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Adsorption kinetic, equilibrium and thermodynamic investigations of Zn(II) and Ni(II) ions removal by poly(azomethinethioamide) resin with pendent chlorobenzylidine ring

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This paper reports the application of poly(azomethinethioamide) (PATA) resin having the pendent chlorobenzylidine ring for the removal of heavy metal ions such as Zn(II) and Ni(II) ions from the aqueous solutions by adsorption technology. Kinetic, equilibrium and thermodynamic models for Zn(II) and Ni(II) ions adsorption were applied by considering the effect of contact time, initial metal ion concentration and temperature data, respectively. The adsorption influencing parameters for the maximum removal of metal ions were optimized. Adsorption kinetic results followed the pseudo-second order kinetic model based on the correlation coefficient (R^2) values and closed approach of experimental and calculated equilibrium adsorption capacity values. The removal mechanism of metal ions by PATA was explained with the Boyd kinetic model, Weber and Morris intraparticle diffusion model and Shrinking Core Model (SCM). Adsorption equilibrium results followed the Freundlich model based on the R^2 values and error functions. The maximum monolayer adsorption capacity of PATA for Zn(II) and Ni(II) ions removal were found to be 105.4 mg/g and 97.3 mg/g, respectively. Thermodynamic study showed the adsorption process was feasible, spontaneous, and exothermic in nature.

Keywords: adsorption, models, Ni(II) ions, poly(azomethinethioamide), Zn(II) ions.

INTRODUCTION

Heavy metals are non-biodegradable and toxic in nature. Nickel, zinc, chromium, copper, lead, cadmium and mercury are among the most abundant toxic and harmful metals in the wastewater[1–5], because, these metals find many applications in industries which results the generation of metals along with the industrial wastewater. Zinc and nickel metals are most toxic pollutants and are released into the environment largely from various natural and anthropogenic activities such as acid mine drainage, galvanising plants, electroplating, refining and welding industries. Bureau of Indian Standards (BIS) has recommended the maximum permissible limit for zinc and nickel in drinking water as 5 mg/L (BIS 1994) and 0.02 mg/L (BIS 2003), respectively[6–7]. If the concentration of these metals has increased above the permissible limit in the aquatic system then it produces a serious threat to the human health and other living organisms in the environment. Therefore, it is highly important and challenging task to remove these metal ions effectively from the wastewater/water. Even though various processes such as adsorption, chemical precipitation, ion exchange, membrane separation, chemical coagulation, flotation, advanced oxidation, reverse osmosis, electro-winning, electrocoagulation, solvent extraction, evaporation, etc. are used for the removal of metal ions from the wastewater[2, 8–14]. Adsorption remains to be the most popular technique due to its flexibility and simple in design, convenience and ease of operation and higher efficiency in removing heavy metal ions especially at lower concentration. Various adsorbents were employed for the removal of metal ions from the aqueous solutions which includes surface modified *Strychnos potatorum* seeds[2, 13], bael tree leaves[8–9], cashew nut shell[10–11], unmodified *Strychnos potatorum* seeds[12], chitosan–PVA blend[14], rice bran[15], activated carbon from bagasse[16], xanthate modified magnetic chitosan[17], orange peel[18], banana peel[18], coir[19], *Azadirachta indica* bark[20], bagasse fly ash[21], cork biomass[22], physic seed hull[23], lignin[24], lignocellulosic substrate[25], P-tert[(dimethylamino)methyl]-calix[4]arene[26] and etc.

The objective of the present research is to develop an effective polymeric material with maximum adsorption capacity for the removal of Zn(II) and Ni(II) ions from the aqueous solution. Adsorption experiments were carried out under different experimental conditions like varying the solution pH, adsorbent dose, contact time, initial metal ions concentration, and temperature. Kinetic studies and adsorption isotherms were analyzed and various models were used to evaluate the experimental data to elucidate the possible adsorption mechanism. Thermodynamic studies were also done to estimate the adsorption process is an exothermic or an endothermic process.

EXPERIMENTAL

Preparation of metal ions solution

The salts such as $ZnSO_4 \cdot 7H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were supplied by Merck Chemicals, India. All the chemicals were of analytical reagent grade. The stock solutions of Zn(II) and Ni(II) ions were prepared by dissolving a measured quantity of $ZnSO_4 \cdot 7H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ salts in double distilled water, respectively. The concentration of Zn(II) and Ni(II) ions in the solution were determined by atomic absorption spectrometer (AAS, SL176 Model, Elico Limited, Chennai, India). The adsorption experimental test solutions were prepared by using appropriate subsequent dilutions of prepared

stock solution. The pH of the test solution was adjusted to the required value with 0.1 N NaOH or 0.1 N HCl. The pH of test solution before and after the adsorption experiments were measured by using pH meter (Elico Model, India).

Preparation of adsorbent

The dicarboxylic acid monomer 2-(p-chlorobenzalimino terephthalic acid) which contains an azomethine group was prepared by condensing 0.01 mol of 4-chlorobenzaldehyde and 0.01 mol of 2-aminoterephthalic acid in 50 mL of DMF with pyridine (as a catalyst) and heated to a temperature of 110°C for about 4 h. The resultant yellow product such as dicarboxylic acid monomer was filtered, dried and then recrystallised. Polyamide was prepared by using N-methylpyrrolidine as a solvent, and triphenylphosphite and calcium chloride as condensing agents. The prepared dicarboxylic acid monomer and 4,4'bis(thiourea)biphenylether were taken in equimolar amounts along with the triphenylphosphite, pyridine, and hydrochloric acid. The reagents were stirred at a temperature of 140°C in N-methylpyrrolidine for about 6 h. After that the reaction mixture was cooled to a room temperature and this was poured into ethanol to precipitate the polymer. The precipitated polymer was filtered, and washed with dilute sodium carbonate followed by dilute hydrochloric acid to remove the unreacted monomer. This was then washed with water, ethanol, and dried in a vacuum pump. The prepared resin was named as poly(azomethinethioamide) and this resin was abbreviated as PATA. The synthesis reaction scheme of PATA resin and the characterization reports were discussed in our previous research work[27].

