

ORIGINAL ARTICLE

Estimate the effect of Concentration of Polyaniline incorporation on tin cerium Tungstate towards the adsorptive efficiency for dye removal from aqueous solution

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ABSTRACT

Polyaniline was chemically incorporated into the matrix of tin cerium tungstate which was synthesized by coprecipitation method. The study showed its utility as ion exchange in the separation chemistry. The distribution coefficient studies showed its selectivity towards Pb(II) and Co(II) metal ions. UV-Visible absorption spectroscopy recorded the adsorption behavior of the solution after treatment with synthesized composite showing the adsorption capacity of methylene blue dye. The polyaniline mass was the most significant variable affecting the dye removal; the effect of polyaniline mass for the adsorptive efficiency of the composite material was studied. The effect of some important parameters such as pH, initial concentration of dye, contact time and dosage of composite on the removal efficiency was investigated in batch adsorption system. In order to find out the possibility of reuse, desorption study was also carried out in this investigation.

Keywords: Adsorption, Composite, Ion Exchanger, Organic Dye, Polyaniline

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INTRODUCTION

Interest of inorganic exchangers in the industrial applications is increasing day by day. Synthetic inorganic ion exchange sorbents have been used more extensively in the past two decades [1-3]. The inorganic ion exchangers have their own limitations. In order to overcome the limitations researchers tried to incorporate a polymer materials into the matrix of inorganic ion exchanger [4,5]. These materials have conjugate the mechanical properties of the organic polymers with the intrinsic properties of the inorganic compound creating a new class of hybrid organic-inorganic materials with improvement in mechanical properties, chemical inertness, high temperature and radiation stability, reproducibility and high selectivity for harmful ions. These materials are introduced in the field of environmental sciences as an adsorbent for hazardous materials from aqueous solution.

Water pollution due to toxic metals and organic compounds like dyes remains a serious environmental and public problem. Therefore, removal of metal ions and dyes from the wastewater has been an important environmental concern to minimize the water and soil pollution. Here in this paper we tried to incorporate polyaniline conducting polymer into the matrix of inorganic ion exchanger and studied the effect of polyaniline concentration towards the adsorptive dye removal efficiency of composite material.

MATERIALS AND METHODS

Stannic chloride (E.Merck), Ammonium ceric nitrate (E.Merck), Sodium tungstate (LobaChem) and aniline (E.Merck) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

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 analysis were used. UV-Visible Spectrophotometer model JASCO V660 was used for spectrophotometric measurements.

Ammonium ceric nitrate 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 mixtures of ammonium

ceric nitrate solution and stannic chloride solution with constant stirring in volume ratio Sn:Ce:W as 1:2:4. The yellow precipitates were obtained when the pH of the mixtures was adjusted to 1.0 by adding aqueous ammonia or hydrochloric acid with constant stirring. The excess reagents and 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⁺ form by treating with 1.0 M HNO₃ 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.

The different molar concentrations of aniline monomer were added to the yellow tin cerium tungstate solid. The cerium present in the crystal oxidised the aniline and polyaniline is formed into the matrixes of tin cerium tungstate. The supernatant liquid was decanted and solids 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⁺ form by treating with 1.0 M HNO₃ 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.

The ion exchange capacity of the material was determined by column method. The ion exchange capacity of the material was determined by column method. 1.0 g of the exchanger in H⁺ form was taken in a glass column of 1.1 cm diameter. The H⁺ 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 ion exchange capacity, IEC in meqg⁻¹ 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 [6].

The effect of temperature on ion exchange capacity was studied by heating several 1.0 g samples of the exchanger at different temperatures for 3 hrs in an air oven and Na⁺ ion exchange capacity in meqg⁻¹ was determined by the column method after cooling them to room temperature.

Topp and Pepper method [7] 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 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_d 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 [6].

Batch experiments were performed according to Mahanta et al [8]. Briefly, 0.2 g of the SnCeW-PANI composite was agitated with 50 mL of dye solutions individually at 28 °C in a rotary incubated shaker for 1 hr. The shaking speed was maintained at 180 rpm throughout the study. The dye solution was separated from the adsorbent by centrifugation at 6000 rpm. The dye concentration was analyzed by monitoring the absorbance of the dyes using UV-Visible Spectrophotometer (model JASCO V660). Experimental variables considered were (i) the effect of dosage of composite, (ii) initial dye concentration, (iii) effect of contact time and (iv) pH on the adsorption capacities.

