Resource-Efficient Technologies 3 (2017) 317–328

Contents lists available at ScienceDirect

Resource-Efficient Technologies

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

Removal of chlorobenzene and 1,4-dichlorobenzene using novel poly-o-toluidine zirconium(IV) phosphotellurite exchanger ☆

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ARTICLE INFO

Article history:
Received 29 June 2016
Accepted 8 February 2017
Available online 7 March 2017

Keywords:
Poly-o-toluidine
Composite exchanger
Chlorobenzene
Dichlorobenzene
Adsorption

ABSTRACT

Novel hybrid exchanger poly-o-toluidine zirconium(IV) phosphotellurite was synthesized and physicochemical properties of the material were well studied by FTIR, XRD, TGA, SEM-EDX and TEM analysis. The composite exchanger showed good ion exchange capacity and excellent removal potential towards US Environmental Protection Agency listed priority pollutants like chlorobenzene and 1,4-dichlorobenzene. The factors affecting the adsorption like time, pH and temperature were studied in detail using UV spectrophotometry. More than 90% of the pollutants were successfully removed using the exchanger. The composite also showed selectivity towards heavy metal ions, especially mercury ions. The sorption kinetics of the material was studied in detail using pseudo first order and pseudo second order kinetics. The material followed pseudo second order kinetic model indicating chemisorption of the pollutants. The composite can be successfully used for environmental remediation purposes.

1. Introduction

Water is the basic necessity for life but the quality and availability of potable water is decreasing drastically. Water bodies are seriously contaminated by various factors such as heavy metals, noxious chemicals, pesticides and fertilizers, radioactive wastes etc. which are intentionally or unintentionally discharged into it from diverse sources. Adsorption, ion exchange, oxidation, filtration, chemical precipitation, membrane separation, solvent extraction, electrodialysis etc are the various methods adopted for water treatment and purification [1–5]. Among the various pollutants that contaminate water bodies, priority pollutants are a class of compounds of extreme concern. The US Environmental Protection Agency (EPA) has listed 126 pollutants as priority pollutants which include both heavy metals and specific organic compounds. Compounds are categorized under priority pollutants on the basis of their toxicity, degradability, persistence and effect on organisms. This class of pollutants is mainly found in water bodies and possesses high toxicity; hence removal of priority pollutants from water bodies is absolutely relevant [6].

Ion exchange is a simple, attractive and widely used method which has well established its significance in separation science and metal ion recovery. The latest advance in this field is the composite exchangers. Composite exchangers are new class of materials which gained appreciable acceptance by overcoming the major drawbacks of inorganic and organic exchangers. They are materials containing an organic matrix and an inorganic moiety [7]. Applications of composite exchangers include water purification, separation of metal ions, radioactive waste removal, development of fuel cells, ion selective membrane electrodes, catalysis etc [8–10]. Innumerable works has been carried out using newly synthesized composite exchangers and the major application of composite exchangers is their environmental remediation capacity [11]. They are widely used for their ion exchange property and adsorption capacity towards various kind of pollutants. Though water purification has been extensively carried out using composite exchangers, elimination of priority pollutants using composite materials has not been studied much [12]. Only negligible works have been carried out in this area and considering this factor, the newly synthesized exchanger was made used for the removal of priority pollutants.

The hybrid exchanger was studied for its capability to adsorb priority pollutants such as chlorobenzene, 1,4-dichlorobenzene and

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☆ Peer review under responsibility of Tomsk Polytechnic University.

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https://doi.org/10.1016/j.reffit.2017.02.003

mercury ions. Chlorobenzene (CB) and 1,4-dichlorobenzene (DCB) are highly toxic organic compounds and are ranked 7th and 27th in the priority pollutants list. Mercury on other hand is the 10th priority pollutant among the heavy metals [6]. Chlorobenzene is a colorless, flammable liquid widely used in the manufacture of several chemicals such phenol, aniline, nitrochlorobenzene, triphenylphosphene, thiophenol etc. It is primarily used as solvent for paints, resins and is an intermediate in the synthesis of insecticide such as DDT and dyes. Pulp and paper industries, leather tanning industries and chemical industries are the major industries releasing chlorobenzene containing effluents. Inhalation or exposure to CB may cause numbness, muscular spasm and lethal effect on central nervous system.1,4-dichlorobenzene is mainly used as fumigant for the control of moths. It is also used as intermediate for synthesis of dyes, pharmaceuticals, plastics and various other chemicals. They are highly carcinogenic in nature and its toxicity includes mild effects such as headache, nausea, dizziness etc to acute health effects such as damage of liver, kidney, central nervous system etc. Mercury enters water bodies mainly from dental amalgam, thermometer factories, refineries etc. Methyl mercury is the prime organic mercury compound which can enter into food chain and results in biomagnification. It mainly damages the nervous system and is carcinogenic. Elemental mercury is also poisonous since it leads to brain and kidney damage, insomnia, memory loss etc.

