Investigation of Pb(II) Adsorption onto Natural and Synthetic Polymers

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ABSTRACT: Adsorption of toxic metal ion Pb(II) onto two different insoluble humic acids (IHAs) obtained from Beysehir (BIHA) and Ermenek (EIHA) low grade lignites and two synthesized terpolymers: styrene-divinylbenzene-methacrylic acid (SDBM) and styrene-divinylbenzene allyl-methacrylate (SDBAM) were investigated and compared with commercial activated carbon (AC). The synthesized polymers were characterized by FTIR. Effects of pH (in neutral and acidic range), time, and initial metal concentration on the effectiveness of IHAs and terpolymers were determined. All synthesized adsorbents could adsorb Pb(II) with much higher capacity at half of the retention of AC in acidic medium. The adsorption capacities varied in the range of 51–76 mg g^{-1}. The affinity order of polymers in acidic medium for Pb(II) ions was observed as: SDBAM>SDBM>BIHA≈EIHA>AC. IHAs fit Freundlich model while SDB polymers were fitting Langmuir isotherm. The maximum adsorption capacities in neutral medium were 48 mg g^{-1} for SDBM and 15 mg g^{-1} for BIHA. Desorption studies for the polymer of highest performance indicated that about 90% desorption was achieved at 5 h by using EDTA regenerant solution. The polymer can be used repeatedly in Pb(II) adsorption with close capacities to initial use. The higher selectivity of SDBAM to Pb(II) ions in multimetal solution was also indicated in the study. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 716–724, 2012

Key words: radical polymerization; adsorption; FT-IR; Pb(II)

INTRODUCTION

Industrial and municipal effluents usually consist appreciable amounts of heavy metals such as lead [Pb(II)] as toxic materials even in dilute concentrations. Adsorption or ion exchange technology is one of the most effective methods for removing such toxic materials from aquatic environment.[1] Recent growing concerns regarding such toxic materials drive for the development of new, feasible, and chemically less polluting adsorbents. The use of chelating polymers for the removal of toxic metal ions would be of great importance in such an environmental application due to their high selectivity, efficiency, easy handling, and availability. The dire need of the time to reduce the concentration of heavy metals down to acceptable levels in waste streams followed by subsequent reuse of those metals have led to an increasing interest in the development of selective polymeric adsorbents.[2–5]

Among the various wastewater treatment techniques described, adsorption or ion exchange is generally preferred for the removal of heavy metal ions due to the performance of various adsorbents and cost-effectiveness.[6] The ability of insoluble humic acids (IHAs) on sorption of heavy metals has been demonstrated in a number of investigations.[7–9] Madronova et al.[7] investigated the metal binding properties of IHAs obtained from North-Bohemia coal. Ibarra et al.[8] studied the adsorption of Sr(II), Pb(II), and Th(IV) from solution by several IHAs. IHA extracted from clay loam (Ontario) was used for adsorption of heavy metals by Kerndorff and Schnitzer.[9] These adsorption studies were performed under static equilibrium conditions and all reported that, the adsorption capacity depends on the origin of the IHAs and their pretreatment.

Moreover, a great deal of interest has been observed in relation to the applicability of the synthetic polymers for removal, separation, and purification of metal ions from water, due to the ability of them to form polymer-metal complexes. Some organic polymer sorbents, Amberlite XAD, Lewatit, Separon, Polysorb are well known from the literature.[10] Recently, styrene-divinylbenzene-based insoluble resins, gelatinous and macroporous copolymers and crosslinked polymer adsorbents gained vital importance because of their ability to remove high quantities of ions.[11,12]

Therefore, the aims of this study were to obtain IHAs from Beysehir and Ermenek low grade lignites (from Central Anatolian region, Konya-Turkey), to synthesize SDB based terpolymers, and to investigate

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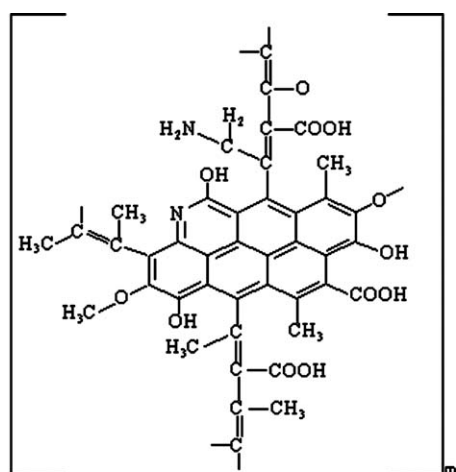
(a)
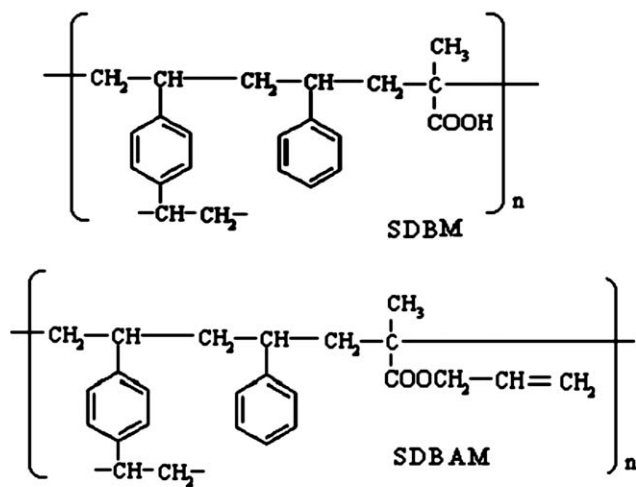
(b)

