 for Ni(II) and pH 7.0 Fe(II) at 30°C. A series of such conical flask were shaken for 120 min at 180 rpm. The samples were filtered and the filtrates were analyzed with AAS.

Adsorption Isotherms

Batch adsorption experiments were conducted using 250 mL conical flask at 30°C. 20 mg of adsorbent was added to each conical flask which consists of 100 ml metal ion solution of various initial concentrations. All the flasks were shaken at 180 rpm in the mechanical shaker for 120 mins, after filtration, the metal ion concentration in the filtrate solution was analyzed using AAS. The amount of metal adsorbed qe (mg/g) was determined by using the following mass

$$\mathbf{q_e = \frac{C_o - C_e}{m} \times V}$$

V is the volume (ml) of the solution; and m is the mass (mg) of the adsorbent.

Adsorption kinetics

Kinetic studies were conducted using a 250 mL conical flask at 30 °C. The experiment was conducted using 20 mL of metal ion solution at the initial metal ion concentration of 300 mg/L. The mixture was shaken continuously and the samples were taken at predetermined time intervals and immediately filtered. The filtrate solution was analyzed for the residual metal ion concentration. The amount of metal adsorbed at time t, qt (mg/g), was calculated by:

$$q_e = \frac{C_o - C_t}{m} \times V$$

Ct is the concentration of metal solution at any time t (mg/L).

Desorption and reusability studies

The recovery and reusability of the adsorbent is an important parameter related to the application of adsorption technology. In this study, the metal loaded PAMA was kept in solution of 2N NaOH for about 6 h, followed by washed with 2N HCl and washed deionized water to remove any residual desorbing solution and utilized for the adsorption cycle. Each adsorption cycle was repeated four times using the same adsorbent.

Result and Discussion

Characterization

FTIR spectrum of PAMA

IR spectrum of **poly(azomethineamide)s [**PAMA] is shown in **Figure 2**. The amide carbonyl (-C=O) and (-N=CH-) stretching frequencies appeared at 1627 cm^{-1} and 1592 cm^{-1} respectively. The –NH stretching frequency and amide (II) band is observed at 3372 cm^{-1} and 1492 cm^{-1} respectively which suggest the formation of amide link in the polymer. The (S=O) and (C-S) stretching vibrations appears at 1014 and 577 cm^{-1} respectively. The above spectrum analysis support the structure of poly(azomethineamide) shown in the Figure 2.

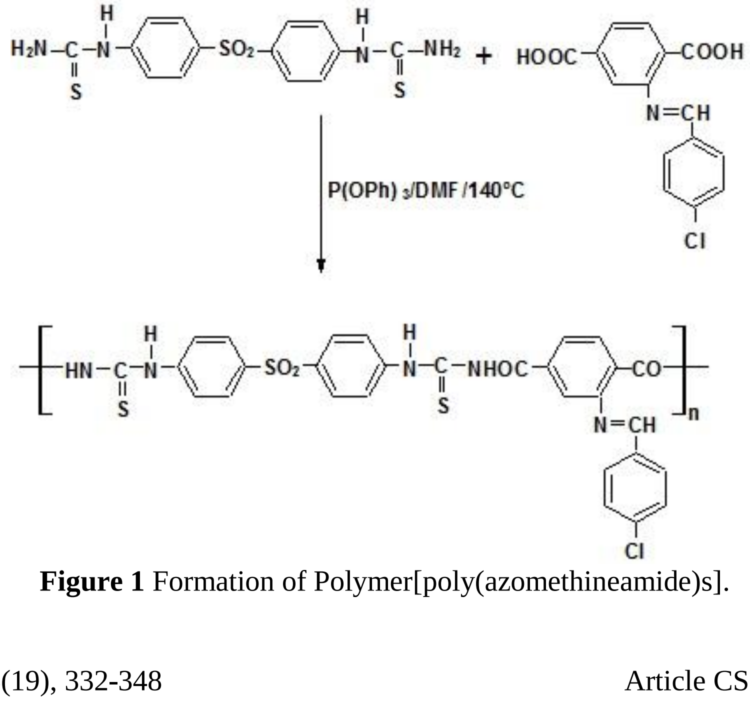

Figure 1 Formation of Polymer[poly(azomethineamide)s].

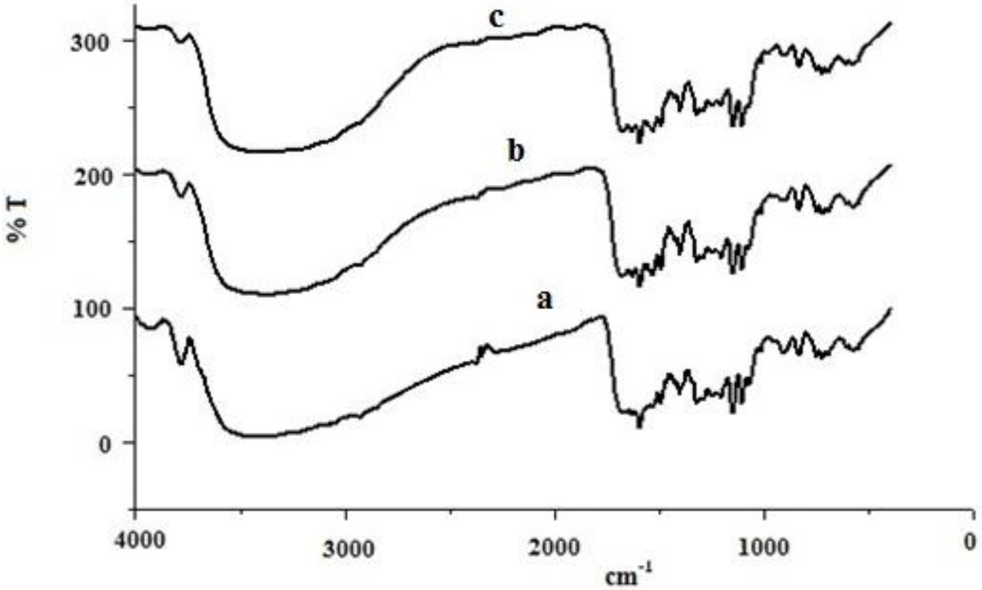

Figure 2 FT-IR spectrum of PAMA (b) Ni and (c) Fe treated PAMA.

SEM analysis

The structural morphology of the PAMA was analyzed using Scanning electron microscope at an accelerating voltage of 10 kV under magnifications of 10 µm and 20 µm. **Figure 3**a and b. Figure 3a shows that the size of the polymer particles ranges between 88.7 nm to 204 nm. The SEM images of the PAMA and metal loaded PAMA are shown in Figure 3c. From Figure 3d irregular image and porous surface could be observed. After metal adsorption, the porous surface on the PAMA gets filled by the metal ions. This observation indicates that metal ions are adsorbed to the functional groups present inside the wall of the PAMA surface. So, the morphological study of metal loaded PAMA confirms that the adsorption takes place inside the wall of the PAMA surface. This fact is further supported by the FT-IR analysis of the metal adsorbed polymer (b) and (c) are shown in Figure 2. When compared to plain polymers the –N-H stretching frequency of amide link (3372 cm^{-1}) shifts to lower wavelength (3371 cm^{-1} and 3366 cm^{-1}) in the metal adsorbed polymer. The –N-CH- stretching frequency also changed in the metal adsorbed polymer.

