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Preparation, Characterization and Ion-Exchange Properties of an Organic-Inorganic Composite Cation Exchanger: Polyaniline-Bi(III) Iodovanadate and Catalytic Properties of Bi(III) Iodovanadate Inorganic Ion Exchanger

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Abstract

Polyaniline based composite cation exchange materials have been used in industrial application for more than 100 years. The organic-inorganic composite cation exchanger was prepared by using sol-gel process. The organic polymer part furnishes the good chemical and mechanical properties, whereas the inorganic part improves the ion-exchange behavior and thermal stability. A new and novel polyaniline-Bi(III) iodovanadate composite cation exchanger prepared by using sol-gel process and was characterized by FT-IR, XRD, SEM-EDS studies. The ion exchange capacity, effect of size and charge of metal ion, eluent concentration, effect of time on IEC elution behavior and oxidizing properties of Bi(III) iodovanadate was also studied by column method. Polyaniline-Bi(III) iodovanadate composite exhibits ion exchange capacity for Na^+ ion is 1.48 meq/g.

Keywords: elution behavior, ion exchange capacity, thermal stability, sol-gel process

1. Introduction

Polyaniline has become one of the most interesting organic conducting polymer due to its high chemical and environmental stability, easy to synthesis in laboratory, feasibility of electrical conductivity and low cost of aniline monomer [1–3]. Literature survey reported that many ion exchange composite cation exchanger used for the separation of some toxic metal ions and dyes from the environment. New organic-inorganic conducting polymer composite cation exchanger developed by incorporation of organic polymer into the inorganic heteropolyacid moiety [4]. It is extensively used in rechargeable batteries, charge storage devices, protector shield

in magnetic fields, sensors, biosensors, catalytic processes, microwave absorption, image processing and infrared optic applications [5–9]. Polymer based composite cation exchanger have extended enormous applications such as ion selective electrode, photocatalyst, antimicrobial, sensors, environmental remediation, etc. Several heteropolyacids are used as a catalyst in organic synthesis and they are extensively used for reagents in qualitative and quantitative analysis [10–12]. This paper deals with preparation, characterization, ion exchange studies, chemical stability and oxidizing ability of Bi(III) iodovanadate and newly fabricated polyaniline-Bi(III) iodovanadate composite cation exchanger. The structural analysis of polyaniline-Bi(III) iodovanadate composite was done by FT-IR, XRD and SEM-EDS studies.

2. Experimental section

2.1 Reagents and instrument

The reagents used for the preparation were analytical grade and used without any further purification. FT-IR spectra were recorded on a JACSO-4100 FT-IR Spectrometer. X-ray diffraction pattern was also recorded by using analytical system Shimadzu XRD-6000 model and the spectrum was recorded 10–90° using Cu-K α radiation. The surface morphology and elemental composition was determined by using scanning electron microscope JSM-6390Lv energy dispersive X-ray detector.

2.2 Preparation of polyaniline-Bi(III) iodovanadate cation exchanger

Polyaniline gel was prepared by 0.2 M solution of aniline and potassium persulfate in 1 M hydrochloric acid [13] with constant stirring. Bi(III) iodovanadate inorganic ion exchanger was prepared by mixing 1:2:3 volume ratio of 0.2 M solution of bismuth nitrate, potassium iodate and sodium meta vanadate. The mixture of solution was adjusted to pH = 1 by using 1 M HNO₃, and the precipitate was stirred for 1 hour [14]. The gel of polyaniline was mixed with inorganic precipitate of Bi(III) iodovanadate and the mixture was stirred thoroughly using magnetic stirrer. The green colored gel was kept for 1 day. The gel was filtered and dried in oven at 50°C. The dried product of composite cation exchanger is crushed and the product is converted into H⁺ form by using 1 M HNO₃ with occasional shaking for 1 day. The product is filtered and dried at 50°C. The H⁺ form of polyaniline-Bi(III) iodovanadate is used for ion exchange and chemical stability studies.

2.3 Ion exchange capacity

The ion exchange capacity of dry H⁺ form of polyaniline-Bi(III) iodovanadate was determined by column process using 0.1 M NaCl as eluent. The liberated H⁺ ion was determined titrimetrically against NaOH solution by using phenolphthalein indicator and IEC was calculated by using formula,

$$\text{IEC} = \frac{(N * V)}{W} \text{ meq/g} \quad (1)$$

where N and V are the normality and volume of NaOH respectively and W is the weight in gram.