Figure 1 Chemical structures of: (a) humic acid; (b) SDB terpolymers.

the effectiveness of all these polymers in Pb(II) adsorption. The performance of the polymers in Pb adsorption were compared with the well known, widely used commercial adsorbent activated carbon (AC).

EXPERIMENTAL

Materials

Lignite samples taken from the coal mine sites, around Beysehir and Ermenek (Konya-Turkey), having large deposits (about 200 million tons) of low grade lignite. Styrene, divinylbenzene, and methacrylic acid were purchased from Merck (Darmstadt, Germany). Lead nitrate [Pb(NO$_3$)$_2$ · 2H$_2$O], potassium hydroxide, azobisizobutironitrile, hydrochloric, and nitric acids were purchased from Fluka (Buchs, Switzerland).

Insoluble humic acid synthesis

Crashed and grinded samples of lignites were first sieved and 80 mesh portion was used in Insoluble humic acid (IHA) synthesis. 1 g of lignite was mixed with 20 mL 5% NaOH and 10 mL distilled water, mixture was heated on a bright flame and boiled for 3 min and cooled immediately under tap water. Cooled mixture was centrifuged several times by adding distilled water until the supernatant became clear. The settled parts were collected into another beaker after each centrifugation. Fifty microliter of distilled water was added to the rest of the solution and the pH value was adjusted to pH 3.0 by adding 5% HCl. IHA precipitated at the bottom of the flask was filtered and dried at 60°C. The chemical structures of the synthesized IHAs were indicated in Figure 1(a).

Synthesis of SDB copolymers

Styrene-divinylbenzene-methacrylic acid (SDBM) and styrene-divinylbenzene-allylmethacrylate (SDBAM) were synthesized by radical suspension polymerization. 9.1 g styrene, 1.3 g divinylbenzene, and 0.321 g other monomer either methacrylic acid or allylmethacrylate (3% by weight) were mixed with 0.21 g azobisizobutironitrile in 60 mL polyvinyl alcohol. The mixture was polymerized at 80°C for 6 h in a setup equipped with a mechanical stirrer and reflux condenser. At the end of reaction to separate the formed terpolymer from other components, it was first settled with methanol, washed with hot water, centrifuged and finally dried at 60°C under vacuum pressure. The structure of synthesized terpolymers was indicated in Figure 1(b).

Characterization of adsorbents

The FTIR spectra of polymers were recorded on a Perkin–Elmer 1605 FT-IR spectrometer. Spectroscopies of IHAs and SDB polymers were indicated in Figures 2 and 3.
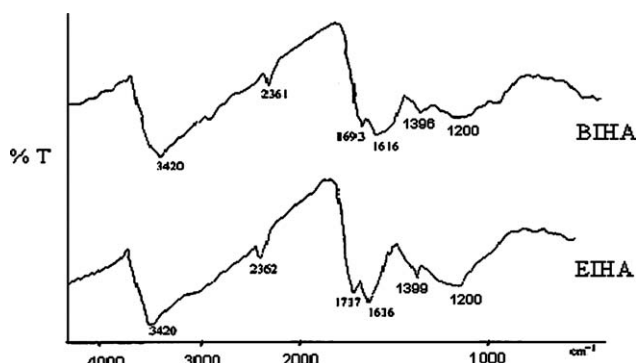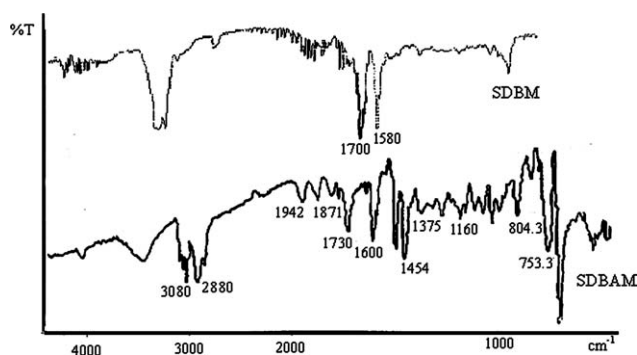

Figure 2 FTIR spectra of IHAs.

Figure 3 FTIR spectra of SDB terpolymers.

