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ORIGINAL PAPER

Adsorption of cadmium ion using a new composite cation-exchanger polyaniline Sn(IV) silicate: kinetics, thermodynamic and isotherm studies

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Abstract A new organic–inorganic composite cation exchanger polyaniline Sn(IV) silicate has been synthesized. The physicochemical properties of this ion exchanger were determined using different analytical techniques including fourier transform infrared spectroscopy, simultaneous thermogravimetry–differential thermogravimetry analyses, X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy and elemental analysis studies. Ion exchange capacity and effect of heating temperature on ion exchange capacity were also carried out on this ion exchange material. Adsorption properties for different metal ions have been investigated and the results revealed that polyaniline Sn(IV) silicate had the highest adsorption capacity for Cd^{2+} ion. It's selectivity was tested by achieving some important binary separations. Dependence of adsorption on contact time, temperature, pH of the solution and exchanger dose had been studied to achieve the optimum conditions. Adsorption kinetic study showed that the adsorption process followed the first order kinetics. Adsorption data were fitted to linearly transformed Langmuir isotherm with R^2 (correlation coefficient) >0.99. The maximum removal of Cd^{2+} was found at pH 9. The adsorption was fast and the equilibrium established within 40 min. Thermodynamic parameters viz- entropy change, enthalpy change and Gibb's free energy change were also calculated.

Keywords Binary separations · Characterization · Langmuir isotherm · Toxic metals

Introduction

Heavy metal pollution occurs in many industrial wastewaters such as those produced by electroplating, nuclear power plants, battery manufacturing process, paints and pigments production and municipal and storm water runoff. The main heavy metals which cause metal ion pollution are Cd, Th, Pb, Cr, As, Hg, Cu and Ni. Unlike most organic pollutants, heavy metals are generally refractory and cannot be degraded or readily detoxified biologically (Sekar et al. 2004). These heavy metals consequently enter in the surrounding soils as well as the ground and surface waters. Public concern over heavy metal pollution has demanded treatment of such effluents before disposal to the environment. Several techniques have been developed for the removal of such metal ions. These techniques include chemical precipitation, physical treatment such as ion exchange, solvent extraction, reverse osmosis and adsorption (Babel and Kurniawan 2003; Wan Ngah and Hanafiah 2008; Bhattacharyya and Gupta 2008; Mahitti and Fuangfa 2008). Although, reverse osmosis is very effective but it is a cost-prohibitive process as the membranes get easily spoiled requiring frequent replacement. Chemical precipitation, however, is not very suitable when the pollutants are present in trace amounts and also a large amount of sludge is produced (Jiang et al. 2010). Solvent extraction or electrolytic processes are also available but they are considered to be cost-effective only for more concentrated solutions (Bhattacharyya and Gupta 2008). Ion exchange is highly effective, promising and widely applied method. Organic–inorganic composite ion exchange materials

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prepared by sol–gel method have attracted a great attention in separation science because they have high selectivity towards toxic metal ions (Khan and Alam 2003; Sahin et al. 2009; Sengupta and Gupta 1997; Nabi et al. 2011; Nabi et al. 2010a, b). Composite materials were considered to be the best way to solve the limitations of poor thermal stability and less chemical stability associated with the use of organic as well as inorganic ion exchange materials, respectively. Composite materials formed by mixing organic polymers and inorganic particles possess all the good properties of both the constituents and an enhanced utility thereof. The combination of organic and inorganic precursors yields composite materials that have mechanical properties not present in the pure materials. A polymeric-inorganic composite cation exchanger polypyrrole Th(IV) phosphate was prepared and used to develop a Pb^{2+} ion-selective membrane electrode (Khan et al. 2005a). It has been established that fibrous polymeric ion exchangers can be impregnated with nanoparticles of hydrated ferric oxide (HFO) which served as a selective sorbent for As(III) and As(V) species from drinking water (Vatutsina et al. 2007). Gupta et al. (2004) studied the adsorption behavior of Hg(II) ions from aqueous solutions on composite of polyaniline with polystyrene as a function of concentration and temperature. The study revealed that the increase of adsorbent concentration (10^{-8}–10^{-3} M) and temperature (293–333 K) enhanced the removal of Hg(II) ions. An organic–inorganic nano-composite poly-*o*-toluidine Th(IV) phosphate was prepared which showed the high selectivity for Hg^{2+} metal ion (Khan et al. 2007).

So, the main objective of our study was to synthesize a new composite material with good ion exchange capacity and high selectivity for heavy toxic metal ions. We have synthesized polyaniline Sn(IV) silicate composite cation exchange material. The material was found to be highly selective for a very toxic metal ion (Cd^{2+}). Cadmium enters in natural water through industrial discharges mainly from electroplating industry and nickel–cadmium battery industry or the deterioration of galvanized water pipes. Cadmium is therefore a potential pollutant in the environment. When excessive amounts of cadmium are ingested, it replaces Zn at key enzymatic sites, causing metabolic disorders, kidney damage, renal dysfunction, anemia, hypertension, bone marrow disorders, cancer and toxicity to aquatic biota (Khan and Alam 2003). Polyaniline Sn(IV) silicate was successfully used for the quantitative separations of Cd^{2+} metal ion from the synthetic mixture of metal ions. Therefore, it was worthwhile to synthesize polyaniline Sn(IV) silicate and investigate its ion exchange properties and applications in a systematic manner. Adsorption kinetic study for polyaniline Sn(IV) silicate was studied which showed that the adsorption process followed the first order kinetics. Adsorption data were fitted to linearly transformed Langmuir isotherm with R^2 (correlation coefficient) >0.99. Studies on thermodynamic parameters viz. Gibb's free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were also carried out to know the feasibility and adsorption process. The effect of various parameters such as time, pH, temperature, adsorbent dose and initial cadmium concentration were also studied. The present research was performed at the Chemistry Department, King Saud University (Riyadh, Kingdom of Saudi Arabia) from January to June 2011.

Materials and methods

Reagents and instruments

Main reagents used for the synthesis were aniline, stannic chloride pentahydrate, sodium metasilicate and potassium persulphate. These reagents were purchased from Sigma Aldrich, Germany. All other reagents and chemicals were of analytical reagent grade.

The main instruments used during the study were a single electrode pH meter (744, Metrohm, Switzerland), FTIR spectrophotometer (Nicolet 6700, Thermo Scientific, USA), an automatic thermal analyzer (V2.2A Du Pont 9900), a PW 1148/89 based X-ray diffractometer (Phillips, Holland), a UV–vis spectrophotometer (Thermo Scientific, England), a water bath incubator shaker (SW22/9550322, Julabo, Germany), high-performance scanning electron microscope with a high resolution of 3.0 nm (JSM-6380 LA, Japan) and muffle furnace (GPC12/65, Carbolite, England).

Preparation of reagent solutions

The solutions of stannic chloride pentahydrate and sodium metasilicate were prepared in de-ionized water (Milli Q). Aniline and potassium persulphate solutions were prepared in 1.0 M HCl. The standard stock solutions of metal nitrates were prepared by dissolving appropriate amounts of their corresponding nitrate or chloride salts in de-ionized (Milli Q) water.