The percentage of removal of dyes was calculated using the following formula:

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

The dye-loaded SnCeW-PANI composite, which were exposed to 50 mgL⁻¹ of dyes at 28 °C, was separated from the solution by centrifugation (6000 rpm) and washed several times with water. Later, composite was dried completely and used for desorption experiments. The dye-loaded composites (0.2 g) were then brought into contact with 1.0 M NaOH, 1.0 M HCl, 1.0 M HNO₃, ethanol (95%), and acetone (99%), separately. The mixture was agitated on a rotary shaker (180 rpm) at 26 °C for 1 hr. After desorption, the supernatant was centrifuged, with the remaining procedure being the same as for the sorption experiments.

RESULTS AND DISCUSSION

A number of samples of 'organic-inorganic' composite cation-exchanger tin cerium tungstate-polyaniline (SnCeW-PANI) were prepared by mixing of different molar ratio of aniline monomer into tin cerium tungstate (Table 1). The composite material formed as black solid material has the ion exchange capacity of 2.29 meqg⁻¹ selected for further study. It was also noticed that the Na⁺ ion-exchange capacity of the composite materials higher as compared to inorganic ion-exchanger tin cerium tungstate (1.43 meqg⁻¹).

Table 1: Synthesis and properties of various samples of exchanger.

Sample	Molar concentration of aniline	Polyaniline weight percentage	pH	Appearance	Ion Exchange Capacity for Na ⁺ (meqg ⁻¹)
SnCeW-PANI 1	0.025	5.0	1	Colourless	1.46
SnCeW-PANI 2	0.050	10.0	1	transparent	2.29
SnCeW-PANI 3	0.100	25.00	1	solid	1.85
SnCeW-PANI 4	0.150	30.00	1		1.15

In order to check the reproducibility of the prepared composite, it was 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 2.29 meqg⁻¹ and $\pm 0.03\%$, respectively.

Fig 1 shows the FTIR spectrum of SnCeW-PANI. In the spectrum of the material, a strong and broad band around 3380 cm⁻¹ is found which can be ascribed to -OH stretching frequency. A sharp peak around 1622 cm⁻¹ can be attributed to H-O-H bending band, which represents the strongly bonded -OH groups in the matrix. An assembly of two sharp peaks in the region 500-800 cm⁻¹ may be due to the presence of metal oxygen bond. Another assembly of two peaks in the region 1300-1400 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 [9]. This indicates that the tin cerium tungstate was modified with polyaniline.

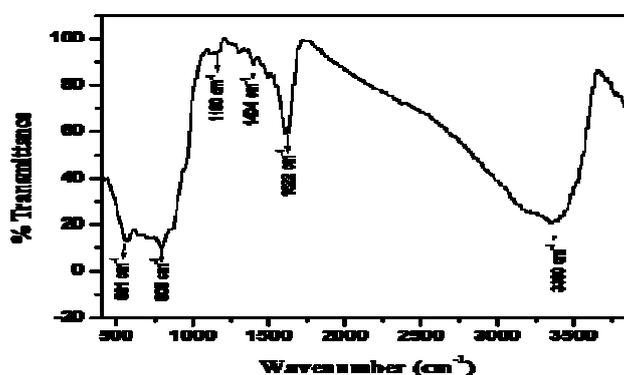


Fig. 1. FTIR of SnCeW-PANI

The TGA curve (Fig 2) of both samples (SnCeW and SnCeW-PANI) recorded continuous weight loss of mass up to 150 °C, which may be due to the removal of external water molecule [10]. In the case of composite material there was a weight loss at 250 °C it may be due to the partial decomposition of organic part. At around 500 °C weight was observed which is due to the complete degradation of organic part.

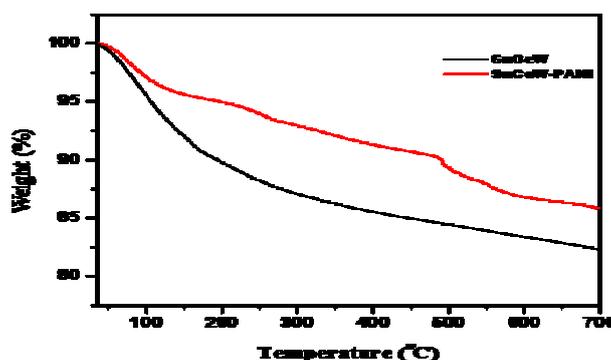


Fig. 2. TGA curves of SnCeW and SnCeW-PANI

X-ray diffractogram (Fig 3) showed no prominent peaks which suggested amorphous nature of the composite material.