Pb(II) removal studies

Preparation of metal ion solution

Stock solutions (1000 mg L^{-1}) of lead were prepared by dissolving analytical reagent grade Pb(II) nitrate in HNO$_3$ in proportion 1 : 1. Then 10 mL concentrated HNO$_3$ and double distilled water were added.

Adsorption studies

Pb^{2+} and other species of Pb(II) were reported to potentially exist in water depending on pH. Without electrolytes, the Pb^{2+} species exists at various pH values.[13] At pH 2.85 to 6.01, Pb^{2+} exists at > 89% of total Pb(II), indicating its predominance in acidic solution. The species of Pb(OH)$_2$, Pb(OH)$_3$, Pb$_2$OH^{3+}, Pb$_3$(OH)$_4{}^{2+}$, and Pb$_4$(OH)$_4{}^{4+}$ do not virtually exist in acidic solution.[14] At pH values higher than 7, Pb^{2+} precipitation occurred simultaneously.[15]

In some of the studies, it was noticed that in acidic pH range the adsorption capacity of various adsorbents for Pb(II) increased with increasing pH, reaching plateau values at around pH 4–6.[1,16–19] Moreover, humic acid is soluble in dilute alkaline medium. Hence, in this study the pH was adjusted to 4.0 as acidic and 7.0 as neutral condition and high pH values were not studied. pH adjustments were made with HNO$_3$ and NaOH.

The adsorption behaviors of Pb(II) onto adsorbents were studied as a function of initial concentration of the adsorbate, pH and contact time in flasks with 100 mL liquid volume. 100 mL solutions containing 10, 20, 30, 40, 50, 60 mg L^{-1} Pb(II) were prepared; 0.05 g polymer was added into each flask; the flasks were placed in a shaker; and they were shaked at 220 rpm at 20°C ± 2°C constant temperature. The change of Pb(II) concentration was followed against time until equilibrium was reached. In all flasks, 240 min was found sufficient to reach equilibrium.

Desorption of Pb(II)

Desorption studies were performed with the polymer which resulted in the highest Pb(II) adsorption per-

formance. After the separation of polymer from the adsorption equilibrium solution in the experiments for polymer, regeneration solutions were added to replace the adsorbed Pb(II). KNO$_3$, HCl, EDTA, and CH$_3$COONa (NaAc) were tried as regenerants for desorption. 0.05 g polymer was regenerated in 50 mL, 0.1M solutions of each chemical. The suspensions were shaken for 24 h at 20°C ± 2°C constant temperature and 1 mL aliquots were taken for Pb analysis.

Adsorption competition

Adsorption competition studies were also performed with the polymer which resulted in the highest Pb(II) adsorption performance. To indicate the adsorption selectivity of the polymer to metals the adsorption competition experiments were performed with a multimetal solution, which was prepared with Pb(II), Fe(II), Cu(II), Co(II), Zn(II), Cr(II), and Mg(II) ions. The concentration of each ion in the mixed solution was 60 mg L^{-1}. 0.1 g polymer was added into a flask containing 200 mL multimetal solution. The flask was placed in a shaker and shaked at 220 rpm at 20°C ± 2°C. The aliquots were taken at varying time periods, and change of each metal concentration was followed against time until equilibrium was reached.

The adsorption capacities, the distribution ratios, and the selectivity coefficients were calculated using the following equations:

$$q_e = (C_o - C_e).V/W;$$
$$D = q_e/C_e;$$
$$\alpha = D_{Pb}/D_{Me};$$

where, Q is the equilibrium adsorption capacity (mg g^1), C_o and C_e are the initial and equilibrium concentrations of metal ions (mmol L^{-1}), W is the mass of adsorbent (g), V is the volume of metal ion solution (L), D is the distribution ratio (L g^{-1}), α is the selectivity coefficient.

Analyses

Pb(II) measurements were performed by an atomic absorption spectrometer GBC SensAA model with an air-acetylene flame (air and acetylene flow rates of 7 and 2 dm^3 min^{-1}, respectively). The pH measurements were made on JENWAY model pH meter, 3305-digital. NUVE SL 350 mechanical shaker having speed control facility was used for batch studies.

