Chemosphere 167 (2017) 44–52

Contents lists available at ScienceDirect

Chemosphere

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

Allyl triphenyl phosphonium bromide based DES-functionalized carbon nanotubes for the removal of mercury from water

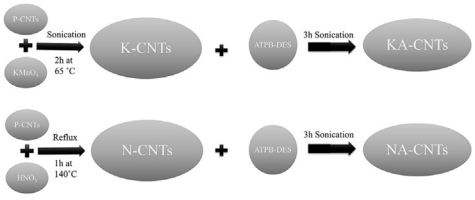
Mohamed Khalid AlOmar [a, b], Mohammed Abdulhakim Alsaadi [b, c, *], Maan Hayyan [a, b], Shatirah Akib [d], Muhammad Ibrahim [c], Mohd Ali Hashim [b, e]

[a] Department of Civil Engineering, University of Malaya, Kuala Lumpur, 50603, Malaysia
[b] University of Malaya Centre for Ionic Liquids (UMCiL), University Malaya, Kuala Lumpur, 50603, Malaysia
[c] Nanotechnology & Catalysis Research Centre (NANOCAT), IPS Building, University of Malaya, 50603, Kuala Lumpur, Malaysia
[d] School of Energy, Geoscience, Infrastructure and Society (EGIS), Heriot-Watt University Malaysia, 62200, Putrajaya, Malaysia
[e] Department of Chemical Engineering, University of Malaya, Kuala Lumpur, 50603, Malaysia

HIGHLIGHTS

- Deep eutectic solvents were used as functionalization agents of CNTs.
- The DES-CNT combination utilized as a novel Hg^{2+} adsorbent.
- The DESs-CNTs adsorbent were characterized by various instrumental methods.
- The effect of operation parameters is optimized utilizing RSM methodology.
- Adsorption isotherm and kinetics were comprehensively investigated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 June 2016
Received in revised form
24 September 2016
Accepted 26 September 2016

Handling Editor: T. Cutright

Keywords:
Deep eutectic solvents
Carbon nanotubes
Functionalization
Mercury adsorption
Ionic liquids

ABSTRACT

Recently, deep eutectic solvents (DESs) have shown their new and interesting ability for chemistry through their involvement in variety of applications. This study introduces carbon nanotubes (CNTs) functionalized with DES as a novel adsorbent for Hg^{2+} from water. Allyl triphenyl phosphonium bromide (ATPB) was combined with glycerol as the hydrogen bond donor (HBD) to form DES, which can act as a novel CNTs functionalization agent. The novel adsorbent was characterized using Raman, FTIR, XRD, FESEM, EDX, BET surface area, TGA, TEM and Zeta potential. Response surface methodology was used to optimize the removal conditions for Hg^{2+}. The optimum removal conditions were found to be pH 5.5, contact time 28 min, and an adsorbent dosage of 5 mg. Freundlich isotherm model described the adsorption isotherm of the novel adsorbent, and the maximum adsorption capacity obtained from the experimental data was 186.97 mg g^{-1}. Pseudo-second order kinetics describes the adsorption rate order.

1. Introduction

Mercury (Hg) is a heavy metal which exists in liquid or vapour phase at room temperature. It is considered to be one of the most toxic element in nature. It mainly affects the neurologic,

* Corresponding author. Nanotechnology & Catalysis Research Centre (NANOCAT), IPS Building, University of Malaya, 50603, Kuala Lumpur, Malaysia.
E-mail address: mdsd68j@gmail.com (M.A. Alsaadi).

http://dx.doi.org/10.1016/j.chemosphere.2016.09.133
0045-6535/

gastrointestinal (GI), and renal organ systems. Hg can be found in three forms, specifically metallic element, organic salt, and inorganic salt (Goldman et al., 2001). This element also exists in seawater, fresh water, and soil (Keating, December 1997). It is extremely hazardous, even at low concentrations, and hence the maximum allowable concentration of Hg in water, according to the World Health Organization (WHO), is 1 μg L^{-1} (Mohan et al., 2001), Different techniques have been utilized to decrease Hg concentrations in water. Examples include solvent extraction, precipitation, ion-exchange, reverse osmosis, membrane separation, coagulation, and photoreduction. However, most of these methods require either high-energy or a large quantities of chemicals (Zhang et al., 2005b). Adsorption processes have been commonly applied in industrial applications, and are consequently the most studied technique for Hg removal from water (Chiarle et al., 2000).

Carbon nanotubes (CNTs) have been shown to be an excellent adsorbent for many pollutants (Ibrahim et al., 2016), including cadmium (Ruthiraan et al., 2015), zinc (Mubarak et al., 2013), lead (Li et al., 2002), cupper (Mubarak et al., 2015), 1,2-dichlorobenzene (Peng et al., 2003), fluoride (Li et al., 2003), and trihalomethanes (Lu et al., 2005). However, despite all the extraordinary physicochemical properties of CNTs, they have many flaws with regards to solubility, aggregation, and difficulty of manipulation. On the other hand, CNTs have shown a great affinity for interaction with different compounds (Andrews et al., 2002; Sun et al., 2002; Lin et al., 2003; Hirsch and Vostrowsky, 2005; Mubarak et al., 2014; Ihsanullah et al., 2016) . Consequently, the need for new types of economical and environmentally friendly functionalization agents is crucial in many applications (Martínez et al., 2003; Hayyan et al., 2015).

