

## EVALUATION ON THE EFFECT OF PREPARATION STRATEGY FOR ADSORPTION EFFICIENCY OF POLYANILINE – TIN CERIUM PHOSPHATE CATION EXCHANGE MATERIAL

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### ABSTRACT:

A novel composite cation exchange material was synthesized by incorporating polyaniline into inorganic ion exchange material, tin cerium phosphate in three different ways. The materials were characterized using FTIR, XRD, TGA and SEM. The material synthesized by in-situ method was highly crystalline, the other materials which was formed by ex-situ and chemical modification way showed amorphous in nature. The SEM analysis depicted the different morphology for three composite materials. The material was formed by in-situ polymerization has needle like structure, where as composite was prepared by ex-situ method having fiber morphology and the third one has spherical morphology. Ion exchange capacity (IEC) study of these three materials indicated that there was no much difference in capacity ( $\sim 1-1.3 \text{ meqg}^{-1}$ ). The temperature effect on IEC described the difference in the thermal stability of these materials. The distribution coefficient study exposed that the order of selectivity towards different metal ions (  $\text{Pb(II)} > \text{Bi(III)} > \text{Co(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Ca(II)} > \text{Mn(II)} > \text{Ni(II)} > \text{Hg(II)} > \text{Mg(II)}$  ) was not vary for three materials, but the quantity of distribution coefficient was different for composites. pH titration study of three composite materials showed bifunctional nature for all. The prepared composites were used as adsorbents for the removal of methylene blue (MB) dye from aqueous solutions. Comparison between the removal of the dye by using three composite materials formed by different ways was investigated by UV-Visible absorption spectroscopy. The results indicated that composite was formed by in-situ polymerisation method is a very efficient adsorbent material for adsorption of dye from aqueous solutions compared to other two materials. The findings demonstrated the importance of the introduced composite material in dye removal technology..

**Keywords:** *Composite material, Polyaniline, Adsorption, Dye, Methylene blue*

### [I] INTRODUCTION

The chemical contamination of water from a wide range of toxic derivatives, in particular heavy metals, aromatic molecules and dyes, is a serious environmental problem owing to their potential human toxicity. About 15% of the total world production of dyes is lost during the dyeing process and is released as liquid effluents.<sup>1</sup> Some

dyes are either toxic or mutagenic and carcinogenic pollutants which must be strictly controlled in the water system because of their threat to human physiology and ecological systems even at low concentrations. Hence, their presence in wastewater is unwarranted, and it is desirable to remove coloring material from

effluents, before their discharge in the environment. Among the various methods for the removal of dyes, adsorption by ion exchanger is the most versatile and eco-friendly technique. Thus, the safe removal of such a dye is the prime aim of our present research and this is accomplished by using a novel ion exchanger.

The organic–inorganic composite ion exchangers are modern materials in the chromatographic field, as the merits of organic and inorganic moieties can be combined in the composites. This hybrid material was introduced to overcome the limitation suffered by the organic and inorganic ion exchangers. Many investigators have introduced organic–inorganic composite ion exchangers consisting of inorganic materials and organic binding matrices.<sup>2-4</sup> In literature, various methods for preparing these hybrid materials have been reported.<sup>5-7</sup> Composite materials formed by mixing organic polymers and inorganic salts possess all the good properties of both the constituents and an enhanced utility. In designing composite ion exchanger, scientists and engineers have ingeniously combined various inorganic metal salts, metal oxide and polymers to produce a new generation of extraordinary materials that encompass a wide variety of applications. The present study undertaken to evaluate the efficiency of a composite ion exchanger, polyaniline – tin cerium phosphate prepared in three different ways for the removal of dye in aqueous solution. Methylene blue as a typical basic textile dye was selected as a test probe. The material has also been successfully used for the separation of metal ions quantitatively. Hence, the objective of the present work was to develop simple, cost-effective, and environmentally benign method for the removal of organic dyes from aqueous solution using composite ion exchanger.

## [II] MATERIALS AND METHODS

### 2.1. Reagents

Stannic chloride (E.Merck), Ammonium ceric nitrate (E.Merck), Sodium dihydrogen phosphate

(Loba Chem) and aniline (E.Merck) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

### 2.2. Apparatus and Instrumentations

A glass column was used for column operations. ELICO LI613 pH meter was used for pH measurements. FT-IR Spectrometer model Thermo-Nicolet Avtar 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/DTA Analysis System for thermogravimetric/derivative thermogravimetric analysis were used. UV-Visible Spectrophotometer model JASCO V660 was used for spectrophotometric measurements.

