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# Removal of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> ions by the synthesized sodium dodecyl benzene sulphonate-based tin (IV) phosphate (SDBS-SnP) cation exchanger

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## ABSTRACT

The newly synthesized cation exchanger sodium dodecyl benzene sulphonate (SDBS)-based tin (IV) phosphate, SDBS-SnP, has been found to be a good cation exchange material for the removal of  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$  ions from water sample. The cation exchanger, SDBS-SnP, was synthesized and was characterized by using the physical techniques like infrared spectroscopy, X-rays diffraction (XRD), scanning electron microscopy and thermal and differential thermogravimetric analysis. The XRD studies indicated that the SDBS-SnP is an amorphous material. The elemental analysis of the material was also performed on the ion exchange material to ascertain the presence of surfactants and inorganic constituents. The ion exchange material. The concentration behaviour showed that 1.0 M NaNO<sub>3</sub> was the optimum concentration for the complete removal of H<sup>+</sup>-ions from SDBS-SnP. The H<sup>+</sup>-ions were eluted by 160 mL of 1.0 M NaNO<sub>3</sub> solution. The ion exchange material retained more than 95% of its initial values of ion exchange capacity on heating to 100°C for an hour. The cationic exchanger is found to be highly selective for  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$  ions, and can be used for the separation of  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$  ions from the solution containing acid, alkalis or alkaline earth metals.

*Keywords:* Fibrous ion exchanger; Sn (IV) phosphate; Sodium dodecyl benzene sulphonate; SDBS-SnP; Adsorption studies; Water treatment

# 1. Introduction

The studies on the synthesis and ion exchange behaviour of composite materials comprising the surfactants and inorganic ion exchange materials have gained popularity in the recent years [1–7]. The surfactant-based cation exchangers have been capable of exchanging and adsorbing the metal ions through the surfactant and inorganic constituents. The presence of surfactant molecules in the inorganic matrix enhanced the ion exchange capacity and also made the ion exchangers chemically and thermally more stable. The intercalation of surfactant molecules into

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the inorganic matrix makes the composite material environment friendly. The earlier studies [8-10] have shown that the surfactant-inorganic interaction is the result of direct co-condensation of anionic inorganic species with a cationic surfactant (S<sup>+</sup>I<sup>-</sup>), cooperative condensation of cationic inorganic species with an anionic surfactant (S<sup>-</sup>I<sup>+</sup>), condensation of ionic inorganic species with surfactants having the similar charge and the condensation mediated by the counter ions of opposite charge of surfactant headgroup  $(S^+X^-I^+ \text{ and } S^-M^+I^-, \text{ where } X^- \text{ denotes anions such }$ as Cl<sup>-</sup> or Br<sup>-</sup>, and M<sup>+</sup> denotes cations like K<sup>+</sup> or Na<sup>+</sup>). These nano-pororous materials possessed the surface area in order of magnitude greater than nanoparticles and were capable of binding a broad range of ions/ molecules [11,12]. They specifically adsorb heavy metals and were reported to be effective for the removal of mercury and other metals such as cadmium, silver and molybdenum from soil and sludge [13]. The charged headgroup of surfactant molecules removes metal ions by binding with oppositely charged ions through complexion effect, electron attraction and charge neutralization. The surfactant molecules reduce the interfacial tensions [14] between solid and liquid phases and, thereby, it helps to wet the surface properly and facilitates the exchange of metal ions easily and readily from the surface.

The present study describes the synthesis of surfactant based, cationic exchange material capable of exchanging and removing the heavy metal ions from water. It is environment friendly material because SDBS-SnP can be decomposed and recycled after its exhaustion. It presents better alternate for the resinbased or polymer-based ion exchange materials (as they are non-biodegradable in nature and pose environmental problem for its disposal). The ion exchange capacity, stability towards higher temperature and elution and adsorption behaviour of SDBS-SnP cation exchanger have been studied and discussed herewith.

