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Characterization of hydroxybenzoic acid chelating resins: equilibrium, kinetics, and isotherm profiles for Cd(II) and Pb(II) uptake

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Abstract: Chelating ion-exchange resins were synthesized by polycondensation of *ortho*/*para* hydroxybenzoic acid with resorcinol/catechol employing formaldehyde as cross-linking agent at 80±5 °C in DMF. The resins were characterized by FTIR and XRD. The uptake behaviour of synthesized resins for Cd(II) and Pb(II) ions have been studied depending on contact time, pH, metal ion concentration and temperature. The sorption data obtained at optimized conditions were analyzed by the Langmuir and Freundlich isotherms. Experimental data of all metal–resin system were best represented by the Freundlich isotherm. The maximum obtained sorption capacity for cadmium was 69.53 mg g^{-1} and 169.32 mg g^{-1} for lead. The adsorption process follows first order kinetics and the specific rate constant K_r was obtained by the application of the Lagergan equation. Thermodynamic parameters ΔG^{ads}, ΔS^{ads} and ΔH^{ads} were calculated for the metal–resin systems. The external diffusion rate constant (K_s) and the intra-particle diffusion rate constant (K_{id}) were calculated by the Spahn–Schlunder and Weber–Morris models, respectively. The sorption process was found to follow an intra-particle diffusion phenomenon.

Keywords: chelating resin; SEM; kinetics; isotherm; distribution coefficient.

INTRODUCTION

In recent years, there has been a growing concern for the immobilization of metal ions introduced into water and wastewater bodies by increasing human technological activities. It has been established beyond doubt that heavy metal ions in the environment (water, soil and air) pose a very serious threat to human health. With the exponentially increasing population, there is a need for control-

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ling heavy metal discharge before the toxic metal ions enter the complex ecosystem.

Separation, removal, and enrichment of trace metals in aqueous solutions play an important role in the analysis of wastewaters, industrial and geological samples. Solid phase extraction of metal ion has gained rapid acceptance because of its various advantages over other methods. The extraction of metal ions using chelating ion exchange resin is a green analytical method since it does not involve the use of toxic chlorinated organic solvents, which are very frequently used in conventional liquid–liquid extraction techniques. The main objective of most of the research on chelating resins was the preparation of insoluble functionalized polymers that can provide more flexible working conditions together with good stability and high capacity for metal ions.

The use of modified clay minerals for the adsorption of metal ions from aqueous solutions for water purification or industrial wastewater treatment has been widely studied. These clay minerals, when used as colloids or powders, have been found to be equally efficient as ion exchange resin but it is difficult to recover such adsorbents from filters after use. This further renders the regeneration and possible reuse of clay adsorbents very difficult.

The kinetics of the adsorption of toxic metal ions is required in order to predict the rate at which the toxic metal ions are removed from the aqueous solution. Adsorption kinetics also provides an insight into the mechanism of adsorption.[1]

A number of kinetic investigations have been performed on the adsorption of Pb(II) onto peat,[2] Pb(II) onto decaying leaves,[3] Cd(II) onto hydrous ferric oxide,[4] Cu(II) and Pb(II) onto a polysulphone and algae complex,[5] Cr(IV) onto peat,[6] Pb(II) on palm kernel fibre,[7] Pb(II) onto orthophosphate-modified Kaolinite clay,[8] Pb(II) and Cd(II) onto tripolyphosphate-modified Kaolinite clay,[9] to mention but a few. However, although these adsorbents all showed good potential as low cost adsorbents in the adsorption of metal ions, they either exist in aqueous solution as colloids or dispersed particles that are difficult to recover from filters.

To address the problem of recovery of adsorbent after use from filters, this study focuses on the production of a water-stable and mechanically strong adsorbent by the synthesis of chelating ion exchange resins. These were subsequently employed for the adsorption of Pb(II) and Cd(II).

This study further considers the kinetics of the adsorption of Pb(II) and Cd(II) onto chelating ion exchange resin adsorbents. The effects of pH, metal ion concentration, temperature, the pseudo-second order and pseudo first order rate constants and the kinetics of adsorption of Pb(II) and Cd(II) for all the resins were investigated. The obtained kinetic adsorption data were modelled against existing kinetic adsorption models.

EXPERIMENTAL

Reagents and solutions

Analytical reagent (A.R.) grade chemicals were used unless otherwise stated. Stock solutions (500 mM) of metal ions were prepared by dissolving appropriate amounts of $CdAc_2$ and $PbAc_2$ in deionised water acidified with 5 cm^3 of the corresponding acid. The metal ion solutions were standardized by complexometric titration with ethylenediaminetetraacetic acid (EDTA) using standard procedures.[10] The working solutions of metal ions were obtained by dilution of the stock solutions with deionised water. The solutions were adjusted to a particular pH using buffers. Acetate buffer was used to adjust the pH in the ranges 3.5 to 6.5. The water samples from industry were collected, immediately acidified with 2 % HNO_3, filtered, and stored in glass bottles. Solutions of acids and alkalis were prepared by dissolving appropriate amounts of the particular compound in deionised water and standardized by literature methods.[10]

Instruments

A flame atomic absorption spectrometer (AAS, Electronic Corporation of India Ltd., Hyderabad, India, model 4129) was used for the measurements of the metal concentrations, employing an air–acetylene flame (air and acetylene flow rates: 10 dm^3 min^{-1} and 2.0 dm^3 min^{-1}, respectively). The line selected for monitoring Cd and Pb were 228.8 and 217.0 nm, respectively. The analysis of each metal ion was realised by AAS after appropriate dilution. The infrared spectra of the synthesized resin in KBr pellets were recorded on an FTIR spectrophotometer (Shimadzu, model-8201PC, Japan). The X-ray diffraction (XRD) analysis was performed using an advanced diffractometer (Bruker, AXE D8, UK). The surface morphology was analyzed using an optical microscope (Olympus, SZX12, Japan) and a scanning electron microscope (Philips, XL30, Netherlands) at different magnifications. The sorption–desorption studies of both metal ions were performed by the batch technique and using columns of 0.5 cm internal diameter. For the batch sorption technique, a mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi, India) at a speed of 200 strokes min^{-1} was used throughout the equilibration.

