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Graphene oxide as filter media to remove levofloxacin and lead from aqueous solution

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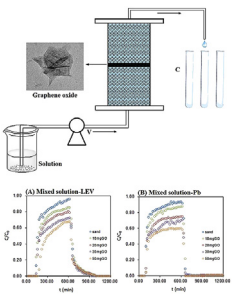
HIGHLIGHTS

- GO showed strong sorption of LEV (256.6 mg g^{-1}) and Pb (227.2 mg g^{-1}).
- GO-sand columns effectively removed LEV and Pb single and mixed solution systems.
- LEV and Pb removal efficiency in GO-sand columns increased with GO content.
- LEV and Pb removal efficiency in GO-sand columns decreased with injection flow rate.
- Column experimental data were well described by BDST model.

GRAPHICAL ABSTRACT



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ABSTRACT

There is an increasing need to develop novel and high-efficiency water purification technologies. This work systematically evaluated the potential of using graphene oxide (GO) directly as filter media for the removal of levofloxacin (LEV), an emerging contaminate, and lead (Pb), a heavy metal, from aqueous solution. Batch and fixed-bed experiments were conducted to determine the sorption behaviors of LEV and Pb onto the GO. In the batch system, GO showed strong sorption of the two contaminants with Langmuir maximum adsorption capacities of 256.6 and 227.2 mg g^{-1}, respectively. The removal of LEV and Pb by GO in fixed-bed columns was high under all tested conditions in both single and mixed solution systems. The removal efficiency of the two contaminants in the GO-sand columns increased with increasing GO content, but decreased with increasing injection flow rate. In the mixed solution system, although LEV and Pb competed for sorption, the GO media still had high removal efficiencies for them. The column experimental data were well described by the Bed Depth Service Time (BDST) model, suggesting the model can be used for the design of GO-sand filters in large-scale applications. Findings from this work demonstrated that GO is a promising nano-adsorbent that can be used as a high-efficiency filter media in water treatment to remove hazardous metal elements and emerging contaminants.

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1. Introduction

Nanotechnology can provide new solutions to solve environmental problems including the development of novel agents for environmental remediation (Dionysiou and Wiesner, 2007). Graphene oxide (GO), which is derived from graphene, is a two-dimensional engineered carbon nanomaterial with great potential for various applications (Zhang et al., 2014). In comparison to other oxidized carbon nanomaterials, such as functionalized carbon nanotubes, GO can be prepared much more cost-effectively (Hummers and Offeman, 1958), making it more suitable for large-scale environmental applications.

Recent studies have already shown that GO and its derivatives can serve as effective adsorbents for both heavy metals (Gollavelli et al., 2013) and organic pollutants in aqueous solutions (Chen et al., 2015). Yang et al. (2010) found that GO has a huge adsorption capacity for copper, which is about ten times of that of activated carbon. Chen et al. (2015) showed that GO can effectively remove sulfamethoxazole and ciprofloxacin from aqueous solutions with a maximum sorption capacity far above 200 mg g^{-1}. The effectiveness of GO as an adsorbent towards other heavy metals (e.g., lead, zinc, and mercury) and organics (e.g., dyes and algal toxins) in aqueous solutions has also been demonstrated (Zhao et al., 2011; Pavagadhi et al., 2013; Cui et al., 2015). Findings from these studies strongly point out that GO and its derivatives can be effective adsorbents for environmental remediation, particularly with respect to water treatment.

Because of its good "solubility", direct application of GO as an adsorbent for contaminant removal from water has been restricted. Although GO nanosheets are effective in the batch or continuous mixing systems, the exhaust adsorbents are difficult to collect due to their extremely small sizes (Tian et al., 2013). Novel GO-based adsorbents, such as GO hydrogels/aerogels and GO-based nanocomposites thus have been developed to take advantage of the strong sorption ability of GO for wastewater treatment (Gao et al., 2011; Zhang et al., 2012, 2013). For instance, Zhang et al. (2013) found that GO-based aerogels with a three-dimensional network of carbon structures have excellent removal ability towards aqueous lead. Gao et al. (2011) found that GO-coated sand in packed columns can effectively remove both heavy metals and organic dyes from water. Although previous studies have shown that carbon nanotubes can be directly packed in sand columns to remove heavy metals and emerging contaminants from aqueous solutions (Tian et al., 2012, 2013), only few studies have explored the potential of GO as a filter media in fixed-bed systems (Ding et al., 2014). The direct application of GO nanosheets as a filter layer in a packed sand column may greatly enhance the filtration performance for various contaminants and thus provide a convenient and cost-effective method for wastewater treatment.