# 2. Experimental

# 2.1. Reagents and chemicals

Tin (IV) chloride (CDH, India), cadmium (II) nitrate (CDH, India), magnesium (II) nitrate (CDH, India) and strontium (II) nitrate (CDH, India) were used during the experiment. Sodium dodecyl benzene sulphonate (SDBS, Merck-Schuchardt, Germany), calcium nitrate (Merck-Schuchardt, Germany), barium nitrate (Merck-Schuchardt, Germany), nickel nitrate (Merck-Schuchardt, Germany) and sodium nitrate (Merck-Schuchardt, Germany) were used as obtained from supplier. Phosphoric acid, copper (II) nitrate and lead (II) nitrate were obtained from Qualigens (India) and mercuric (II) nitrate and zinc (II) nitrate were obtained from Thomas Baker. All other reagents used were of Anal R grade. Doubly distilled demineralized water with specific conductance,  $1-2 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ , was used during the experiments.

# 2.2. Instruments used

The X-ray diffraction was performed on a Philips Analytical X-ray B.V. diffractometer (type PW 170 B. V. The Netherlands) and infrared spectroscopy (IR) spectrum was recorded on Shimadzu 8201 PC spectrophotometer (Japan). The elemental analysis was done by Heraeus Carlo Erba-1108 analyzer (Italy). Differential pulse polarogramme was recorded by using an Elico CL-362 Pulse Polarograph (India) and scanning electron microscopy (SEM) studies were performed on SEM Hitachi-S520, Japan. The thermal and differential thermogravimetric analysis (TGA/DTA/DTG) curves were recorded on Perkin Elmer Pyris Diamond (USA).

# 2.3. Preparation of the reagent solutions

The stock solutions of 0.1 M SDBS, 0.6 M solution of phosphoric acid, 0.1 M sodium hydroxide, 1.0 M sodium nitrate, 0.01 M cadmium nitrate, 0.01 M lead nitrate, 0.01 M zinc nitrate, 0.01 M copper nitrate, 0.1 M sodium nitrate, 0.1 M magnesium nitrate, 0.1 M potassium nitrate and 0.1 M calcium nitrate were prepared in the doubly distilled water. Solution of tin (IV) phosphate was prepared by adding tin (IV) chloride to 0.6 M  $H_3PO_4$ .

### 2.4. Synthesis of the ion exchange material

Samples of sodium dodecyl benzene sulphonate-tin (IV) phosphate (SDBS-SnP) were prepared by adding one volume of 0.30 M tin (IV) chloride solution to two volumes of a (1:1) mixture of 0.60 M H<sub>3</sub>PO<sub>4</sub> and SDBS solutions drop-wise with the constant stirring by using a magnetic stirrer at room temperature. The resulting slurry was stirred for 3.5 h at room temperature, filtered and then washed with demineralized water till  $pH \sim 4$ was achieved. The samples were then left to dry at room temperature. The dried material was having the sheet-like structure. It was then crushed into small pieces. The synthesized material was kept in 1.0 M HNO<sub>3</sub> for 24 h to change it in the form of  $H^+$  form. After keeping in HNO<sub>3</sub>, it was filtered, washed with doublely distilled water several times to remove the residual H<sup>+</sup> ions completely. The material in H<sup>+</sup>-form was left to dry at 45 °C for a day and then sieved to obtain particles of size 50–70 mesh. Then, the ion exchange capacity of the various synthesized samples was determined by column process, and it was found that the sample-3 possessed the highest ion exchange capacity and, therefore, it was selected for further studies.

# 2.5. Ion exchange capacity concentration behaviour and elution behaviour

To determine the number of ionogenic groups present in the synthesized exchanger, 1.0 g of the material (in the H<sup>+</sup>-form) was taken in a glass burette of internal diameter ~1 cm and fitted with glass wool at the bottom. 250 mL of 1.0 M NaNO<sub>3</sub> solution was used as eluent, maintaining a slow flow rate (~0.5 mL min<sup>-1</sup>). The effluent was titrated against 0.1 M NaOH solution using phenolphthalein as an indicator to determine the total H<sup>+</sup>—ions liberated during ion exchange process.

The optimum concentration of eluent needed to complete elution of H<sup>+</sup> ions was determined by passing a fixed volume (250 mL) of different concentrations of NaNO<sub>3</sub> solution containing 1.0 g of the ion exchange material kept in a column. The H<sup>+</sup>-ions eluted out were titrated against a standardized 0.1 M NaOH solution using phenolphthalein as an indicator. To determine the elution behaviour of the material, the above experiment was repeated in which 1.0 g of the cation exchanger was taken in a column and eluted with 1.0 M NaNO<sub>3</sub> solution. The effluents were collected in different 10 mL fractions and the liberated  $H^+$  ions were determine by titrating against 0.1 M NaOH solution using phenolphthalein as an indicator. The above experiments were repeated at least 3-4 times and the observed results were found to be reproducible within ±5%.