Preparation of polyaniline Sn(IV) silicate

Polyaniline gels were synthesized by mixing different volume ratios of 10 % aniline and 0.2 M potassium persulphate with continuous stirring (Alam et al. 2010). Green colored polyaniline gels were obtained by keeping the solution below 10 °C for 1 h. The precipitate of Sn(IV) silicate was prepared at room temperature (25 ± 2 °C) by adding 0.2 M sodium silicate solution gradually into an aqueous solution of 0.2 M stannic chloride pentahydrate. The gels of polyaniline were then added to the inorganic precipitate of Sn(IV) silicate and mixed thoroughly with constant stirring. The resultant gels, so obtained, were kept in mother liquor for 24 h at room temperature for digestion. The supernatant liquid was filtered and washed with Milli Q water to remove adhering ions. The material was dried in an oven at 50 ± 2 °C for 48 h. The dried material was broken into the desired particle size suitable for column separations on immersion in Milli Q water. The granules were converted into H^+ form by placing in 1 M HNO_3 solution for 24 h. The excess acid from the material was removed after several washings with Milli Q water and finally dried at 50 ± 2 °C. In this way, a number of samples of polyaniline Sn(IV) silicate were prepared in different experimental conditions. It was decided to study sample S-5 in detail on the basis of highest ion exchange capacity and reproducibility for Na^+ ions. It was then stored in air tight container and was used for further studies.

Column ion exchange capacity and regeneration study

1.0 g dry cation exchanger (H^+ form) was packed in a column (internal diameter 1.0 cm) fitted with glass wool at the bottom. 250 mL of 0.1 M solution of each metal nitrates was used to elute the H^+ ions completely from the column. The effluent was titrated against a standard solution of 0.1 M NaOH to determine the total amount of H^+ ions released which is equivalent to the cation retained by the material (Varshney et al. 1988).

When the exchange material exhausted, it was regenerated by keeping it overnight in 0.1 M HNO_3. After that, it was washed with Milli Q water till neutral and the ion exchange capacity was determined by standard column process as described above.

Effect of heating temperature on ion exchange capacity

1.0 g polyaniline Sn(IV) silicate in H^+ form was heated at different temperatures in a muffle furnace for 1 h and Na^+ and Cd^{2+} ion exchange capacities were determined after cooling them at room temperature by standard column process as described above.

Instrumental characterization

Simultaneous thermogravimetric analysis-differential thermal analysis (TGA-DTA) studies of the sample were carried out at a heating rate of 10 °C min^{-1} up to 1,100 °C in the air atmosphere. The Fourier transform infrared spectroscopy (FTIR) absorption spectrum was recorded between 500 and 4,000 cm^{-1}. For FTIR analysis, 10 mg (dry mass) of the exchanger in H^+ form was thoroughly mixed with 100 mg (dry mass) of KBr and grinded to a fine powder. A transparent disc was formed by applying a pressure of 80 psi (1 psi = 6,894.76 pa) in a moisture-free atmosphere. For X-ray diffraction (XRD) analysis, manganese-filtered CuKα radiation wavelength (1.54056 Å) at 298 K was used. The instrument was equipped with graphite monochromator and operating at 40 kV and 30 mA. Scanning electron micrographs (SEM) were recorded for polyaniline Sn(IV) silicate using a scanning electron microscope. Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique which utilizes X-rays that are emitted from the specimen when bombarded by the electron beam. This technique is used to identify the elemental analysis or chemical characterization of a sample. The EDX of polyaniline Sn(IV) silicate was recorded.

Chemical stability and chemical composition

200 mg polyaniline Sn(IV) silicate was equilibrated with 20 mL solution of analytical interest at room temperature (25 ± 2 °C) and kept for 24 h. Stannic and silicate released in the solution were determined by standard spectrophotometric methods (Snell and Snell 1959a, 1959b).

For chemical composition, 200 mg polyaniline Sn(IV) molybdate was dissolved in 20 mL hot concentrated hydrochloric acid. The solution was cooled and diluted to 100 mL with Milli Q water. The metal contents in the solution phase were determined spectrophotometrically (Snell and Snell 1959a, 1959b). Carbon, hydrogen, nitrogen and oxygen contents of the material were determined by elemental analysis.

Sorption studies

0.4 g exchanger in H^+ form was treated with 40 mL solution of metal ions in required solvent medium in a 100 mL Erlenmeyer flask for 24 h. The amount of metal ions before and after adsorption was determined by titration against a standard solution of 0.01 M disodium salt of EDTA. The K_d values may be expressed as follows:

$$K_d = \frac{\text{milli equivalent of metal ions/gm of ion} - \text{exchanger}}{\text{milli equivalent of metal ions / mL of solution}}\ \text{mL g}^{-1} \tag{1}$$

$$K_d = \frac{I - F}{F} \times \frac{V}{M}\ \text{mL g}^{-1}$$

where I is the initial amount of the metal ion in the solution phase, F is the final amount of the metal ion in the solution phase, V is the volume of the solution (mL) and M the amount of exchanger (g).

Quantitative separation of metal ions in binary synthetic mixtures

Quantitative binary separations of some metal ions of analytical interest were achieved on polyaniline Sn(IV) silicate composite cation exchange material. 1.0 g polyaniline Sn(IV) silicate (H^+ form) was packed in a glass column (internal diameter 1.0 cm) with a glass wool support at the end. The column was washed thoroughly with Milli Q water. 2.0 ml binary mixture (1 mL of each metal) of the metal ions to be separated was poured on to the column and allowed to flow at a rate of 0.3–0.5 mL min^{-1} till the solution level was just above the surface of the material. The column was then rinsed with Milli Q water. Individual metal ions were eluted using appropriate eluting reagents. The flow rate of the eluent was maintained (0.3–0.5 mL min^{-1}) throughout the elution process. The effluent was collected in 10 mL fractions and was titrated against the standard solution of 0.01 M disodium salt of EDTA.

Removal study of Cd^{2+} ion by batch experiment

Effect of contact time

The equilibration time for maximum adsorption of Cd^{2+} ion on polyaniline Sn(IV) silicate was established by performing a series of adsorption experiments. 1.0 g polyaniline Sn(IV) silicate was stirred with a known amount of cadmium(II) nitrate solution for 10–60 min. The amount of Cd^{2+} ion before and after adsorption was determined by titration against the standard solution of 0.01 M disodium salt of EDTA.

Effect of pH

To study the effect of pH on the adsorption of Cd^{2+} ion, 1.0 g polyaniline Sn(IV) silicate was shaken continuously with a known amount of cadmium(II) nitrate solution for 40 min at pH 1–10. The pH of the solution was adjusted by adding acid, base or buffer of desired pH. The amount of Cd^{2+} ion before and after adsorption was determined by the above method.

