Synthesis and Characterization of Sulfonylamberlite-XAD-16-Based Chelating Resins: Complexation and Application for the Selective Removal of Some Heavy Metals

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Modification of Amberlite XAD-16 using chlorosulfonic acid, aminosalicyclic acid, and formylsalicyclic acid to produce the functionally substituted polymer was investigated to give two ligands, H_2L^1 and H_2L^2. The synthesis and characterization of polymer-bonded metal complexes of Fe^{3+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} with resins of functionalized Amberlite XAD-16 were described. The morphology and surface structure of the chelating resins and their metal complexes were studied by SEM and EDS techniques. The batch equilibrium method was used for studying the metal sorption and selectivity at different pH values and different contact times at room temperature. The sorption tendency of the metal ions through the two resins was found to be: $Fe^{3+} > Hg^{2+} > Cd^{2+} > Pb^{2+}$. Adsorption kinetics was explained based on pseudofirst-order and pseudosecond-order models. The data showed that the sorption of Fe^{3+} and Pb^{2+} on the chelating resins H_2L^1 and H_2L^2 perfectly fit a pseudofirst-order model, while Hg^{2+} and Cd^{2+} perfectly fit a pseudosecond-order model. The selective extraction of Fe^{3+} from binary $Fe^{3+}-Hg^{2+}$, $Fe^{3+}-Cd^{2+}$, and $Fe^{3+}-Pb^{2+}$ mixtures was studied, and the data showed that separation factors ($K_{Fe^{3+}/M^{2+}}$) are in the order $Fe^{3+}-Hg^{2+} < Fe^{3+}-Cd^{2+} < Fe^{3+}-Pb^{2+}$ for both chelating resins. The resins were used to determine the different metal ions in real water samples.

Introduction

The tremendous increase in the use of heavy metals during the last few decades has led to the increase of metallic contents in the environment. Solid phase extraction (SPE) is one pretreatment method, which has been widely used in the analysis of various samples[1−4] and in the field of wastewater[5,6] enrichment of trace metal ions prior to instrumental analysis,[7] solvent purification from ions, and hardness removal from seawater.[8−10] In addition, SPE using chelating resins is preferable over all other separation techniques due to the selectivity, eco-friendliness, reusability, and high preconcentration factors.[11−15] The selectivity of a chelating resin for metal ions is mainly referred to the nature of the immobilized structure of the polymer matrix.[16] However, since ligand groups are chemically bound to the rigid polymer matrix, their free motions are greatly restricted. As a result, the complex formation of a chelating resin tends to be different from that observed in the homogeneous analogue.[17,18] Tanco et al.[5] and Kumagi et al.[19] have reported the synthesis, metal uptake, and selectivity of different chelating resins with different spacer groups.

Polymer modification has become a major mechanism to improve properties and widen polymer application. The modification of Amberlite is a method used to enhance the performance where it converts the Amberlite into a functionally substituted polymer, which improves its metal uptake and ion selectivity. Commercially available resins of the Amberlite series[20−23] have been found to be very promising as a support for designing chelating resins due to their good physical properties such as their porosity, uniform pore size distribution, high surface area, chemical homogeneous nonionic structure, and good adsorbent properties for great amounts of uncharged compounds. The most widely used matrix materials for immobilization of ligands are Amberlite XAD-2, XAD-4, and XAD-16. Amberlite XAD-16 upon ligand immobilization gave chelating resins of better sorption capacities than the others[24,25] due to its higher surface area. To design new chelating resins with high selective and metal capacities toward different metal ions, the extraction process can be made green by replacing the use of large quantities of carcinogenic solvents, which are used in a liquid−liquid extraction, with the reuse of the modified resin. In continuation of our research in this area, we aim to (i) synthesize and characterize the newly created chelating resins (H_2L^1, H_2L^2), (ii) study their ligating behavior toward different metal ions, (iii) study their metal sorption capacities and selectivities under different conditions, and (iv) study the use of these chelating resins for the sorption of trace metals from Gulf water samples.

Experimental Section

Materials and Solvents. All chemicals used in this work were of analytical grade from Merck (Darmstadt, Germany). Commercially available Amberlite XAD-16 was obtained from Aldrich and was thoroughly washed with 4.0 M HNO_3, 1.0 M NaOH, and double-distilled water successively and well dried before use. Ethylenediamine, 4-aminosalicylic acid, 5-formylsalicylic acid, and chlorosulfonic acid, $Cd(NO_3)_2\cdot 4H_2O$, $Hg(NO_3)_2\cdot H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, and $Pb(NO_3)_2$, were purchased from Aldrich and used without further purification. Working metal ion solutions (0.1 M) of Fe^{3+}, Cd^{2+}, Pb^{2+}, and Hg^{2+} were prepared by dissolving $Cd(NO_3)_2\cdot 4H_2O$, $Hg(NO_3)_2\cdot H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, and $Pb(NO_3)_2$ in acidified double distilled water. The glassware used was soaked in 10 % HNO_3 overnight before use and cleaned repeatedly with double distilled water.

Elemental Analysis and Physical Measurements. CHN analysis was performed on a LECO CHNS-932 elemental analyzer. The concentration of the metal ions was determined

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by an inductively coupled plasma optical emission spectrometer (ICP-OES Varian Vista-MPX ICP-OES system, axial ICP system), and the wavelength used for the analysis of Fe^{3+}, Cd^{2+}, Pb^{2+}, and Hg^{2+} was in the range of (200 to 700) nm. The instrument is calibrated by using ICP standards (Inorganic Ventures) for all metals that were analyzed. The process of calibration needs 5 min, and the correlation coefficient of the calibration curves is confirmed to be greater than 0.995. A few drops of 1 % HNO_3 were added to all standard samples to avoid any matrix interference. A digital Orion pH/ISE meter, model 710 A, was used for the pH measurements. The pH values of the solutions were adjusted with monochloroacetic acid/acetate buffer in the pH range of 2.5 to 4, acetate buffer in the pH range of 4 to 7, and ammonia−ammonium chloride in the pH range of 7 to 10. Hydrochloric acid and sodium hydroxide were used to adjust the pH below 2.5 and above 10, respectively. Fourier Transform Infrared (FT-IR) spectra of the chelating resins and their complexes as KBr discs were recorded with a Schimadzu 2000 FT-IR spectrophotometer. Electronic spectra of the chelating resins and their complexes were recorded with a Cary Varian 5 UV/vis/NIR spectrophotometer. The shapes and surface morphology of the resins and their metal complexes were examined on a JEOL's JSM-3600 Scanning Electron Microscope (SEM) and the attached Energy Dispersive Spectroscope (EDS) for elemental X-ray microanalysis. Thermal analysis (TG and DTG) of the ligands and their complexes was carried out on a Shimadzu Thermal system 50 consisting of TGA-50 and DTA-50 with a heating rate of 10 °C·min^{-1} under N_2 atmosphere and temperature range up to 800 °C.

