

Polyaniline embedded tin zirconium tungstate composite ion exchange material for the removal of heavy metal ion and organic pollutant from aqueous solution

Vinisha P.Valsaraj^{1*}, C.Janardanan²

Post Graduate and Research Department of Chemistry, Sree Narayana College, Kannur-670 007, Kerala, (INDIA)

E-mail: vinipunep@gmail.com

ABSTRACT

A new composite material has been synthesized by the incorporation of conducting polymer into the inorganic matrix. It was characterized by using various instrumental techniques. The ion exchange characteristics of material were studied. Physicochemical properties, pH titrations, effect of temperature on the ion exchange capacity, effect of eluent concentration, and elution behavior were studied to exploit the ion-exchange capability of composite. The hybrid material exhibits improved thermal stability. Sorption behaviour of metal ions on the material was studied in different solvents at different concentration. On the basis of distribution values, composite material was found to be selective for Pb(II) ions. Some analytically important binary separation of the metal ions has been achieved on the column of this composite. This composite material has been fruitfully applied for the treatment of heavy metals from synthetic mixture and industrial waste water samples. The UV-Visible spectrophotometric studies revealed the enhanced adsorption ability of this material towards organic pollutants like dyes. The effect of some important parameters such as initial concentration of dye, adsorbent dosage, and contact time on the uptake of organic dye from aqueous solution was also investigated. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Composite;
Ion exchange capacity;
Distribution coefficient;
Binary separation;
Wastewater treatment;
Adsorption.

INTRODUCTION

Organic-inorganic composite materials have attained a great deal of attention because of their useful integration of properties encompassing both organic and inorganic characteristics within a single molecular-scale^[1]. A composite material consists of two or more physically distinct components and ex-

hibits properties that are entirely different from their original components. They have been used as sorbents^[2], ion exchanger^[3], catalyst^[4] and ion selective electrode^[5]. Composite exchangers are being preferred over organic and inorganic ion-exchangers as they overcome two major drawbacks from which the latter suffers. One serious limitation of organic resin is its poor thermal and chemical stability (less stable in highly acidic and basic

Full Paper

medium) while the use of inorganic ion-exchanger is limited by its non-reproducibility^[6]. Furthermore, insoluble acid salts of polyvalent metals produced by mixing rapidly the elements of groups of III, IV and V of periodic table possessing ion exchange properties are reported to be not very much reproducible and granular thereby limiting their suitability for column operation^[7]. Recently, polyaniline (PANI) as an organic binder has been used to prepare new composites. The organic binder polymer is inert and the active component which possesses the ion-exchange property is inorganic ion-exchanger.

Water pollution caused by heavy metal ions from various industrial effluents is serious threat to the living world^[8]. These metals when present beyond the certain concentration are not only toxic but also can lead to serious health problems^[9]. So every care should be taken to treat wastewaters before flowing into public sewage, rivers and on land to prevent environmental pollution. Therefore, it is big deal to develop appropriate method for the removal of metal ions to decrease the pollution load on the water system. For this purpose, various competent technologies have been developed for the removal of these metals from polluted water such as solvent extraction, membrane process, precipitation, adsorption and ion-exchange^[10-12]. However, an ion-exchange technique has been widely adopted in the removal and determination of heavy metal ions in wastewater because of its simplicity and low operation cost^[13]. Many industries such as textile, rubber, leather, paper, cosmetics, plastics, food, and pulp extensively use synthetic organic dyes which create significant problem to the human health because of its toxic, mutagenic and carcinogenic nature^[14,15]. Therefore, removal of dyes from the wastewater has been an important environmental concern to minimize the water and soil pollution. Among the various method for the removal of dyes from wastewaters adsorption by ion exchanger is the most prominent and economic method^[16].

Tin zirconium tungstate is new member in the family of tetravalent based ion exchanger. By modifying its mechanical and ion-exchange properties, the new organic-inorganic composite, tin zirconium tungstate-polyaniline (SnZrW-PANI) was synthesized

and characterized for ion exchange properties to explore the utility of this material in the environmental remediation.

EXPERIMENTAL

Reagents

Stannic chloride (E.Merck), zirconium oxychloride (E.Merck), and sodium tungstate (Loba Chem) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

Apparatus and instruments

A glass column was used for column operations. FT-IR Spectrometer model Thermo-Nicolet Avatar 370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies, JEOL Model JSM - 6390LV for scanning electron microscopic analysis, TG Perkin Elmer Diamond TG Analysis System for thermogravimetric analysis were used. UV-Visible Spectrophotometer model JASCO V660 was used for spectrophotometric measurements

Synthesis

(a) Tin zirconium tungstate (SnZrW)

Zirconium oxychloride solution (0.05 M), stannic chloride solution (0.05 M) and sodium tungstate solution (0.05 M) were prepared. Sodium tungstate solution was added to the mixture of zirconium oxychloride solution and stannic chloride solution with constant stirring in different volume ratios so that final volume was 500 mL. The resulting white gel, tin zirconium tungstate (SnZrW) was kept for 24 hrs at room temperature maintaining the pH at 1. pH was adjusted with 1.0 M NaOH/1.0 M HNO₃. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H⁺ form by treating with 1.0 M HNO₃ for 24 hrs with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60- 100 mesh.

(b) Polyaniline (PANI)

150 mL of Polyaniline gels were prepared by mixing acidic solutions of 0.05 M aniline and 0.05 M

ammonium persulphate with continuous stirring by a magnetic stirrer keeping the temperature below 10 °C for half an hour. Green coloured polyaniline gels were obtained that were kept overnight in refrigerator.

(c) Tin zirconium tungstate-polyaniline (SnZrW-PANI)

Tin zirconium tungstate slurry prepared by above method is mixed with prepared gel of polyaniline and the pH of the mixture was adjusted to 1.0 by adding aqueous ammonia and hydrochloric acid with constant stirring. The dark green coloured gel obtained was then filtered, washed with deionized water and dried. The exchanger was then converted into the H⁺ form by treating with 1.0 M HNO₃ for 24 hrs with occasional shaking and intermittent changing of acid. The excess acid was removed by washing with deionized water and then dried and sieved to obtain particles of 60- 100 mesh.

