Journal of Molecular Liquids 220 (2016) 142–149

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Application of polyrhodanine modified multi-walled carbon nanotubes for high efficiency removal of Pb(II) from aqueous solution

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ARTICLE INFO

Article history:
Received 20 January 2016
Received in revised form 1 April 2016
Accepted 16 April 2016
Available online xxxx

Keywords:
MWCNTs
Polyrhodanine
Adsorption
Pb(II) ion removal
Thermodynamics

ABSTRACT

In the present work, multiwall carbon nanotubes (MWCNTs)/polyrhodanine nanocomposite was fabricated through one-step chemical oxidation polymerization. The synthesized nanocomposite was characterized by using Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). In addition, the adsorption performance of MWCNTs/polyrhodanine toward Pb(II) ions removal from aqueous solution was explored. Factors influencing the uptake of Pb(II) ions including solution pH, initial concentration of Pb(II) ions, contact time and temperature were investigated systematically in batch experiments. The adsorption isotherm of Pb(II) onto MWCNTs/polyrhodanine fitted well to both Langmuir and Freundlich isotherm models and from the Langmuir isotherm, the maximum monolayer adsorption capacity was found to be 8118 mg/g. The rate of Pb(II) adsorption encountered a rise with increasing solution temperature and followed the pseudo second-order kinetics, suggesting that the adsorption mechanism might be a chemisorption process. Various thermodynamic parameters, such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were calculated and the obtained values demonstrated that adsorption was spontaneous and endothermic in nature.

1. Introduction

Metallic elements are generally classified into two groups: ions playing essential roles in the function of living organisms such as iron and calcium, and those that are poisonous or nonessential such as mercury and lead. Toxic metals are not metabolically degradable and their accumulation in living tissues can cause death or serious health problems [1]. In this regard, Lead is a cumulative, non-biodegradable general poison which has the ability to replace with the calcium in bones and has a long-term maintenance in living organisms, this is one of the most insidious effects of inorganic lead [2]. The main sources of Lead in wastewater are battery manufacturing, activities involving arts and crafts, peeling paint, and renovations resulting in dust or fumes from paint [3].

In order to both decrease the amount of metal-containing wastewater generated by industrial activities and improve the quality of treated effluents, various methods for the treatment of lead-containing wastewater have been developed in recent years. Treatments, such as chemical precipitation, coagulation–sedimentation, ion exchange, membrane filtration and adsorption onto proper adsorbent have been employed to remove heavy metals from contaminated wastewater, each with their own advantages and limitations in application [1]. Among all the wastewater treatment methods, adsorption is considered quite attractive due to its easy handling, low operational costs and improved selectivity for specific metals ions [4]. Adsorbents are either of natural origin or engineered. Natural or low-cost adsorbents might be interesting due to their low prices, but their adsorption capacities are much lower than engineered adsorbents and are limited to very specific applications [1,4]. Various materials have been used for removal of Pb(II) ions, including natural zeolite [5], activated carbon [6,7], fly-ash [8], chitosan [9], biomass [10] MWCNTs [11], etc. The above mentioned adsorbents were used in raw state or with modified surface.

Carbon nanomaterials including active carbon, carbon nanotubes (CNTs) and fullerenes, are studied extensively in terms of potential applications in environmental remediation applications. In this sense, CNTs, in particular, are considered as promising materials for use as adsorbents in adsorption technology [12].

Since their discovery in 1991, CNTs have opened up a new chapter in carbon chemistry because of their unique properties such as high thermal and electrical conductivities, high strengths, and high stiffness [13]. CNTs have cylindrical pores, which makes their adsorption potential significantly higher than that of other materials with slit-shaped pores of the same dimension. Furthermore, CNTs are highly graphitized with an aromatic surface structure and a high density of π electrons. Considering these factors, it is expected that CNTs can adsorb molecules more strongly than activated carbon [12,14,15].

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http://dx.doi.org/10.1016/j.molliq.2016.04.065
0167-7322/

Combination of excellent properties of CNTs with high structural flexibility of polymers leads to the formation of high-efficiency CNTs/polymer nanocomposites with multi-functional properties [16,17]. However, formation of aggregates and poor interaction between CNTs and the polymer matrix had severely limited the full reinforcing potential of CNTs [13,14,18]. Presence of electrostatic interaction and van der Waals forces results in particle agglomeration, which induces defect sites in the composite and drastically weakens the composites. Thus, in order to achieve the highest reinforcing efficiency, these problems needed to be resolved [19–21]. Mechanical approaches such as ultrasonication and high shear mixing and surface chemical modification of CNTs with surfactants can significantly enhance the adhesion characteristics and improve the compatibility of CNTs with the target medium [21–23]. The physically adsorbed surfactant on the surface of CNTs s reduces the surface tension and prevents agglomeration [24,25].

Several studies have focused on the improvement of the adsorption capacity of CNTs based adsorbents toward metal-containing aqueous solutions. Kosa et al. [26] used MWCNTs modified by 8-HQ to enhance the adsorption and removal efficiency of Cu(II), Pb(II), Cd(II) and Zn(II) ions from aqueous solutions. Additionally, Shao et al. [27], reported due to strong affinity of polyaniline (PANI) functional groups (amine and imine) with Pb(II) ions, the adsorption capacity of MWCNTs composite toward Pb(II) ions enhanced after Aniline molecules were polymerized on MWCNTs and formed (PANI)/MWCNTs composite. Also, MWCNTs was used for the synthesis of MWCNT/Al_2O_3 composites for lead removal through batch and fixed-bed sorption experiments, in which, the coated nanotubes exhibit better removal ability over uncoated [28]. Therefore, searching for new promising adsorbents with high adsorption capacities and efficiencies have been the aim of many researchers.

