Poly-o-toluidine cerium(IV) arsenate nanocomposite ion exchanger: Synthesis, characterisation and applications

Aparna Mohan[1]*, C.Janardanan[2]

Post Graduate & Research Department of Chemistry, Sree Narayana College, Kannur, Kerala, India, 670007

E-mail: aparnakaryat@gmail.com

ABSTRACT

Nanocomposite ion exchanger was synthesised by using poly-o-toluidine as organic counterpart and cerium(IV) arsenate as inorganic counterpart. The ion exchange capacity of the material was found to be 1.7meqg^{-1}. Effect of temperature and resusability of the exchanger were studied. The material was characterised using various instrumental techniques like FT-IR, XRD, SEM and TG-DTA. Partition coefficient studies shows the material has high affinity towards Hg(II) ions. Binary separations and waste water treatment were successfully carried out using the exchanger. The exchanger is a promising material for heavy metal removal from water.

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KEYWORDS

Nanocomposite;
Mercury;
Ion exchange;
Waste water treatment;
Separation

INTRODUCTION

Pollution and contamination of water and water bodies has become a major universal issue. Water pollution management and development of more efficient methods and materials for water treatment is hence a necessity. Various successful methods have been developed for waste water treatment and processing[1-3]. One among the different methods available is the use of nanocomposite exchangers[4]. Composite materials are hybrid materials having both organic and inorganic counterparts[5]. Composite ion exchangers have added advantages than organic or inorganic ion exchangers since they show better mechanical and thermal stability, high selectivity and various environmental remediation methods. The applications of composite exchangers include water purification, sensors, catalysts, fuel cells, ion selective electrodes etc[6]. All these applications lead to the synthesis of a variety of composite materials having noticeable pertinence in the field of analytical chemistry.

Prominent water contaminating agents include organic and inorganic pollutants, sewage water, pharmaceutical effluents, detergents, heavy metals, pesticides etc. Heavy metal contamination is a leading cause of water pollution. Industrial effluents contain heavy metals like mercury, cadmium, nickel, cobalt, lead, aluminium, copper etc. Among these, mercury is a toxic heavy metal which has been reported as a priority pollutant by the US Environmental Protection Agency (EPA)[7]. Even trace amount of mercury can cause several health problems in living systems. Mercury poisoning may lead

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to respiratory failure, damage of gastrointestinal tract, nervous system, functioning of kidney and even death. Organic mercury, mainly methyl mercury (CH_3Mg), has the capacity for bioaccumulation and biomagnifications in aquatic food chain, especially in fishes[8]. Through the consumption of these fishes, the poisoning extends to humans. Hence removal of mercury from water using composite exchangers is an impressive application.

The present study comprises of the synthesis, characterisation and applications of Poly-o-toluidine cerium(IV) arsenate nanocomposite exchanger (POT CeAs). The material showed high selectivity for heavy metal ion mercury. The significance of the material was figured out by the removal of mercury and cadmium from industrial waste effluents and also by carrying out some binary separation.

EXPERIMENTAL

Materials

Ammonium ceric(IV) nitrate (E.Merck), Sodium arsenate (Loba Chemie, India), O-toluidine (Loba Chemie, India) and Ammonium peroxodisulfate (E.Merck) were used for the synthesis of the exchanger. All other reagents and chemicals used were of analytical grade.

Instrumentation

For IR studies, FT-IR spectrometer model Thermo Nicolet Avtar370 was used, X-ray diffraction studies were conducted by Bruker AXS D8 Advance with Cu Kα radiations, TG Perkin Elmer Diamond TG/DTA Analysis System was used for thermogravimetric/ derivative thermogravimetric analysis by using Nitrogen atmosphere at a rate of 10 p C and Jeol Model JSM - 6390LV was used for Scanning Electron Microscopic analysis. For stirring purposes, magnetic stirrer (Remi Equipments) was used, an electric shaking machine for shaking and a glass column of 1.1 cm diameter was used for column operations.

SYNTHESIS OF NANOCOMPOSITE EXCHANGER

Synthesis of Cerium(IV) arsenate

The inorganic counterpart Cerium(IV) arsenate was prepared by slow and constant addition of 0.05M sodium arsenate to the solution of 0.05M ceric ammonium nitrate at room temperature. The pH of the solution was maintained at 2. The yellow coloured gel formed was kept for 24hours in room temperature for digestion.

Synthesis of Poly-o-toluidine

The polymerisation of o-toluidine was carried out by chemical oxidative polymerisation using ammonium persulfate. Similar volume ratios of 0.4 M ammonium persulfate prepared in 4.0 M HCl was added to 10% o-toluidine prepared in 2.0 M HCl with continuous stirring by a magnetic stirrer for 2 hours at 0 p C. A green coloured gel thus obtained was kept for 24 hours at 0 p C[9].

