Batch metal removal by modified hydrous titanium (IV) oxide gel: Kinetics and thermodynamics

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The adsorption ability of polyacrylamide grafted hydrous titanium(IV) oxide gel for heavy metals in aqueous solutions has been investigated by means of batch adsorption tests. The adsorbent material on IR spectral characterization showed the presence of peripheral - COOH group and exhibits a very high adsorption potential for Pb(II), Hg(II) and Cd(II). Kinetic measurements have been made as a function of agitation time, initial metal concentration, adsorbent dose, pH and temperature. The process follows a first - order kinetics. The intraparticle diffusion of metal ions through pores in the adsorbent was shown to be the main rate limiting step. The sorbent is effective for the quantitative removal of metal ions at pH 6.0. Temperature dependence indicates the endothermic nature of the process. A Langmuir isotherm model fits the equilibrium data well. Thermodynamic parameters were calculated for predicting the nature of adsorption. The method was applied for synthetic wastewaters. Acid regeneration of the adsorbent has been tried.

The processes developed to remove heavy metals from wastewater include chemical precipitation, coagulation, complexing, solvent extraction, ion exchange and adsorption. At low concentrations, the removal of such pollutants is more effective by ion exchange or adsorption on solid adsorbents. Different types of polymeric materials and synthetic resins are used as adsorbents for the removal of metal pollutants from chemical process industries in certain developed countries[1]. Surface modifications by chemical treatment of the adsorbent materials usually improve the physical characteristics and adsorption efficiency of the adsorbents[2,3]. Silica gel modified with pyridinium ions[4] and clay impregnated with 2-mercaptobenzothiazol[5] have been developed for the adsorption of heavy metals from water. Formaldehyde polymerized onion skin[6], tree bark[7], tea leaves[8] and sawdust[9] were also used as adsorbents for heavy metals.

Previous research has suggested that polymer coated metal oxide gels represent a new and promising class of sorbent materials for the removal of heavy metals from waste waters. The materials such as silica gel[10], iron (III) oxide[11], tin

(IV) oxide[12] and chitosan[13] have already been used as polymer support for the preparation of adsorbents. Carboxylate functional group substituted on the backbone of the polymerised materials increase the number and change the nature of sites capable of adsorbing metals in solutions[13]. Zorin and Stoyamova[14] have investigated the applicability of using weak carboxylic acid cation exchangers for water treatment. Comparison of ion exchange capacities had showed that the weak carboxylic acid exchangers were competitive with certain conventional strong acid exchangers[14]. Hydrous titanium(IV) oxide gel (HyTiO) has attracted considerable attention as an ion exchanger owing to its high sorption selectivity for certain metal ions[15]. Even though the relative cost of HyTiO is higher than that of silica gel and iron(III) oxide HyTiO has been used as polymer support, because it has high chemical stability and resistance to degradation in extreme environment such as high temperature and the presence of ionizing radiation[16].

Studies have also been reported on the use of commercial weak carboxylic cation exchangers such as Amberlite IRA-64, Amberlite IRP-88, Amberlite CG-50 and Duolite ES-468 for water

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treatment which are available for Rs. 740, Rs.836, Rs.1520 and Rs. 760 per 100 g of resin[17] respectively. Recently, a weak carboxylic cation exchanger has been developed by grafting polyacrylamide on hydrous titanium (IV) oxide gel (PGHyTiO-COOH) which may be utilized in removing heavy metals from water and wastewaters[18]. Cost of this material was calculated and was found to be Rs. 420 per 100g. The relative cost of this material used in the present study is lower than that of certain commercial resins. This paper describes the results of our detailed investigation of the adsorption characteristics for the removal of Pb(II), Hg(II) and Cd(II) from water and wastewater onto PGHyTiO-COOH. Desorption studies have also been carried out.