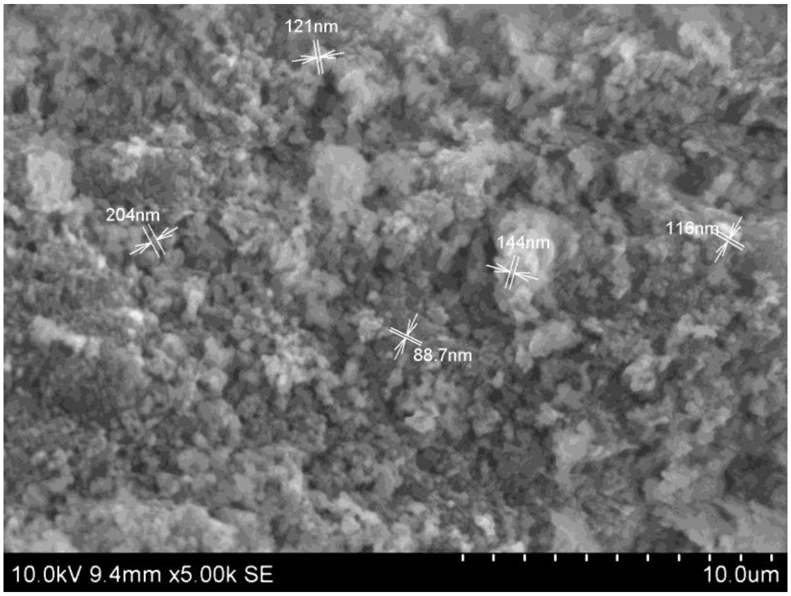

Figure 3 The structural morphology of the PAMA using Scanning electron microscope.

SEM-EDX

The EDX images of PAMA and metal loaded PAMA are shown in **Figure 4**a, 4b and 4c respectively.

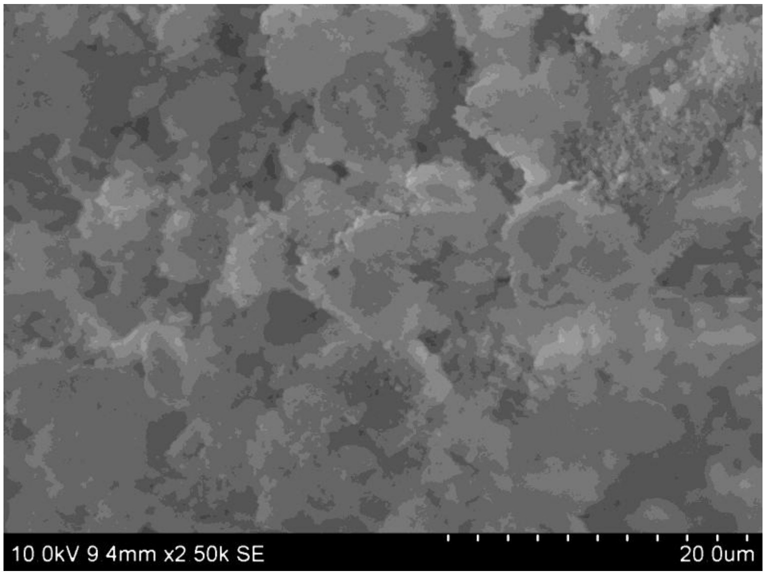

Figure 4 The SEM images of the PAMA.

Effect of pH on metal ion adsorption

The solution pH is an important controlling parameter that affects the adsorbent capacity of heavy metals. The influence of hydrogen ion concentration on the adsorption of Ni and Fe was investigated by varying the pH of metal solution in the range of 3.0-8.0.The effect of pH on heavy metal ions such as Ni(II) and Fe(II) adsorption was shown in **Figure 5**. The adsorption capacity is high at pH 6.0 and it decreases as the solution pH increases or decreases. The maximum removal efficiencies of Ni(II) and Fe(II) ions were 89.96%, 98.59% respectively concentration of H+ ions far exceeds that of the metal ions and hence H+ ions compete with would hinder the metal ions from reaching the binding sites of the adsorbent caused by repulsive forces. However, the metal ions removal is minimum presumably due to enhanced competition of H+ with metal ions for the binding sites and complex formation. When pH 6 the functional groups present in the adsorbent are deprotonated and their metal binding capacity increases. Hence the optimal pH value of 6 was fixed for further adsorption experiments.

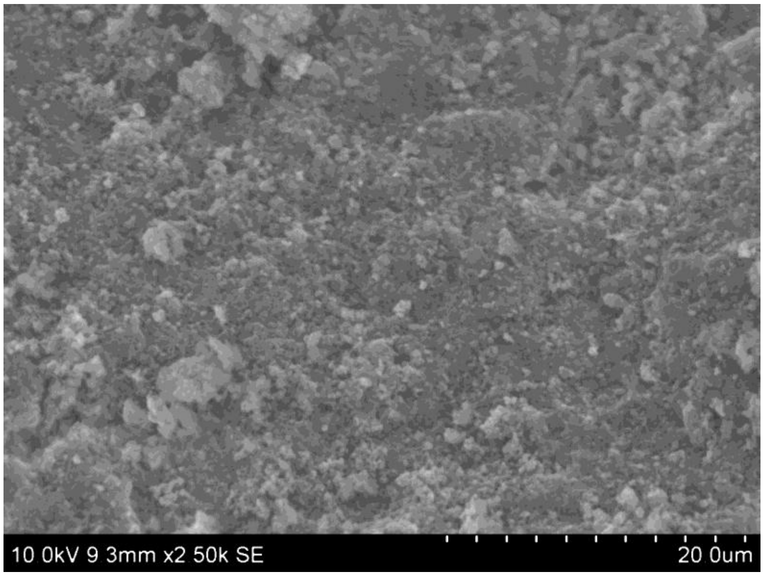

Figure 5 Ni (II) loaded PAMA.

Effect of adsorbent dose on metal ions adsorption

The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration. The adsorption efficiency for Ni(II) and Fe(II) ions as a function of adsorbent dosage was investigated. It was observed from the result **Figure 6** that percent removal of metal ion increases with increase in adsorbent dosage. This is because of the availability of more binding site on the surface at higher concentration of the adsorbent for complexation of metal ions. The increase in adsorbent dose for Ni(II), and Fe(II) from 10 to 50 mg resulted in an increase of Ni(II) ions from 71.4% to 95.23%, and for Fe(II) ions from 65.9% to 98.65% respectively.

