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A biopolymer-based hybrid cation exchanger pectin cerium(IV) iodate: synthesis, characterization, and analytical applications

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ABSTRACT

Pectin cerium(IV) iodate (PcCeI) and cerium(IV) iodate (CeI) cation ion exchange materials were synthesized via sol–gel methods. The materials were characterized by using Fourier transform infrared spectroscopy, X-ray diffractometer, thermogravimetric analysis, and scanning electron microscopy. The ion exchange capacity (IEC), thermal stability, distribution coefficient (K_d), and pH titrations were investigated to recognize the cation exchange behavior of the materials. The IEC of pectin-cerium(IV) iodate (PcCeI and cerium(IV) iodate CeI were reported as 1.80 meq/g and 0.92 meq/g, respectively. The higher distribution coefficient values of 250.01 and 219.14 mg/L confirmed the selectivity of pectin-cerium(IV) iodate hybrid ion exchanger for As^{3+} and Zn^{2+}. The antibacterial activity of synthesized ion exchangers was explored for *E. coli* bacteria and observed relatively higher for PcCeI as compared to CeI.

Keywords: Hybrid cation exchangers; Inorganic ion exchanger; Toxic metal ions; Removal; Antimicrobial activity

1. Introduction

Synthetic inorganic ion exchangers based on tetravalent metals have been subject of considerable interest in recent years because of their selectivity and intercalation properties [1]. The ion exchangers have been extensively used in petrochemical, pharmaceutical, semiconductor, power, and a host of other industries [2–4]. They have definite advantages such as great thermal stability at elevated temperature and resistant to high radiation fields over organic resins. They also have high chemical stability and compatibility with the final waste forms. However, the inorganic ion exchangers have their own limitations such as non-reproducible in nature, fabrication for the column is difficult, and less mechanical strength [5]. In order to overcome these limitations, the interest has been generated in the preparation of inorganic–organic hybrid materials of high mechanical stability and enhanced ion exchange capacity (IEC) [6]. The hybrid ion exchangers have good chemical, mechanical, and thermal stability which was due to the presence of organic species in

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inorganic ion exchange material. The synthesis of hybrid materials represents the one of the most fascinating improvement in material chemistry, in recent years. Many of such material based on cerium(IV) and thorium(IV) possess fibrous nature [7,8]. Fibrous ion exchangers are of great importance in industrial and environmental applications due to versatility in their properties. They can be used to prepare thin layers chromatogram suitable for chromatographic separations without binder.

The heavy metals and dye pollutants are ever growing threat increasing with alarming rate due to industrialization [9–13]. The different conventional and non-conventional adsorbents have been used for treatment of these pollutants [14–17]. The hybrid ion exchangers are promising materials for environmental pollution remediation. Many organic and inorganic hybrid materials have been investigated for their chemical, biological, and environmental significance [18–22]. The new applications of hybrid materials have been explored in the field of catalysis, protective coating, solid polymer electrolyte membrane, fuel cell, ion selective electrodes, ion transport, and ion exchange [23–26]. The major advantage of these materials is that they have a rigid inorganic backbone and the flexibility of organic groups provides the wide range of properties [27]. Various methods have been reported for the synthesis of hybrid ion exchanger but among these chemical method was most important and widely used [28–30]. The important applications of ion exchangers in separation science have been described, elsewhere, in the literature [31].

Pectin is a natural, non-toxic, amorphous carbohydrate found in the cell walls of all plant tissues, functions as an intercellular and intracellular cementing material. Pectin is both inexpensive and abundantly available. Therefore, pectin is an excellent material for eco-friendly biodegradable applications [32]. The ion exchangers have been used extensively in the chemical decontamination process for metal ion recovery and removal of the formulation chemicals from the coolant [33] which are capable of removing toxic substances from aqueous effluent [34]. Inorganic antibacterial agents have attracted a lot of attention, since the 1990s. They possessed so many outstanding properties, such as long-lasting effects, broad-spectrum antibiosis, and better heat resistance compared to organic antibacterial agents.

