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CELLULOSE ACETATE-Sn(IV) MOLYBDOPHOSPHATE: A BIOPOLYMER SUPPORTED COMPOSITE EXCHANGER FOR THE REMOVAL OF SELECTED HEAVY METAL IONS

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ABSTRACT. Cellulose acetate-tin(IV) molybdophosphate (CATMP) composite exchanger was prepared by mixing biopolymer celluloseacetate with its inorganic counterpart tin(IV) molybdophosphate (TMP) using sol-gel method. The physical characterization of the as synthesized exchanger was carried out by FTIR, XRD, BET, TGA-DTG and SEM-EDX techniques. Chemical properties such as ion exchange capacity, chemical stability, pH and distribution behavior were carried out. The average IEC of the composite material, as determined by batch equilibrium, was found to be 2.43 meq/g for Na⁺ ion; higher than its inorganic counterpart, i.e. 1.41 meq/g. This exchanger was also found to be stable in water, acids and organic solvents, but unstable in basic medium. The distribution study (K_d) of the exchanger in different solvent systems showed promising separation potential of the exchanger towards metal ions of analytical interest from a given mixture of toxic heavy metal ions. The sorption studies revealed that the material was selective for Cr(III) and Cd(II) ions and moderately selective for Co(II) ion in solvents employed in this work. Its selectivity was examined by achieving some important binary separations of metal cations on its column indicating its promising application in environmental pollution abatement.

KEY WORDS: Cation exchanger, Biopolymer, Organic-inorganic hybrid, Sol-gel method, Binary distribution

INTRODUCTION

Clean water scarcity is a global challenge that has been intensified with growing economies, increasing population, agricultural expansion, urbanization, and climatic change [1]. This has contributed to the spread of water scarcity worldwide. Wastewater recycling is one of the feasible approaches to reduce this scarcity and increase the amount of clean water supply. Nonetheless, the treated volumes of wastewater may still contain trace amounts of several contaminants including heavy metals that are harmful to humans and the environment [2-4]. The detection and quantification of heavy metal ions are important in many applications including environmental monitoring, waste management and clinical toxicology [5].

Various techniques have been employed for removing heavy metals from wastewater including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption [6]. Each technique has its own limitations like, high capital and difficult operational methods and there are problems in disposing the residual metal slugs. Ion exchange is the most common and effective process, when compared with other processes, for removal of heavy metals from drinking water and wastewater even at very low concentrations. Ion exchange is also most successful technique in separation of ionic species from a complex mixture [7, 8].

Ion exchangers are classified as organic and inorganic ion exchangers. The main advantages of organic ion-exchange resins are their high capacity, wide applicability, wide versatility and low cost relative to some inorganic media and their limitations are having limited radiation and thermal stabilities [9]. Inorganic ion exchangers (IIEs) are the materials that have higher selectivity to treat the large amounts of nuclear waste around the world [10]. Inorganic ion

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exchangers have good properties such as chemical, thermal and radiation stability, resistance to oxidation, unique selectivity to certain ions than that of the well known and traditionally used organic resins [11, 12]. However, the inorganic ion exchangers also have their own limitations e.g. non-suitable for column operation because of non-granulometric nature and their high cost when compared with the organic ion exchange. Besides this disadvantage, the inorganic exchangers are also hydrolyzed with aqueous solvents [13, 14].

To overcome the limitations in both sides, hybrid/composite ion-exchangers have been introduced with conjugate mechanical properties of polymer with intrinsic properties of inorganic compound that have been extensively developed in the past decades. Composite materials are materials made up of two or more physically distinct components and exhibit properties that are entirely different from their original components [13, 14]. The organic polymer in composite material increases the mechanical strength and provides more exchangeable sites or greater number of active donor sites by increasing the surface area while the inorganic part provides selectivity toward some specific metal ions [15, 16]. Therefore, the development of organic-inorganic composite ion exchanger can lead to materials whose properties differ considerably from those of their individual isolated components that have interesting ability to detect hazard pollutants [17-20]. Investigation of composite ion exchange material is always of interest because of their applications in diverse fields such as adsorption [21, 22], ion selective electrode [23-26], antimicrobial activity [27], photocatalysis [28, 29], sensors [26], and removal of heavy metal ions from wastewater [30, 31].

Cellulose-based nanocomposites are materials of extraordinary interest due to their low cost, high-volume application, renewable nature, and possibility of recycling. Number of polymer nanocomposite material based on cellulose derivatives have been reported in the last few years [32]. It has been documented that the biopolymer-based materials were used efficiently and economically for wastewater treatment [21]. Several cellulose acetate based composite ion exchange materials have been synthesized in recent years such as, cellulose acetate-Zr(IV) molybdophosphate [33], cellulose acetate-tin(IV) phosphate [34], cellulose acetate-Sn(IV) molybdate [15], and cellulose acetate-Zr(IV) phosphate [35].

Recently, we reported a novel organic-inorganic composite exchanger, polyaniline tin(IV) molybdophosphate with demonstrated selectivity for Cu(II) and Pb(IV) ions from aqueous solution [36]. We have also synthesized a new inorganic exchanger, nano-titanium(IV) tungstomolybdate with promising separation potential towards metal ions such as Pb(IV), Cr(III) and a radionuclide UO_2^{2+} [37]. To the best of the researchers' knowledge, no work has been done on the composite exchanger considering cellulose acetate as a biopolymer support to the inorganic exchanger counterpart Sn(IV) molybdophosphate. The objective of this work was therefore to evaluate the ion exchange property of cellulose acetate-Sn(IV) molybdophosphate (CATMP) composite cation exchanger for the determination of selected heavy metals from artificially contaminated aqueous system. In this work, new organic-inorganic composite cation exchanger was prepared by sol-gel method by mixing cellulose acetate as biopolymer matrix and Sn(IV) molybdophosphate as inorganic counterpart. The as-obtained material was characterized by TGA-DTG, FTIR, XRD, BET and SEM-EDX. The ion exchange property of the material was studied through batch equilibration technique and the nanocomposite cation exchanger was also effectively used for the separations of Cr^{3+} and Cd^{2+} ions from the synthetic mixtures of other metal ions.