Resin synthesis

Salicylic acid/*p*-hydroxybenzoic acid (13.5 g, 0.1 mol) was taken in a 250 cm^3 round bottom flask and dissolved in dimethyl formamide (DMF) solvent (20 cm^3) to give a clear solution. A solution of resorcinol/catechol (11 g, 0.1 mol) in 10 cm^3 DMF was added to the solution and stirred for 2 h. Formaldehyde (0.3 mol, 37 %) was added and stirred for an hour. The salicylic acid–formaldehyde–resorcinol (SFR), salicylic acid–formaldehyde–catechol (SFC), *p*-hydroxybenzoic acid–formaldehyde–resorcinol (*p*HFR) and *p*-hydroxybenzoic acid–formaldehyde–resorcinol (*p*HFC) resins were synthesized by refluxing the corresponding mixture at 80±5 °C in a water bath for 2–3 h under constant stirring, during which the mixture gelled to a soft dark brown mass. A gel was separated from the reaction vessel and cured in an oven at 80–90 °C for 12 h. As carboxylic acid groups normally decompose above 100 °C, the resin was cured below 90 °C. The resulting resins were washed with DMF to remove monomer impurities and finally with deionised water. After the complete washing cycle, the yields of the resins were in the range 78–85 %. These purified and dried resins were finely ground and passed through a 50-mesh sieve and then a 20-mesh sieve to obtain a uniform particle size (20–50 mesh). The sieved resins were again washed with water, air dried at room temperature and stored in airtight polyethylene bottles.

To convert the resin samples into the H^+ form, resins of uniform particle size were equilibrated with 1 M HCl solution for 24 h and washed with deionised water until chloride-free, checked with silver nitrate solution. The H^+ form of the resins were used for the batch and column studies. The physico-chemical properties, *viz*. moisture content, % solid, apparent density, true density, void volume fraction and sodium exchange capacity were studied according to literature methods.[11]

Batch sorption experiments

The sorption properties, *i.e*., as the effect of contact time, the effect of pH, the effect of metal ion concentration and the effect of temperature, were studied by the batch equilibration method at 30±2 °C according to literature methods.[12]

To study the effect of contact time on the sorption of Cd(II) and Pb(II), accurately weighed (0.250±0.001 g) amounts of the H^+ form of the dry resins with a uniform particle size (20–50 mesh) were taken in different glass-stoppered flasks and equilibrated with buffer solutions of optimum pH value (pH of the highest exchange) for 6 h. After decanting the buffer solution, 50 cm^3 (200 mM) of metal ion solutions of the same pH were added. After the equilibration time, the solutions were filtered through a 0.02 µm membrane filter to separate the resin and solution. The amounts of non-adsorbed metal ions were determined by AAS at fixed time intervals.

To study the effect of pH on the uptake of Cd(II) and Pb(II), different sets of accurately weighed (0.250±0.001 g) dry resin were equilibrated with buffers of different pH values in glass-stoppered flasks for 6 h for the resin to attain the desired pH value. After 6 h, the buffer solutions were decanted and 50cm^3 of 200 mM metal ion solutions of varying pH from 3 to 7 were added. The metal ion solutions were equilibrated at room temperature (30±2 °C) for 6 h with intermittent shaking. The pH of the filtrate was measured and it was found that the pH remained stable throughout the experiment (±0.2). The non-adsorbed metal ions were estimated after filtration.

To study the effect of metal ion concentration on the uptake of Cd(II) and Pb(II) ions by the synthesized resins, accurately weighed (0.250±0.001 g) buffered resins were equilibrated with different concentrations of metal ion solutions (50 cm^3) in the range 50–300 mM at the same pH value at room temperature for 6 h with intermittent shaking. After 6 h, the metal ion solutions were filtered and the residual metal ions were estimated by AAS.

To study the effect of temperature, equilibrium experiments were performed at fixed metal ion concentration (200 mM) for a fixed resin loading (0.250±0.001g) and initial pH (different optimum pH for different resins for Cd(II) and Pb(II) ions) at four different temperatures: 30, 40, 50 and 60 °C.

Column chromatography

Column/ion exchange chromatography is a technique in which the separation of components of a mixture is realised by taking advantage of their different selectivity coefficients/retention capacity of the column adsorbent/resin. The differences in the selectivity coefficient/retention capacity lead to different migration rates on through the column. The study of column chromatography for the separation of mixtures and industrial effluents provides an idea of its application on a large scale.

A calibrated 50cm^3 glass column (0.5cm internal diameter) fitted with a glass wool plug at the lower end was used as ion exchange column. The resin having various particle sizes (20–50 mesh) was used to avoid choking of the column. The glass column was filled with a slurry of the resin in hot deionised water whereby air entrapment was avoided. The column was then backwashed with deionised water to ensure no air bubbles remained in the column and that the resin was uniformly distributed. This column was used for the separation of Cd(II) and Pb(II) from the mixtures.

RESULTS AND DISCUSSION

Physico–chemical properties

The physico–chemical properties of all four synthesized resins are presented in Table I. The moisture content of a resin furnishes a measure of its water loading capacity or its swelling capacity. The moisture content depends on many factors, such as the composition of the resin matrix, the degree of cross-linking or the nature of the active groups and the ionic form of the resin. The degree of cross-linking of a resin has an impact on the moisture content of the resin and the moisture content, in turn, has an impact on the selectivity. In a resin with a high moisture content, the active groups are spaced further apart from each other, for example, strong acid cation resins contain about 50 % moisture. The percentage moisture content of synthesized resins, as shown in Table I, ranged from 6.2–8.7 %. Thus, these resins have low range of percentage moisture content compared to the commercial resins. Resins synthesized from salicylic acid–furfuraldehyde–benzidine and *p*-hydroxybenzoic acid–furfuraldehyde–benzidine[13] had lower moisture contents (4.01 and 4.9 % respectively) than the present synthesized resins. The resin synthesized from salicylic–furfuraldehyde–hexamine[14] and salicylic acid–formaldehyde–*m*-cresol[15] exhibited slightly higher moisture contents (15.11 and 9.4 %, respectively) than SFR, SFC, pHFR and pHFC resins. The difference in moisture content may be due to the different experimental conditions, such as the media in which the resins were synthesized, the polymeric backbones, the degree of cross linking and functional groups involved.