Synthesis of the Chelating Resins. (a) Synthesis of Chlorosulfonated Polystyrene, PS−SO_2Cl.[21] To a swelled Amberlite XAD-16 (5 g) in $CHCl_3$ (50 mL) for 2 h, $ClSO_3H$ (50 mL) in $CHCl_3$ (50 mL) was added, and the mixture was stirred for 24 h at room temperature and then filtered off and washed thoroughly with dry CH_2Cl_2 followed by drying in a vacuum at 60 °C for 72 h.

(b) Synthesis of the Chelating Resins H_2L^1. The dry PS−SO_2Cl (5.0 g) was treated with 4-aminosalicylic acid (3.347 g) in acetone (20 mL). The reaction mixture was refluxed for 48 h. The product was filtered off and washed with acetone (3 × 15 mL) and diethyl ether (3 × 15 mL) followed by drying in vacuum at 60 °C for 24 h.

(c) Synthesis of Aminated PS−SO_2Cl. The dry PS−SO_2Cl (5.0 g) was mixed with ethylenediamine (0.731 mL, 0.657 g) in 250 mL of dry CH_2Cl_2 for 24 h at room temperature. The reaction mixture was then refluxed for a further 48 h. The reaction product was filtered off and washed with dioxane (3 × 5 mL) and double distilled water (3 × 15 mL) followed by drying in vacuum at 60 °C for 24 h.

(d) Synthesis of the Chelating Resins H_2L^2. The dry product of aminated PS−SO_2Cl (5.0 g) was treated with 5-formylsalicylic acid (1.86 g) in acetone or chloroform (20 mL). The reaction mixture was refluxed for 48 h. The obtained product was filtered off and washed with acetone (3 × 15 mL) and diethyl ether (3 × 15 mL) followed by drying in vacuum at 60 °C for 24 h.

Synthesis of the Metal Complexes. The metal complexes were synthesized by two methods.

Method A. To a solution of metal salt, $Cd(NO_3)_2\cdot4H_2O$, $Hg(NO_3)_2\cdot H_2O$, $Fe(NO_3)_3\cdot9H_2O$, or $Pb(NO_3)_2$ ($5\cdot10^{-4}$ mol) in methanol (20 mL) was added H_2L^1 (0.345 g, $6.42\cdot10^{-4}$ mol) or H_2L^2 (0.606 g, $1.02\cdot10^{-3}$ mol). The reaction mixture was refluxed and stirred for 24 h. The obtained complex was filtered, washed by methanol (5 × 10 mL) and diethyl ether (10 × 10 mL), and then dried in vacuum at 60 °C for 24 h.

Method B. To a solution of $Cd(NO_3)_2\cdot4H_2O$, $Hg(NO_3)_2\cdot H_2O$, $Fe(NO_3)_2\cdot9H_2O$, or $Pb(NO_3)_2$ ($5\cdot10^{-4}$ mol) in double distilled water (100 mL) was added H_2L^1 (0.345 g, $6.42\cdot10^{-4}$ mol) or H_2L^2 (0.606 g, $1.02\cdot10^{-3}$ mol). The reaction mixture was shaken for 24 h. The obtained complex was filtered off, washed by diethyl ether (10 × 10 mL), and then dried in an oven at 60 °C for 24 h.

The complexes were also obtained from the batch method.

Effect of pH on the Metal Sorption. The batch method was used to determine the metal ion uptake from aqueous solution containing $1\cdot10^{-4}$ mmol of Fe^{3+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} ions in triplicate. To a 50 mL of solution of the metal ion (0.002 M) in a stoppered glass bottle, 100 mg of H_2L^1 or resin H_2L^2 was added. The pH of the solution was adjusted in the range of 1.5 to 8.0 for Pb^{2+} and Cd^{2+}, 1.5 to 4.0 for Hg^{2+}, and 1.5 to 4.5 for Fe^{3+}. The mixture was shaken at a shaking rate of 200 rpm at (25 ± 1) °C for 1 h then filtered off. An appropriate volume of each solution of the filtrate was analyzed by ICP-OES. The metal uptake was calculated from eq 1

$$q_t = (C_o - C_t)V/m \qquad \text{mmol}\cdot\text{g}^{-1} \tag{1}$$

where V (L) is the volume of the solution in the flask; C_o and C_t (mmol·L^{-1}) are the concentrations of the metal ion in the aqueous phase at start and at time t, respectively; and m is the mass of the chelating resin (g).

Effect of Shaking Time on the Metal Sorption. The metal sorption capacity was determined in triplicate at an initial pH of 4.0 for Fe^{3+}, 3.6 for Hg^{2+}, and 7.0 for Cd^{2+} and Pb^{2+}, which were determined as the optimum pH values for the metal ions. To 50 mL of solution of the metal ion (0.002 M) in a stoppered glass bottle was added 50 mg of resin H_2L^1 or resin H_2L^2. The whole system was shaken at a constant shaking rate of 350 rpm at (25 ± 1) °C at appropriate intervals in the range of (2 to 120) min and then filtered off. An appropriate volume of each solution of the filtrate of the metal ion was determined by ICP-OES. The kinetic data were analyzed by Vermeulen's approximation.[26]

Separation of Fe^{3+} from Mixtures. To an aqueous solution (25 mL) containing $Fe^{3+}-Hg^{2+}$, $Fe^{3+}-Cd^{2+}$, and $Fe^{3+}-Pb^{2+}$ binary mixtures of 0.1 mg·mL^{-1} of each metal ion, 10 mg of dry resin was added in a stoppered glass bottle. The mixtures were automatically shaken for 30 min. After remaining motionless for 2 h and filtered off with deionized water, the filtrate and washings were recovered into a 100 mL volumetric flask, and deionized water was added to the mark. The concentration of each ion was determined by ICP-OES. The results of the average of triplicate measurements with a precision in most cases are very close to ± 1.1 %. The separating factor K was calculated by using eq 2

$$K = (C_{A1} - C_{A2})C_{B2}/(C_{B1} - C_{B2})C_{A1} \tag{2}$$

where C_{A1} and C_{A2} are the concentration of the metal ion A (Fe^{3+} in this case) before and after separation, respectively, while C_{B1} and C_{B2} are the concentration of the second metal ion (Cd^{2+} and Pb^{2+}) before and after separation, respectively.

Regeneration of the Resins. The regeneration of the resin loaded with a known amount of Fe^{3+}, Cd^{2+}, or Pb^{2+} was performed with a 2.0 M HNO_3 solution. After the heavy metal ions were recovered from the resins, the resins were washed

Table 1. Elemental Analysis of Ligands

	% C	% H	% N	% S
compound	calcd (found)	calcd (found)	calcd (found)	calcd (found)
$[PS{-}SO_2Cl \cdot H_2O]_n$	48.68 (48.36)	4.46 (5.55)	-	12.98 (13.42)
$[H_2L^1 \cdot H_2O]_n$	58.37 (58.92)	4.50 (5.80)	2.60 (2.89)	11.53 (12.00)
$[PS{-}SO_2Cl + en]$	59.40 (59.56)	5.40 (5.26)	6.30 (6.20)	14.40 (13.95)
$[H_2L^2 \cdot 2H_2O]_n$	57.32 (57.30)	5.09 (5.30)	5.09 (4.79)	10.19 (10.12)

with enough distilled water and then regenerated with 2 M HNO_3 solution. These regenerated resins were used again for the retention of the metal ions.