### 2.3. Synthesis

#### a) Polyaniline-tin cerium phosphate (SCP-Pe)

*Synthesis of polyaniline:* Polyaniline gels were prepared by mixing of the acidic solutions of 10% aniline and 0.1 M ammonium persulphate in different volume ratios with continuous stirring by a magnetic stirrer keeping the temperature below 10 °C for half an hour. Green colored polyaniline gels were obtained that were kept overnight in a refrigerator.

*Synthesis of tin cerium phosphate:* ammonium ceric nitrate solution (0.05 M), stannic chloride solution (0.05 M) and sodium dihydrogen phosphate solution (0.05 M) were prepared. Sodium dihydrogen phosphate solution was added to the mixtures of ammonium ceric nitrate solution and stannic chloride solution with constant stirring in volume ratios 1:2:3 corresponding to Sn:Ce:PO<sub>4</sub> and formed tin cerium phosphate gel.

*Synthesis of polyaniline-tin cerium phosphate (SCP-Pe):* The gels of polyaniline were added to the yellow inorganic precipitates of tin cerium phosphate and mixed thoroughly with constant stirring. The resultant green colored gels were kept for 24 hrs at room temperature (25±2 °C) for

digestion. The supernatant liquid was decanted and gels were filtered under suction. The excess acid was removed by washing with demineralized water (DMW) and the material was dried in an air oven at 50 °C. The dried products were immersed in DMW to obtain small granules. They were converted to H<sup>+</sup> form by treating with 1.0 M HNO<sub>3</sub> for 24 hrs with occasional shaking, intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and the material was dried at 50 °C. The particle of the size of the range (~125 µm) of the material was obtained by sieving and kept in desiccators for further studies.

*b) Polyaniline-tin cerium phosphate (SCP-Pc)*

*Synthesis of tin cerium phosphate:* Tin cerium phosphate gel was prepared in the same way described above. The pH of the mixtures was adjusted to 1.0 by adding aqueous ammonia or hydrochloric acid with constant stirring. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H<sup>+</sup> form by treating with 1.0 M HNO<sub>3</sub> 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.

*Synthesis of polyaniline-tin cerium phosphate (SCP-Pc):* The crystals of tin cerium phosphate are kept in the 10% solution of aniline monomer. The cerium present in the crystal oxidized the aniline and polyaniline is formed into the matrixes of tin cerium phosphate. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H<sup>+</sup> form by treating with 1.0 M HNO<sub>3</sub> 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.

*c) Polyaniline - tin cerium phosphate (SCP-Pi)*

*Synthesis:* Tin cerium phosphate gel was prepared in the same way described above. For

the synthesis of composite we added acidic solution of aniline monomer to the gel of tin cerium phosphate. Due to the redox activity of cerium present in the inorganic gel oxidized the aniline monomer to polyaniline and it was formed in the interlayer of tin cerium phosphate. The resulting gel was kept for 24 hrs at room temperature maintaining the pH at 1.0 by solution of 1.0 M NaOH/1.0 M HNO<sub>3</sub>. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H<sup>+</sup> form by treating with 1.0 M HNO<sub>3</sub> 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.

**2.4. Ion exchange capacity**

The ion exchange capacity of the material was determined by column method. 1.0 g of the exchanger in H<sup>+</sup> form was taken in a glass column of 1.1 cm diameter. The H<sup>+</sup> ions were eluted by percolating 100 mL of 1.0 M NaCl solution. The effluent was collected and titrated against standard sodium hydroxide solution. The exchange capacity in meqg<sup>-1</sup>, IEC was calculated using the formula,

$$IEC = \frac{av}{w}$$

Where, *a* is the molarity, *v* is the volume of alkali used during titration and, *w* is the weight of the exchanger taken.<sup>8</sup>

**2.5. Thermal Effect on Ion-exchange Capacity (I.E.C.)**

To study the effect of drying temperature on the I.E.C., 1.0 g samples of the composite cation exchange materials in the H<sup>+</sup> form were heated at various temperatures in a muffle furnace for 2 hrs and the Na<sup>+</sup> ion-exchange capacity was determined by column process after cooling them at room temperature.

**2.6. pH Titrations**

Topp and Pepper method<sup>10</sup> 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<sup>-</sup> added.