# 2.6. Thermal stability

The thermal stability of the cation exchanger was determined by taking several 1.0 g samples of SDBS-SnP and heating them at different temperatures e.g. 100, 150, 200 and 300°C in a muffle furnace for an hour. After cooling to room temperature, their ion exchange capacity was determined.

# 2.7. Adsorption studies

The adsorption behaviour of SDBS-SnP was determined by taking 200 mg of the synthesized material in H<sup>+</sup>—form in a conical flask containing 20.0 mL of metal nitrate solutions  $(1.0 \times 10^{-3} \text{ M})$ . The conical flask was thermostated at room temperature  $(25.0 \pm 0.5 \text{ °C})$  for 24 h, with shaking intermittently to achieve equilibrium. The concentration of the metal ions was determined before and after the equilibrium was achieved. The concentrations of Hg<sup>2+</sup>, Ni<sup>2+</sup>, Ba<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Sr<sup>2+</sup> ions were determined by titration with standardized disodium salt of EDTA solution [15]. The concentrations of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions were determined by measuring the diffusion current [16]. The concentration of Fe<sup>2+</sup> was determined by spectrophotometric method using hydroxyl amine, sodium acetate and 1,10-phenanthroline. Iron(II) gave a complex having orange-red colour with  $\lambda_{max}$  at 510 nm. The absorbance of the solution was recorded before and after achieving the equilibrium at 510 nm wavelength.

The distribution coefficient  $(K_d)$  for these metal ions was calculated by using the following relationship:

$$K_{\rm d} = \frac{I - F \ V}{F \ M} \ (\rm{mL} \ g^{-1})$$

where  $K_d$  = distribution coefficient (mL g<sup>-1</sup>), *I* = initial amount of metal ions in the solution, *F* = final amount of metal ions in the solution, *V* = volume of the solution (mL), *M* = amount of the exchanger taken (g).

## 2.8. Metal ions separations

The binary separations for metal ions were carried out by column method. 2.0 g of the synthesized material was taken into the column with internal diameter  $\sim$ 0.6 cm. The column was washed thoroughly with the doubly distilled water and then the mixture containing  $Hg^{2+}-Ni^{2+}$ ,  $Hg^{2+}-Ba^{2+}$ ,  $Hg^{2+}-Mg^{2+}$  and  $Hg^{2+}-Sr^{2+}$ to be separated was loaded onto it, maintaining a flow rate of  $\sim 12-15$  drops min<sup>-1</sup>. The separation was achieved by passing a suitable solvent through the column as eluent and the metal ions in the effluent were determined quantitatively by EDTA titrations. Quaternary separations for Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions were carried out using a column with internal diameter  $\sim\,0.6\,\text{cm}$  containing 2.0 g of the synthesized material. The column was washed thoroughly with the demineralized water and the mixture containing Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions was loaded onto it with a flow rate of  $\sim$  12–15 drops min<sup>-1</sup>. The separations for Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions before and after adsorption were determined by recording the differential pulse polarogramme.

# 2.9. Separation in presence of acid, alkali and alkaline earth metals

To study the effectiveness of SDBS-SnP for the removal of  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$  and  $Pb^{2+}$  ions in the

presence of acid, alkalis and alkaline earth metals, the above experiments were repeated by taking a mixture of  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$  ions in the solutions containing 0.01 and 0.1 M acid, alkalis or alkaline earth metals.

