An investigation into the sorption of heavy metals from wastewaters by polyacrylamide-grafted iron(III) oxide

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Abstract

An adsorbent for heavy metals was synthesized by introducing carboxylate functional group into polyacrylamide-grafted hydrous iron(III) oxide. The product exhibits a very high adsorption potential for Pb(II), Hg(II) and Cd(II). The removal of metal ions by adsorption on adsorbent has been found to be contact time, concentration, pH and temperature dependent. The process follows first-order reversible kinetics. The intraparticle diffusion of metal ions through pores in the adsorbent was shown to be the main rate-limiting step. The optimum pH range for the removal of metal ions was found to be 5.0–6.0. The thermodynamic parameters such as free energy change, enthalpy change and entropy change have been calculated to predict the nature of adsorption. The adsorption data were fitted using the Langmuir equation and maximum adsorption for each metal was estimated using their respective Langmuir equation constants. The method was applied for synthetic wastewaters. NaCl regeneration has been tried for several cycles with a view to recover the adsorbed metal ions and also to restore the sorbent to its original state. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Effective removal of toxic heavy metals, in connection with wastewater treatment strategy, still remains a major topic of present research. Many methods have been proposed for the removal of heavy metals. Chemical precipitation, membrane filtration, coagulation, complexing, solvent extraction, ion exchange and adsorption are some of the commonly used processes, but each has its own merits and demerits in its application [1]. Adsorption

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or ion exchange using different polymeric materials and synthetic resins is the method of choice in many wastewater treatment process for removing metals from chemical process industries in certain developed countries [2]. Studies have been reported on the use of hydrous metal oxides as adsorbents for the removal of metals from aqueous solutions [3,4]. Surface modification by chemical treatment of the adsorbent materials usually improve the physical characteristics and sorption efficiency of the adsorbents. Silica gel modified with pyridinium ions [5] and clays impregnated with 2-mercaptobenzothiazole [6] have been developed for the adsorption of heavy metals from aqueous solutions. Polymer coated agricultural by products were also used as adsorbents for heavy metals [7,8].

The use of polymer grafted metal oxides for the removal of toxic heavy metals from wastewater has been continued to attract considerable attention in recent years, particularly because they are capable of binding heavy metals by adsorption and ion exchange even at higher temperature [9]. The materials such as chitosan [10], silica gel [11], iron [12] and tin(IV) oxide [13] have already been used as polymer support for the preparation of adsorbent. Carboxylate functional group substituted on the backbone of the polymerized materials increases the number and change the nature of sites capable of adsorbing metals in solutions [14].

The weak carboxylic cation exchanger such as Amberlite IRA-64, Amberlite IRP-88, Amberlite CG-50 and Duolite ES-468 are the better ion exchanger options, most commonly used in many water treatment application. However, these ion exchange resins are relatively expensive (US$ 21–45 per 100 g of resin) and lower cost alternatives have been sought for these materials. Recently, we have developed a weak carboxylic cation exchanger by grafting polyacrylamide on hydrous iron(III) oxide (PGHyFeO–COOH), which may be utilized in removing some water and wastewater cation contaminants. Cost of this material was calculated and found to be US$ 7 per 100 g. The relative cost of this material used in the present study is lower than that of certain commercial resins. The present work explores the possibility of using PGHyFeO–COOH to remove Pb(II), Hg(II) and Cd(II) from water and wastewater by studying its metal removal properties in a series of laboratory experiments. Desorption studies have also been carried out.

2. Materials and methods

2.1. Sorbent preparation

Hydrous iron(III) oxide (HyFeO) was precipitated from a solution of iron(III) chloride (100 ml) by adding concentrated ammonia solution until pH becomes 7.0 [15]. The air dried precipitate was grafted with polyacrylamide using the procedure described by Shigetomi et al. [12] and then functionalised it with carboxylate groups (Scheme1). About 25 g of HyFeO (1) was immersed in 300 ml aqueous solution containing 5 g N,N'-methylenebisacrylamide (2) and 1.5 g potassium peroxydisulphate. Then 17.5 g of acrylamide (3) was added to the reaction mixture. The grafting was performed at $70\,°C$. After the desired reaction time, the polymerized product (4) was taken out and washed thoroughly with water and acetone. The dried mass was refluxed with 25 ml ethylenediamine (en)$_2$ in toluene for 8 h. Then washed with toluene and dried. To functionalise it with carboxylate groups, one part

by weight of the above material was refluxed with equal part by weight of succinic anhydride in 1,4-dioxane at pH 4.0 for 6 h. The excess succinic anhydride was washed out with 1,4-dioxane and finally with ethanol and dried. The carboxylic acid bound polyacrylamide grafted HyFeO (PGHyFeO–COOH) was ground and sieved to average diameter of 0.096 mm. The graft yield was calculated as the percentage increase in weight over the original weight of HyFeO.

2.2. Adsorption experiments

All the experiments for the adsorption were carried out by the following procedure, unless otherwise stated. About 0.1 g of the adsorbent was shaken with 50 ml metal solution (nitrate salt) of varying concentration in different stoppered conical flasks. Initial pH of the solution was adjusted using 0.05 M solution of HNO_3 and NaOH. The contents were continuously agitated in a temperature controlled flask shaker. At the end of pre-determined time intervals, the sorbent was centrifuged and supernatant was analyzed. Lead and cadmium were estimated using atomic absorption spectrophotometer (Perkin-Elmer, 2380 Model). Mercury was determined using mercury analyzer (Perkin-Elmer, MAS-50A). All the chemicals used were of analytical grade and were obtained from BDH, Fluka and Merck.

