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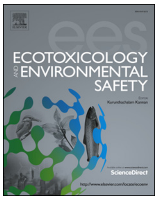

# Graphene oxide encapsulated polyvinyl alcohol/sodium alginate hydrogel microspheres for Cu (II) and U (VI) removal

Xiaofeng Yi*, Fuliang Sun, Zhenhua Han, Fuhao Han, Jiarui He, Minrui Ou, Junjie Gu, Xiaoping Xu*

*College of Chemistry, Fuzhou University, Fuzhou 350108, China*

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ABSTRACT

In this work, a novel sodium alginate (SA)/polyvinyl alcohol (PVA)/graphene oxide (GO) hydrogel microspheres were prepared by a simple method. Sodium alginate was physically crosslinked by $Ca^{2+}$; GO was encapsulated into the composite to strengthen the hydrogels; PVA played a significant role in well dispersing of GO in SA. The SA/PVA/GO (SPG) hydrogels were employed as an efficient adsorbent for removal of Cu (II) and U (VI) from aqueous solution. Batch experiments with the subject of the pH, initial metal ion concentration, competing ions and contact time were investigated. Structure characterization was successfully conducted by FTIR, SEM, EDX, BET and XPS. Furthermore, the sorption kinetics of $Cu^{2+}$ and $UO_2^{2+}$ followed pseudo-second order model and exhibited 3-stage intraparticle diffusion model. Equilibrium data were best described by Langmuir model and the obtained maximum adsorption capacities of SPG hydrogel microspheres for $Cu^{2+}$ and $UO_2^{2+}$ were 247.16 and 403.78 mg/g, respectively. The difference in adsorption capacity can be confirmed by the percentage of elements in EDX spectra and the intension of peak of elements in XPS spectra. The SPG sorbent exhibited excellent reusability after 5 adsorption-desorption cycles. All results suggested that the prepared adsorbents could be considered as effective and promising materials for removal of Cu (II) and U (VI) in wastewater.

## 1. Introduction

Water pollution by various toxic chemicals from industrialization is representing a global problem due to the high toxicity of these elements and their tendency to accumulate in living tissues through the food chain, affecting the health of the people (Awual, 2015a). The toxic chemicals including dyes, organics, heavy metals and pharmaceuticals are of highly concerned (Awual and Hasan, 2015a; Tan et al., 2017; Zheng et al., 2017). Non-biodegradable metal ions are one of the most significant water pollutants. For example, copper, one of the essential nutrients in trace amounts, can produce health problems when it presents at a high levels (Awual, 2017; Awual et al., 2016c). Uranium (U (VI), as $UO_2^{2+}$), an important actinide element, is another toxic heavy metal ion which can be hazardous to ecosystem and human health (Shao et al., 2016). Therefore, methods for removal of copper and uranium ions from wastewater are of great significance.

The ion-exchange (Chitpong and Husson, 2017), membrane filtration (Al-Abri et al., 2010), solvent extraction (Domanska and Rekawek, 2009), and adsorption (Awual, 2016b; Awual et al., 2015c; Kolbasov et al., 2017) have been developed for removal of metal ions from aqueous solution. Among these methods, adsorption is considered to be a suitable and promising method to remediate heavy metals from wastewater owning to its simple operation, high efficiency and low cost (Awual et al., 2017; Zhao et al., 2016). Since adsorbents have a critical role in sorption process, it is a key point to develop environment-friendly and efficient sorbents.

Hydrogels consisting of biopolymers such as alginate, chitosan and cellulose have been widely studied for removal of heavy metal (Karthik and Meenakshi, 2015; Monier and Abdel-Latif, 2013). Sodium alginate (SA), a linear biopolymer, is nontoxic, biodegradable and rich in carboxyl and hydroxyl groups. Thus, it is an effective candidate for heavy metal removal. SA may be converted into a hydrogel by crosslinking with $Ca^{2+}$ (Ghasemi et al., 2011; Yi et al., 2017a, 2017c), However, the alginate hydrogel microspheres are usually fragile, which are unfavorable in adsorption processing. Recently, an effective and simple method has been developed to solve this problem by blending SA with polyvinyl alcohol (PVA) (Hua et al., 2010). The excellent properties of PVA including high-quality dispersant, compact molecular packing, high degree of crystallinity, good biodegradability and high chemical resistance make this polymer be an appropriate choice to enhance the flexibility, durability and chemical stability of SA (Zain et al., 2011).

SA/PVA-based hydrogels are still restricted for some applications

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* Corresponding authors.
*E-mail addresses:* 927208329@qq.com (X. Yi), xu@fzu.edu.cn (X. Xu).

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because of their improper stability and mechanical strength. Composite materials are growing attention for diverse metal ions removal based on their specific functionality in adsorption technique. It has been reported that the addition of reinforcing fillers into SA/PVA hydrogels is an easy and effective method to improve the mechanical performance and stability (Lv et al., 2013; Ou et al., 2015; Yue et al., 2016). Among popular fillers, graphene oxide (GO), one of the most commonly used carbon materials in recent years, arouses widespread concern due to its superior processability, excellent flexibility, good thermal stability and outstanding mechanical properties (Jiao et al., 2016). According to former researches, the use of GO fillers to enhance the stability and mechanical strength of SA has attracted much interest. For instance, researchers found that introducing GO into SA can not only increase the mechanical property but also improve the thermal stability of SA/GO composite films (Ionita et al., 2013; Liu et al., 2017). However, GO can disperse unevenly in the SA hydrogel. Fortunately, PVA can be used as an effective dispersing agent in composites (Khosroshahi and Ghazanfari, 2012; Reddy et al., 2009). To our knowledge, there has not been any works concerned with the crosslinking PVA and SA using calcium chloride with the presence of GO. In the present study, GO is designed to enhance physicochemical properties of SA, PVA is used to disperse the GO in SA and to optimize the performance of SA.

