Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Fabrication of electrically conductive membrane electrode of gelatin-tin (IV) phosphate nanocomposite for the detection of cobalt (II) ions

Deepak Pathania [a,*], Manita Thakur [a], Vanita Puri [b], Shefali Jasrotia [a]

[a] School of Chemistry, Shoolini University, Solan 173212, Himachal Pradesh, India
[b] Department of Chemistry, National Defense Academy, Khadakwasla, Pune, Maharashtra, India

ARTICLE INFO

Article history:
Received 4 April 2017
Received in revised form 8 September 2017
Accepted 15 January 2018
Available online xxxx

Keywords:
Nanocomposite
Gelatin
Methylene blue
Heavy metals
Ion selective electrode

ABSTRACT

Gelatin-tin (IV) phosphate nanocomposite (GT/TPNC) ion exchanger was synthesized by mixing gelatin gel into the precipitates of tin (IV) phosphate using sol–gel method. GT/TPNC was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The ion exchange capacity of GT/TPNC was reported to be1.44 meq/g. The material was found monofunctional as indicated from pH titration curves. The distribution coefficient of different metal ions such as Zn^{2+} (42.10), Cd^{2+} (37.93), Mg^{2+} (33.33), Cu^{2+} (33.21), Al^{3+} (14.28), Pb^{2+} (6.06), Ni^{2+} (12.50) and Co^{2+} (50.0) was studied using GT/TPNC ion exchanger. The distribution studies confirmed the selectivity of GT/TPNC for Co (II). The photocatalytical degradation of MB was found to be 78% within 5 h of solar illumination using GT/TPNC. Some binary separations such as Co^{2+}–Pb^{2+}, Cd^{2+}–Ni^{2+}, Co^{2+}–Mg^{2+}, Mg^{2+}–Zn^{2+}, Pb^{2+}–Zn^{2+}, Cu^{2+}–Al^{3+}, Al^{3+}–Cd^{2+}, Ni^{2+}–Cu^{2+} were attempted using GT/TPNC ion exchanger. GT/TPNC was explored for the fabrication of ion-sensitive membrane electrode for the determination of Co (II) in the water system. The membrane electrode was found mechanically more stable with quick response time (30 s) and a wide pH working range (4.0–7.0).

1. Introduction

The industrial development, urbanisation and uncontrolled agricultural practices caused serious environmental problems. The organic and inorganic pollutants continuously contaminated the drinking water. The chemical industries such as battery manufacturing, metal plating, fertilizer, mining, paper and pesticides, metallurgical, mining, fossil fuel etc. are the major sources of noxious pollutants which affects the quality of drinking water. The discharge of industrial wastes contain agriculture runoff, pathogens, radioactive pollutants, heavy metals, synthetic dyes, phenols, buffers, bleaching agents, water softeners, surfactants, acids, pesticides and detergents are affecting our flora and fauna [1].

Among the various pollutants, heavy metal ions and dyes are carcinogenic and non-biodegradable in nature [2]. The release of heavy metals into the environment posed a serious threat to human beings, animals and plants because of their bioaccumulation, non-biodegradable and toxicity. The heavy metals such as aluminum, chromium, cadmium, lead, mercury and arsenic are discharged into the environment directly through industrial effluents [3,4]. The accumulation of these toxic heavy metals caused severe harmful effects to the living organisms. Also, the presence of organic dyes causes a number of problems such as nausea, hypertension, hemolysis and respiratory problems in living organisms [5]. Therefore, it is essential to find out appropriate methods for the removal of these pollutants from aquatic system before getting mixed with air, water and soil. Different methods such as membrane process, reverse osmosis, precipitation, electro sorption, adsorption and ion exchanger process have been reported for the removal of pollutants [6]. Among all these methods, ion exchange is most important and cost effective for waste water treatment [7].

The inorganic ion exchangers have been used for the removal of pollutants. But due to some drawbacks such as high costs, limited chemical stability at extreme pH ranges, non-reproducible, less stable in acidic and basic medium, costly, inefficient to treat large volume of waste effluents and non-suitability for column operations limit their applicability in different fields [8]. While, the organic ion exchangers have certain limitations such as instability at high temperature and ionization radiation, poor thermal and radiation stability [9–11]. Hence, attempt has been made to synthesize composite ion exchangers by the incorporation of organic

---

* Corresponding author at: Department of Environmental Sciences, Central University of Jammu, Rahya Suchani, Bagla, Distt. Samba, Jammu and Kashmir, 181143, India

E-mail address: dpathania74@gmail.com (D. Pathania).

https://doi.org/10.1016/j.apt.2018.01.009

Please cite this article in press as: D. Pathania et al., Fabrication of electrically conductive membrane electrode of gelatin-tin (IV) phosphate nanocomposite for the detection of cobalt (II) ions, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.01.009

part into the inorganic matrix. The obtained materials have better stabilities, reproducibility and good selectivity towards organic and inorganic pollutants. The composite ion exchange materials have a wide range of properties such as mechanical, chemical, environment stability, optical activity, catalytic activity and good selectivity for heavy metals [12–16]. In recent years, polymer based composite ion exchange materials have been attracted more attention due to their advanced properties such as toughness, chemical selectivity, mechanical and thermal stability [17,18]. But the composites with nano-scale dimensions have wide utility in diverse fields such as ion selective electrode [18–21], photocatalysis [22–25], antimicrobial [26,27], sensor [20,28], drug delivery, adsorbent, photocatalysis, thermal stability, chromatography, antimicrobial activity, ion selective electrodes and environmental remediation [29–36].