EXPERIMENTAL

Chemicals and reagents

The reagents employed during the synthesis of the composite exchanger were orthophosphoric acid (H_3PO_4), tin(IV) chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$); cellulose acetate all from BDH, England; sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), sodium chloride, potassium chloride and barium chloride

procured from Blulux, India; calcium chloride, magnesium chloride, phenolphthalein indicator, disodium salts of EDTA each obtained from BDH, England. HCl (35.4%), H₂SO₄ (98%), from Blulux, India; HNO₃ (69%), from Breckland Scientific Supplies, UK; Formic acid was purchased from Fisher Scientific Company, USA. Other chemicals used were DMF, NaOH, KOH, CaCO₃, ammonia solution (25%), ethanol, Eriochrome Black T (EBT), methanol, chloroform, petroleum ether. In addition to this, different salts of heavy metals such as Pb(II), Ni(II), Cu(II), Cd(II), Ag(I), Zn(II), Cr(III), Fe(III), and Co(II) were also used during laboratory work. All the reagents and chemicals were of analytical grade and used with no further purification.

Instruments

The instruments used in this study included the following: FT-IR spectrometer (Shimadzu 1730, Japan), pH meter (Mettler Toledo, MP 220, Switzerland); Powder X-ray diffractometer (XRD) using X'Pert Pro PANalytical; scanning electron microscope (SEM) using a Hitachi TM1000 with EDX detector. N₂ adsorption isotherms; thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer PerkinElmer TGA7.

Preparation of cellulose acetate-Sn(IV) molybdophosphate

The gel like solution of cellulose acetate was prepared by dissolving cellulose acetate in concentrated formic acid (4 wt %/volume) [33, 38].

Preparation of Sn(IV) molybdophosphate

Sn(IV) molybdophosphate was prepared by mixing equal volumes of Na₂MoO₄·2H₂O (0.1 M), H₃PO₄ (0.1 M) and SnCl₄·5H₂O (0.2 M) solutions gradually with continuous shaking of the mixture in varying mixing ratios [33, 36]. The mixture was stirred for 1 h to get a precipitate of Sn(IV) molybdophosphate. The pH variation was adjusted by adding 1 M nitric acid or 1 M ammonia solution to maintain the desired pH. At the end of the reaction, a yellow precipitate of Sn(IV) molybdophosphate was obtained.

Preparation of cellulose acetate-Sn(IV) molybdophosphate

Cellulose acetate-Sn(IV) molybdophosphate composite cation exchanger was prepared by the sol-gel mixing of the cellulose acetate (as anorganic polymer) with the above inorganic precipitate of Sn(IV) molybdophosphate with constant stirring for 1 h. The resultant mixture was kept for 24 h at room temperature for digestion. Then, the product cellulose acetate-Sn(IV) molybdophosphate based composite cation exchanger gel was obtained, washed thoroughly with DIW several times to remove excess acid and the gel was dried at 50 °C in an oven. It was then converted to its H⁺ form by keeping it in 1 M HNO₃ solution for 24 h with occasional shaking and intermittently replacing the supernatant liquid (was filtered off). Excess acid was removed after several washings with deionized water. The material was finally dried at 50 °C and sieved to obtain particles of a specific size range [33, 38]. The composite cellulose acetate Sn(IV) molybdophosphate cation exchanger was prepared in six proportions labeled S₁-S₆ by varying the synthetic parameters (Table 1). On the basis of Na⁺ ion exchange capacity (IEC), its yield and physical appearance, one of the composites was selected for further studies.

Ion exchange capacity (IEC)

IEC is defined as a measure of the hydrogen ion liberated by neutral salt that low through the composite cation exchanger [39]. IEC of the synthesized composite cation exchanger was deter-

mined by acid-base titration. EC of the cellulose acetate-Sn(IV) molybdophosphate (CATMP) material in H⁺ form was determined in such a way that 0.5 g of the exchanger, was soaked in 50 mL of 1 M NaCl solution for 12 h with continuous shaking at room temperature. Then the solution was filtered off and the exchanged ions in the solution were titrated against standard solution of 0.1 M NaOH solution using phenolphthalein as indicator to determine the total H⁺ ions released. The IEC was calculated using the equation:

$$\text{IEC (mg/g)} = \frac{C \times V}{W}$$

where IEC is the ion exchange capacity, C and V (mL) are concentration in molarity and volume of NaOH solution, respectively. W (g) is the amount of CATMP [20, 37, 40].

Thermal stability

The effect of temperature on the IEC of CATMP was determined in such a way that, 0.5 g samples of the composite ion-exchange material in the H⁺ form was heated at various temperatures from 50 °C to 700 °C in a muffle furnace for 1 h and the Na⁺ ion-exchange capacity was determined by batch process and IEC of the material was determined after cooling at room temperature [40].

Chemical stability

Chemical dissolution of cellulose acetate-Sn(IV) molybdophosphate composite cation-exchanger in H⁺ form was determined by treating each of 0.4 g portions of the composite separately with 50 mL of 0.1M in different reagent solutions such as: HNO₃, H₂SO₄, HCl; bases such as, NaOH, KOH; and organic solvents such as, ethanol, methanol, chloroform, petroleum ether and finally deionized water for 24 h with occasional shaking. After removal of excess reagent, the composite was dried in oven at 50 °C. The ion exchange capacity of the remaining material was determined by the batch method [40, 41].

pH-titration

The pH-titration of composite ion-exchanger (CATMP) was performed by Topp and Pepper method [49]. In this method, typically 500 mg portions of the ion-exchanger in the H⁺ form was placed in each of several 250 mL conical flasks, followed by the addition of equi-molar solutions of alkali metal chlorides and their hydroxides (NaCl-NaOH) in different volume ratios, the final volume being 50 mL to maintain the ionic strength constant. pH of the solutions were recorded every 24 h until equilibrium was attained. The pH of each solution was determined after equilibration and plotted against milliequivalents of OH ions added [13].

Distribution study and selectivity

The relative selectivity of ion exchange materials is determined by distribution studies in a suitable solvent. As a result, when the value of distribution coefficient (K_d) in a specific type of solvent concentration yields relatively larger value, then the ion exchanger is said to be highly selective towards that metal ions [37]. Therefore, the distribution coefficient (K_d) values of various metal ions on the composite ion exchanger were determined by the batch method in various solvent systems of analytical interest. A portion (0.2 g) of the exchanger in H⁺ form was placed into a 100 mL conical flask containing 20 mL solution of different metal ions concentration. The mixture was kept for 24 h with continuous shaking in a temperature controlled incubator shaker at room temperature to attain equilibrium. The amount of metal ion

left in the solution was determined by EDTA titration. Distribution coefficient values were calculated using the following relationship.

$$K_d = \frac{\text{metal ions (mequiv.)}/\text{ion-exchanger (g)}}{\text{metal ions (mequiv.)}/\text{solution (mL)}}$$

$$K_d = \frac{I-F}{F} \times \frac{V}{M}$$

where I is the initial amount of the metal ion in the solution phase and F is the final amount of the metal ion in the solution phase, V is the volume of the solution (mL) and M is the amount of cation-exchanger (g) [42].