Adsorption studies

Process parameter optimization

All the adsorption experiments were carried out in a temperature controlled incubation shaker by mixing accurately calculated amounts of PATA resin with metal ions solution of specific concentrations in series of 100 mL conical flasks to optimize the process parameters which affects the adsorption process such as solution pH, adsorbent dose, contact time, initial metal ions concentration and temperature. The agitation speed of the incubation shaker was set at 180 rpm. The adsorption mixtures were kept and operated at an equilibrium conditions in an incubation shaker. When the adsorption system reached equilibrium, the adsorption mixtures were separated by using centrifugation operation. The supernatant was analysed by using AAS to measure the final concentration of the metal ions in the solution. The percentage removal of metal ions was calculated by using the following equation.

$$\%\,\text{Removal of metal ions} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \tag{1}$$

where C_o (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of metal ions in the solution, respectively.

Adsorption studies on kinetics and mechanism

The removal of metal ions [Zn(II) and Ni(II)] from the aqueous solution by PATA resin was carried out by adding 0.2 g of PATA resin in a series of 100 mL conical flasks which consists of 100 mL of different metal ions concentration ranging from 50 mg/L to 250 mg/L. The adsorption mixtures in conical flasks were placed in an incubation shaker and the agitation speed was set at 180 rpm. The sampling was carried out at specified times (5, 10, 15, 20, 25, 30, 40, 50 and 60 min) and the adsorption mixtures were collected and centrifuged. The supernatant was analyzed by using AAS. From the results, the adsorption capacity (q_t) at time t and the equilibrium adsorption capacity (q_e) were calculated by using the following equation.

$$q_t = \frac{(C_o - C_t)V}{m} \tag{2}$$

$$q_e = \frac{(C_o - C_e)V}{m} \tag{3}$$

where, q_t is the adsorption capacity at time t (mg/g), C_t is the concentration of metal ions in the solution at time t (mg/L), C_e is the concentration of metal ions in the solution at equilibrium time (mg/L), V is the volume of metal ions solution (L) and m is the mass of the adsorbent (g).

The adsorption process was characterized by fitting the pseudo-first order and pseudo-second order kinetic models to the adsorption experimental data. The pseudo--first order kinetic model[28] is represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

where q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at any time t (mg/g), k_1 is the pseudo-first order rate constant (min^{-1}) and t is the time (min). The pseudo-second order kinetic model[29] is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

where k_2 is the pseudo-second order rate constant (g/mg · min) and $k_2 \cdot q_e^2 = h$, is the initial adsorption rate (mg/g · min).

The mechanism for the removal of metal ions from the aqueous solution by the adsorbent was described by the different models such as intraparticle diffusion[30], Boyd kinetic[31] and shrinking core models[32–34] to fit the adsorption kinetic data. The Weber and Morris intraparticle diffusion model is represented as:

$$q_t = k_p t^{1/2} + C \tag{6}$$

where q_t is the adsorption capacity at any time t (mg/g), k_p is the intraparticle diffusion constant (mg/g · $min^{0.5}$), t is the time (min), C is a constant related to the thickness of the boundary layer (mg/g) and r is the radius of the adsorbent. The Boyd kinetic model is represented as:

$$-0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) = Bt \tag{7}$$

The effective diffusivity, D_i (m^2/s) values were determined by using the following equation:

$$B = \frac{\pi^2 D_i}{r^2} \tag{8}$$

where B is the slope the Boyd kinetic plot. The shrinking core model (SCM) was successfully employed to fluid--particle chemical reactions by Levenspiel[32]. For film diffusion control, the model equation is represented as:

$$X = \frac{3D}{\delta\, r\, C}\alpha \tag{9}$$

where δ is the fluid film thickness. If the film diffusion is controlled in the removals of metal ions by adsorbent then the plot of X versus α yield a straight-line. For particle diffusion control, the model equation is represented as:

$$F(X) = 1 - 3(1-X)^{\frac{2}{3}} + 2(1-X) = \frac{6D}{r^2 C^o}\alpha \tag{10}$$

If the particle diffusion is controlled in the removal of metal ions by the adsorbent then the plot of F(X) versus α give a straight-line. The diffusivity values can be determined from the slope of the plots.

$$D = (\text{Slope})\frac{C^o r^2}{6} \tag{11}$$

Where

$$X \text{ is the extent of reaction} = \frac{(C_o - C)}{(C_o - C_{eq})} \tag{12}$$

$$\alpha = \int_0^t C\, dt \tag{13}$$

where C_o is the initial concentration of metal ions in the solution (mg/L), C^o is the average metal ions binding site density of the adsorbent (mg/L), C is the final metal ions concentration (mg/L), C_{eq} is the equilibrium concentration of metal ions (mg/L), D is the diffusion coefficient (m^2/s) and r is the radius of the adsorbent particles (m).

Adsorption equilibrium studies

Adsorption equilibrium studies were conducted by adding 0.2 g of adsorbent dose into the series of 100 mL of known metal ion concentration (50–250 mg/L) in the conical flasks at an optimum condition. The adsorption mixtures were kept in an incubation shaker at the agitation speed of 180 rpm and the mixtures were shaken till its equilibrium time. After that the mixtures were separated by centrifugation operation and the concentration of metal ions in the supernatant was analyzed by AAS. The adsorption equilibrium data were fitted to the different adsorption isotherm models such as Langmuir[35], Freundlich[36], Temkin[37] and Dubinin-Radushkevich[38] models to explain the adsorption process. The Langmuir adsorption isotherm model is represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{14}$$

where q_e is the equilibrium adsorption capacity (mg/g), q_m is the maximum monolayer adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir constant related to the affinity of the metal ions to the adsorbent (L/mg) and C_e is the equilibrium concentration of metal ions in the solution (mg/L). The adsorption equilibrium parameter is represented as:

$$R_L = \frac{1}{1 + K_L C_o} \tag{15}$$

The Freundlich adsorption isotherm model is represented as:

$$q_e = K_F C_e^{1/n} \tag{16}$$

where K_F is the constant [(mg/g)(L/mg)$^{(1/n)}$] related to the adsorption capacity of the adsorbent and n is the constant related to the intensity of the adsorption (g/L).