RESULTS AND DISCUSSION

Characterization of adsorbents

Figure 2 shows FTIR spectrum of IHA's. IHA's were formed from condensed aromatic systems having double bonds of quinoid type inside of their
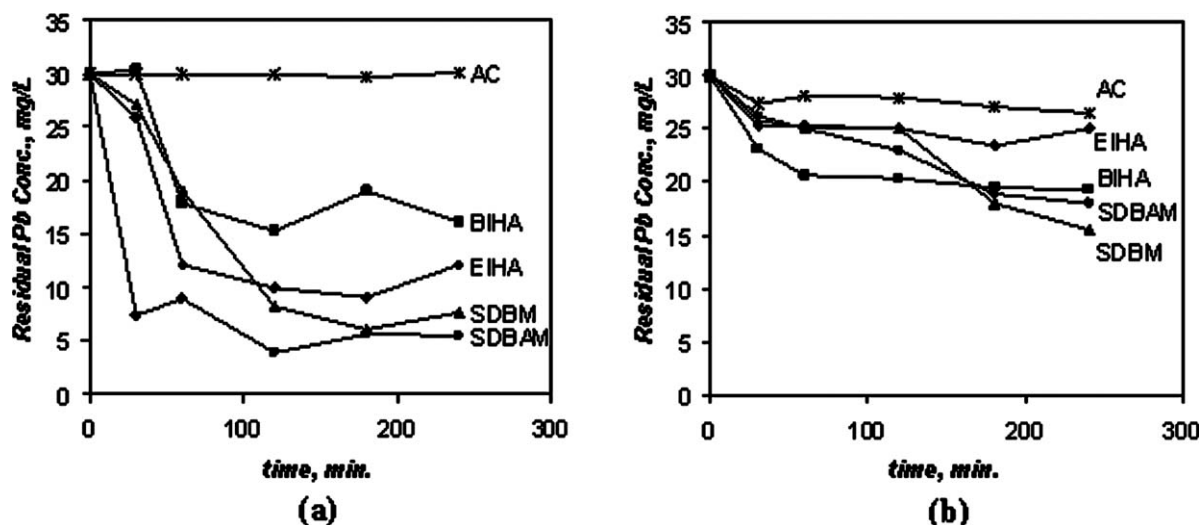
Figure 4 Change of Pb(II) removal with time: (a) in acidic medium; (b) in neutral medium (amount of polymer 0.05 g; volume of sorption medium 100 mL; temperature 20°C ± 1°C; stirring rate 220 rpm; initial metal concentration 30 mg L^{-1}).

molecular structure [Fig. 1(a)]. Strong peaks were observed in both ranges of the spectrums. These indicated that Konya lignite is rich in humic acids. Major spectra bands were assigned as follows: 3420 cm^{-1} (N-H stretching and OH stretch of OH groups), 1693 and 1717 cm^{-1} (carboxyl and ketonic carbonyl stretching), 1616 cm^{-1} (aromatic C=C and conjugated carbonyl C=O), 1396 and 1399 cm^{-1} (antisymmetric stretching of COO, O—H deformation, C=O stretching of phenolic groups and aliphatic C—H deformation) and 1200 cm^{-1} (—O—CH$_3$ group, C—OH stretching of aromatic groups and C—O—C stretching of aryl ethers and phenols).[20–24]

To confirm the copolymerization of methacrylic acid and allylmethacrylate with styrene and divinylbenzene [Fig. 1(b)] and the functional groups of terpolymers, FTIR spectra of SDBM and SDBAM were compared in Figure 3. Both terpolymers showed medium to very weak peaks of aromatic C—C multiple bonds stretching at 1580 and 1600 cm^{-1}. In the FTIR spectrum of SDBM the peak at 3100–3160 cm^{-1} shows the —OH group of acid and existence of peak at 1700 cm^{-1} indicate C=O group of acid. Compared with the spectra of SDBM, the new characteristic bands in the spectrum of SDBAM at 1730 cm^{-1} and 1160 cm^{-1} attributing to the ester C=O and C—O stretching of (—CO—O—) appeared. Further the absorption band at 3080 cm^{-1} due to =CH$_2$ group vibration. The absorption bands at 1454 and 1375 cm^{-1} were attributed to —CH$_2$ and —CH deformation and bending vibration. The absorption band near 3080 cm^{-1} was caused by the stretching vibrations of the vinyl group.

Pb(II) removal

Effect of contact time

The effect of contact time on the adsorption of Pb(II) ions onto IHAs and SDB based polymers was stud-

ied by taking 0.05 g resin with 100 mL of the 30 mg L^{-1} metal solution in different stoppered flasks at initial solution pH 4 or 7. The flasks were shaken for different time intervals (30–240 min) in a temperature controlled shaker.

Figure 4 indicates the change of Pb(II) concentration with time for all studied adsorbents under neutral and acidic pH conditions. In both conditions, the metal sorption proceeds with time with a rapid decrease in the first 60 min in acidic and 120 min in neutral pH after which adsorption of metal ions reached the plateau. The initial adsorption rate was very fast may be due to the existence of greater number of polymer sites available for metal ions adsorption. As the remaining vacant surface sites decreasing, the adsorption rate slowed down due to formation of repulsive forces between the metals on the solid surface and in the liquid phase.