TABLE I. Physico–chemical properties of the synthesized resins

Property	*SFR*	*SFC*	*p*HFR	*p*HFC	*SD*
Moisture content, %	7.0	6.2	8.7	6.5	0.5
Solid content, %	93	93.8	91.3	93.5	0.5
True density, d_{res} / g cm^{-3}	1.126	1.210	1.689	1.391	0.03
Apparent density, d_{col} / g cm^{-3}	0.842	0.883	0.931	0.916	0.006
Void volume fraction	0.453	0.483	0.448	0.341	0.005
Sodium exchange capacity, mmol g^{-1} dry resin	4.931	4.027	3.822	3.497	0.2
Concentration of fixed ionogenic groups, mmol cm^{-3}	5.02	4.473	5.893	4.548	0.200
Volume capacity, mmol cm^{-3}	2.67	2.209	3.247	2.997	0.05

The true densities of the synthesized resins, which were in the range 1.126 to 1.689 g cm^{-3}, are given in Table I. The true density of commercial resins generally lies between 1.1 to 1.7 g cm^{-3}. To avoid the floating of resin particles, the true density must be more than one. Floating of resin particles is undesirable in chromatographic studies, as it hampers the formation of a compact column. The optimum density and uniform particle size enable perfect column packing and performance of the column. The measurement of the column density, or apparent density, is necessary as commercially resins are sold on a volume basis and packed on a weight basis. The apparent densities of the synthesized polymers are given in Table I, from which it can be seen that the apparent densities of all the resins were in the range of 0.84 to 0.93 g cm^{-3}, which is comparable to the density of commercial resins. This may be because of changes in the polymeric matrix, different functional groups and the method of synthesis. The apparent density parameter gives an idea of the required length of a packed column for an ideal column chromatographic study. The values of void volume fraction of resin are also given in Table I. The void volume fraction of the synthesized resin was in the range of 0.341 to 0.483. The appreciable values of the void volume fraction help the diffusion of the exchangeable ion on the resin and hence increase the rate of exchange of ions. The minimum essential void volume provides better diffusion of exchangeable ions and thus gives feasibility to column operation.

FTIR Spectra of resins

The FTIR spectra of the SFR, SFC, *p*HFR and *p*HFC resins are displayed in Fig. 1. The strong band at 3446–3452 cm^{-1} is attributed to ν(O–H) stretching of the phenolic group. The presence of a medium band at 2920–2926 cm^{-1} is due to the ν(C–H) stretching of the methylene group.[16] The medium strong band at 1630–1653 cm^{-1} can be assigned to ν(C=O) stretching of the aromatic acid

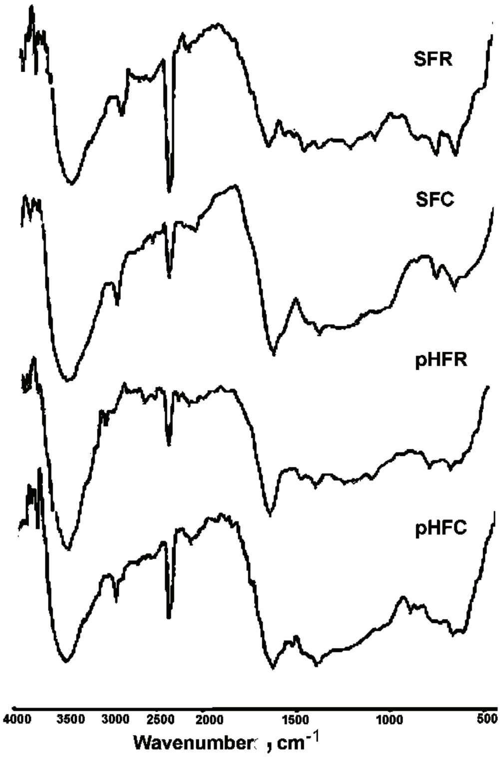


Fig. 1. FTIR Spectra of the synthesized resins.

group. The weak medium band at 1390–1462 cm^{-1} is due to δ(C–H) deformation of the methylene group.[15,17] The medium band at 769–775 cm^{-1} is due to the δ(C–H) bending of the 1,2,3,4-tetra substituted benzene ring.[18] The medium band at 664–667 cm^{-1} is attributed to the δ(C–H) bending of poly ethylene –(CH_2)– bridges.

X-Ray diffraction analysis

XRD Patterns of a compound provide information about its crystalline or amorphous nature and the regions of the compound that may co-exist.[19] The XRD patterns of all four resins (SFR, SFC, pHFR and pHFC) are shown in Fig. 2. No sharp peaks were observed in the diffractograms of the resins, which exhibited an irregular pattern, which is characteristic an amorphous compound. A phenol–formaldehyde resin exhibited a similar XRD pattern, which confirms the amorphous nature of the four synthesized resins.[20]

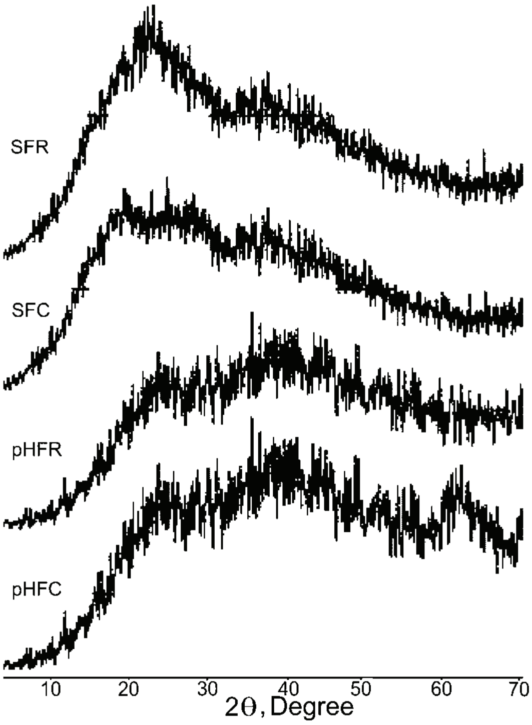
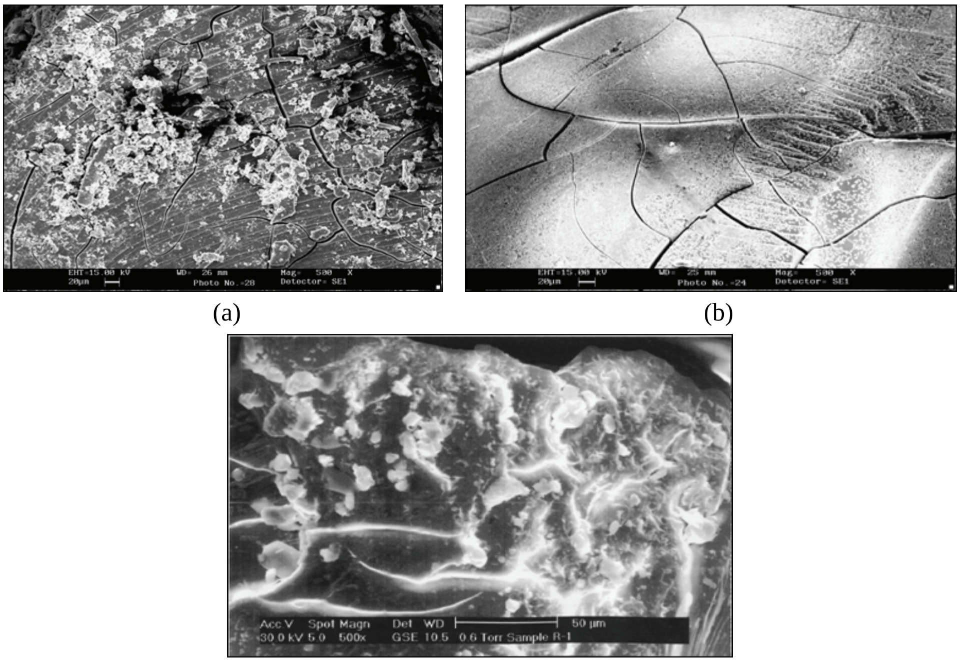


Fig. 2. XRD Patterns of the synthesized resins.

