Chemical Engineering Journal 175 (2011) 8–16

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Heavy-metals separation from industrial effluent, natural water as well as from synthetic mixture using synthesized novel composite adsorbent

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ARTICLE INFO

Article history:
Received 14 September 2010
Received in revised form
31 December 2010
Accepted 5 January 2011

Keywords:
Composite adsorbent
Polyaniline
Ti(IV) tungstate
Characterizations and environmental applications

ABSTRACT

A new amorphous composite cation exchange material has been synthesized at pH 1.0 by sol–gel method. The experimental parameters such as mixing volume ratio, concentration and pH were established for the synthesis of the material. Exchange capacity of the composite material was determined for alkali and alkaline earth metals. The exchanger was characterized on the basis of FTIR, XRD, SEM, TGA and CHNO analysis. This composite material exhibits improved ion-exchange capacity, chemical and thermal stability. It can withstand up to 300 °C with 98% of initial ion-exchange capacity retained. The distribution coefficient studies of metal ions on the composite material were performed in non-ionic, cationic and anionic surfactants systems of varying concentrations. On the basis of distribution coefficient values, the material was found to be selective for Pb(II), Hg(II), Bi(III) and Zr(IV) ions. The limit of detection (LOD) and the limit of quantification (LOQ) for Pb(II) metal ion was found to be 0.85 and 2.85 $\mu g\,L^{-1}$. Some analytically important, selective separations of metal ions have been successfully applied for the analysis of industrial effluent and natural water on the columns of this exchanger.

1. Introduction

Water pollution by heavy metals remains an important environmental issue having a major negative impact on the public health and the ecosystem. It has been reported [1] that in terms of the quantity of water needed to dilute such wastes to drinking-water standards, the annual toxicity of all heavy metals mobilized exceeds the combined total toxicity of the radioactive and organic wastes generated every year. Major contributors to environmental pollution with toxic metals comprises of anthropogenic sources such as galvanization, metallurgical, metal shining, electroplating, mining, power generation, and tannery industries [2]. With regard to heavy metal pollution, there have been growing interests in the development of new ion-exchange materials for the removing of toxic metal ions even in low concentration from the contaminated water. Pure organic and inorganic ion-exchangers have good ion-exchange capacity, yet they suffer from certain drawbacks. One serious limitation encountered with organic resin is its poor thermal and chemical stability (less stable in highly acidic and basic medium) while inorganic ion-exchanger obtained in fine powdery form is not suitable for column studies [3]. To overcome all these drawbacks much attention has been paid to synthesized organic–inorganic composite ion-exchangers because of its excellent ion-exchange capacity, selectivity, chemical and thermal stability. Composite ion-exchangers exhibit very different properties from their original components (organic polymer and inorganic materials). These materials should be considered as next generation composite materials that will encompass a wide variety of applications. They have been used as sorbent [4], ion exchanger [5], catalyst [6] and ion selective electrode [7,8]. In our laboratory a large number of titanium and tungstate based hybrid ion exchangers have been synthesized [9–12] that possessed all such characteristics discussed earlier and are highly selective for toxic metals in the environment.

Surfactants play an important role in modifying the adsorption behaviour of ion exchangers [13]. In aqueous solutions, at concentrations above the CMC values, the cationic and anionic surfactants form micelles which are approximately spherical and dynamic, aggregate with a highly anisotropic interface composed of head groups, counter ions and water between their hydrocarbon cores and the surrounding bulk aqueous phase [14]. In the presence of surfactants, the adsorption of metal ions on the exchange sites is affected by the charge density of the interface.

The present paper reports synthesis, characterization and ion-exchange behaviour of Polyaniline Ti(IV) tungstate cation exchanger and their analytical applications for the removal of toxic metal ions from industrial effluents.

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doi:10.1016/j.cej.2011.01.022

Table 1
Conditions for the synthesis of Polyaniline Ti(IV) tungstate cation exchanger.

S. no.	A ($M L^{-1}$)	B ($M L^{-1}$)	C (%, v/v)	Mixing ratio (v/v/v)	Temperature	pH	Appearance of bead	IEC ($meq g^{-1}$) for Na^+	Yield (g)
T-1	0.25	0.1	–	1:1	25 ± 2 °C	0.5	White granular	0.25	1.68
T-2	0.25	0.1	–	1:1	25 ± 2 °C	1.0	White granular	0.60	1.96
T-3	0.25	0.1	–	1:1	100 ± 2 °C	1.0	White granular	0.40	1.85
T-4	0.25	0.1	10	1:1	25 ± 2 °C	1.5	Green granular	0.35	2.95
T-5	0.25	0.1	10	1:1:1	25 ± 2 °C	0.5	Green granular	0.65	2.33
T-6	0.25	0.1	10	1:1:1	25 ± 2 °C	1.0	Green granular	0.85	2.99
T-7	0.25	0.1	10	1:1:1	100 ± 2 °C	1.0	Green granular	0.70	3.00
T-8	0.25	0.1	10	1:1:1	25 ± 2 °C	1.5	White granular	0.55	3.25

A, sodium tungstate; B, titanium tetrachloride; C, polyaniline; IEC, ion exchange capacity.