Ion exchange capacity

The ion exchange capacity of the material was determined by column method^[17] and the effect of temperature on ion exchange capacity was studied. The chemical resistivity of the sample was assessed in mineral acids like HCl, HNO₃ and H₂SO₄, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this, 0.5 g of the sample was soaked in 50 mL of different solvents, kept for 24 hrs and changes in colour, nature and weight of the sample were noted.

pH titration

Topp and Pepper method^[18] was used for pH titrations using NaOH/NaCl, KOH/KCl, systems. 0.5 g of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. At equilibrium (after equilibration), pH of the solutions was measured and plotted against the milliequivalents of OH⁻ added.

Distribution coefficient (K_d)

Selectivity studies were carried out for various metal ions in demineralized water by batch process^[17]. The effect of temperature on distribution value of metal ions was studied.

Elution behavior

To find out the optimum concentration of the eluent for complete elution of H⁺ ions, a fixed volume (100 ml) of NaCl solution of varying concentrations was passed through a column containing 1.0 g of the exchanger in the H⁺ form with a flow rate of 0.5 ml min⁻¹. The effluent was titrated against a standard alkali solution of 0.1 M NaOH for the H⁺ ions eluted out. Since an optimum concentration of 1.0 M NaCl for a complete elution of H⁺ ions was observed for sample, a column containing 1.0 g of the cation exchanger in H⁺ form was eluted with NaCl solution of this concentration in different 10 ml fractions with minimum flow rate as described above. Each fraction of 10 ml effluent was titrated against a standard alkali solution for the H⁺ ions eluted out, to find out the elution behavior.

Binary separation

Quantitative separations of some important metal ions were achieved on tin zirconium tungstate-polyaniline columns. 1.0 g of exchanger in H⁺ form was packed in a glass column (0.5 cm, internal diameter) with a glass wool support at the bottom. The column was washed thoroughly with demineralized water and the mixture of two metal ions (each with initial concentration of 0.1 mol L⁻¹) was loaded onto it and allowed to pass through the column at a flow rate 5–20 drops min⁻¹ until the level was just above the surface of the material. The process was repeated twice or thrice in order to ensure the complete sorption of metal ions on the bead. The separation of metal ion was achieved by collecting the effluent in 10 ml fraction and titrated against the standard solution of disodium salt of EDTA (0.01 mol L⁻¹).

Waste water treatment

Industrial wastewater was collected from battery industries. Samples were first filtered to remove any solid particles and then it was neutralised. The colour producing substances were removed by adsorption using charcoal. The treated samples were then chemically treated for the detection and separation of any heavy elements presents. 100 ml of the sample was passed and repeated 3-4 times using effluent collected at the bottom. This was for the maximum uptake of cation. Care was taken to restrict the flow by

Full Paper

0.5 ml/minutes. The eluent used for Pb(II) was 0.5 M HNO_3 . Finally the ions were eluted out using respective eluents and then determined titrimetrically with EDTA solution.

Adsorption Experiments

The adsorption study was conducted in a batch system in which 200 mg tin zirconium tungstate-polyaniline adsorbent was mixed with 50 mL of MB dye solution of 20 mgL^{-1} for 2 hrs in a 100 mL conical flask and the mixture was shaken in an electrical shaker at a constant agitation speed. The sample solution withdrawn from each flask after 1 hr were then analysed by using UV-Visible diffuse reflectance spectrophotometer with 1 cm path length quartz cell by measuring absorbance at λ_{max} of dyes (MB – 663 nm). All experiment results were conducted in duplicate and the average value was used in the data analysis.

The experiments were repeated by varying the following parameters: contact time, temperature, adsorbent concentration, pH and dye concentration.

The amount of dye sorbed at any time, q_t , was calculated from;

$$q_t = (C_i - C_t) \frac{V}{W}$$

At equilibrium, $q_t = q_e$ and $C_i = C_e$; therefore, the amount of sorbed dye q_e was calculated from

$$q_e = (C_i - C_e) \frac{V}{W}$$

Where C_i , C_t and C_e are the initial concentration, concentration at any time and equilibrium concentrations of dye solution (mgL^{-1}), respectively, V is the volume of solution (L) and W is the mass of adsorbent (mg).

The dye removal percentage can be calculated as follows:

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100$$

Desorption study

The dye adsorbed exchangers were separated from the solution and dried completely and used for desorption experiments. The dye-loaded materials (200 mg) were then brought into contact with 10 mL of 1.0 M NaOH, 1.0 M HNO_3 , and ethanol (95%), separately. The mixture was kept for 24 hrs. After desorption, the supernatant liquid was collected and estimated.

RESULTS & DISCUSSION

The composite exchanger tin zirconium tungstate-polyaniline obtained is dark green in colour and is found to be stable in mineral acids and organic solvents. Chemical composition analysis, EDS measurement (Figure 1) and CHN analysis of SnZrW-PANI

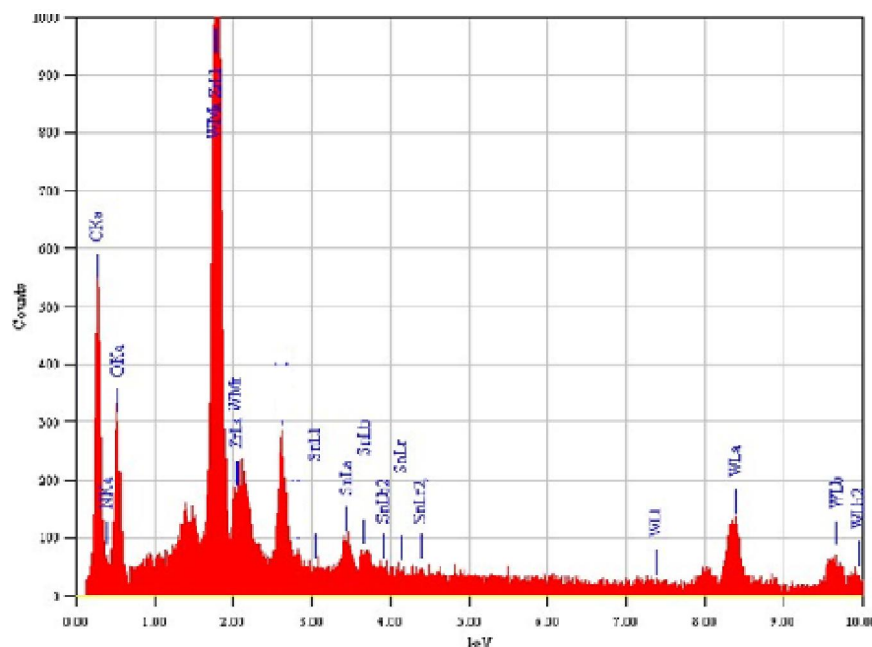


Figure 1 : EDS of SnZrW-PANI

show the atom percent composition of Sn, Zr, W, C, H, O and N is 13.61, 14.05, 32.32, 16.13, 1.61, 19.53 and 2.75. Sodium ion exchange capacity of composite prepared is 1.37 meqg^{-1} .