2.4 Chemical stability

To find out extent of dissolution of composite cation exchange material, chemical stability was studied in different organic and inorganic solvents. Two fifty

milligram of H^+ form of polyaniline-Bi(III) iodovanadate mixed with 25 ml of different solvents and kept for 24 hours. After 24 hours the composite material was filtered and dried. The stability of composite cation exchanger was determined by change in color and weight of composite cation exchanger.

2.5 Inorganic heteropolyacid as oxidizing agent

The catalytic function of heteropoly compounds has attracted much attention, particularly in the last two decades, because their acidic and redox properties can be controlled at atomic/molecular levels. As for the phase of these catalytic systems, various systems are possible: homogenous liquid, liquid/liquid (phase transfer), liquid/solid, gas/solid systems, and so on. There are actually several large-scale industrial processes that use heteropolyacid catalysts.

Polyaniline gel was prepared by 0.2 M solution of aniline and potassium persulfate in 1 M hydrochloric acid with constant stirring. About 0.5 g of Bi(III) iodovanadate inorganic ion exchanger were added to the solution of acidic aniline with constant stirring for 1 hour. Aniline was polymerized into the green color polyaniline. The product of polyaniline was filtered and washed with DMW, ethanol, acetone and dried at $50^\circ C$.

3. Results and discussion

The incorporation of organic polymer polyaniline into the inorganic matrix of Bi(III) iodovanadate was confirmed by carrying out FT-IR spectral studies. The characteristic peaks of polyaniline and Bi(III) iodovanadate were observed in the FT-IR spectrum of polyaniline-Bi(III) iodovanadate composite shown in **Figure 1b**. The FT-IR peak observed at 3400 cm^{-1} is due to the -OH stretching vibrations. The benzenoid and quinoid stretching frequency obtained at 1477 and 1560 cm^{-1} [15]. Peaks at 1270 and 1654 cm^{-1} as singed to -CN stretching and -NH bending vibration in neighboring quinoid ring [16]. The characteristic bands at 878 , 784 and 671 cm^{-1} may be assigned to M-O stretching [17].

The XRD pattern of polyaniline shows broad peak at two theta value of 25.43° which indicate low crystallinity of the conducting polymer XRD pattern of polyaniline-Bi(III) iodovandate composite (**Figure 2b**) exhibit high intensity peaks at two theta values 26.09 , 33.6 and 32.8° . The observation in the XRD pattern of polyaniline composite shows that the composite is crystalline nature and calculated particle size is 14.96 nm .

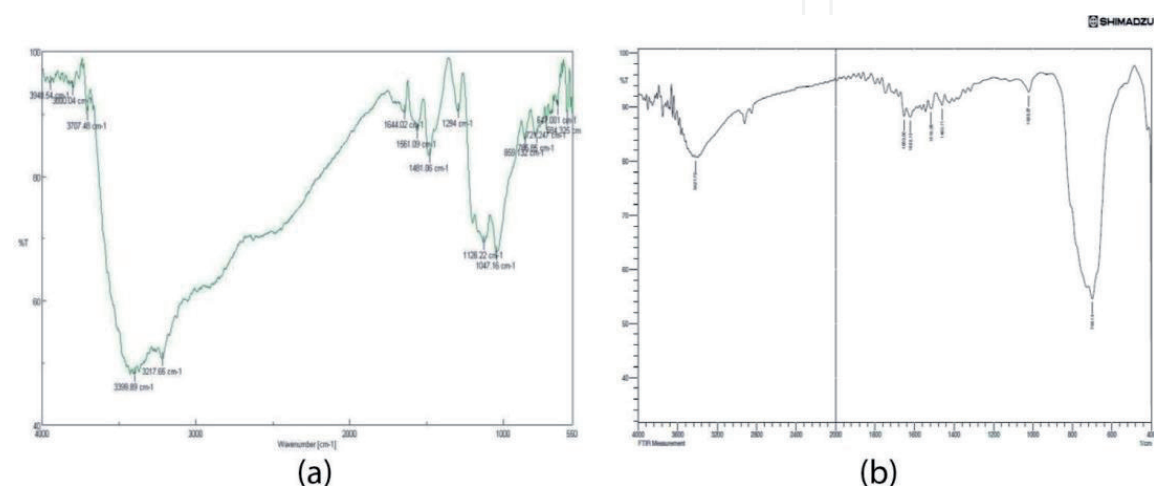


Figure 1.
(a) FT-IR spectrum of polyaniline; (b) FT-IR spectrum of polyaniline-Bi(III) iodovanadate.