Quantitative separation of metal ions in binary mixture

Quantitative binary separations of some metal ions of analytical interest were achieved on cellulose acetate-Sn(IV) molybdophosphate exchanger. A portion of the exchanger (1.0 g) in H⁺ form was packed in a glass column (internal diameter = 1.0 cm) with a glass wool support at the end. The column was washed thoroughly with deionized water. Then binary mixture of two metal ions was poured onto the top of the column till the solution level was just above the surface of the material. The columns were then rinsed 2-3 times with DIW. The effluents from each column were recycled three times to ensure complete adsorption of the metal ions. An individual metal ion was eluted using appropriate eluting reagents. The flow rates of the eluents were maintained a flow rate of 0.20 mL min⁻¹ or about 3 drop per min. The effluent was collected and titrated against the standard solution of 0.01M disodium salt of EDTA [37, 38].

Physical characterization of the composite exchanger

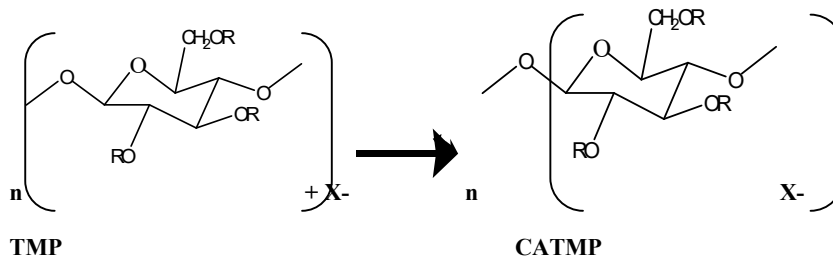
FTIR study of cellulose acetate-Sn(IV) molybdophosphate sample was performed by the KBr disc method. Accordingly, 10 mg of the exchanger in H⁺ form was thoroughly mixed with 100 mg of KBr to a fine powder. Then the IR absorption spectra of the sample were recorded in the range of 400-4000 cm⁻¹ region. X-ray diffractometer (XRD) was used for the characterization of the synthesized powder. For X-ray diffraction analysis, nickel filtered CuK α radiation wavelength (0.1542 nm) at 298 K was used. The instrument is equipped with a graphite monochromator and operating at 40 kV and 30 mA. Scanning electron microphotographs of CATMP was recorded at different magnifications using scanning electron microscope hyphenated with energy dispersive X-ray (SEM-EDX). Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (Perkin Elmer, TGA7). The samples to be analyzed were heated at a rate of 20 °C min⁻¹ to a maximum temperature of 700 °C in a flowing atmosphere of oxygen. The surface area of the as synthesized composite cation exchanger was determined by Brunauer–Emmett–Teller (BET) analysis. N₂ sorption properties were measured at -196 °C (77 K) in a Micromeritics instrument ASAP 2420 device. Typically, before measurements of any isotherms, approximately 100 mg of each sample were prepared and out gassed at 150 °C under vacuum for 16 h.

RESULTS AND DISCUSSION

Synthesis of cellulose acetate-Sn(IV) molybdophosphate

Cellulose acetate-Sn(IV) molybdophosphate cation exchanger was prepared by sol-gel method from the organic part cellulose acetate and inorganic part tin(IV) molybdophosphate. The physical appearance of the material resembles more the inorganic part Sn(IV)

molybdophosphate which is yellow powder. The binding of cellulose acetate into the matrix of Sn(IV) molybdophosphate (assumed as X in the reaction) can be given as shown in scheme below:



Scheme 1. Proposed binding for the synthesis of cellulose acetate-Sn(IV) molybdophosphate nanocomposite.

The samples of cellulose acetate-Sn(IV) molybdophosphate were synthesized under varying conditions such as mixing ratios keeping pH and temperature constant. In our case, we maintained ambient temperature; and pH close to unity based on literature evidence [33, 38, 43]. Accordingly, we synthesized six samples (S₁-S₆) by varying mixing ratios (molar ratio of the reactants) (Table 1). From these samples, the sample prepared with 1:1:2:2 (CA: (SnCl₄: Na₂MoO₄: H₃PO₄)) ratios at pH 1 was found to be the sample with high yield and good ion exchange capacity. The ion exchange capacity was noted to increase with increase in anionic phosphate group (concentration of orthophosphoric acid) and sodium molybdate. Based on its high percentage yield, IEC, and chemical stability, sample S₆ was selected for subsequent studies. This sample showed good ion exchange capacity as evident from the fact that the material obtained from various batches did not show any appreciable deviation in its percentage of yield and ion exchange capacities. This composite cation exchange material possessed a better Na⁺ ion-exchange capacity of 2.43 meq/g compared to its inorganic counterpart, Sn(IV) molybdophosphate, the IEC of which is found to be 1.41 meq/g. The improvement in ion exchange property of this organic-inorganic composite cation exchanger may be due to the binding of organic polymer (cellulose acetate) with inorganic moiety of Sn(IV) molybdophosphate.

Table 1. Synthesis condition and ion exchange capacity of different sample of the composite cation exchanger (S₁-S₆).

S. No.	CA	SnCl ₄	H ₃ PO ₄	NaMoO ₄ .H ₂ O	Mixing ratio (v/v)	pH	Appearance after dried	Yield (g)	IEC meq/g
S-1	1	1	1	1	1/1:1:1	1	Yellow	4.58	1.28
S-2	2	1	1	1	2/1:1:1	1	Light yellow	4.96	1.47
S-3	1	2	1	1	1/2:1:1	1	Yellow	5.48	1.68
S-4	1	1	2	1	1/1:2:1	1	Yellow	5.62	1.92
S-5	1	1	1	2	1/1:1:2	1	Yellow	5.76	1.76
S-6	1	1	2	2	1/1:2:2	1	Yellow	6.87	2.43

CA, cellulose acetate; IEC, ion exchange capacity.