The overarching objective of this work was to evaluate the potential of using GO as a filter media to for the removal of emerging contaminants and hazardous metal elements from aqueous solutions. Two common water pollutants, levofloxacin (LEV) and lead (Pb) were selected to represent emerging and heavy metal contaminants, respectively. LEV is one of most commonly used antibiotics for bacterial infections and is frequently detected in wastewater and nature water bodies (Sarmah et al., 2006). Lead is among the most common aqueous heavy metal pollutants that have been extensively studied (Jarup, 2003). Both batch and fixed-bed experiments were conducted to measure the removal ability of the contaminants by GO. The specific objectives were as follows: 1) determine the maximum sorption capacity of GO to the contaminants; 2) measure the filtration and transport of single contaminant in GO enabled sand columns under various conditions; 3) measure the filtration and transport of mixed contaminants in GO enabled sand columns under various conditions; and 4) test the bed depth service time model (BDST) for simulating the performances of the GO media in the sand columns.

2. Materials and methods

2.1. Materials

Single-layer GO prepared with the modified Hummers method was purchased from ACS Material (Medford, MA). As reported by the manufacturer, the lateral diameter of the GO is 1–5 μm, layer thickness is 0.8–1.2 nm, and purity and single layer ratio are all around 99%.

Quartz sand (Unimin-Le Sueur, MN, USA) was sieved into grain size 0.35–0.45 mm and washed sequentially with tap water, 10% nitric acid (v:v), and deionized (DI) water to remove impurities and metal oxides, and then oven dried at 40 °C following the procedure of Tian et al. (2010).

Levofloxacin hydrochloride (>98.5%, Dalian Meilun Biology Technology, Ltd) was used to prepare the stock solution of LEV. Chemical structures and properties of LEV are reported in Figure S1 (Supporting Information). Lead nitrate (analytical grade, Shanghai Chemical Reagent Co., Ltd) was used to prepare the Pb stock solution. For preparing the LEV and Pb stock solutions, 100 mg of levofloxacin hydrochloride and 1000 mg of lead nitrate into 1000 mL deionized (DI) water, respectively. The solutions were diluted to 5 mg L^{-1} of LEV or Pb solutions with DI water right before each experiment. In addition, a mixed solution containing both LEV (5 mg L^{-1}) and Pb (5 mg L^{-1}) were prepared. Nitric acid and sodium hydroxide solutions were used to adjust the pH of the solutions to 5.6.

2.2. Batch sorption experiments

Adsorption of LEV or Pb onto GO and sand were conducted in polytetrafluoroethylene centrifuge tubes at room temperature (25 ± 1 °C). For each GO sorption experiment, the tubes were first filled with 10 mL GO suspension (40 mg L^{-1}) as the adsorbent. After that, 10 mL of LEV or Pb solutions of seven different concentrations (i.e., LEV: 1, 2, 5, 10, 20, 30, and 40 mg L^{-1}; and Pb: 1, 2, 5, 10, 20, 40, and 60 mg L^{-1}) were added into the tubes, to serve as the adsorbates. For the sand experiments, 5 g of sand and 30 mL of adsorbate solutions (LEV: 0.5, 1, 2.5, 5, 10, 15, and 20 mg L^{-1}; and Pb: 1, 2.5, 5, 10, 20, and 30 mg L^{-1}) were used. The mixtures were shaken for 24 h in a rotary shaker, and then were immediately filtered through 0.22 um polytetrafluoroethylene membrane filters (Millipore, USA). The filtrates were collected for analysis of the adsorbate concentrations. The concentration of LEV was detected using a high performance liquid chromatography (HPLC, Agilent 1200, Agilent Technologies, Co., California, USA) system. A polarized Zeeman atomic absorption spectrophotometer (AAS, Z-2000, Hitachi, Japan) was used to determine the concentration of Pb in the filtrates. The amounts of sorbed adsorbate per unit adsorbent mass were calculated based on the differences between initial and final aqueous solution concentrations. Every batch sorption experiment was conducted in triplicate, and the average values were reported.

2.3. Column experiments

Column experiments were conducted to quantitatively evaluate the removal of LEV and Pb in water flowing through the GO filters. Acrylic columns (1.5 cm inside diameter and 5 cm height) were used to hold the quartz sand GO. Stainless steel membranes with 50 μm pores were used at both inlet (bottom) and outlet (top) to

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