Determination of Metal Ions in Water Samples. A real sample of Gulf water (5000 mL) was preconcentrated to a final volume of 40 mL. The amount of different metal ions was determined by ICP-OES. Three portions of 50.0 mL of the preconcentrated sample were adjusted to pH 6, 5, and 4 and treated with 300 mg of the investigated resins under a shaking rate of 350 rpm for (6 to 24) h. The mixture in each case was filtered and the resin washed several times with doubly distilled water. The results of ICP-OES measurements before and after treatment and the percent sorption of metal ions onto the chelating resins are computed according to eq 3

$$\% \text{ sorption} = [C_i - C_f/C_i] \cdot 100 \qquad (3)$$

where C_i and C_f are the initial and final concentration of the metal ion ($mg \cdot L^{-1}$) before and after treatment, respectively. The results are the average of triplicate measurements, and the precision in most cases is very close to ± 1.6 %.

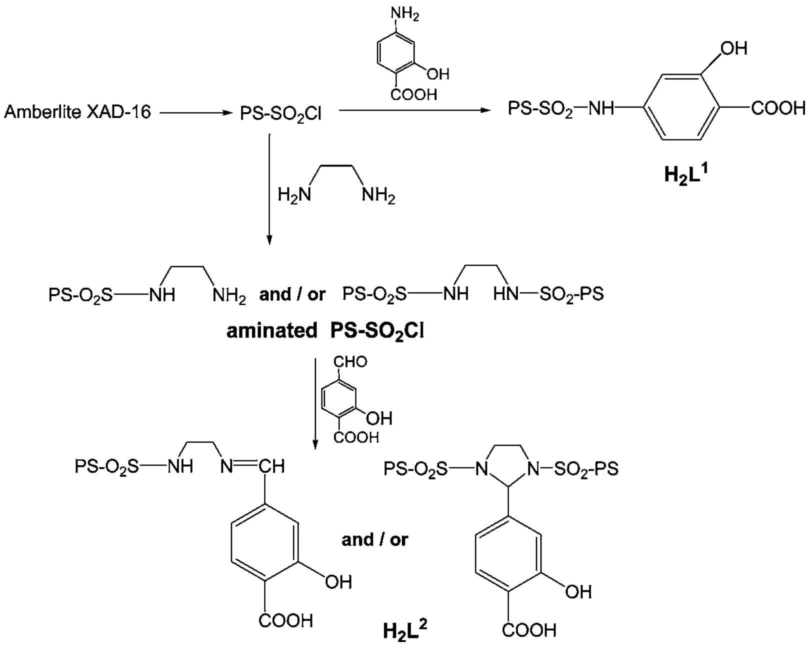
Results and Discussion

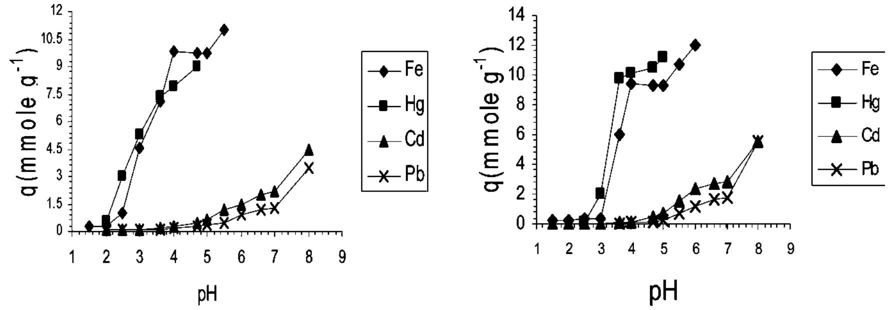
Characterization of the Chelating Resins. Elemental Analysis. Although the sulfonamide hydrogen has low reactivity, a long refluxing time of 24 h assisted this group to react with another chlorosulfonated moiety which is consistent with other published results.[27−32] The elemental analyses of the two chelating resins, H_2L^1 and H_2L^2, are included in Table 1. Both sulfur and nitrogen contents deliver useful information on loading capacities such as, for example, the sulfonyl group contents or diamine or salicylic moieties, respectively. From data presented in Table 1, it is possible to calculate the first step modification of Amberlite-XAD-16 to chlorosulfonated Amberlite, which delivers the product with about 4 mmol of sulfonyl groups per gram. With the neglect ion of possible partial cross-linking of the resin, the second stages of transformation were performed with stoichiometric quantities of ethylenediamine and 4-aminosalicyclic acid. The percentage of conversion is calculated based on the percentage of nitrogen, which was found to be 5.15 and 7.89, respectively. The elemental analysis reflects the formation of compounds H_2L^1 and H_2L^2 according to Scheme 1. $PS{-}SO_2Cl$ was a sulfur analysis of 13.42 %, which agrees with the formula $PS{-}SO_2Cl \cdot H_2O$. Transformation of compound $PS{-}SO_2Cl$ to derivative H_2L^1 was confirmed based on a nitrogen analysis of 2.89 %, which agrees with the structure H_2L^1 in the hydrated form $H_2L^1 \cdot H_2O$. In addition, the percent of nitrogen increases upon using ethylenediamine to 6.20 % in agreement with the aminated $PS{-}SO_2Cl$ structure. Similarly, compound H_2L^2 was confirmed (cf. Scheme 1 and Table 1).

IR Spectra of the Polymer and Modified Polymer. The FT-IR spectrum of aminated $PS{-}SO_2Cl$ displays a broad band at 3430 cm^{-1} which can be assigned to $\nu_{(NH)}$. The spectrum exhibits a weak band at 3045 cm^{-1} due to the aromatic C−H, while those at (2998, 2977, and 2913) cm^{-1} are assigned for the aliphatic C−H. The spectra of resins H_2L^1 and H_2L^2 display broad bands at (3436 and 3433) cm^{-1} for H-bonded OH. The carbonyl of the carboxylic group in both resins is assumed to be involved in a hydrogen bonding of the type $-C{=}O \cdots HO-$ as indicated from its shape and position at (1710 to 1662) cm^{-1}. The bands at (1476, 1450, 897 and 1490, 1456, 889) cm^{-1} for resins H_2L^1 and H_2L^2, respectively, could be taken as evidence for the presence of the sulfonamide moiety in both resins.