In the present study, cerium(IV) iodate and pectin-cerium(IV) iodate cation exchangers were synthesized. The materials were characterized using some instrumental techniques. The synthesized materials have also been successfully used as antibacterial agents against *E. coli* bacteria.

2. Experimental

2.1. Material and apparatus

All the reagents used were of analytical reagent grade and used as received. Double distilled water was used for preparation of all the solutions. An electric thermostat oven (Microsil, India) was used for drying the samples. Thermo Orion Model 420-A) pH meter was used for pH measurements. X-ray diffractograms were taken from Phillips (England), X-ray diffractometer. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer (1730, USA) using KBr disc method. Electric furnace (Microsil, India) was used for heating the samples at elevated temperatures. Thermogravimetric analysis (TGA) was carried out using the Mettler-Tolledo Star system at rate of 100°C/min. The external morphology of ion exchangers was measured by scanning electron microscopy (SEM) (model JSM-6100). The absorption spectra were recorded with UV–visible spectrometer (Shimadzu UV-1601).

2.2. Synthesis of cerium(IV) iodate (CeI)

Cerium(IV) iodate (CeI) was prepared by adding 0.2 M aqueous solutions of potassium iodate (KIO_3) dropwise with constant stirring to aqueous solution of 0.05 M solution of ammonium ceric nitrate ($NH_4Ce(NO_3)_6$) in molar ratio of 1:1 at room temperature. The pH of the solution was adjusted to 0–1 by adding 0.1 M $NaOH/HNO_3$. This mixture was kept for digestion for 24 h at room temperature. The precipitates were filtered, washed with distilled water, and dried in hot air oven at 50°C. The material was then converted into H^+ form by treating with 0.1 M HNO_3 for 24 h with occasional shaking. The material was washed with distilled water to remove the excess acid and finally dried at 50°C in a hot air oven.

2.3. Synthesis of pectin-cerium(IV) iodate (PcCeI)

Pectin-cerium(IV) iodate (PcCeI) hybrid ion exchanger was prepared by simple sol–gel method. In this method, 0.2 M potassium iodate (KIO_3) and 0.05 M ammonium ceric nitrate solution were mixed in 1:1 M concentration with constant stirring at room temperature. The gel of pectin (0.2 g pectin in 10 mL DMW) was added to the above reaction mixture. The resulting mixture was stirred for 4 h at temperature 50–60°C. The pH of the mixture was adjusted between 0 and 1 by adding 0.1 N $NaOH/HNO_3$ [35]. This mixture was kept for 24 h at room temperature for digestion, filtered off, and then washed with distilled water. The precipitates were dried at 50°C in hot air oven. The material was then converted into H^+ form by treating with 0.1 N HNO_3 for 24 h with occasional shaking. After decanting off the supernatant liquid, the resulting precipitates were washed with distilled water to remove the excess of acid and finally dried at 50˚C in hot air oven.

2.4. Ion exchange capacity

The IEC of CeI and PcCeI cation exchange materials was determined by column method using 1.0 g of the exchanger in H^+ form [36]. The H^+ ions were eluted by percolating 0.1 M NaCl solution. The flow rate was kept 20 drops/min. The collected effluent was titrated against a standard sodium hydroxide solution using phenolphthalein indicator. The H^+ ions released were then calculated as follows:

$$\mathrm{IEC} = \frac{N \times V}{W}\left(\frac{\mathrm{meq}}{\mathrm{g}}\right) \tag{1}$$

where N is the normality of alkali, V is the volume of alkali, and W is the weight of exchanger taken.

2.5. pH titration

The pH titration studies of CeI and PcCeI ion exchanger materials were performed by the method of Topp and Pepper using NaCl–NaOH system [37].The 0.5 g of ion exchangers in H^+ form was placed in several 250 mL conical flasks, followed by the addition of equimolar solution of alkali and their hydroxide in different volume ratios. The final volume was adjusted to 50 mL to maintain the ionic strength constant. The pH of each solution was recorded after 24 h till the equilibrium was established.

2.6. Thermal stability

The effect of temperature on the IEC of CeI and PcCeI was studied by heating 1.0 g ion exchangers in the H^+ form at various temperatures in a muffle furnace for 1 h and then IEC was determined by the column process.

