Journal of Hazardous Materials 260 (2013) 313–322

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

Preparation and characterization of 5-sulphosalicylic acid doped tetraethoxysilane composite ion-exchange material by sol–gel method

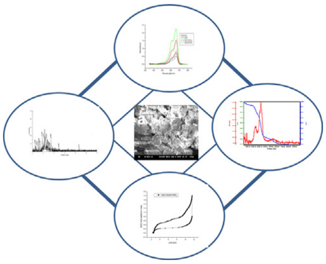
Suhail-ul Rehman, Nasarul Islam, Sozia Ahad, Syed Zeeshan Fatima, Altaf Hussain Pandith*

Department of Chemistry, University of Kashmir, Hazratbal, Srinagar 190 006, J&K, India

HIGHLIGHTS

- Sulphosalicylic acid doped tetraethoxysilane composite is prepared by sol–gel method.
- Its X-ray diffraction studies suggest that it is crystalline in nature.
- This material shows selectivity for Mg(II) and Ni(II) ions in aqueous solutions.
- Separation of Ni(II) from binary mixtures was successfully achieved on this material.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 December 2012
Received in revised form 20 May 2013
Accepted 21 May 2013
Available online 27 May 2013

Keywords:
Ion exchangers
Silicates
Tetraethoxysilane
Sulphosalicylic acid
Maleic acid

ABSTRACT

In this manuscript, we report the preparation and characterization of sulphosalicylic doped tetraethoxysilane (SATEOS), composite material by sol–gel method as a new ion exchanger for the removal of Ni(II) from aqueous solution. The fine granular material was prepared by acid catalyzed condensation polymerization through sol–gel mechanism in the presence of cationic surfactant. The material has an ion exchange capacity of 0.64 mequiv./g(dry) for sodium ions, 0.60 mequiv./g(dry) for potassium ions, 1.84 mequiv./g(dry) for magnesium ions, 1.08 mequiv./g(dry) for calcium ions and 1.36 mequiv./g(dry) for strontium ions. Its X-ray diffraction studies suggest that it is crystalline in nature. The material has been characterized by SEM, IR, TGA and DTG so as to identify the various functional groups and ion exchange sites present in this material. Quantum chemical computations at DFT/B3LYP/6-311G (d,p) level on model systems were performed to substantiate the structural conclusions based ion instrumental techniques. Investigations into the elution behaviour, ion exchange reversibility and distribution capacities of this material towards certain environmentally hazardous metal ions are also performed. The material shows good chemical stability towards acidic conditions and exhibits fast elution of exchangeable H^+ ions under neutral conditions. This material shows remarkable selectivity for Ni(II) and on the basis of its K_d value (4×10^2 in 0.01 M $HClO_4$) some binary separations of Ni(II) from other metal ions are performed.

1. Introduction

The ever increasing economic growth and industrialization has ushered the human civilization into a new era of consumerism and urbanization, thereby posing a severe threat to our environment and ecology. The unabated pollution of our water bodies,

---

* Corresponding author. Tel.: +91 194 2424900; fax: +91 194 2421357.
E-mail address: altafpandit23@gmail.com (A.H. Pandith).

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.05.036

particularly, warrants the development of efficient and cheap methods of analysis and monitoring of pollution levels of these water bodies. Ions of heavy metals such as nickel, copper, lead, and zinc have a significant impact on our aqueous environments. Contamination of aquatic media by heavy metals is a serious environmental problem, mainly introduced into water bodies in the form of effluents from nickel plating plants, silver refineries, zinc industries, storage batteries and oil industry [1–3]. Nickel complexes are mostly soluble in water and, therefore, may be readily absorbed into living organisms. Nickel is the fifth most abundant element in the earth's crust by weight after iron, oxygen, magnesium and silicon, comprising about 3% of the composition of the earth [4]. More recently, nickel is reported to be used in nuclear power plants, gas turbine engines and cryogenic containers [5]. Nickel is a potent carcinogen and causes cancer in lungs, nose, stomach and bone. Prolonged contact of skin with nickel can cause a very painful disease known as nickel itch which may result in sudden death [6]. Several methods such as evaporation, electro-deposition, solvent extraction, reverse osmosis, membrane separation process and activated carbon adsorption have been employed for the removal of heavy metal ions from wastewater [7]. Conventional methods for the removal of Ni(II) from wastewaters include chemical precipitation, chemical reduction, flocculation, filtration, evaporation, solvent extraction, biosorption, activated carbon adsorption, ion-exchange, reverse osmosis, electro-dialysis and membrane separation processes. The chemical precipitation is the most cost-effective treatment technology. The possibility to precipitate metals in the form of insoluble compounds, mostly metal hydroxides, in solutions containing complexing agents depends on the stability constant of the complex and the hydroxide solubility product [8]. A broad range of biomass types including bacteria, algae, yeast, fungi, activated sludge, anaerobic sludge, digested sludge, peat have also been used as bio-sorbents to remove Ni(II) metals from aqueous solution [9–16].