### 2.7. Distribution Coefficient (K<sub>d</sub>)

Distribution studies were carried out for various metal ions in demineralized water by batch process. In this method, 0.1 g of the exchanger (60-100 mesh) was equilibrated with 20 mL of the metal ion solutions for 24 hrs at room temperature. The metal ion concentrations before and after sorption were determined spectrophotometrically/ complexometric titration against standard EDTA solution. In the complexometric method, the K<sub>d</sub> values were calculated using the formula,

$$K_d = \frac{(I - F)}{F} \times \frac{V}{W}$$

Where, I is the initial volume of EDTA used, F is the final volume of EDTA used, V is the volume of the metal ion solution (mL) and W is the weight of the exchanger.<sup>9</sup>

### 2.8. Batch experiments for dye removal

Batch experiments were performed according to Mahanta et al.<sup>11</sup> The initial and final concentrations of methylene blue solutions were determined by measuring absorbance at 664 nm using UV-visible absorption spectroscopy. Methylene blue solutions (50 mL) of different concentrations (50 mg L<sup>-1</sup> to 250 mg L<sup>-1</sup>) were mixed with 0.2 g of material and kept for 2 hrs and measured its absorbance. The effect of pH, contact time and adsorbent dosage was carried out. The percentage removal of dye from solution was calculated by the following:

$$\% \text{Removal} = \frac{(C_o - C_t)}{C_o} \times 100,$$

Where, C<sub>o</sub> and C<sub>t</sub> (mg L<sup>-1</sup>) are the initial dye concentration and concentration at time *t*, respectively.

### 2.9. Desorption study

The dye-loaded exchanger which was exposed to 50 mg L<sup>-1</sup> of dye was separated from the solution. Later, cation exchanger was dried completely and used for desorption experiments. The dye-loaded materials (0.2 g) were then brought into contact with 1.0 M NaOH, 1.0 M HNO<sub>3</sub>, and ethanol (95%), separately. The mixture was kept for 24 hrs. After desorption, the supernatant liquid was collected, with the remaining procedure being the same as for the sorption experiments.

## [III] RESULTS AND DISCUSSION

The organic-inorganic polyaniline-tin cerium phosphate was formed by three different methods are similar in appearance. The composite materials possessed ion exchange capacity of 1.28 meqg<sup>-1</sup> for SCP-Pi, 1.25 meqg<sup>-1</sup> for SCP-Pe and 1.15 meqg<sup>-1</sup> for SCP-Pc. In order to check the reproducibility of the prepared composites, they were synthesized four times under identical conditions of the concentration of reagents, mixing ratio and drying temperature. Ion-exchange capacity and yield of each product were examined. The averages and standard deviation of the ion-exchange capacity and yield were found to be x meqg<sup>-1</sup> and ± 0.04%, respectively. It was observed that on heating at different temperatures for 2 hrs, the ion-exchange capacities of the exchangers were changed as the temperature increased (Fig. 1). The order of thermal stability of exchanger at 300 °C is SCP-Pi > SCP-Pc > SCP-Pe. The solubility experiment indicated that the composite materials have reasonable good chemical stability in solutions of different acids, bases, organic solvents, salts, etc. The chemical stability may be due to the presence of binding polymer, which can prevent the dissolution or leaching of any constituent element into the solution.

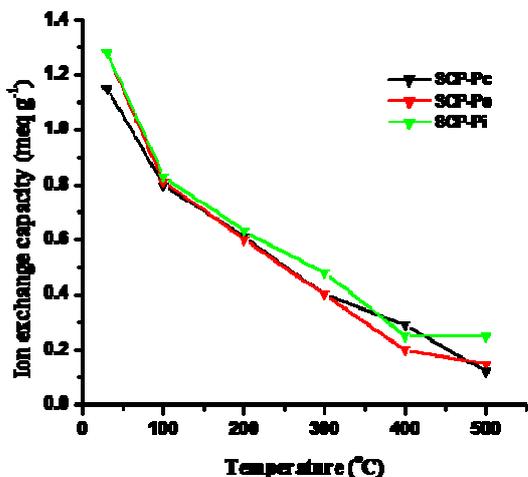


Fig. 1. Effect of temperature on IEC of SCP-Pc, SCP-Pe and SCP-Pi

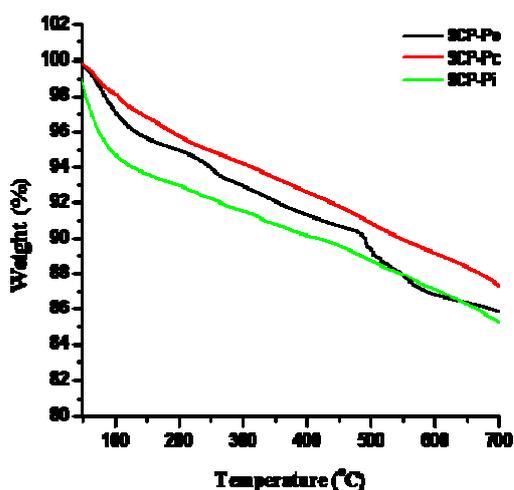


Fig. 2. TGA of SCP-Pc, SCP-Pe and SCP-Pi

The TGA curve (Fig. 2) of three samples recorded continuous weight loss of mass up to 150 °C, which may be due to the removal of external water molecule.<sup>12</sup> In the case of SCP-Pe there was a sudden weight loss at 250 °C, may be due to the partial decomposition of organic part. While considering other two materials this weight loss was not observed which may be due to the lower polymer content than in the first one which was supported by EDS data. Likewise at around 500 °C a sudden weight loss was observed which

may be due to complete degradation of polymer molecule present in the composite.