2.7. Thermal analysis

TGA of ion exchange materials was carried out by heating the samples up to 800˚C at a constant rate of 10˚C/min in nitrogen atmosphere using TGA.

2.8. Scanning electron microscopy

Electron micrographs of ion exchange materials were recorded using SEM operated at 15 kV at different magnifications.

2.9. FTIR Studies

The FTIR spectrum was recorded in the range of 400-4,000 cm^{-1}. For this study, 10 mg of ion exchanger in H^+ form was mixed with 100 mg of KBr and ground to a very fine powder. A pellet was made by applying a pressure of 80,000 psi and then FTIR spectra were recorded.

2.10. X-ray analysis

X-ray diffraction analysis was done using manganese filter CuKα radiation at 298 K. The instrument was operated at 40 kV and 30 mA.

2.11. Distribution coefficient (K_d)

Distribution studies were carried out using the method as descried earlier [38]. In this method, 0.1 g of ion exchangers in H^+ form were taken in 50 mL of different metal ion concentrations. It was kept for 24 h with continuous shaking at room temperature to attain the equilibrium. The amount of metal ions before and after adsorption was determined using standard method. The K_d values were determined from the formula as:

$$K_d = \frac{I - F}{F} \times \frac{V}{W}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) \tag{2}$$

where I = initial amount of metal ion in the solution, F = final amount of metal ion in the solution after treatment with exchanger, V = the volume of metal ion solution (mL) taken for analysis, and W = the dry weight of ion exchangers taken (g).

2.12. The antibacterial activity

The antibacterial activity of CeI and PcCeI ion exchangers was determined by using optical density method. In this method, *E. coli* bacteria were aerobically cultured at 30˚C for 24 h in nutrient broth (NB). 13% of NB was prepared in distilled water and autoclaved. Hundred milliliter was taken in three different flasks and the culture of bacteria was added. To these flasks, 0–200 μg/mL concentrations of CeI and PcCeI were added. Then the flasks were kept in the incubator shaker at 30˚C. Three milliliters of suspension from each flask was taken to determine the optical density at 600 nm to monitor the bacterial concentration. The growth curves were obtained by plotting optical density against time of incubation.

3. Results and discussion

It has been observed that Na^+ IEC of PcCeI (1.80 meq/g) was higher than CeI (0.92 meq/g) at 50℃. The improvement in the IEC of this hybrid cation exchanger (PcCeI) compared to inorganic ion exchangers (e.g. CeI) may be due to the binding of organic polymer (pectin) with inorganic moiety (CeI). The effect of temperature on the IEC was shown in Table 1. It is evident that the physical nature and the IEC of dried cation exchangers changed on heating at different temperature. It was observed that the IEC decreased with the increase in temperature.

The FTIR spectra of CeI and PcCeI are shown in Fig. 1(a) and (b). A sharp peak at 3,400 cm^{-1} was due to the presence of external water molecules. Another absorption strong peak at 1,690 cm^{-1} may be due to H–O–H bonding [39]. A sharp peak at 2,348 cm^{-1} was due to CO_2 atmosphere. The stretching band in the region of 830–500 cm^{-1} indicated the presence of iodate and metal oxide groups [40]. A band at 750 cm^{-1} corresponded to O–Ce–O bond. The absorption band in the region of 584 cm^{-1} may be due to Ce–O. The FTIR spectrum of PcCeI Fig. 1(b) confirmed the presence of metal oxide and metal hydroxide band at 582 cm^{-1}. The absorption band at 3,433 cm^{-1} may be due to symmetric and asymmetric O–H stretching. The band at 2,388 cm^{-1} indicated the C–H stretching and carbon. The band at 1,710 cm^{-1} was due to the presence of C=O stretching of ester. The absorption bands at 1,038 cm^{-1} indicated the C–O stretching in PcCeI. The absorption peak at 1,625 cm^{-1} was due to stretching bands of COO^- groups of pectin. Fig. 2 shows the pH titration curve of CeI and PcCeI in NaOH/NaCl system. The pH titration curve indicated the mono-functional behavior of ion exchangers. The IEC obtained from the pH titration curve was in agreement with the result obtained from the column method.