SEM and optical microscopy

Surface analysis is of great use for the understanding of the surface features of a material. Several observations were made of the resins before the photographs (SEM and optical) were taken to ensure that the photographed regions were representative of the overall resin. The optical photographs of synthesized resins showed that the SFR resin was red in colour, whereas the pHFR resin appeared brown in colour with a rough surface, while the SFC and pHFC resins were black in colour with a smooth surface. This indicates that salicylic acid-containing resins exhibit a reddish–brown colour and the catechol-containing resins were black in colour.

The SEM photographs of all the resins are shown in Fig. 3 at 500× magnification. The SEM photographs indicate that the resin exhibits angular edges with regular fringes. The morphology of the resin shows a fringed micelle model of the crystalline–amorphous structure. The fringes represent the transition material between crystalline and amorphous phases. The SEM photographs exhibits such spherulites, which are the aggregate of some crystallites present along with some amorphous regions. SFC is more amorphous than *p*HFC, while *p*HFR is least amorphous. All four resins exhibited an amorphous character, which was confirmed by their XRD patterns.



(a) (b)

(c)

Fig. 3. SEM Photographs of the synthesized resins at 500× magnification; a) *p*HFC, b) *p*HFR and c) SFC.

Effect of contact time

The rate of exchange of metal ions on the resin changed in a time dependent manner as can be seen in Fig. 4. Thus, the time required for 50 % exchange ($t_{1/2}$) of Cd(II) for the SFR and SFC resins was 50 min, for *p*HFR about 60 min and for *p*HFC 65min. The time required for 50 % exchange ($t_{1/2}$) of Pb(II) for SFR was 45 min, for SFC 55 min, *p*HFR about 55 min and for *p*HFC 60 min. The fast rate of exchange at the beginning can be explained based on the law of mass action.[21] A faster rate of exchange is facilitated by column chromatographic separation. The kinetics of metal ion exchange mainly depends on various physical properties, such as particle size, pore size, physical core structure and diffusion of the counter ion.[15,17] Complete uptake of Cd(II) took 21 h with SFR, *p*HFR and *p*HFC and 15 h with SFC. Complete uptake of Pb(II) 12 h with SFR, 15h with SFC and 18 h with pHFR and pHFC. Hence, 24 h was considered as the optimum time for complete equilibration of Cd(II) and Pb(II) ions and was used for all further experiments.

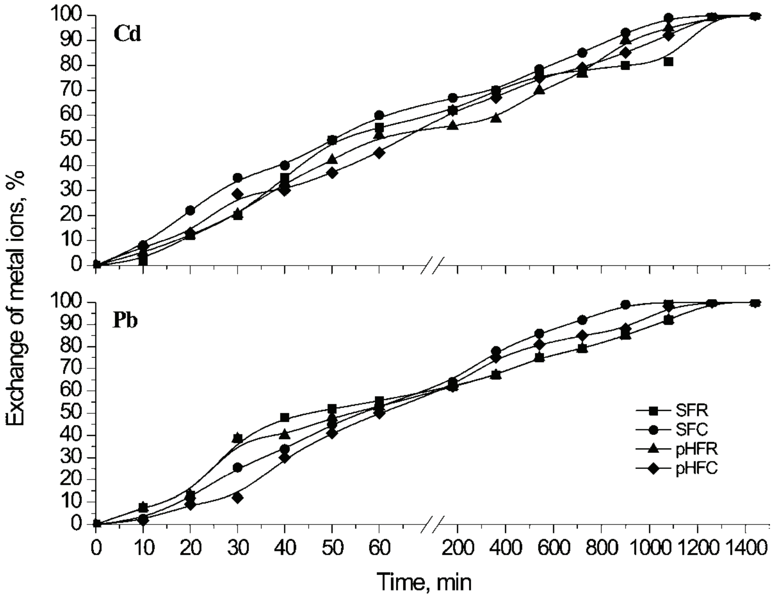


Fig. 4. Time dependence of the fraction of metal ion uptake by the synthesized resins. Conditions: c_0 = 200 mM, w = 0.25 g, V = 50 cm^3, t = 30±2 °C.

Effect of pH on the exchange capacity

The effect of pH variation on chelating ability of the synthesized resins towards Cd(II) and Pb(II) ions was studied. The removal of metal ions from aqueous solution was highly dependent on the pH of the solution that also affected the surface charge of the sorbents. The results are presented in Fig. 5 as exchange capacity against pH for both the studied metal ions. The results show that the uptake of Cd(II) and Pb(II) ions increased with increasing pH up to a certain value and thereafter decreased. The nature of the observed trend indicates that the cation exchange behaviour of these resin was similar to that of weak acid cation exchangers,[17] because in weak acid cation ion exchanger, the exchange capacity is pH dependent.[19] The maximum uptake of SFR for Cd(II) and Pb(II) occurred at pH 5 and of SFC at pH 5.5, while *p*HFR exhibited a maximum capacity for Cd(II) at pH 5.5 and for Pb(II) at pH 5 and *p*HFC a maximum capacity for Cd(II) at pH 5 and for Pb(II) at pH 5.5.