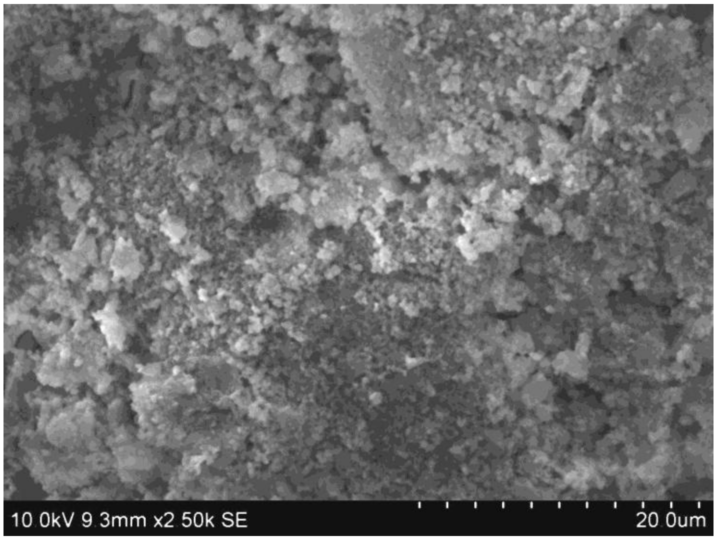

Figure 6 Fe (II) loaded PAMA.

Effect of contact time on metal ions adsorption

Contact time is one of the important parameters for successful use of the adsorbent for practical application and rapid sorption is among the desirable parameters. **Figure 7** shows the effect of contact time on the adsorption of Ni (II) and Fe (II), ions onto PAMA. The adsorption efficiency of Ni (II) and Fe (II) ions increased considerably with increasing contact time up to 160 mins later, it was almost constant. For instance, during 120 mins, when the adsorption efficiency was 89.99, 95.9 for Ni (II) and Fe (II) ions, respectively, then it was 90.52, 96.05 respectively, for 250 min. Therefore, the optimum contact time was fixed as 120 mins for further experiments.

Effect of initial metal ion concentration on metal ions adsorption

The rate of adsorption is a function of the initial concentration of the metal ions, which makes it an important factor to be considered for effective adsorption. The percentage removal of metal ion such as Ni (II) and Fe (II), at a different metal ion concentration (50-250 mg/L) using PAMA is presented in **Figure 8**. The initial metal ions concentration were increased from 50 to 250 mg/L, the percentage of adsorption was slightly decreased for Ni (II) 89.96%, 80.39% and for Fe(II) from 92.59%, 87.34%).This may be due to the saturation of active adsorption sites on PAMA.

Adsorption isotherms

Adsorption isotherms are the basic requirements for designing any sorption systems. The distribution of metal ions between the liquid pH and adsorbent is a measure of the position of equilibrium in the adsorption process and can generally be expressed by one or more of a series of isotherm models. In order to adopt for the considered systems, an adequate model that can reproduce the experimental result obtained, equations of Langmuir [7] , Freundlich [8], Redlich Peterson [9], and Koble Corrigan have been considered. The maximum adsorption capacity of metal ions q_m, for the adsorbent used in this study along with that of other adsorbents are presented. The adsorption capacity of PAMA was much higher than that of other potential adsorbent such as Bagasse, carbon, Bone char, Aniline formaldehyde coated, Tree fern and Fly ash.

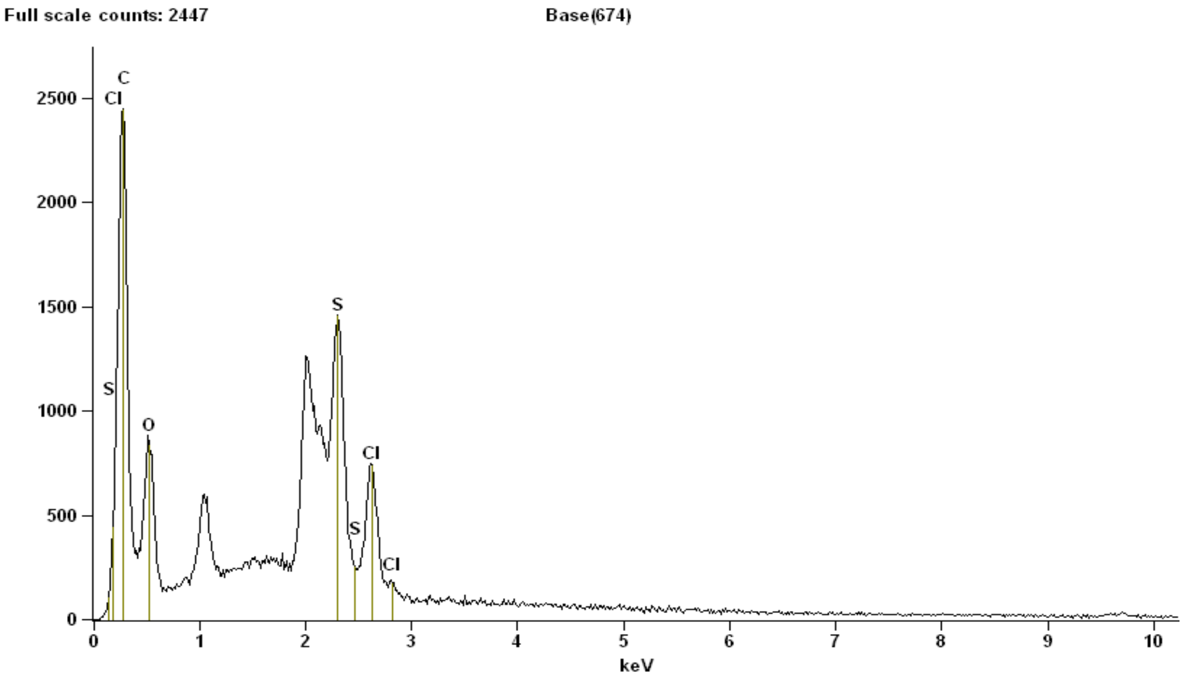

Figure 7 The EDX images of PAMA.