2.3. Potentiometric titration

About 100 mg of PGHyFeO–COOH was placed in 250 ml conical flask containing 50 ml of double distilled water. The mixture was titrated with standard 0.01 M NaOH. Duration of 30 min after each addition of NaOH equivalent to 0.5 meq./g was allowed before a pH reading was taken. The same procedure was adopted for titration with PGHyFeO–COOH containing different heavy metal cations.
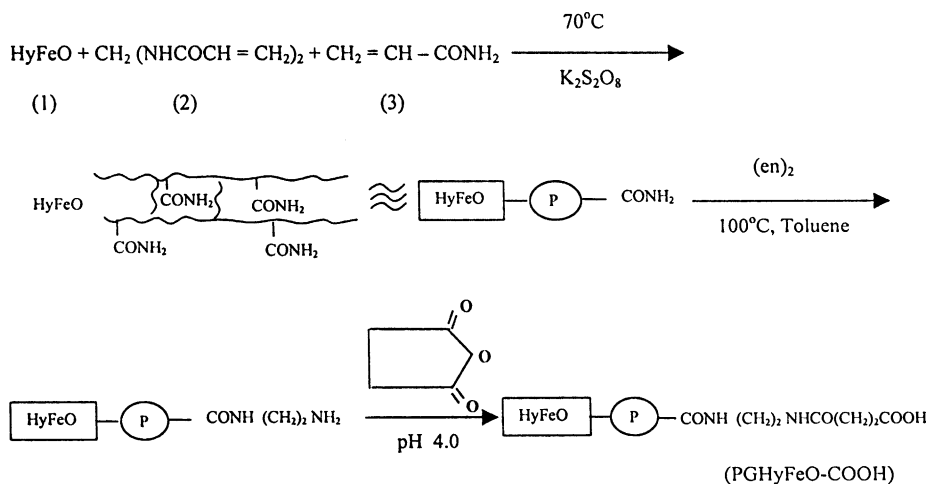
2.4. Desorption experiments

For desorption study, 0.1 g of metal-loaded adsorbent was agitated with 50 ml of 0.2 M HCl or 0.2 M NaCl for 4 h. Then the supernatant was centrifuged and analyzed for metals. The sorbent sample, thus, regenerated and reused for adsorption purpose. The loading and regeneration cycle was repeated three times. After each cycle, the sorbent was washed with distilled water and dried. All the experiments were performed in duplicate and mean values are presented.

3. Results and discussion

3.1. Sorbent characterization

The IR spectra of HyFeO and PGHyFeO–COOH were recorded on a Shimadzu FTIR 1801 spectrophotometer. HyFeO shows a broad absorption band at wave number range 3200–3400 cm^{-1}, which is attributed to the sum of the contribution from water and hydroxyl bonding to iron. The absorption band at 620 cm^{-1} is due to Fe–O-bond. The IR spectrum

$$HyFeO + CH_2(NHCOCH=CH_2)_2 + CH_2=CH-CONH_2 \xrightarrow[\text{K}_2\text{S}_2\text{O}_8]{70^\circ C}$$

$$(1)\qquad\qquad (2)\qquad\qquad\qquad (3)$$

Scheme 1. Preparation of carboxylated polyacrylamide grafted HyFeO.

of PGHyFeO–COOH shows a broad spectrum around $3400\,cm^{-1}$ representing overlap of O–H, C–H, N–H and C–O stretching vibrations. The peaks at 1653 and $1699\,cm^{-1}$ indicate the presence of aliphatic amide (N–H) and methylene (C–H) groups, respectively. The additional peaks at $1734\,cm^{-1}$ ($\nu_{C=O}$) and $1465\,cm^{-1}$ (ν_{C-O}) indicate the presence of COOH group in PGHyFeO–COOH [16]. Based on these results, the structure of PGHyFeO–COOH is represented in Scheme 1. The physical and surface properties of PGHyFeO–COOH were carefully determined by standard methods [7]. The characteristics of the sorbent are: apparent density, $2.26\,g/ml$, moisture content 3.8%, cation exchange capacity $2.16\,meq./g$, surface area $97.16\,m^2/g$, grafting 68.8%, porosity $0.49\,ml/g$ and pH_{ZPC} 5.8.

3.2. pH titration

Fig. 1 shows the potentiometric titration curves for PGHyFeO–COOH with NaOH alone and those in the presence of different metal cations. The starting pH of the titration depresses by the addition of heavy metal cations. This clearly indicates that hydrogen ions are released from the adsorbent. Additionally, the titration curves in the presence of heavy metal cations are shifted to the right, tending to rise more slowly in pH. More OH^- ions are used up in raising the pH of the solution compared with the titrations with NaOH alone. PGHyFeO–COOH is a weak acid cation exchanger having ionogenic –COOH functional groups. The exchange reaction for the system containing NaOH alone can be expressed as:

$$PGHyFeO-COOH + Na^+ \leftrightarrows PGHyFeO-COONa + H^+ \qquad (1)$$
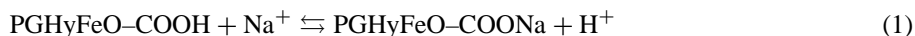
The following exchange reactions are occurred in the presence of divalent cations (M^{2+}).