Effect of pH on Metal Sorption. The effect of pH on metal sorption of the Fe(III), Hg(II), Cd(II), and Pb(II) ions onto H_2L^1 and H_2L^2 was investigated for fixed concentrations of the four cations and ionic strength. The data obtained are shown in Figure 1. The observed extraction of the metal ions is attributed to the complex formation with the introduced salicylic acid chelating ligand since Amberlite XAD-16 itself does not retain these metal ions. The complexation of the chelating resins with the different

Scheme 1





(A) (B)

Figure 1. Effect of pH on the sorption of Fe^{3+}, Hg^{2+}, Cd^{2+}, and Pb^{2+} by (A) H_2L^1 and (B) H_2L^2.

Table 2. Separation Factors ($K_{Fe^{3+}/M^{2+}}$) of Fe^{3+} over Hg^{2+}, Cd^{2+}, and Pb^{2+}

resin	mg·mL^{-1} of M^{n+}		$Fe^{3+}-Hg^{2+}$		$Fe^{3+}-Cd^{2+}$		$Fe^{3+}-Pb^{2+}$	
H_2L^1	C_{Fe}	C_{B1}	518	520	520	520	520	520
	$K_{Fe/M}$		4.53		42.98		59.32	
	C_{Fe}	C_{B2}	354	486	37	509	38	512
H_2L^2	C_{Fe}	C_{B1}	520	520	520	516	520	519
	$K_{Fe/M}$		2.90		38.53		47.47	
	C_{Fe}	C_{B2}	356	469	43	504	35	509

Table 3. ICP-OES Results of a Gulf Ocean Water Sample before and after Treatment with the Chelating Resins H_2L^1 and H_2L^2 [a]

	H_2L^1			H_2L^2	
metal ion	C_i	C_f	% sorption	C_f	% sorption
[b]Na^+	16427.550	2506.550	84.742	2793.483	82.995
[b]K^+	763.900	178.260	76.664	1144.760	81.049
[b]Mg^{2+}	1611.400	164.580	89.787	213.380	86.758
[b]Ca^{2+}	509.500	16.870	96.689	17.390	96.587
[c]Co^{2+}	2.540	0.273	89.252	ND	
[c]Ni^{2+}	13.750	0.173	98.737	0.838	93.391
[c]Cu^{2+}	13.700	0.154	98.876	0.194	91.285
[c]Cd^{2+}	BDL	ND		ND	
[c]Pb^{2+}	74.200	25.148	66.108	33.997	54.182
[c]Fe^{3+}	1.070	0.014	98.692	0.0138	98.103
[c]Hg^{2+}	15.100	0.885	94.139	0.938	93.788

[a] ND = not detected; BDL = below detection limit. [b] C_i in mg·L^{-1}. [c] C_i in μg·L^{-1}.

metal ions is due to the bonding with the carboxylate−carbonyl oxygen and the hydroxyl−oxygen atoms as proved from the FT-IR spectra of the isolated complexes for these chelating resins.

At low pH (1.5 to 3.0), the metal complex formation is in competition with the formation of the hydronium ion, making the resins unsatisfactory for complexing the metal ion.[33,34] At pH > 4.0, the complexing groups are deprotonated and manage to overcome the hydrophobic effect of the matrix.

The highest metal uptake values were recorded at a pH prior to the precipitation limit of the metal hydroxide, Hg^{2+} (4.0), Fe^{3+} (5.0), Cd^{2+} (8.1), and Pb^{2+} (7.5). The observed sudden increase in the uptake with increasing pH at more than the precipitation limit is attributed to the formation of insoluble metal hydroxides.

The metal capacities of the two resins are similar which could be due to the similarity in the chelating centers, while the spacer arms appeared to have no effect. Both chelating resins have high capacities toward Fe^{3+} and Hg^{2+} but lower capacities toward Cd^{2+} and Pb^{2+}. The capacities can be ordered as: $Fe^{3+} > Hg^{2+} > Cd^{2+} > Pb^{2+}$. This is consistent with the reported formation constants of the free chelating organic ligands with these metal ions. In general, the effect of solution pH on the metal ion retention is due to the modification of both metal ion concentration and the ratio between the acid form (−COOH) and basic form (−COO$^-$) of the carboxylic groups.[35−37]

The effect of the adsorption/desorption cycles on the metal uptake by these two resins showed an increase in the metal capacity of H_2L^1 and H_2L^2 up to two cycles for both. This observation is a positive aspect of these newly synthesized H_2L^1 and H_2L^2 because in most cases the metal capacity of the chelating resins usually decreases upon the regeneration of the resins.[38] The increased metal capacity of these resins upon regeneration could be discussed on the basis of the increased accessibility of the metal ions to the salicylic acid moiety. Furthermore, this result could be assigned to the increase of the chain flexibility in the whole matrix.

Effect of Shaking Time. The variation of shaking time on metal uptake by H_2L^1 and H_2L^2 was studied. Complete saturation was reached for: (i) Fe^{3+} after 30 min at pH 4.0 for both resins, (ii) Cd^{2+} after 50 min at pH 7.0, (iii) Pb^{2+} after 90 min at pH 7.0 for both resins, and (iv) Hg^{2+} after (25 and 20) min for H_2L^1 and H_2L^2, respectively, at pH 3.6. Furthermore, the chelating resins exhibit similar absorption characterization with respect to the four metal ions. It was found that the percent sorption increases with increasing shaking speed and attains a maximum sorption at 350 rpm and decreases again upon increasing the shaking speed more than 350 rpm. Therefore, all other studies are carried out at a speed of shaking of 350 rpm for all metal ions with the two chelating resins.

Sorption Selectivity. The chelating resins H_2L^1 and H_2L^2 are used to study the possibilities of their potential uses for the

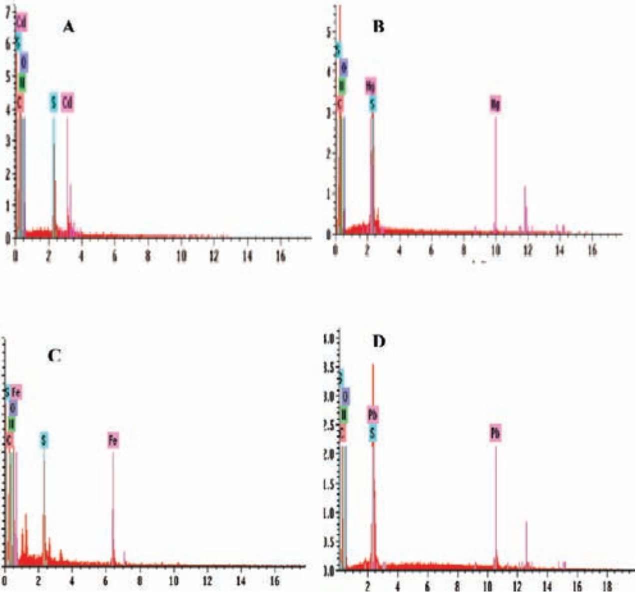


Figure 2. EDS analysis for (A) H_2L^1−Cd, (B) H_2L^1−Hg, (C) H_2L^1−Fe, and (D) Pb.