In the FT-IR spectrum of the SCP-Pc (Fig. 3), a strong and broad band around 3400 cm<sup>-1</sup> is found which can be ascribed to -OH stretching frequency but the intensity of the same peak was less in the other materials which may be due to the higher amount of polyaniline insertion into the matrix of inorganic counter parts. Likewise in the case of SCP-Pc, a sharp peak around 1600 cm<sup>-1</sup> can be attributed to H-O-H bending band, which represents the strongly bonded -OH groups in the matrix which is not prominent in the other two materials. In the case of other two materials, the -OH stretching bands was merged together and shifted to lower frequency side. An assembly of two sharp peaks in the region 500–800 cm<sup>-1</sup> may be due to the presence of metal oxygen bond. Another assembly of two peaks in the region 1300–1400 cm<sup>-1</sup> may be ascribed due to the stretching vibration frequency of C-N in the materials,<sup>13</sup> as it also resembles the stretching vibration frequencies for C-N found in polyaniline. This proved that the SCP-Pi and SCP-Pe contains considerable amount of polyaniline where as in the case of SCP-Pc the intensity of peaks at the above region was less indicating the low polyaniline content in this material.

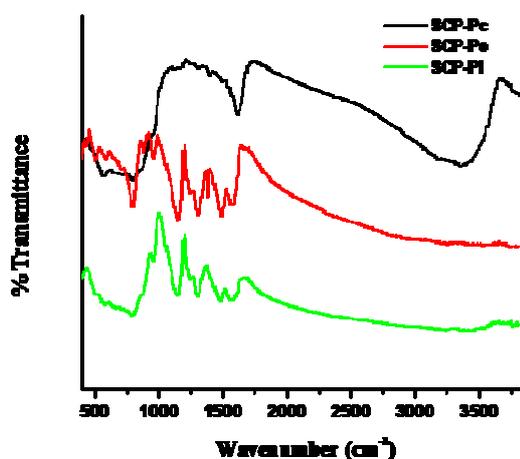


Fig. 3. FTIR of SCP-Pc, SCP-Pe and SCP-Pi

The XRD patterns of SCP-Pi, SCP-Pe and SCP-Pc are shown in Fig. 4. X-ray diffraction pattern of the SCP-Pe and SCP-Pc showed no observable peaks which conformed amorphous nature of the material. XRD analysis displayed crystalline nature of the SCP-Pi with high intensity peak of  $2\theta$  value and the average crystalline size was found to be 30-40 nm ranges which is in the nano range. The crystallinity may be developed by the intercalation of polyaniline in between the SnCeP layer because of the in-situ preparation and which gave the stability to the SnCeP. The intercalation of polyaniline was proved with the support of d

value of the composite material.<sup>14</sup> The particle size was calculated from the full width at half-maximum of the peak using Debye Scherer equation,

$$D = \frac{0.9\lambda}{\beta_{2\theta} \cos \theta_{max}}$$

Where, D is the average crystal size in nm,  $\lambda$  is the characteristic wavelength of X-ray used,  $\theta_{max}$  is the diffraction angle and  $\beta_{2\theta}$  is the angular width in radians at an intensity equal to half of the maximum peak intensity.

