Desalination 276 (2011) 175–183

Contents lists available at ScienceDirect

Desalination

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

Pb^{2+} selective and highly cross-linked zirconium phosphonate membrane by sol–gel in aqueous media for electrochemical applications

Shalini Singh [a], Parimal Patel [b], Vinod K. Shahi [a,*], Uma Chudasama [b]

[a] *Electro-Membrane Processes Division, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), G. B. Marg, Bhavnagar-364002, India*
[b] *Applied Chemistry Department, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara-390001, India*

A R T I C L E   I N F O

Article history:
Received 23 November 2010
Received in revised form 4 March 2011
Accepted 16 March 2011
Available online 8 April 2011

Keywords:
Lead selective membrane
Electrodialysis
Selective lead separation
Electrochemical process for lead removal

A B S T R A C T

Zirconium diethylene triamine pentamethylene phosphonic acid (ZrD) was synthesized and showed high adsorption capacity for Pb^{2+}. Cross-linked ZrD nanocomposite Pb^{2+} selective membrane was prepared by sol–gel using poly(vinyl alcohol) (PVA) as plasticizer in aqueous media. Developed ZrD nanocomposite membrane showed good thermal, mechanical and chemical stabilities, which are essential parameters for its durability. Furthermore, conductivity and counter-ion transport studies of these membranes suggested their potential application for separating Pb^{2+} by electrodialysis (ED). Electro-dialytic studies revealed very high Pb^{2+} flux across ZrD membranes in comparison with other bi-valent metal cations (Cu^{2+}, Cd^{2+} and Ni^{2+}). Relatively high retention of Pb^{2+} in the membrane phase was attributed to its controlled cross-linked structural morphologies, and completely intermingled and well connected network between the metal phosphonates and the polymeric backbone. Furthermore, high separation factor (2.0–3.0) for separating Pb^{2+}/Cu^{2+}, Pb^{2+}/Cd^{2+}, and Pb^{2+}/Ni^{2+}, suggested practical applications of developed membrane for electro-dialytic fractionation/removal of Pb^{2+} from industrial waste water.

1. Introduction

The mounting stratum of heavy metals in the environment represents a serious intimidation to the living world including human health, other living resources and ecological systems. Since they are considered to be importunate, hazardous as well as bio-accumulative, proper measures should be taken to remove them from wastewater before discharging [1,2]. Heavy metal species, such as lead, cadmium and mercury have lethal effects on the biological world especially [3]. Pb^{2+}, Cu^{2+}, Cd^{2+}, and Ni^{2+} ions are common pollutants introduced into natural water from variety of industrial wastewaters including those from the textile, leather tanning, electroplating and metal finishing industries [4,5]. The guideline of lead concentration recommended by WHO is less than 10 ppb (ppb = μg dm^3) for drinking water and for environmental water [6]. Particularly, lead is toxic to the brain, kidneys, reproductive system, and cardiovascular system. Exposures can cause impairments in intellectual functioning, kidney damage, infertility, miscarriage, and hypertension [7]. Lead is a special hazard for young children.

Development of sensitive and mature technologies for the removal of lead and other heavy metal ions from aqueous solutions is an important scientific endeavor during recent past years. Several separation methods such as ion exchange resins [8,9], ion selective electrode [10–12], liquid membrane separation [13,14], polymer inclusion membranes [15,16], neutral ionophore based crown ether [17,18], ion exchange membrane based technology [19–21] etc., are available in the literature. But many of these technologies suffered because of poor mechanical strength, low chemical stability, high cost as well as low selectivity or efficiency. Ion exchange membranes are stepping over and above all of them and making a great market boom due to their comparatively high durability, mechanical stability, chemical sustainability, selectivity, ionic conductivity [22] along with their low cost and maintenance expense. Stable and specific metal ion selective membranes with controlled IEC, surface charge density, hydrophilicity/hydrophobicity and porosity, are extremely desirable for the removal of metal ion contamination. Organic–inorganic nanocomposite membranes with fascinating properties like specific chemical reactivity, flexibility, and mechanical and thermal stability, have great potential to solve many problems in separation and purification engineering [23–27].