Experimental procedure

Sorbent preparation—Hydrous titanium(IV) oxide gel (HyTiO) was precipitated from a solution of $TiCl_4$ (50mL) by adding 400 mL of 2.8M NaOH solution[15]. The air dried gel has been identified as $TiO_2 1.81$ $H_2O^{15,18}$. The gel was grafted with polyacrylamide using the procedure described by Shigetomi *et al.*[11] The polymerized product then washed with water and dried at 80°C and then refluxed with `25 mL ethylenediamine in toluene for 8h.To functionalize 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 *p*H 4.0 for 6h. The *p*H was maintained using 0.1M solution of potassium hydrogen phthalate and HCl. The excess succinic anhydride was washed out with 1,4-dioxane and finally with ethanol and dried. The carboxylic acid bound polyacrylamide grafted hydrous titanium(IV) oxide gel (PGHyTiO-COOH) was ground and to the average diameter 0.096 mm.

Adsorption experiments—Adsorption experiments were performed by shaking 0.1 g of the adsorbent with 20 mL metal solutions (nitrate salts) of varying concentration at 100 rpm for predetermined time intervals and at 30° C using a temperature controlled shaking water bath. Initial *p*H of solution was adjusted using 0.05 M solution of HNO_3 and NaOH. The contents were centrifuged and the supernatant was analysed for metal content. Lead and cadmium were estimated by atomic absorption spectrophotometry. Mercury

was determined spectrophotometrically using eosin method[19].

Desorption experiments—For desorption study 0.1 g of metal-loaded adsorbent was agitated with 20 mL of distilled water/ or 0.5 M HCl for 6h. Then the supernatant was centrifuged and analysed for metal. The sorbent samples thus regenerated was reused for the 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.

Results and Discussion

The IR spectra of HyTiO and PGHyTiO-COOH were recorded on a Shimadzu FTIR-1801 spectrometer. HyTiO shows a broad asymmetric absorption band at wave number range 3300-3400 cm^{-1}, which is attributable to the sum of the contribution from water and hydroxyl groups bonding to titanium. The absorption bands at 865 and 490 cm^{-1} are due to Ti-O bond. IR spectrum of PGHyTiO-COOH shows a broad spectrum around 3470 cm^{-1} representing the overlap of -OH, C-H, N-H and C-O stretching vibrations. The peaks at 1693 and 1673 cm^{-1} for PGHyTiO-COOH is due to the aliphatic amide groups. The sharp absorption band at 2955 cm^{-1} is attributable to the contribution

Table 1—Physical and surface properties of modified and non-modified adsorbents

parameters	Magnitude	
	HyTiO	PGHyTiO-COOH
Apparent density, g/mL	1.61	1.76
Moisture content, %	14.5	3.82
Cation exchange capacity, meq/g	0.86	1.91
Grafting, %	--	82.5
Surface area, m^2/g	30.4	71.6
Porosity, mL/g	0.22	0.36
Zero point charge (pH_{zpc})	5.0	5.8
Particle size, mm	0.096	0.096
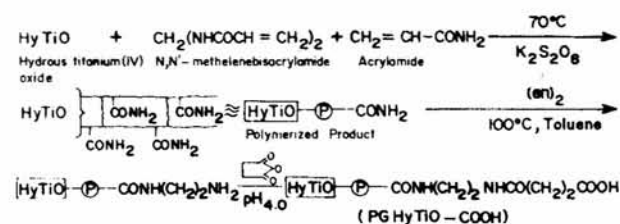
Scheme 1—Preparation of carboxylated polyacrylamide grafted HyTiO.

of C-H stretching from CH_2 group. The additional peaks at 1745 cm^{-1} ($\sqrt{c}=0$) and 1460 cm^{-1} ($\sqrt{c}=0$) indicate the presence of COOH group[20] in PGHyTiO-COOH. Based on these results, the structure of the PGHyTiO-COOH is represented in Scheme 1. The results of the physical and surface characteristics of the modified and non-modified gels are given in Table1. Although PGHyTiO-COOH is grafted with a polymer, the specific surface area remains considerably low, i.e., 71.6 m^2/g.This indicates that most of the pores are clogged with polymer, presumably because the inner surfaces of the pores are not uniformly covered with polymer network.