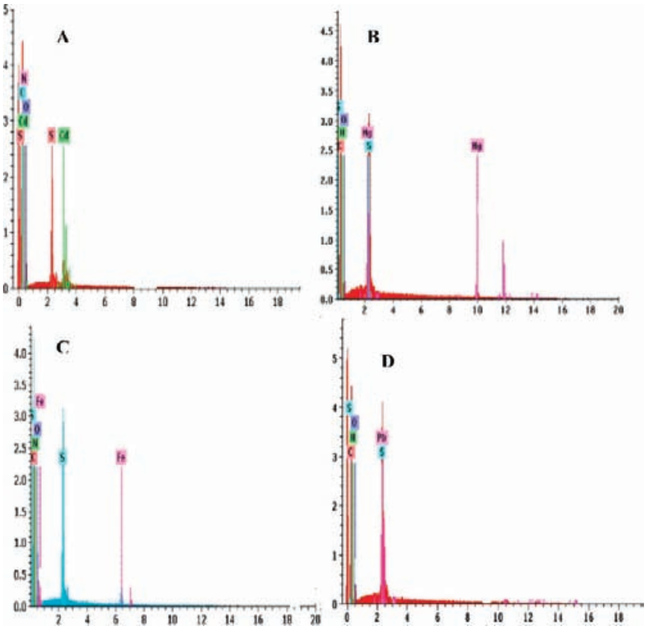


Figure 3. EDS analysis for (A) H_2L^2-Cd, (B) H_2L^2-Hg, (C) H_2L^2-Fe, and (D) H_2L^2-Pb.

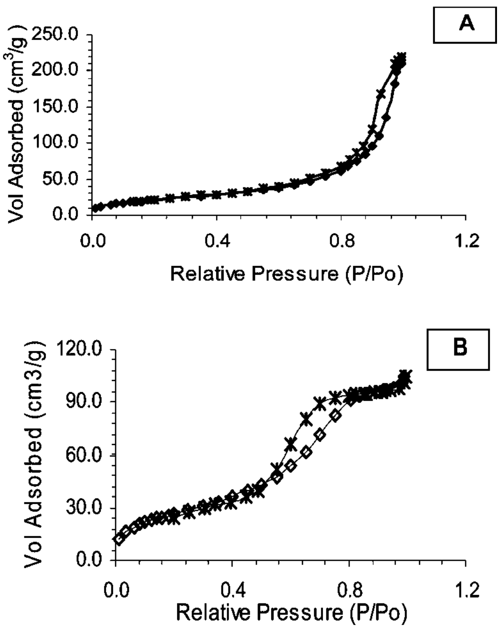


Figure 4. Nitrogen adsorption/desorption isotherms of (A) H_2L^1 and (B) H_2L^2.

selective separation of Fe^{3+} present in binary mixtures with other ions utilizing the batch method. The method was applied for separation of Fe^{3+} from the binary mixtures, $Fe^{3+}-Hg^{2+}$, $Fe^{3+}-Cd^{2+}$, and $Fe^{3+}-Pb^{2+}$ at pH 5 and a shaking time of 30 min. The data given in Table 2 show that: for the same resin, the iron can be separated to an extent of about (92 ± 1) % in the presence of Cd^{2+} or Pb^{2+}. That is to say that iron can be separated to a high extent in the presence of either of these two metal ions. This could be explained on the basis of the interaction of the harder and more strongly polarizing Fe^{3+} ion with the hard donor oxygen atoms in the chelating resins. (ii) The presence of Hg^{2+} retards the separation of Fe^{3+} although it is a soft ion. This could be attributed to the formation of some organo-mercury compounds which compete with the complexation of iron. (iii) For the same binary mixture the values of the separation factors ($K_{Fe^{3+}/M^{2+}}$) are in the order $H_2L^1 > H_2L^2$.

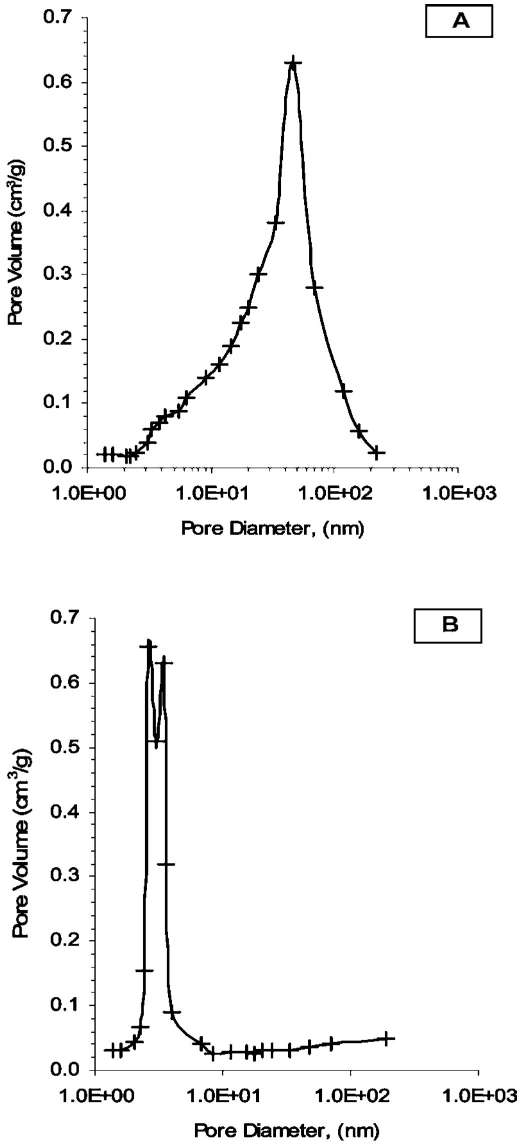


Figure 5. BJH desorption pore size distributions of (A) H_2L^1 and (B) H_2L^2.