# 3. Results and discussion

The ion exchange capacity of the sample of ion exchange material synthesized with different amount of SDBS is given in Table 1. The ion exchange capacity increased from 1.50 (for Sn (IV) phosphate) to 1.63 meq/g for SDBS-SnP having 0.0001 M SDBS. The ion exchange capacity (i.e.c.) was highest for the sample (No. 3) having 0.001 M SDBS. At 0.01 M SDBS, the i.e.c. values decreased, may be due to the blocking of the some of the ion-exchanging site of tin (IV) phosphate by the surfactant molecules. Thus, the addition of surfactant to the tin (IV) phosphate ion exchanger increased the ion exchange capacity for the Na<sup>+</sup> ions from 1.50 to 2.20 meq/g [17]. The strength of the interaction between the ion exchange material and mobile ions is determined by the nature, ionic size and number of the charges on the metal ion and on the functional group of the ion exchanger. Ions that have a stronger ionic interaction require a higher salt concentration and elute later in the gradient. The elution behaviour of the cation exchanger for H<sup>+</sup>-ions reveals that the process of exchange is quite fast and almost all the H<sup>+</sup> ions were eluted out in the first 160 mL of the effluent from a column of 1.0 g exchanger (Fig. 1). At lower salt concentrations, H<sup>+</sup>-ions with the weak ionic interactions starts to elute first from the column and H<sup>+</sup>-ions that have a stronger ionic interaction require a higher salt concentration and elute later in the gradient. Thus, the optimum concentration of NaNO<sub>3</sub> required to remove H<sup>+</sup> ions completely from the exchanger was found to be 1.0 M (Table 2).

The study on variation on ion exchange capacity at different temperatures reveals that SDBS-SnP is thermally stable till it attains temperature  $\sim 150$  °C, where the exchange capacity of 91.36% is retained by the material. On heating it further in the temperature

Table 1 Ion exchange capacity of various samples of SDBS-SnP

Sample number	SDBS used (moles)	Na <sup>+</sup> ion-exchanging capacity (meq/g)
Sample-1	0.0	1.50
Sample-2	0.01	1.03
Sample-3	0.001	2.20
Sample-4	0.0001	1.63



Fig. 1. Histogrammes showing the elution behaviour of SBDS-SnP.

Table 2

Variation in ion exchange capacity of SDBS-SnP cation exchanger with varying eluant concentrations

Concentration of NaNO <sub>3</sub> (M)	Ion exchange capacity (meq/g			
0.2	0.86			
0.4	1.24			
0.6	1.62			
0.8	1.91			
1.0	2.20			
1.2	2.20			

range 150-200°C, the ion exchange capacity is decreased to about 59.09%, may be due to the disruption in the bonding pattern of sulphonic part of SDBS from where the exchange of ions occurs. On heating to 300°C, the material possesses only 43.18% of ion exchange capacity of its initial value (i.e. before heating) may be due to exchange capacity of tin (IV) phosphate. The results are summarized in Table 3. The thermal behaviour of SDBS-SnP was further explored by thermogravimetric studies. The thermogravimetric and differential thermal analysis of SDBS-SnP show two-step mass losses, 11.4 and 7.9% up to the temperature 200°C with endo effect at 77°C which confirm the removal of external water molecules associated with the ion exchange material. The curves show 2.5 and 0.9% weight losses at 540°C due to thermal decomposition of SDBS and volatilization of alkyl part of SDBS [18]. A large weight loss of 19.1% was observed in the temperature range of 558-561°C due to the decomposition in the residual part of SDBS (i.e. benzene sulphonate groups) and Sn (IV) phosphate

Thermal stability and appearance of SBDS-SnP cation exchanger after heating at different temperatures for 1 h						
Heating temperature (°C)	Na <sup>+</sup> -ion exchange capacity (meq/g)	Physical appearance	% Retention in ion exchange capacity			
100	2.10	White	95.45			
150	2.01	White shiny	91.36			
200	1.30	Creamish white	59.09			
300	0.95	Yellow	43.18			



Fig. 2. TGA/DTA curve of SDBS-SnP.

[18]. At further high temperature, the weight of the substance becomes almost constant on heating up to 1,020°C with slight weight losses of 1.7% at 701°C, 0.5% at 850 C and finally 0.1% at 1,020 C. The residual mass of material is due to the formation of tin (IV) oxide (Fig. 2).

SDBS-SnP cation exchanger has been observed to possess higher selectivity towards Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and  $Hg^{2+}$  ions. The  $K_d$ -value signifies the ease with which one species sorbs onto a surface. Thus, higher the K<sub>d</sub>-value is, the more readily the species are sorbed to the surface. From the Table 4, it is observed that the values of  $K_d$  is very high for  $Hg^{2+}$  ions as compared to other metal ions in demineralized water, HClO<sub>4</sub> and acetic acid media. Therefore, it can be predicted that Hg<sup>2+</sup> ions can readily be sorbed onto SDBS-SnP surface in the aqueous and acidic media of perchloric acid and acetic acid. It is also observed that the  $k_d$  value is higher for the metal ion in aqueous solution but its value decreases in the acidic media or on increasing the acid strength due to the competition between the metal ions and hydrogen ions for the binding to the active site of the exchange materials. The high value of  $k_d$  for Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> ions in the presence of respective Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> ions (Table 5) makes SDBS-SnP a suitable candidate for the removal of transition metal ions in the presence of alkali and alkaline earth metals. The cation exchanger removes  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  in the presence of 0.1 and .01 M solutions of nitric acid, acetic acid and perchloric acid, respectively, (Fig. 3). The SDBS-SnP removes Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> ions in