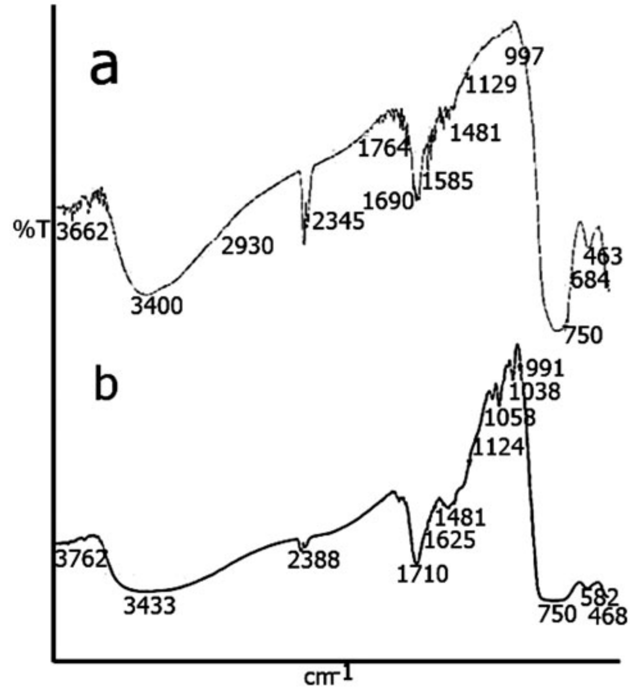

Fig. 1. (a) FTIR spectra of CeI and (b) FTIR spectra of PcCeI.

Thermogravimetric curve of CeI and PcCeI are shown in Fig. 3(a) and (b). It was observed that the weight loss in CeI occurred in three steps while PcCeI lost in the weight was observed in four steps. The small loss in the weight occurred up to 125℃ may be due to the removal of external water molecules from the exchanger [41]. Beyond this temperature, the condensation of the material started, resulted in the removal of strongly coordinated water molecules from the frame work of exchangers, which continued up to 300 and 500℃ for CeI and PcCeI, respectively. The weight loss in the region of 600–650℃ in PcCeI was due to the complete decomposition of organic part of the exchanger (Fig. 3(b)). After 750℃, a smooth horizontal section showed the complete formation of oxide from of the material in PcCeI. The SEM images of CeI and PcCeI are shown in Fig. 4 (a)–(d) at different magnifications. It was inferred that CeI surface was

Table 1
Effect of temperatures on the ion exchange capacities of CeI and PcCeI cation exchangers

Drying temperature (℃)	IEC (meq/g)		Change in colour	
	PcCeI	CeI	PcCeI	CeI
50	1.80	0.92	Yellow	Light yellow
75	0.98	0.71	Yellow	Light yellow
100	0.60	0.32	Faded yellow	Faded yellow
125	0.36	0.13	Light green	Faded brown

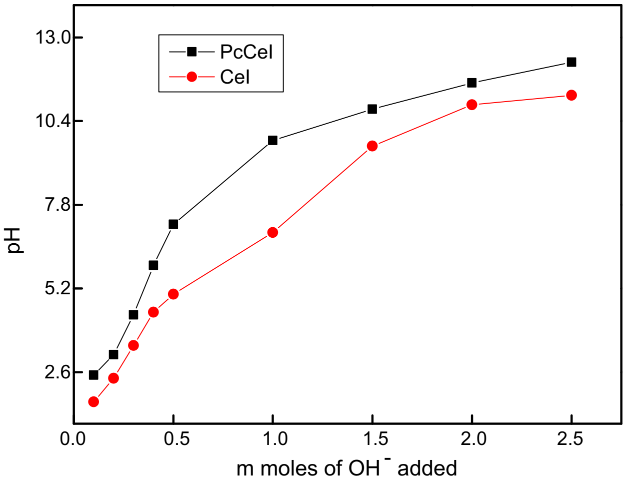

Fig. 2. pH titration curves for CeI and PcCeI.