Recently, attention has been engendered for preparing organic based inorganic ion exchange membranes, because of the compatible properties of organic and inorganic constituents, which make specific ion selective separation membrane. Anchoring of organic units in the backbone of tetravalent metal acid salts is of particular interest, since the resulting material has the added advantage of both its counterparts in terms of IEC as well as thermal and chemical stability [28]. Zr(IV) phosphate has been widely used as a cation exchanger which shows a number of advantages as an ideal host lattice. Tetravalent metals (such as Zr) phosphonate (—H or —OH of $—PO(OH)_3$ groups

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* Corresponding author. Tel.: +91 278 2569445; fax: +91 278 2567562/2566970.
E-mail addresses: vkshahi@csmcri.org, vinodshahi1@yahoo.com (V.K. Shahi).

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doi:10.1016/j.desal.2011.03.048

were replaced by —R (—R=alkyl/aryl)) can also be used as specific ion exchanger for separation processes, because of their close relation with phosphates, ability to retain Pb^{2+}, and controlled structural morphologies [29]. Incorporation of Zr phosphonate into polymer matrix by sol–gel ensures the formation of completely intermingled and connected network between metal phosphonates and polymeric backbone due to proper chemical interaction at the nano-level. This hydrophilic and charged membrane may be cross-linked for better stabilities and used with advantages for the separation of metal ions in aqueous media.

Herein, Pb^{2+} selective ZrD nanocomposite membranes prepared by sol–gel are reported with exceptionally high selectivity towards Pb^{2+} over other bi-valent metal ions. Developed membranes were found to be suitable and efficient for electro-dialytic separation of separation/removal of Pb^{2+} from other metal cations.

2. Experimental

2.1. Chemicals and reagents

Diethylene triamine pentamethylene phosphonic acid (DETPMP), $ZrOCl_2$, HNO_3, Poly(vinyl alcohol) (PVA, Mw: 125 000; degree of polymerization: 1700, degree of hydrolysis: 88%), methanol, formaldehyde, hydrogen peroxide, Na_2SO_4, NaCl etc. of AR grade were received from S.D. fine chemicals, India, and used without any further purification. Deionized (DI) water was used in all experiment.

2.2. Synthesis of Zirconium DETPMP and membrane preparation

ZrD-PVA nanocomposite cation exchange membranes were prepared by a three step methodology: preparation of ZrD gel, sol–gel processing, and chemical crosslinking of —OH groups via formal reaction. ZrD gel was prepared by drop wise mixing aqueous solutions of DETPMP (0.1 M) and $ZrOCl_2$ (0.1 M) at 30 °C under continuous stirring. Obtained white gelatinous precipitate was assessed by FTIR. ZrD–PVA hybrid CEM was prepared by acid catalyzed sol–gel followed by chemical crosslinking via formal reaction. A 10 wt.% of PVA solution was prepared in DI water at room temperature under stirring. ZrD gel (inorganic precursor) of fixed weight percentage was mixed with PVA solution slowly. The solution was stirred at room temperature under acidic conditions for 12 h to obtain a viscous white colored gel. This resulting gel was transformed into thin film of uniform thickness on a clean glass plate and dried under IR lamps at ambient temperature for 24 h followed by vacuum drying at 60 °C for the next 12 h. This film was further crosslinked with formal solution ($HCHO + H_2SO_4$ in 1:1.6 v/v ratios in water) at 60 °C for 2 h. The resulting membrane was washed thoroughly by DI water and conditioned in 1.0 M HCl and NaOH solutions, successively. Finally, the conditioned membrane was stored for further characterization and applications. In this way, membranes with different weight percentage of ZrD were prepared and designated as ZrD-X, where X denotes weight percentage of ZrD (X corresponds to 45, 55 and 65 wt.% of ZrD).