Literature review suggests that only few studies have been carried out for the removal and adsorption of chlorobenzene and 1,4-dichlorobenzene. Adsorption of CB using activated carbon has been discussed and the adsorption kinetics has been detailed [13,14]. In another study, carbon nanotubes and graphene has been used for the adsorption of chlororbenzene [15]. Use of other adsorbents such as marine sediments [16] γ-Al_2O_3 has also been reported for the removal of CB [17]. The degradation of 1,4-dichlorobenzene in acetonitrile-water solution has been investigated and reported by Qi Liu et al. [18]. The present study focuses on the synthesis and characterization of novel composite exchanger poly-o-toluidine zirconium(IV) phosphotellurite (POT ZrPTe) and its efficacy in removing priority pollutants from aqueous system. Effect of various parameters that affect the adsorption and the kinetic aspects of removal of the CB and DCB using the proposed composite exchanger has also been studied and discussed.

2. Materials and methods

2.1. Chemicals and reagents

The main chemicals used were Zirconium oxychloride (E. Merck), Sodium tellurite (E. Merck), Sodium orthophosphate (Loba Chemie, India), O-toluidine (Loba Chemie, India), Chlorobenzene (Loba Chemie, India) and 1,4-dichlorobenzene (Loba Chemie, India). All other reagents and chemicals used for the synthesis were of analytical grade. Double distilled water was used throughout the synthesis process.

2.2. Instrumentation

For IR studies, FTIR spectrometer model IR Tracer-100, Shimadzu was used. X-ray diffractometer Rigaku Rint TTR-III for X-ray diffraction studies and Shimadzu DTG-60H was used for thermogravimetric analysis. SEM images were taken using Jeol JSM-7500F and UV-Visible spectrophotometer model JASCO V660 was used for spectrophotometric measurements. The transmission electron micrographs (TEM) of the sample was acquired using a JEOL/JEM-3200FS.

2.3. Synthesis of composite exchanger

2.3.1. Synthesis of poly-o-toluidine

Simple oxidative polymerization technique was used for the polymerization of o-toluidine. 0.4 M ammonium persulfate prepared in 4.0 M HCl was continuously added to 10% o-toluidine prepared in 2.0 M HCl with stirring using a magnetic stirrer for 2 hours at 0 C till a dark green colored gel was obtained. The gel obtained was kept for 24 hours at 0 C [19].

2.3.2. Synthesis of zirconium(IV) phosphotellurite

For the synthesis of inorganic part zirconium(IV) phosphotellurite, 0.05M solution of sodium orthophosphate and sodium tellurite were mixed vigorously by constant stirring maintaining the pH in acidic range. The clear solution formed was then added to 0.05M aqueous solution of zirconium oxychloride until a white gelatinous precipitate was formed. The slurry was kept for digestion for 24 hours at room temperature.

2.3.3. Synthesis of poly-o-toluidine zirconium(IV) phosphotellurite composite (POT ZrPTe)

The ex-situ polymerized gels of poly-o-toluidine were added to the white gelatinous inorganic precipitate of zirconium(IV) phosphotellurite carefully with constant stirring at room temperature until a green colored thick slurry was formed . The slurry was then kept for digestion at room temperature. The gel was filtered and the excess acid was removed by continuous washing with demineralized water (DMW). The filtered out material was dried in an air oven at 30 C. After drying, the material was converted to H^+ form by keeping it in 1.0 M HNO_3 solution for 24 hours with occasional shaking, intermittently replacing the supernatant liquid with fresh acid. The excess acid was again removed using DMW and then dried at 30 C and kept in desiccator.

2.4. Ion exchange capacity (IEC)

Column method was used for the determination of ion exchange capacity [20]. A glass column of 1.1 cm diameter plugged with cotton wool at the bottom was taken, to which 1g of the material in H^+ form was added. 100 mL of 1.0 M NaCl solution was poured to it in order to elute the H^+ ions from the exchanger, maintaining the flow rate at 1 mL min^{-1}. The H^+ ion content in the effluent was then determined by titrating it against a standard solution of 0.05M NaOH solution. From the titre value, the ion exchange capacity in meqg^{-1} was calculated using the relation,

$$\mathrm{IEC} = \mathrm{av/w}$$

where a and v are the molarity and volume of NaOH used during titration and w is the weight of the exchanger taken [20].

2.5. Distribution studies

Distribution coefficient, K_d is defined as the ratio of the concentration of a metal ion in the exchanger and in the solution [20]. Distribution coefficient of the composite exchanger for various metal ions in DMW was studied by batch method [21]. For this, 0.1 g of the exchanger was equilibrated with 20 mL of the metal ion solutions for 24 hours at room temperature. The metal ion concentration before and after sorption were determined by complexometric titration against standard EDTA solution. In the complexometric method, the K_d values were calculated using the formula,

$$K_d = \frac{(I - F)}{F} \times \frac{V}{W}$$