Journal of the Taiwan Institute of Chemical Engineers 000 (2016) 1–10

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Tartaric acid modified graphene oxide as a novel adsorbent for high-efficiently removal of Cu(II) and Pb(II) from aqueous solutions

Zhi-Hang Wang[a,1], Bao-Yu Yue[a,1], Jie Teng[b,1], Fei-Peng Jiao[a], Xin-Yu Jiang[a], Jin-Gang Yu[a,*], Ming Zhong[c], Xiao-Qing Chen[a]

[a] *College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China*
[b] *College of Materials Science and Engineering, Hunan University, Changsha, Hunan 410082, China*
[c] *School of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang, Hunan 414006, China*

ARTICLE INFO

Article history:
Received 1 March 2016
Revised 18 May 2016
Accepted 18 June 2016
Available online xxx

Keywords:
Graphene oxide
Tartaric acid
Functionalization
Adsorption
Copper
Lead

ABSTRACT

A novel adsorbent, tartaric acid modified graphene oxide (GO-TA), was successfully prepared by a simple esterification reaction and applied to remove Cu(II) and Pb(II) metal ions from aqueous solutions. The obtained composites were characterized by Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM). Batch experiments were carried out to investigate the effect of pH value, contact time, concentration of metal ions and temperature on Cu(II) and Pb(II) adsorption. The maximum adsorption capacities for Cu(II) and Pb(II) are 374.53 mg g^{-1} and 125.63 mg g^{-1}, respectively, which were higher than those of pristine graphene oxide (GO). The obtained experimental data showed a good correlation with the Langmuir adsorption model. The adsorption kinetics of Cu(II) and Pb(II) onto GO-TA composite was found to be well fit for the pseudo-second-order model. Moreover, thermodynamic parameters including $\Delta G^{\theta} < 0$, $\Delta H^{\theta} > 0$ and $\Delta S^{\theta} > 0$, indicating that the adsorption of Cu(II) and Pb(II) onto GO-TA composite was spontaneous and endothermic in nature. All these results indicated that GO-TA composite with such high adsorption efficiency and fast adsorption equilibrium could be used to clean up heavy metal pollution in the future.

1. Introduction

The presence of toxic heavy metals in water is mainly caused by mining, metallurgy, electroplating, landfill and other related industries. As one of the major environmental concerns, the water contamination from heavy metal pollutants has a profound effect on the whole society and people's life [1,2]. Due to the non-biodegradabilility and the good chemical stability, heavy metal ions are easy to accumulate in the organisms, which have already produced undesirable effects on human health and ecological environment [3]. As time goes on, increasing attention has been given to monitor and process these compounds due to their highly toxic properties.

Two of the most toxic contaminants of water bodies, copper (Cu) and lead (Pb), are included in the class of heavy metal pollutants. The excessive indigestion of the Cu or Pb contaminated water may cause symptoms such as pain, vomiting, cramps, convulsions or more serious toxicological problems such as death [4]. To remove these heavy metal ions from wastewater, various treatment technologies such as chemical precipitation [5], filtration [6,7], ion exchange [8–10], adsorption [11,12], coagulation [13,14], flocculation [15] and electroflotation [16,17] have been developed and used in practical applications. Especially, the adsorption technologies have received more and more attention in recent years due to their wide availability, low cost and high efficiency [18–21]. The immobilization of divalent metal ions by various adsorbents has been extensively investigated [22–28]. Among these adsorbents, the carbon-based nanomaterials are believed to be one of the most widely used adsorbents due to their extensive porosity and large surface area [29, 30]. Specially, carbon nanomaterials functionalized with sulfonic groups (SO_3H–) or with carboxylic acid groups (–COOH) would exhibited relatively better adsorption capacities because of the coordination effects between the metal ions and the introduced functional groups [31–33]. That is to say, if proper building blocks are chose and modified rightly onto carbon nanomaterials to tune the coordination interactions, it is possible to enhance the adsorption performance of the adsorbents for metal ions [34,35].

In the previous work, we have investigated the removal of copper ions [Cu(II)] using the synthesized tartaric acid modified CNT

---

[*] Corresponding author. Tel./fax: +86 731 88879616.
E-mail address: yujg@csu.edu.cn (J.-G. Yu).

[1] These three authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jtice.2016.06.018
1876-1070/© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

(CNT-TA) composite. Compared with pristine CNTs, oxidized CNTs and other adsorbents, CNT-TA composite showed better performance to adsorb and retain Cu(II) from aqueous solutions because the plentiful carboxyl groups on its surface could provide more coordination sites for Cu(II) [12,36]. Based on the research we have done before, we designed and implemented TA modified GO (GO-TA) composite for more efficient Cu(II) and Pb(II) adsorption. The present study is an extension of our research on the possible use of TA-based nanocomposites as available adsorbents for divalent metals removal. The main objective of our work is to investigate the kinetic, thermodynamic and equilibrium models of Cu(II) and Pb(II) removal by GO-TA composite. The characterization of GO-TA composite was described to evaluate the synthetic effectiveness.

2. Experimental

2.1. Materials

Natural flake graphite was purchased from Nantong Xianghai Carbon Product Co., Ltd. Sulfuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4, 85%), hydrogen peroxide solution (H_2O_2, 30%), hydrochloric acid (HCl, 37%), 1-Ethyl-3-(3-dimethylamino-prophy) carbondiimide hydrochloride (EDC•HCl) and dimethylaminopyridine (DMAP) were obtained from Sinopharm Chemical Reagent Co., Ltd. N,N-dimethyl formamide (DMF) was supplied by Chingsun Specialty Products Co., Ltd. Tartaric acid (TA) was provided by Tianjin Kemiou Chemical Reagent Co., Ltd. Copper nitrate ($Cu(NO_3)_2$ •$3H_2O$) and $Pb(NO_3)_2$ were purchased from Tianjin Fuchen Chemical Reagent Factory, which are analytical grade and used without further purification.