Preliminary investigation shows a high uptake of metal ions on PGHyTiO-COOH in comparison with HyTiO. It was found that for the quantitative removal of 50 mg/L metal in 20 mL, a minimum adsorbent dosage of 150,175 and 250 mg of PGHyTiO-COOH or 350, 500 and 700 mg of HyTiO is required for Pb(II), Hg(II) and Cd(II) respectively. The data clearly show that PGHyTiO-COOH is 2.3, 2.9 and 2.8 times more effective than HyTiO for the removal of Pb(II), Hg(II) and Cd(II) respectively. This may be due to the higher porosity and moderate ion exchange capacity of PGHyTiO-COOH compared to HyTiO. As such subsequent investigations with metal ions were made only on the modified sample.

Fig. 1 shows that the removal of Pb(II) Hg(II) and Cd(II) by PGHyTiO-COOH increased from 9.14, 8.02 and 7.39 mg/g to 33.17, 25.97 and 18.98 mg/g by increasing concentration from 50 to 250 mg/L at *p*H 6.0. It is also clear that increasing agitation time increased the metal uptake and it remained constant after the saturation time of 5h.

Table 2—Adsorption kinetic parameters for the sorption of Pb(II), Hg(II) and Cd(II) onto PGHyTiO-COOH at different temperatures

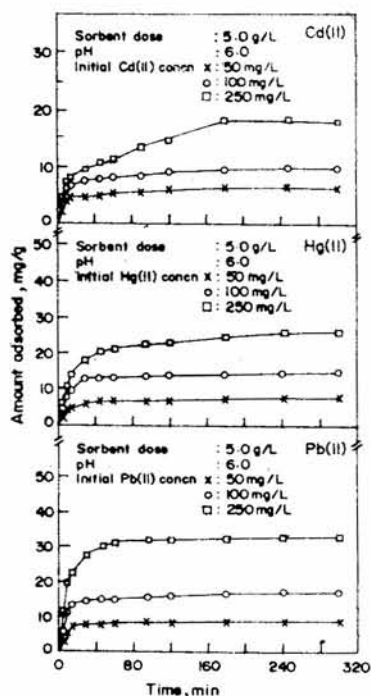| Temperature °C	k_{ad}, min^{-1}			k_{id}, mg/g/min$^{-1/2}$		
	Pb(II)	Hg(II)	Cd(II)	Pb(II)	Hg(II)	Cd(II)
30	1.40×10^{-2}	1.17×10^{-2}	1.40×10^{-2}	4.36×10^{-1}	3.21×10^{-1}	3.10×10^{-1}
40	1.84×10^{-2}	1.47×10^{-2}	1.50×10^{-2}	7.82×10^{-1}	4.80×10^{-1}	4.10×10^{-1}
50	2.14×10^{-2}	1.81×10^{-2}	2.04×10^{-2}	9.16×10^{-1}	7.20×10^{-1}	6.92×10^{-1}
60	2.90×10^{-2}	2.85×10^{-2}	2.20×10^{-2}	10.16×10^{-1}	9.61×10^{-1}	8.80×10^{-1}

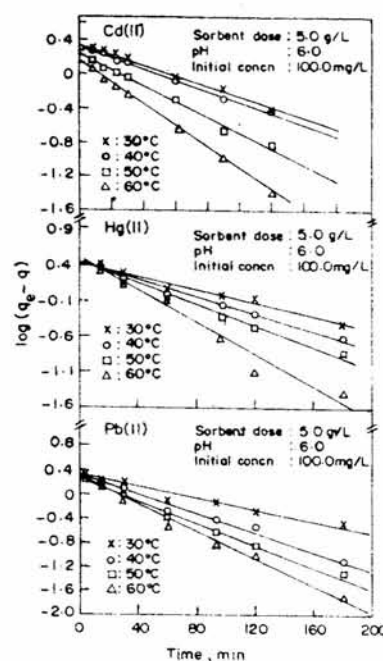Fig.1—Effect of agitation time and initial concentration for the adsorption of metals on PGHyTiO-COOH.