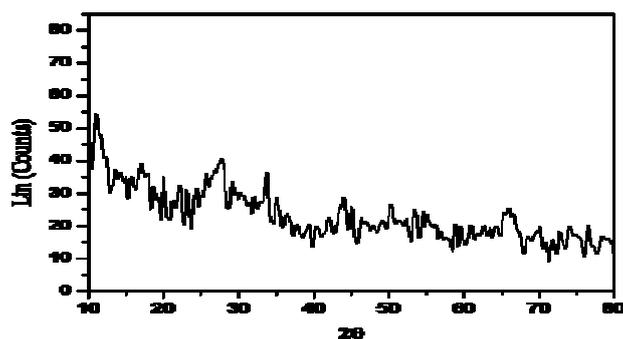


Fig. 3. XRD of SnCeW-PANI

The SEM images (Fig 4) showed that the surface morphology of composite material was not that much different from their individual inorganic components.

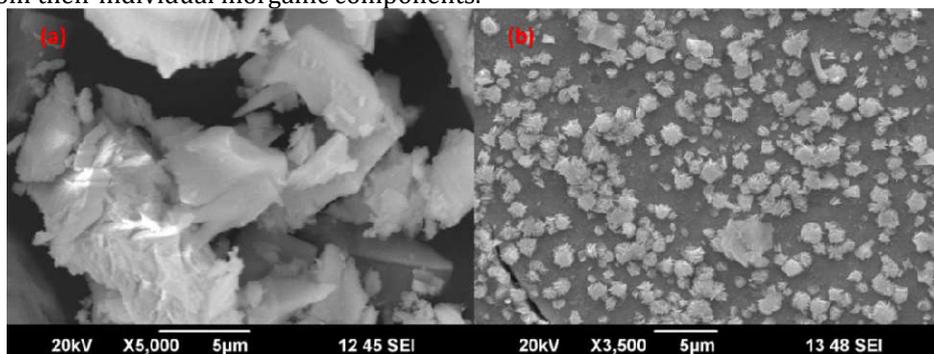


Fig. 4. (a) SEM image of SnCeW and (b) SEM image of SnCeW-PANI

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 material (Fig 5). It appears to be a strong cation exchanger as indicated by a low pH (~2.1) of the solution when no OH ions were added to the system. The exchange capacity obtained from the curve is in agreement with that obtained by the column method.

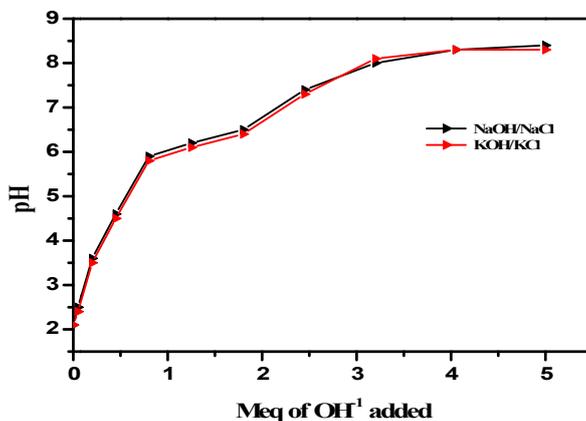


Fig. 5. pH titration curve of SnCeW-PANI

It was observed that on heating at different temperatures for 3 hrs, the mass, and ion-exchange capacity of the exchanger were changed as the temperature increased (Fig 6). The composite cation exchange material was found to possess good thermal stability as the sample maintained about 33% of the initial mass by heating up to 400 °C. However, in respect to ion exchange capacity, this material was found to possess better thermal stability as the sample maintained 56% of the ion-exchange capacity up to 200 °C and it retained 26% up to 500 °C where as tin cerium phosphate retained only 7% of ion exchange capacity up to 500 °C.