Over the years, hybrid materials have been the objects of considerable interest, because of their excellent chemical and thermal stability and their potential application in the field of environmental analysis and monitoring. Their use in the field of ion exchange, intercalation, catalysis, ionic conductivity and recovery of domestic and industrial wastes from aqueous systems stimulates new research on this class of compounds. Intercalation of organic molecules/polymeric materials into an inorganic host matrix provides new class of hybrid ion exchangers with enhanced ion exchange capacity, high stability, reproducibility, and selectivity for heavy metal ions. These materials may possess improved mechanical strengths, chemical inertness, reproducibility, selectivity and higher stability at elevated temperatures and ionizing radiation fields. Fibrous and membranous hybrid ion exchange materials have found wider applications in chemical analysis and can be produced in many forms such as thin films, conveyer belts and as ion selective electrodes. Recently, organic–inorganic hybrid materials have attracted much interest as intercalation and non-intercalation ion-exchangers and sorbents for applications in chemical analysis, separation processes, and waste cleanup under harsh conditions of pH, temperature and ionizing radiation fields [17–21]. Large number of hybrid materials using organic moieties such as n-butyl acetate [22], acrylonitrile [23], acrylamide[24], polyaniline [25], styrene [26], triethylammonium [27], polymethylacrylate [28], nylon 6-6 [29,30] and EDTA [31] have been synthesized and used in separation, purification and detection of heavy metal ions.

Organic–inorganic hybrid materials prepared by the sol–gel method have rapidly become a fascinating new field of research in material sciences. The explosion of activity in this area in the past decade has made tremendous progress in both the fundamental understanding of the sol–gel process and the development and applications of new organic–inorganic hybrid materials [32–34]. The advantage of sol–gel process is that tailor made size, shape, and charge selective materials having specialized applications in chemical analysis can be easily prepared by simple manipulation of reaction conditions. The sol–gel process has so far been one of the most attractive ways of synthesizing these porous materials because of the mild synthesis conditions. Ion-exchange sites can be incorporated into the inorganic skeleton for the preparation of highly selective sorbents for preferential uptake of metal ions. The mild reaction conditions provide the possibility to incorporate various functionalized moieties and molecules such as proteins, enzymes, dyes, organic and organo-metallic reagents into the inorganic host matrix [35–40]. This is achieved by doping the reagent into the sol prior to its gelation [41] or by using organo-silicon derivatives [42–44]. The materials with enhanced chemical and mechanical stabilities, better optical properties, controlled pore size, and pore size distribution, surface area, and polarity can be prepared in a variety of sizes and shapes, including thin films, monoliths, fibres and powders [45]. In recent past, many new adsorbent and ion exchange materials have been developed for the removal of heavy metal ions such as lead, cadmium and mercury from wastewaters [46–48]. However, to our best information, no major works are reported in the literature regarding the preparation of hybrid ion-exchangers/adsorbents for selective removal of Ni(II) from aqueous solutions.

Therefore, the main motivation of this work has been to synthesize cheap and cost-effective crystalline hybrid composite material, by using the simple synthetic methods, for the removal of nickel from drinking and industrial wastewaters. By using sol–gel method, we have synthesized a new composite material by incorporating 5-sulphosalicylic acid into tetraethoxysilane matrix, which is crystalline in nature and shows improved functionalities in terms of ion-exchange and adsorption behaviour. The material is a relatively low cost ion-exchanger/adsorbent having promising ion exchange/adsorption characteristics. We find that the material is highly selective for Ni(II) absorption from aqueous solutions and, therefore, may have potential applications in the recovery and removal of Ni(II) from aqueous media

2. Materials and methods

2.1. Materials

Tetraethoxysilane and hexadecyltrimethylammonium chloride were obtained from Merck, Germany. Sulphosalicylic acid and ethyl alcohol were obtained from Glaxo Laboratories, India. Other reagents and chemicals were of analytical grade and were used without any further purification.

2.2. Instrumentation

pH measurements were performed using an Eutech Instrument PC 5500. X-ray diffraction spectra were recorded on a Bruker AXS D8 Advance diffractometer. Analysis of C, H, S and N were determined on an Elemental Vario Micro CHNS analyser. IR spectra were recorded on Interspec-2020 FTIR spectrophotometer. Electron micrographs were recorded with a Hitchi-S3000H scanning electron microscope. An incubator shaker Yellow Line OSC with a temperature variation of ±0.5 °C was used for equilibrium studies. Exstar 6000 TGA/DTG instrument from SIINT, Japan was used for thermal studies.

2.3. Synthesis of the ion exchange material

A number of samples of the composite ion exchange material were prepared from silica sol using sol–gel method. The silica sol was prepared from tetraethoxysilane, deionised water, ethanol,