Fig.2—Lagergren plots for the adsorption of metals on PGHyTiO-COOH at different temperatures.

The curves are smooth and continuous indicating the possibility of monolayer coverage of metal ions on the surface of the adsorbent.

The Lagergren's rate equation as cited by Wasay et al[21] was employed for the rate constant study of the systems under taken:

$$\log (q_e-q)=\log q_e-(k_{ad}/2.303)t \qquad \ldots (1)$$

The linear plots of $\log(q_e-q)$ vs t (Fig. 2) show the fitness of the Lagergren's model, consequently the first-order nature of the process involved herein. The values of adsorption rate constant (k_{ad}) calculated from the slope of the plots are given in Table 2. The rate constant was higher at higher temperatures. The activation energy, E_a was determined using Arrhenius equation[9]. The plots of $\ln k_{ad}$ vs $1/T$ were found to be linear. The E_a values as calculated from the slope of the plots were found to be 25.8, 24.0 and 24.8 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.
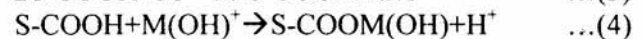
Owing to the porous nature of the adsorbent, the intraparticle transport is supposed to be the rate controlling step. The rate constant for intraparticle diffusion k_{id} is given by Weber and Morris[22].

$$q=k_{id}t^{1/2} \qquad \ldots (2)$$

Where q is the amount adsorbed (mg/g) at time t, k_{id} values were obtained from the slope of the linear portion of q vs $t^{1/2}$ plots for each temperature (Table 2). k_{id} was higher at higher temperatures. Since diffusion is an endothermic process, the rate of sorption will increase with increased solution temperature, when intraparticle transport is the rate limiting step. The results of this study reinforce the conclusion that metal adsorption on PGHyTiO-COOH is controlled by pore diffusion.

In order to examine the effects of pH on metal uptake, experiments were conducted using two different initial concentrations of 50 and 250 mg/L. The percentage removal of metal ion by PGHyTiO-COOH increased with an increase in pH upto a certain value and then decreased with further increase of pH. In the case of low concentration of 50 mg/L the maximum removal of 91.2% for Pb(II), 80.3% for Hg(II) and 75.1% for Cd(II) was observed at pH 6.0. Below and above this pH, a decreasing trend in removal was observed. The same pH phenomena was also found at higher

concentration. The perusal of Pb(II), Hg(II) and Cd(II) speciation diagrams[23-25] clearly indicates that in the range of the highest removal efficiency the dominant species were M^{2+} and M(OH)$^+$. The final pH of the reaction mixture remained between 2.4 and 7.2 during the experiments, while the initial pH of the reaction mixture varied from 2 to 9. Hence the effect of pH on metal ion can be explained as due to the exchange behaviour of H$^+$ ions from Peripheral-COOH groups. The removal of metal ions by PGHyTiO-COOH may be represented as

$$2S\text{-}COOH+M^{2+}\rightarrow 2S\text{-}COOM+2H^+ \qquad \ldots (3)$$
$$S\text{-}COOH+M(OH)^+\rightarrow S\text{-}COOM(OH)+H^+ \qquad \ldots (4)$$

$S \rightarrow$ polymerized surface.

Decrease in removal of metal ions at low pH is apparently due to the higher concentration of protons in the reaction mixture which compete with metal ions for the adsorption sites on the sorbent surface. Decrease in removal of metal ions at higher pH is due to the formation of soluble hydroxy complexes[26].