Thus, in this study the synthesis gelatin-tin (IV) phosphate (GT/TPNC) ion exchanger have been reported. It has been characterized by different techniques such as FTIR, XRD, SEM and TEM. GT/TPNC was explored for the separation of heavy metals and photocatalytic degradation of methylene blue (MB). On the basis of distribution studies, GT/TPNC was explored for the fabrication of ion selective electrode for the detection of Co (II) ions in aqueous system.

2. Experimental

2.1. Reagents and instruments

Gelatin (Spectrochem Pvt. Ltd., India), orthophosphoric acid (SD Fine-Chem. Ltd., India), tin (IV) chloride (Sigma-Aldrich, India), sodium chloride, sodium hydroxide, ethylene diamine tetra acetic acid, ammonium chloride, ammonium hydroxide, cu-PAN, phenolphthalein eriochrome black-T were purchased from Hi Media Pvt. Ltd. India. Tetrahydrofuran (THF), cobalt nitrate, nickel nitrate, lead nitrate, cadmium nitrate, aluminium nitrate, copper nitrate, zinc nitrate, magnesium nitrate and poly vinyl chloride (PVC) were purchased from Otto Chemie. Pvt. Ltd. India. All the reagents used in this study are of analytical grade and dilutions were made using double distilled water.

2.2. Instrumentation

FTIR spectrum of GT/TPNC ion exchanger was recorded by Perkin Elmer SpectrumBX, USA using KBr disc method. In this, 10 mg of material was thoroughly mixed with definite amount of KBr and appropriate pressure was exerted to form a transparent disc. The FTIR spectrum of GT/TPNC ion exchanger was recorded in the ranged from 400 to 4000 cm^{-1}. The X-ray diffraction pattern of GT/TPNC was recorded by X'pert Pro Analytical diffractometer. SEM images of GT/TPNC were studied by QUANTA 250 FEI D9393 scanning electron microscope at different magnifications. In TEM analysis, 0.01 mg of material was added to minimum quantity of ethanol to form fine suspension and sonicated in ultrasonic cleaner for 30 min. Then, the drop of suspensions was placed onto a carbon copper grid and analyzed using high resolution transmission electron microscopy Hitachi, H7500, Germany.

2.3. Synthesis of tin (IV) phosphate (TP)

Tin (IV) phosphate was synthesized by mixing 0.1 N tin (IV) tetrachloride and 0.1 N orthophosphoric acid in 1:2 vol ratio with constant stirring at constant temperature. The pH of the solution was adjusted to 0–1 by adding 0.1 N HNO_3. The resulting precipitates were kept overnight in the mother liquor with occasional shaking. Then, the precipitates were filtered and washed with double distilled water to remove the excess of acid. Then, the precipitates were dried at 50 °C in an oven.

2.4. Synthesis of gelatin-tin (IV) phosphate nanocomposite (GT/TPNC) ion exchanger

Gelatin-tin (IV) phosphate nanocomposite ion exchanger was synthesized in two steps. In first step, 0.1 N tin (IV) chloride and 0.1 N orthophosphoric acid were mixed with constant stirring at room temperature in volume ratio 1:2. The pH of resulting mixture was adjusted to 0–1 by adding 0.1 N HNO_3. In the second step, the gel of gelatin was prepared in hot water and added to the precipitates of tin (IV) phosphate (TP) drop wise with continuous stirring. The resultant mixture was stirred for 2 h on a magnetic stirrer. This mixture was kept for digestion for 24 h with occasional shaking. Then the precipitates were filtered and washed with double distilled water several times to remove the impurities. The precipitates of gelatin-tin (IV) phosphate thus obtained were dried at 50 °C in a hot air oven. The dried precipitates were converted into H^+ by adding in 0.1 N HNO_3 solution for 24 h with occasional shaking. Then the precipitates were filtered and washed with distilled water to remove the excess of the acid. Similarly, different samples of GT/TPNC ion exchanger were synthesized and the sample with highest ion exchange capacity was selected for further detail study as shown in Table 1.

3. Physicochemical properties

3.1. Ion exchange capacity (IEC)

The ion exchange capacity of GT/TPNC ion exchanger was investigated by standard column process as discussed earlier [18]. In this process, 0.1 g of nanocomposite in H^+ form was taken in a glass column. 1 M solution of alkali and alkaline earth metal nitrate was used to elute the H^+ ions from the ion exchanger. The flow rate of effluent was adjusted to 0.5 mL/min. The collected effluent was titrated against a standard sodium hydroxide solution using phenolphthalein as an indicator. Ion exchange capacity of GT/TPNC was calculated by formula as given below:

$$\text{Ion exchange capacity (IEC)} = \frac{N \times V}{W}\ \text{meq/g}$$

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

3.2. 2Effect of eluent concentration

The optimum concentration of eluent for complete elution of H^+ ions from GT/TPNC was determined by column method. In this, 250 mL of $NaNO_3$ solution of different concentration (0.3 M, 0.6 M, 0.9 M, 1.2 M, 1.5 M and 1.8 M) were passed through a columns containing 1.0 g of ion exchanger at flow rate 0.5 mL/min. The effluents were collected and titrated against standard NaOH solution [18].

3.3. Elution behavior

In this method, 1.0 g of GT/TPNC ion exchanger in H^+ form was eluted with 0.9 M $NaNO_3$ solution. The effluent was collected in fractions of 10 mL at a flow rate of 0.5 mL/min. Each collected fraction was titrated against standard 0.1 M NaOH solution in order to determine the total amount of released H^+ ions.

Please cite this article in press as: D. Pathania et al., Fabrication of electrically conductive membrane electrode of gelatin-tin (IV) phosphate nanocomposite for the detection of cobalt (II) ions, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.01.009