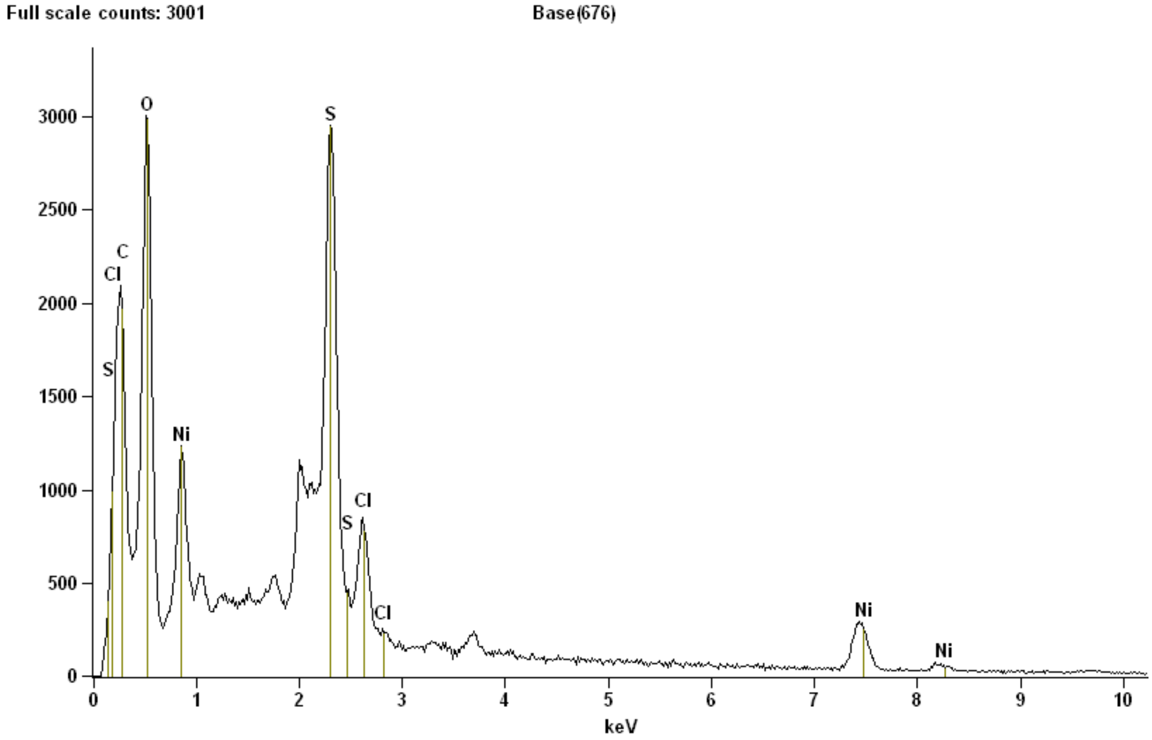

Figure 8 The EDX images of Ni (II) loded PAMA.

The Langmuir isotherm

The theoretical Langmuir sorption isotherm is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The non-linear equation of Langmuir isotherm model is expressed as follow:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Where C_e is the supernatant concentration at the equilibrium state of the system (mg/L), q_m and k_L are the Langmuir constants, representing the maximum adsorption capacity for the solid pH ase loading and the energy constant related to the heat of adsorption respectively.

The Freundlich isotherm

The Freundlich isotherm model is the earliest known relationship describing the sorption process. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation which can be employed to describe heterogeneous systems and is expressed as follows:

$$q_e = k_f C_e^{1/n}$$

where K_f is the Freundlich constant ((mg/g) (L/g) $^{(1/n)}$ related to the bonding energy. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbent for unit equilibrium concentration.1/n is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if n=1 then the adsorption value is below to unity, this implies that adsorption process is chemical; if the value is above unity adsorption is a favorable pH physical process.

The Redlich – Peterson isotherms

The Redlich – Peterson isotherms is a combination of Langmuir Freundlich model. It approaches the Freundlich model at higher concentration and is in accordance with the lower concentration limit of the Langmuir equation. The equation follows as:

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{\beta}}$$

Where K_R is Redlich –Peterson isotherms constant (L/g), α_R is Redlich-Peterson isotherm constant (L/mg) and β is the exponent which lies between 0 and 1. The constant β can characterize the isotherm as: if β =1 the Langmuir will be the preferable isotherm, while if β =0,the Freundlich isotherm will be the preferable isotherm.

The Koble-Corrigan isotherm

The Koble-Corrigan isotherm [10] has been used in the following form:

$$q_e = \frac{\alpha \ C_e^n}{1 + bC_e^n}$$

Where a, b, c are Koble-Corrigan parameters

The experimental data on the effect of an initial concentration of metal ions on the PAMA of the test medium were fitted to the isotherm models using MATLAB 7.1 and the graphical representations of these models are presented in **Figure 9**(a), and (b) . All of the constants are presented in **Table 1**. Since the value of R^2 is nearest to 1 this indicates that the respective equation fits the experimental data best. The representations of the experimental data by all the model equations result in non-linear curve with R^2 values as tabulated in Table 1. The experimental data yielded excellent fits based on its correlation coefficient values of Koble-Corrigan, Redlich-Peterson, Freundlich, and

Langmuir isotherms for Ni(II), and Redlich-Peterson, Freundlich, Langmuir and Koble-Corrigan for Fe(II) ions. Koble-Corrigan isotherm has fits better compare to other three isotherms for Ni(II) and Redlich-Peterson for Fe(II). The plotted equations obtained from the graphs were presented in Table 1.

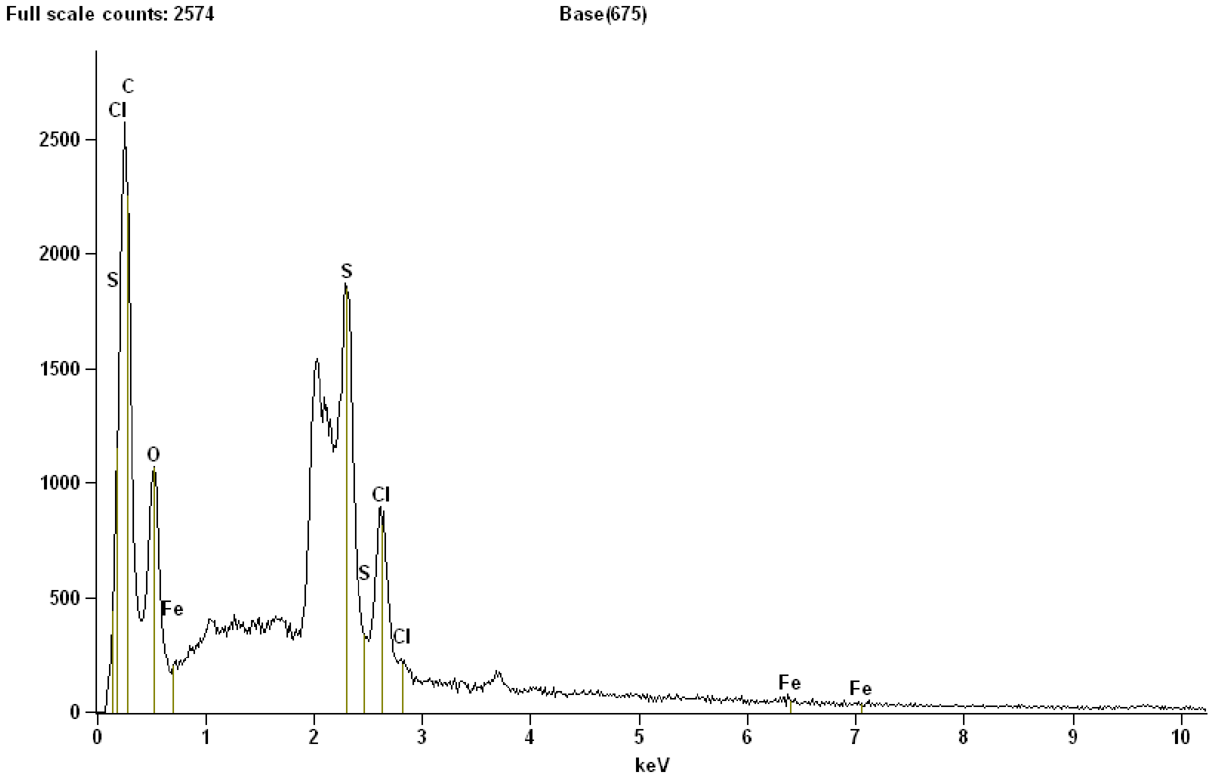

Figure 9 The EDX images of Fe (II) loded PAMA.