Synthesis of Poly-o-toluidine cerium(IV) arsenate nanocomposite (POT CeAs)

The synthesis of the composite exchanger POT CeAs was carried out by simple stirring method. The dark green coloured polymer gels of poly-o-toluidine were added drop wise to the yellow coloured inorganic precipitate of cerium(IV) arsenate under constant stirring resulting in the formation of green coloured slurry. The slurry was kept for digestion in room temperature for 24hours. The gel was then filtered and excess acid was removed by washing with demineralised water (DMW). The material was then dried in an air oven at 30 p C. It was then converted to H^+ form by treatment with 1.0M HNO_3, intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed by washing with DMW and then dried at 30 p C and was kept in desiccator.

CHARACTERISATION OF COMPOSITE EXCHANGER

Ion-exchange capacity (IEC)

IEC is the milli-equivalents of hydrogen ions liberated by unit weight of the exchanger. The ion exchange capacity of the material was determined by column method. 1g of the exchanger in H^+ form was taken in a glass column of 1.1cm diameter. 100 mL

of 1 M sodium chloride solution was added to the column and the H^+ ions were eluted using it. The effluent collected was titrated against standard sodium hydroxide solution. The ion exchange capacity in $meqg^{-1}$ can be 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[10].

Effect of temperature on IEC and study of reusability

The effect of temperature on ion exchange capacity was studied by heating the material at different temperature for 3hours in an air oven and the ion exchange capacity was determined by column process after cooling them at room temperature.

The reusability of the material was studied by immersing the used ion exchange material in 1.0 M HNO_3 and keeping it overnight. The material was then dried and the ion exchange capacity was again calculated by the usual procedure.

Adsorption or Partition Coefficient studies K_d

The distribution coefficient (K_d), is the ratio of concentration of the metal ion in the exchanger to the solution with which it is in contact. K_d of various metal ions on POT CeAs was determined by batch method in various solvent systems. In this method, 0.1g of the exchanger was equilibrated with 20 mL of the metal ion solution for 24hours at room temperature. The metal ion concentrations before and after sorption were determined either spectrophotometrically or by 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[10].

BINARY SEPARATIONS

Quantitative separations of some important metal

ions were achieved on POT CeAs column. A glass column of internal diameter 0.5cm was packed with 1.0 g of exchanger in the H^+ form, with a porous plug at the bottom. The column was washed thoroughly with demineralised water in order to ensure that no air bubbles get stuck. The mixture of two metal ions, each with an initial concentration of 0.1 mol/L was loaded on to it. The flow rate was adjusted to 5-20 drops per minute, until the level was just above the surface of the exchanger. The process was repeated for maximum sorption of metal ions on to the material. The effluent was collected and was titrated against standard solution of di-sodium salt of EDTA.

WASTE WATER TREATMENT

The raw materials and fossil fuel used in cement industry causes significant emission of heavy metals like mercury, cadmium, lead etc. Hence waste water effluent from cement factory was collected. The sample was first filtered to remove any solid particles present and then neutralised. It was then treated with charcoal to decolourise the solution. The treated sample was analysed to detect the heavy metal ions present in it. To a column packed with granular POT CeAs exchanger, the sample was allowed to pass through. 100 mL of the sample was passed through the column with a flow rate maintained at 0.3-0.5 mL/min. The process was repeated thrice to ensure maximum sorption of metal ions. The ions present in the sample were eluted using suitable solvent and the amount was quantitatively determined by titrimetric method using standard EDTA solution.

RESULTS AND DISCUSSIONS

The nanocomposite exchanger POT CeAs was obtained as dark green coloured solid. The ICE of the inorganic counterpart cerium(IV) arsenate was 1.2 $meqg^{-1}$ and the nanocomposite POT CeAs showed an improved exchange capacity of 1.7 $meqg^{-1}$.

The study of effect of temperature reveals that the exchange capacity decreases with increase in temperature (TABLE 1). About 40% of the exchange

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TABLE 1 : Effect of temperature on IEC