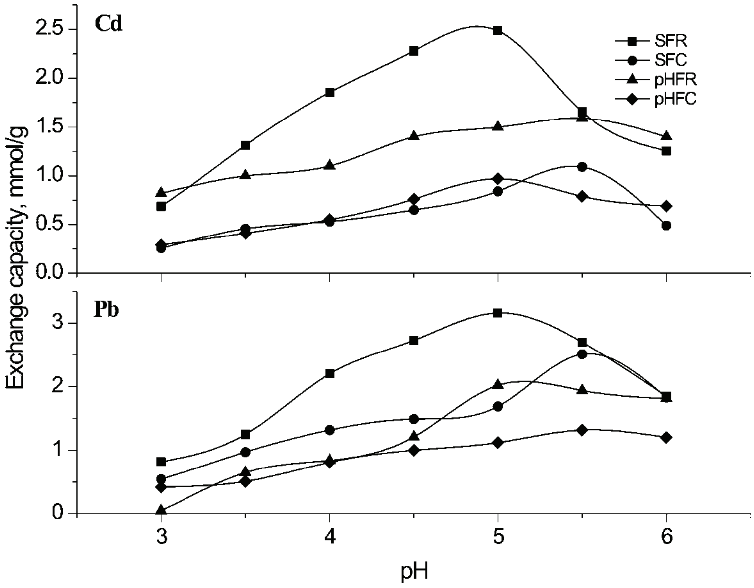


Fig. 5. Metal ion uptake capacity of the synthesized resins as a function of pH. Conditions: c_0 = 200 mM, w = 0.25 g, V = 0 cm^3, t = 30±2 °C.

The selectivity order for Pb(II) was SFR > SFC > *p*HFR > *p*HFC and for Cd(II), it was SFR > *p*HFR > SFC > *p*HFC. Chelation and ion exchange, are more favourable for the uptake of Pb(II) in case of the salicylic acid-containing resin due to its smaller hydrated ion radius. An increase in pH increased the negatively charged nature of the sorbent surface. This leads to an increase in the electrostatic attraction between the positively charged metal ions and the negatively charged sorbent, which results in an increase in the uptake of metal ions. The decrease in the removal of metal ions at lower pH is due to the higher concentration of H^+ present in the reaction mixture, which compete with the metal ions for the sorption sites on the resin surface. The observed decrease in sorption at higher pH is due to the formation of insoluble hydroxy complexes of the metal ions.[22]

Though SFC and pHFC were found to possess low cross-linking in their backbones, they exhibit comparatively higher exchange than a salicylic acid–formaldehyde–*m*-cresol resin.[15] This is due to tiny cracks and channels, which were clearly seen on the surface of the SFC and pHFC resin (SEM photographs, Fig.

3). The breaking of large particles tends to open tiny cracks and channels on the particle surface of the material, resulting in better diffusion owing to the smaller particle size.

SFR exhibited a higher exchange capacity for both Cd(II) and Pb(II), while pHFC showed a lower exchange capacity for Cd(II) and Pb(II) as compared to other synthesized resins (SFC and *p*HFR). The exchange capacity for Cd(II) was lower as compared to Pb(II) for all the synthesized resins (SFR, SFC, *p*HFR and *p*HFC). This can be explained based on the hydrated radius of Cd(II) and Pb(II), cadmium having a larger hydrated ion radius than Pb(II) ion. This results in a decrease in the electrostatic attraction between the Cd(II) and coordinating group, a lower complex stability and hence a lower the capacity.

Effect of initial metal ion concentration on the exchange capacity

The amount of metal ion uptake first increased with increasing concentration of metal ions and then remained constant with further increasing of the metal ion concentration (results not shown). At lower concentrations of metal ions, the number of metal ions available in solution was lower than the number of available sites on the sorbent.[23] However, at higher concentrations, the available sites of exchange remained the same whereas more metal ions were available for sorption and subsequently the exchange finally become almost constant. A similar trend in the sorption data was previously reported for lead and chromium onto bagasse fly ash[24] and for heavy metals onto a salicylic acid–formaldehyde–*m*-cresol chelating resin.[15] At a Cd(II) concentration of 250 mM, the sorption/ion exchange attained a limiting value for the SFR, SFC and *p*HFC and *p*HFR resins. In case of Pb(II), the uptake became constant for SFR and *p*HFC after a concentration of 200 mM, while for SFC and *p*HFC, the limiting value was reached at a concentration of 250 mM. Therefore, a 200 mM concentration was considered as the optimum concentration for all the resins and this concentration was used in the further experiments.

Effect of electrolyte concentration and pH on the distribution coefficients of the metal ions

The distribution coefficient (K_d) values of the metal ions as a function of pH and concentration of electrolyte solution were studied. The K_d value decreased with increasing the electrolyte concentration and increased with increasing pH, which is presented in Table II. In the present investigation, the distribution studies were limited up to a certain pH for each metal ion to prevent hydrolysis of the metal ions at higher pH values. To achieve a more distinct separation of metal ions in a shorter time, the maximum difference in the K_d value should be selected for optimized chromatography conditions.

TABLE II. K_d values for the synthesized resins in tartaric acid at different pH values and concentrations

Resin	Metal ion	Tartaric acid concentration, mol dm^{-3}	pH				
			3.0	3.5	4.0	5.0	6.0
SFR	Cd(II)	0.1	565.00	443.00	299.80	143.31	87.50
		0.2	370.81	215.70	153.80	98.98	50.99
		0.3	252.11	170.77	101.02	53.00	19.27
		0.5	98.23	50.09	31.13	–	–
		1.0	31.47	22.57	10.68	–	–
	Pb(II)	0.1	828.23	587.62	440.84	310.51	247.10
		0.2	517.00	473.74	301.77	250.67	189.74
		0.3	390.32	295.00	220.22	181.37	121.84
		0.5	152.71	210.13	187.15	120.91	92.31
		1.0	171.13	145.70	90.27	52.64	11.09
SFC	Cd(II)	0.1	69.5	54.3	33.5	21.3	17.5
		0.2	52.1	37.8	21.5	13.5	12.5
		0.3	29.3	21.5	14.3	9.2	–
		0.5	17.4	15.8	–	–	–
		1.0	–	–	–	–	–
	Pb(II)	0.1	143.1	129.7	103.5	81.5	52.6
		0.2	118.2	110.4	84.8	62.7	45.3
		0.3	72.9	63.1	57.6	48.3	37.5
		0.5	–	–	–	31.2	24.8
		1.0	–	–	–	–	
*p*HFR	Cd(II)	0.1	55.5	62.2	68.6	22.2	19.4
		0.2	42.3	57.2	31.7	39.3	13.6
		0.3	29.7	20.5	27.8	14.5	
		0.5		–	–	–	–
		1.0	–	–	–	–	–
	Pb(II)	0.1	96.3	81.1	74.2	54.2	33.8
		0.2	78.5	68.2	62.8	49.0	30.1
		0.3	69.2	60.5	54.8	31.5	22.0
		0.5	54.2	49.7	44.0	37.4	18.8
		1.0	–	–	–	–	–
*p*HFC	Cd(II)	0.1	37.5	22.0	30.2	19.5	19.0
		0.2	24.9	18.0	15.5	10.9	15.6
		0.3	19.5	15.0	9.5	–	–
		0.5	16.2	12.9	–	–	–
		1.0	–	–	–	–	–
	Pb(II)	0.1	60.5	39.5	28.4	25.5	16.5
		0.2	32.1	22.0	20.3	16.5	15.4
		0.3	15.1	13.6	10.1	15.2	–
		0.5	8.5	10.2	–	–	–
		1.0	–	–	–	–	–