Table 1 The value of parameters for each isotherm models used in this study.

Isotherm Model	**Ni (II)**		**Fe (II)**	
	Parameter	**R^2**	**Parameter**	**R^2**
Langmuir	q_m = 173.3 K_L = 0.0515	0.9732	q_m = 167.2 K_L = 0.0820	0.9303
Freundlich	$K_{F\,=}$26.75 n =2.643	0.9816	K_F =31.7 n =2.801	0.9767
Redlich	K_R =19.96 α_R =0.3796 β = 0.7556	0.9894	K_R =108.5 α_R =2.956 β =0.6732	0.9772
Koble-Corrigen	α =19.15 β =0.07346 n =0.6308	0.9900	α =3.0 β =0.02061 n =1.68	0.8262

Adsorption kinetics

Lagergren pseudo-first-order [11], pseudo-second-order [12] Elovich kinetic [13] and intraparticle diffusion [14] models were used to test the experimental data and explain the adsorption kinetic process.

Lagergren pseudo-first order kinetic model

Lagergren pseudo-first order equation is the most popular kinetics equation and used only for the rapid initial pH phase. The pseudo-first order equation is given by

$$\log (q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303}\, t$$

where q_t is the adsorption capacity at time t (mg/g) and k_{ad} (min^{-1}) is the rate constant of the pseudo-first order adsorption, was applied to the present study of Ni(II), Fe(II) ion adsorptions onto PAMA. The rate constant, k_{ad} and correlation coefficients of the metal ions under single concentration were calculated from the linear plot of $\log(q_e - q_t)$ versus t **Figure 10** and listed in **Table 2**. The correlation coefficients for the pseudo-first-order kinetic model are low. Moreover, a large difference of equilibrium adsorption capacity (q_e) between the experiment and calculation was observed, indicating a poor pseudo first-order fit to the experimental data.

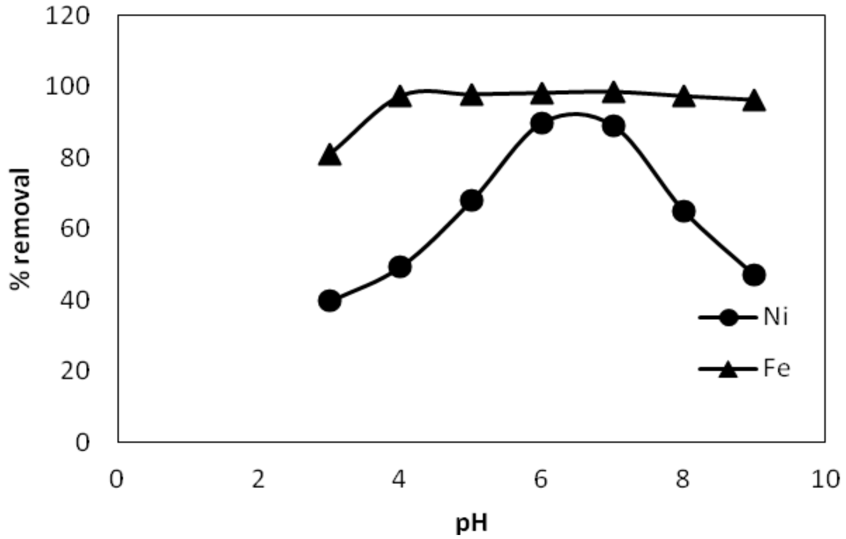

Figure 10 Effect of pH on heavy metal ions such as Ni (II), Fe(II) adsorption.

Table 2 Kinetic models and other statistical parameters.

Kinetic model	Parameters	Metal ions solution (50 mg/L)	
		Ni (II)	**Fe (II)**
Pseudo-first-order equation	k_{ad} (h^{-1})	0.0162	0.0092
	$q_{e,}$ cal (mg/g)	28.18	17.53
	R^2	0.959	0.847
Pseudo-second-order equation	k (g mg^{-1} h^{-1})	7.617×10^{-4}	10.227×10^{-4}
	q_e ,cal (mg/g)	52.63	52.63
	h (mg g^{-1} h^{-1})	2.1097	2.8328
	$q_{e,}$ exp (mg/g)	45.49	48.05
	R^2	0.998	0.998
Elovich equation	α (mg/g.h)	10.33	20.78
	β (g/mg)	0.1214	0.1298
	R^2	0.951	0.923
Intraparticle diffusion	k_p (mg/g.$h^{1/2}$)	1.558	1.441
	C	23.50	28.05
	R^2	0.896	0.850

The pseudo second-order kinetic model

The pseudo second-order model is more likely to predict the kinetic behavior of adsorption with chemical sorption being the rate controlling step. This equation is in the following form:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}\, t$$

where h=kq_e^2 (mg g^{-1} min^{-1}) can be regarded as the initial adsorption rate as t→0 and k is the rate constant of pseudo second- order adsorption (g mg^{-1} min^{-1}). The plot of t/q_t versus t **Figure 11** should give a straight line if the pseudo-second-order kinetics is applicable to the adsorption of metal ions onto PAMA. The values q_e, k and h can be determined from the slope and intercept of the plot. At studied initial metal ion concentration, the straight lines with extremely high correlation coefficients (0.998) were obtained and presented in Table 2. In addition, the calculated q_e values also agreed with the experimental data in the case of pseudo-second order kinetics. This suggests that the adsorption data are well represented by pseudo-second-order kinetics and supports the assumption that the rate-limiting step of metal ions onto PAMA may be chemisorption process.