2. Experimental

2.1. Materials and methods

2.1.1. Reagents and solutions

The main reagents for the synthesis were aniline, potassium persulphate, titanium tetrachloride, carbon tetrachloride, triton, cetyl trimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) from E-Merck (India), sodium tungstate (CDH, India). All other reagents and chemicals were of analytical grade. A solution of sodium tungstate (0.25 M) was prepared in demineralized water and 1% solution of $TiCl_4$ was prepared in CCl_4 while, 10% solution (v/v) of aniline and 0.1 M potassium persulphate were prepared in 1 M HCl.

2.2. Apparatus

A digital pH meter Elico EL-10 (Elico India) was used for pH measurements. Infrared (IR) spectra were recorded on a Fourier Transform-IR Spectrometer from Perkin Elmer (1730, USA) using KBr disc method. Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA) analysis was carried out by DTG–60 H; C305743 00134, (Schimadzu, Japan) analyzer at a rate of $10\,^{\circ}C\,min^{-1}$ in nitrogen atmosphere. An X' Pert PRO analytical diffractometer (PW-3040/60 Netherlands, Holland with CuKα radiation $\lambda = 1.5418$ Å) was used for X-ray diffraction (XRD) measurement. Scanning Electron Microscope (SEM; LEO, 435 VF) instrument was used for SEM images of the material at different magnifications. CHNO analysis was carried out on Carlo Erba EA1108 (Milan, Italy) elemental analyzer. FAAS measurements were made with a Model GBC-932-Plus flame atomic absorption spectrometer (GBC Scientific, Australia). A temperature controlled shaker (MSW-275, India) was used for shaking. Muffle furnace (Narang Scientific works-India) was used for heating samples at different temperatures.

2.3. Synthesis of Polyaniline Ti(IV) tungstate composite

2.3.1. Synthesis of Ti(IV) tungstate

Inorganic precipitate of Ti(IV) tungstate was prepared by mixing 0.1 M solution of titanium tetrachloride to a solution of sodium tungstate (0.25 M) gradually with constant stirring (using magnetic stirrer) at room temperature for 1 h whereby gel type slurries were obtained. The pH of the solution was maintained by adding dilute HCl or HNO_3 solution. The resulting white precipitate so formed was kept overnight in the mother liquor for digestion.

2.3.2. Synthesis of polyaniline

The polymerization of the monomer aniline was initiated by the addition of potassium persulphate into 10% solution of aniline in 1:1 ratio under constant stirring below 4 °C for 1 h [15]. A dark green gel of polyaniline was obtained.

2.3.3. Synthesis of Polyaniline Ti(IV) tungstate composite

The composite ion-exchange material was prepared by adding gel of polyaniline to the white precipitate of Ti(IV) tungstate in a volume ratio of 1:1 mixed thoroughly with continuous stirring for 1 h at 25 ± 2 °C. The resultant green gel obtained was kept for 24 h at room temperature for digestion. The supernatant liquid was decanted and the gel was filtered under suction. The excess acid was removed by washing with demineralized water and the material was dried in an oven at 50 ± 2 °C. The dried material was grounded into small granules, sieved and converted into H^+ form by treating with 1.0 M nitric acid solution for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess of acid was removed after several washings with demineralized water and finally dried at 50 ± 2 °C in an oven. Thus a number of samples of 'Polyaniline Ti(IV) tungstate' composite were prepared under different condition of mixing ratio, pH and temperature (Table 1). On the basis of better ion-exchange capacity, percentage yield and physical appearance of the beads sample T-6 was selected for detailed studies. The proposed structure of the composite material is shown in Scheme 1.

2.4. Ion exchange capacity

For determination of ion-exchange capacity, one gram of the exchanger in H^+ form was taken into a glass column (internal diameter, 0.5 cm) plugged with glass wool at the bottom. The exchanger was stripped off H^+ ions by allowing alkaline earth metal nitrates solutions (0.1 M) to pass through the column at the flow rate of $1.0\,mL\,min^{-1}$. The H^+ ions content of the effluent was then determined by titrating against a standard solution of sodium hydroxide ($0.1\,mol\,L^{-1}$).

2.5. pH titration

In order to determine the nature of the ionogenic group of Polyaniline Ti(IV) tungstate, pH titrations studies were done by using Topp and Pepper method [16]. In this method 0.5 g of the exchanger in H^+ form was taken in each of several 50 mL conical flasks which are followed by the addition of equimolar solution of alkali and alkaline metal chlorides and their corresponding hydroxides as NaCl–NaOH, KCl–KOH and $CaCl_2$–$Ca(OH)_2$, $BaCl_2$–$Ba(OH)_2$ systems. The final volume was adjusted to 50 mL to maintain the ionic strength.

2.6. Chemical composition

The composition of the sample was determined by dissolving portion of 0.25 g in 15 mL hot concentrated hydrochloric acid. The solution was then cooled and diluted to 100 mL with distilled water. Titanium and tungstate were determined spectrophotometrically using standard procedures [17,18].