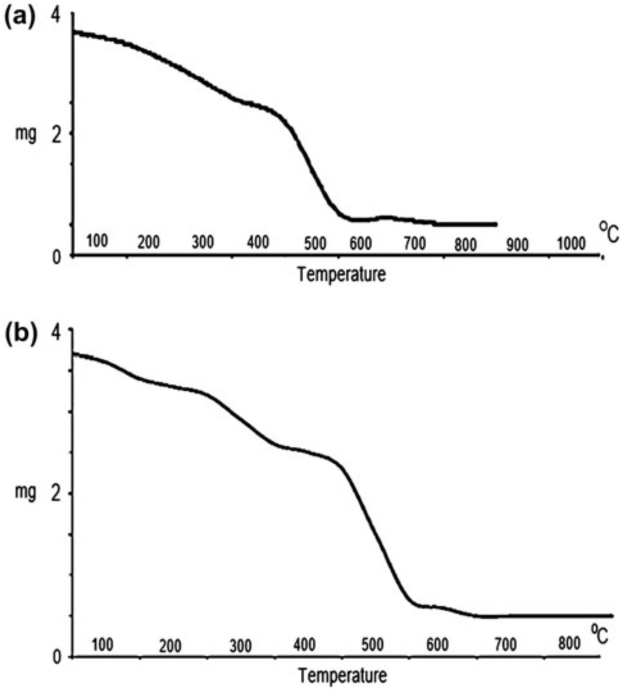

Fig. 3. (a) TG curve of CeI and (b) TG curve of PcCeI.

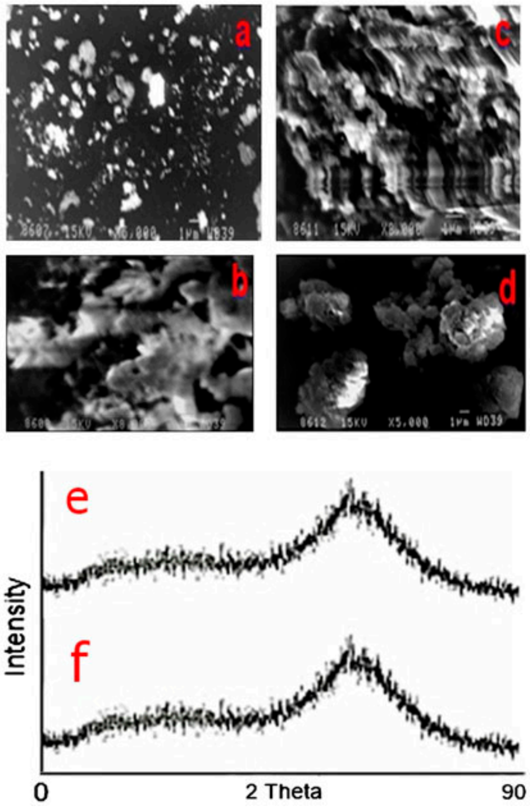

Fig. 4. Scanning electron micrographs (a and b) CeI and (c and d) PcCeI at different magnifications (e) X-ray Diffraction of CeI and (f) X-ray Diffraction of PcCeI.

smooth and porous, changed after binding of organic polymer with inorganic cerium(IV) iodate.

X-ray diffraction pattern of CeI and PcCeI are shown in Fig. 4(e) and (f). It is evident that both the ion exchanger was amorphous in nature.

In order to explore the potentiality of the cation exchange material for the separation of metal ions, the distribution studies for some metal ions were performed in water systems (Table 2). It was observed that CeI is selective for As^{3+} ion and PcCeI is selective for As^{3+} and Zn^{2+} ions. Table 3 shows the various ion exchangers and their selective nature for particular metal ion. The selectivity of the ion exchange materials for metal ions reflects their potential for the separation of metal ions from water system.