The affinity sequence for alkali and alkaline earth metal ions on SnZrW-PANI has found to be the order ie $\text{Li(I)} < \text{Na(I)} < \text{K(I)}$ and $\text{Mg(II)} < \text{Ca(II)} < \text{Ba(II)}$, respectively (TABLE 1). This sequence is in accordance with the hydrated ionic radii. Usually at low aqueous concentrations and ambient temperature the extent of exchange increases with increasing valence of ingoing ions i.e. $\text{Ca(II)} > \text{Na(I)}$. The ion exchange capacity should increase with decreasing hydrated radii and increases with electrode potential. The ions with smaller hydrated ionic radii easily enter the pores of exchanger, resulting in higher sorption.

It was observed that on heating at different temperatures for 2 hrs, the ion-exchange capacity of the

dried sample material was changed as the temperature increased as shown in Figure 2. The composite cation-exchange material was found to possess higher thermal stability as the sample maintained about 40.4% of the initial mass by heating up to 300°C . However, in respect to ion exchange capacity, this material was found to possess thermal stability as the sample maintained 60% of the ion-exchange capacity up to 100°C .

The composite was found reasonably stable in some organic solvents (ethanol, acetonitrile), acids (HCl , HNO_3 , H_2SO_4) and bases (sodium hydroxide, potassium hydroxide) up to 1.0 M. Thus, the exchanger was chemically resistant to these solvents and could be successfully used with these solvents in column operation.

FTIR spectra of SnZrW-PANI (Figure 3a) show a broad band in the region $\sim 3444 \text{ cm}^{-1}$ which is assigned to symmetric and asymmetric $-\text{OH}$ stretching^[19].

TABLE 1 : Effect of hydrated ionic radii and charge on IEC

Metal ion	Hydrated ionic radii (\AA°)	IEC (meqg^{-1})
Li(I)	3.40	1.22
Na(I)	2.76	1.37
K(I)	2.32	1.45
Mg(II)	7.00	1.21
Ca(II)	6.30	1.79
Ba(II)	5.90	2.11