$$PGHyFeO-COOH + Na^+ \leftrightarrows PGHyFeO-COONa + H^+$$

$$2PGHyFeO-COOH + M^{2+} \leftrightarrows (PGHyFeO-COO)_2M + 2H^+ \qquad (2)$$
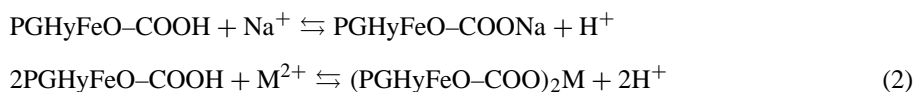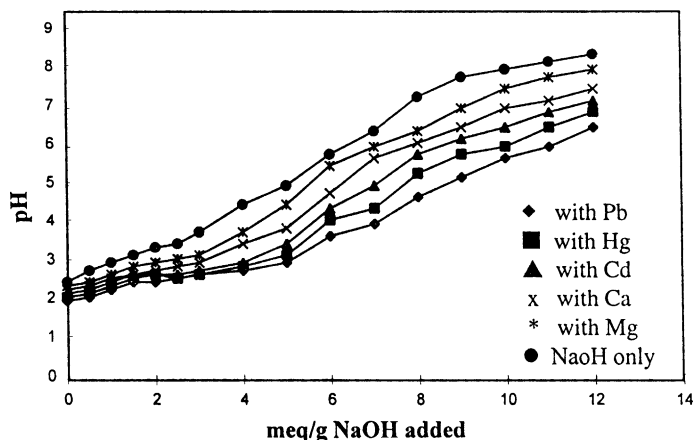
Fig. 1. Potentiometric titration curves of PGHyFeO–COOH.

$$2PGHyFeO–COONa + M^{2+} \leftrightarrows (PGHyFeO–COO)_2M + 2Na^+ \qquad (3)$$

A greater amount of NaOH is required to increase the pH of solutions containing divalent cations compared with that of the titration with NaOH alone. The different divalent cations differ in their ability to replace the hydrogen from the adsorbent. The titration curves in the presence of Pb(II), Hg(II), and Cd(II) are found more to the right of those in the presence of Ca(II) and Mg(II). This indicates that Pb, Hg and Cd are preferred over that of the two other divalent cation. The observed order of uptake for the metal ions is the same (Pb > Hg > Cd > Ca > Mg) as for their increasing stability complexes formed by metal ions with –COOH group in adsorbent and also for their increasing ionic radii [4,17].

3.3. Effect of pH

In order to examine the effect of pH on metal uptake, experiments were conducted using an initial concentration of 50 mg/l (Fig. 2). The percentage removal of metal ions by PGHyFeO–COOH increased with increase in pH upto a certain value and then decreased with further increase in pH. The maximum removal of Pb(II) (95.7%) was observed at an optimum pH of 6.0, whereas, the maximum removal of 84.9% for Hg(II) and 81.0% for Cd(II) was observed at pH 5.0. Below and above this pH, a decreasing trend in removal was observed. The possible sites on PGHyFeO–COOH for specific adsorption in acidic pH includes H^+ ions in –COOH functional groups. Hence, the effect of pH on metal ions can be explained as due to the exchange behavior of H^+ ions from peripheral –COOH groups. The perusal of Pb(II), Hg(II) and Cd(II) speciation diagrams [18–20] clearly indicate that in the range of highest removal efficiency the dominant species were M^{2+} and $M(OH)^+$. It has been shown that final pH is always less than the initial pH. The final pH of the reaction mixture remained between 1.8 and 5.2, during the experiments, when the initial pH of the reaction mixture varied between 2.0 and 6.0. This indicates that as the metal ions are bound on the adsorbent, H^+ ions are released into the solution and it leads to the conclusion that
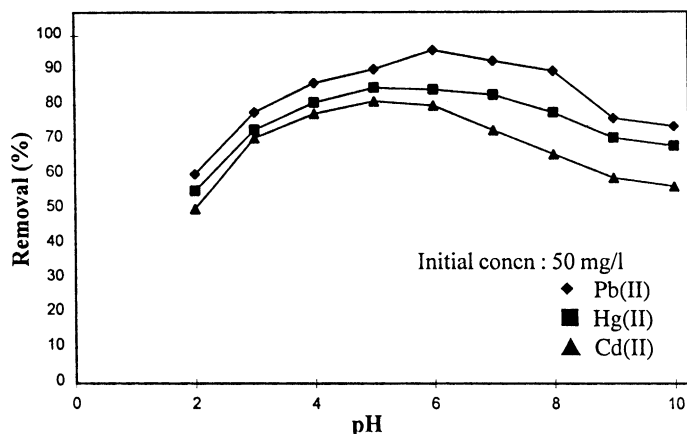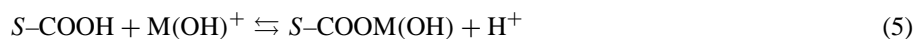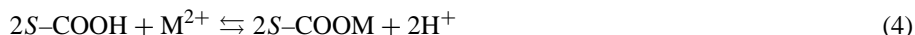
Fig. 2. Effect of pH on the removal of metals by PGHyFeO–COOH.

PGHyFeO–COOH probably act as an acid form ion exchanger. The removal of metal ions by PGHyFeO–COOH may be represented as:

$$2S\text{–COOH} + M^{2+} \leftrightarrows 2S\text{–COOM} + 2H^+ \tag{4}$$

$$S\text{–COOH} + M(OH)^+ \leftrightarrows S\text{–COOM(OH)} + H^+ \tag{5}$$

where S is the polymerized surface.