Effect of pH

The removal of metal ions from aqueous solution by adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate.[25] Weak acid cation adsorbents are much dependent on pH value of solution. Weak acid cation adsorbents are nonionized at low pH value of solution and cannot be operated for long time below a pH of 2.0.[26] Liu and Erhan reported that the sorption of divalent metal ions on ESOT-II resin to fall drastically at pH levels below 3. These results were in agreement with the observation that weakly acidic ion-exchange resins absorb hydrogen ion more strongly than corresponding metal ions. Therefore, the addition of H$^+$ ions in a slight excess to the solution may displace all other cations from
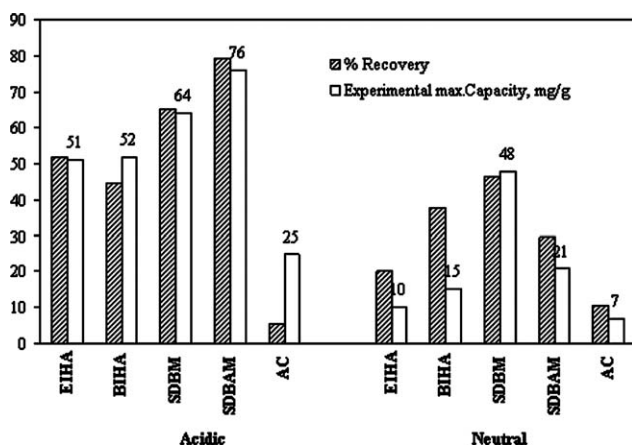
Figure 5 Comparison of Pb(II) recovery performances of all conditions.

the resin.[27] Pehlivan and Altun[28] determined that Pb(II), Cu(II), Zn(II), Cd(II) and Ni(II) ions were poorly adsorbed at pH < 4 for weak acid cation exchange resins. Martyniuk and Wieckowska[24] reported that even at pH (3.5–5.4), the Pb, Ag, Hg, and Cu ions would react with humic acids's carboxylic and phenolic groups as well. Kerndorff and Schnitzer[9] studied adsorption of 11 metal ions on humic acids within the reaction range of pH 4.4–5.8. Polymers used in this study, such as IHAs and SDBM had weak acid groups. In reactions of IHAs with metal ions, the main part was carboxylic groups. Based on data from the literature, the pH values below 4 and above 7 were not studied in this study. Average recoveries were calculated from the results and compared with experimental maximum capacities in Figure 5. Both were parallel to each other and indicated that acidic conditions enhance the Pb(II) adsorption.

IHAs found effective with adsorption capacities 52 mg g^{-1} for Beysehir IHA and 51 mg g^{-1} for Ermenek IHA for Pb(II) removal under acidic pH conditions; adsorption capacities of IHAs under neutral pH conditions were 15 mg g^{-1} and 10 mg g^{-1}, respectively. This can be explained with the chemical structure of IHA. The basic structural units of humic acid are aromatic rings and alkyl chains contain a wide variety of functional groups [—COOH, —OH, —NH$_2$, as seen in Fig. 1(a)]. These groups can bind strongly to metals and give humic acid a high adsorption capacity for metals. The metal ions bind to humic matter through oxygen-containing groups, especially enolate and carboxilate groups. Single-valenced ions are removed with a simple cation-exchange by carboxyl salts, while multi-valenced cations can compose coordinated bonds with organic molecules. Examination of IR spectra of metal-humic preparations showed that metal ions react mainly with carboxylic groups of the humic acids.[24] Accord-

ing to Manunza et al.,[29] the considerable affinity of the Pb(II) ions to humic acids was attributed to their easy complex formation. The formation of Pb-HA complexes occurs more readily at low pH regions.[30] Alvarez-Puebla et al.[31] have found that in FTIR spectrum for pH 4.11, the increase of asymmetric and symmetric COO stretchings and the reduction of the O-H stretching of H-bonded, C=O stretching and C—O stretching and O—H deformation in COOH suggest that the formation of complexes with carboxylic acid groups is the preferred adsorption mechanism.

In our previous study, the carboxylic group contents of prepared IHAs were determined as 13.55% for Beysehir and 11.58% for Ermenek IHA.[32] Accordingly the slightly higher affinity of BIHA in both pH for Pb(II) ions was observed. But it was observed that for the BIHA and EIHA in acidic medium 1.8 and 1.42 meq g^{-1} COOH groups, in neutral medium 2.52 and 2.22 meq g^{-1} COOH groups were unbound. These groups were probably hidden and inaccessible for metal ions coordination in the macromolecular matrix of IHA.[33]

SDBM also contains carboxyl groups [see Fig. 1(b)] and metal ions mainly bound to these. The adsorptive capacity of SDBAM and SDBM were found experimentally as 76 and 64 mg g^{-1} under acidic, 21 and 48 mg g^{-1} under neutral conditions respectively, which are considerably good quantities (Fig. 5). SDBM recovered Pb(II) better than SDBAM under neutral conditions but at low pH vice versa. The performance of both synthetic polymers was higher at low pH. This may be arisen from structural difference indicated in Figure 1(b).