The Temkin adsorption isotherm model is represented as:

$$q_e = B_T \ln (A\, C_e) \tag{17}$$

where B_T = RT/b, is the constant related to the heat of adsorption, b is the heat of adsorption (kJ/mol), R is the gas constant (8.314 J/mol · K), T is the temperature (K) and A is the adsorption equilibrium binding constant related to the maximum binding energy (L/mg).

The Dubinin-Radushkevich adsorption isotherm model is represented as:

$$q_e = q_{m,D} \exp\left(-\beta\left(RT \ln\left(1 + 1/C_e\right)^2\right)\right) \tag{18}$$

where $q_{m,D}$ is the Dubinin-Radushkevich monolayer adsorption capacity (mg/g) and β is a constant related to adsorption energy.

The mean free energy, E is represented as:

$$E = \frac{1}{\sqrt{2\beta}} \tag{19}$$

The best fitting of the model to the adsorption equilibrium data was compared by the best coefficient of correlation (R^2) values and the less error values (SSE, sum of squared error and RMSE, root mean squared error).

Adsorption thermodynamic studies

Adsorption thermodynamic studies were conducted by adding 0.2 g of adsorbent dose in a series of 100 mL of known metal ion concentration (50–250 mg/L) in the conical flasks at an optimum condition. The adsorption mixtures were placed in an incubation shaker and this adsorption system was operated at different temperatures (303 K to 333 K) and at the agitation speed of 180 rpm. The adsorption mixtures were operated till its equilibrium time in an incubation shaker. After that the adsorption mixtures were separated by centrifugation operation and the concentration of metal ions in the supernatant was analyzed by the AAS.

The thermodynamic parameters such as change in free energy (ΔG^o), change in enthalpy (ΔH^o) and change in entropy (ΔS^o) were estimated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{20}$$

$$\Delta G^o = -RT \ln K_c \tag{21}$$

$$\log\left(\frac{C_{Ae}}{C_e}\right) = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \tag{22}$$

where K_c is the adsorption equilibrium constant, C_{Ae} is the amount of metal ions adsorbed onto the adsorbent per liter of solution at an equilibrium (mg/L), C_e is the concentration of metal ions in the solution at an equilibrium (mg/L), R is the gas constant (8.314 J/mol · K) and T is the temperature (K).

RESULTS AND DISCUSSION

Estimation of optimum parameters

Figure 1(a) shows the effect of pH on the removal of metal ions from the aqueous solution by the PATA. The contact time and agitation speed are properly set at 30 min and 180 rpm, respectively, for the initial metal ion concentration of 100 mg/L at an adsorbent dose of 0.2 g and at the temperature of 30°C. The adsorption experiments were carried out in the initial pH range of 2.0–6.0 to avoid the formation of metal hydroxide at pH>6.0. At very low pH, the removal of metal ions is very low as the number of hydronium ions is high in the solution and the metal ions has to compete with the hydronium ions for the active sites of the adsorbent. Point of zero charge (pH_{pzc}) is the pH at which the surface charge of the adsorbent becomes neutral. At pH>pH_{pzc}, the negative charge density on the adsorbent surface gets increased and hence the cation adsorption capacity of the adsorbent gets increased[39–40]. The pH_{pzc} of the PATA was found to be 4.5. The pH_{pzc} of the adsorbent was estimated by mass titration method suggested by Noh and Schwas[41]. The adsorption of metal cation was preferred when the solution pH is higher than the pH_{pzc} of the adsorbent. This may be due to that the surface of the adsorbent is positively charged when the solution pH is less than the pH_{pzc}. It was indicated that the removal of metal ions was increased with the increase in solution pH above the pH_{pzc} because the metal ions are cationic in nature. It was also found that the metal ions gets precipitated when the solution pH was increased above 6.0. Based on the results, it was observed that the pH of 6.0 is an optimum pH for the present adsorption system.

Figure 1(b) shows the effect of adsorbent dose on the removal of metal ions by the PATA. The contact time and agitation speed are properly set at 30 min and 180 rpm, respectively, for the initial metal ion concentration of 100 mg/L at a pH of 6.0 and at the temperature of 30°C. It was observed that the removal of metal ions