At very low pH, the competition between M^{2+} and the higher concentration of H^+ ions for sorption sites is in favor of H^+, and as a result, less removal efficiency was observed at low pH. With increase of the pH (up to optimum pH), the enhancement of adsorption is apparently due to the hydrolysis of the exchanging cations, since the hydroxy complex, that is $M(OH)^+$ is sorbed in preference to the uncomplexed cations [21]. The point of zero charge(pH_{ZPC}) for the PGHyFeO–COOH was found to be 5.8, the adsorbent surface is negatively charged and the metal ions are still present as M^{2+} and $M(OH)^+$ ions upto pH 8.0. Under this condition adsorption must be occurring due to electrostatic attraction between positively charged species and negatively charged adsorbent surface. Decrease in the removal of metal ions at higher pH (above pH 8.0) is due to the formation of soluble hydroxy complexes [22].

3.4. Kinetic studies

The important physicochemical parameters that help defining the type of sorption and evaluate the process of sorption are sorption kinetics and sorption equilibria. Adsorption kinetic experiments were carried out using an initial concentration range of 100–400 mg/l for Pb(II) and 50–200 mg/l for Hg(II) and Cd(II). Preliminary investigation on the removal of metal ions with time on PGHyFeO–COOH (at optimum pH) indicated the process of adsorption proceeds quite rapidly and attain equilibrium gradually. This contention can also be supported by comparing the percent removal of metals for the first 30 min of reaction

time with that for the following 240 min. Depending upon variation in initial concentration of metal ions, 64.7–76.1% for Pb(II), 57.3–77.4% for Hg(II) and 56.3–68.3% for Cd(II) was achieved during the first 30 min of reactions time, while only additional removal of 14.6–17.0% Pb(II), 8.9–20.0% Hg(II) and 15.3–17.8% Cd(II) occurred in the following 240 min of reaction time.

The sorption of metal ions from liquid phase to solid phase can be considered as a reversible reaction with an equilibrium being established between two phases. A batch adsorption kinetic model was used to analyze the batch adsorption data in order to obtain estimates for the rate constants. A simple diffusion controlled first-order reversible kinetic model previously developed by Bhattacharya and Venkobachar [23] has been adopted to model metal adsorption onto PGHyFeO–COOH. The simple way to describe the metal removal by adsorbent is:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \tag{6}$$

The rate equation for the above reaction is expressed as:

$$\frac{dC_B}{dt} = \frac{-dC_A}{dt} = k_1(C_{A_0} - C_{A_0}X_A) - k_2(C_{B_0} + C_{A_0}X_A) \tag{7}$$

in which C_B is the concentration of metal ions on the adsorbent and C_A is the concentration of metal ions in solution at any time, C_{B_0} and C_{A_0} are the initial concentrations of heavy metals on adsorbent and solution, respectively. X_A is the fraction of metal adsorbed onto the adsorbent and k_1 and k_2 are the first-order adsorption and desorption rate constants, respectively. At equilibrium conditions:

$$K_c = \frac{k_1}{k_2} = \frac{C_{B_0} + C_{A_0}X_{A_e}}{C_{A_0} - C_{A_0}X_{A_e}} \tag{8}$$

in which X_{A_e} is the fraction of metal adsorbed at equilibrium.

The rate equation in terms of equilibrium conversion can be represented by the following equation [23]:

$$\ln\left(1 - \frac{X_A}{X_{A_e}}\right) = -k't = -(k_1 + k_2)t = -\left(k_1 + \frac{k_1}{K_c}\right)t \tag{9}$$

in which k' is the overall rate constant.

In a rapidly stirred batch reactor, the adsorbate species are most probably transported from the solution to solid phase through intraparticle transport which is often the rate limiting step, in many adsorption processes [24]. When the rate of a reaction is controlled by the intraparticle diffusion process, the kinetics of adsorption are modelized according to the following equation [25,26]:

$$1 - \frac{X_A}{X_{A_e}} = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D_i}{r^2}\right)t \tag{10}$$

in which X_A/X_{A_e} is the fractional attainment of equilibrium, and D_i is the effective diffusion coefficient. The values of D_i were calculated from the slope of the linear plots of ln
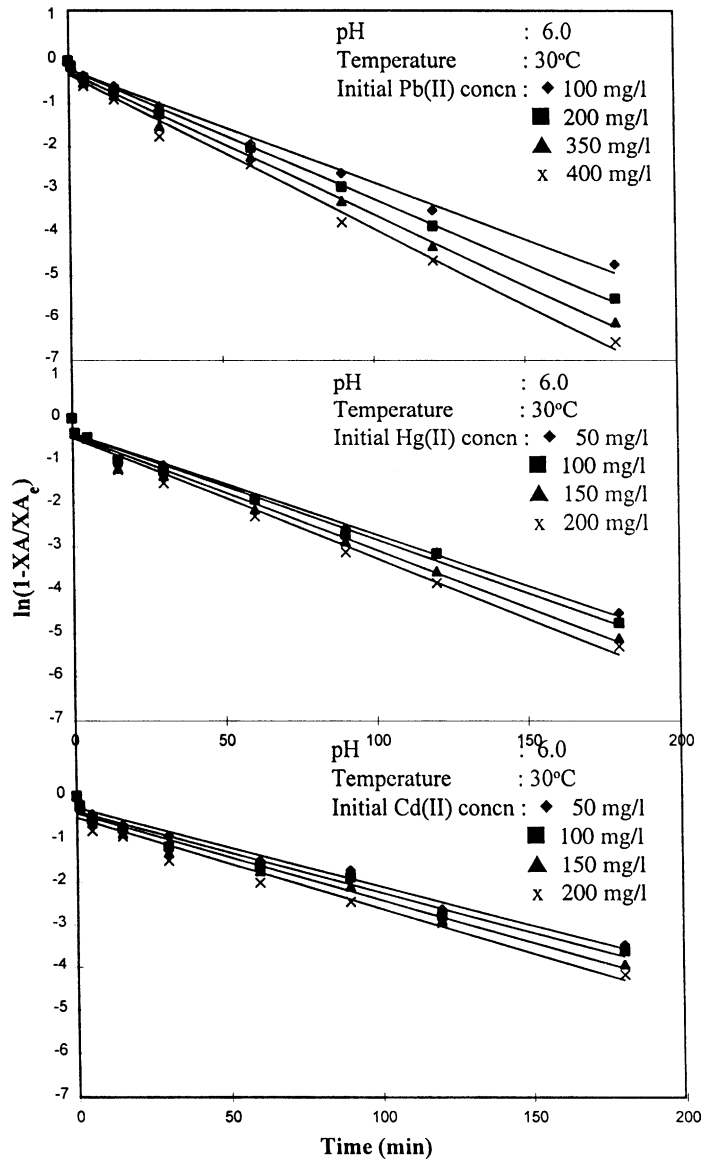
Fig. 3. First-order reversible kinetic fit for metals at different concentrations.

