Chemical Engineering Journal 257 (2014) 248–252

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Short communication

Filtration and transport of heavy metals in graphene oxide enabled sand columns

Zhuhong Ding [a,b], Xin Hu [c,b], Verónica L. Morales [d], Bin Gao [b,*]

[a] School of Environment, Nanjing Tech University, Nanjing 211816, PR China
[b] Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611-0570, United States
[c] State Key Laboratory of Analytical Chemistry for Life Science, Center of Material Analysis and School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China
[d] SIMBIOS Centre, University of Abertay, Dundee, DD1 1HG, UK

HIGHLIGHTS

- GO enabled sand columns showed good filtration ability to Pb and Cu.
- Increase in injection flow rate decreased metal removal efficiency of the columns.
- Increase in the amount of GO enhanced metal removal efficiency of the columns.
- Pb and Cu competed for adsorption sites in the columns.

ARTICLE INFO

Article history:
Received 15 June 2014
Received in revised form 9 July 2014
Accepted 10 July 2014
Available online 19 July 2014

Keywords:
Graphene oxide
Fixed-bed column
Filtration
Cu
Pb

ABSTRACT

A fixed-bed sand column with graphene oxide (GO) layer was used to remove heavy metals (Cu(II) and Pb(II)) from an aqueous solution injected under steady flow. Due to the time constrained kinetic process of heavy metal sorption to GO, removal efficiency was affected by the injection flow rate. When injection flow rate changed from 1 to 5 mL min^{-1}, the removal efficiency of the two metals decreased from 15.3% to 10.3% and from 26.7% to 19.0% for Cu(II) and Pb(II), respectively. Provided a fixed concentration of heavy metals in the injected flow, an increase in GO in column from 10 to 30 mg resulted in an sharp increase in the removal efficiency of Pb(II) from 26.7% to 40.5%. When Cu(II) and Pb(II) were applied simultaneously, the removal efficiency of the two metals was lower than when applied by individually. GO-sand column performance was much better for the removal of Pb(II) than for Cu(II) in each corresponding treatment. When breakthrough curve (BTC) data were simulated by the convection-dispersion-reaction (CDER) model, the fittings for Cu in every treatment were better than that of Pb in corresponding treatment. Considering the small amount of GO used to enable the sand columns that resulted in a great increase in k value, compared to the GO-free sand columns, the authors propose GO as an effective adsorption media in filters and reactive barriers to remove Pb(II) from flowing water.

1. Introduction

Lack of clean water resources has become a highly pervasive worldwide problem due to rapid urbanization and industrialization [1]. A growing number of contaminants have direct entryways into freshwater resources, causing numerous environmental and health problems. There is therefore a need to find innovative and cost-effectively solutions to water purification and wastewater reutilization with new materials and techniques [1]. As a derivative of graphene nanosheets, graphene oxide (GO) has become one of the most intensively studied engineered nanomaterials in the last decade due to its tremendous potential in environmental applications; particularly with respect to water purification [2–5]. It has been reported in the literature that GO and GO-based sorbents have strong sorption ability to various water contaminants, including heavy metals and organic pollutants [6–9].

GO has a sheet structure with an abundance of oxygen atoms on the graphitic backbone in the form of epoxy, hydroxyl, and carboxyl functional groups [10]. These functional groups are the essential chemical skeletons for an ideal adsorbent of heavy metals because of their strong affinity to cations, especially multivalent metal ions [11–13], through both electrostatic and coordinate approaches [14].

---

[*] Corresponding author. Tel.: +1 352 392 1864x285; fax: +1 352 392 4092.
E-mail address: bg55@ufl.edu (B. Gao).

http://dx.doi.org/10.1016/j.cej.2014.07.034
1385-8947/

Laboratory batch sorption experiments have been used to determine the sorption ability of GO to a variety of heavy metal ions, including Pb(II), Cu(II), Cd(II), Co(II), Zn(II), Eu(III), and Th(IV) in aqueous solutions [15–18]. Most of these studies were focused on exploring the sorption characteristics and mechanisms of GO to heavy metals in single sorbate solution systems. Only few studies have examined the competitive sorption of different heavy metals on GO in aqueous solutions [16]. Findings from the batch sorption studies have demonstrated the great potential of using GO as an effective sorbent to remove heavy metals from water. Because almost all batch sorption experiments are conducted under ideal sorption conditions (e.g., full contact and sufficient reaction time), fix-bed adsorption experiments are often used to evaluate the sorbents as packed media in filter systems [19–21]. In the literature, however, only few studies have investigated the filtration of heavy metals by GO enabled fix-bed columns [3].

In general, engineered nanomaterials, including GO, may not be applied directly as filter media because of their small size. To take advantage of the great sorption ability of engineered nanomaterials, several methods have been developed to combine them with other sorbents such as sand for improved filter performance [3,19,20,22–24]. For example, Gao et al. [3] found that GO can be used to coat sand surfaces and the GO-enabled sand retains at least 5-fold higher concentration of heavy metal and organic dye than pure sand. Recently, Tian et al. [19,20] evaluated the effect of different packing methods of carbon nanotubes (CNTs) in sand columns on their removal of heavy metals and antibiotics from aqueous solutions and found that CNT packed together with natural sand can effectively and safely remove metallic and pharmaceutical contaminants from water. Furthermore, their results also suggested that functionalized carbon nanomaterials may be applied as a layer within natural sand columns to filter contaminants from water.