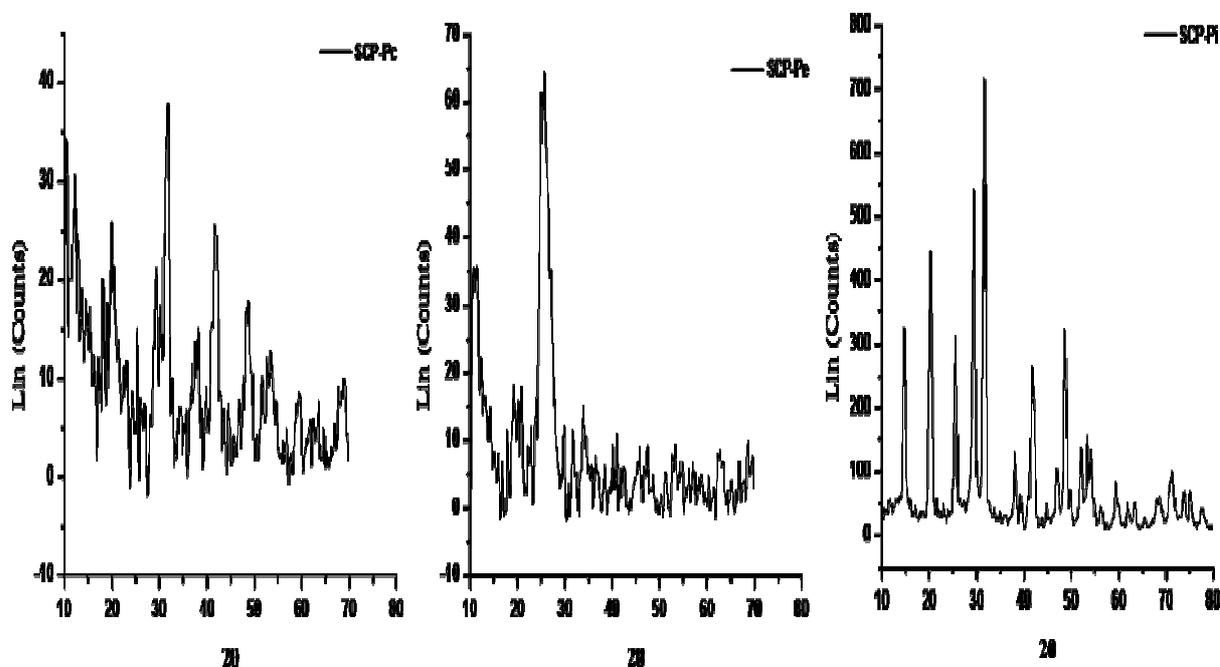
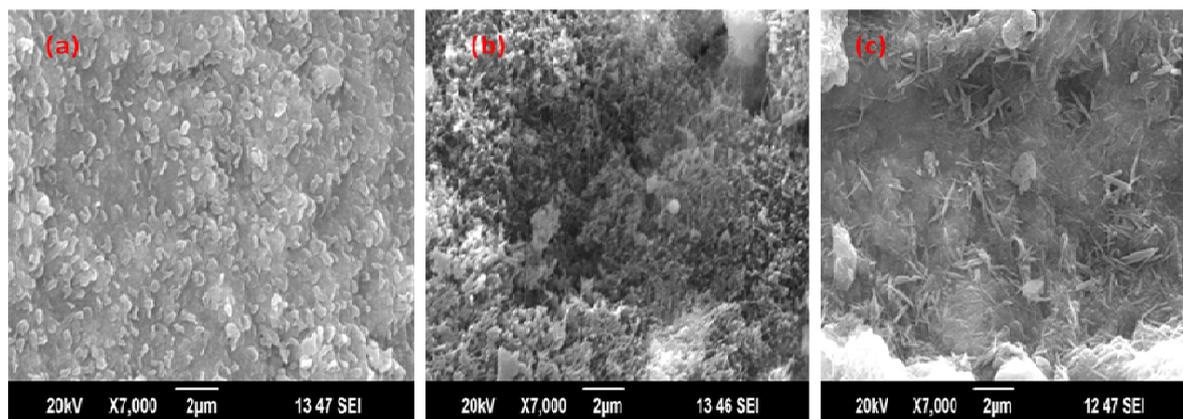


Fig: 4. XRD of SCP-Pc, SCP-Pe and SCP-Pi

Scanning electron microscope (SEM) photographs of SCP-Pc, SCP-Pe and SCP-Pi are shown in Fig. 5. The SEM pictures demonstrated the difference in surface morphology of three