$(1 - X_A/X_{A_e})$ versus t. The slope can be expressed as:

$$k' = \frac{\pi^2 D_i}{r^2} \qquad (11)$$

in which k' is the overall rate constant.
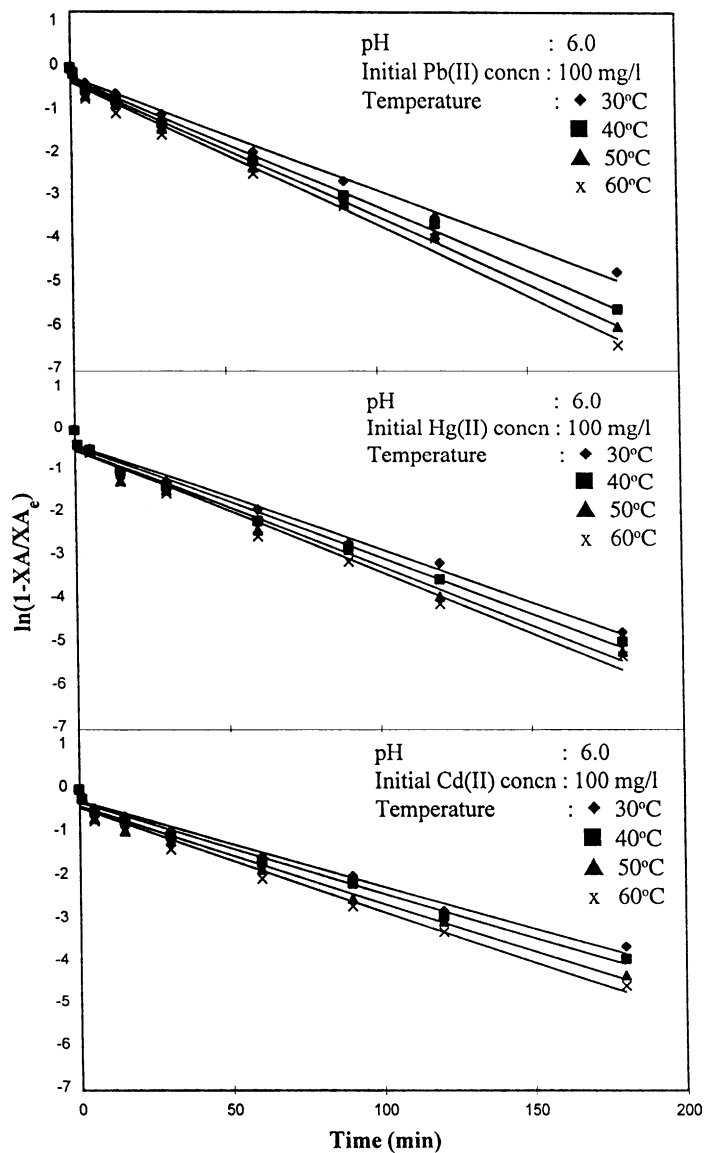
Fig. 4. First-order reversible kinetic fit for metals at different temperatures.

The straight line plots of $\ln(1 - X_A/X_{A_e})$ versus t (Figs. 3 and 4) observed at different concentrations and temperatures indicate the validity of first-order reversible kinetics for the present system of investigation. The increase in the slope of the straight line plots and, hence, in the rate of adsorption, with the increase in concentration of metal and temperature suggest that the rate of adsorption is governed by the diffusion of ions within the exchanger

Table 1
Values of rate constants at different concentrations

Metal ions	Initial concentration (mg/l)	Overall rate constant k' (min^{-1})	Forward reaction rate k_1 (min^{-1})	Reverse reaction rate k_2 (min^{-1})
Pb(II)	100	0.0241	0.0223	0.0018
	200	0.0257	0.0231	0.0027
	300	0.0282	0.0238	0.0044
	400	0.0305	0.0243	0.0062
Hg(II)	50	0.0227	0.0196	0.0031
	100	0.0230	0.0192	0.0039
	150	0.0256	0.0207	0.0050
	200	0.0269	0.0208	0.0061
Cd(II)	50	0.0146	0.0122	0.0024
	100	0.0150	0.0120	0.0230
	150	0.0160	0.0124	0.0036
	200	0.0167	0.0124	0.0043

particles. The values of k' along with other constants k_1 and k_2 calculated using Eqs. (8) and (9) are summarized in Tables 1 and 2. The k_1 values are (3.4–6.0 times for Pb(II), 3.4–6.0 times for Hg(II) and 2.8–5.0 times for Cd(II)) greater than the k_2.