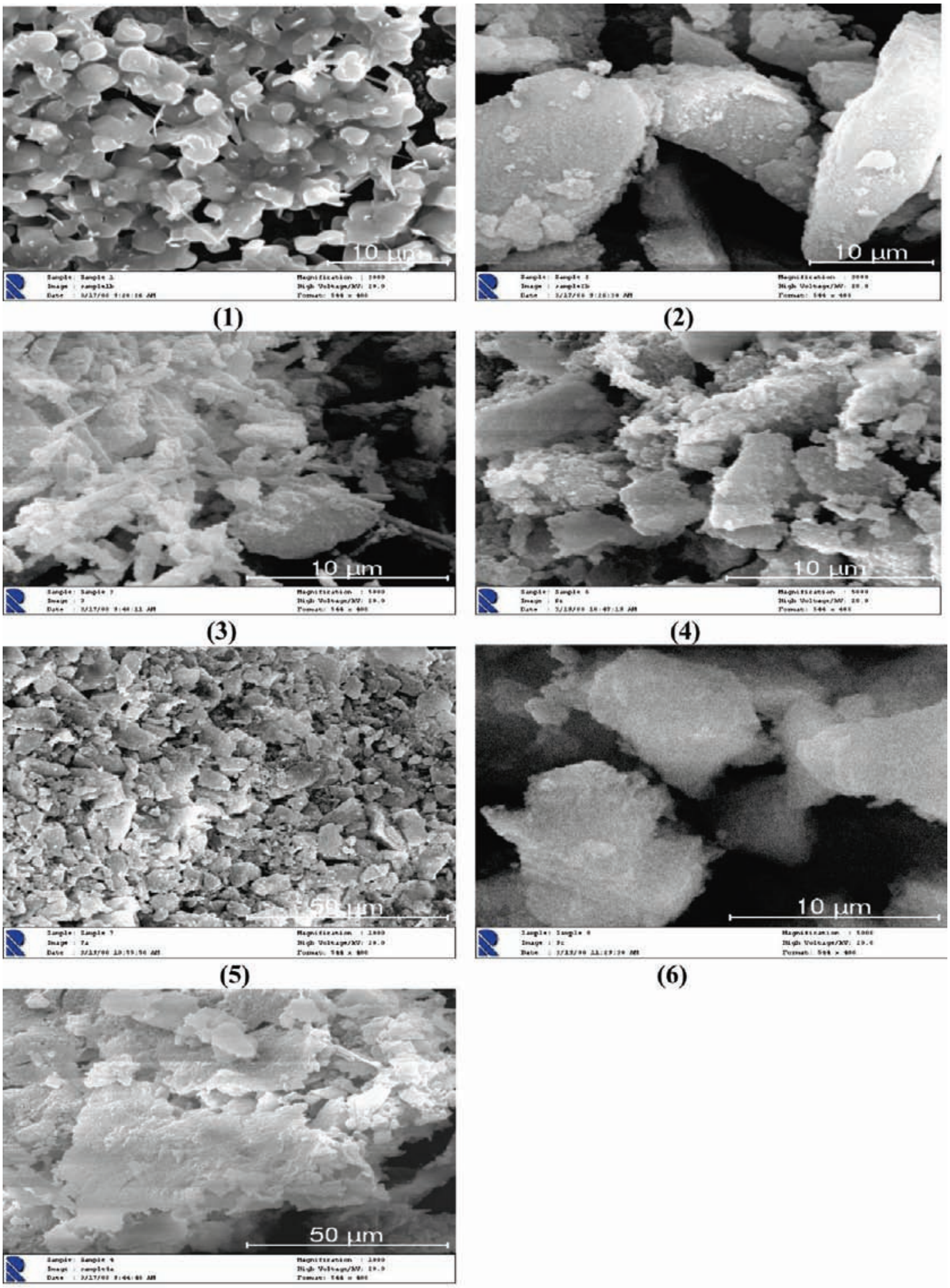
Application of the Chelating Resins for Gulf Ocean Water Analysis. The synthesized and characterized chelating resins were used to determine different metal ions in a real sample of Gulf ocean water. Table 3 shows that the resins are able to remove 11 elements, namely, Na, K, Mg, Ca, Co, Ni, Cu, Cd, Pb, Fe, and Hg from the ocean water.

Thermal Stability. TGA of H_2L^1, H_2L^2, and their metallopolymer complexes has revealed that the weight loss percent (wt %) for the polymers and their complexes over the temperature range (25 to 200) °C is due to the loss of water absorbed or adsorbed within the compound and H-bonding in the polymeric material. The total weight loss was obtained under nitrogen with a heating rate of 10 $°C\cdot min^{-1}$.

The TGA of H_2L^1 and its metallopolymer complexes showed that the thermal stability of Cd is the highest, while the Pb-complex is the lowest. The following arrangement shows the thermal stability sequence: $H_2L^1-Cd > H_2L^1-Hg > H_2L^1-Fe > H_2L^1 > H_2L^1-Pb$.

On the other hand, the thermal stability of H_2L^2 and its metallopolymer complexes is arranged as follows: $H_2L^2-Hg > H_2L^2 > H_2L^2-Cd > H_2L^2-Fe > H_2L^2-Pb$.

In both cases the Pb^{2+} complex was the least stable, while Cd^{2+} and Hg^{2+} showed the most stable complexes. The metal



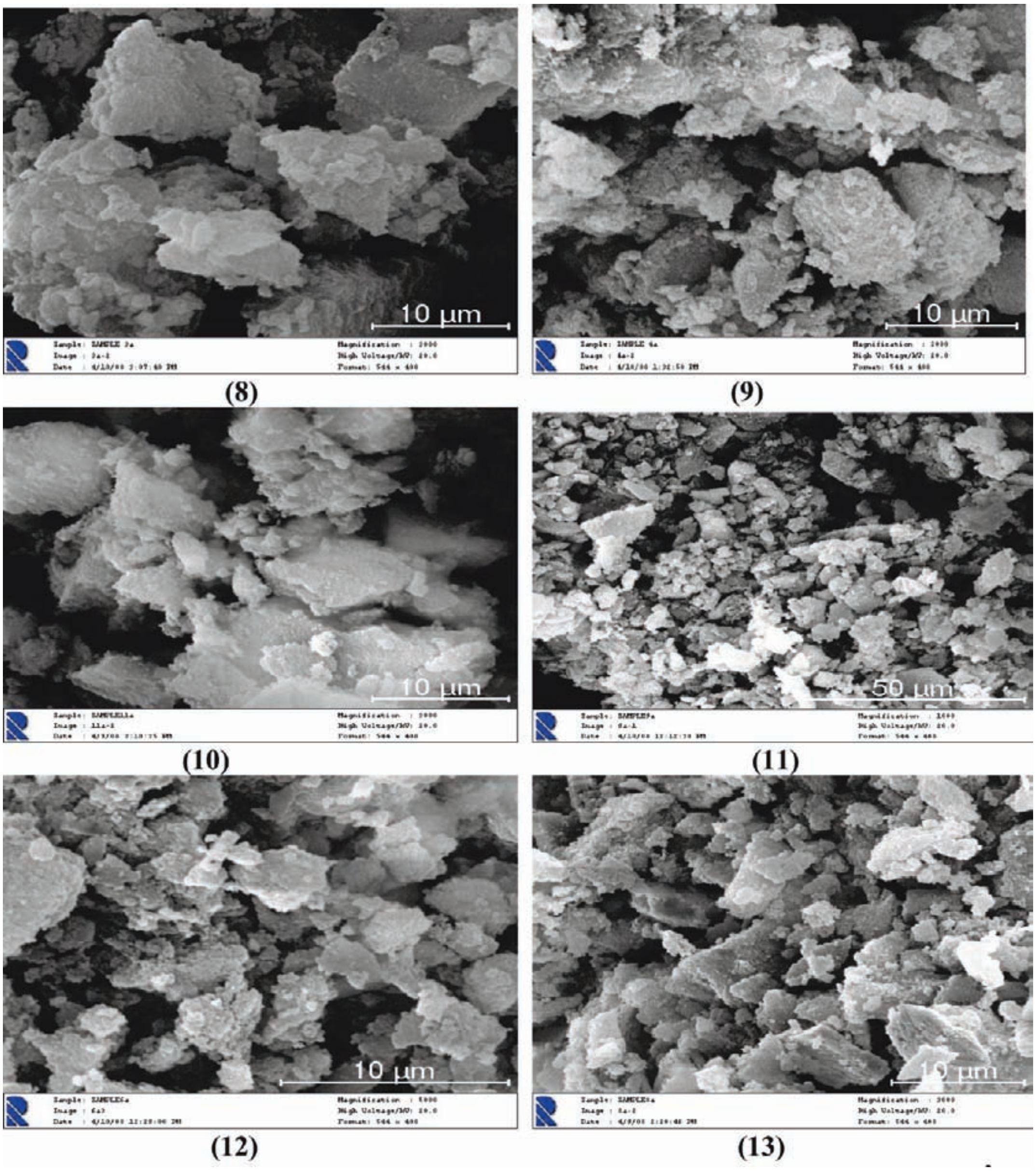
(1) (2) (3) (4) (5) (6) (7)