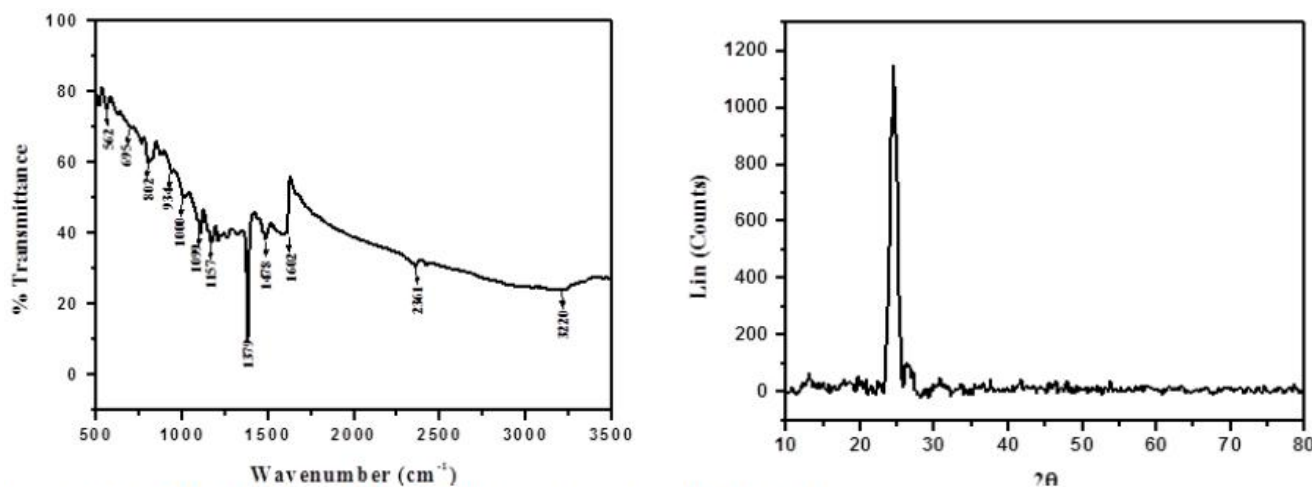| Temperature(^{o}C)	Duration (hrs)	Na$^+$-IEC (meqg^{-1})
50	3	1.7
100	3	1.53
200	3	1.39
300	3	1.22
400	3	1.09
500	3	1.02

Figure 1 : (a) FT-IR and (b) XRD images of POT CeAs

capacity was lost after heating the exchanger for 3 hours at elevated temperatures and the result obtained is in agreement with the TG-DTA analysis. The re-usability study shows that about 65% of the capacity was retained after reuse for 3 times.

The FTIR spectrum of POT CeAs (Figure 1(a)) shows a number of peaks. The peak at ~3220cm^{-1} can be attributed to the stretching frequency of N-H stretching of amine group, the peak at ~2361cm^{-1} can be due to the presence of alkyl group[11]. Multiple peaks between 1400-1600cm^{-1} is due to the presence of benzenoid and quinoid rings[12]. The presence of bands along the region 562-934cm^{-1} indicates metal oxygen bonding.

The X-ray diffraction study (Figure 1 (b)) shows a prominent intense peak at 2θ value 24.519 shows monocrystalline nature of the material. The particle size calculated by Debye Scherrer equation is 8.29nm.

The TG-DTA data of the sample is shown in Figure 2 (a). A 5% loss in weight upto 100°C is observed, which may be due to the evaporation of water molecules present in the material. Further weight loss of about 20% is observed due to the decomposition of organic part. On further heating of the material, gradual weight loss is observed and 60% weight of the material was retained even after heating to 800°C. The SEM images (Figure 2 (b)) exhibits granular morphology for the material. The granular porous feature of the material makes it a good scavenger of metal ions.

TABLE 2 gives the distribution study data of various metal ions on the nanocomposite exchanger in water and other electrolytes. The K$_d$ values varies with concentration and type of electrolyte. The selectivity was found to be in the order Hg(II)> Cd(II)> Mg(II)> Co(II)> Cu(II)> Ni(II)> Zn(II)> Th(IV)> Pb(II)> Bi(III)> Mn(II). It was found that the selectivity towards Hg(II) and Cd(II) ions were appreciably high in all electrolytes and the selectivity towards other metal ions were comparatively poor. The effect of electrolyte concentration on distribution studies shows that the value decreases with increase in electrolyte concentration.