Physical characterization techniques

FTIR spectra of the organic polymer (cellulose acetate), inorganic moiety (Sn(IV) molybdophosphate) and composite cation exchanger (cellulose acetate Sn(IV) molybdophosphate) are

shown in Figure 1a-c. The composite cation exchanger (Figure 1c) indicates the presence of external water molecules in addition to the metal-oxygen and OH groups. The broad band around 3420 cm^{-1} indicates the presence of OH functional group in the exchanger. A sharp peak at 1627 cm^{-1} corresponds to the deformation vibration of free water molecules (water of crystallization) and strongly bonded OH group in the matrix [33]. A broad peak at 1063 cm^{-1} may be due to the presence of PO_4^{3-} , HPO_4^{2-} and H_2PO_4^- [18, 33, 36, 43]. A band at 1384 cm^{-1} can be assigned to stretching vibration of carbonyl group of cellulose acetate [33]. The peak $\sim 964\text{ cm}^{-1}$ may be usually assigned to an out of plane bending vibration of C-H bond of cellulose acetate [44].

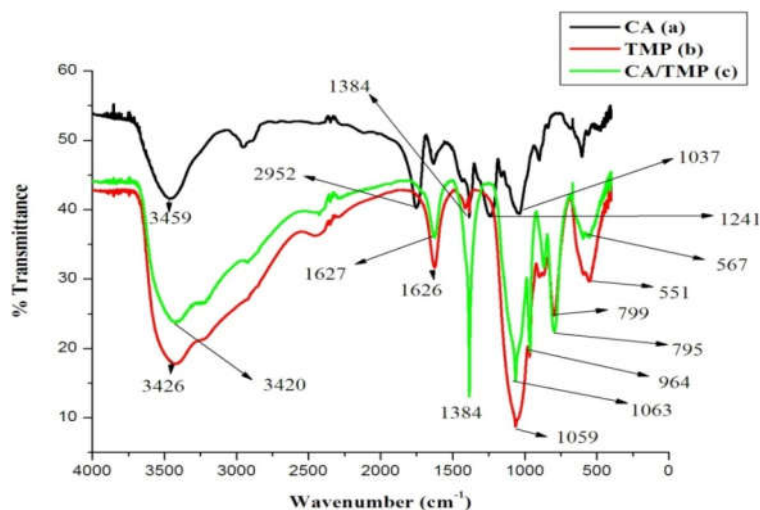


Figure 1. FTIR spectra of cellulose acetate (CA (a)), tin(IV) molybdophosphate (TMP (b)), and composite, (CA/TMP (c)).

A sharp peak $\sim 795\text{ cm}^{-1}$ is due to the presence of molybdate group [4, 33, 36, 44] and an assembly of two sharp peaks in the region $500\text{--}570\text{ cm}^{-1}$ is due to Sn-O bond vibrations [36]. The region of $1100\text{--}400\text{ cm}^{-1}$ could be connected to the superposition of metal-oxygen stretching vibrations which show the binding of inorganic precipitate with organic polymer and formation of 'organic-inorganic' hybrid cellulose acetate Sn(IV) molybdophosphate [33]. Generally the change in peak intensities and position clearly indicated the binding of organic polymer with inorganic counterpart.

The XRD patterns of cellulose acetate (CA), Sn(IV) molybdophosphate (TMP) and the composite cation exchanger (CATMP) are shown in Figure 2. The X-ray diffraction of the composite cation exchanger (Figure 2c) shows sharp, intense and symmetry peaks that indicated a well ordered crystal structure of the composite.

The XRD peaks for the CATMP are similar to the characteristic peaks of the Keggin structure as evidenced at $2\theta = 10.7, 26.7$ and 30.8° . The composite showed better crystallinity compared with the inorganic counterpart revealing the formation of well dispersed crystals in the polymer matrix. The as-synthesized materials is different from the earlier synthesized hybrid ion exchange material such as cellulose acetate Zr(IV) molybdophosphate [33], cellulose acetate tin (IV) phosphate [34], cellulose acetate tin(IV) molybdate [15] and cellulose acetate Zr(IV) phosphate [35] which showed amorphous or semi-crystalline nature.

The average particle size of the nanocomposite was estimated by using Scherrer formula:

$$D(\text{nm}) = \frac{K\lambda}{\beta \cos \theta}$$

where D is the average size of the crystallite, assuming that the grains are spherical, K is 0.9, λ is the wavelength of X ray radiation, β is the peak full width at half maximum (FWHM) and θ is the angle of diffraction. Accordingly, the crystal size of the cellulose acetate-Sn(IV) molybdophosphate nanocomposite is found to be around 16 nm where as the crystal size of the inorganic part is found to be close to 50 nm.

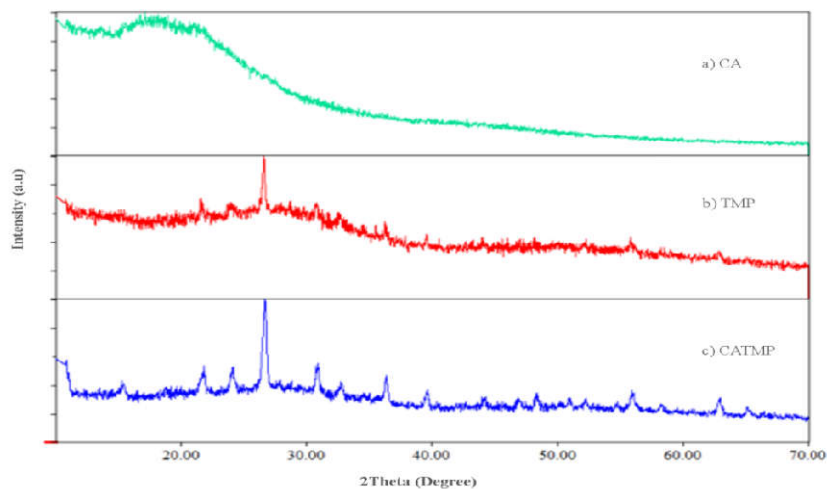


Figure 2. XRD patterns of cellulose acetate (CA), inorganic (TMP) and composite (CATMP).