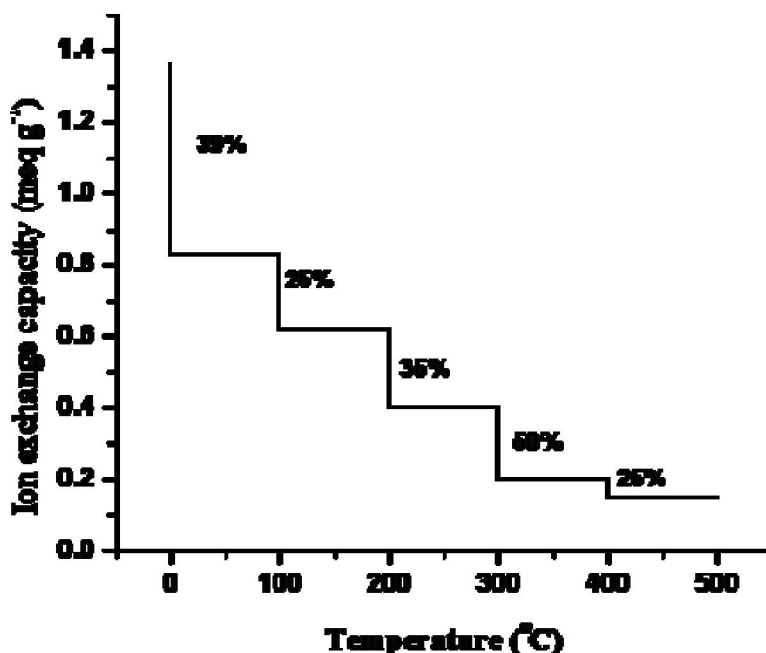


Figure 2 : Effect of temperature on IEC

Full Paper

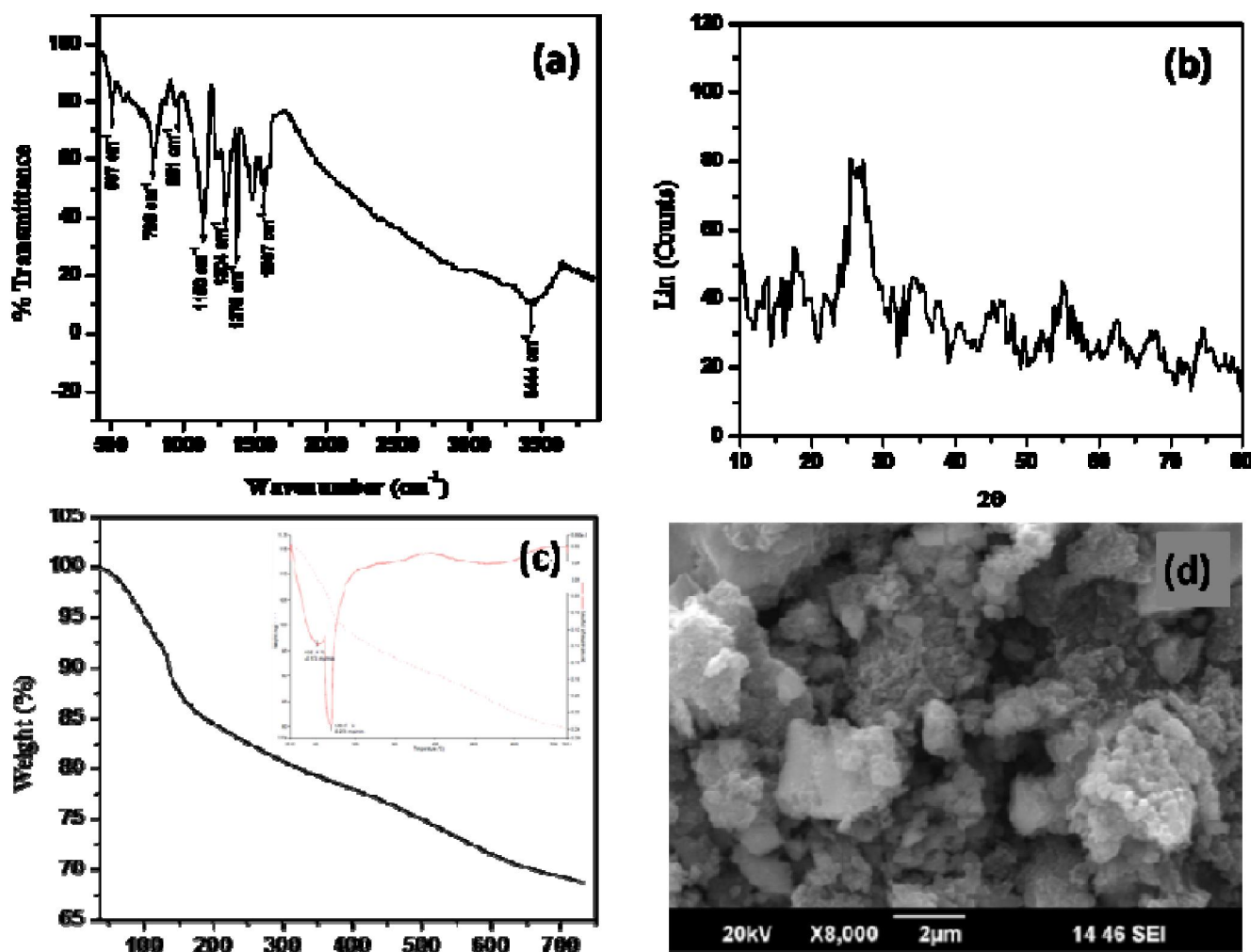


Figure 3 : a. FT-IR, b. XRD, c. TGA and d. SEM image of SnZrW-PANI

Bands at $\sim 507\text{ cm}^{-1}$ may be due to the presence of metal oxygen bond. A band at 798 cm^{-1} indicates the out of plane C-H bending mode. In plane C-H bending bands occur in the region $1000\text{--}1200\text{ cm}^{-1}$. Another assembly of peaks in the region $1300\text{--}1400\text{ cm}^{-1}$ may be ascribed due to the stretching vibration frequency of C-N in the material, as it also resembles the stretching vibration frequencies for C-N found in polyaniline^[20]. This confirms the formation of tin zirconium tungstate-polyaniline composite.

X-ray diffractogram (Figure 3b) shows amorphous nature of the composite material. Scanning electron microscopy (SEM) study was performed to examine the surface morphology of composite material. SEM photograph of SnZrW-PANI depicted its irregular shape (Figure 3d) and the rough surface with pleats.

The thermogram of SnZrW-PANI (Figure 3c) showed that the weight loss (about 25%) of the ion

exchanger up to 150°C is due to the removal of free external water molecules^[21]. Further, a gradual loss of mass (about 7%) up to 400°C may be due to the condensation of hydroxyl groups along with the slight degradation of organic part. An endothermic peak at 600°C is observed in the case of SnZrW-PANI which suggests the polyaniline degradation.

The pH-titration curves of SnZrW-PANI were obtained under equilibrium conditions with NaCl/NaOH and KCl/KOH (Figure 4). The functionality of the ion-exchanger was determined with the help of these curves. However, it is a general observation that the shape of the titration curves and the functionality depend upon the time of contact of the solution containing OH^- ions with the ion exchanger until equilibrium is obtained. Sometimes the system takes several days if it is at room temperature with intermittent shaking. In the present case, for attaining equilib-