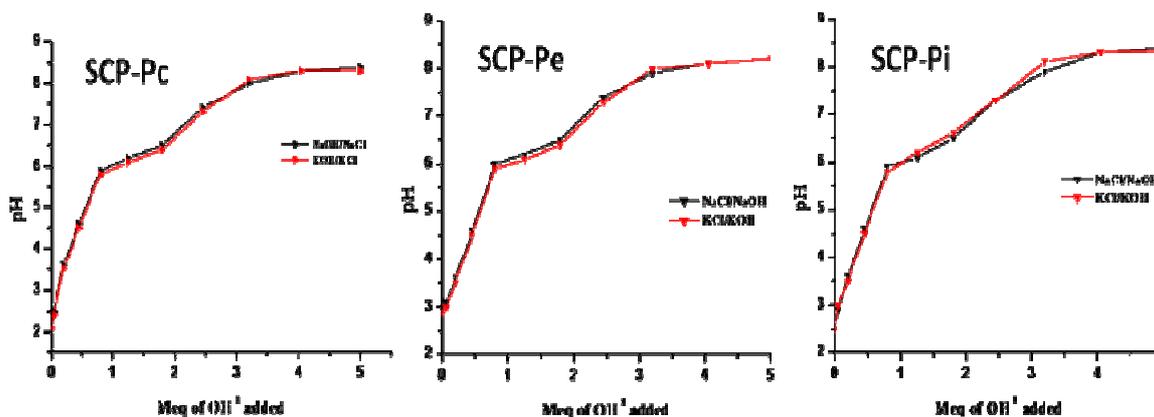
materials. SCP-Pc has granular structure where as SCP-Pe has the fiber like morphology. The morphology of SCP-Pi has been changed to needle like structure which may be due to in-situ preparation strategy.



**Fig. 5.** SEM of (a) SCP-Pc, (b) SCP-Pe and (c) SCP-Pi pH titration curve obtained under equilibrium conditions for each of NaOH/NaCl and KOH/KCl system showed two inflection points which indicate the bifunctional behaviour of the materials (Fig. 6). These appear to be strong cation exchangers as indicated by a low pH (~2 – 4) of the solution when no OH<sup>-</sup> ions were added

to the system. The exchange capacity obtained from the curve is in agreement with that obtained by the column method.

**Fig. 6.** pH titration curve for SCP-Pc, SCP-Pe and SCP-Pi



SCP-Pc		SCP-Pe		SCP-Pi	
Metal ion	DMW	Metal ion	DMW	Metal ion	DMW
Pb(II)	300.00	Pb(II)	333.60	Pb(II)	336.00
Bi(III)	185.00	Bi(III)	255.00	Bi(III)	260.20
Co(II)	75.75	Co(II)	160.00	Co(II)	166.00
Cu(II)	72.00	Cu(II)	129.60	Cu(II)	139.60
Zn(II)	40.00	Zn(II)	90.00	Zn(II)	90.00
Ca(II)	38.00	Ca(II)	85.90	Ca(II)	85.95
Mn(II)	27.00	Mn(II)	80.12	Mn(II)	83.40
Ni(II)	17.00	Ni(II)	75.88	Ni(II)	79.80
Hg(II)	14.00	Hg(II)	65.45	Hg(II)	71.90
Mg(II)	8.50	Mg(II)	50.40	Mg(II)	55.40
Cd(II)	NA	Cd(II)	34.40	Cd(II)	50.40

**Table 1.** K<sub>d</sub> of different metal ion on SCP-Pc, SCP-Pe and SCP-Pi

In order to understand the potentiality of the composite cation exchange material in the separation of metal ions, distribution studies for 11 metal ions were performed in demineralised water (DMW) (Table 1). The SCP-Pi composite ion exchanger has wide variety of  $K_d$  value for different metal ions and have higher selectivity towards Pb(II) and Bi(III) in comparison to other metal ions studied. The selectivity was found to be in the order Pb(II) > Bi(III) > Co(II) > Cu(II) > Zn(II) > Ca(II) > Mn(II) > Ni(II) > Hg(II) > Mg(II) > Cd(II) for all three materials. The distribution coefficient of different metal ions on three materials was different and it was decreased in the order SCP-Pc < SCP-Pe < SCP-Pi.

The adsorption of the dye, methylene blue (MB), cationic in nature was used for comparative study of the effect of preparation methods of composite exchangers under the same conditions of amount of adsorbent, contact time, temperature and pH. The adsorption experiment of MB using diffuse reflectance uv-visible spectroscopy was conducted for all three materials.

The effect of adsorbent dosage on the removal of MB was studied at  $50 \text{ mgL}^{-1}$  concentration of dye solution (Fig. 7a) for 2 hrs at neutral pH and  $30 \text{ }^\circ\text{C}$ . Removal of dyes with increasing adsorbent dosage was observed which is due to the availability of reactive sites<sup>15</sup> and above 0.4 g there is not much observable difference in the percentage adsorption. The percentage of removal efficiency was observed about ~ 98% even at 0.1 g adsorbent dosage. The higher removal efficiency of SCP-Pi compared with SCP-Pe and SCP-Pc is mainly due to the nano sized needle shape morphology and crystalline structure of adsorbent which provide high surface area for the adsorption of the dye molecule. For further study fixed the amount of adsorbate as 0.2 g and studied the effect of concentration of MB.