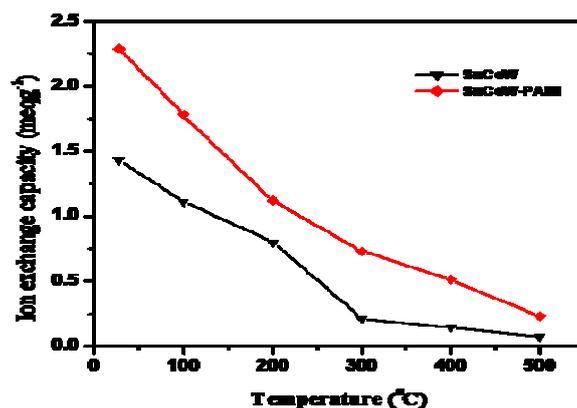


Fig. 6. Temperature effect on Ion exchange capacity of SnCeW and SnCeW-PANI

Table 2: K_d values of various metal ions in different electrolyte

Metal ion	DMW	0.001M HNO ₃	0.01M HNO ₃	0.1M HNO ₃	0.001M NH ₄ NO ₃	0.01M NH ₄ NO ₃	0.1M NH ₄ NO ₃
Pb(II)	800.00	756.00	500.00	266.00	788.00	501.00	356.00
Zn(II)	22.84	15.00	2.12	NS	15.00	1.20	NS
Mn(II)	24.00	11.90	2.32	NS	22.00	3.67	NS
Ni(II)	86.48	44.12	13.13	NS	45.00	14.21	NS
Hg(II)	16.16	2.19	NS	NS	10.00	NS	NS
Cd(II)	NS	NS	NS	NS	NS	NS	NS
Co(II)	201.00	64.12	34.00	19.01	70.12	59.00	29.12
Cu(II)	64.96	56.99	23.70	14.55	70.01	59.90	24.50
Bi(III)	134.12	177.12	134.22	100.00	182.34	123.90	99.90
Mg(II)	20.32	NS	NS	NS	NS	NS	NS

NA: no observable adsorption

In order to explore the potentiality of the new composite cation exchange material in the separation of metal ions, distribution studies for different metal ions were performed in different solvent systems shown in Table 2. The distribution studies of metal ions showed that the exchanger has very high affinity towards Pb(II) and Co(II) ions in comparison to other metal ions studied. The selectivity was found to be in the order Pb(II) > Co(II) > Bi(III) > Ni(II) > Cu(II) > Mn(II) > Zn(II) > Mg(II) > Hg(II). The effect of electrolyte concentrations on distribution coefficients showed that the value decreases with increase in electrolyte concentrations.

Methylene blue (MB) was selected for this study. We selected composite material with different concentration of polyaniline for the study of effect of polyaniline concentration on tin cerium tungstate towards the adsorption of MB. The study showed that the adsorptive capacity of composite material was decreased with increasing concentration of polyaniline. The sample 2 showed an efficient adsorptive efficacy for the removal of dye from aqueous solution (Fig 7). So for further study for different parameter effect on dye adsorption, sample 2 was chosen.

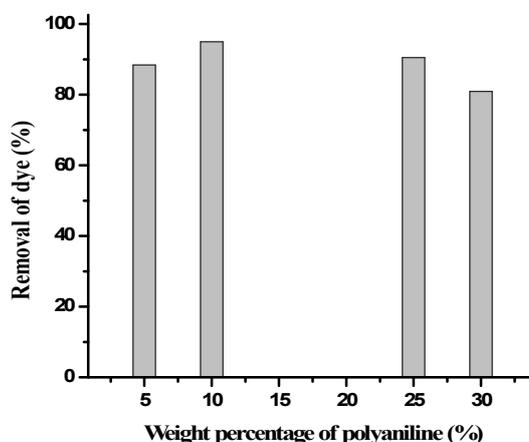


Fig. 7. Effect of polyaniline concentration on dye removal

Adsorbent dosage is an important factor which must be carefully optimized during wastewater treatment. The effect of adsorbent dosage (0.1–0.5 g) on 50 mgL⁻¹ concentration of MB dye solution was studied at

28 °C and neutral pH for 1 hr, and the results are presented in Fig 8(a). Initially, a rapid removal of dyes with the increasing adsorbent dosage was attributed to the availability of reactive sites [11]. A further increase in the composite dosage from 0.2 g to 0.5 g did not show much increase in the removal rate and adsorption equilibrium. Thus, further experiments were carried out using 0.2 g of the adsorbent, as it exhibits appreciable removal capacity for the optimization of adsorption parameters.

The adsorption of MB dye solution on composite at different initial concentrations (50–250 mgL⁻¹) was analyzed for 1 hr at 28° C and neutral pH. The removal rate of the MB was varied according to the initial concentration of dye (Fig 8(b)). At low concentration (50 mgL⁻¹), 95% of dye was adsorbed by the composite. 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 (250 mgL⁻¹) the removal rate was decreased (71%) because the dye molecules needed to diffuse to the adsorbent sites by intraparticle diffusion. In addition, steric repulsion between the solute molecules could slow down the adsorption process and there by decreases the removal rate. A similar trend was observed for the adsorption of methyl violet by agricultural waste [12].