The order of the performance for all adsorbates was SDBAM>SDBM>BIHA≈EIHA>AC for acidic and SDBM>SDBAM>BIHA>EIHA>AC for neutral pH medium. As seen from Figure 5, there was a considerable effect of solution pH on the adsorption of Pb(II). It was strongly adsorbed in acidic medium on all four polymers, indicating their very high complexation ability for Pb(II) and SDB terpolymers were better adsorbents for Pb(II). This can be explained as follows: at lower pH value, H$^+$ ions at higher concentration compete with heavy metals for the negatively charged sites of carboxylic acid groups of polymers. But at higher pH value such as pH 4, H$^+$ ions which are at lower concentration than pH 2–3, are binding on negatively charged sites of polymers and they are exchanged by positively charged heavy metal ions. As the pH increased above 4–5, there would be a decrease in the positive surface active sites, which would lower the electrostatic repulsion between the positively charged heavy metal ions and the surface of the adsorbent, thus favoring adsorption. The decrease of the amount of removed metal ions at higher pH, may be accounted for the diminution of free ions due to

TABLE I
Sorption % Values of Pb(II) in Different Initial Metal Concentrations in Acidic Medium (Polymer Amount 0.05 g; Solution Volume 100 mL; Time 240 min)

Polymers	Initial Pb(II) concentrations, mg L^{-1}					
	10	20	30	40	50	60
SDBAM	95	94	83.3	72.5	72	64.1
SDBM	60	70	73.3	61.3	64	51.6
BIHA	45	55	60	52.5	46	39.2
EIHA	40	47.5	45	42.5	42	41.6
AC	0	5	0	0	4.5	0

TABLE II
Sorption % Values of Pb(II) in Different Initial Metal Concentrations in Neutral Medium (Polymer Amount 0.05 g; Solution Volume 100 mL; Time 240 min)

Polymers	Initial Pb(II) concentrations, mg L^{-1}					
	10	20	30	40	50	60
SDBAM	45	30	36.6	36	23	14.6
SDBM	65	42.5	48.3	43.7	41	40
BIHA	25	20	18.3	15	12.5	11.6
EIHA	7.5	7.5	10	8.7	8	7.5
AC	25	2.5	8.3	5	2	5

formation of soluble hydroxyl complexes, too.[34] It is important to mention that the commercial AC used in the study was unable to adsorb Pb(II) under both pH conditions. A significant improvement in the separation of Pb(II) was observed with natural and synthetic polymers.

Effect of initial metal concentration

Adsorption (ion exchange) of the acidic groups increases with atomic number, valence and degree of ionization of the exchange metal ion. The ionic radius changes in the order of Ni^{2+} <Cu^{2+} <Zn^{2+} <Cd^{2+} <Pb^{2+}.[35,36] Small ions, which have a higher charge density can bound more strongly.[37] To investigate effect of initial metal concentrations on adsorption percentage, 0.05 g polymer was used. The effect of the initial Pb(II) concentration on the Pb(II) adsorption capacity of the polymers at 293 K and pH 4 or 7 was studied with a contact time of 240 min. The results given in Tables I and II indicated that with increasing initial Pb(II) concentration, the adsorption percentage decreased, whereas the residual Pb(II) concentration increased. The percentages of sorption in acidic medium were signifi-

cantly higher than neutral. The results indicated that the most suitable metal concentration for maximum recovery of Pb(II) ions was 20 mg L^{-1}.

Adsorption isotherms

The ion-exchange isotherms were plotted between the capacity (mg g^1) and the amount of metal ions left in equilibrium solution, C_e, mg L^{-1}. Resultant isotherm curves were given in Figure 6 for both neutral and acidic conditions. The isotherm curves for neutral and acidic conditions were similar to each other and correspond to a favorable adsorption under both conditions. Resultant capacities under neutral conditions were lower than capacities under acidic conditions. Adsorption capacities of all synthesized adsorbents were higher under acidic conditions. The highest recovery capacity was determined for SDBAM.

The determination coefficients (R^2) of the data fittings to each adsorption model were indicated in Table III together with the values of the characteristic parameters for both isotherm models. According to R^2 both models provided reasonable fittings for the data of Pb(II) adsorption of the polymers but not
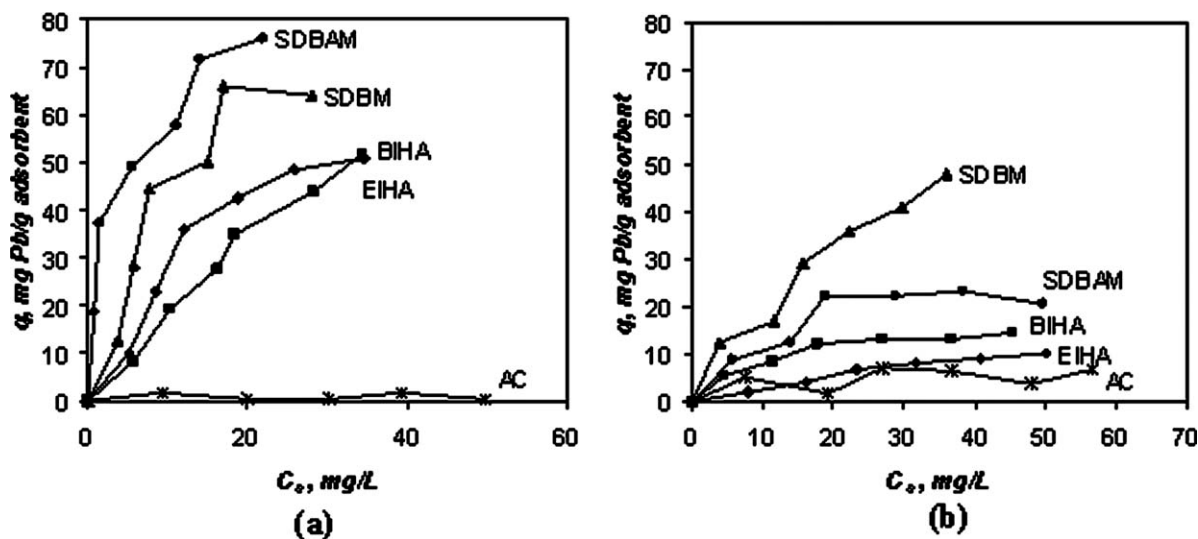