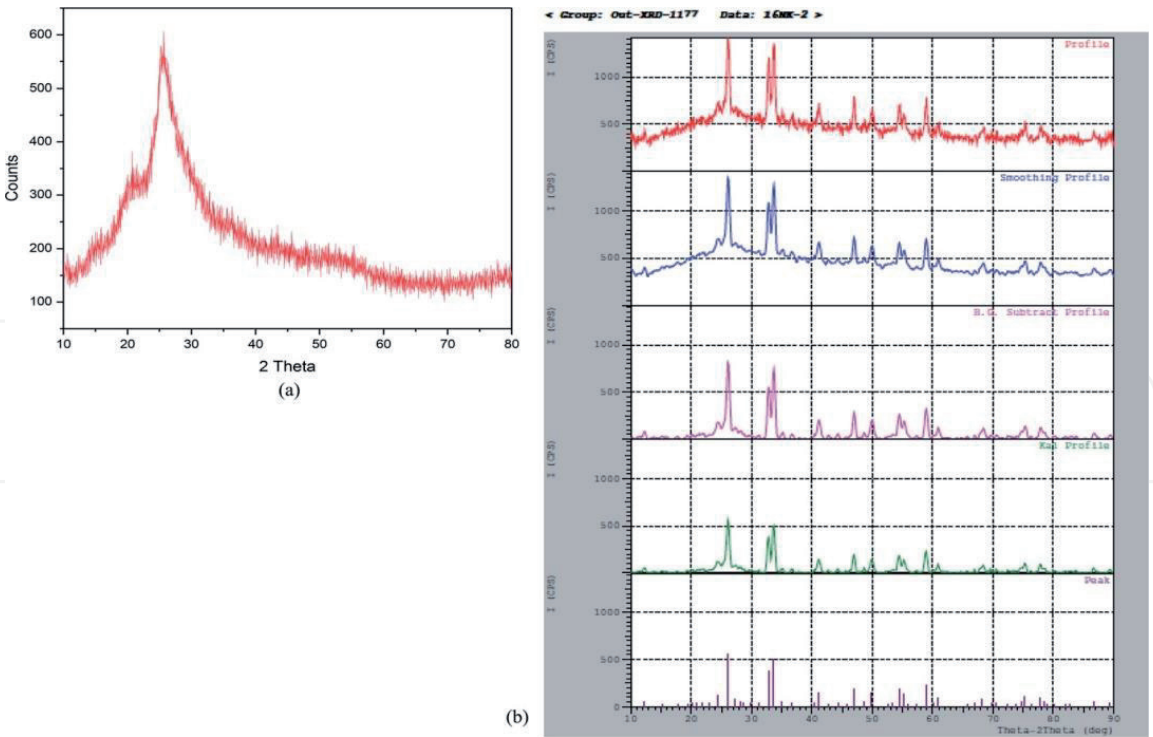


Figure 2.
(a) XRD pattern for polyaniline; (b) XRD pattern for polyaniline-Bi(III) iodovanadate.