Fig. 7b shows the percentage sorption of dyes at different concentration of dyes in the presence of 0.2 g of exchanger at neutral pH and  $30 \text{ }^\circ\text{C}$  for 2 hrs. From the figure, it was revealed that there was significant removal of dyes even at higher concentration also possible with the exchanger. The enhanced removal at low concentration could be due to the faster movement of dye into the activated sites of composite.<sup>16</sup> The percentage of adsorption was decreased with increasing concentration of dyes ( $50 \text{ mgL}^{-1}$  –  $250 \text{ mgL}^{-1}$ ). However, in higher concentration ( $250 \text{ mgL}^{-1}$ ) the removal rate was decreased (30-50%) 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.<sup>17</sup>

The adsorption of MB was analysed as a function of contact time on  $50 \text{ mgL}^{-1}$  concentration of dye solution (Fig. 7c) at neutral pH and  $30 \text{ }^\circ\text{C}$ . The slow removal was observed for SCP-Pe and SCP-Pi compared with SCP-Pc during the first 20 minutes due to the fiber and needle like morphology of molecule of SCP-Pe and SCP-Pi respectively which slow down the diffusion of dye molecule and gradually increased the adsorption of MB on exchanger. After reaching 2 hrs the equilibrium time for dye adsorption was achieved.

Several studies reported the significant role of pH in adsorption reaction. Crini et al.<sup>18</sup> reported that the pH of the solution influences the surface charge and functional groups of the adsorbent. In addition, pH influences the degree of ionization of the materials present in the solution and solution chemistry. Hence, 0.2 g of the composite exchanger was mixed with 100 mL of dye solutions ( $50 \text{ mgL}^{-1}$ ) at different pH values (2–12). The results (Fig. 7d) showed that increasing

solution pH increases the extent of dye removal. 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.<sup>19</sup> 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 was increased at higher pH. Finally the adsorption process proceeded through

the electrostatic attraction between the two counter ions. The amount of dye adsorbed,  $Q_e$  ( $mg\ g^{-1}$ ) onto unit mass of SCP-Pi, SCP-Pe and SCP-Pc are equal to  $5.38\ mg\ g^{-1}$ ,  $4.98\ mg\ g^{-1}$ , and  $3.61\ mg\ g^{-1}$ , respectively.  $Q_e$  was calculated from the mass balance equation given by:

$$Q_e = (C_0 - C_e)Vm^{-1}$$

Where  $C_0$  is the initial dye concentration in liquid phase,  $C_e$  is the liquid phase dye concentration at equilibrium,  $V$  is the volume of dye solution used, and  $m$  is the mass of adsorbent used.