6692

Table 3

$K_{\rm d}$ values of metals ions on SDBS-SnP cation exchanger in demineralized water and in acidic media									
Metal ions	K <sub>d</sub> values								
	Demineralized water	0.1 M HNO <sub>3</sub>	0.01 M HNO <sub>3</sub>	0.1 M HClO <sub>4</sub>	0.01 M HClO <sub>4</sub>	0.1 M CH₃COOH	0.01 M CH <sub>3</sub> COOH		
Mg <sup>2+</sup>	446.44	171.42	212.00	346.18	500.85	81.10	120.85		
Ca <sup>2+</sup>	533.30	62.50	128.57	87.72	107.90	52.19	135.32		
Ba <sup>2+</sup>	200.00	183.33	191.50	61.66	87.51	95.82	110.48		
$\mathrm{Sr}^{2+}$	500.00	127.77	291.66	65.72	126.42	75.00	113.33		
Ni <sup>2+</sup>	850.00	260.00	733.33	88.58	170.27	102.46	150.02		
Fe <sup>2+</sup>	342.00	81.81	233.33	_	_	-	-		
Hg <sup>2+</sup>	1350.0	220.00	516.20	425.00	960.00	340.00	1060.40		

Table 4  $K_4$  values of metals ions on SDBS-SnP cation exchanger in demineralized water and in acidic media

[Metal ion] =  $1.0 \times 10^{-3}$  M, final volume = 20.0 mL, temperature =  $25.0 \pm 0.5$  °C.

#### Table 5

 $K_d$  values of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> on SDBS-SnP cation exchanger in the presence of 0.1 M alkali/alkaline earth metals

0.1 M alkali/alkaline	K <sub>d</sub> value				
earth metal ions	Cu <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>		
Na <sup>+</sup>	261.721	112.71	2429.03		
K <sup>+</sup>	507.906	149.02	1661.79		
Mg <sup>2+</sup>	785.353	555.90	468.11		
Ca <sup>2+</sup>	745.078	207.38	2,293.89		

the presence of 0.1 M alkali metals (Na<sup>+</sup> and K<sup>+</sup>), 0.1 M alkaline earth metals (Mg<sup>2+</sup> and Ca<sup>2+</sup>) and other transition metal ions (e.g. 0.01 M Zn<sup>2+</sup>, etc.). Thus, these studies show that the material can be used to remove Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> ions from waste water during its treatment in the presence of ambient environmental pollutants. Shao et al. observed that the adsorption capacity of Vulcan XC-72 for Pb2+ is increased when grafted with SDBS [19]. They grafted SDBS over carbon (XC-72 carbon) using a plasma technique, and observed that XC-SDBS possessed higher adsorption capacity than XC-72 carbon. They suggested the suitability of XC-SDBS for the immobilization of heavy metal from large volumes of aqueous solutions in environmental pollution cleaning. Pb<sup>2+</sup> is removed by the negatively charged SDBS molecules by complexion effect, electron attraction and charge neutralization between the dodecyl benzene sulphonate anion headgroup and Pb<sup>2+</sup> ion [20]. Tagashira et al. extracted Pb<sup>2+</sup> using SDBS from the mixture of  $Sn^{2+}$  [21]. They extracted  $Pb^{2+}$  quantitatively in presence of NaCl also. SDBS appears to have a lamellar structure with alternating head-to-head (hydrophilic layer) and tail-to-tail (hydrophobic layer) arrangements. Water molecules and Na<sup>+</sup> counter ions exist between the heads of the hydrophilic layer. During



Fig. 3. Differential pulse polarogramme curves for  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  ions before (upper curve) and after (lower curve) passing through the column containing the SDBS-SnP ion exchanger.