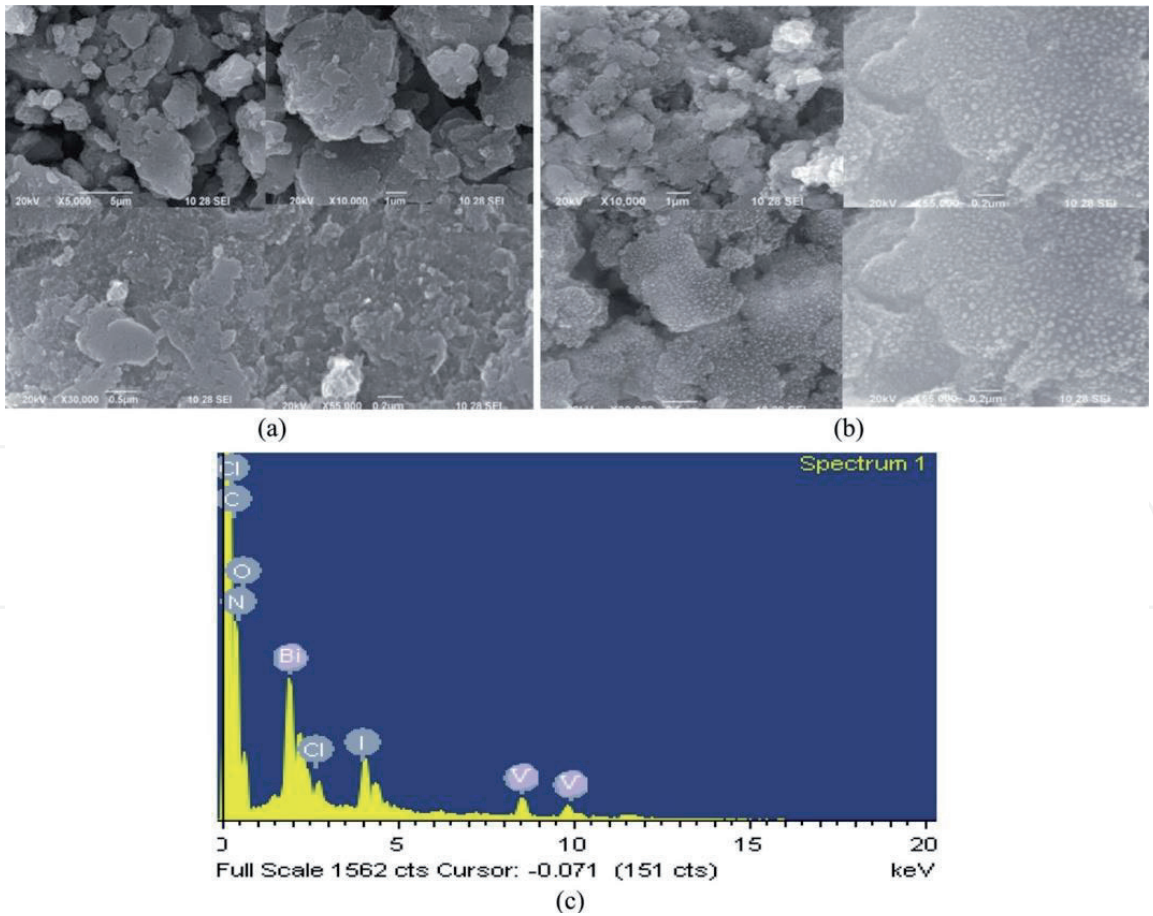


Figure 3.
(a) SEM photograph for polyaniline; (b) SEM photograph for polyaniline-Bi(III) iodovanadate; (c) EDS analysis for polyaniline-Bi(III) iodovanadate.

Figures 3a, b represents SEM photographs of polyaniline and polyaniline-Bi(III) iodovanadate composites, respectively. SEM photograph of polyaniline salt suggests that agglomerates are randomly distributed on its surface, whereas polyaniline-Bi(III)

iodovanadate composite have porous morphology with granular structure [18]. It is clearly evident from SEM study, inorganic ion exchanger homogeneously distributed on the surface of polyaniline. **Figure 3c** shows that presence of all the elements present in the material which shows purity of composite.

The ion exchange capacity is affected by the size and charge of metal ions. Ion exchange capacity of polyaniline-Bi(III) iodovanadate composite for various alkali and alkaline earth metal cations follows the order $K^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Mg^{2+}$ respectively. The ions with smaller hydrated ionic radii easily enter the pores of cation exchanger resulting in higher adsorption. Similar observation was observed by Mesalem et al. and Nachood et al. [19, 20]. Elution behavior was carried out to find out the volume of eluent (NaCl) required for complete elution in H^+ ion from 1 g composite cation exchanger on H^+ form and represented in **Figure 4b**. It is clear from **Figure 4b** 120 ml of NaCl is enough for complete elution of H^+ ions.

Eluent concentration is main factor which affects the Na^+ ion exchange capacity. The minimum molar concentration of eluent was found to be 0.1 M. The effect of time on ion exchange capacity shows constant: ion exchange capacity after 60 minutes. The observed datas of eluent concentration and effect of time show in (**Figure 5**).

Chemical stability study was carried out to find the stability of prepared composite cation exchanger in different solvents of interest such as DMW, 2 M HCl, H_2SO_4 , NaOH, ether, 1,2-dichloroethane, cyclohexane and benzene. The polyaniline-Bi(III) iodovanadate composite was more stable in DMW, Partially stable in mineral acid and organic solvents and unstable in 2 M NaOH because of dedoped form of ion exchanger.