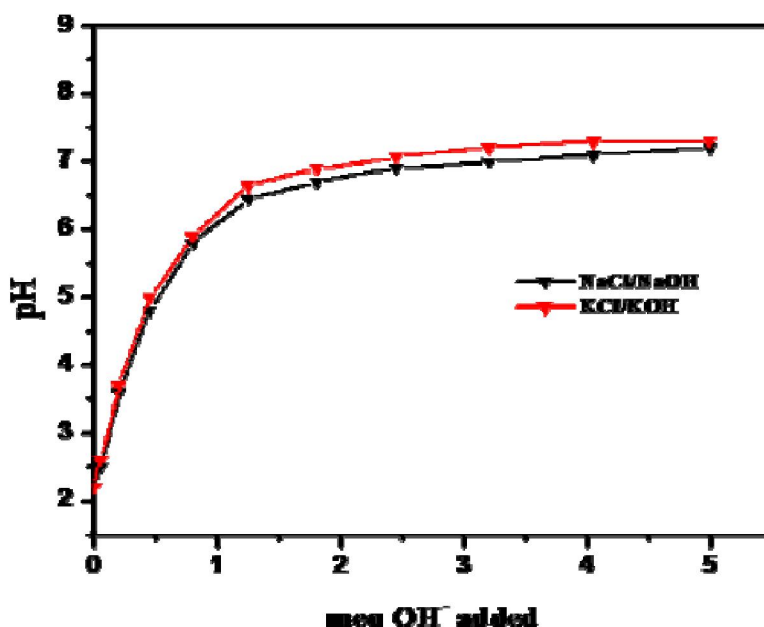


Figure 4 : pH titration curve of SnZrW-PANI

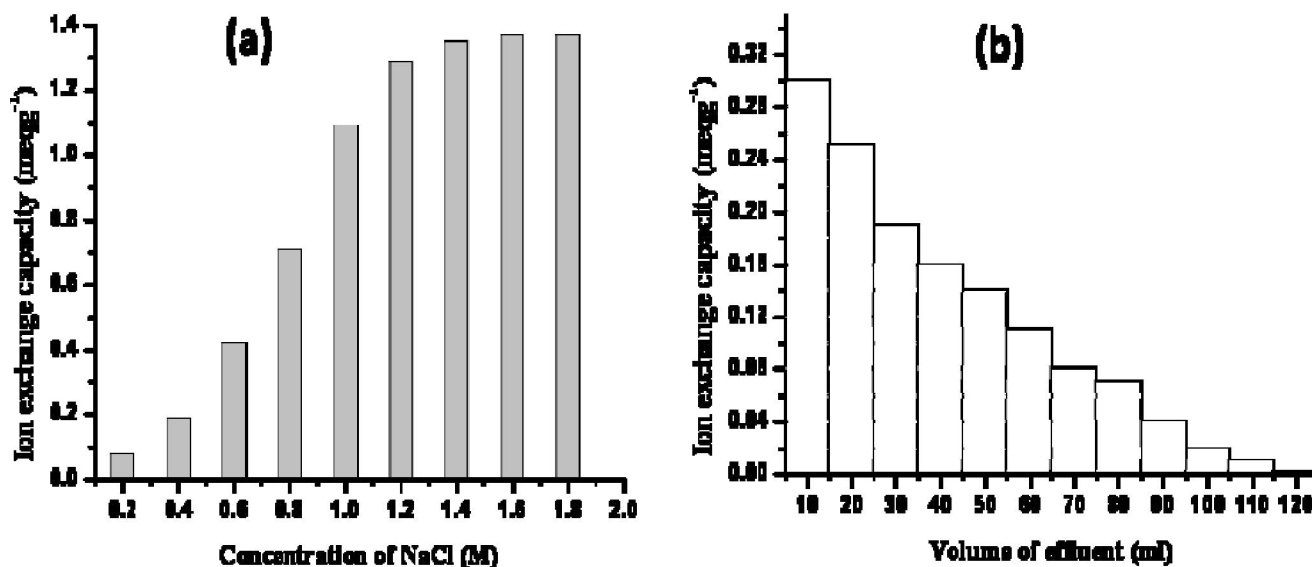


Figure 5 : a. Effect of eluent concentration on ion-exchange capacity, and b. Elution behavior of SnZrW-PANI

rium almost 3 days was taken which is close agreement with the above mentioned factor. The functionality of the systems was observed to be monofunctional in nature as shown in Figure 3. This showed that the composite material is a strong cation-exchanger as indicated by a low pH (~ 2) of the solutions, when no OH^- ions were added to the system. With the addition of NaOH, the solution is progressively neutralized and at the same time the ion-exchange is driven to completion. Thus, the pH titration curve of this ion-exchanger showed a gradual rise in pH at the early stage of titration and a steep rise at the point of complete neutralization of the

cation-exchanger i.e. strong acidic groups of the composite cation-exchanger are completely converted to the Na^+ form. Thus, the maximum capacity (theoretical capacity) of the strong acidic groups of the composite was calculated as 1.35 meqg^{-1} , from the amount of titrant added up to the point where the steep rise in the pH occurs i.e. at equilibrium.

The column elution experiment indicated a dependence of the concentration of the eluent on the rate of elution, which is a usual behavior, for such materials. A maximum elution was observed with the concentration of 1.0 M NaCl as indicated in Figure 5a. The elu-

Full Paper

tion behavior of the exchanger (Figure 5b) reveals that the rate of exchange is quite fast as only 100 mL of NaCl solution (1.0 M) is sufficient for almost complete elution of H^+ ions from the column containing 1.0 g exchanger. Hence, fast kinetic would facilitate the operation of the column for the separation of metal ions.

In order to explore the potentiality of the new hybrid cation-exchange material in the separation of metal ions, distribution studies for metals ions were performed in different solvent systems (Figure 6). It is clear from the data given in Figure 6 that the K_d values vary with the composition and nature of the contacting solvents. The selectivity for metal ions is in the order of $Pb(II) > Hg(II) > Mn(II) > Cd(II) > Cu(II) > Ni(II) > Mg(II) >$

$Co(II) > Bi(III) > Zn(II)$. It was observed from the K_d value studies that the uptake of $Pb(II)$ is exceptionally high in all solvents, while the remaining metal ions are poorly sorbed. Thus, the composite cation-exchanger can be very well utilized for the separation of lead ions from waste effluents. The temperature effect on K_d value showed that the K_d value was not changed even after high temperature treatment with the exchanger. While considering the IEC value it was slightly decreasing with temperature. Even though the retaining of K_d value of exchanger may be due to the structural change of the material with the organic part present on it. Due to the slight decomposition of the organic part may help to develop the pore in the surface of the exchanger. So on

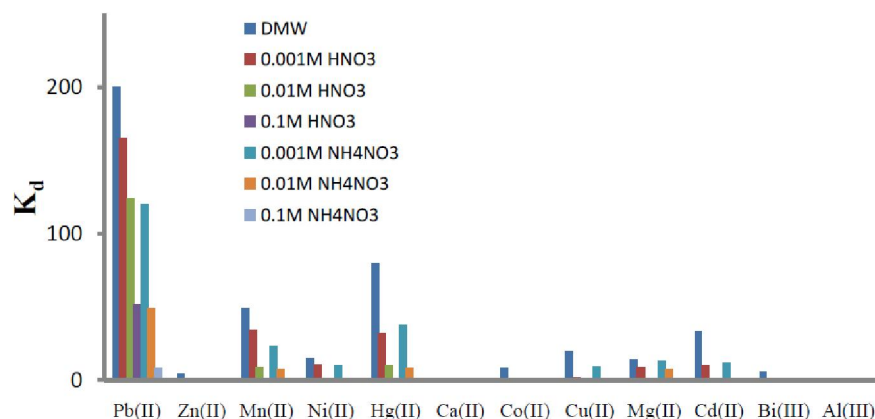


Figure 6 : K_d values of various metal ions in different electrolyte

TABLE 2 : Binary separation of metal ions on SnZrW-PANI

Materials	Separation achieved	Separation Factor	Eluent	Metal ion (mg)		% Efficiency
				Loaded	Eluted	
SnZrW-PANI	Co(II)	25.64	0.001 M HNO_3	1.92	1.90	98.96
	Pb(II)		0.3 M HNO_3 + 0.2 M NH_4NO_3	2.80	2.75	98.21
	Ni(II)	13.37	0.01 M HNO_3	3.20	3.10	96.88
	Pb(II)		0.3 M HNO_3 + 0.2 M NH_4NO_3	2.80	2.67	95.36
	Cu(II)	10.20	0.01 M HNO_3 0.3	2.80	2.72	97.14
	Pb(II)		M HNO_3 + 0.2 M NH_4NO_3	2.80	2.69	96.07
	Zn(II)	51.54	0.001 M HNO_3 0.3	2.80	2.77	98.93
	Pb(II)		M HNO_3 + 0.2 M NH_4NO_3	2.80	2.75	98.21

TABLE 3 : Selective separation of Pb(II) from synthetic mixtures containing Pb(II), Cu(II) [2.57 mg], Mg(II) [2.97 mg], Hg(II) [4.70 mg] and Ni(II) [1.93 mg]

Amount of metal ion loaded (mg)	Amount of metal ion found (mg)	Recovery (%)	Eluent used	Volume of eluent (mL)
4.10	4.03	98.29	0.5 M HNO_3	70
3.92	3.85	98.21	0.5 M HNO_3	50

higher temperature treated exchanger; adsorption may also play the major role for the separation of metal ions.