At any pH, the experimental results on the single ion system showed that the adsorption capacity of the sorbent for the various metal ions decreased in the order Pb(II)>Hg(II)>Cd(II)>. 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 smaller
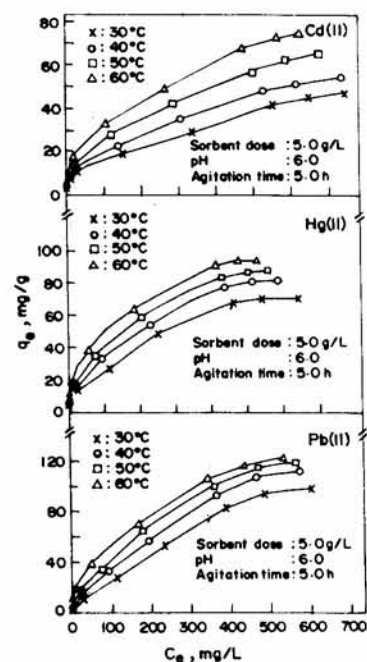

Fig.3—Adsorption isotherms of metals on PGHyTiO-COOH.

the hydrated ionic radius, the greater its affinity to active groups of the sorbent. This suggests that the energy required for the dehydration of the metal ions, so that they could occupy a site in the sorbent, plays an important role in determining selectivity series for the metal ions.

Adsorption isotherm studies were performed for the initial concentration ranges between 25 and 1000 mg/L (Fig.3). The L-type nature of the curve[27] as obtained in the present investigation, is favourable to adsorption, and it indicates the strong tendency in the process for monolayer formation. With L-type isotherm, the adsorption sites in the PGHyTiO-COOH are gradually filled and subsequent adsorption becomes difficult so that adsorption tends to be limited.

The equilibrium data for the removal of metal ions by adsorption on PGHyTiO-COOH at all temperatures were fitted in the rearranged Langmuir isotherm.

$$\frac{C_e}{q_e} = \frac{1}{Q^{ob}} + \frac{C_e}{Q^o} \qquad \qquad ...(5)$$

Where C_e is the equilibrium concentration in mg/L and q_e is the amount adsorbed at equilibrium in mg/g. Q^o is the adsorption capacity and b is the energy of adsorption. The linear plots of C_e/q_e vs. C_e at different temperatures (Fig.4) indicate the applicability of Langmuir adsorption isotherm. Q^o and b values calculated from the plots are given in Table 3. Adsorption capacity of Pb(II) is greater than that of Hg(II) and Cd(II) and increases with temperature.

Thermodynamic equilibrium constant, K_o for the adsorption process was determined by the method of Khan and Singh[28] by plotting $\ln q_e / C_e$ vs q_e and

Table 3—Langmuir constants for the sorption of Pb(II), Hg(II), and Cd(II) onto PGHyTiO-COOH

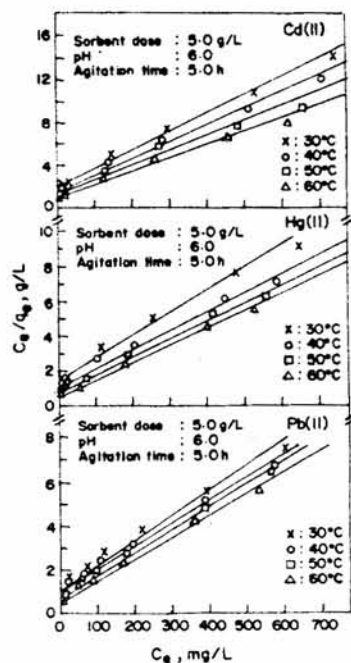| Temperature, °C	Langmuir constants					
	Pb(II)		Hg(II)		Cd(II)	
	Q^o mg/g	b L/mg	Q^o mg/g	b L/mg	Q^o mg/g	b L/mg
30	84.0	3.2×10^{-2}	75.1	9.6×10^{-3}	53.5	6.9×10^{-3}
40	90.9	3.3×10^{-2}	92.6	9.7×10^{-3}	63.7	8.6×10^{-3}
50	100.0	3.8×10^{-2}	97.1	12.0×10^{-3}	100.2	8.7×10^{-3}
60	111.1	4.0×10^{-2}	107.8	15.0×10^{-3}	103.1	9.6×10^{-3}