SEM-EDX study was performed to examine the morphology of the as-prepared materials. The micrograph on Figure 3a exhibited fibrous like compact structure packed in a layer form for cellulose acetate. The inorganic Sn(IV) molybdophosphate and the composite, cellulose acetate Sn(IV) molybdophosphate, exchangers showed no distinct morphologies (Figure 3b and c). The difference in the surface morphology after incorporation of the organic polymer into the inorganic precipitate indicates the binding of the inorganic ion exchange material into the organic polymer, thus the formation of a composite material. The EDX spectra confirm the presence of Mo, Sn and P both in the inorganic and composite forms of the exchangers. The average amounts of elements found in the composite material were 34% (Mo), 57% (Sn) and 9% (P).

The stability and structural integrity of inorganic (TMP) and the composite (CATMP) exchangers were further studied by TGA (Figure 4). The inorganic exchanger (TMP) showed a total weight loss of approximately 20% up to 700 °C. The TGA analysis of TMP shows stepwise weight loss prior to the complete conversion of the material to the corresponding metal oxides. The sharp weight loss of approximately 15% in the temperature range 25-200 °C is due to removal of internal and external water molecules. Slight weight loss in the temperature range of 200-530 °C corresponds to the conversion of phosphate to pyrophosphate. The weight loss above 530 °C appeared constant which might be due to the complete conversion of the material to the corresponding metal oxides [36]. CATMP composite cation-exchanger showed a total weight loss of approximately 30% up to 700 °C. The sharp weight loss of approximately from 25-170 °C could be attributed to the removal of external and internal water molecules that is caused by condensation of -OH groups. The curve shows a stability plateau in the range of 170-258 °C in which the plateau is the region of the TGA where the weight is constant, this gives the

thermal stability information of the sample under given conditions. Such a temperature range reveals the high thermal stability of CATMP composite cation exchanger. The sharp weight loss in the temperature range of 258 to 300 °C corresponds to the conversion of inorganic phosphate to pyrophosphate. Further sharp loss between 300 to 456 °C might be due to decomposition of the organic material [45]. There was no further weight loss above 456 °C which might be due to the complete conversion of the material to the corresponding metal oxides.

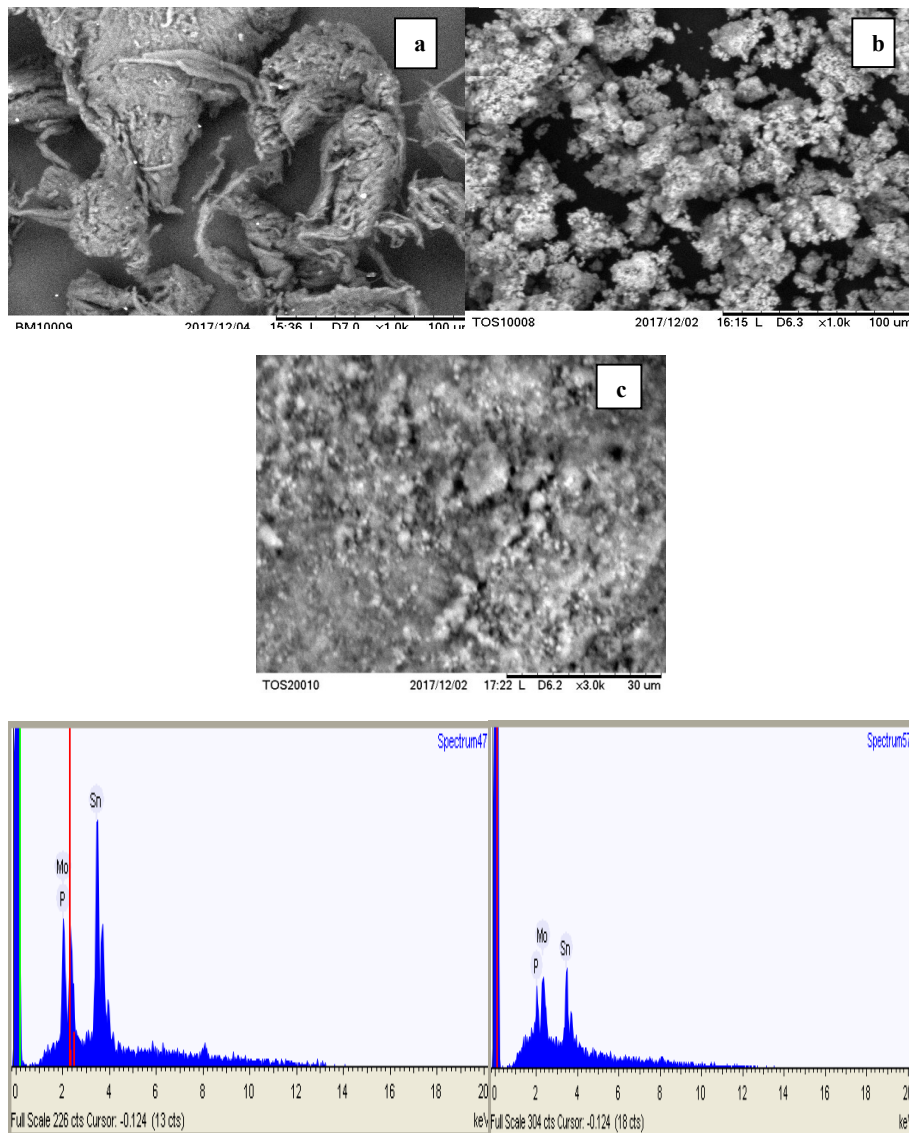


Figure 3. SEM-EDX images of CA (a), inorganic TMP (b) and CA/TMP composite cation exchanger (c).

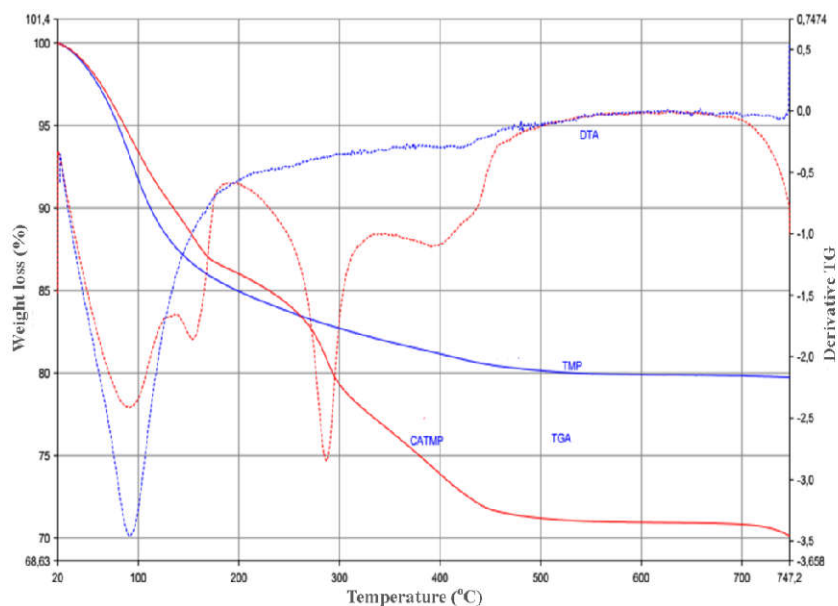


Figure 4. TGA/DTG curve of cellulose acetate-tin(IV) molybdophosphate (CATMP).