MB solution (50 mL, 50 mgL⁻¹) was treated with 0.2 g of exchanger for different periods of time (10-60 min) at 28° C and neutral pH. The rapid removal was observed during the first 10 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 Fig 8(c) that the contact time needed to attain the equilibrium condition for MB was about 1 hr.

Several studies reported the significant role of pH in adsorption reaction. Crini et al. [13] 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 was mixed with 50 mL of dye solutions (50 mgL⁻¹) at different pH values (2–12) and kept for 1 hr shaking. The pH was measured before the addition of the composite. From Fig 8(d), it was observed that in basic pH composite adsorbs dye molecules, while in acidic pH the dye adsorption is comparatively low. The maximum adsorption of dyes (99%) was observed at pH 12 and minimum adsorption (78.8%) was observed at pH 2. Lower adsorption percentage of MB on composite at highly acidic conditions is probably due to the presence of high concentration of H⁺ ions on the surface of adsorbent competing with methylene blue (cationic dye) for adsorption sites in the adsorbent. With an increase in the solution pH, the electrostatic repulsion between the positively charged methylene blue and the surface of adsorbent is lowered. Consequently removal efficiency is increased.

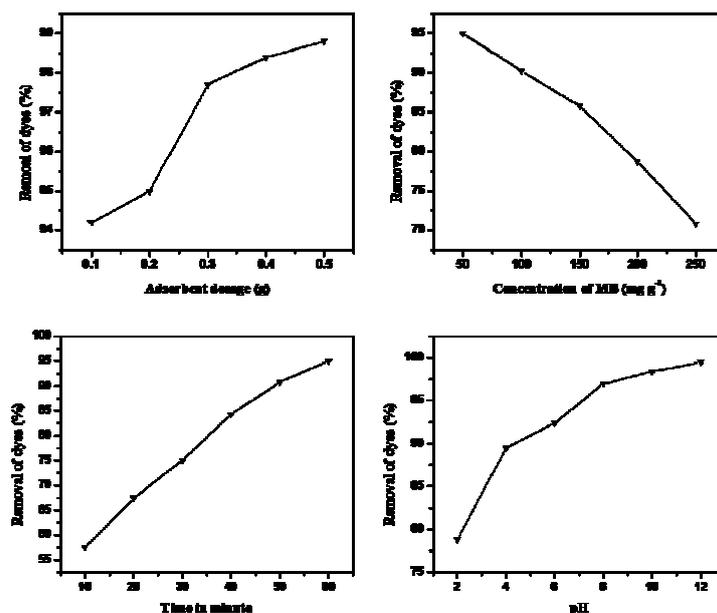


Fig. 8. (a) Effect of adsorbent dosage, (b) effect initial dye concentration, (c) effect of contact time and (d) effect of pH on the removal methylene blue by SnCeW-PANI

After confirming the fact that SnCeW-PANI is capable of adsorbing the dye molecules onto its surface, it becomes necessary to know the process by which the dye molecules remain adhered to the surface of the composite. The adherence of dye molecules onto the surface of the composite was purely chemical interactions, involving chemical binding of the substances. The chemical bonding can be elicited by subjecting the adhered material to desorption and regeneration process [14]. In this study, desorption experiments were conducted using 1.0 M NaOH, 1.0 M HCl, 1.0 M HNO₃, ethanol, and acetone to ascertain the nature of binding of dye molecules onto the composite surface. Treatment with HNO₃ (1.0 M) shows the considerable recovery of the dyes (84%). Under acidic condition, the positively charged sites increase onto the composite surface, and it acts as a driving force for the elution of dye by electrostatic repulsion. However, negligible recovery of dyes was observed after treatment with 1.0 M NaOH. In the series of five sorption and desorption cycle, the loss in the sorption capacity was less than 7%. Hence, composite can be easily regenerated and reused for the practical purposes.

CONCLUSION

A novel polyaniline composite ion exchange material was easily synthesized by chemical oxidation method directly into the matrix of tin cerium tungstate. The adsorption experiments indicated that adsorbent used in this paper was effective in removing methylene blue from aqueous solution. The study evinced that the polyaniline concentration effect on adsorptive efficacy of the composite material where the optimum level for polyaniline weight percentage is 10%. Advantages such as environmentally friendly material, low cost and its high regeneration percentage make it a suitable adsorbent for removal of metal ions and dyes such as MB from textile wastewaters or other industries dealing with metal ions, dyes and dyeing.

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