the extraction process, Na<sup>+</sup> ions are replaced by cationic complex of Pb<sup>2+</sup>. The exchange of Na<sup>+</sup> ions with  $(Pb(TU)_n)^{2+}$  ions changes the thickness of the hydrophilic layer. The metal ions are bonded to SDBS molecule through SO group. The bonding between SO group and metal ion is ionic in nature. The incorporation of SDBS into tin (IV) phosphate makes it more selective for Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> ions than tin (IV) phosphate alone [5,8]. The adsorption of the ionic species to the ion exchanger is driven by the ionic interaction between the oppositely charged ionic groups in the mobile phase and the functional group available in the cation exchanger (SDBS/SnP/SDBS-SnP). The selectivity possessed in SDBS-SnP for these ions may be attributed to the replacement of sodium



Fig. 4. SEM photograph of SDBS-SnP.

ions from SDBS molecules of SDBS-SnP. This process results into the replacement of Na<sup>+</sup> from the SDBS molecules by Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> ions and leads to the formation of Cu<sup>2+</sup>-DBS, Cd<sup>2+</sup>-DBS, Pb<sup>2+</sup>-DBS and Hg<sup>2+</sup>-DBS ion-pairs. The strong electrostatic attractive force is responsible for the binding between the oppositely charged bivalent Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> ions and dodecyl benzene sulphonate anion (DBS<sup>-</sup>). The presence of SDBS in the ion exchanger was confirmed by elemental analysis of the synthesized material. The SDBS molecules coat the tin (IV) phosphate matrix to form an intercalated inorganicorganic fibrous ion exchanger as shown by the SEM photograph in Fig. 4. The cationic exchange material exists in the variable size ranging from 50 to 500 µm.

The IR spectrum of the material in Fig. 5 indicates the presence of phosphate and metaphosphate groups by the appearance of peak at  $511.73 \text{ cm}^{-1}$  [22]. The appearance of S=O stretching vibration bands was observed at 1,063.35 and 1,408.60 cm<sup>-1</sup> [23,24]. The peak at 1,642.74 cm<sup>-1</sup> represents the water of crystallization and the bands beyond at 3408.13 cm<sup>-1</sup> correspond to –OH groups [1,25]. The XRD study of the material has been carried out by using Rigaku Cu K $\alpha$ radiation with the wavelength of 1.54 A. The absence of defined peak for the material shows that the material is amorphous in nature.



Fig. 5. IR spectrum of SDBS-SnP.

effectively removed from the mixture containing,  $Zn^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  ions in HNO<sub>3</sub>,  $CH_3COOH$  or HClO<sub>4</sub> when passed through the thoroughly washed column. The enhanced adsorption of  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$  by SDBS-SnP exchanger may be attributed to the formation of ion-pair complexes of surfactant with



Fig. 6. Chromatogrammes of binary separations of metal ions on SDBS-SnP cation exchanger columns. Eluents 0.1 M CH<sub>3</sub>COOH and 0.1 M HClO<sub>4</sub> were for the separation of (A)  $Hg^{2+}-Ba^{2+}$ , (B)  $Hg^{2+}-Ni^{2+}$  and 0.1 M CH<sub>3</sub>COOH and 0.1 M HNO<sub>3</sub> were used for the separation of (C)  $Hg^{2+}-Mg^{2+}$  and (D)  $Hg^{2+}-Sr^{2+}$ .

Binary separation	s of metal ions	achieved on	SDBS-SnP	cation	exchanger	column

Table 6

S. no	Separation achieved	Eluant used	Volume of eluent used (mL)	Amount loaded (µg)	Amount recovered (µg)	Error (%)
1	Hg <sup>2+</sup>	0.1 M CH <sub>3</sub> COOH	70	6852.4	6766.7	-1.25
	$Mg^{2+}$	0.1 M HNO <sub>3</sub>	70	5128.2	5166.6	+0.74
2	Hg <sup>2+</sup>	0.1 M CH <sub>3</sub> COOH	70	6852.4	6732.4	-1.75
	Ba <sup>2+</sup>	0.1 M HClO <sub>4</sub>	60	5226.8	5148.3	-1.50
3	$Hg^{2+}$	0.1 M CH <sub>3</sub> COOH	60	6852.4	6852.4	0
	$\mathrm{Sr}^{2+}$	0.1 M HNO <sub>3</sub>	70	4232.2	4126.7	-2.49
4	Hg <sup>2+</sup>	0.1 M CH <sub>3</sub> COOH	60	6852.4	6749.6	-1.50
	Ni <sup>2+</sup>	0.1 M HClO <sub>4</sub>	80	5816.2	5816.2	0