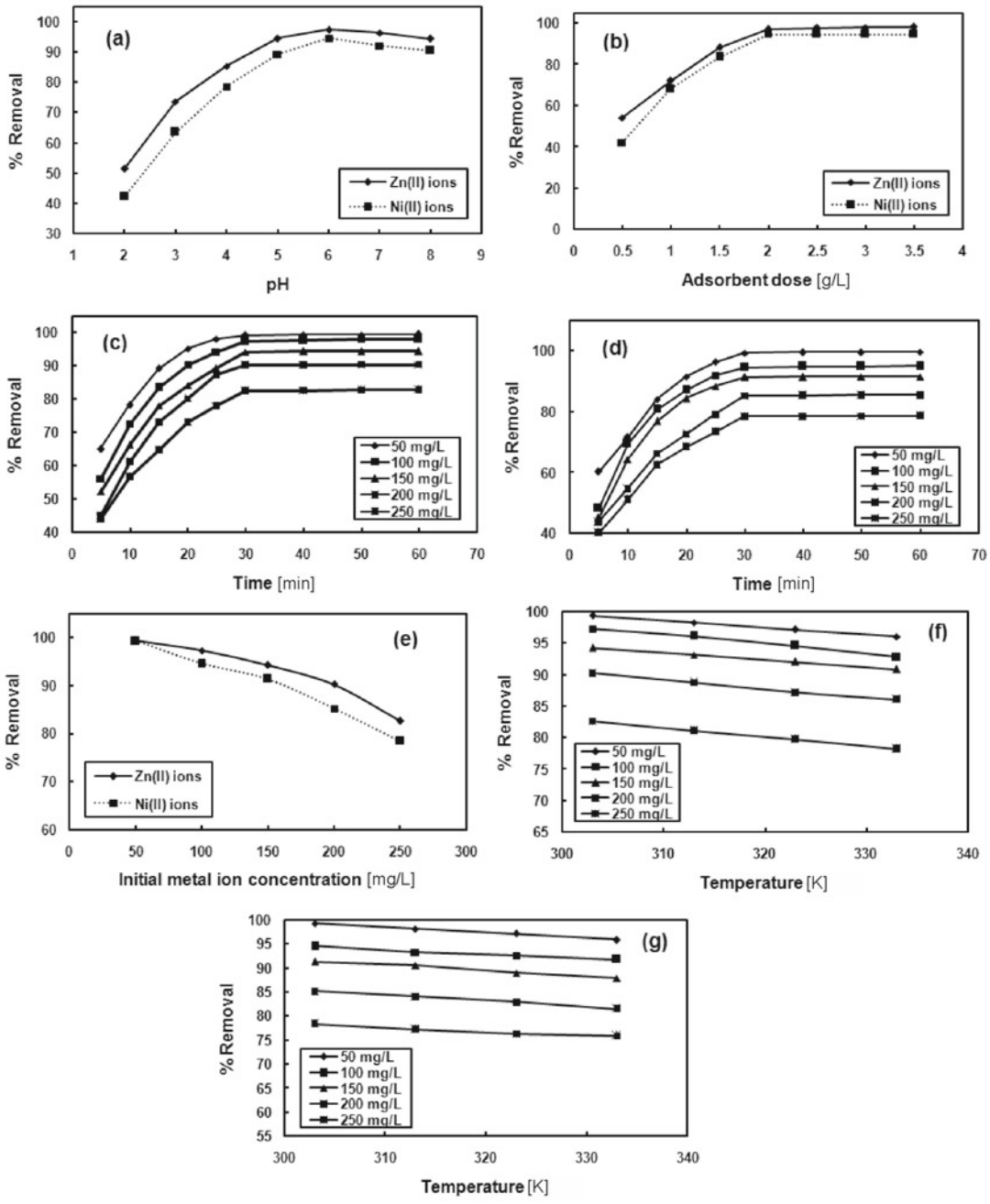

Figure 1. Effect of operating parameters on the adsorption of heavy metals onto PATA

was increased with the increase in adsorbent dose. This may be due to the increase in the availability of more adsorption sites for the adsorption process because of the increase in the adsorbent amount. The maximum removal of metal ions was observed at an adsorbent dose of 2.0 g/L. After the dose of 2.0 g/L, the removal of metal ions was measured as constant, because, at the higher dosage of the adsorbent the ratio of metal ions to the adsorbent sites gets decreased. The optimum dose of adsorbent for the present adsorption system was found to be of 2.0 g/L.

Figure 1(c) and (d) shows the effect of contact time on the removal of Zn(II) and Ni(II) ions by the PATA, respectively. The agitation speed and temperature are properly set at 180 rpm and 30°C, respectively, for the initial metal ion concentration of 50–250 mg/L, at an adsorbent dose of 2.0 g/L and at a pH of 6.0. It can be seen that the removal of metal ions was increased with the increase in contact time and the adsorption system was reached the equilibrium time of 30 min. At very less contact time, the less removal of metal ions was observed and this may be due to less residential time between the adsorbent and the metal ions and vice versa.

Figure 1(e) shows the effect of initial metal ion concentration on the removal of metal ions by the PATA. The agitation speed, contact time and temperature are properly set at 180 rpm, 30 min and 30°C, respectively, for the initial metal ion concentration of 50–250 mg/L, at an adsorbent dose of 2.0 g/L and at a pH of 6.0. From the Figure 1(e), it was observed that the removal of metal ions was decreased with increase in initial metal ion concentration. At lower metal ion concentration, most of the metal ions in the solution may be adsorbed onto the adsorbent surface and which facilitated the complete adsorption of metal ions. At higher metal ion concentration, more metal ions are left unadsorbed in the solution which may be due to the saturation of available adsorption sites.

Figure 1(f) and (g) shows the effect of temperature on the removal of Zn(II) and Ni(II) ions by the PATA, respectively. The agitation speed and contact time are properly set at 180 rpm and 30 min, respectively, for the initial metal ion concentration of 50–250 mg/L, at an adsorbent dose of 2.0 g/L and at a pH of 6.0. The results show that the removal of metal ions was decreased with increase in temperature which indicates the present adsorption process is an exothermic. The reason may be due to the weakening of the adsorptive forces between the adsorbent surface and the metal ions and also between the adjacent metal ions of the adsorbed metal ions on the adsorbent surface. The maximum removal of metal ions was observed at a temperature of 30°C.

The optimum condition for the present adsorption system was found to be: pH of 6.0, adsorbent dose of 2.0 g/L, contact time of 30 min, temperature of 30°C for the initial metal ion concentration of 50–250 mg/L.

Estimation of kinetic and mechanism parameters

The adsorption kinetic data were fitted with pseudo-first order and pseudo-second order kinetic models and these results were shown in Figure 2(a)–(d). From the slope and intercept of the plots of kinetic data fitted pseudo--first order and pseudo-second order kinetic models, the values of k_1, k_2, h, q_e,exp, q_e,cal and R^2 were estimated and these values were listed in Table 1. A linear relationship with high R^2 values was observed, illustrating that the adsorption kinetic data were well fitted with the pseudo-second order model than the pseudo-first order