Figure 6 Isotherm curves for: (a) acidic; (b) neutral conditions.

Condition	Adsorbent	Langmuir isotherm			Freundlich isotherm		
		b	q_m	R^2	K	$1/n$	R^2
Neutral	EIHA	0.009	35	0.662	1.52	0.86	0.976
	BIHA	0.101	18	0.989	1.65	0.42	0.945
	SDBM	0.030	87	0.685	1.99	0.63	0.931
	SDBAM	0.101	27	0.909	1.88	0.46	0.786
	AC	0.036	9	0.245	1.49	0.19	0.059
Acidic	EIHA	0.023	123	0.536	3.43	0.82	0.879
	BIHA	0.002	833	0.036	1.64	1.00	0.971
	SDBM	0.046	125	0.604	2.28	0.76	0.818
	SDBAM	0.332	84	0.978	4.07	0.37	0.905
	AC	0.009	2	0.014	2.36	0.58	0.040

for AC. AC fit neither of them as it was unable to adsorb Pb(II). The structural differences of polymers affect the adsorption mechanisms. EIHA and SDBM fit Freundlich model, which indicates the heterogeneous multilayer adsorption, under both acidic and neutral conditions. Heterogeneous adsorption energies at mutlilayer physical adsorption increased under acidic conditions which is represented by higher sorption capacity constant (K). Sorption intensities were not affected from pH conditions as $1/n$ constants were close to each other. SDBAM fit Langmuir model, which represents monolayer, homogeneous coverage by chemical forces, under both conditions with a much higher maximum Pb(II) adsorption capacity at acidic pH as 84 mg g^{-1} (Table III). These findings were parallel to the literature.[38–40] BIHA exerted the unsteady behavior such that the homogeneity under neutral conditions was shifted to heterogeneity with acidification and possess an acceptable Freundlich model. The polymeric adsorbents predominantly consist of functional groups such as —COOH, —OH, —NH$_2$ etc. These all have negative charges on the surface and have tendency to form metal complexes. Changes in these structures with acidification changed the adsorption properties resulting in different isotherm model.
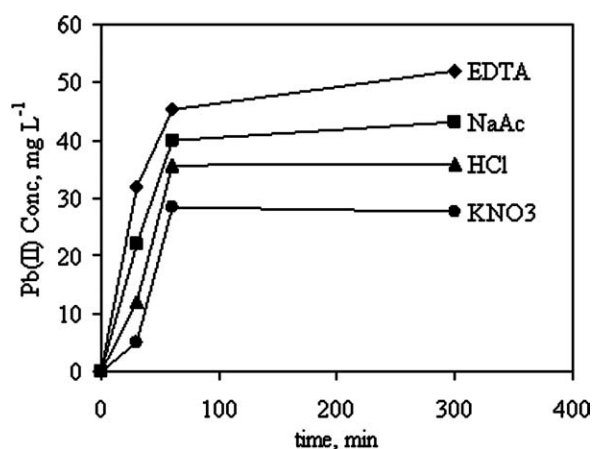

Figure 7 The desorption via alternative regenerant solutions (0.1M each).

Desorption of Pb(II) from the polymers

The effectiveness of the desorption chemical depends upon the mechanism of adsorption. If the ions were adsorbed by their electrostatic attraction to the polymer, they can be desorbed by KNO$_3$ which is an unbuffered salt.[41] The HCl was used to elute metal ions adsorbed through chemical interaction as electrostatic or covalent interaction.[42] EDTA is a common chelator, which can bind metals via the formation of covalent bonds; the NaAc is a strong electrolyte to show the amount of ion-exchange.[43]

Because of highest capacity SDBAM was used for desorption and competition studies. About 90% desorption could be achieved by 0.1M EDTA solution in 5 h (Fig. 7). The desorption percentages of other chemicals were 73%, 60%, and 49% for NaAc, HCl, and KNO$_3$, respectively, in 5 h. The highest percentage in EDTA and lower percentage in NaAc may suggest that Pb(II) adsorption is predominately determined by complexation with organic ligands, whereas ion-exchange effect merely accounts for a small part of adsorption mechanism. The desorption percentage of Pb(II) in KNO$_3$ represent the relative contribution of the electrostatic adsorption to the total adsorption.