The average specific surface area of CA, TMP and CATMP were found to be $3.2816 \pm 0.0157 \text{ m}^2/\text{g}$, $119.6420 \pm 0.6797 \text{ m}^2/\text{g}$, $146.4150 \pm 1.0676 \text{ m}^2/\text{g}$, respectively. The specific surface area of cellulose acetate we obtained is similar with many of the literature results reviewed by Suhas *et al.* [50]. The as-synthesized exchanger showed relatively high specific surface area as evidenced by the XRD result i.e. small particle size results large surface area. Both the inorganic, tin(IV) molybdophosphate and composite, cellulose-acetate tin(IV) molybdophosphate exchangers, showed relatively high specific surface area when compared with the value reported by Bezabih *et al.* [37] for titanium(IV) tungstomolybdate ($1.46 \text{ m}^2/\text{g}$). The morphological change exhibited by CA in the composite formation could be the cause for the enhanced specific surface area of the composite exchanger as witnessed in the SEM micrograph of the same in Figures 3a and c.

Ion exchange capacity

The exchange capacity for Na^+ is a general parameter used as a measure for the ion exchange capacity of cation exchange materials [46]. The CATMP nanocomposite cation-exchange material possessed better IEC for Na^+ (2.43 meq/g) as compared to the inorganic counterpart TMP (1.41 meq/g), measured under similar conditions. The improvement in its ion exchange capacity may be due to the organic polymer in the composite material (cellulose acetate) which increases the mechanical strength and provides more exchangeable sites or greater number of active donor sites by increasing the surface area [15]. The sodium ion exchange capacities of composite exchangers from literature and the present work are depicted on Table 2. Cellulose acetate-Sn(IV) molybdophosphate (S_6), was found to have higher IEC compared to other composite cation exchangers (Table 2), except the one reported by Khan *et al.* [44].

Table 2. Sodium ion (Na⁺) exchange capacity in milliequivalent per gram of different composite cation exchanger materials.

No	Ion exchange material	Na ⁺ IEC (meq/g)	References
1	Cellulose acetate-Zr(IV) molybdophosphate	1.96	[33]
2	Cellulose acetate-tin (IV) phosphate	1.51	[34]
3	Cellulose acetate-tin (IV) molybdate	1.56	[15]
4	Cellulose acetate Zr(IV) phosphate	1.40	[35]
5	Poly-o-toluidine-thorium (IV) molybdophosphate	1.22	[4]
6	Polyaniline tin (IV) molybdophosphate	1.79	[36]
8	Polyaniline titanium (IV) molybdophosphate	2.46	[44]
9	Cellulose acetate-Sn(IV) molybdophosphate	2.43	Present work

Ion exchange capacity of CATMP for alkali and alkaline earth metal ions

The affinity sequence for alkali metal ions is found to be in the order $K^+ > Na^+$ and for alkaline earth metal ions in the order $Ba^{2+} > Ca^{2+} > Mg^{2+}$ (data not shown). This sequence is in accordance with the hydrated ionic radii [43]. The attraction between anions and cations in ionic crystals obeys coulomb's law, which demands that for cations of equal charge a small ion be attracted with a greater force and held more tightly than a large ion [36]. The extent of ionic hydration and the hydrated ionic size are inversely proportional to the atomic radius of the metal ion. IEC increases with the decrease in hydrated ionic radii down the group; thus, ions with smaller hydrated radii easily enter the pores of the exchanger resulting in higher degree of adsorption [22].

Effect of temperature (thermal stability)

To apply the exchanger materials for practical industrial waste water treatment, the exchanger needs to be stable thermally since industrial effluents are hot in nature. Therefore, thermal stability that is studied under certain temperatures is an important parameter for any ion exchanger materials. Based on this principle, cellulose acetate-Sn(IV) molybdophosphate sample was heated at a temperature from 50 °C to 700 °C for 1 h and Na⁺ ion exchange capacity was determined after cooling them at room temperature. The color of this sample was changed from yellow to different colors at each temperature; the loss of mass increases and the IEC decreases (data not shown). However, the exchanger exhibited considerable thermal resistance/stability up to 500 °C. It has been revealed that CATMP ion exchanger was thermally stable and retained about 46% of its total ion exchange capacity up to 500 °C.

Chemical stability

Chemical stability of synthetic ion-exchange materials plays an important role in their analytical applications. Exchangers, who have a high solubility in water, as well as in acidic media, may not be very useful for separation studies. It is, therefore, advisable to have a rough guide of the solubility of an ion exchanger [26]. The solubility experiments of this exchanger showed that the material has reasonably good chemical stability. The results indicated that the material is stable in dilute mineral acids and organic solvents and fairly moderate stability in water (Table 3). However, it showed weak stability in strong base, like NaOH, KOH. In the basic medium, the material shows very high weight loss and extreme decrease in its IEC which shows high dissolution in basic medium. This may be related to the hydrolysis of exchanger or the high solubility of exchanger at higher pH. Therefore, the solubility experiment shows the exchanger exhibits considerable resistance to most of chemicals it is treated with.

Table 3. The chemical dissolution of CATMP under different 0.1 M solution.