Effect of temperature on Cd $^{2+}$ ion sorption

To determine the effect of temperature on the adsorption of metal ions, 1.0 g polyaniline Sn(IV) silicate was equilibrated with cadmium(II) nitrate solution at pH 9 for 40 min and different temperatures 25, 35, 45 and 55 °C. The amount of metal ion before and after adsorption was determined by the above method.

Effect of polyaniline Sn(IV) silicate dose

To determine the effect of ion exchange material dose for the removal of Cd^{2+} ion, different amount (0.2–1.0 gm) of polyaniline Sn(IV) silicate was stirred with a known amount of cadmium nitrate solution for 40 min at pH 9 and 45 °C temperature. The amount of metal ion before and after adsorption was determined by the above method.

Effect of initial Cd^{2+} concentration

The adsorption of Cd^{2+} ion onto polyaniline Sn(IV) silicate was studied by varying initial cadmium concentration (200–1,000 mg/L) using optimum adsorbent dose (0.5 g) at ambient temperature (45 °C) for a contact time of 40 min and pH 9. The amount of metal ion before and after adsorption was determined by the above method.

Study of interferences

It is important to study the interference of competitive ions like Cu, Mg, Ca, Zn and Pb on the adsorption of cadmium, because these ions are commonly found in drinking water as well as industrial effluent. Varying concentration of these solutions was prepared from their nitrate and chloride salts. The initial concentration of cadmium was fixed at 1,000 mg/L while the initial concentration of copper, magnesium, calcium, zinc and lead cations varied from 100 to 500 mg L^{-1}.

Results and discussion

Different samples of polyaniline Sn(IV) silicate were prepared by incorporating polyaniline into the matrix of inorganic precipitate (Sn(IV) silicate) under changeable conditions. Table 1 shows that the mixing ratio of the reactants and pH affected the ion exchange capacity of the material. Among them, sample S-5 possessed better Na^+ ion exchange capacity, high mechanical and thermal stability. The material (sample S-5) has good reproducible behavior because it was synthesized in various batches and it did not show any considerable change in ion exchange capacities. So sample S-5 was selected for detailed studies.

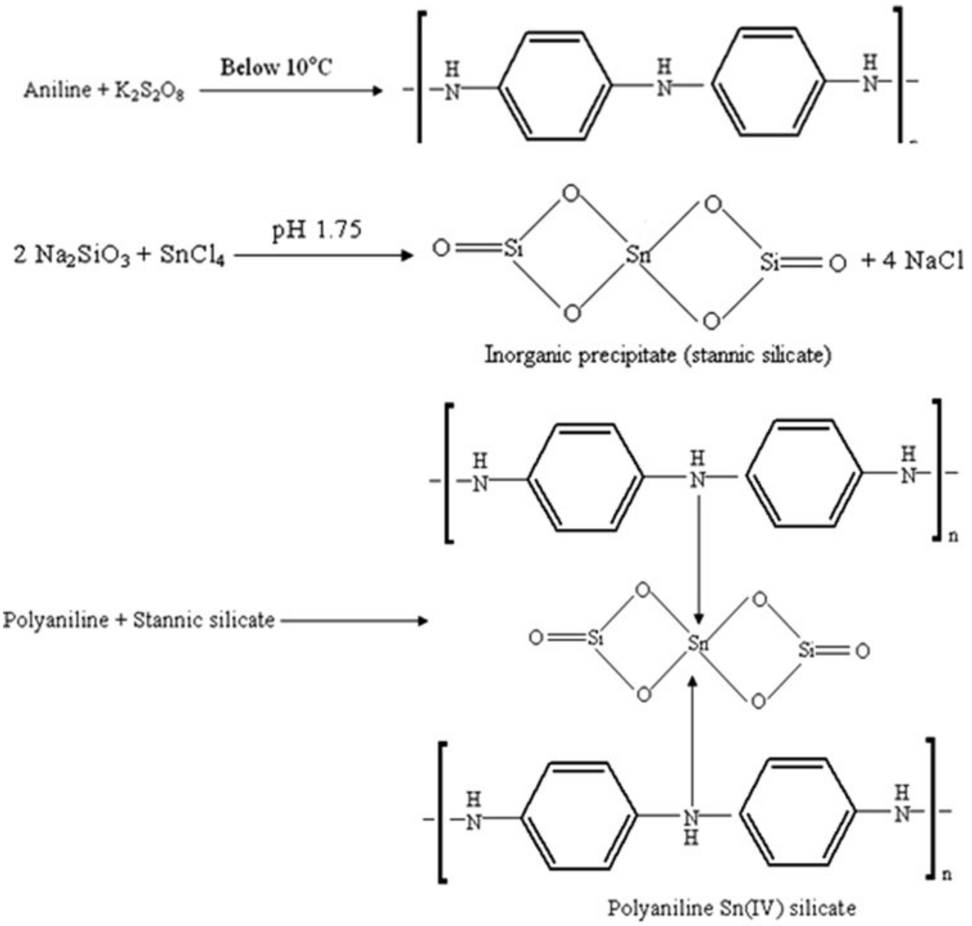
Polyaniline gel was prepared by oxidative coupling using $K_2S_20_8$ in acidic aqueous medium (Alam et al. 2010). The binding of polyaniline into the matrix of Sn(IV) silicate may be given as Scheme 1.

Ion exchange capacities for mono and bivalent metal ions have been studied (Table 2). It was found that the material showed the highest affinity for Cd^{2+} ion. The reusability of polyaniline Sn(IV) silicate was investigated after regenerating this ion exchange material by keeping it

Table 1 Synthesis of polyaniline Sn(IV) silicate composite cation exchange material in different conditions

Sample code	Mixing volume ratios (V/V)		pH of inorganic precipitates	Mixing volume ratios (V/V)		Drying temperature (°C)	Heating time (h)	Ion exchange capacity for Na^+ ion (meq g^{-1})
	A	B		0.2 M $K_2S_2O_8$ in 1.0 M HCl	10 % aniline in 1.0 M HCl			
S-1	1 (0.2 M)	2 (0.2 M)	0.5	1	1	50 ± 2	2	No precipitate
S-2	1 (0.2 M)	2 (0.2 M)	1.0	1	1	50 ± 2	2	No precipitate
S-3	1 (0.2 M)	2 (0.2 M)	1.2	1	1	50 ± 2	2	No precipitate
S-4	1 (0.2 M)	2 (0.2 M)	1.5	1	1	50 ± 2	2	1.0
S-5[a]	1 (0.2 M)	2 (0.2 M)	1.75	1	1	50 ± 2	2	1.75
S-6	1 (0.2 M)	2 (0.2 M)	1.9	1	1	50 ± 2	2	1.25
S-5	2 (0.2 M)	1 (0.2 M)	1.75	1	1	50 ± 2	2	1.50
S-6	1 (0.2 M)	1 (0.2 M)	1.75	1	1	50 ± 2	2	1.12

A stannic chloride pentahydrate, *B* sodium silicate, *S-5*[a] selected for detailed studies