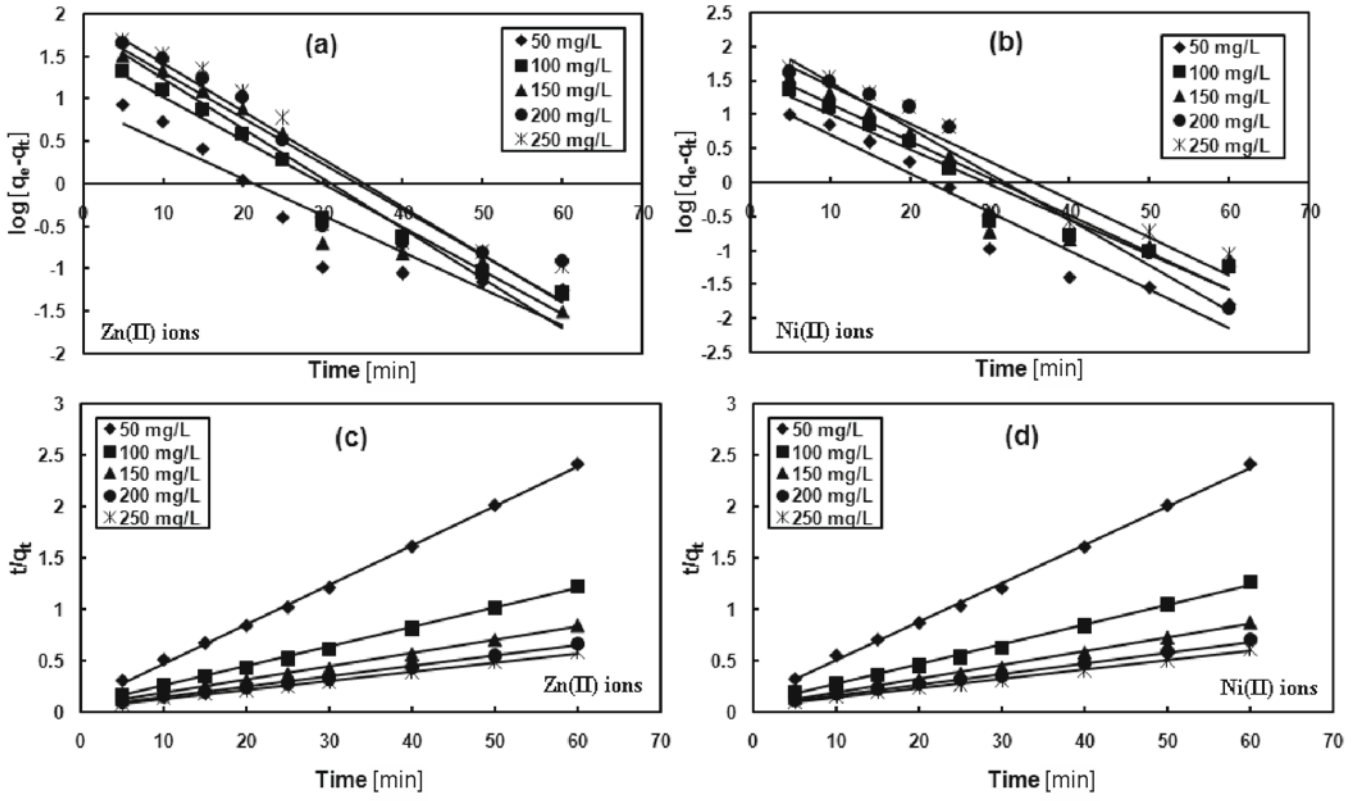

Figure 2. Kinetic plots for the adsorption of heavy metals onto PATA (Initial metal ions concentration = 50–250 mg/L, pH = 6.0, adsorbent dose = 0.2 g, volume of sample = 100 mL and temperature 30°C)

model. And also, the q_e,cal values for pseudo-second order model closely approaching the q_e,exp values. This also further confirms that the pseudo-second order model provides the best fits to the adsorption kinetic data.

It is essential to calculate the rate controlling step in the adsorption process to elucidate the adsorption mechanism. For a solid – liquid adsorption process, the solute transfer is characterized by either external mass transfer (external diffusion) or internal mass transfer (internal diffusion or intraparticle diffusion or particle diffusion) or both. The rate controlling step in the adsorption process was estimated by fitting the adsorption kinetic data to the different models such as intraparticle diffusion, Boyd kinetic and shrinking core models.

The diffusion of the metal ions from the solid – liquid interface to the interior part of the solid particles plays an important role in the adsorption of metal ions. The adsorption kinetic data for Zn(II) and Ni(II) ions removal by the PATA were fitted to the intraparticle diffusion model and the results were shown in Figure 3(a) and (b), respectively. If the adsorption of metal ions onto the PATA was controlled by the intraparticle diffusion then the plot of q_t versus $t^{1/2}$ should be a straight line that must be passes through the origin and also the line should covers almost all the experimental data points. But for the present adsorption system, the line is not covered all the points and also the line is not passes through the origin. This indicates that the intrapartic-

Table 1. Kinetic parameters, equilibrium adsorption capacities and coefficient of determination values for the adsorption of metal ions onto PATA

Heavy metals	Co [mg/L]	Kinetic models							
		Pseudo-first order model			Pseudo-second order model				
		k_1 [min^{-1}]	$q_{e,}$ cal [mg/g]	R^2	k_2 [g $mg^{-1}min^{-1}$]	q_e ,cal [mg/g]	h [mg $g^{-1}min^{-1}$]	$q_{e,}$exp [mg/g]	R^2
Zn(II)	50	0.099	8.336	0.866	0.0150	26.246	10.395	24.925	0.9988
	100	0.115	33.728	0.964	0.0050	52.910	14.064	49.031	0.9985
	150	0.133	66.988	0.915	0.0028	77.519	17.035	70.914	0.9978
	200	0.122	71.400	0.886	0.0019	100	19.230	90.542	0.9962
	250	0.126	93.067	0.887	0.0016	114.942	22.123	103.556	0.9968
Ni(II)	50	0.131	19.081	0.933	0.0098	26.881	7.137	24.911	0.998
	100	0.117	32.218	0.932	0.0044	51.813	12.033	47.522	0.9972
	150	0.125	48.752	0.887	0.0028	75.757	16.207	68.689	0.9964
	200	0.154	140.08	0.943	0.0017	96.153	15.723	85.504	0.9959
	250	0.128	96.805	0.901	0.0016	109.890	19.342	98.324	0.9964