The separation capability of the material has been demonstrated by achieving some analytically important binary separations of some important metal ions viz Co(II)-Pb(II), Ni(II)-Pb(II), Cu(II)-Pb(II) and Zn(II)-Pb(II) (TABLE 2). TABLE 2 summarizes the salient features of these separations. The separation was based on sequential elution of ions through the column depending upon the metal-eluting ligand (eluent) stability. It was also observed that Pb(II) retained strongly on the cation-exchanger column. The weakly retained metal ions get eluted first, followed by the stronger one. It is evident from data that the separations are quite sharp, quantita-

tive and reproducible.

The practical utility of the composite material was demonstrated by separating lead and cadmium from synthetic mixtures (TABLE 3 & 4) as well as from paper and battery industrial wastes water respectively (TABLE 5).

Around 1.0 mg/ 100mL lead metal ions were separated from the paper and battery industrial effluents using SnZrW-PANI ion exchanger column.

Removal of methylene blue

Methylene blue (MB) has wider applications due to its good solubility, like coating for paper stock, coloring paper, coloring leather products, dyeing

TABLE 5 : Quantitative removal of Pb(II) from textile industry effluent using column of SnZrW-PANI

Sample	Metal Ion	Eluent used	In mg/100mL
Sample A	Pb(II)	0.5 M HNO ₃	1.15
Sample B	Pb(II)	0.5 M HNO ₃	1.23

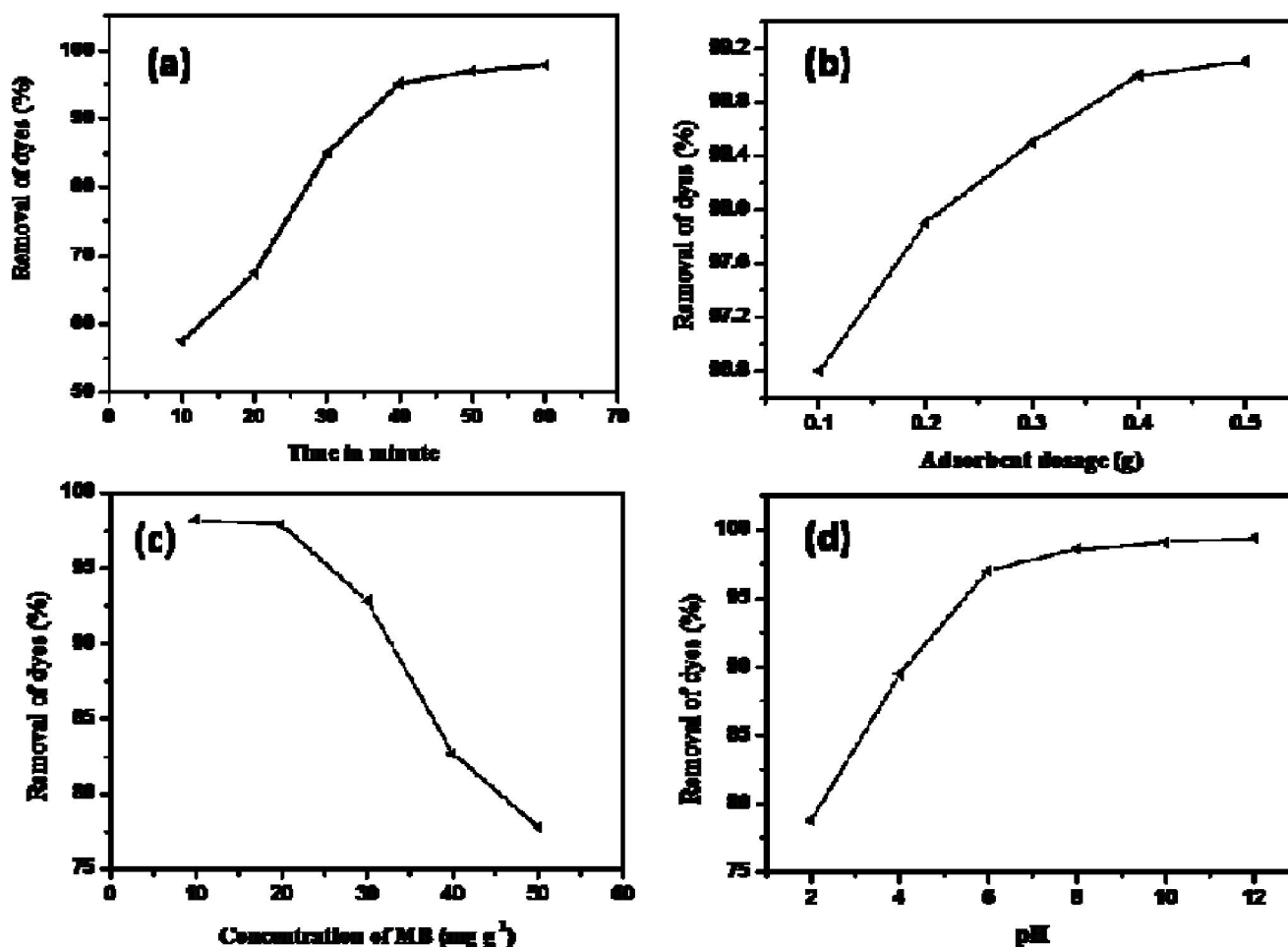


Figure 7 : (a) effect of contact time, (b) effect of adsorbent dosage, (c) effect of initial dye concentration and (d) effect of pH on the removal methylene blue by SnZrW-PANI

Full Paper

cottons, wools, and temporary hair colorant, etc. Although MB is not strongly hazardous, it can render several harmful effects. Acute exposure to MB will cause increased heart rate, shock, Heinz body formation, vomiting, quadriplegia, cyanosis, jaundice, and tissue necrosis in humans^[22,23]. It is harmful when it is breathed and in contact with skin and when it is swallowed^[24]. The composite tin zirconium tungstate-polyaniline exhibits good adsorption ability for the removal of MB from aqueous solution. The adsorption capability of tin zirconium tungstate-polyaniline were analysed experimentally.