2.2. Preparation of GO-TA composite

GO was prepared by a modified Hummer's method. In a typical reaction, 0.3 g of graphite and 1.5 g of $KMnO_4$ were added into a round-bottom flask (100 ml). Then, 36 ml of concentrated H_2SO_4 and 4 ml of H_3PO_4 was blended and added slowly into the above mixture. The dark green solution was heated to 50 °C and stirred for 12 h. The reaction was then cooled to room temperature, and 30% H_2O_2 (0.6 ml) was added in the reaction to reduce the residual $KMnO_4$. After that, the mixture was centrifuged (8000 rpm for 20 min) and the supernatant was decanted away. Furthermore, the solid residue was washed in succession with HCl (1.0 mol l^{-1}) and water for at least three times, respectively. Finally, the solid residue was freeze-dried at -50°C to obtain GO which is sponge-like layer.

The experimental procedure for preparing GO-TA composite could be indicated as follows: 0.5 g of the as-prepared GO, 2.0 g of TA, 0.11 g of DMAP and 2.0 g EDC•HCl were dispersed in 50 ml of anhydrous DMF and then sonicated for 10 min to form a colloidal suspension, which was kept stirring at 50 °C for 37 h. After that, it was centrifuged and the residue was harsh washed with deionized water and diluted hydrochloric acid (0.5 M) for several times. The final products of GO-TA composite were freeze-dried at −50 °C for 36 h, and then stored in desiccator for further experiments.

2.3. Characterization methods

The morphology of the as-obtained products was observed by TEM images acquired from a Jeol JEM-2100 200 kV high-resolution transmission electron microscopy (HR-TEM). Fourier transform infrared (FTIR) spectroscopy was measured in the wavenumber range of 4000–400 cm^{-1} on a Thermo-Nicolet Nexus 670 FT-IR spectrometer. Raman spectra of GO-TA composite was measured using a Renishaw Micro-Raman System 2000 Spectrometer operated at the argon laser wavelength of 514.5 nm. The concentrations of metal ions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) on an Optima 8300 ICP-OES Spectrometer. And the pH values of the solutions were measured on a HI5222 pH Meter.

2.4. Adsorption studies

The two stock solutions of Cu(II) and Pb(II) were prepared by dissolving the appropriate amount of $Cu(NO_3)_2$•$3H_2O$ and $Pb(NO_3)_2$ in deionized water, respectively. To perform the adsorption kinetic studies, adsorption experiments were carried out by adding 0.0020 g of GO-TA composite with 20 ml (concentration of 50 μg/ml for Cu(II) and 25 μg/ml for Pb(II)) solution in 50 mL conical flasks at 25°C with a contact time ranging from 0 h to 1.5 h. The conical flasks containing these mixtures were shaken at 200 rpm in a thermostatic shaker. After that, the mixtures were filtered through a 0.45 μm pore size membrane at specific time intervals. Finally, the remaining Cu(II) or Pb(II) concentration was obtained by ICP-AES.

The isotherm-models analysis on adsorption of Cu(II) or Pb(II) onto GO-TA composite from aqueous solution was investigated. 20 ml of Cu(II) or Pb(II) solutions with six different initial concentrations of 10 μg/ml to 100 μg/ml were added into a conical flask (50 ml), then 0.0020 g of GO-TA composite was added. The adsorption was conducted for 1.5 h at 25 °C, 35 °C and 45 °C, respectively. After the adsorption, the concentrations of Cu(II) or Pb(II) solutions were measured by ICP-AES.

The adsorption capacity (q_e, mg g^{-1}) and the adsorption percentage [$R(\%)$] were obtained from Eqs. (1) and (2), respectively.

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where V is the volume of the solution (L); m is the weight of adsorbent (g); C_0 and C_e are the concentrations of Cu(II) or Pb(II) ions in the initial aqueous solution and equilibrium solution, respectively; is the removal percentage of Cu(II) or Pb(II).

The effect of solution pH on adsorption was measured using the same procedures mentioned above. In briefly, 0.0020 g of GO-TA composite was added into 20 ml of Cu(II) or Pb(II) solutions, and the pH of the solutions were adjusted to 2.0, 3.0, 4.0, 5.0, 6.0 at 25 °C. Solutions of 0.1 M NaOH and 0.1 M HCl were used for controlling the solution pH values. All of the adsorption was conducted for 1.5 h.

3. Results and discussion

3.1. Characterization of GO-TA composite

3.1.1. FI-IR spectrum

The FTIR spectra of GO and GO-TA composite are presented in Fig. 1. The characteristic peaks of GO (Fig. 1A) appeared at 1741 cm^{-1}, 1625 cm^{-1}, 1394 cm^{-1} and 1113 cm^{-1} can be attributed to the C=O double bond of carboxyl group, C=C bond of aromatic ring, –OH group, C–O–C bond of epoxide group, respectively. These characteristic peaks indicate that large amounts of oxygen-containing functional groups exist on the surface of GO. The emerging absorption band at 1697 cm^{-1} of GO-TA composite (Fig. 1B) is due to COO– bond stretching vibration of the ester. The FT-IR results proved that TA was successfully grafted onto the surface of GO.

Please cite this article as: Z.-H. Wang et al., Tartaric acid modified graphene oxide as a novel adsorbent for high-efficiently removal of Cu(II) and Pb(II) from aqueous solutions, Journal of the Taiwan Institute of Chemical Engineers (2016), http://dx.doi.org/10.1016/j.jtice.2016.06.018