The values of D_i increased from 4.026×10^{-13} to 4.439×10^{-13} m^2/s for Pb(II), 3.587×10^{-13} to 4.304×10^{-13} m^2/s for Hg(II) and 2.338×10^{-13} to 2.815×10^{-13} m^2/s for Cd(II) as the temperature varies from 30 to 60 °C (Table 2). According to earlier workers [27–29], if pore diffusion is to be rate limiting then the pore diffusion coefficients should be in the range of 10^{-12}–10^{-14} m^2/s. As per this, the rate limiting steps appears to be pore diffusion for the present system. There are only limited data available in the literature reporting effective diffusion coefficients (using Eq. (11)) for the adsorption of metal ions. Values of D_i have been given in the literature based on different initial solute concentration, different particle size of the adsorbent and different adsorbent mass/solution volume ratios. These include 6.31×10^{-13}, 1.25×10^{-12}, 1.41×10^{-12} and 1.99×10^{-12} m^2/s for the adsorption of Zn^{2+}, Mn^{2+}, Co^{2+} and Fe^{2+} onto stannic oxide (particle size: 0.100 mm) at 30 °C, respectively [27], 7.01×10^{-12}, 1.12×10^{-11} and 2.62×10^{-11} m^2/s for the adsorption of Th^{4+}, Y^{3+} and Sr^{2+} onto tantalum arsenate (particle size: 0.216 mm), respectively [28]. The D_i values for the adsorption of vanadium(IV) have been reported by Jansson-Charrier et al. [29] in the range between 4.30×10^{-15} and 1.65×10^{-13} m^2/s for chitosan with particle range between 0.125 and 0.750 mm. Other values of 4.15×10^{-15} and 2.97×10^{-15} m^2/s were obtained by Saraswat et al. [30] for the adsorption of $[Co(NH_3)]^{3+}$ and $[Co(en)_3]^{3+}$ onto chromium ferrocyanide gel (particle size: 0.134 mm), respectively. Further experimental work is in progress to understand the variation of D_i values with initial solute concentration, particle size of the adsorbent, adsorbent dose/solution volume ratios and agitation speed. The activation energy (E_a) of adsorption was calculated from the slope of linear curve obtained in the Arrhenius plot of $\ln k_1$ versus $1/T$ and the values were found to be 2.65, 4.92 and 5.28 kJ/mol for Pb(II), Hg(II) and Cd(II), respectively. Relatively low E_a values suggest that metal adsorption is a diffusion controlled process [31].

Table 2
Values of rate constants and effective diffusion coefficient at different temperatures

| Temperature ($^\circ$C)	Overall rate constant k' (min^{-1})			Forward reaction rate k_1 (min^{-1})			Reverse reaction rate k_2 (min^{-1})			Diffusion coefficient D_i (m^2/s)		
	Pb(II)	Hg(II)	Cd(II)	Pb(II)	Hg(II)	Cd(II)	Pb(II)	Hg(II)	Cd(II)	Pb(II)	Hg(II)	Cd(II)
30	0.0258	0.0230	0.0150	0.0223	0.0191	0.0120	0.0017	0.0038	0.0029	4.026×10^{-13}	3.587×10^{-13}	2.338×10^{-13}
40	0.0271	0.0251	0.0158	0.0259	0.0215	0.0135	0.0012	0.0034	0.0023	4.227×10^{-13}	3.921×10^{-13}	2.474×10^{-13}
50	0.0278	0.0263	0.0172	0.0271	0.0233	0.0149	0.0006	0.0026	0.0027	4.338×10^{-13}	4.106×10^{-13}	2.681×10^{-13}
60	0.0285	0.0276	0.0181	0.0280	0.0250	0.0159	0.0005	0.0019	0.0021	4.439×10^{-13}	4.304×10^{-13}	2.815×10^{-13}
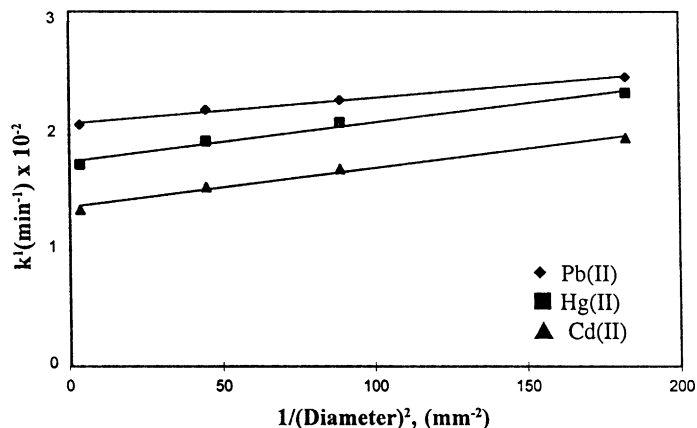
Fig. 5. Effect of particle size of PGHyFeO–COOH on rate of adsorption.

The effect of particle size on the adsorption rate was also studied at different particle sizes, namely 0.074, 0.106, 0.149 and 0.508 mm. The results of variation in rate constant at these particle sizes are shown in Fig. 5. As per Eq. (11) the rate of the reaction should vary with the reciprocal of the square of particle radius if the mechanism of uptake is controlled by intraparticle diffusion [26,27]. As shown by other workers, the increase in sorption rate of the metal ion support the contention that particle diffusion is the rate controlling mechanism [27]. Smaller particles have a larger surface area available for adsorption per unit mass of adsorbent than larger particles and one could anticipate higher k' values. The assumption that the large surface area presented by smaller particles results in lower driving force per unit area remains very plausible [32]. Therefore, more functional groups on PGHyFeO–COOH can be used to bind metal ions. It is interesting to note that Rawat and Thind [28] concluded, based on their studies on sorption of metal ions by tantalum arsenate, that for larger particle size the rate is slow and diffusion through the particle as the rate determining step is independent of particle size. The contradiction on this effect may be due to range of particle size chosen. In the latter case, the particle size range was only between 0.122 and 0.210 mm (1.7 times variation) whereas, in the present study the range was between 0.074 and 0.508 mm (6.9 times variation).