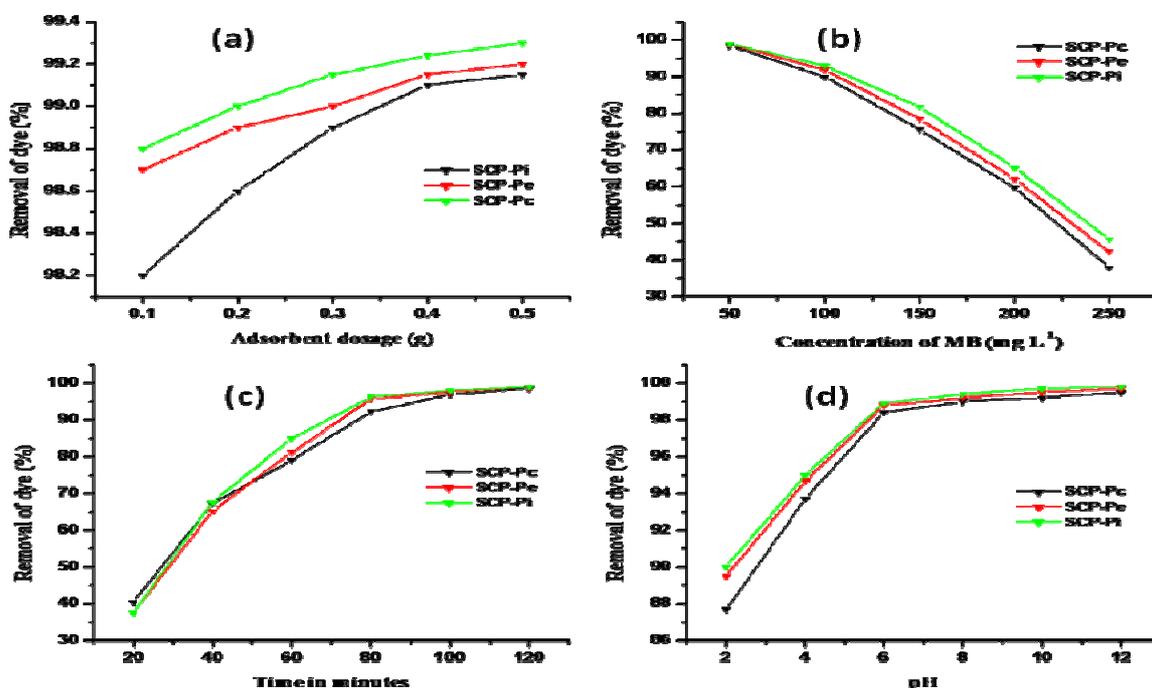


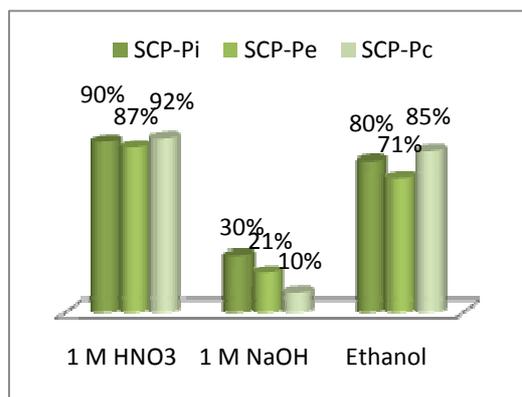
Fig: 7. (a) Effect of adsorbent dosage, (b) effect of initial dye concentration, (c) effect of contact time and (d) effect of pH on the removal methylene blue by SCP-Pc, SCP-Pe and SCP-Pi

After confirming the fact that SCP-P was 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 was purely chemical interactions, involving chemical binding of the substances. The increasing efficiency of exchanger towards dye

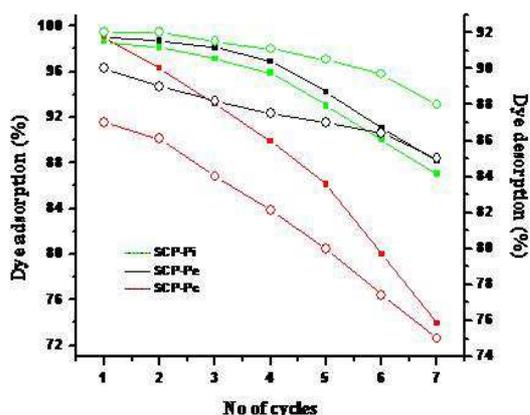
removal was due to both the cation exchange nature of the sorbent and cationic nature of the dye. SCP-P possessed structural hydroxyl groups. Therefore the dyes could bond to the sorbent either by hydrogen bonds or weak van der Waals forces. The chemical bonding can be elicited by subjecting the adhered material to desorption and regeneration process.<sup>18,20</sup> In this study, desorption experiments were conducted using NaOH (1.0 M),  $HNO_3$  (1.0 M), and ethanol to ascertain the

nature of binding of dye molecules onto the exchanger composite surface. Treatment with NaOH (1.0 M), ethanol and HNO<sub>3</sub> (1.0 M) showed the considerable recovery of the dyes (10% - SCP-Pc, 21% - SCP-Pe, 30% - SCP-i), (85% - SCP-Pc, 71% - SCP-Pe, 80% - SCP-Pi) and (92% - SCP-Pc, 87% - SCP-Pe, 90% - SCP-Pi) respectively (Fig. 8). Under acidic condition, the positively charged sites increased onto the exchanger surface, and it acted as a driving force for the elution of dye by electrostatic repulsion.

After five series of sorption- desorption cycle, the loss in the sorption capacity was only 7-25% (Fig. 9). Hence, the cation exchanger could be easily regenerated and reused for the practical purposes.



**Fig. 8.** Percentage of desorption of dye on SCP-Pc, SCP-Pe and SCP-Pi in 1.0 M HNO<sub>3</sub>, 1.0 M NaOH and Ethanol



**Fig. 9.** Percentage of dye adsorption and desorption on SCP-Pc, SCP-Pe and SCP-Pi with respect to no of cycles

## [V] CONCLUSION

Three different methods were chosen to prepare a novel polyaniline – tin cerium phosphate composite cation exchanger. The materials have high selectivity towards bismuth and lead metal ions. The adsorption efficacy of composite exchangers was carried out and compared the preparation strategy towards the adsorption. The in-situ prepared composite has the excessive up taking power for methylene blue from aqueous solution than the other two. It may be due to the nano size and needle type morphology of the material. Thus, this composite material can effectively used for the removal of metal ions (Pb(II) and Bi(III)) as well as methylene blue dye from waste water.

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