Figure 6. SEM micrographs of (1) polystyrene, (2) chlorosulfonated polystyrene, (3) H_2L^1 and its complexes, (4) H_2L^1-Cd, (5) H_2L^1-Fe, (6) H_2L^1-Hg, and (7) H_2L^1-Pb.

residual percent could be arranged in the case of H_2L^1 as follows: H_2L^1-Hg (9.706 %) > H_2L^1-Cd (5.562 %) > H_2L^1-Pb (4.799 %) > H_2L^1-Fe (2.37 %). That of H_2L^2 showed the following sequence: H_2L^2-Pb (33.184 %) > H_2L^2-Cd (4.146 %) > H_2L^2-Hg (2.445 %) > H_2L^2-Fe (1.453 %).

Energy Dispersive Spectroscopy (EDS). Energy dispersive spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. Figure 2 showed the energy dispersive spectroscopy (EDS) of the H_2L^1 and its metallopolymer complexes. The metal uptake by H_2L^1 has been confirmed by EDS spectra which reveals the presence of different metal ions. In addition, EDS spectra (Figure 3) of H_2L^2 and its complexes confirm the presence of the metal ions. All of these data confirm the formation of complex products. Thus, EDS analysis of both resins supports the formation of the proposed chelating resins.

Porosity of the Synthesized Polymer and Its Metallopolymer Complexes. The amount of pores on the surface of H_2L^1 and H_2L^2 is found to be more than that on the surface of $PS-SO_2Cl$, and the amount of pores on H_2L^2 is more than H_2L^1. The existence of these pores would provide convenient



(8) (9) (10) (11) (12) (13)

Figure 7. SEM micrographs of (8) ammoniated chlorosulfonated polystyrene, (9) H_2L^2 and its complexes, (10) H_2L^2−Cd, (11) H_2L^2−Fe, (12) H_2L^2−Hg, and (13) H_2L^2−Pb.

diffusion channels for metal ions into the interior of the resins. The porous structure parameters of the chelating resins H_2L^1 and H_2L^2 are determined by a nitrogen adsorption experiment at 77.33 K. The adsorption−desorption isotherms of both resins are shown in Figure 4. According to the IUPAC classification and as reported,[34] pores within porous materials are classified into: (i) micropore (width less than 2 nm), (ii) mesopore width between (2 and 50) nm, and (iii) macropore (width greater than 50 nm). It can be seen from Figures 4 and 5 that there was almost no dinitrogen adsorbed at lower relative pressure (P/P^o) which is due to the mechanism of meso- and micropore filling. This indicates that there are no micropores in both resins. Furthermore, the shape of the curves of the dinitrogen adsorption−desorption could be taken as evidence for the mechanism of capillary condensation, suggesting a quite large contribution of mesopores in both resins. In the entire region of relative pressure, the nitrogen volume adsorbed by H_2L^2 is nearly twice that of H_2L^1, indicating that H_2L^2 is of lower porosity than H_2L^1 which is consistent with SEM.

Morphology of the Synthesized Polymer. Molecular shape and the way molecules are arranged in a solid are important factors in determining the properties of the polymers. The SEM images of the PS−SO_2Cl, H_2L^1, H_2L^2, and their complexes, Figures 6 and 7, show the morphological differences.

(a) The surface of PS seemed to be like beans in its shape.

(b) Change in the surface due to sulfonation was observed where the surface seemed to be like a big platelet.

(c) Another clear change in the surface has been observed. A small and big cavity were observed in the case of H_2L^1 and the Cd complex. Fine surface-like particles were observed in the case of the Fe complex. A cloudy like surface in the case of the Hg and Pb complexes was observed. Little change was observed upon treating chlorosufonated XAD-16 with ethylenediamine, while treatment with 5-formylsalicylic acid showed a clear cavity. Complex formation with H_2L^2 showed fine particles in the case of Pb, Hg, and Fe, while in the case of Cd a swelled cotton shape was observed.

Kinetic Studies. Kinetics of Sorption. Successful application of adsorption demands innovation of cheap, easily available,

Table 4. Kinetic Parameters for the Adsorption of Fe^{3+}, Hg^{2+}, Cd^{2+}, and Pb^{2+} on H_2L^1

		pseudofirst-order			pseudosecond-order		
	q_e (exptl)	k_1	q_e		k_1	q_e	
metal ion	$(mmol \cdot g^{-1})$	(mni^{-1})	$(mmol \cdot g^{-1})$	R^2	$(g \cdot mol^{-1} \cdot mni^{-1})$	$(mmol \cdot g^{-1})$	R^2
Fe^{3+}	9.80	$8.03 \cdot 10^{-2}$	9.77	0.9991	$6.58 \cdot 10^{-3}$	10.10	0.7741
Hg^{2+}	7.35	$4.58 \cdot 10^{-2}$	6.98	0.7767	$6.23 \cdot 10^{-2}$	7.33	0.9997
Cd^{2+}	2.20	$2.33 \cdot 10^{-2}$	2.34	0.8616	$3.49 \cdot 10^{-2}$	2.19	0.9992
Pb^{2+}	1.30	$5.53 \cdot 10^{-2}$	1.31	0.9994	$2.67 \cdot 10^{-2}$	1.41	0.6247