Solvent	Wt. before treatment (g)	Wt. After treatment	% retention in wt.	CBT	CAT	IEC (meq/g)	% retention in IEC
H ₂ SO ₄	0.4	0.34	85	Yellow	Yellow	2.20	90.5
HNO ₃	0.4	0.33	82.5	Yellow	Yellow	1.67	68.7
HCl	0.4	0.29	72.5	Yellow	Yellow	1.82	74.9
NaOH	0.4	0.12	30	Yellow	White	0.31	12.8
KOH	0.4	0.05	12.5	Yellow	White	0.06	2.5
Ethanol	0.4	0.32	80	Yellow	Yellow	1.62	66.7
Methanol	0.4	0.36	90	Yellow	Light green	1.05	43
Chloroform	0.4	0.33	82.5	Yellow	Yellow	1.12	46
Petroleum ether	0.4	0.39	97.5	Yellow	Yellow	1.27	52
DIW	0.4	0.35	87.5	Yellow	Yellow	0.78	32

Wt; weight, CBT; color before treatment, CAT; color after treatment, IEC; ion exchange capacity.

pH titration curve

The effect of pH was studied under equilibrium condition of equimolar solutions of alkali metal chlorides and their hydroxides. pH titration curve (Figure 5) was obtained under equilibrium conditions for 0.1 M NaCl-NaOH system. As shown in the figure, the exchanger, cellulose acetate-Sn(IV) molybdophosphate, appears to be strong cation exchanger as indicated by low pH (~2.06) of the solution when no OH ion was added.

As the volume of NaOH added to the system is increased, more OH ions are consumed suggesting in the increase of the rate of ion exchange in basic medium due to the removal of H⁺ ions from the external solution. From pH titration curve, the points at pH 4 and 7 are two inflections points that show the cellulose acetate-Sn(IV) molybdophosphate behaves as bifunctional ion exchange materials. Thus, it exhibits two plateaus corresponding to the replacement of two hydrogen ions per mole of cellulose acetate-Sn(IV) molybdophosphate.

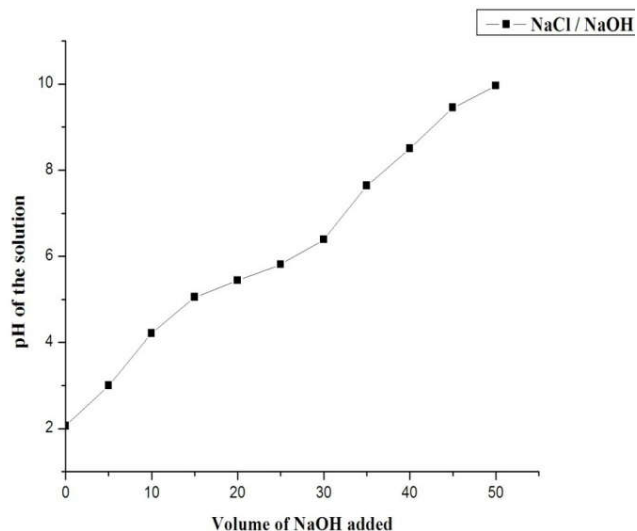
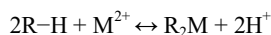


Figure 5. pH titration curve under equilibrium conditions for 0.1 M NaCl-NaOH.

Distribution studies

Whenever an ion is removed out of an aqueous solution and is replaced by another ionic species, it is generally referred to as “ion exchange”. The distribution behavior of metal ions plays an important role in the determination of selectivity of the material. The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase [30]. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution coefficients of the counter ions. The distribution coefficient, K_d , is the measure of the affinity of the cation exchanger towards different metal ions. Hence, the ion-exchange properties of the cation exchanger were studied by measuring the distribution coefficients (K_d) of nine metal ions using batch experiments in different solvent system (Table 4). In addition to the nature of the ion exchanger, various factors such as swelling, formation of complexes, nature of the chemical bond, composition and nature of the solvent, pH, etc. may be responsible for the wide variation in the distribution coefficient values [47, 48]. The K_d values vary with the composition and nature of the solvent system. The exchange of ions between ion exchanger materials and contacting metal ions may be represented by the following reaction:



The distribution coefficient (K_d values) of various metal ions on CATMP (S_6) was determined by batch method in various solvent systems. Some solvents favor the release of the hydrogen ions from the exchanger and enhance sorption of metal ions on it. However, on mixing these solvents, the K_d value for most of the metal ions showed a significant decrease. This may probably be due to an increase in polarity of the mixed systems. The increase in polarity of the solvent increases the interaction between metal ion and solvent due to ion-dipole interaction as a result exchange of metal ion between solvent phase and exchanger phase will be less [36, 37]. Further, the K_d values in strong electrolyte media are lower as compared to weak electrolyte media as well as aqueous medium. This may be attributed to high competition among ions for exchange in strong electrolyte media. It is apparent from the distribution coefficients given in Table 4 that the exchanger has differential selectivity for metal ions, possibly because of the formation of metal complexes with different stability constants.

Table 4. K_d values of some metal ions on cellulose acetate-Sn(IV) molybdophosphate composite cation-exchanger loaded in column in different solvent system.

Metal ions	Solvents				
	DIW	0.1 M DMF	0.1 M FA	0.1 M H ₂ SO ₄	0.1 M DMF+H ₂ SO ₄
Ag ⁺	395.02 ^{dc*}	848.3 ^{bd*}	1309.8 ^{ad*}	725.03 ^{cl*}	25.20 ^{eg*}
Cd ²⁺	1601.70 ^{ccb*}	2300.4 ^{baa*}	2500.2 ^{ab*}	1400.85 ^{cc*}	1450 ^{ca*}
Zn ²⁺	151 ^{ch*}	35.3 ^{di*}	661.8 ^{bg*}	800.70 ^{ac*}	10.24 ^{ci*}
Pb ²⁺	291.70 ^{dg*}	285 ^{ci*}	945 ^{bc*}	1300 ^{ad*}	500 ^{cd*}
Co ²⁺	1190 ^{dc*}	1435 ^{bc*}	651 ^{eg*}	1551 ^{ab*}	1376 ^{cb*}
Cu ²⁺	725 ^{ad*}	325 ^{dc*}	461 ^{ch*}	696 ^{bg*}	100.8 ^{ci*}
Cr ³⁺	1941 ^{ca*}	1700.4 ^{db*}	2906 ^{aa*}	2845.6 ^{ba*}	1245.7 ^{cc*}
Fe ³⁺	15.1 ^{ci*}	150 ^{di*}	1409.7 ^{ac*}	310.6 ^{bn*}	275 ^{ce*}
Ni ²⁺	350 ^{at*}	250 ^{bg*}	141 ^{ci*}	250.3 ^{bi*}	15 ^{dh*}

The values are the average of three replicate measurements. a, b, c, d, and e means that the values in the same row with the same letter are not significantly different at $P < 0.05$. a*, b*, c*, d*, e*, f*, g*, h* and i* : means that the values in the same column with the same letter are not significantly different at $P < 0.05$. Letters having * sign were used to compare the K_d values of each metal ions in the same solvent system i.e. down the column.