the metal ions and also due to the reduction in interfacial tensions between the solid and liquid phases by amphiphilic nature of surfactant [1]. The sequential elution of the ions from the column depends upon the metal-ligand stability. The elution profiles of metal ion separated are shown in Fig. 6. The weakly retained metal ions were eluted first and strongly retained metal ions were eluted in the last. The separations are quite sharp, and recovery of metal ions was quantitative and reproducible. The results are summarized in Table 6. It is easy to synthesize, durable in nature and capable of removing the  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$  ions from the waste water. It is also cost-effective as the synthesis includes simple method and easily available materials like tin salt, SDBS etc. The high selectivity of material towards Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> ions will be much helpful in analytical and environmental chemistry for the separation and removal of Cu2+, Cd2+, Pb2+ and Hg<sup>2+</sup> ions during the treatment of waste water during its recycling.

# 4. Conclusion

The synthesized cation exchanger, SDBS-SnP, possessed higher ion exchange capacity (2.20 meq/g) than the tin (IV) phosphate (1.50 meq/g). The addition of SDBS to the matrix of Sn (IV) phosphate improved the mechanical and thermal stability. The cation exchanger is found to be quite selective for the removal of  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$  ions, and can be used in presence of other impurities like acid, alkalis, alkaline earth and other metal ions. The higher and better selectivity possessed of SDBS-SnP is attributed to the formation of ion-pair between metal ions and surfactant molecules. SDBS-SnP is clean, environment friendly and cost-effective material. The cationic exchange material can be recycled once it is exhausted and will not pose any threat to the environment.

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# References

 K.G. Varshney, M.Z.A. Rafiquee, A. Somya, Synthesis, characterization and adsorption behaviour of TX-100 based Sn(IV) phosphate, a new hybrid ion exchanger: Separation of Ni (II) from Hg (II), Pb(II) and Fe (III) on its column, J. Therm. Anal. Cal. 90 (2007) 663–667.