The antibacterial activity of CeI and PcCeI cation exchangers against *E. coli* bacteria are shown in

Table 2
Distribution coefficient (K_d) of different metal ions on CeI and PcCeI cation exchangers in DMW

		Distribution coefficient (K_d)	
Sr. no.	Metal ions	CeI	PcCeI
1	Mg^{2+}	33.78	20.69
2	Ni^{2+}	110	66.25
3	Ca^{2+}	197.22	100
4	As^{2+}	232.51	250.01
5	Zn^{2+}	44.02	219.14

Table 3
Various ion exchangers and their selectivity for particular metal ions

Ion exchanger	Selectivity	Distribution coefficient value	Reference
Cellulose acetate–tin (IV) phosphate	Cd^{2+}	568.2	[20]
Polyaniline Th(IV) tungstomolybdophosphate	Cu^{2+}	207.85	[29]
Poly-*o*-toluidine Th(IV) phosphate	Pb^{2+}	425.0	[31]
n-Butylacetatezirconium (IV) iodate	Pb^{2+}	600.0	[6]
Poly-*o*-toluidine Zr(IV) tungstate	Hg^{2+}	600.0	[37]
Acrylamide zirconium (IV) arsenate	Pb^{2+}	650.0	[42]
Pectin zirconium (IV) selenotungstophosphate	Cu^{2+}	299.99	[34]
Pectin cerium (IV) iodate	As^{2+}	250.01	In present study

Fig. 5(a) and (b). The result indicated that both the materials were effective antibacterial agent at low and high concentration. At high concentration of the ion exchange materials, the antibacterial activity was found higher. It was inferred that PcCeI has better antibacterial property than CeI. Thus, PcCeI and CeI could be effectively used for the removal of *E. coli* from water system.

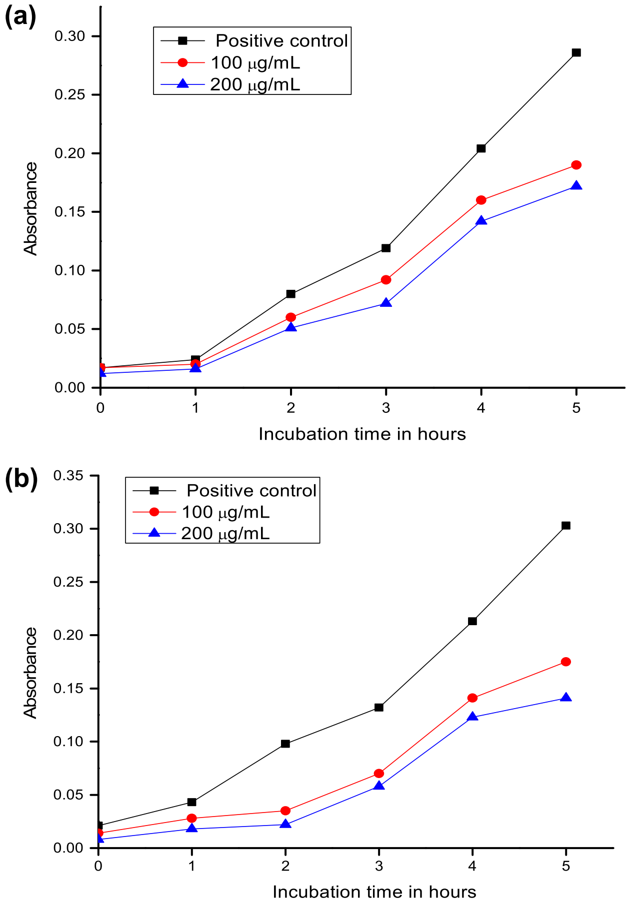

Fig. 5. Growth curve of *E. coli* in presence of (a) CeI and (b) PcCeI.

4. Conclusions

CeI and PcCeI cation exchangers were synthesized by simple sol–gel method. It was observed that both the ion exchangers were amorphous in nature. The SEM images inferred that the morphology of PcCeI hybrid cation exchanger was changed after the binding of organic polymer (pectin) with CeI. PcCeI hybrid cation exchanger showed the better IEC and thermal stability in comparison to its inorganic counterpart. The distribution coefficient values revealed that PcCeI was selective for Zn^{2+}. Furthermore, CeI and PcCeI showed the significant antibacterial activity for *E. coli*.

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