2.3. Instrumental analysis

FT-IR spectra of ZrD were recorded by KBr technique in the range of 4000–400 cm^{-1}, while ATR technique was used for dried membranes with spectrum GX series 49387 spectrometer in the range of 4000–600 cm^{-1}. Scanning electron microscopy (SEM) images of ZrD particles (obtained after drying the ZrD gel) and dried membranes were recorded using a LEO Instruments (Kowloon, Hong Kong) microscope after the gold sputter coatings on desired membrane samples.

The thermal degradation and stabilities of ZrD particles and ZrD composite membranes were investigated using a thermogravimetric analyzer (TGA, Mettler Toledo TGA/SDTA851 with *Star*^{c} software) under N_2 atmosphere with 10 °C/min heating rate with a temperature range from 40 to 600 °C. Differential scanning calorimetry (DSC) measurements of the membranes were carried out in 30–450 °C with 5 °C/min heating rate. The dynamic mechanical stabilities of the hybrid membranes were evaluated by Mettler Toledo dynamic mechanical analyzer 861^{c} instrument with *Star*^{c} software under nitrogen with 10 °C/min heating rate between 30 and 300 °C, to observe the effect of the silica content on membrane mechanical stability.

2.4. Physicochemical and stabilities analysis of ZrD composite membranes

The detailed procedures for the determination of water uptake, dimensional change (swelling %) and ion-exchange capacity (IEC) are reported earlier [30–32].

To explore the stability of these membranes in harsh oxidative, hot aqueous and acidic environment, long-term aging experiments were carried out in respective mediums. The oxidative stability of nanocomposite membranes was evaluated in Fenton's reagent at 80 °C for a specific time period. It served as an accelerated test to simulate the strong oxidative water splitting conditions and membrane degradation by oxiactive radicals [33]. For the hydrolytic stability test, small pieces of membranes were boiled in water for 24 h at 120 °C in a pressurized closed vial. The oxidative and hydrolytic stabilities were evaluated by loss in weight, ion-exchange capacity and physical appearance of the test samples [34]. Membrane stability was also assessed in HCl of different concentrations for a fixed time period, and its swelling parameter was recorded.

2.5. Electrochemical characterizations

The counter-ion transport number in the membrane phase (t_i^m) was obtained by Hittorf method as reported earlier [35,36].

Membrane conductivity measurements for ZrD membranes equilibrated in different electrolytic environment (0.01 M) were carried out using a potentiostat/galvanostat frequency response analyzer (Auto Lab, Model PGSTAT 30, EcoChemie, B.V. Utrecht, The Netherlands). The membranes were sandwiched between two in house made circular electrodes (4.0 cm^2) of stainless steel. Direct current (dc) and sinusoidal alternating currents (ac) were supplied to the respective electrodes for recording the frequency at a scanning rate of 1 μA/s within a frequency range of 10^6 to 1 Hz. The membrane resistances were obtained from Nyquist plots [37].

Electro-osmotic permeability measurements were carried out in a two-compartment cell (25 cm^3), made of acrylic glass and separated by AEM (24.0 cm^2), as reported earlier [38].

2.6. Metal ion adsorption studies

Different electrolytic stock solutions (10 mM) were prepared by dissolving in DI water and batch process for the adsorption was carried out. Dry ZrD particles (0.1 g) were placed in 20 ml solution of different electrolytic content in conical flasks for 24 h at room temperature in a shaker incubator at 100 rpm. Ionic concentrations in the supernatant solution were determined by EDTA titration to estimate the adsorbed amount of ions. Measuring error for the estimation of metal ion concentration was 0.1 mg/l.

2.7. Metal ion transport studies

Schematic diagram of the experimental setup used for metal ion transport studies is depicted in Fig. 1. ED cell is contained of two cell pair of ion-exchange membrane and is divided into five compartments viz., catholyte, anolyte, compartment 1 and 3 (metal ion depleted stream) and 2 (metal ion concentrated stream). All streams were connected through separate tanks to recirculate all streams with the help of