Scheme 1

overnight in 0.1 M HNO_3. It was observed that the ion exchange capacity decreased about 30 % of its original ion exchange capacity after reuse for four times. It confirmed that polyaniline Sn(IV) silicate has a good reusability. Ion exchange capacity of the material was also affected by heating. On heating at different temperatures for 1 h, the ion exchange capacity of the dried material decreased as the temperature increased. But, the material was quite

Table 2 Ion-exchange capacity of various exchanging ions on polyaniline Sn(IV) silicate composite cation exchange material

Exchanging ions	Salt solution used	IEC (meq g^{-1})
Li^+	Lithium nitrate	0.80
Na^+	Sodium nitrate	1.75
K^+	Potassium nitrate	1.80
Mg^{2+}	Magnesium nitrate	1.20
Ca^{2+}	Calcium nitrate	1.54
Sr^{2+}	Strontium nitrate	1.60
Ba^{2+}	Barium nitrate	1.90
Pb^{2+}	Lead nitrate	2.00
Cd^{2+}	Cadmium nitrate	2.40

IEC ion exchange capacity

Table 3 Thermal stability of polyaniline Sn(IV) silicate after heating to various temperatures for 1 h

Heating temperature (°C)	IEC for Na^+ ion (meq g^{-1})	% retention of IEC	IEC for Cd^{2+} ion (meq g^{-1})	% retention of IEC
50	1.75	100	2.40	100
100	1.70	97.0	2.35	95.8
200	1.55	88.6	2.00	83.3
300	1.40	80.0	1.87	77.9
400	1.20	68.6	1.30	54.2
500	0.80	45.71	1.0	41.6
600	0.50	28.6	0.64	26.6
700	0.32	18.3	0.42	17.5

stable and retained more than 40 % ion exchange capacity up to a temperature of 500 °C. The thermal stability of polyaniline Sn(IV) silicate was found to be more than normal inorganic ion exchangers, which may be due to it's hybrid nature. The sodium and cadmium ion exchange capacities at different temperatures are shown in Table 3.

TGA curve (Fig. 1) of the polyaniline Sn(IV) silicate showed a continuous weight loss of mass 11 % up to 160 °C which may be due to loss of external water molecules from the exchanger (Duval 1963). The second weight loss (about 8 %) up to 500 °C is attributed to the removal of structural water molecules (Nilchi et al. 2006). Further weight loss (about 12.76 %) between 500 and 1,000 °C may be due to decomposition of the organic part of the material. From 1,000 °C onwards, a smooth horizontal section represented the complete formation of the oxide form of the material. DTA and DTG analyses (Fig. 1), which were used as complimentary techniques, supported these conclusions. The ion exchange capacity data also supported these findings as the material lost ~59 % ion exchange capacity (for Cd^{2+} ion) up to 500 °C. Decrease in ion exchange capacity with increasing temperature is attributed to the condensation of structural hydroxyl groups (Qureshi et al. 1977; Thakkar et al. 2007). The FTIR spectrum of the prepared polyaniline Sn(IV) silicate is shown in Fig. 2a. It is concluded from the figure that the broad band in the region of 3,300–3,600 refers to the stretching vibration of interstitial water (Al-Othman et al. 2011a). A sharp peak at 1,600 cm^{-1} corresponds to H–O–H bending band, being also representative of the strongly bonded –OH groups in the matrix (Khan et al. 2005b). The O–H stretching bands merged together and shifted to lower frequency in the spectrum of the exchanger. This was due to the possibility of H-bonding. A band at about 1,400 cm^{-1} can be due to stretching vibration of C–N (Rao 1963) and a band around 3,000 cm^{-1} may be related to the stretching of NH bonds of benzenic and quinonic rings (Tang et al. 1988). A sharp peak at 1,096 cm^{-1} attributed to silicate (Nabi et al. 2010a, b) ion and a broad peak in the region between 500 and 800 cm^{-1} was due to metal–oxygen bond (Al-Othman et al. 2011b). The XRD pattern (Fig. 2b) was recorded in powdered sample which showed low intense peaks at different 2θ values. The analysis of these small signal peaks suggested the semi-crystalline nature of polyaniline Sn(IV) silicate. The SEM image of polyaniline Sn(IV) silicate (Fig. 3a) showed a rough morphology with irregular particle size. The EDX spectrum of polyaniline Sn(IV) silicate (Fig. 3b) showed the peaks of Sn and Si, along with peaks for O and C. The spectrum indicated that Sn was the major component.

Polyaniline Sn(IV) silicate was found reasonably stable in some organic solvents (dimethylformamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide), acids (nitric acid, formic acid, acetic acid, succinic acid) and bases (sodium hydroxide, potassium hydroxide) up to 1 M. Thus, the exchanger was chemically resistant to these solvents and could be successfully used with these solvents in column operation. The molar ratio of Sn, Si, C, H, N and O, in polyaniline Sn(IV) silicate was estimated to be 1, 2, 13, 3, 1 and 8.

To investigate the potentiality of this composite material in the separation of metal ions, distribution studies for different metal ions were performed in several acid mediums viz. 0.1 M oxalic acid, 0.1 M citric acid, 0.1 M formic acid and 0.1 M succinic acid (Table 4). The effect of the dielectric constant of these solvent systems on K_d values was studied and it was found that the increase in dielectric constant of solvents caused the decrease in distribution coefficient of almost all the metal ions studied except Sr^{2+} and Hg^{2+}, where no regular trend was observed. All metal ions had the lowest K_d values in oxalic acid medium than other acidic mediums (0.1 M citric acid, 0.1 M formic acid and 0.1 M succinic acid). It was due to the presence of high concentration of H^+ ions in oxalic acid medium, which

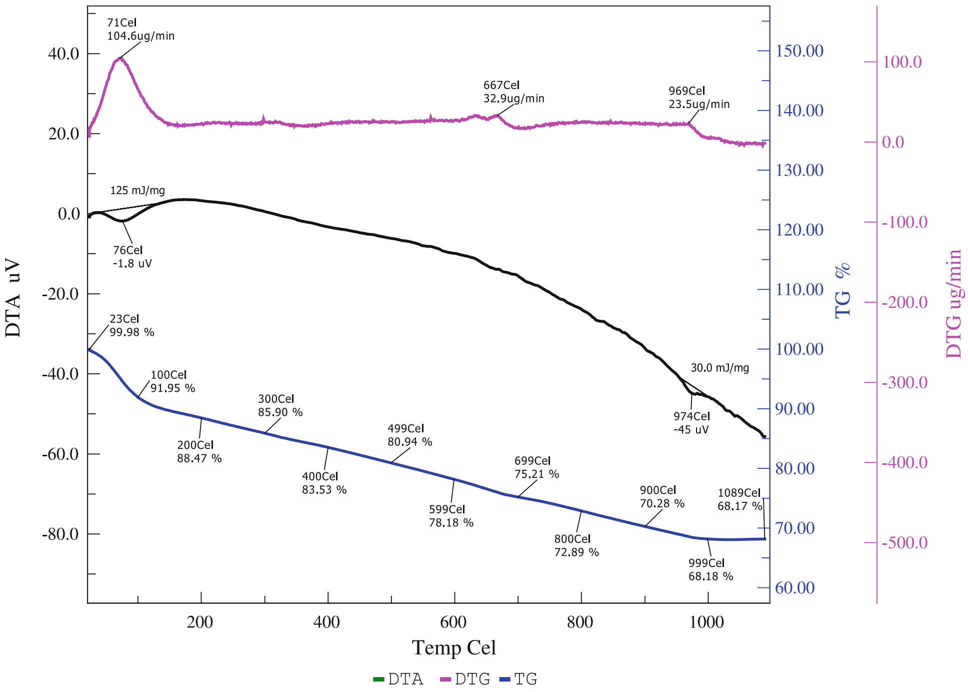


Fig. 1 TGA-DTA curves of polyaniline Sn(IV) silicate composite cation exchange material