Among all the resins under investigation, the SFR resin showed the highest K_d values, where pHFC exhibited the lowest K_d values. This may be explained based on the stability constants or the difference in the energy of the complexes according to Irving and Williams.[25] Chromatographic separation of these two metal ions was employed using the SFR resin. From Table II, it is clear that Pb(II) had a distribution coefficient of 120.91 as compared to Cd(II) (0.0) at pH 5.0 and tartaric acid concentration of 0.5 M, indicating the feasibility of the chromatographic separation of these two metal ions. Chromatographic separation of the metal ions was achieved and the recovery of Cd(II) was 90.7 % and of Pb(II) 96.20 %, which is shown in Fig. 6.

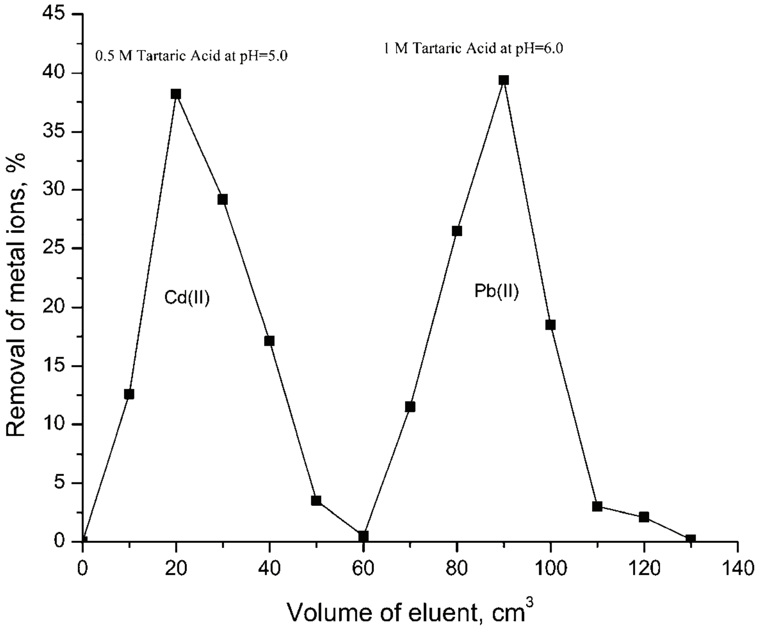


Fig. 6. Chromatographic separation of the metal ions on the SFR resin.

Effect of temperature and thermodynamic parameters

The effect of temperature on the uptake of both Cd(II) and Pb(II) on synthesized resins was studied using the optimized conditions determined in the previous experiments. The temperature was varied from 30 °C to 60 °C. It was observed that the uptake of Cd(II) and Pb(II) ions increased with increasing temperature (results not shown) for all the metal–resins systems. The exchange was enhanced due to the increased kinetic energy.[26] The phenomenon of an ion-exchange depends on the metal ion concentration and temperature. The surface energy of the SFC resin increases with temperature. Similar results were also reported previously for the ion exchange of Ni(II), Cu(II), Zn(II),Cd(II) and Pb(II) with Dowex 50[28] and Amberlite IR 120.[27]

The values of ΔH^{exch}, ΔS^{exch} and ΔG^{exch} were also calculated from the slope and intercept of the Van't Hoff plot of the exchange of metal ions on the

SFC resin using the following linear variation of ln K_d with reciprocal temperature $1/T$:

$$\ln K_d = (\Delta S^{exch}/R) - (\Delta H^{exch}/RT) \tag{1}$$

where, ΔS^{exch} and ΔH^{exch} are the entropy and enthalpy change for the process, respectively. The free energy of the adsorption ΔG^{exch} was calculated using the following Van't Hoff Equation:

$$\Delta G^{exch} = -RT\ln K_d \tag{2}$$

The value of ΔH^{exch} was negative which indicates an exothermic ion exchange process and it is likely that the chelation mechanism dominates (Table III).[28] The entropy (ΔS^{exch}) is positive corresponding to an increase in degree of freedom of the system due to release of two hydrogen ions for the divalent metal ions under study.[29] The negative values of ΔG^{exch} indicate the feasibility of the process and also the spontaneity of the ion exchange process. The amount of metal ions uptake at equilibrium must increase with increasing temperature, because ΔG^{exch} decreases with increasing solution temperature.

TABLE III. Thermodynamic parameters for Cd(II) and Pb(II) adsorption on the synthesized resins

Metal ion	Resin	T / K	K_d	ΔG / kJ mol^{-1}	ΔH /kJ mol^{-1}	ΔS / J K^{-1} mol^{-1}
Cd(II)	SFR	293	7.92±0.2	–5.041	–6±0.2	17±0.2
		303	8.12±0.2	–5.276		
		313	8.41±0.2	–5.541		
		323	8.67±0.2	–5.799		
	SFC	293	4.65±0.2	–3.622	–7±0.2	19±0.2
		303	4.95±0.2	–3.712		
		313	5.10±0.2	–3.739		
		323	5.29±0.2	–4.801		
	*p*HFR	293	5.19±0.1	–4.371	–7±0.1	18±0.1
		303	5.32±0.1	–4.391		
		313	5.49±0.1	–4.406		
		323	5.69±0.1	–4.409		
	*p*HFC	293	4.41±0.1	–3.701	–5±0.1	13±0.1
		303	4.67±0.1	–3.722		
		313	4.93±0.1	–3.735		
		323	5.06±0.1	–3.739		
Pb(II)	SFR	293	9.65±0.2	–4.803	–5±0.2	11±0.2
		303	9.92±0.2	–4.812		
		313	10.51±0.2	–4.835		
		323	10.87±0.2	–4.853		
	SFC	293	8.05±0.2	–3.845	–4±0.2	12±0.2
		303	8.27±0.2	–3.892		
		313	8.63±0.2	–3.911		
		323	8.79±0.2	–3.923		

TABLE III. Continued

Metal ion	Resin	T / K	K_d	ΔG / kJ mol^{-1}	ΔH /kJ mol^{-1}	ΔS / J K^{-1} mol^{-1}
Pb(II)	*p*HFR	293	7.47±0.1	–2.588	–7±0.1	20±0.1
		303	7.61±0.1	–2.591		
		313	7.92±0.1	–2.607		
		323	8.11±0.1	–2.615		
	*p*HFC	293	7.12±0.1	–4.782	–5±0.1	15±0.1
		303	7.56±0.1	–5.094		
		313	7.73±0.1	–5.311		
		323	8.02±0.1	–5.492		

Sorption isotherms

Equilibrium can be described by isotherm equations such as the Langmuir and Freundlich isotherms. A preliminary screening of the corresponding equations showed that the Langmuir and Freundlich models best fit the experimental data and the following equations were used for the modelling of results.