The type of solvent used also affect the ease of complexation. The studies of the adsorption of different metal ions in diverse solvent systems revealed many interesting features. It is also

interesting to note that K_d values for most of the metal ions in this studies are exceptionally high in organic solvents and acidic solvents. This behaviour of metal ions may again be because of the formation of more stable metal complexes with exchanger. It was also observed from the distribution studies (K_d values) that the Cr^{3+} and Cd^{2+} were highly adsorbed in all solvents, while remaining metal ions were poorly adsorbed. The high uptake of Cr^{3+} ions in all solvents demonstrates not only the ion exchange properties but also the adsorption and ion-selective characteristics of the cation exchanger towards this metal ion. Thus, the K_d value indicates that this nanocomposite cation exchanger is highly selective for Cr(III) ions and can be utilized for the determination and separation of Cr(III) ions from waste effluents.

Quantitative separation of metal ions in binary mixture

Separation of the metal ions was performed by an elution technique. On the basis of the different K_d values of those selected metal ions, several binary separations were achieved on columns packed with this material, by selecting appropriate mobile phases (Table 5). The guide for clear separation is the separation factor α . For the preferential uptake of metal ion in a mixture of two metal ions, separation factor is to be determined [36]. It can be defined and calculated as:

The separation factor (α_B^A) is defined by $\alpha_B^A = \frac{K_d(A)}{K_d(B)}$

where $K_d(A)$ and $K_d(B)$ are the distribution coefficients for the two competing ionic species, A and B in the exchanger phase. Thus on the basis of individual K_d values of metal ions in different solvent media, the separation factor for a binary metal solutions of A and B can be calculated. If the ion A is preferred, factor (α_B^A) is larger than unity, and if B is preferred the factor is smaller than unity [6].

Table 5. Binary separation of metal ions achieved by CATMP filled in a column.

Separation achieved	α	Amount of metal ion loaded (mg)	Amount of metal ion found (mg)	Eluent used	% Recovery
Cr^{+3}	2.23	10.81	10.50 ± 0.40	0.1M DMF+H ₂ SO ₄	97.13
Pb^{+2}		6.62	6.50 ± 0.30	0.1M DMF	98.18
Cr^{+3}	3.63	10.81	10.01 ± 0.04	0.1M DMF+H ₂ SO ₄	92.60
Zn^{+2}		5.95	5.65 ± 0.00	0.1M DMF+H ₂ SO ₄	94.96
Cd^{+2}	3.45	6.2	5.37 ± 0.10	0.1M DMF+H ₂ SO ₄	86.61
Cu^{+2}		4.99	4.43 ± 0.00	0.1M DMF+H ₂ SO ₄	88.69
Cd^{+2}	3.12	6.2	5.98 ± 0.00	0.1M DMF+H ₂ SO ₄	96.45
Zn^{+2}		5.95	5.60 ± 0.10	0.1M DMF+H ₂ SO ₄	94.12
Co^{+2}	4.43	5.82	4.96 ± 0.14	0.1M Formic acid	85.22
Ni^{+2}		4.75	3.97 ± 0.80	0.1M DMF+H ₂ SO ₄	83.54
Co^{+2}	2.14	5.82	4.80 ± 0.07	0.1M Formic acid	82.5
Cu^{+2}		4.99	4.31 ± 0.48	0.1M DMF+H ₂ SO ₄	86.30

The values are the average of three replicate measurements. Note: $\alpha = K_{d1}/K_{d2}$, where K_{d1} and K_{d2} are K_d values of metal 1 and metal 2 in aqueous media. % Recovery = (concentration of metal ion eluted/concentration of metal ion loaded) \times 100.

In the present work, separations of some selected metal ions were achieved based on the above principles. Based on separation factor α and distribution study (K_d) value, binary separations have been carried out for six sets of metal ions: Cr(III)–Pd(II), Cr(III)–Zn(II), Cd(II)–Zn(II), Cd(II)–Cu(II), Co(II)–Ni(II), Co(II)–Cu(II). The selections of solvents (eluent) for these separations were also done based on the K_d values of both metal ions [36]. The details

of these separation studies are presented in Table 5. To elute Cr(III) and Cd(II), (0.1 M) DMF + H₂SO₄ was preferably used while, for Co(II), 0.1 M formic acid was preferably used. This was due to the low K_d values of these metals in (0.1 M) DMF+H₂SO₄ and 0.1 M formic acid, respectively which enables quantitative elution for these metals. For Cr(III)–Pb(II) binary system, 0.1 M DMF was used to elute Pb(II), from Cr(III)–Pb(II) binary system. For Cr(III)–Zn(II) binary system (0.1 M) DMF+H₂SO₄ was used to elute Zn(II) from Cr(III)–Zn(II) mixture.

CONCLUSION

In the present study, cellulose acetate-Sn(IV) molybdophosphate cation exchanger nanocomposite was synthesized by a sol-gel approach and characterized by using different instrumental techniques. The FTIR spectrum confirmed that the synthesized exchanger is associated with adsorbed water and hydroxyl group in addition to its major functional groups. The XRD study revealed that the exchanger shows sharp, intense and symmetrical peaks which indicate a good crystalline nature of the as-synthesized cation exchanger. This new composite exchanger exhibited better CEC (2.43 meq/g) compared to its inorganic counterpart (1.41 meq/g). This new class of 'organic-inorganic' hybrid ion exchanger possesses fairly good yield, good ion exchange behavior, higher stabilities and selectivity for specific heavy metal ions such as Cr(III) and Cd(II) showing its potential for environmental applications. Cellulose acetate- Sn(IV) molybdophosphate obtained as yellow powder was found to be stable in water, quite stable in strong acids and organic solvents. However, its stability in strong base solution is poor. The pH titration curve indicates the as-synthesized nanocomposite is a bifunctional strong cation exchanger which was indicated by low pH (~2.06) of the solution when no OH ion was added. The distribution coefficient of the exchanger towards metal ions was also studied in different solvent systems and showed good separation possibilities of metal ions of analytical interest from a given mixture for toxic heavy metal ions. These materials could be used as good cation exchangers for the recovery and preconcentration of toxic metal ions (Cd²⁺ and Cr³⁺) in aqueous solutions.

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