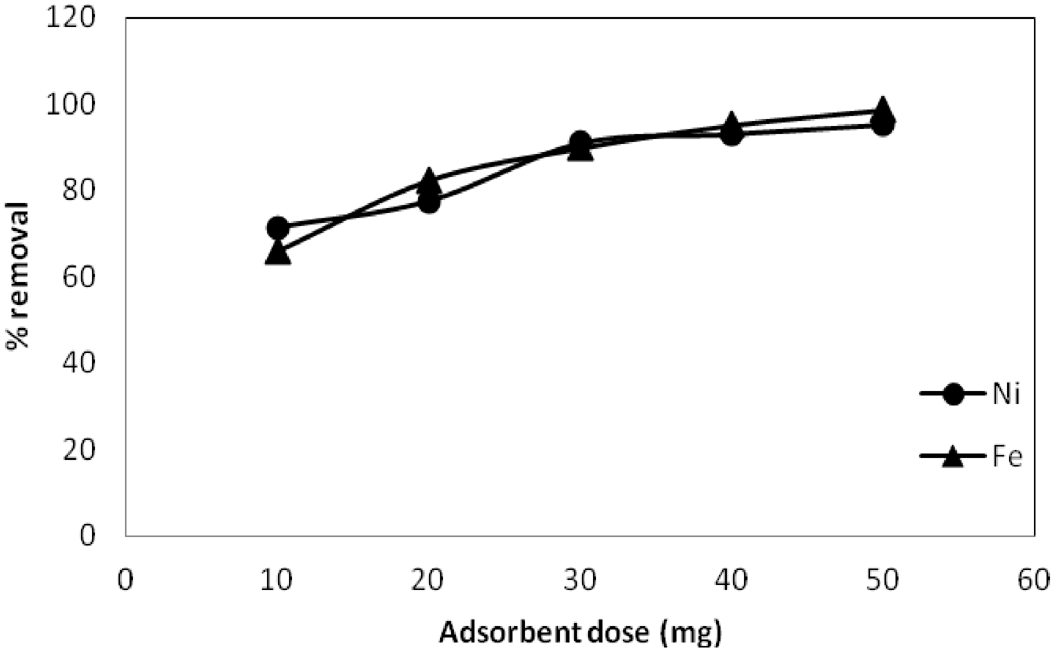

Figure 11 Effect of adsorbent dose on metal ion such as Ni(II), Fe(II) adsorption.

The Elovich kinetic model

The equation defining the Elovich kinetic model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. The linear form of Elovich equation is given by

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$$

where α and β known as the Elovich coefficients, α represent the initial sorption rate in mg/(g min) and β is related to the extent of the surface coverage and activation energy for chemisorption (g/mg), respectively. The Elovich coefficients could be computed from the plot of qt versus ln t (**Figure 13**). Ni(II), and Fe(II) ion adsorption kinetics onto PAMA were also tested with Elovich kinetic model by plotting qt versus ln t. Recorded R^2 values are low which indicates that the experimental data does not fit the Elovich kinetic model and metal ions removal using PAMA under study cannot be described using this model.

The intraparticle diffusion model

Taking into account that the kinetic results are fitted very well to a chemisorption model, the intraparticle diffusion model was plotted in order to verify the influence of mass transfer resistance on the binding of metal ions to the PAMA. The kinetic results were analyzed by the Weber and Morris intraparticle diffusion model to elucidate the diffusion mechanism, which is expressed as:

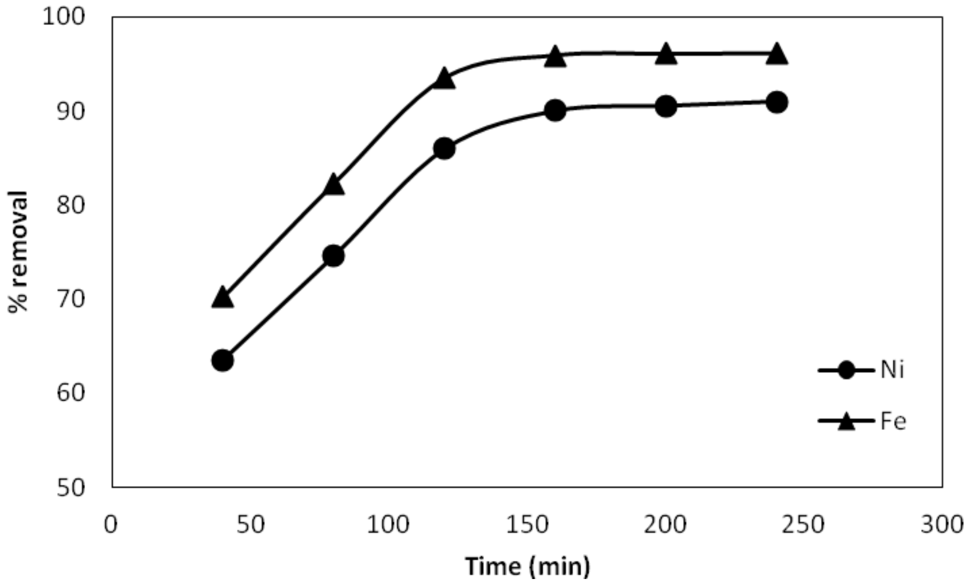

Figure 12 Effect of contact time on metal ion such as Ni (II), Fe (II) adsorption.

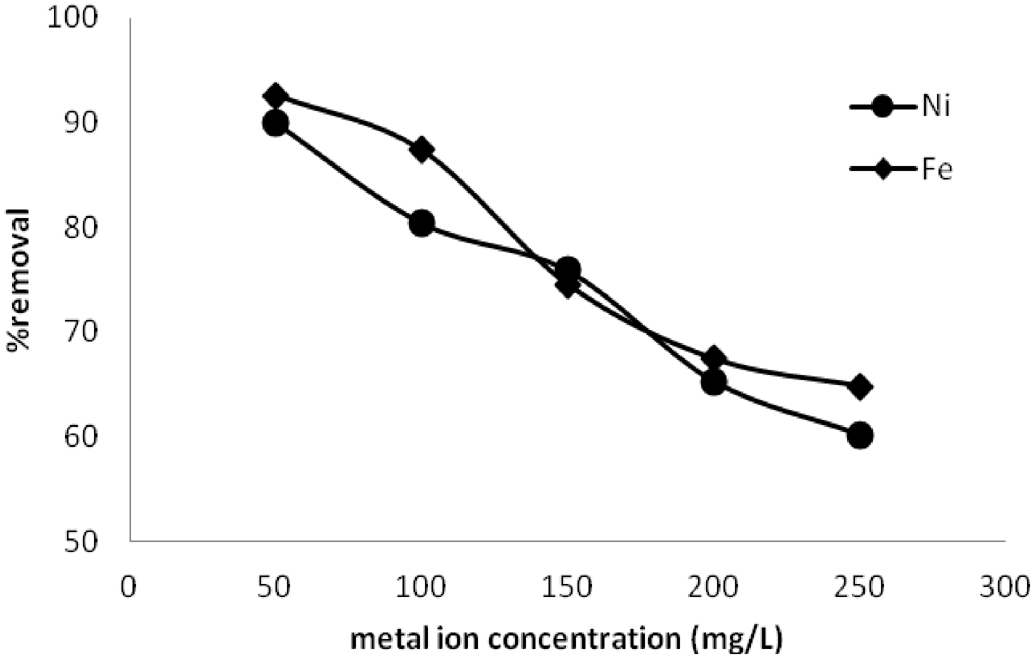

Figure 13 Effect of initial metal ion concentration on metal ion such as Ni (II) , Fe (II) adsorption.