Langmuir model: $$(c_e/Q_e) = (1/Q^0b) + (c_e/Q^0) \quad (3)$$

Freundlich model: $$\log q_e = \log k_f + (1/n)\log c_e \quad (4)$$

where c_e is the equilibrium concentration (mmol g^{-1}), Q_e is the amount adsorbed at equilibrium (mmol g^{-1}) and Q^0 and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The liner plots of c_e/Q_e *vs.* c_e (not shown) indicate that ion uptake obeys the Langmuir model. The constants Q^0 for Cd(II) were calculated as 69.53, 43.23, 52.47 and 38.84 mg g^{-1} as the maximum capacity for SFR, SFC, *p*HFR and *p*HFC, respectively. The constant Q^0 for Pb(II) by SFR, SFC, pHFR and pHFC were calculated as 169.32, 143.23, 122.47 and 101.84 mg g^{-1}, respectively. These results are comparable to those of the commercial resin Duolite GT-73 reported by Vaughan *et al.*[30] The Q^0 value of Duolite GT-73 for Cd(II) and Pb(II) were 106 and 122 mg g^{-1},[30] respectively. The values of Q^0 for a synthetic methacrylic acid–co–ethyleneglycol dimethacrylate resin were 416.67 and 588.24 mg g^{-1} for Cu(II) and Ni(II) respectively.[23] The sorption energy constant of Cd(II) for SFR, SFC, *p*HFR and *p*HFC are 0.1048, 0.0721, 0.0831 and 0.0593 dm^3 mg^{-1}, respectively. The sorption energy constant of Pb(II) for SFR, SFC, *p*HFR and *p*HFC are 0.2732, 0.2461, 0.2382 and 0.1984 dm^3 mg^{-1}, respectively The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor or equilibrium parameter, R_L.[31] The value indicates the isotherm to be either unfavourable ($R_L < 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of R_L obtained for all the metal–resin systems investigated are given in Table IV. The R_L values for both the metals Cd(II) and Pb(II)) under study were between 0 and 1, indicating the sorption to be favourable.

TABLE IV. Langmuir and Freundlich isotherms constants for the metal–resin systems

Metal ion	Resin	Langmuir constant				Freundlich constant		
		b/ dm^3 mg^{-1}	Q^0/ mg g^{-1}	R_L	R^2	k_f / dm^3 g^{-1}	1/n	R^2
Cd(II)	SFR	0.1048	69.53	0.219	0.9627	35.41	0.4152	0.9886
	SFC	0.0721	43.23	0.202	0.9787	68.72	0.7215	0.9934
	*p*HFR	0.0831	52.47	0.2141	0.9791	54.70	0.5123	0.9862
	*p*HFC	0.0593	38.84	0.198	0.9687	21.35	0.5216	0.9912
Pb(II)	SFR	0. 2732	169.32	0.341	0.9892	71.75	0.7023	0.9925
	SFC	0.2461	143.23	0.322	0.9974	66.23	0.6230	0.9914
	*p*HFR	0.2382	122.47	0.281	0.9972	54.11	0.5834	0.9887
	*p*HFC	0.1984	101.84	0.263	0.9983	39.63	0.4982	0.9974

The specific rate constant, K_r, for the sorbent was determined by the Langergan Equation:

$$\log (q_e - q) = \log q_e - K_r t/2.303 \tag{5}$$

where q_e and q (mg g^{-1}) are the amounts of metal ions adsorbed at equilibrium and at time t (min), respectively. The straight-line plot of log (q_e–q) *vs*. time t, (not shown) indicates the validity of the Lagergren equation for the system and explains that the process follows first order kinetics. The values of K_r for the Cd(II)–resin systems were found to be 17.123×10^{-3}, 14.315×10^{-3}, 15.217×10^{-3}, 11.831×10^{-3} min^{-1} for SFR, SFC, *p*HFR and SFC, respectively. The values of K_r for the Pb(II)–resin systems were found to be 9.187×10^{-3}, 12.501×10^{-3}, 15.157×10^{-3} and 15.331×10^{-3} min^{-1} for SFR, SFC, pHFR and SFC, respectively. Similar K_r values were reported by Prasad *et al*. for Cu(II) (11.3×10^{-3} min^{-1}) and Ni(II) (9.9×10^{-3} min^{-1}) with a synthetic methacrylic acid–co–ethyleneglycol dimethacrylate resin.[23]

Diffusion models

Sorption kinetics are mainly controlled by various factors including *i*) solute transfer from the solution to the boundary film of the particle (bulk diffusion), *ii*) diffusion from the film to the surface of the sorbent (external diffusion), *iii*) diffusion from the surface to the intraparticular sites (intra-particle diffusion) and *iv*) solute adsorption by complexation or physico–chemical sorption or ion exchange.

By providing sufficient agitation to avoid particle and solute gradients in the batch reactor, enables bulk diffusion to be ignored.[23] The processes of intra-particle diffusion and external diffusion may be the rate controlling steps. Several models have been described to discuss the effect of external diffusion and intra-particle diffusion of solute on an adsorbent. In the present work, the Spahn and Schlunder model[33] and the Weber and Morris model[34] were chosen to describe the external diffusion and intra-particle diffusion on the resin, respectively.

The Spahn and Schlunder model

If external diffusion of metal cations (within the diffuse layers outside the sorbent) is the rate limiting step then the sorption data can be fitted by the following equation:[23,37]

$$\ln (c_t/c_0) = -K_s At/V \tag{6}$$

where K_s is the external diffusion coefficient, c_0 is the initial metal ion concentration, c_t is the concentration at sorption time t, A is the external sorption area and V is the total solution volume. The external diffusion coefficient can be calculated from the slope of the straight line obtained from a plot of ln (c_t/c_0) *vs*. t (not shown). The external diffusion model shows excellent correlation with the sorption data, with high correlation coefficients (Table V). This would indicate that the sorption of Cd(II) and Pb(II) ions under study is a probably a surface process occurring on the exterior of the resin particle. The external diffusion coefficient (K_s) values of Cd(II) and Pb(II) for SFR, SFC, *p*HFR and *p*HFC were calculated and the values are given in Table V. The values for the external diffusion coefficient (K_s) for the synthesized resins are in the range of 0.00125–0.00425 mmol h^{-1} for Cd(II) and 0.00249–0.00680 mmol h^{-1} for Pb(II). Similar results were observed by Anand *et al*.[23] while studying the uptake behaviour of Cu(II) and NI(II) on a methacrylic acid–co–ethylene glycol dimethacrylate polymer.