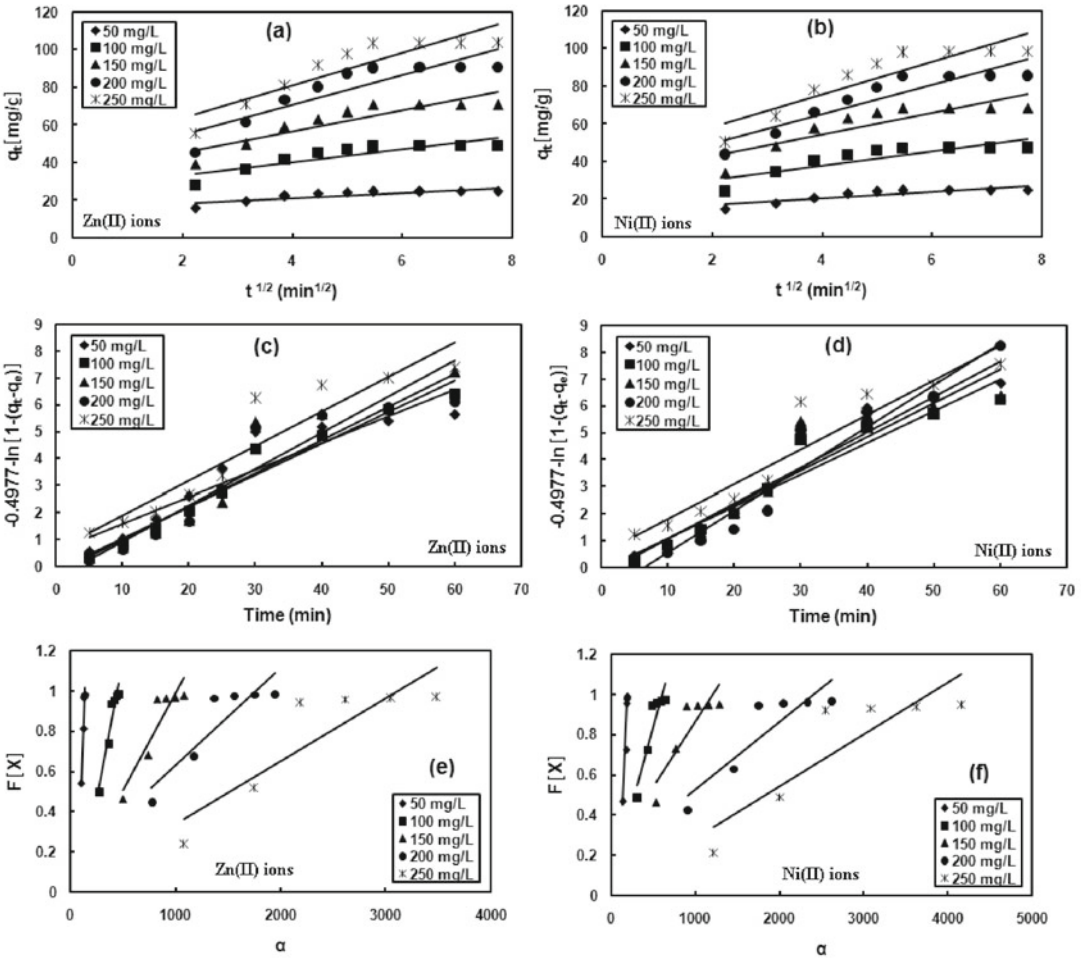

Figure 3. Mechanism for the adsorption of heavy metals onto PATA (Initial metal ions concentration = 50–250 mg/L, pH = 6.0, adsorbent dose = 0.2 g, volume of sample = 100 mL and temperature 30°C)

Table 2. Mechanism parameters and coefficient of determination values for the adsorption of metal ions onto PATA

Heavy metals	Co [mg/L]	Intraparticle diffusion model			Boyd kinetic model			Shrinking core model	
		k_p [mg/g · min$^{1/2}$]	C [mg/g]	R^2	B	D_i [x 10^{-11} m^2/s]	R^2	D [x 10^{-9}m^2/s]	R^2
Zn(II)	50	1.422	15.71	0.724	0.099	2.108	0.867	0.129	0.950
	100	3.5069	26.085	0.771	0.117	2.481	0.965	5.409	0.935
	150	5.5663	34.271	0.808	0.135	2.865	0.915	2.763	0.847
	200	7.8595	39.11	0.787	0.124	2.625	0.886	1.753	0.814
	250	8.693	46.154	0.821	0.129	2.731	0.887	1.205	0.783
Ni(II)	50	1.756	13.409	0.789	0.132	2.789	0.933	9.588	0.883
	100	3.779	22.969	0.742	0.118	2.502	0.932	2.801	0.855
	150	5.735	31.494	0.745	0.125	2.653	0.887	1.615	0.777
	200	7.737	34.105	0.842	0.155	3.287	0.943	0.981	0.804
	250	8.687	40.897	0.822	0.129	2.729	0.901	1.134	0.777

le diffusion may not be the rate controlling factor in determining the adsorption process because there is a boundary layer resistance. The intraparticle diffusion rate constant, k_p and the boundary layer thickness, C values were calculated from the slope and intercept of the plots of q_t versus $t^{1/2}$ (Fig. 3(a) and (b)) and these values were listed in Table 2. The dual nature of the plots was observed in the Figure 3(a) and (b). From the figure, it was observed that the first linear portion of the plot was due to the external diffusion (or film diffusion) and the second linear portion of the plot was due to the internal diffusion (or intraparticle diffusion).

The diffusion of metal ions from the bulk liquid phase to the surface of an adsorbent might also play an important role in estimating the rate controlling steps in the adsorption of metal ions onto the adsorbent. The actual slowest in this adsorption process was further discussed by Boyd kinetic model. The adsorption kinetic data for Zn(II) and Ni(II) ions were applied to the Boyd kinetic model and the results were shown in Figure 3(c) and (d), respectively. From the fitted Boyd kinetic plots, it was observed that the plots are linear but the lines are not passes through the origin. This gives an idea about the adsorption process may be controlled by external diffusion or internal diffusion. The effective diffusivity values (D_i) were estimated and the values were listed in Table 2.