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. In physical adsorption, most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. MB solution (50 mL, 20 mg L⁻¹) was treated with 0.2 g of exchanger for different periods of time (10-60 min) at 30° C and neutral pH. The rapid removal was observed during the first 20 min and gradually decreased with laps of time until equilibrium. The increased activity at initial stage could be due to the availability of more adsorption sites on composite surface, and gradual occupancy of these sites reduced the reaction rate and the adsorption becomes less efficient. At this point, the amount of dye being adsorbed onto the composite was in a state of dynamic equilibrium with the amount of dye desorbed from the composite. The time required to attain this state of equilibrium was termed as equilibrium time, and the amount of dye adsorbed at the equilibrium time reflected the maximum adsorption capacity of the adsorbent under these particular conditions. It is evident from Figure 7a that the contact time needed to attain the equilibrium condition for MB was about 1 hr.

The effect of adsorbent dosage on the removal of MB has shown in the Figure 7b. To study the effect of adsorbent dose on dye adsorption, different amounts of adsorbents varying from 100 mg to 500 mg were respectively added to initial concentration of 20 mg L⁻¹ of MB solution of 50 mL and kept for 1 hr. Removal of dye with increasing adsorbent dosage was observed

which is due to the availability of reactive sites^[25]. The removal of MB ranged from 96.8 to 99.1 % for 1 hr when treated with different doses of exchanger.

The studies on the removal of MB by exchanger were carried out at different concentration of dye from 10 mg L⁻¹ to 50 mg L⁻¹ by keeping the fixed adsorbent dosage of 200 mg at 30° C and neutral pH shown in Figure 7c. The percentage of removal decreased with the increase in initial concentration. From the figure, it was revealed that there was significant removal of dyes even at higher concentration also possible with this exchanger. The percentage removal decreases with the increase in dye concentration indicated that there exists a reduction in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of dye. The enhanced removal at low concentration could be due to the faster movement of dye into the activated sites of composite. However, in higher concentration (50 mg L⁻¹) the removal rate was decreased to 77.8 % because the dye molecules needed to diffuse to the adsorbent sites by intra particle diffusion. In addition, steric repulsion between the solute molecules could slow down the adsorption process and thereby decreases the removal rate. A similar trend was observed for the adsorption of methyl violet by agricultural waste^[26].

pH of the solution influences the surface charge and functional groups of the adsorbent and it has significant role in the adsorptive removal of dye^[27]. In addition, pH influences the degree of ionization of the materials present in the solution and solution chemistry. The results (Figure 7d) show that by increasing solution pH, the extent of dye removal increases. Lower adsorption percentage of MB on exchangers at highly acidic conditions is probably due to the presence of high concentration of H⁺ ions on the surface of adsorbent, competing with MB (a cationic dye) for adsorption sites in the adsorbent^[28]. With an increase in the solution pH, the electrostatic repulsion between the positively charged MB and the surface of adsorbent is lowered. Consequently removal efficiency is increased at higher pH. Finally the adsorption process proceeds through the electrostatic attraction between the two counter ions.

Figure 8 shows the effect of temperature on ad-

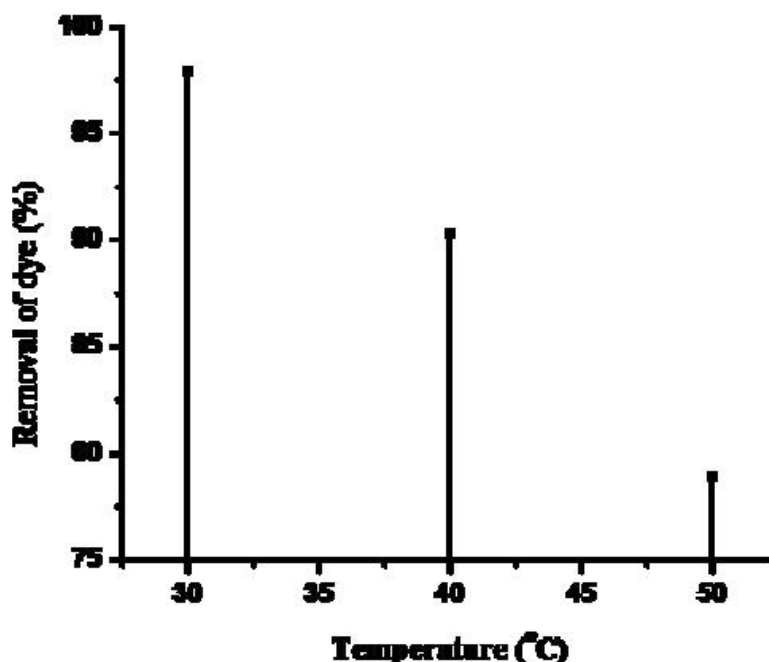


Figure 8 : Effect of temperature on the removal methylene blue by SnZrW-PANI

sorption of dye onto exchanger. The increase in temperature (from 30 to 50 °C) leads to a decrease in dye uptake. With increasing temperature, the decrease in the uptake indicates that an exothermic process controls the adsorption of dye^[29]. The adsorption capacity decreases with increasing temperature indicating that the adsorption process occurs through physical interactions.

After confirming the fact that tin cerium phosphate-polyaniline composites is capable of adsorbing the dye molecules onto its surface, it became necessary to know the process by which the dye molecules remain adhered to the surface of the exchanger. The adherence of dye molecules onto the surface of the exchanger is a purely chemical interaction, involving chemical binding of the substances exchanger and the dye. All the three composites possess structural hydroxyl groups. Therefore the dyes can bond to the sorbent either by hydrogen bonds or weak Van der Waals forces. The bonding nature between the adsorbent and dye was checked by subjecting the adhered material to desorption and regeneration process^[30]. Treatment with NaOH (1.0 M), ethanol and HNO₃ (1.0 M) shows the considerable recovery of the dyes which is represented in Figure 9. Under acidic condition, the positively charged sites increase on the surface of exchanger, and this act as a

driving force for desorption of dye by electrostatic repulsion.