3.5. Adsorption isotherm

The effect of temperature on the adsorption of metal ions by PGHyFeO–COOH at 30, 40, 50 and 60 °C was studied for concentration range between 25 and 500 mg/l. Langmuir adsorption isotherm model was applied for adsorption equilibrium at all temperatures.

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \tag{12}$$

where C_e is the equilibrium concentration in mg/l and q_e is the amount adsorbed at equilibrium in mg/g. Q° is the adsorption capacity and b is the energy of adsorption. The values of

Q° and b at different temperatures were determined from the slope and intercept of the linear plots of C_e/q_e versus C_e (Fig. not shown) and are given in Table 3. The adsorption capacity Q° increases with increase in temperature. Although direct comparison of PGHyFeO–COOH with other adsorbent materials is difficult, owing to different applied experimental conditions, it was found, in general, that the adsorption capacities of PGHyFeO–COOH for metals, using equilibrium experiments at 30 °C, determined to be around 211.4 mg for Pb(II), 155.0 mg for Hg(II) and 147.2 mg for Cd(II) per g of adsorbent, are higher than 150.3 mg Pb(II) for tea leaves [33], 109.9 mg Hg(II) for peanut hull carbon [34] and 11.1 mg Cd(II) for straw activated carbon [35]. At any temperature, the experimental results showed that the adsorption capacity of the sorbent for the various metal ions decreased in the order Pb > Hg > Cd. The observed order of uptake for metal ions was the same as that of their increasing ionic radii, i.e. their decreasing hydrated ionic radii. The hydrated radii of the metal ions studied are as follows: Pb^{2+} 0.401, Hg^{2+} 0.413 and Cd^{2+} 0.426. The smaller the hydrated ionic radius, the greater its affinity to penetrate into smaller pores and, thus, have greater access to active groups of the adsorbent. The relative preference for these cations may also be explained by the higher stability of the complex formed by Pb(II) with carboxylate groups in PGHyFeO–COOH compared with those formed by Hg(II) and Cd(II) [17].

3.6. Thermodynamic parameters

The thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the process can be estimated using the following equations

$$\Delta G^\circ = -RT \ln K_c \tag{13}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{14}$$

The values of equilibrium constant K_c at different temperatures were calculated using Eq. (8). The plots of $\ln K_c$ versus $1/T$ for the adsorption process were found to be linear. ΔH° and ΔS° as calculated from the slope and intercept of the plots were found to be 42.66 kJ/mol and 162.11 J/mol/K for Pb(II), 26.34 kJ/mol and 99.98 J/mol/K for Hg(II) and 16.45 kJ/mol and 66.49 J/mol/K for Cd(II), respectively. The positive values of ΔH° indicate the endothermic nature of adsorption. The negative values of ΔG° indicate (Table 3) the feasibility of the process and spontaneous nature of adsorption. Further, the values of ΔG° decrease with rise in temperature showing increase in feasibility of adsorption at higher temperatures. The positive values of ΔS° show the increased randomness at the solid/solution interface during adsorption. The relatively small positive ΔS° values in the system under investigation, indicate that as a result of adsorption no significant structural change occurs in the adsorbent material.

3.7. Testing with synthetic wastewaters

The utility of the adsorbent material has been demonstrated by treating with synthetic wastewaters. The results are shown in Table 4. The amount of adsorbent for the complete

Table 3
Langmuir constants and thermodynamic parameters for the adsorption of metal ions onto PGHyFeO–COOH

Temperature (°C)	Langmuir constants						Thermodynamic parameters					
	Q° (mg/g)			b (l/mg)			K_c			ΔG° (kJ/mol)		
	Pb(II)	Hg(II)	Cd(II)	Pb(II)	Hg(II)	Cd(II)	Pb(II)	Hg(II)	Cd(II)	Pb(II)	Hg(II)	Cd(II)
30	211.42	155.01	142.71	0.0256	0.0246	0.0206	12.624	4.949	4.012	−6.38	−4.02	−3.49
40	213.22	157.45	146.26	0.0327	0.0341	0.0265	20.929	6.326	5.727	−7.91	−4.81	−4.54
50	216.17	160.17	149.89	0.0409	0.0451	0.0286	41.017	9.101	6.549	−9.97	−5.92	−5.05
60	218.53	163.21	151.47	0.0538	0.0598	0.0317	55.818	12.610	7.425	−11.13	−7.01	−5.64

Table 4
Composition of synthetic wastewater and the amount of adsorbent for complete removal of metals from 50 ml solution