TABLE V. External and intra-particle diffusion rate constants for the metal–resin systems

Metal ion	Resin	External diffusion		Intra-particle diffusion		
		K_s	R^2	K_{id}	I	R^2
Cd(II)	SFR	0.00425	0.978	0.102	0.029	0.987
	SFC	0.00125	0.977	0.0310	0.063	0.990
	*p*HFR	0.00193	0.938	0.0504	0.094	0.992
	*p*HFC	0.00187	0.987	0.0301	0.039	0.990
Pb(II)	SFR	0.00680	0.942	0.134	0.119	0.989
	SFC	0.00355	0.963	0.0807	0.187	0.997
	*p*HFR	0.00249	0.993	0.0443	0.173	0.978
	*p*HFC	0.00283	0.983	0.0439	0.062	0.995

Weber and Morris model

An empirically found functional relationship, common to the most sorption processes, is that the uptake varies almost proportionally with $t^{1/2}$, the Weber and Morris plot:[34]

$$q_t = k_{id}t^{1/2} + I \tag{7}$$

where, q_t is the amount of sorbate retained at time t, k_{id} is the intra-particle diffusion rate constant and I is thickness of the boundary layer. According to Eq. (7), a plot of q_t *vs*. $t^{1/2}$ (not shown) should be a straight line with slope k_{id} and intercept I when sorption mechanism follows an intra-particle diffusion process.

The values of intercept give an idea about the thickness of the boundary layer, *i.e.*, the larger the intercept, the greater is the boundary layer effect.[35] The values of I for all the resins for Cd(II) and Pb(II) were found in the range 0.029–0.187 mmol dm^{-3} h$^{-1/2}$. The obtained values of the intra particle coefficient ($K_{\rm id}$) and I are given in Table V. From the external diffusion and intra-particle diffusion data, it can be concluded that diffusion process was mainly controlled by intra-particle diffusion.

Analytical application

Removal of toxic metal from industrial effluents. The efficiency of metal ion recovery from industrial effluent was examined using SFR as the representative of all the synthesized resins. The effluents were collected from D. P. Chemicals Pvt. Ltd. GIDC, Ankleshwer and the Plate Well, Padra Road, Atladara, Baroda for Cd(II) and Pb(II), respectively. The initial concentrations of Cd(II) and Pb (II) in the effluents were found to be 185 and 106 mg dm^{-3}, respectively.

Industrial effluent analysis was performed in a simple way using the synthesized resins. The SFR resin was filled in a column (diameter is 0.5 cm) to a length of 15 cm. The filled resin was pre-equilibrated at pH 5.0.

The pH of the industrial effluent containing Cd(II) (100 cm^3) was adjusted to 5.0 using buffer solution and passed through the resin column at flow rate of 1 cm^3 min^{-1}, followed by a thorough washing with water. The chelated cadmium was eluted with 1 M tartaric acid solution at pH 5.0. It was found that the removal and recovery of cadmium from the effluent were quantitative.

The pH of the Pb-containing effluent was adjusted to 5.0 and pass through the resin column at a flow rate 1 cm^3 min^{-1}, followed by thorough washing with deionised water. The chelated lead was eluted with 1 M tartaric acid solution at pH 6.0.

The results showed 94.3 % Cd(II) and 95.1 % Pb(II) recovery from the industrial effluents using the SFR resin. The synthesized resins can be adopted for the treatment of industrial wastewater.

CONCLUSIONS

The synthesized resins exhibited great amorphous character with cracks and channels on their surfaces. The low moisture contents of the resins indicate high degrees of cross-linking. The resins showed quite high capacities for metal uptake. The void volume fractions of the resins were relatively lower than other reported resins, indicating a lower rate of exchange. The chelating ability of the resins for Cd(II) was SFR > *p*HFR > SFC > *p*HFC and for Pb(II) was SFR > SFC > > *p*HFR > *p*HFC. The uptake of metals proceeds by both physical and chemical phenomenon, confirmed by the applicability of the Langmuir and Freundlich isotherms. Diffusion studies shows that the process of metal ion uptake is mainly governed by an intra-particle diffusion process. These synthesized resins can be used for the removal of toxic heavy metals from aqueous media and industrial wastewater containing Cd(II) and Pb(II). The recovery of the metals from Industrial effluents gives an indication of the utilization potential of the synthesized resins for wastewater treatment.

ИЗВОД

КАРАКТЕРИЗАЦИЈА ХЕЛАТНЕ СМОЛЕ ХИДРОКСИБЕНЗОЕВЕ КИСЕЛИНЕ: РАВНОТЕЖА, КИНЕТИКА И ИЗОТЕРМСКИ ПРОФИЛ ЗА ВЕЗИВАЊЕ Cd(II) И Pb(II)

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Хелатна јоно-измењива смола је синтетисана на 80±5 °C поликондензацијом *орто*/*пара*-хидроксибензоеве киселине и ресорцинолом/катехолом уз формалдехид у DMF као умрежавајући агенс. Смола је била карактерисана FTIC и XRD методама. Испитана је способност синтетисаних смола (SFR, SFC, *p*HFR и *p*HFC) да вежу Cd(II) и Pb(II) јоне у зависности од времена контакта, pH, концентрације јона метала и температуре. Селективност синтетисаних смола у везивању јона Pb(II) расте у низу SFR > SFC > *p*HFR > *p*HFC, а за Cd(II) SFR > > *p*HFR > SFC > *p*HFC. Сорпциони подаци добијени за оптимизоване услове су анализирани применом Langmuir-ове и Freundlich-ове изотерме. Експериментални подаци за све метал–смола системе су у најбољем слагању са Freundlich-овом изотермом. SFR показује максимални сорпциони капацитет за кадмијум од 69,5 mg/g и олово 169,3 mg/g. Адсорпциони процес је реакција првог реда, а константа брзине је одређена применом Lagergan-ове једначине. Израчунати су термодинамички параметри метал–смола система. Константе дифузије за спољашњу дифузију и дифузију унутар честице су израчунате применом Spahn–Schlunder и Weber–Morris модела, редом. Дифузија унутар честица је одговорна за процес сорпције.

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