- [2] K.G. Varshney, M.Z.A. Rafiquee, A. Somya, TX-100 based cerium(IV) phosphate, as a new Hg(II) selective, surfactant based fibrous ion exchanger: Synthesis, characterization and adsorption behaviour, Colloids Surf., A 317 (2008) 400–405.
- [3] A. Somya, M.Z.A. Rafiquee, K.G. Varshney, Synthesis, characterization and analytical applications of sodium dodecyl sulphate-cerium (IV) phosphate: A new Pb (II) selective, surfactant based intercalated fibrous ion exchanger, Colloids Surf., A 336 (2009) 142–146.
- [4] A. Somya, M.Z.A. Rafiquee, K.G. Varshney, Effect of surfactant on the adsorption behavior of cerium (IV) phosphate, cation exchanger for alkaline earths and heavy metal ions, Colloids Surf., A 301 (2007) 69–72.
- [5] N. Iqbal, M.Z.A. Rafiquee, Synthesis and characterization of lead(II) selective sodium dodecyl benzene sulphonate–cerium (IV) phosphate ion exchanger, Colloids Surf., A 364 (2010) 67–71.
- [6] N. Iqbal, M. Mobin, M.Z.A. Rafiquee, Synthesis and characterization of sodium bis(2-ethylhexyl) sulfosuccinate based tin (IV) phosphate cation exchanger: Selective for Cd<sup>2+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup> ions, Chem. Eng. J 169 (2011) 43–49.
  [7] N. Iqbal, M. Mobin, M.Z.A. Rafiquee, H.A. Al-Lohedan, Char-
- [7] N. Iqbal, M. Mobin, M.Z.A. Rafiquee, H.A. Al-Lohedan, Characterization and adsorption behaviour of newly synthesized sodium bis(2-ethylhexyl) sulfosuccinate-cerium (IV) phosphate (AOT-CeP) cation exchanger, Chem. Eng. Res. Des 90 (2012) 2364–2371.
- [8] Q.S. Huo, D.I. Margolese, U. Ciesla, P. Feng, T.E. Gier, P. Sieger, R. Leon, P.M. Petroff, F. Schuth, G.D. Stucky, Generalized synthesis of periodic surfactant/inorganic composite materials, Nature 368 (1994) 317–321.
- [9] Q.S. Huo, D.I. Margolese, G.D. Stucky, Surfactant control of phases in the synthesis of mesoporous silica-based materials, Chem. Mater. 8 (1996) 1147–1160.
- [10] S. Mann, G.A. Ozin, Synthesis of inorganic materials with complex form, Nature 338 (1996) 313–318.
- [11] A.B.D. Nandiyanto, F. Iskandar, K. Okuyama, Nano-sized polymer particle-facilitated preparation of mesoporous silica particles using a spray method, Chem. Lett 37 (2008) 1040–1041.
- [12] A.B.D. Nandiyanto, S.G. Kim, F. Iskandar, K. Okuyama, Synthesis of spherical mesoporous silica nanoparticles with nanometer-size controllable mesopores and outer diameters, Microporous Mesoporous Mater. 120 (2009) 447–453.
- [13] S.V. Mattigod, X.D. Feng, G.E. Fryxell, J. Liu, G. Meiling, Separation of complexed mercury from aqueous wastes using self-assembled mercaptan on mesoporous silica, Sep. Sci. Technol. 34 (1999) 2329–2345.
- [14] K.G. Varshney, M.Z.A. Rafiquee, A. Somya, M. Drabik, Synthesis and characterization of a Hg(II) selective n-butyl acetate cerium(IV) phosphate as a new intercalated fibrous ion exchanger: Effect of surfactants on the adsorption behaviour, Ind. J. Chem. 45A (2006) 1856–1860.
- [15] C.N. Reiliy, R.W. Schmidt, F.S. Sadek, Chelon approach to analysis: I. Survey of theory and application, J. Chem. Edu. 36 (1959) 555–564.
- [16] J. Mendham, R.C. Denney, J.D. Barnes, M.J.K. Thomas, Vogel's Quantitative Chemical Analysis, sixth ed., The School of Chemical and Life sci., University of Greenwich, London, 2000.
- [17] M. Bouraada, M. Lafjah, M.S. Ouali, L.C. de Menorval, Basic dye removal from aqueous solutions by dodecylsulfate- and dodecyl benzene sulfonate-intercalated hydrotalcite, J. Hazard. Mater. 153 (2008) 911–918.
- [18] A.V. Streltsov, O.V. Morozova1, N.A. Arkharova, V.V. Klechkovskaya, I.N. Staroverova, G.P. Shumakovich, A.I. Yaropolov, Synthesis and characterization of conducting polyaniline prepared by laccase-catalyzed method in sodium dodecylbenzenesulfonate micellar solutions, J. Appl. Polym. Sci. 114 (2009) 928–934.

- [19] D. Shao, Z. Jiang, X. Wang, SDBS modified XC-72 carbon for the removal of Pb(II) from aqueous solutions, Plasma Process. Polym. 7 (2010) 552–560.
- [20] J. Lin, W.H. Gao, SDBS@BaSO<sub>4</sub>: An efficient wastewater-sorbing material, J. Mater. Chem., 19 (2009) 3598–3601.
  [21] S. Tagashira, S. Kimoto, K. Nozaki, Y. Murakami, Surfactant
- [21] S. Tagashira, S. Kimoto, K. Nozaki, Y. Murakami, Surfactant gel extraction of gold(III), palladium(II), platinum(II), and lead(II) as thiourea-complexes, Anal. Sci. 25 (2009) 723.
- [22] K.C. Sobha, K.J. Rao, Investigations on sodium tin phosphate and tin pyrophosphate glasses, J. Chem. Sci. 107 (1995) 573–580.
- [23] K. Suri, S. Annapoorni, Tandon, phase change induced by polypyrrole in iron-oxide polypyrrole nanocomposite, Bull. Mater. Sci. 24 (2001) 563–567.
- [24] D.W. Chang, G.J. Sohn, L. Dai, J-B Baek, Reversible adsorption of conjugated amphiphilic dendrimers onto reduced graphene oxide (rGO) for fluorescence sensing, Soft Matter 7 (2011) 8352–8357.
- [25] M. Ristoval, P. Naumov, B. Soptrajanov, The FTIR spectrum of water in aqua(malonate)cadmium(II) hydrate, Bull. Chem. Tech. Macedonia 21 (2002) 147–150.