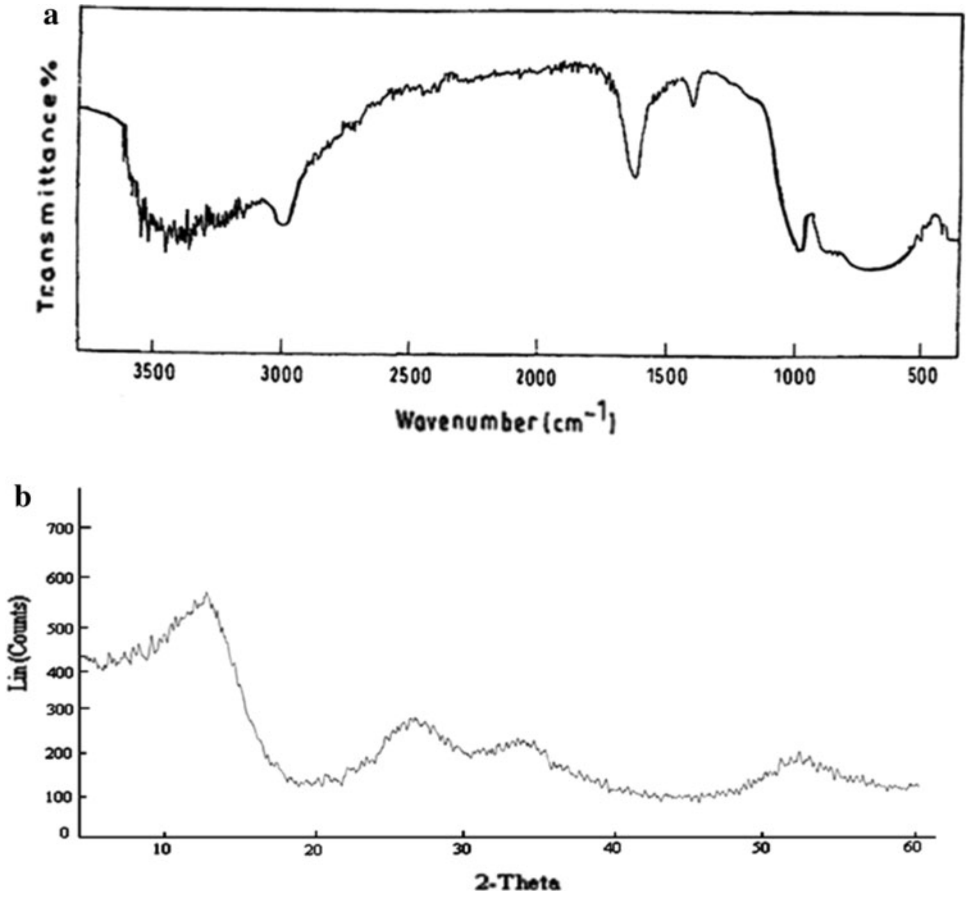


Fig. 2 Polyaniline Sn(IV) silicate composite cation exchanger. **a** FTIR spectra of **b** powder X-ray diffraction pattern

reversed the process of adsorption and the process of regeneration predominates over the process of removal. Further, Cd^{2+} ion showed relatively higher K_d values in all the solvents as compared to other metal ions. The difference in the K_d values of metal ions indicated the separation possibilities of certain metal ions of analytical interests.

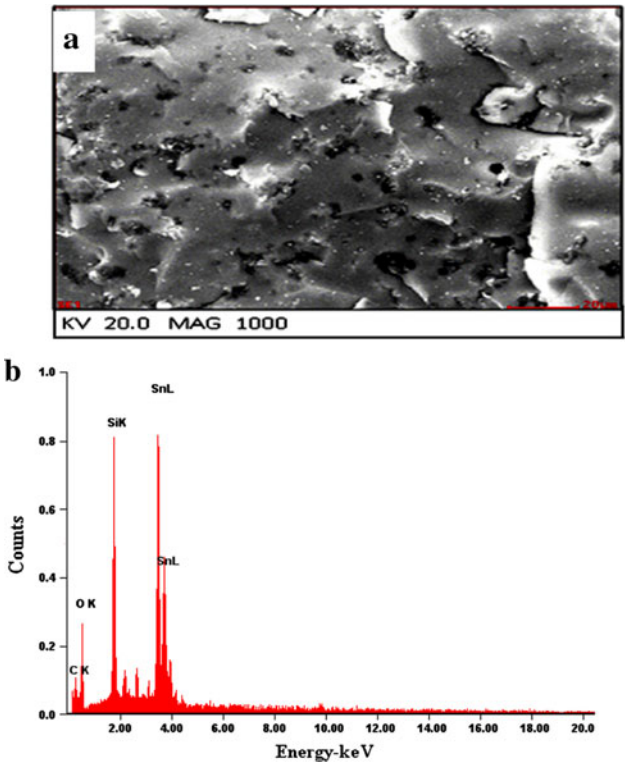


Fig. 3 Polyaniline Sn(IV) molybdate composite cation exchanger. **a** SEM image, **b** EDS spectra

The separation capability of the material has been demonstrated by achieving some important binary separations (Table 5). The sequential elution of ions through column depends upon the metal–ligand stability. The weakly retained metal ions eluted first and strongly retained at last. Elution behavior of metal ions towards polyaniline Sn(IV) silicate was studied in various eluting reagents and it was observed that 0.1 M succinic acid was the best eluent for all metal ions in which about 58–85 % metal ions were recovered. So 0.1 M succinic acid was selected as eluting reagent for the elution of metal ions (Table 6).