Metal ions	No. of samples	Composition (mg/l)	Amount of adsorbent (mg)
Pb(II)	1	Pb: 25; Na^+: 10; K^+: 10; Mg^{2+}: 10; Ca^{2+}: 10; NH_4^+: 10; Cl^-: 15; NO_2^-: 10; SO_4^{2-}: 40; NO_3^-: 30; CH_3COO^-: 35	150
	2	Pb: 25; Na^+: 15; K^+: 20; Mg^{2+}: 5; Ca^{2+}: 10; NH_4^+: 5; Cl^-: 20; NO_2^-: 20; SO_4^{2-}: 20; NO_3^-: 15; CH_3COO^-: 15	150
	3	Pb: 50; Na^+: 10; K^+: 10; Mg^{2+}: 10; Ca^{2+}: 10; NH_4^+: 10; Cl^-: 15; NO_2^-: 10; SO_4^{2-}: 40; NO_3^-: 30; CH_3COO^-: 35	300
Hg(II)	1	Hg: 25; Na^+: 10; K^+: 10; Mg^{2+}: 10; Ca^{2+}: 10; NH_4^+: 10; Cl^-: 15; NO_2^-: 10; SO_4^{2-}: 40; NO_3^-: 30; CH_3COO^-: 35	200
	2	Hg: 25; Na^+: 15; K^+: 20; Mg^{2+}: 5; Ca^{2+}: 5; NH_4^+: 5; Cl^-: 20; NO_2: 20; SO_4^{2-}: 20; NO_3^-: 15; CH_3COO^-: 15	200
	3	Hg: 50; Na^+: 10; K^+: 10; Mg^{2+}: 10; Ca^{2+}: 10; NH_4^+: 10; Cl^-: 15; NO_2^-: 10; SO_4^{2-}: 40; NO_3^-: 30; CH_3COO^-: 35	500
Cd(II)	1	Cd: 25; Na^+: 10; K^+: 10; Mg^{2+}: 10; Ca^{2+}: 10; NH_4^+: 10; Cl^-: 15; NO_2^-: 10; SO_4^{2-}: 40; NO_3^-: 30; CH_3COO^-: 35	250
	2	Cd: 25; Na^+: 15; K^+: 20; Mg^{2+}: 5; Ca^{2+}5; NH_4^+: 5; Cl^-: 20; NO_2^-: 20; SO_4^{2-}: 20; NO_3^-: 15; CH_3COO^-: 15	250
	3	Cd: 50; Na^+: 10; K^+: 10; Mg^{2+}: 10; Ca^{2+}: 10; NH_4^+: 10; Cl^-: 15; NO_2^-: 10; SO_4^{2-}: 40; NO_3^-: 30; CH_3COO^-: 35	600

removal of Pb(II), Hg(II) and Cd(II) from 50 ml synthetic wastewaters containing 25 mg/l metal and several foreign ions (samples 1 and 2) were found to be 150, 200 and 250 mg, respectively, the corresponding amount of adsorbent for 50 mg/l metal (sample 3 of each metal) were found to be 300, 500 and 600 mg. The results are in good agreement with those obtained from batch experiments mentioned above. The results also indicate that the presence of other ions have either no interference or very little interference on the adsorption of metal ions by PGHyFeO–COOH.

3.8. Competition among cations

The 150 ml of solution containing 50 mg/l each of Pb(II), Hg(II) and Cd(II) was shaken with 0.1 g of PGHyFeO–COOH. After adsorption equilibrium was reached, the contents were centrifuged and supernatant was analyzed for Pb(II), Hg(II) and Cd(II). The adsorption of these metals was found as: Pb(II) = 14.56 mg/g, Hg(II) = 9.76 mg/g and Cd(II) = 8.31 mg/g. For ions of the same valence, sorbent prefers the metal with higher atomic number [4].

3.9. Desorption and regeneration studies

To make the adsorption process more economical, it is necessary to regenerate the spent adsorbent. Solutions of (1) 0.5 M HCl and (2) 0.2 M NaCl were evaluated for desorption of metals from PGHyFeO–COOH into aqueous phase again. Desorption experiments were carried out by shaking 0.1 g of PGHyFeO–COOH saturated with metal ions in (1) 50 ml of 0.5 M HCl and (2) 50 ml of 0.2 M NaCl. A reaction time of 4 h was maintained in the regeneration study. The desorption and regeneration data are presented in Table 5 . The Na^+ ions are easily displaced by metal ions bonded to sorbent during adsorption experiments. This is an indication of an ion-exchange process. An efficiency of 98.3% Pb(II), 93.1% Hg(II) and 90.1% Cd(II) was obtained by using 0.2 M NaCl and is therefore suitable for regeneration of metal ions from spent PGHyFeO–COOH. The small fraction of sorbed

Table 5
Desorption and regeneration data

Metal ions	No. of cycles	Adsorption		Desorption in 0.2 M NaCl (mg/g)	Recovery in 0.2 M NaCl (%)
		mg/g	%		
Pb(II)	1	23.79	95.2	23.39	98.3
	2	23.33	93.3	22.51	96.5
	3	22.04	88.2	20.51	93.1
Hg(II)	1	21.38	85.5	19.92	93.2
	2	20.72	82.9	18.64	90.0
	3	19.83	79.3	16.96	86.8
Cd(II)	1	21.03	84.1	18.04	90.1
	2	20.46	81.9	17.23	88.5
	3	19.68	78.7	15.91	85.2

metals not recoverable by regeneration presumably represents the metal which is bound through strong interaction and, as a result, the sorption capacity is reduced in subsequent cycles.

4. Conclusions

The following conclusions may be drawn on the basis of present studies. PGHyFeO–COOH can be a suitable adsorbent for the removal of metals from water and wastewaters as both kinetics and capacity is highly favorable. The process of uptake was found to be pH dependent and follows first-order reversible kinetics. The presence of diverse ions does not affect the adsorption of metals. Thermodynamic parameters have been calculated and the adsorption data fits with the Langmuir isotherm equation. Quantitative removal of Pb(II), Hg(II) and Cd(II) from synthetic wastewaters confirms the validity of the results obtained in batch wise studies. Spent adsorbent can be regenerated using 0.2 M NaCl treatment.

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