The overarching objective of this work was to determine the removal efficiency of GO-enabled sand filters for aqueous heavy metal cations. GO-enabling consisted of thin layering of GO material in a quartz sand bed to create the fixed-column. The filtration and transport of Pb(II) and Cu(II) in GO-enabled and pure sand columns (the control) were investigated under various conditions. The specific objectives were as follows: (1) determine the effect of GO on the removal of two types of heavy metals in the fix-bed sand columns under single and dual sorbate conditions; (2) determine the effect of flow rate and GO loading on heavy metal removal; and (3) model the filtration and transport of heavy metals in the fix-bed columns.

2. Materials and methods

2.1. Materials

GO was obtained from ACS Material (Medford, MA) and used as received. According to the manufacturer, it was prepared by the modified hummer's method. The physical dimensions of GO were determined previously, where an average thickness and average square root of the area was reported as 0.92 ± 0.13 nm and 582 ± 111.2 nm, respectively [25].

Quartz sand (Standard Sand & Silica Co.) of grain size 0.5–0.6 mm was washed sequentially with tap water, 10% nitric acid (v:v), and deionized (DI) water, followed by oven drying at 70 °C following the procedure of Tian et al. [26] to remove loose impurities and metal oxides.

Copper nitrate and lead nitrate were used to prepare the heavy metal stock solutions. Individual metal solutions were prepared at concentrations of 10 mg L^{-1} of Cu^{2+} or Pb^{2+}. In addition, a dual metal solution containing 10 mg L^{-1} of Cu^{2+} and Pb^{2+}, each, was also prepared. Inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2100 DV, PerkinElmer Inc., Waltham, MA) was used to determine the metal concentration in the solutions. Nitric acid and sodium hydroxide solutions were used to adjust the pH of the metal solutions to 5.6.

2.2. Fixed-bed column experiment

Fixed-bed column experiments were used to quantitatively evaluate the removal of heavy metals dissolved in water. GO was packed as a thin layer in the middle of the fixed-bed contained in an acrylic column (1.5 cm inside diameter and 5 cm height) holding approximately 16.5 g of quartz sand (Table 1). Packing of the GO-enable fixed-bed column entailed filling half of column with sand by wet-packing into the acrylic column, carefully layering 10 or 30 mg of GO on top of the packed sand, and finally wet-packing the rest of the sand into the column. Membranes with 50 lm pores (Spectra/Mesh, Spectrum Laboratories, Inc.) were used at the column inlet and outlet to distribute the flow and seal the column. Sand columns packed without GO were also prepared to be used as controls. Because only small amount of GO (0.06% w/w or 0.18%w/w of GO/sand) were used in the fixed-bed columns, the bed porosity of all the columns was assumed to remain at 0.45.

After packing, the columns were first flushed with DI water (pH 5.6, adjusted with nitric acid) for 1 h to remove potential impurities. They were then subjected to pulses of single or dual metal solutions and the removal efficiency was determined through mass balance calculations. Fig. 1 illustrates the setup of the fix-bed column experiment. The BTC experiments consisted of two injection stages. At stage one, the single (Cu(II) or Pb(II)) or dual (Cu(II) and Pb(II)) metal solutions were injected into the bottom of the column at a steady flow rate (1 mL min^{-1} or 5 mL min^{-1}) for 28 or 140 min. At stage two, the influent was switched to metal-free DI water for an additional 2 h to elute residual heavy metals in the pore water. Effluent samples were collected discretely with a fraction collector and the metal concentrations were measured with the ICP-OES. All treatments were tested in duplicate, and average values were reported.

2.3. Model heavy metal transport in the columns

Filtration and transport of the heavy metals in the GO-enabled and pure sand columns were simulated by the convection-dispersion-reaction (CDER) model. The governing equation can be written as [27]:

$$R\frac{\partial C}{\partial t}+\frac{\rho_b}{\theta}\frac{\partial q}{\partial t}=D\frac{\partial^2 C}{\partial z^2}-v\frac{\partial C}{\partial z} \tag{1}$$

$$\frac{\rho_b}{\theta}\frac{\partial q}{\partial t}=kC \tag{2}$$

where R is the retardation factor (dimensionless), C is the sorbate concentration in pore water (mg L^{-1}), t is the time (min), ρ_b is the medium bulk density (g L^{-1}), θ is the dimensionless volumetric moisture content, q is the concentration of heavy metal adsorbed onto the column (as sand or sand + GO combination) (mg g^{-1}), z is the distance traveled in the direction of flow (cm), D is the dispersion coefficient (cm^2 min^{-1}), v is the average linear pore-water velocity (cm min^{-1}), and k is the first-order removal rate constant (min^{-1}). Eqs. (1) and (2) were solved numerically using the finite difference method with a zero initial concentration, a pulse-input and a zero-concentration-gradient boundary conditions for the whole column. The Levenberg-Marquardt algorithm was used to estimate the value of the model parameters by minimizing the sum-of-the-squared differences between model-calculated and