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

where C is the intercept and k_p is the intraparticle diffusion rate constant, (mg/g min1/2), which can be evaluated from the slope of the linear plot of qt versus $t^{(1/2)}$ **Figure 14**. The intercept of the plot reflects the boundary layer effect. The larger the intercept is the greater is the contribution of the surface sorption in the rate controlling step. The calculated intraparticle diffusion coefficient k_p values are listed in Table 2. If the regression in the plot of qt versus $t^{(1/2)}$ is linear and pass through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plot at each concentration did not pass through the origin. This deviation from the origin is perhaps being due to difference in the rate of mass transfer in the initial and final stages of adsorption. This is indicative of some degree of boundary layer control and this further showed that the intraparticle diffusion was not only rate-limiting step, but also may be controlling the rate of sorption or all may be operating simultaneously.

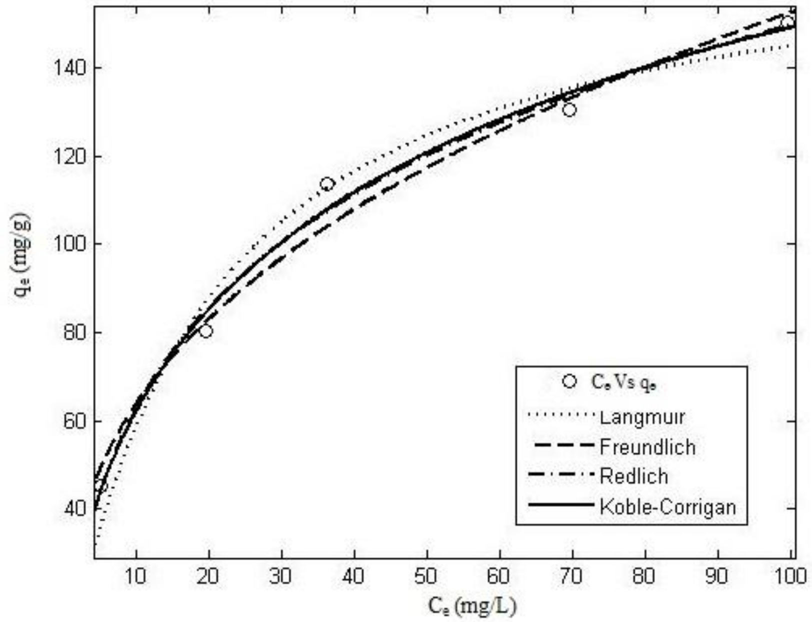

Figure 14 Adsorption isotherms of PAMA with Ni (II) ion.

Thus based on the high correlation coefficient values (Table 2), it can be inferred that adsorption of metal ions onto PAMA followed pseudo-second order model than that of the intraparticle diffusion model, pseudo-first order model.

Regeneration

Desorption studies helps to elucidate the mechanism of adsorption and the recovery of the adsorbent. The metals under study is acidic in nature and exhibits good attraction toward basic medium and therefore an aqueous solution of NaOH (2N) is capable of eluting the metals from the PAMA. The regenerated PAMA was used again up to three adsorption cycles and the results are illustrated in **Figure 15**. From the results, it is clear that the efficiency of PAMA drops a little after each cycle. This might be due to the ignorable amount of PAMA lost during the adsorption process. Regeneration studies show that the adsorption process using PAMA is a reversible process.

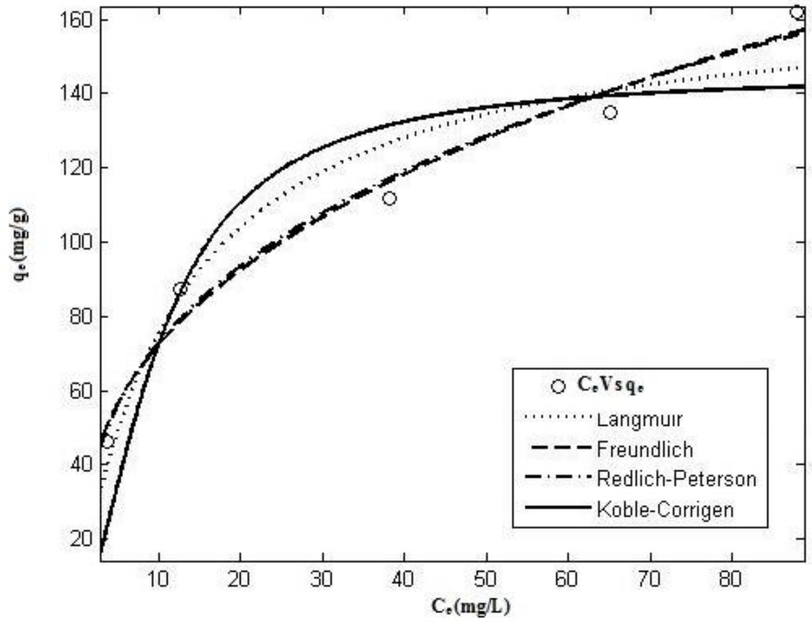

Figure 15 Adsorption isotherms of PAMA with Fe (II) ion.

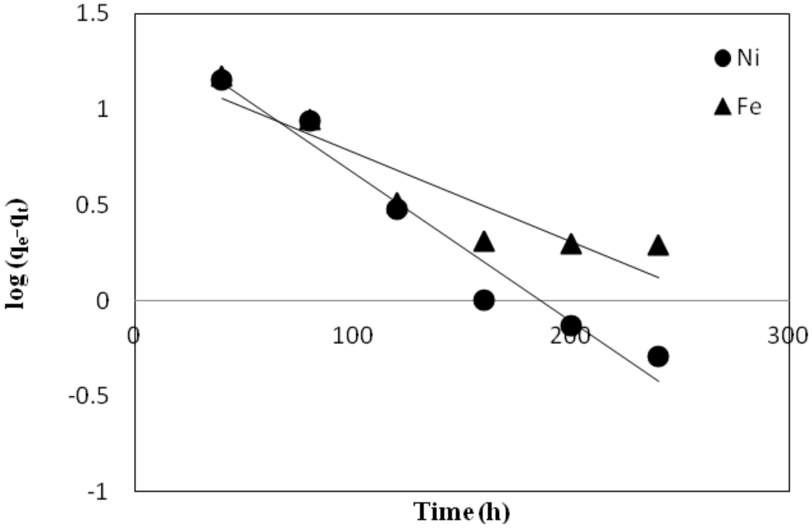

Figure 16 Lagergren pseudo-first order kinetic model in Ni (II), Fe (II) ions.