Table 4 Distribution coefficients of different metal ions on polyaniline Sn(IV) silicate composite cation exchange material columns in different solvent systems

Metal ion	Oxalic acid (0.1 M)	Citric acid (0.1 M)	Formic acid (0.1 M)	Succinic acid (0.1 M)
Mg^{2+}	57	70	121	205
Ca^{2+}	57	76	230	234
Sr^{2+}	140	86	148	190
Ba^{2+}	148	420	420	490
Hg^{2+}	82	102	96	119
Cd^{2+}	215	927	965	1,583
Pb^{2+}	300	413	440	455
Zn^{2+}	86	132	134	210
Mn^{2+}	83	120	146	217
Cu^{2+}	38	56	56	200
Al^{3+}	237	412	541	679
Ni^{2+}	31	61	161	235
Fe^{3+}	130	135	167	178
Co^{2+}	124	129	154	182
La^{3+}	168	168	174	186

The utility of polyaniline Sn(IV) silicate to remove Cd^{2+} ions by sorption at different time, pH, temperature and ion exchange material dose was studied. It was observed that instant adsorption was achieved within 10 min and goes on increasing up to 40 min and equilibrium was established after 40 min (Fig. 4a). The difference in the rate of adsorption may be due to the fact that initially all adsorbent sites were vacant and so the adsorption was high. Later, due to the decrease in number of adsorption sites as well as cadmium concentration, the cadmium uptake rate by polyaniline Sn(IV) silicate was decreased significantly (Islam and Patel 2007, 2008). The optimum pH for maximum removal of Cd^{2+} ion using polyaniline Sn(IV) silicate column was found to be 9 (Fig. 4b). At pH lower than 2, the removal was very low. This is due to high H^+ ion concentration, which reversed the process of adsorption and the process of regeneration predominated over the process of removal (Islam and Patel 2008). At higher pH (i.e. ≥ 9), 86 % removal was achieved. This was due to combined effect of adsorption and precipitation as cadmium hydroxide. It was also interesting to note that the uptake of Cd^{2+} ions by the exchanger was favored with the increase in temperature up to 45 °C and after that it became constant (Fig. 4c). The removal of Cd^{2+} increased from 63 to 80 % for 25–45 °C. The continuous increase in the percentage removal of Cd^{2+} up to 45 °C indicated that adsorption was endothermic in nature (Ofomaja and Ho 2008; Ajmal et al. 2000). The effect of polyaniline Sn(IV) silicate dose for the removal of Cd^{2+} ions was studied and it was noted that 0.5 g polyaniline Sn(IV) silicate was optimum dose for the removal of maximum Cd^{2+} ions (79 %). After 0.5 g dosage, there was no considerable change in the percentage of Cd^{2+} ions removal (Fig. 4d). It may be due to the overlapping of active sites at higher dosage. So, there was not any increase in the effective surface area resulting in the conglomeration of exchanger particles (Islam and Patel 2008). The adsorption of Cd^{2+} onto polyaniline Sn(IV) silicate exchanger was studied by varying initial cadmium concentration (200–1,000 mg L^{-1}). It was found that as the concentration of cadmium increased; the percentage removal was decreased from 92 to 80 %. It may be due to less availability of adsorption sites of exchanger at higher dose of cadmium. The effect of interfering cations like copper, magnesium, calcium, zinc and cadmium was studied. It was found that the presence of these cations reduced the adsorption of Cd^{2+} ion

Table 5 Quantitative separations of metal ions in binary mixtures on polyaniline Sn(IV) silicate composite cation exchange material columns

Separations achieved	Separation factor $\alpha = Kd_1/Kd_2$	Amount loaded (mg)	Amount found[a] (mg)	% recovery	Volume of eluent (mL)
Zn^{2+}	7.54	6.54	4.79	73.27	70
Cd^{2+}		11.24	8.94	79.50	80
Ni^{2+}	6.74	5.87	4.76	81.14	70
Cd^{2+}		11.24	8.94	79.50	80
Hg^{2}	13.30	20.05	16.19	80.77	40
Cd^{2+}		11.24	8.94	79.50	80
Mg^{2+}	7.72	2.43	1.86	76.42	60
Cd^{2+}		11.24	8.94	79.50	80
Pb^{2+}	3.48	10.64	8.35	78.44	70
Cd^{2+}		11.24	8.94	79.50	80
Cu^{2+}	7.92	6.3	5.36	84.49	60
Zn^{2+}		6.54	4.79	73.27	70
Mg^{2+}	3.31	6.53	5.55	84.95	60
Al^{3+}		2.70	2.16	80.19	70

0.1 M succinic acid is used as eluent

[a] Average of three replicate determinations

Table 6 Elution behaviour of metal ions towards polyaniline Sn(IV) silicate composite cation exchange material

Separations achieved	% E/Ev	Oxalic acid (0.1 M)	Citric acid (0.1 M)	Formic acid (0.1 M)	Succinic acid (0.1 M)
Zn^{2+}	% E	58.00	69.14	70.30	73.27
	Ev	50	50	60	70
Ni^{2+}	% E	70.10	73.40	79.20	81.14
	Ev	60	60	70	70
Cd^{2+}	% E	70.80	72.40	75.50	79.50
	Ev	70	70	80	70
Hg^{2+}	% E	70	75.64	78	80.77
	Ev	50	50	50	50
Al^{3+}	% E	73.18	75.00	79.24	80.19
	Ev	80	80	70	70
Pb^{2+}	% E	70	73.50	75.50	78.44
	Ev	70	80	70	70
Cu^{2+}	% E	78	80	82.40	84.49
	Ev	70	60	60	60
Mg^{2+}	% E	77.14	80	82	84.95
	Ev	70	60	60	60

Ev volume of eluent, *%E* percentage elution

appreciably. The cations decreased the cadmium adsorption in the order of $Pb^{2+} > Zn^{2+} > Ca^{2+} > Mg^{2+} > Cu^{2+}$.

Adsorption kinetics

The adsorption of Cd^{2+} ion was rapid at first and it was slowed down as the equilibrium approached. The rate constant K_{ad} for the sorption of Cd^{2+} ion was studied by Lagergren rate equation (Das et al. 2005; Sujana et al. 1998).

$$\log(qe - q) = \log qe - k_{ad}\left({}^{t}\!/_{2.303}\right) \qquad (2)$$

where qe and q (both in mg/g) are the amounts of cadmium adsorbed at equilibrium and at time 't', respectively. The plot of log ($qe - q$) versus 't' at different time intervals was almost linear, indicated the validity of Lagergren rate equation of first order kinetics. The adsorption rate constant (K_{ad}), calculated from the slope of the above plot is presented in Table 7.