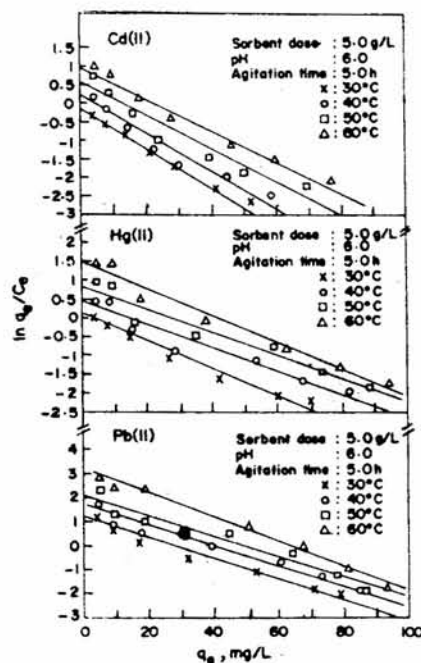Fig.4—Langmuir adsorption isotherm for metals on PGHyTiO-COOH.

Fig.5—Plots of $\ln q_e/C_e$ vs q_e for the adsorption of metals on PGHyTiO-COOH.

Table 4—Thermodynamic parameters for the sorption of Pb(II), Hg(II), and Cd(II) onto PGHyTiO-COOH

Tempe-rature, °C	Pb(II)				Hg(II)				Cd(II)			
	K_o	$\Delta G°$, kJ/mol	$\Delta H°$, kJ/mol	$\Delta S°$, J/mol K	K_o	$\Delta G°$, kJ/mol	$\Delta H°$, kJ/mol	$\Delta S°$, J/mol K	K_o	$\Delta G°$, kJ/mol	$\Delta H°$, kJ/mol	$\Delta S°$ J/mol K
30	3.34	−3.04			1.15	−0.36			0.86	−0.38		
40	5.62	−4.04			1.60	−1.22			1.27	−0.61		
50	8.06	−5.60	53.45	182.8	2.34	−2.29	37.05	121.8	1.80	−1.58	30.76	100.1
60	25.25	−8.94			4.49	−4.16			2.63	−2.67		

Table 5—Composition of synthetic wastewater and the amount of adsorbent for the complete removal of metals from 20 mL solution

Metal ions	No of samples	Composition, mg/L	Amount of adsorbent, mg
	1	Pb:50; Na:50; K:50; NH$_4$:60; Mg:50; Ca:40; Cl:300, NO$_3$:135; CH$_3$COO:80, SO$_4$:100	150
Pb(II)	2	Pb:50; Na:50; K:15; Mg:15; Ca:20; Cl:65; NO$_2$:60; NO$_3$:30; H$_2$PO$_4$:50; SO$_4$:50	150
	3	Pb:100; Na:140; K:70; NH$_4$:30; Mg:50; Ca:60; Cl:80; NO$_3$:90; CH$_3$COO:100; SO$_4$:50	250
	1	Hg:50; Na:50; K:50; NH$_4$:60; Mg:50; Ca:40; Cl:300; NO$_3$:115; CH$_3$COO:80; SO$_4$:100	200
Hg(II)	2	Hg:50; Na:50; K:15; Mg:15; Ca:20; Cl:65; NO$_2$:60; NO$_3$:30; H$_2$PO$_4$:50; SO$_4$:50	200
	3	Hg:100; Na:140; K:70; NH$_4$:30; Mg:50; Ca:60; Cl:80; NO$_3$:90; CH$_3$COO:100; SO$_4$:50	400
	1	Cd:50; Na:50; K:50; NH$_4$:60; Mg:50; Ca:40; Cl:300; NO$_3$:105; CH$_3$COO:80; SO$_4$:100	250
Cd(II)	2	Cd:50; Na:50; K:15; Mg:15; Ca:20; Cl:65; NO$_2$:60; NO$_3$:55; H$_2$PO$_4$:50; SO$_4$:50	250
	3	Cd:100; Na:140; K:70; NH$_4$:30; Mg:50; Ca:60; Cl:80; NO$_3$:140; CH$_3$COO:100; SO$_4$:100	550

extrapolating to zero q_e (Fig.5). The standard free energy $\Delta G°$ for the interaction of PGHyTiO-COOH with metal ion was calculated as $\Delta G° = -RT \ln K_0$. The standard enthalpy, $(\Delta H°)$ and entropy $(\Delta S°)$ changes were computed using the following equation.