This work aims (i) to prepare a novel type of dual functional adsorbent by encapsulating graphene oxide into PVA/SA hydrogel microspheres for Cu (II) and U (VI) removal, respectively. Also, graphene oxide was synthesized from purified natural graphite using a modified Hummers' method (Marcano et al., 2010); (ii) to characterize the adsorption mechanism by FTIR, SEM, EDX, BET and XPS; (iii) to evaluate the adsorption behavior of $Cu^{2+}$ and $UO_2{}^{2+}$ in batch experiments; (iv) and to explore the adsorption process via investigating various adsorption isotherms and kinetic models.

## 2. Materials and methods

### 2.1. Materials

Sodium alginate and calcium chloride were provided by Sinopharm Chemical Reagent Co., Ltd. Polyvinyl alcohol was supplied by Aladdin Industrial Corporation. All chemicals were of analytical grade and were used without further purification. Solutions were prepared with distilled water (was prepared by Fuzhou University).

Cu (II) and U (VI) stock solution (1000 mg/L) was prepared by dissolving 3.906 g $CuSO_4{\cdot}5H_2O$ and 1.859 g $UO_2\ (NO_3)_2{\cdot}6H_2O$ in 1000 mL distilled water, respectively. The solutions of different concentrations used in various experiments were obtained by dilution of the stock solutions.

### 2.2. Preparation of graphene oxide encapsulated polyvinyl alcohol/sodium alginate (SPG) hydrogel microspheres

Graphene oxide flakes were synthesized by the modified Hummers' method and subsequently 0.25 g GO was dispersed in 100 mL deionized water. The GO solution was treated with ultrasound for 2 h to obtain a GO aqueous dispersion. Next, 2 g PVA powder was slowly mixed into aqueous dispersion of GO flakes with magnetic stirring. And then, 2 g SA powder was slowly mixed into GO/PVA aqueous dispersion under constant mechanical stirring. An SA/PVA-only hydrogel was also prepared in parallel. Briefly, The SA/PVA/GO mixture was sonicated for 20 min and was then dropped through a silicon tube, using a peristaltic pump, into a beaker containing 300 mL of calcium chloride solution obtained by dissolving 6.6 g of calcium chloride anhydrous. The formed SPG hydrogel was kept in calcium chloride solution for overnight. The prepared SPG hydrogels were spherical microspheres with the same size, and the diameter of microspheres was about 3 mm. The obtained SPG hydrogel microspheres were then filtered, rinsed with distilled water several times and stored at 4 °C. A SPG aerogel was obtained by lyophilizing the SPG hydrogel.

### 2.3. Characterization

FTIR spectra were performed by using a FTIR spectrophotometer. The FTIR spectrum was recorded with a spectrometer in the range of 4000–400 $cm^{-1}$ using an attenuated total reflectance technique. The morphologies and elemental analysis of the samples were characterized using a scanning electron microscope (SEM, Nova Nano 230). $N_2$ adsorption–desorption isotherms were obtained on a ASAP 2020 M analyzer at 77 K. Pore size distribution were originated from the desorption branches of the isotherms based on BJH model. X-ray photoelectron spectroscopy (XPS) was measured by ESCALAB 250Xi.

### 2.4. Adsorption experiments

Batch sorption experiments were generally carried out by agitating the conical flasks containing 5.0 mg dry sorbent and 10.0 mL solution of heavy metal ions on a rotary shaker. Each experiment was performed at room temperature (25 °C) and shaking rate of 150 rpm. After the adsorption processes, the residual concentration of $Cu^{2+}$ was determined using a UV–vis spectrophotometer at $\lambda = 546$ nm after complexation with dicyclohexanoneoxaly dihydrazone (Yang et al., 2010), and the analyses of U (VI) cations were conducted at a wavelength of 650 nm using Arsenazo-III as the complexing agent by UV–vis spectrophotometer (Wei et al., 2007). In each batch experiment, the adsorption capacity of the adsorbent, $q_t$ (mg/g), was calculated by using the following expression:

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

where, m (g) is the weight of adsorbent and V (L) is the volume of the cation solution. $C_0$ and $C_e$ (mg/L) are initial and equilibrium concentration of $Cu^{2+}$ and $UO_2{}^{2+}$, respectively.

All the experiments were carried out in triplicate and the means of the data were used for results and discussion.

#### 2.4.1. Effect of pH

The pH effect experiments were conducted at metal ions concentrations of 100 mg/L by adjusting the initial pH in the range of 1.0–5.0 for Cu (II) and U (VI) using 0.1 M $HNO_3$ and NaOH. The contact time was 6 h and concentrations of metal ions were 100 mg/L.

#### 2.4.2. Effect of contact time and adsorption kinetics study

For the study of the effect of contact time and adsorption kinetics, 15 mg SA/PVA/GO was added to a 30 mL solution of 100 mg/L $Cu^{2+}$ and $UO_2{}^{2+}$. At designed contact time, samples were withdrawn and diluted for absorbance measurements.

The pseudo-first order model, pseudo-second order model and intraparticle diffusion model were employed to simulate the experimental data to evaluate the kinetic mechanism involved in the sorption process. The pseudo-first order model assumes that physisorption exists between the adsorbents and adsorbates (Wang et al., 2016). The pseudo-second order model is used to describe the chemisorption behavior between the adsorbate and the adsorbents (Srivastava et al., 2008). The intraparticle diffusion model is employed to decide if pore or film diffusion was the controlling step in the adsorption (Yi et al., 2017b). The mathematical expressions of the kinetic models were based on Eqs. (2)–(4):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

$$q_t = k_i t^{1/2} + C \tag{4}$$