Table 5. Kinetic Parameters for the Adsorption of Fe^{3+}, Hg^{2+}, Cd^{2+}, and Pb^{2+} on H_2L^2

		pseudofirst-order			pseudosecond-order		
	q_e (exptl)	k_1	q_e		k_1	q_e	
metal ion	$(mmol \cdot g^{-1})$	(mni^{-1})	$(mmol \cdot g^{-1})$	R^2	$(g \cdot mol^{-1} \cdot mni^{-1})$	$(mmol \cdot g^{-1})$	R^2
Fe^{3+}	9.450	$8.36 \cdot 10^{-2}$	9.46	0.9995	$1.01 \cdot 10^{-2}$	10.010	0.8038
Hg^{2+}	9.745	$2.99 \cdot 10^{-2}$	8.81	0.8261	$3.52 \cdot 10^{-2}$	9.742	0.9998
Cd^{2+}	2.805	$2.30 \cdot 10^{-2}$	2.50	0.8091	$3.02 \cdot 10^{-2}$	2.821	0.9994
Pb^{2+}	1.800	$3.15 \cdot 10^{-2}$	1.78	0.9997	$1.50 \cdot 10^{-2}$	1.928	0.5991

and abundant adsorbents of known kinetic parameters and adsorption characteristics. Adsorption kinetics can be modeled by several models, including the pseudofirst-order Lagergren eq 4 and the pseudosecond-order rate eq 5

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

$$t/q_t = 1/k_2 q_e^{\,2} - (1/q_e)t \tag{5}$$

where k_1 is the pseudofirst-order rate constant (min^{-1}); q_e and q_t are the adsorption capacities of the metal ion in $mmol \cdot g^{-1}$ at equilibrium and at time t (min), respectively; and k_2 is the pseudosecond-order rate constant ($g \cdot mmol \cdot L \cdot min^{-1}$).

The two models basically consider the external film diffusion, intraparticale diffusion, or interaction step for the sorption process of the metal ions by the chelating resins. Accordingly, the rate-determining step of the sorption may be one of these three steps. The effect of the external film diffusion could be reduced or minimized by shaking or stirring. Therefore, the sorption process will be mainly controlled by intraparticale diffusion or the interaction step. The values of R^2 (Tables 4 and 5), which are regarded as a measure of the goodness-of-fit of the experimental data on the kinetic models, showed that the sorption of Fe^{3+} and Pb^{2+} on the chelating resins H_2L^1 and H_2L^2 perfectly fit a pseudofirst-order model, while Hg^{2+} and Cd^{2+} perfectly fit the pseudosecond-order model. The data also indicate that the kinetic behavior of both resins indicates that the textural properties of the resin are the most effective factor on the rate of metal sorption. This effect is confirmed from the plot of the quantity of metal ion sorbed at time intervals (q_t, $mmol \cdot g^{-1}$) and the square root of time ($t^{0.5}$) by applying eq 6

$$q_t = X_i + K_{dif} t^{0.5} \tag{6}$$

where X_i is the boundary layer diffusion effects (external film resistance) and K_{dif} is the intraparticale diffusion rate constant ($mmol^{-1} \cdot g \cdot min^{-1/2}$), which is usually used to compare the mass transfer rates. The plots (Figure 8) hold good for all metal ions with the two different chelating resins but deviate as the shaking time is increased. The straight line obtained in each case indicates that the sorption rate is mainly controlled by the intraparticle diffusion process.[39] In general, as the value of X_i decreases, the effect of external diffusion on the sorption rate decreases. As shown from the data given in Table 6, the values of X_i values vary from −2.303 to −0.186 for the sorption of Fe^{3+} and Pb^{2+} by H_2L^1 and H_2L^2. These negative values indicate that boundary layer effects (external film resistance) have a negligible or no role on the rate of diffusion in the case of these two metal ions. Therefore, the sorption of Fe^{3+} and Pb^{2+} by the two chelating resins is mainly controlled by intraparticle diffusion and interaction step.[40] On the other hand, the positive values of X_i (+0.039 to +0.058) in the case of Hg^{2+} and Cd^{2+} by both chelating resins indicate that the rate of diffusion is slightly controlled by the external film diffusion. The dependence of the sorption rate on the external film diffusion could be taken as a reason of the shift of the reaction mechanism toward a pseudosecond-order model in the case of Hg^{2+} and Cd^{2+}.

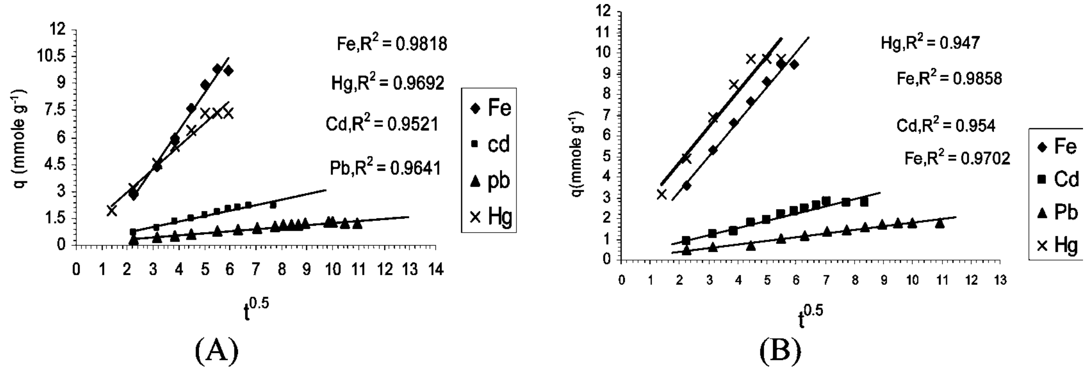


Figure 8. Intraparticle diffusion kinetics model for the adsorption of Fe^{3+}, Hg^{2+}, Cd^{2+}, and Pb^{2+} by (A) H_2L^1 and (B) H_2L^2.

Table 6. External Film Resistance (X_i) and Intraparticale Diffusion Rate Constant Values

	H_2L^1(a)		H_2L^2(b)	
metal ion	K_{diff}	X_i	K_{diff}	X_i
Fe^{3+}	2.667	−2.303	1.859	−0.402
Hg^{2+}	1.380	+0.082	2.108	+0.039
Cd^{2+}	0.412	+0.056	0.176	+0.058
Pb^{2+}	0.113	−0.256	0.368	−0.186

Conclusion

Chlorosulfonated Amberlite XAD-16 is functionalized by aminosalicylic acid and formyl salicylic acid, giving chelating resins H_2L^1 and H_2L^2. These ligands are able to coordinate metal ions through the carboxylate and phenolic oxygen atoms. Their metal sorption and selectivity showed that both chelating resins can separate iron from lead easier than from cadmium but with difficulty from a mercury mixture with selectivity factors for H_2L^1 more than H_2L^2. The metal capacities of the two resins are ordered as: $Fe^{3+} > Hg^{2+} > Cd^{2+} > Pb^{2+}$. Adsorption kinetics proceeds through pseudofirst-order for the sorption of Fe^{3+} and Pb^{2+} and pseudo-second-order for the sorption of Hg^{2+} and Cd^{2+} by the two chelating resins. The chelating resins are used to determine different metal ions in a real sample of Gulf ocean water, and they are able to remove 11 elements, namely, Na, K, Mg, Ca, Co, Ni, Cu, Cd, Pb, Fe, and Hg, from the sample.

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