$$\ln K_0 = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad ...(6)$$

The plots of $\ln K_0$ vs $1/T$ for Pb(II), Hg(II) and Cd(II) were found to be linear. The values of $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of the plots and are given in Table 4. The positive values of $\Delta H°$ suggest the endothermic nature of the process. The negative values of $\Delta G°$ indicate the feasibility of the process and spontaneous nature of adsorption. Further, the free energy change decrease with rise in temperature showing increase in feasibility of adsorption at higher temperatures. The positive values of $\Delta S°$ show the increased randomness at the solid/solution interface during the adsorption.

The utility of the adsorbent material has been demonstrated by treating synthetic wastewaters. The results are shown in Table 5. The amount of adsorbent for the complete removal of Pb(II), Hg(II) and Cd(II) from 20 mL synthetic wastewaters containing 50 mg/L metal and several foreign ions (samples 1 and 2 of each metal) were found to be 150, 200 and 250 mg respectively; the corresponding amount of adsorbent for 100 mg/L metal (sample 3 of each metal) were found to be 250, 400 and 550 mg. The results are in good agreement with those obtained from the batch experiments mentioned above. The data also show that the presence of other ions have either no interference or very little interference on the adsorption of metal ions by PGHyTiO-COOH.

Recovery of the adsorbed material as well as the regeneration of adsorbent is also an important aspect of wastewater treatment. Attempts have been made to reuse the exhausted sorbent after regeneration by acid treatment. The desorption of metals by distilled water was found to be insignificant. Only 8.4% Pb(II), 5.6% Hg(II) and 6.4% Cd(II) desorption took place in distilled water whereas 96.8% Pb(II), 95.2% Hg(II) and 95.6% Cd(II) desorption were observed in 0.5M HCl. This is an indication of ion exchange nature of adsorption process. After two cycles, the adsorption capacity of PGHyTiO-COOH declined by 6.8%; on other hand, recovery of Pb(II) in 0.5M HCl decreased from 96.8% in the first cycle to 90.3% in the third cycle. The absolute adsorption capacities of the adsorbent for Hg(II) and Cd(II) removal after two cycles decreased by 8.4 and

11.7% respectively. The recovery of Hg(II) ions in 0.5 M HCl decreased from 95.2% in the first cycle to 89.6% in the third cycle, whereas in the case of Cd(II) ions it decreased from 95.6 to 90.5%.The small fraction of sorbed metals not recoverable by regeneration presumably represents the metal which are bound through strong interaction and, as a result, the sorption capacity is reduced in subsequent cycles. The results show that spent PGHyTiO-COOH can be effectively regenerated by 0.5M HCl.

Conclusion

PGHyTiO-COOH is a suitable adsorbent for the removal of heavy metals from aqueous solution. Sorption of metals is *p*H dependent and the best results are obtained in the *p*H range 5-7. Equilibrium partitioning of metals onto the sorbent can be described by the Langmuir isotherm. Percentage metal removal at equilibrium increased with increasing adsorbent dose. Quantitative removal of metal ions from synthetic wastewaters confirms the validity of the results obtained in the batch mode studies. Spent adsorbent can be regenerated by acid treatment and can be reused. In order to quantify the specific treatment costs associated with the proposed treatment method, further experimentation on a pilot-scale is required, where the preliminary batch experiments presented in this paper would be compared with process modifications in a more technological way, such as the application of packed or column beds instead of batch mode and also using real industrial wastewater.

Acknowledgment

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