Thermodynamic parameters

Some thermodynamic parameters were also studied to know the ion exchange kinetics of this material. The values of ΔG, ΔH, ΔS and equilibrium constant (K_c) of adsorption were calculated using the following equations (Messina and Schulz 2006; Namasivayam and Sangeetha 2006):

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (3)$$

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

The K_c value was calculated using the following equation (Eren and Afsin 2008; Islam and Patel 2007):

$$K_c = \frac{C_e}{C_o} \qquad (5)$$

where C_e and C_o were the amount of cadmium ion adsorbed per unit mass of adsorbent and in aqueous phase, respectively. Values of ΔH and ΔS were evaluated from the slope and intercept of a linear Van't Hoff plot which was

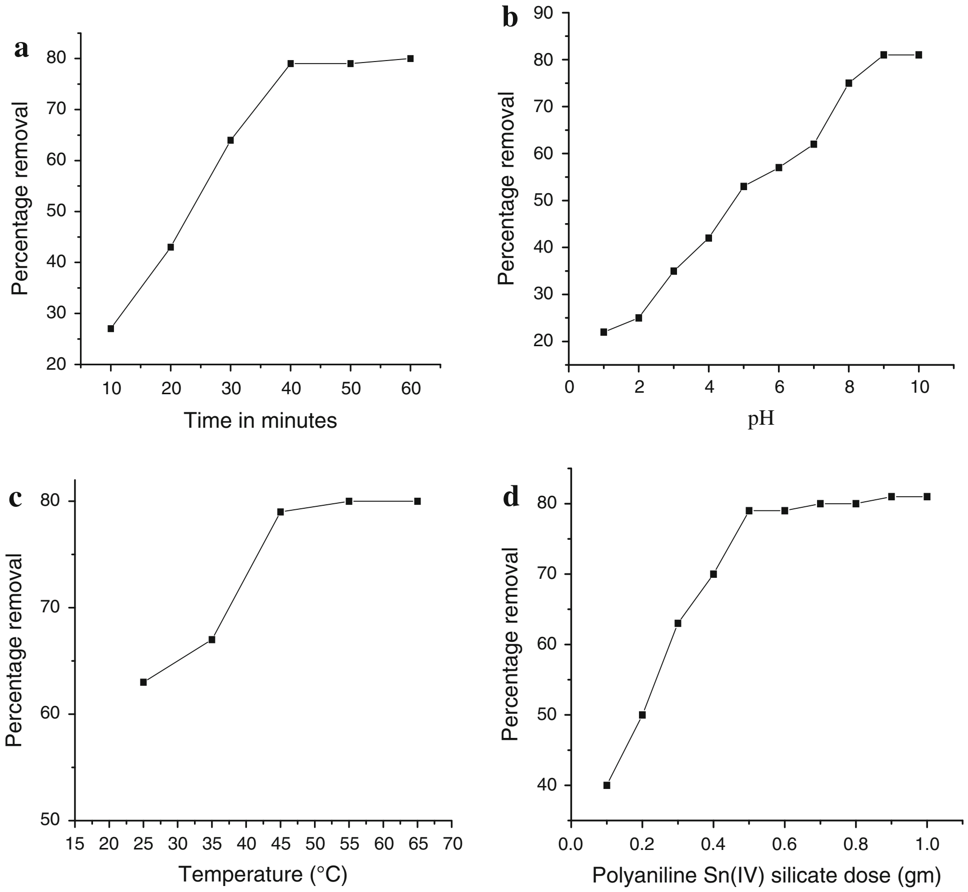


Fig. 4 Percentage removal of cadmium at different **a** time, **b** pH, **c** temperature and **d** exchanger dose

plotted between log K_c and $1/T$. Table 7 showed the positive value of entropy which showed the increase in randomness of the ongoing process and hence a good affinity of cadmium with polyaniline Sn(IV) silicate and the negative value of ΔG indicated the feasibility and spontaneity of the reaction of ongoing adsorption. A decrease in values of ΔG with the increase in temperature suggested more adsorption of cadmium at higher temperature. The endothermic nature of the process was once again confirmed by the positive value of ΔH.

Adsorption isotherm

The adsorption data were fitted to linearly transformed Langmuir isotherm. The linearized Langmuir equation, which is valid for monolayer sorption onto a surface with finite number of identical sites, is given by the following equation (Eren and Afsin 2008; Islam and Patel 2007):

$$\frac{1}{qe} = \frac{1}{qobCe} + \frac{1}{qo} \tag{6}$$

where qo is the maximum amount of the cadmium ion per weight of polyaniline Sn(IV) silicate to form a complete monolayer on the surface (adsorption capacity), Ce denotes equilibrium adsorbate concentration in solution, qe is the amount adsorbed per unit mass of adsorbent, and b is the binding energy constant. The linear plot of $1/Ce$ versus $1/qe$ (Fig. 5) with $R^2 = 0.993$ indicated the applicability of Langmuir adsorption isotherm. The values of Langmuir parameters qo and b were 250 mg/g and 0.0625 L/mg, respectively. To predict the adsorption efficiency of the

Table 7 Lagergren rate constant (K_{ad}) and thermodynamic parameters for Cd^{2+} adsorption on polyaniline Sn(IV) silicate composite cation exchange material

Lagergren rate constant (K_{ad})	ΔH (KJ mol^{-1})	ΔS (KJ/K mol)	ΔG (KJ mol^{-1})					R^2
			25 °C	35 °C	45 °C	55 °C	65 °C	
0.124	65.28	0.24	−7.104	−9.533	−11.962	−14.391	−16.820	0.993

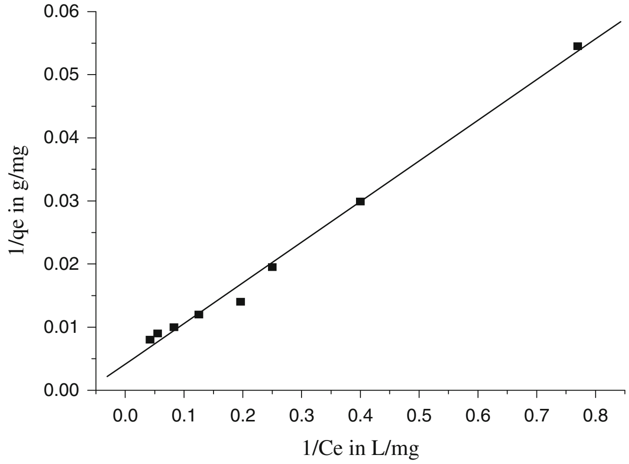


Fig. 5 Langmuir adsorption isotherm, 1/*C*e versus 1/*q*e

adsorption process, the dimension less equilibrium parameter (r) was determined using the following equation (Islam and Patel 2008):

$$r = \frac{1}{1 + bCo} \tag{7}$$

where Co is the initial concentration. Values of $r < 1$ represent favorable adsorption. The "r" value was found to be 0.016. The values indicated a favorable system.

Conclusion

Polyaniline Sn(IV) silicate composite cation exchanger, prepared in the present study, showed high selectivity for Cd^{2+} metal ion. Moreover, it's high thermal and chemical stabilities and feasibility of regeneration by the diluted HNO_3 solution also help to be an excellent candidate for removal of heavy metals from aqueous media. The proposed material was semi-crystalline in nature. The values of ΔS, ΔH and ΔG were determined on this cation exchanger successfully. Some important binary separations were also performed using the packed column of this material. It is clear from the results that the quantitative and efficient separations of various metal ions are feasible on polyaniline Sn(IV) silicate columns. So, this cation exchange material is a potential candidate for removing heavy metal ions and specially Cd^{2+} ion from contaminated water to control the pollution. The adsorption of Cd^{2+} metal ion was found to follow the first order kinetics.