In the present work, poly vinyl pyrrolidone (PVP) doped MWCNTs/polyrhodanine nanocomposite was prepared by one-step chemical oxidation polymerization. Polyrhodanine is a less-known conductive polymer which possess strong metal binding sites (one nitrogen, two sulfur and one oxygen) in its structure [29]. This makes it a proper candidate for antimicrobial [30], antibacterial [31] and anticorrosion applications [32] and as a scaffold in drug delivery. Both polyrhodanine and CNTs have the capability to be applied as adsorbents in separation processes [33]. Hence, the adsorption performance of poly (vinyl pyrrolidone) doped MWCNTs/polyrhodanine nanocomposites for the removal of Pb(II) from aqueous solution was evaluated. The isotherm, kinetic and thermodynamic of the Pb(II) adsorption onto the MWCNTs/polyrhodanine nanocomposite have also been investigated.

2. Materials and methods

2.1. Chemicals

All chemicals used in the experiments were of analytical grade. Multi-walled carbon nanotubes (MWCNTs) with purity 95% and outer diameter of 10–20 nm were purchased from US Research nanomaterials Inc. (United States). Potassium permanganate ($KMnO_4$) (99%) was purchased from Chadwell Heath Essex England. Rhodanine (97%), PVP and lead nitrate $Pb(NO_3)_2$ were all obtained from Merck, Germany. $Pb(NO_3)_2$ was used to prepare Pb(II) stock solution of 1000 mg/L. Further, lead solutions of different initial concentrations were prepared by diluting the stock solution to the desired concentrations. HCl and NaOH were used to adjust the initial pH of the solutions.

2.2. Synthesis of CNTs/polyrhodanine nanocomposite

0.15 g of Rhodanine monomer was added to 50 mL of deionized water and stirred. Along with stirring, the mixture was heated slowly until Rhodanine monomers, which are insoluble in water at room temperature, completely dissolve (usually occurs between 60–70 °C). After that, the solution was left to cool down to about 35–40 °C. In order to prevent aggregation and adherence phenomena, prior to polymerization, 0.2 g of MWCNTs was sonicated with 0.1 g of PVP in 20 mL deionized water for 30 min. PVP is a polymeric surfactant which tends to wrap or twist around CNTs due to its flexible or semi-flexible backbones and as a result debundles CNTs via steric or electrostatic repulsions. The prepared solution was added to the solution containing Rhodanine. Then, the oxidant solution consisting of 0.5 g $KMnO_4$ dissolved in 30 mL deionized water was added drop wise. The in-situ-oxidative polymerization of Rhodanine with MWCNTs was carried out at room temperature for 20 h under constant stirring on a magnetic stirrer. The product was washed thoroughly with deionized water several times to remove the traces of reactants and polyrhodanine oligomers. Finally, the prepared nanocomposites was dried in an oven at 50 °C for 24 h and stored for further experiments.

2.3. Characterization techniques

The surface functional groups of prepared materials were investigated using Fourier transform infrared (FT-IR) spectroscopy (Bruker Tensor 27, Germany) in the frequency range of 4000–400 cm^{-1} by pelletizing a homogenized powder of the synthesized particles and KBr. The Transmission electron microscope (TEM) images were taken using a Zeiss EM10C (Germany) with an accelerating voltage at 80 K.

2.4. Adsorption studies

In order to study the adsorption performance of MWCNTs/polyrhodanine nanocomposite for Pb(II) cations, the influence of effluent pH, initial concentration, contact time and temperature, a series of experiments were performed using batch equilibration technique. Before adsorption, 1598.45 mg of $Pb(NO_3)_2$ (as a source of Pb(II)) was dissolved in distilled water in 1 L volumetric flask up to the mark to obtain stock solution of 1000 mg/L. Further, different concentrations of Pb(II) solution were prepared from stock solution by appropriate dilutions. Adsorption process accomplished by mixing 10 mg of adsorbent with 40 mL of Pb(II) solutions with the required concentration (50–500 mg/L) in 125 mL glass tubes with good sealed plastic screw cap on a shaker, operating at 300 rpm for 2 h at room temperature. After shaking for 2 h, which was determined as the adequate time to ensure equilibration, the sorbents were separated from the resultant solutions through simple filtration, and the residual concentration of Pb(II) was determined by ICPS-7000 sequential plasma spectrometer. All experiments were performed in triplicate, and the mean values were reported. The removal efficiency and adsorption capacity of MWCNTs/polyrhodanine nanocomposites were calculated using the following expressions:

$$\%RE = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \tag{2}$$

where RE is the absorptivity (%), Q_e is the MWCNTs/polyrhodanine equilibrium adsorption capacity in mg (metal ions)/g (adsorbent), V is the metal ions solution volume in L, m is the weight of adsorbent in g and C_0 and C_e are the concentrations of metal ions before adsorption and at equilibrium, respectively, both in mg/L.

Generally, adsorption capacity is affected by several operational factors such as solution pH, initial ion concentration, contact time and temperature [4]. In this study, the effects of these factors on lead adsorption with MWCNTs/polyrhodanine were examined, and the results were presented.