Some important binary separations were carried out using the exchanger. TABLE 3 summarizes the
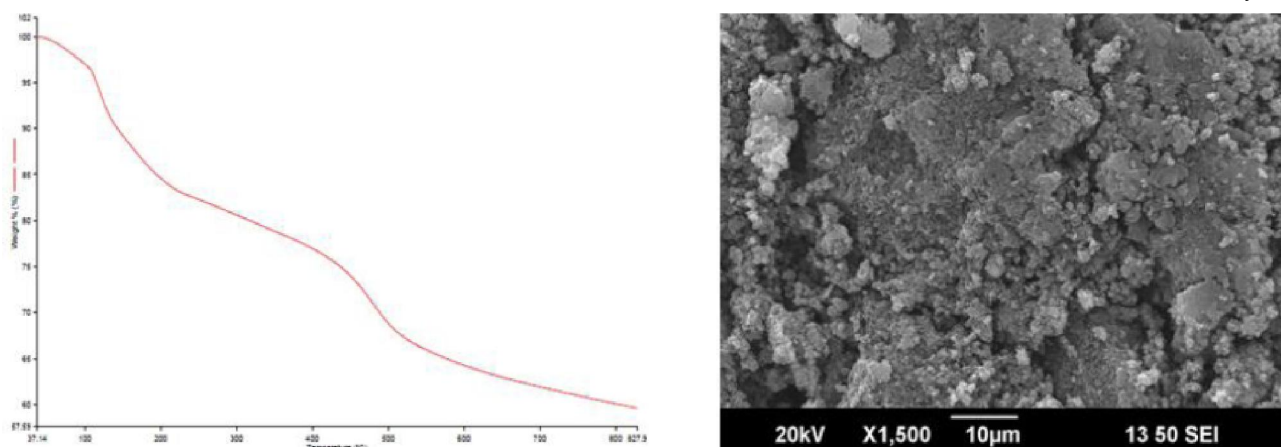
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Figure 2: (a) TGA and (b) SEM images of POT CeAs

TABLE 2: K_d values of various metal ions in different electrolytes

Metal ion	DMW	0.001M HNO₃	0.01M HNO₃	0.1M HNO₃	0.001M NH₄NO₃	0.01M NH₄NO₃	0.1M NH₄NO₃
Hg(II)	540	510.6	490	450.33	525.84	478.1	431
Cd(II)	160.42	152	136	122.04	148	129.8	110.6
Mg(II)	91.3	85.67	78	67.8	80.1	75.4	61
Co(II)	42	37.42	31.59	29.7	30.3	21	14.8
Cu(II)	40.02	30.3	27.46	21.8	27.6	22.02	17
Ni(II)	35.8	29.78	20.3	12.09	23.1	11.8	10.5
Zn(II)	20.34	18.56	11.6	9.42	12.3	7.5	3.6
Th(IV)	11.45	9.4	5.7	1.8	5.5	3.2	NS
Pb(II)	9.1	5.2	2.9	NS	3.5	NS	NS
Bi(III)	5.06	2.44	NS	NS	2.02	NS	NS
Mn(II)	4.02	1.3	NS	450.33	NS	NS	NS

NS: No observable sorption

TABLE 3 : Binary separation of metal ions on POT CeAs

Separations achieved	Separation factor	Eluent used	Metal ion	% Efficiency		Separations achieved
				Loaded	Eluted	
Pb(II)	59.34	0.01M NH₄NO₃	2.21	2.02		91.4
Hg(II)		0.5MHNO₃+0.1M NH₄NO₃	2.46	2.1		85.3
Zn(II)	26.53	0.01M NH₄NO₃	2.5	2.17		86.8
Hg(II)		0.5MHNO₃+0.1M NH₄NO₃	2.4	2.04		85
Th(IV)	47.16	0.01M NH₄NO₃	2.6	2.32		89.2
Hg(II)		0.5MHNO₃+0.1M NH₄NO₃	2.3	2		86.95

binary separations of some metal ions viz. Pb(II)-Hg(II), Zn(II)-Hg(II) and Th(IV)-Hg(II) using POT CeAs. On carrying out binary separation, as the material has high affinity towards Hg(II) ions, it remains firm on the exchanger and the other metal ion gets eluted easily using appropriate eluent.

The analysis of industrial effluents (TABLE 4) collected from cement factory confirmed the presence of heavy metals Hg(II) and Cd(II) ions. 100 mL of the samples were allowed to pass through the column containing POT CeAs and around 1.5g of Hg(II) ions and 1 g of Cd(II) ions were successfully sepa-

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TABLE 4: Waste water treatment on POT CeAs

Samples	Metal ions	Eluents	Amounts in mg/100mL
1	Hg(II)	0.5M HNO_3	1.63
	Cd(II)	0.5M HNO_3	1.1
2	Hg(II)	0.5M HNO_3	1.42
	Cd(II)	0.5M HNO_3	0.98
3	Hg(II)	0.5M HNO_3	1.5
	Cd(II)	0.5M HNO_3	0.86

rated out from the samples.

CONCLUSION

Nanocomposite exchanger poly-o-toluidine cerium(IV) arsenate synthesised showed a good ion exchange capacity of $1.7 meqg^{-1}$. The reusability, temperature effect and the distribution study on the exchanger were carried out. FTIR, XRD, TG-DTA and SEM characterisations of the composite were conducted. The material has monocrystalline nature and has high affinity towards Hg(II) ions. Some important binary separations were achieved on the column of the exchanger. The environmental utility of the material was analysed by separating out Hg(II) and Cd(II) ions from cement industry effluents. POT CeAs can thus be considered as an effective material of environmental remediation processes.

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