A desorption study is also important because it is useful in the recycling of the adsorbent and recovery of heavy metals. The results (Fig. 7) indicated that Pb(II) adsorption was reversible and can be desorbed easily by using EDTA. The polymer was used in the second cycle adsorption after desorption in the EDTA solution,

TABLE IV
Adsorption Competition in Multimetal Solution

Metal	q_e (mg g^{-1})	D (L g^{-1})	α
Pb(II)	81	8.44	1
Zn(II)	21	0.66	13
Fe(II)	20	0.40	21.1
Cu(II)	5	0.11	77
Mg(II)	1.22	0.69	12.2
Cr(II)	0.38	0.05	169
Co(II)	0.19	0.02	422

TABLE V
Comparison of the Results with Other Styrene Based and Natural Polymers

Adsorbent	Condition	Max. Pb(II) Adsorption capacity (mg g^{-1})	Reference
Humic acids		220–262	Martyniuk and Wieckowska[24]
Macroreticular SDB copolymer beads grafted with various poly(ethylene glycols) and containing thiol groups as chelating functions		3.3	Lezzi et al.[44]
Poly-SDB based resin functionalized with bis-(N,N'-salicylidene) 1,3-propanediamine ligands		79	Dev and Rao[45]
Polystyrene microbeads modified with dithiocarbamate		6.2	Denizli et al.[46]
Humic acid isolated from soil	pH 4	33.22	Baker and Khalili[47]
	pH 5	39.21	
SDBAM	pH 4	84	This study
SDBM		64	
BIHA		52	
EIHA		51	

and the Pb(II) adsorption capacity was calculated as 73 mg g^{-1}, which is sufficiently close to the first cycle capacity indicated in Figure 5. Thus the polymer can be employed repeatedly in the Pb(II) adsorption.

Adsorption competition

As shown in Table IV, the q$_e$ and D value of SDBAM for Pb(II) were 81 mg g^{-1} and 8.44 L g^{-1}, respectively. These high values decreased significantly for Zn(II), Fe(II), Cu(II), Mg(II), Cr(II), Co(II). The higher the q$_e$ and D the higher the selectivity of the adsorbent to that metal. The nearest competing metal to the Pb(II) was Zn(II) with 21 mg g^{-1} capacity.

α, the selectivity coefficient, was calculated from Pb(II) point of view as the ratio of distribution ratio (D) of Pb(II) to D of each metal, therefore, it was 1 for Pb(II) itself. If all these α values in Table IV were close to and/or less than unity that would indicate strong adsorption towards variety metal ions without selectivity, or random distribution of ligand functionalities in the polymeric network. However, α value for all other metals were much higher than unity [e.g., 12.2 for Mg(II) and 422 for Co(II)]. This demonstrated that synthesized SDBAM had a higher selectivity for Pb(II).

Comparison with other studied polymers

In the literature, various styrene-based and natural polymers have been studied with a wide range of adsorption capacities for Pb(II) ions.[24,44–47] The results of this study are compared with them in Table V. The sorption capacities of the present polymers are varied in the range of 51–84 mg g^{-1} for acidic and 10–48 mg g^{-1} for neutral pH conditions. Therefore, the synthesized polymers exhibited better capacity values in comparison to most of the other styrene based and natural polymer adsorbents.

CONCLUSIONS

Two natural and two synthetic polymers were synthesized and their structures were determined. Adsorption of Pb(II) onto lignite-synthesized IHA's (as natural polymers) and SDB-based synthesized terpolymers were studied in neutral and acidic conditions. The time required to reach equilibrium was 60 min in acidic and 120 min in neutral pH medium for all adsorbents. Adsorption capacities of all synthesized adsorbents were higher than activated carbon under acidic conditions. The order of the performance for all adsorbates was SDBM>SDBAM>BIHA>EIHA>AC for neutral and SDBAM>SDBM>BIHA≈EIHA>AC for acidic pH medium. General isotherm tendencies were to Freundlich model, whereas SDBAM fit Langmuir model in all pH conditions. SDBAM was the polymer achieved to the highest Pb(II) adsorption capacity, 84 mg g^{-1}. The 90% desorption could be achieved via 0.1M EDTA solution in 5 h, and the SDBAM polymer can be used repeatedly in Pb(II) adsorption in acidic medium. Selectivity of SDBAM to Pb(II) in multimetal solution was also investigated with higher distribution ratio and lower selectivity coefficient.

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