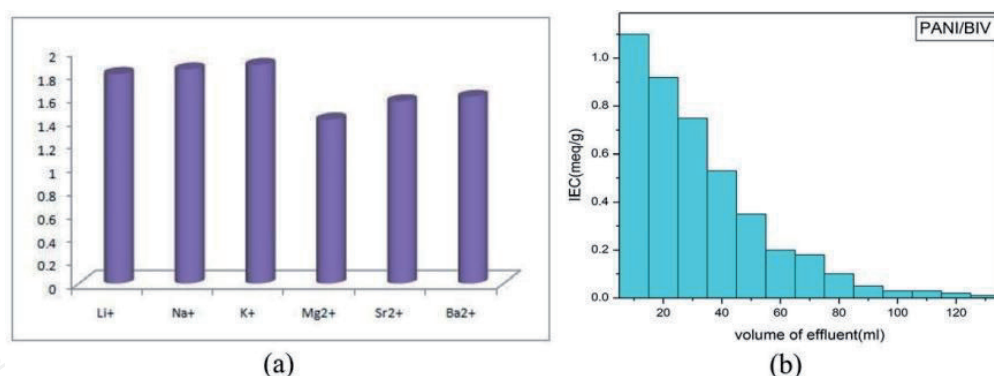


Figure 4. (a) IEC of polyaniline-Bi(III) iodovanadate composite for various metal ions; (b) elution behavior of polyaniline-Bi(III) iodovanadate composite.

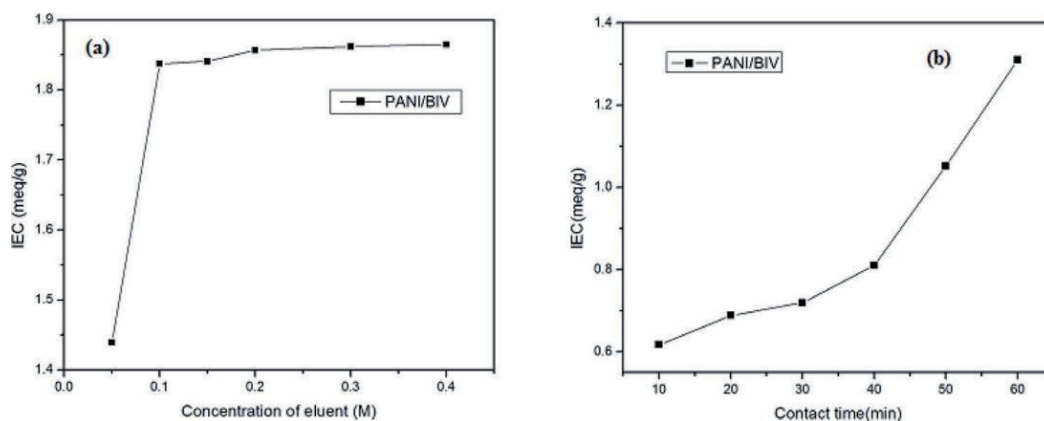


Figure 5. Na^+ + IEC for polyaniline-Bi(III) iodovanadate as a function of (a) eluent concentration; (b) contact time.

3.1 Bi(III) iodovanadate as oxidizing agent

The hetropolyacid (iodovanadate) unit of inorganic ion exchanger like Bi(III) iodovanadate is made up of oxygen and hydrogen with some metals and nonmetal (iodine and vanadium). Bi(III) iodovanadate can act as a oxidizing agent, to the polymerization of aniline monomer into green colored polyaniline gels without adding oxidizing agent [10, 21–24].

4. Conclusion

In this present paper, polyaniline-Bi(III) iodovanadate composite cation exchanger have enhanced Na^+ ion exchange capacity compared to polyaniline and Bi(III) iodovanadate. The composite cation exchanger was prepared successfully by using sol-gel method. FT-IR and SEM-EDS studies confirmed that the inorganic ion exchanger incorporated into polyaniline matrix. XRD spectral studies proved that the composite cation exchanger is in nano size range and crystalline nature. Ion exchange capacity and chemical stability studies proved that the composite material act as good ion exchanger and stable in mineral acid and organic solvents. It was concluded that polyaniline-Bi(III) iodovanadate composite act as good potential for environmental remediation.

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