The influence of particle diffusion in the adsorption of Zn(II) and Ni(II) ions onto the PATA was further analyzed by fitting the adsorption experimental data to the shrinking core model and the results were shown in Figure 3(e) and (f), respectively. It can be seen that the particle diffusion may also influence in the removal of metal ions by the PATA. The diffusivity (D) values were estimated and are listed in Table 2. Based on the adsorption mechanism results, it can be concluded that both external and internal diffusion may be controlling the adsorption process.

Estimation of adsorption isotherm parameters

Adsorption isotherms are the basic needs to design the adsorption system. The distribution of adsorbate between the liquid phase and the solid phase is a measure of the position of the equilibrium in the adsorption process and that can be commonly expressed by one or more adsorption isotherm models. The adsorption isotherm data for Zn(II) ions and Ni(II) ions were applied to the different adsorption isotherm models such as Langmuir[35], Freundlich[36], Temkin[37] and Dubinin-Radushkevich[38] by using MATLAB R2009a and the results are shown in Figure 4 (a) and (b), respectively. The adsorption isotherm parameters (q_m, K_L, K_F, n, B, A, $q_{m,D}$ and β), coefficient of correlation (R^2) values and the error values (SSE and RMSE) were listed in Table 3. The results

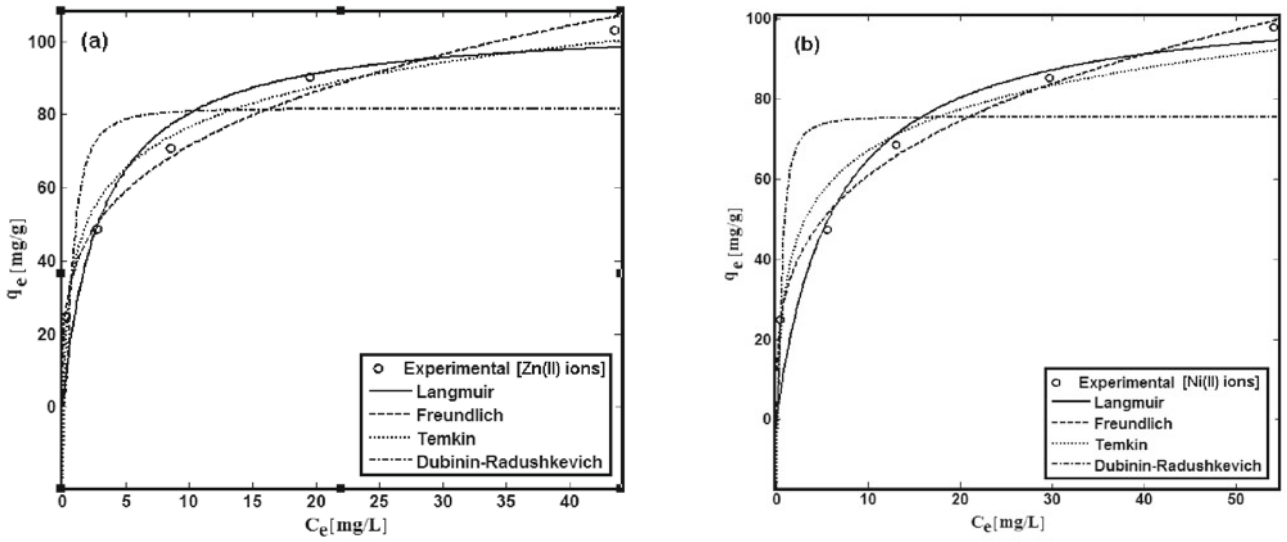

Figure 4. Isotherm plots for the adsorption of heavy metals onto PATA (Initial metal ions concentration = 50–250 mg/L, pH = 6.0, adsorbent dose = 0.2 g, volume of sample = 100 mL, equilibrium time = 30 min and temperature 30°C)

Table 3. Isotherm parameters, coefficient of determination values and error values for the adsorption of metal ions onto PATA

Isotherm Model	Parameters	Heavy metals	
		Zn(II)	Ni(II)
Langmuir	q_m [mg/g]	105.4	97.3
	K_L [L/mg]	0.3218	0.1608
	R^2	0.9206	0.8914
	SSE	315.7	373.4
	RMSE	10.26	11.16
Freundlich	K_F [[mg/g][L/mg] $^{(1/n)}$]]	38.13	31.26
	n [g/L]	3.664	3.449
	R^2	0.9887	0.9916
	SSE	44.82	28.93
	RMSE	3.865	3.106
Temkin	A [L/mg]	12	9.426
	B_T	6.948	6.413
	b [kJ/mol]	0.363	0.393
	R^2	0.9744	0.9426
	SSE	101.9	197.3
	RMSE	5.829	8.11
Dubinin-Raduskevich	$q_{m,D}$ [mg/g]	81.72	75.54
	β	3.345×10^{-8}	2.201×10^{-8}
	R^2	0.6074	0.6038
	SSE	1561	1362
	RMSE	22.81	21.31

from Table 3 show that Freundlich equation is valid for multilayer adsorption onto a completely heterogeneous surface. The results indicated that the Freundlich model was the best option among the other adsorption isotherm models to describe the adsorption behaviour of metal ions onto the PATA. The importance of the n value is given as follows: n = 1 (linear); n < 1 (chemical process); n > 1 (physical process). From the Table 3, it was found that the value of n lie between 1 and 10, indicates that the adsorption was a physical process[42]. The maximum monolayer adsorption capacity (q_{max}) of the adsorbent for Zn(II) and Ni(II) ions were found to be 105.4 and 97.3 mg/g, respectively. The importance of the R_L value is given as follows: $R_L = 0$ (irreversible); $0 < R_L < 1$ (favorable); $R_L = 1$ (linear); $R_L > 1$ (unfavourable). The R_L value for the adsorption of Zn(II) and Ni(II) ions onto the PATA were in the range of 0–1 which indicate that the adsorption process was favourable[43]. The value of heat of adsorption (b) for the adsorption of metal ions onto the PATA was calculated to be less than 8 kJ/mol. This may be due to the weak interaction between the metal ions and the PATA. The results indicate the adsorption process was a physical process[44]. The importance of mean free energy (E) value is given as follows: E < 8 kJ/mol (physical adsorption)[45], 8 < E < 16 kJ/mol (ion-exchange)[46] and 20 < E < 40 kJ/mol (chemisorption)[45]. The calculated E value for the adsorption of metal ions onto the PATA was found to be less than 8 kJ/mol. This indicates the adsorption of metal ions onto the PATA followed physical adsorption[45].