CONCLUSION

Tin zirconium tungstate-polyaniline composite material showed thermal stability with respect to the ion exchange capacity loss with increasing temperature. pH titration studies revealed a strong acidic

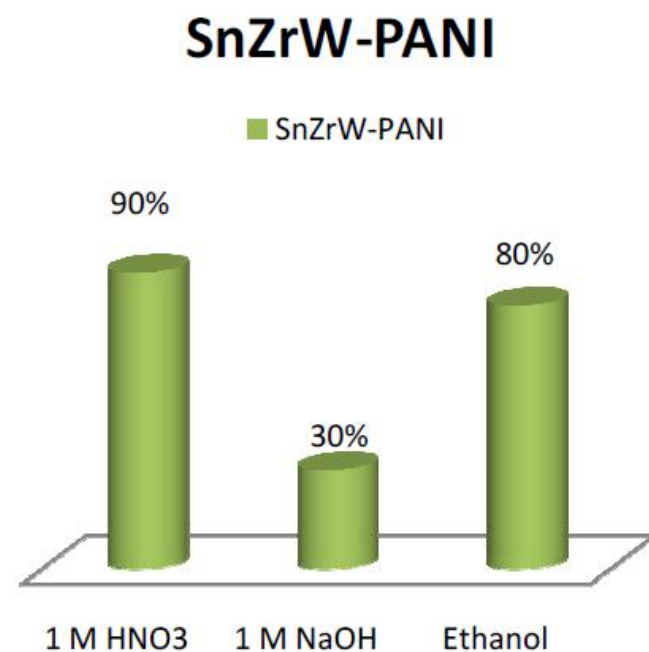


Figure 9 : Percentage of desorption of dye (recovery of dye) from SnZrW-PANI

Full Paper

nature. The distribution studies depicted that the material is highly selective for the Pb(II). It is evident from the results that the quantitative and efficient separations of lead from various metal ions are feasible on tin zirconium tungstate-polyaniline column. The results presented in this work have shown that the exchanger can be used for the adsorption of dye even at low as well as higher concentration of dye. In addition the adsorbent can be recycled thrice without any loss in its capacity and efficiency by treatment with 1.0 M HNO₃ solution. The selective behavior of this composite cation exchanger is important from the environmental pollution chemistry point of view, where an effective separation method is needed for Pb(II) as well as organic pollutant like dye from other pollutants.

ACKNOWLEDGMENTS

Author gratefully acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi, for the award senior research fellowship. Instrumental support received from STIC, Kochi is also gratefully acknowledged.

REFERENCES

- [1] A.Khan, Abdullah M.Asiri, Malik Abdul Rub, Naved Azum, Aftab Aslam Parwaz Khan, Imran Khan, Pijush K.Mondal; *Int.J.Electrochem.Sci.*, **7**, 3854 (2012).
- [2] M.Vatutsina, V.S.Soldatov, V.I.Sokolova, J.Johann, M.Bissen, A.Weissenbacher; *React.Funct.Polym.*, **67**, 184 (2007).
- [3] S.A.Nabi, A.H.Shalla; *J.Hazard.Mater.*, **163**, 657 (2009).
- [4] R.Niwas, A.A.Khan, K.G.Varshney; *Colloids Surf.A.*, **150**, 7 (1999).
- [5] S.A.Nabi, A.H.Shalla, S.A.Ganai; *J.Sep.Sci.*, **43**, 164 (2008).
- [6] K.G.Varshney, N.Tayal, A.A.Khan, R.Niwas, *Colloids Surf.A: Physicochem.Eng.Aspects.*, **181**, 123 (2001).
- [7] W.A.Siddiqui, S.A.Khan, Innamuddin; *Colloid.Surf.A.*, **295**, 193 (2007).
- [8] N.Sankararamakrishnan, A.K.Sharma, R.Sanghi; *J.Hazard.Mater.*, **148**, 353 (2007).
- [9] P.W.Davidson, G.J.Myers, B.Weiss; *Pediatrics.*, **113**, 1023 (2004).
- [10] A.Dabrowski, Z.Hubicki, P.Podkoscielny, E.Robens; *Chemosphere.*, **56**, 91 (2004).
- [11] M.Perez-Collado, C.Molero, E.Larrondo; *React.Funct.Polym.*, **64**, 139 (2005).
- [12] P.Woodberry, G.Stevens, I.Snape; *Solvent Extr.Ion Exch.*, **24**, 603 (2006).
- [13] A.P.Gupta, Renuka; *Ind.J.Chem.*; **36**, 1073 (1997).
- [14] D.Pak, W.Chang; *Water Science and Technology*, **40**, 115 (1999).
- [15] I.M.Banat, P.Nigam, D.Singh, R.Marchant; *Bioresource Technology*, **58**, 217 (1996).
- [16] Lei Wang, Xi-Lin Wu, Wei-Hong Xu, Xing-Jiu Huang, Jin-Huai Liu, An-Wu Xu; *Applied Material Interfaces*, **4**, 2686 (2012).
- [17] A.I.Vogel; *A text book of quantitative inorganic analysis.*(Longman Group Limited, London) (1975).
- [18] N.E.Topp, K.W.Pepper; *J.Chem.Soc.*, **690**, 3299 (1949).
- [19] P.Vinisha Valsaraj, C.Janardanan; *International Journal of Advanced Chemistry*, **2**, 6 (2014).
- [20] C.Duval; *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 315 (1963).
- [21] Y.Nuhoglu, E.Malkoc, A.Gurses, N.Canpolat; *Bioresour.Technol.*, **85**, 331 (2002).
- [22] K.V.Kumar, V.Ramamurthi, S.Sivanesan; *J.Colloid Interface Sci.*, **284**, 14 (2005).
- [23] D.Ghosh, K.G.Bhattacharyya; *Appl.Clay Sci.*, **20**, 295 (2002).
- [24] C.A.P.Almeida, N.A.Debacher, A.J.Downs, L.Cottet, C.A.D.Mello; *J.Colloid.Interface Sci.*, **332**, 46 (2009).
- [25] B.H.Hameed; *J.Hazard.Mater.*, **154**, 204 (2008).
- [26] G.Crini, H.N.Peindy, F.Gimbert, C.Robert; *Sep.Purif.Tech.*, **53**, 97 (2007).
- [27] M.Banimahd Keivani, K.Zare, H.Aghaie, R.Ansari; *J.Phy.Theoret.Chem.IAU Iran.*, **6**, 50 (2009).
- [28] A.Gurses, C.Dogar, M.Yalcin, M.Acikyildiz, R.Bayrak, S.Karaca; *J.Hazard.Mater.*, **131**, 217 (2006).
- [29] Kalpana Maheria, Uma Chudasama; *J.Sci.Ind.Res.*, **66**, 1047 (2007).