Recently, deep eutectic solvents (DESs) have gain great interest, owing to their involvement in many applications (Smith et al., 2014). DESs are involved in nanotechnology through many approaches, such as media for synthesis of nanoparticles (Chen et al., 2013; Chakrabarti et al., 2015; Jia et al., 2015; Xiong et al., 2015; Karimi et al., 2016; Xu et al., 2016), electrolyte in nanostructure sensors (Zheng et al., 2014), and electrolyte in nanoparticle deposition (Abbott et al., 2009, 2012; Gu and Tu, 2011; Wei et al., 2012a; Wei et al., 2012b, 2013; You et al., 2012; Guo et al., 2014; Renjith et al., 2014).

In this work, we introduce novel Hg^{2+} adsorbent based on DES-functionalized CNTs. Allyl triphenyl phosphonium bromide (ATPB) based DES was successfully synthesized by using glycerol (Gly) as the hydrogen bond donor (HBD). Subsequently, the novel DES/CNT combination was characterized using Raman spectroscopy, XRD diffraction, FTIR, FESEM, TEM, EDX, TGA, BET surface area, and zeta potential. An optimization study was performed using Response surface methodology (RSM) to optimize the removal conditions for Hg^{2+} adsorption. Moreover, kinetics and isotherm studies were also performed according to the potential optimal conditions.

2. Experiment

2.1. Chemicals and materials

MWCNTs with specifications of D × L 6–9 nm × 5 μm ˃95% (carbon) were supplied by SIGMA-ALDRICH. Gly, nitric acid (65%), potassium permanganate, sodium hydroxide pellets, and hydrochloric acid (36.5–38%) were also supplied by SIGMA-ALDRICH. ATPB and 1000 mg L^{-1} mercury standard solution was supplied by MERCK.

2.2. Functionalization of CNTs

Two types of primary oxidation were performed to oxidize the surface of the pristine CNTs (P-CNTs). The first involved sonication with $KMnO_4$ for 2 h at 65 °C (AlSaadi et al., 2016). The resulting oxidized CNTs are referred to as K-CNTs in this study. The second method involved refluxing with HNO_3 (65%) for 1 h at 140 °C, and the resulted acidified CNTs are referred to as N-CNTs in this study.

The DESs were synthesized by mixing ATPB with Gly (HBD) using magnetic stirring at 400 rpm and 80 °C until the DES became homogeneous liquid without any visual precipitate. The details of synthesis, characterization, and choosing of molar ration is based on our previous study (AlOmar et al., 2016c). Next, functionalization with DESs was performed by sonicating 200 mg of P-CNTs, K-CNTs, and N-CNTs separately with 7 ml of DES for 3 h at 65 °C. The resulting functionalized CNTs are referred to as PA-CNTs, KA-CNTs, and NA-CNTs, respectively. It should be noted that after each functionalization step, the functionalized CNTs were repeatedly washed and filtered using a vacuum pump and a PTFE 0.45 μm membrane with distilled water until the filtrate water pH was neutral.

2.3. Characterization of functionalized CNTs

To obtain Raman shift spectra, all adsorbents were characterized using Raman spectroscopy (Renishaw System 2000 Raman Spectrometer). Fourier transform infrared (FTIR) spectroscopy, via a PerkinElmer® FTIR spectrometer, was used to study the surface modifications and functional groups that resulted from the functionalization processes. The structure phases were analyzed using an X-ray powder diffraction (XRD) Shimadzu XRD 6000. Furthermore, the surface charge was measured by conducting zeta potential tests using a Zetasizer (Malvern, UK). A fully Automated Gas Sorption System (micromeritics ASAP2020, TRISTAR II 3020 Kr) was used to study the selected samples surface area, based on the method of Brunauer-Emmett-Teller (BET). A Field-Emission Scanning Electron Microscope (Quanta FEG 450, EDX-OXFORD) was used to obtain high resolution nano-sized images for studying the morphology of all selected samples, along with an energy-dispersive X-ray spectrometer (EDX). The functionalization effect on the CNTs layers was explored using Transmission electron microscopy (TEM). Finally, the effect of thermal oxidation was investigated using thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) with a Thermal Analyzer (STA-6000, PerkinElmer®).

2.4. Adsorption experiments

Initially, 10 mg of P-CNTs, K-CNTs, N-CNTs, PA-CNTs, KA-CNTs and NA-CNTs were individually added to 50 ml of Hg^{2+} stock solution at a concentration of 5 mg L^{-1}, in a 250 ml flask. The screening study was carried out at two pHs, 2.0 and 6. The flasks were placed in a mechanical shaker system for 30 min at room temperature at a shaking speed of 180 rpm. The adsorbent with the highest removal percentage was chosen for further studies.

3. Result and discussion

Fig. 1 plots the removal percentage of each adsorbent according to the primary screening study. The results demonstrated that functionalization with ATPB-based DES significantly increases the removal percentage at both pH (2.0 and 6.0). The removal percentage increased with increasing pH, indicating that removal may be pH dependent. KA-CNTs achieve the highest removal percentage compared to the other adsorbent.