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References

Ajmal M, Rao RAK, Ahmad R, Ahmad J (2000) Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater. J Hazard Mater 79(1–2):117–131

Alam Z, Inamuddin, Nabi SA (2010) Synthesis and characterization of a thermally stable strongly acidic Cd(II) ion selective composite cation exchanger: polyaniline Ce(IV) molybdate. Desalination 250(2):515–522

Al-Othman ZA, Naushad Mu, Nilchi A (2011a) Development, characterization and ion exchange thermodynamics for a new crystalline composite cation exchange material: application for the removal of Pb^{2+} ion from a standard sample (rompin hematite). J Inorg Organomet Polym 21(3):547–559

Al-Othman ZA, Naushad Mu, Inamuddin (2011b) Organic–inorganic type composite cation exchanger poly-*o*-toluidine Zr(IV) tungstate: preparation, physicochemical characterization and its analytical application in separation of heavy metals. Chem Engg J 172(1):369–375

Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater 97(1–3):219–243

Bhattacharyya KG, Gupta SS (2008) Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Adv Colloid Interface Sci 140(2):114–131

Das N, Pattanaik P, Das R (2005) Defluoridation of drinking water using activated titanium rich bauxite. J Colloid Interface Sci 292(1):1–10

Duval C (1963) Inorganic Thermogravimetric Analysis. Elsevier, Amsterdam

Eren E, Afsin B (2008) Investigation of a basic dye adsorption from aqueous solution onto rawand pre-treated bentonite surfaces. Dyes Pigm 76(1):220–225

Gupta RK, Singh RA, Dubey SS (2004) Removal of mercury ions from aqueous solutions by composite of polyaniline with polystyrene. Sep Purif Techn 38(3):225–232

Islam M, Patel RK (2007) Evaluation of removal efficiency of fluoride from aqueous solution using quick lime. J Hazard Mater 143(1–2):303–310

Islam M, Patel R (2008) Polyacrylamide thorium (IV) phosphate as an important lead selective fibrous ion exchanger: synthesis, characterization and removal study. J Hazard Mater 156(1–3): 509–520

Jiang MQ, Jin XY, Lu XQ, Chen ZL (2010) Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay. Desalination 252(1–3):33–39

Khan AA, Alam MM (2003) Synthesis and characterization and analytical applications of a new and novel 'organic–inorganic' composite material as a cation exchanger and Cd(II) ion-selective membrane electrode: polyaniline Sn(IV) tungstoarsenate. React Funct Polym 55(3):277–290

Khan AA, Inamuddin, Alam MM (2005a) Preparation, characterization and analytical applications of a new and novel electrically conducting fibrous type polymeric–inorganic composite material: polypyrrole Th(IV) phosphate used as a cation exchanger and Pb(II) ion-selective membrane electrode. Mat Res Bull 40(2):289–305

Khan AA, Inamuddin, Alam MM (2005b) Determination and separation of Pb2+ from aqueous solutions using a fibrous type organic–inorganic hybrid cation exchange material: polypyrrole thorium(IV) phosphate. React Funct Polym 63(2):119–133

Khan AA, Khan A, Inamuddin (2007) Preparation and characterization of a new organic–inorganic nano-composite poly-*o*-toluidine Th(IV) phosphate: Its analytical applications as cation exchanger and in making ion-selective electrode. Talanta 72(2):699–710

Mahitti P, Fuangfa U (2008) Preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg(II) ions. J Hazard Mater 154(1–3):578–587

Messina PV, Schulz PC (2006) Adsorption of reactive dyes on titania–silica mesoporous materials. J Colloid Interface Sci 299(1):305–320

Nabi SA, Bushra R, Naushad Mu, Khan A (2010a) Synthesis, characterization and ion exchange behavior of composite material, poly-*o*-toluidine stannic molybdate and its use in the separation of toxic metal ions. Chem Engg J 165(2):529–536

Nabi SA, Ganai SA, Naushad Mu (2010b) Preparation and characterization of a new inorganic cation exchanger: zirconium (IV) iodosilicate: analytical applications for metal content determination in pharmaceutical sample and synthetic mixture. Desalin Water Treat 16(1–3):29–38

Nabi SA, Bushra R, Al-Othman ZA, Naushad Mu (2011) Synthesis, characterization and analytical applications of a new composite cation exchange material Acetonitrile stannic(IV) selenite: adsorption behavior of toxic metal ions in nonionic surfactant medium. Sep Sci Techn 46(5):847–857

Namasivayam C, Sangeetha D (2006) Removal of molybdate from water by adsorption onto $ZnCl_2$ activated coir pith carbon. J Bioresour Technol 97(10):1194–1200

Nilchi A, Maalek B, Kanchi A, Maragheh MG, Bagheri A (2006) Cerium (IV) molybdate cation exchanger: synthesis, properties and ion separation capabilities. Radiat Phys Chem 75(2): 301–308

Ofomaja AE, Ho YS (2008) Effect of temperature and pH on methyl violet biosorption by Mansonia wood sawdust. Bioresour Technol 99(13):5411–5417

Qureshi M, Gupta AP, Khan T (1977) Synthesis and ion exchange properties of a semicrystalline, magnesium-selective niobium antimonite. J Chrom A 144(2):231–244

Rao CNR (1963) Chemical applications of infrared spectroscopy. Academic Press, New York, p 250

Sahin M, Gorcay H, Kır E, Sahin Y (2009) Removal of calcium and magnesium using polyaniline and derivatives modified PVDF cation exchange membranes by Donnan dialysis. React Funct Polym 69(9):673–680

Sekar M, Sakthi V, Rengaraj S (2004) Kinetics equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. J Colloid Interface Sci 279(2):307–313

Sengupta S, Gupta AKS (1997) Heavy-metal separation from sludge using chelating ion exchangers with nontraditional morphology. React Funct Polym 35(1–2):111–134

Snell FD, Snell CT (1959) Colorimetric methods of chemical analysis including photometric methods, vol 11. D. Van. Nostrand, New Jersey, p 135

Snell FD, Snell CT (1959) Colorimetric methods of chemical analysis including photometric methods, vol 11. D. Van. Nostrand, New Jersey, p 586

Sujana MG, Thakur RS, Rao SB (1998) Removal of fluoride from aqueous solution by using alum sludge. J Colloid Interface Sci 206(1):94–101

Tang J, Jing X, Wang B, Wang F (1988) Infrared spectra of soluble polyaniline. Synth Met 24(3):231–238

Thakkar R, Patel H, Chudasama U (2007) A comparative study of proton transport properties of zirconium phosphate and its metal exchanged phases. Bull Mater Sci 30(3):205–209

Varshney KG, Agrawal K, Agrawal S, Saxena V, Khan A (1988) Synthetic, kinetic and analytical studies on titanium (IV) arsenosilicate ion exchanger: separation of lead from its synthetic alloys. Colloids Surf A Physchem Engg Aspects 29(2): 175–189

Vatutsina OM, Soldatov VS, Sokolova VI, Johann J, Bissen M, Weissenbacher A (2007) A new hybrid (polymer/inorganic) fibrous sorbent for arsenic removal from drinking water. React Funct Polym 67(3):184–201

Wan Ngah WS, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresour Technol 99(10):3935–3948