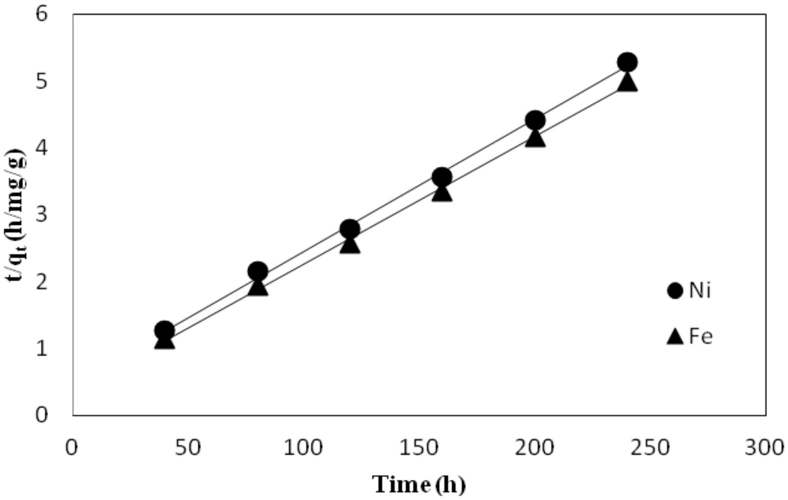

Figure 17 The pseudo second-order kinetic model in Ni (II), Fe (II) ions.

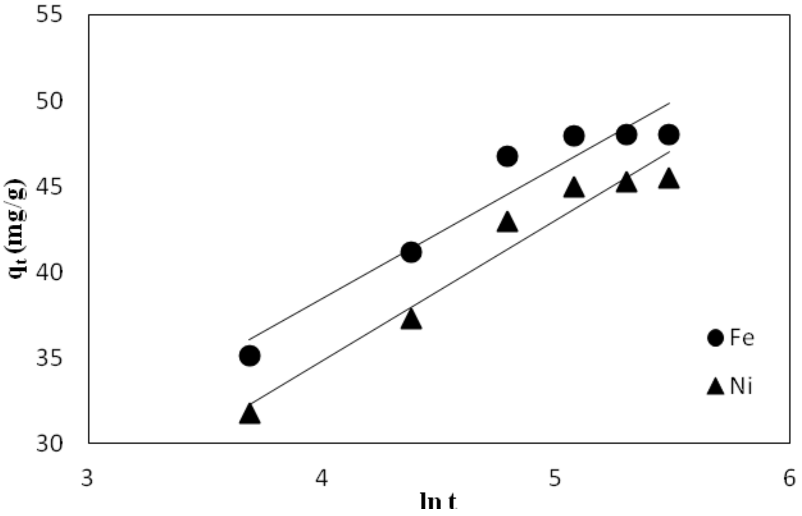

Figure 18 The Elovich kinetic model in Ni (II), Fe (II) ions.

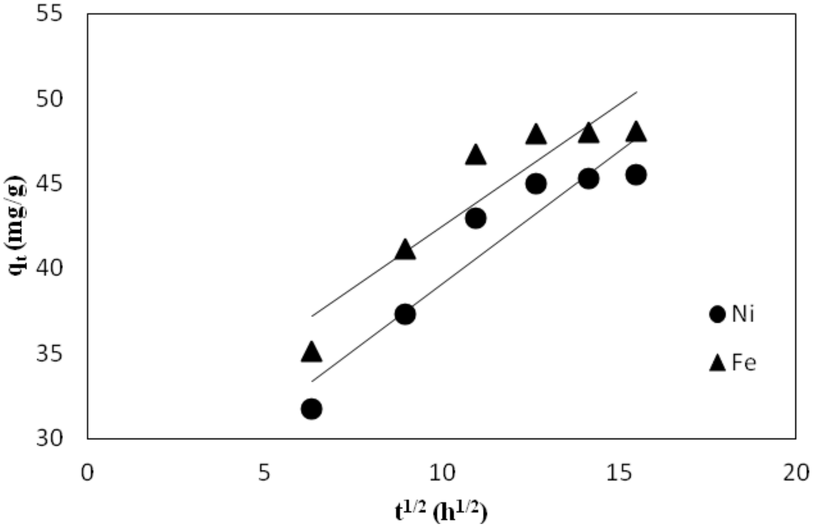

Figure 19 The intraparticle diffusion model in Ni (II), Fe (II) ions.

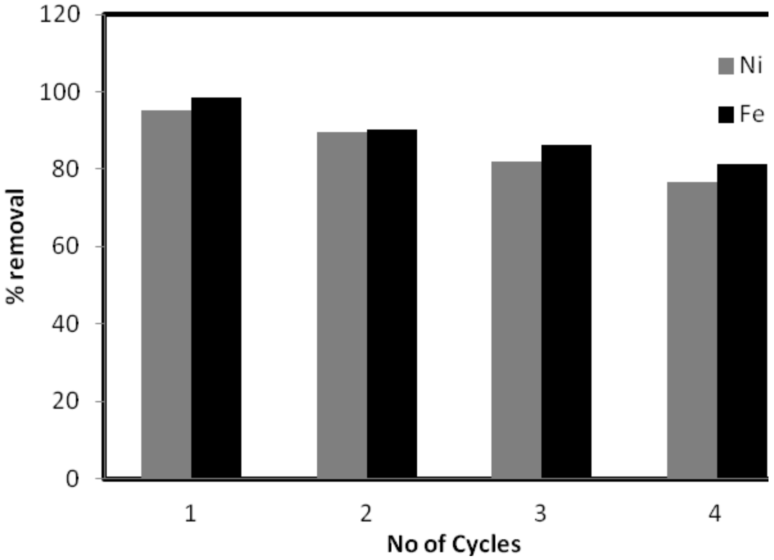

Figure 20 Regeneration of PAMA.

Conclusion

The results of the present investigation show that poly azomethineamides (PAMA) adsorbents have considerable potential for the removal of metal ions such as Ni(II), and Fe(II) from the aqueous solutions. The pH has a greater influence on the adsorption efficiency. At low pH value, the adsorption efficiency was relatively low due to the protonation of the chelating groups; whereas at higher pH values almost 90% metal ions were adsorbed. The adsorbed amount of metal ions increased with increase in contact time and equilibrium could be reached within 160 min. Equilibrium and kinetic studies were conducted for the adsorption of metal ions such as Ni(II), and Fe(II) ions by PAMA. The experimental data shows excellent fits within the following isotherms order for Ni(II), and Fe(II) ions: Koble-Corrigan, Redlich-Peterson, Freundlich, and Langmuir and, Redlich-Peterson, Freundlich, Langmuir and Koble-Corrigan, respectively, based on its correlation coefficient values. From kinetic studies, it is found that the pseudo-second order equation provides the best correlation coefficient and agrees between the calculated q_e values and the experimental data, rather than other three kinetic equations. Finally, it was concluded from the result that the PAMA is an excellent sorbent for the removal of heavy metal ions from the aqueous solution due to its high selectivity, high thermal stability and absolute insolubility in water.

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