Estimation of thermodynamic parameters

The thermodynamic parameters such as standard free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) have been estimated to evaluate the feasibility of the adsorption process. The adsorption thermodynamic data for Zn(II) and Ni(II) ions removal by PATA were fitted to the thermodynamic equations and the results were shown in Figure 5(a) and (b), respectively. The thermodynamic parameters were calculated from the slope and intercept of the plot of log Kc versus 1/T and the values are listed in Table 4. The negative value of ΔG^o indicates the feasibility and spontaneity of the adsorption process. From Table 4, it was observed that the decrease in the negative value of ΔG^o with the increase in the temperature indicates the adsorption process was more favorable at lower temperatures. The negative values of ΔH^o indicate the exothermic nature of the adsorption process and the negative values of ΔS^o indicate the randomness in the system interface solid/solution during the adsorption process.

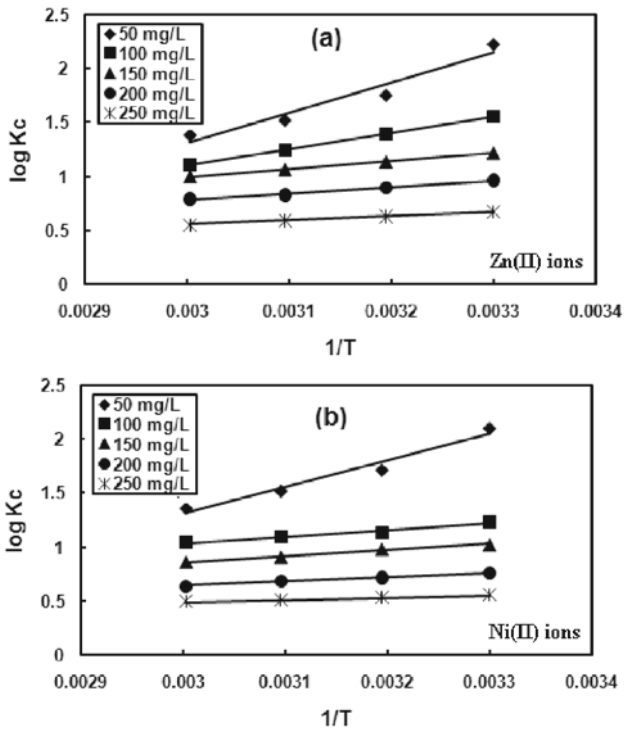

Figure 5. Thermodynamic plots for the adsorption of metal ions onto PATA (Initial metal ions concentration = 50–250 mg/L, pH = 6.0, adsorbent dose = 0.2 g, volume of sample = 100 mL and equilibrium time = 30 min)

Table 4. Thermodynamic parameters for the adsorption of metal ions onto PATA

Heavy metals	Co [mg/L]	ΔH° [kJ/mol]	ΔS° [J/mol · K]	ΔG° [kJ/mol]			
				30°C	40°C	50°C	60°C
Zn(II)	50	– 53.353	–134.958	–12.915	–10.528	–9.438	–8.857
	100	–28.697	–65.002	–9.011	–8.346	–7.679	–7.069
	150	–14.042	–23.076	–7.059	–6.804	–6.584	–6.365
	200	–11.382	–19.162	–5.597	–5.375	–5.141	–5.042
	250	–7.652	–12.313	–3.920	–3.792	–3.686	–3.545
Ni(II)	50	–47.071	–116.104	–12.207	–10.292	–9.419	–8.679
	100	–11.802	–15.526	–7.174	–6.821	–6.781	–6.680
	150	–10.856	–16.123	–5.935	–5.881	–5.609	–5.485
	200	–7.416	–9.895	–4.405	–4.329	–4.243	–4.102
	250	–4.051	–2.728	–3.244	–3.181	–3.135	–3.173
Heavy metal ions			Co (mg/L)	Kc values			
Zn(II)			50	168.491	57.139	33.602	24.510
			100	35.764	24.706	17.450	12.850
			150	16.482	13.662	11.610	9.964
			200	9.224	7.888	6.782	6.178
			250	4.740	4.293	3.945	3.597
Ni(II)			50	127.205	52.191	33.364	22.980
			100	17.248	13.749	12.495	11.165
			150	10.547	9.582	8.074	7.250
			200	5.747	5.277	4.854	4.399
			250	3.625	3.395	3.214	3.145

CONCLUSION

In the present study, the PATA as a new novel adsorbent was successfully applied for the removal of metal ions such as Zn(II) and Ni(II) ions from the aqueous solutions. The adsorption of metal ions onto the PATA was found to be influenced by several operating parameters such as solution pH, PATA dose, contact time, initial metal ion concentration, and temperature. Of all these factors, the removal of metal ions by PATA was highly dependent on pH of the solution. The removal of metal ions was increased with increase in pH and it was reduced after the system was attained the optimum pH of 6.0 due to the formation of metal hydroxides at a higher pH. The removal of metal ions by PATA was found to be increased with increase in PATA dose and it was decreased with the increase in initial metal ion concentration. With regard to contact time, the removal of metal ions was increased up to the contact time of 30 minutes and remained almost constant for further increase in time. The optimized condition for the maximum removal of metal ions was found to be: pH of 6.0, contact time of 30 min; PATA dose of 2.0 g/L and temperature of 30°C. The adsorption kinetic data was well described by the pseudo-second order kinetic model. The removal of metal ions by the PATA was controlled by both film and particle diffusion. The adsorption equilibrium data was fitted well with Freundlich model. The adsorption temperature data was applied to the thermodynamic equations and the evaluated parameters indicated that the adsorption process was feasible and exothermic in nature. The overall results reveal that the PATA can be used as an effective adsorbent for the removal of metal ions from the wastewater.

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