



## Adsorption behavior of $\text{Cu}^{2+}$ from aqueous solutions onto starch-g-poly (acrylic acid)/sodium humate hydrogels

Yian Zheng<sup>a,b</sup>, Shuibo Hua<sup>a,b</sup>, Aiqin Wang<sup>a,\*</sup>

<sup>a</sup> Center of Eco-materials and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China

<sup>b</sup> Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

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### ABSTRACT

A series of starch-g-poly(acrylic acid)/sodium humate (St-g-PAA/SH) hydrogels were prepared and used to adsorb  $\text{Cu}^{2+}$  from the aqueous solution. The batch adsorption experiments were carried out by varying contact times (0–90 min), initial  $\text{Cu}^{2+}$  concentration (0.003–0.02 mol/L), and pH values (2.0–5.0). The effects of ion strength (5, 10 mmol/L NaCl) and competitive ion (5, 10 mmol/L  $\text{Pb}(\text{NO}_3)_2$ ) on the adsorption capacity were investigated. The results indicated that the addition of 5% SH into St-g-PAA polymeric networks could not only improve the initial adsorption rate and final adsorption capacity for  $\text{Cu}^{2+}$ , but also make a remarkable contribution to regeneration ability. St-g-PAA/SH hydrogels exhibited high adsorption capacity within a wide pH range and the adsorption data could be well described by the pseudo-second-order kinetic model and Langmuir isotherm model. FTIR spectra before and after adsorption of  $\text{Cu}^{2+}$  on the hydrogels revealed that complexation was considered as the main adsorption mechanism.

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### 1. Introduction

Adsorption is a conventional but important separation process and has been used widely in the chemical, biological, analytical, and environmental fields [1–3]. In most cases, the adsorbents have large internal porosities to ensure adequate surface area for adsorption. However, the diffusion limitations within the particles lead to decreases in the adsorption rate and the available capacity [4]. So, it is interesting to develop a novel adsorbent with a small diffusion resistance and a high adsorption capacity.

Polymeric hydrogels are crosslinked three-dimensional network structure of hydrophilic homopolymers or copolymers [5–7]. Due to the super-hydrophilicity characteristics, they can swell quickly in the aqueous solution, which is beneficial for shortening the time to reach the adsorption equilibrium [8]. Polymeric hydrogels can be prepared with different functional groups such as carboxylic acid, amine, hydroxyl, amidoxime and sulfonic acid groups. These groups attached onto the polymeric networks can be tailored easily for a specific application. Owing to higher adsorption rate and adsorption capacity, polymer hydrogels can provide many advantages as a novel type, fast-responsive, and high-capacity adsorbent materials in an adsorption process [9,10].

With the development of polymer hydrogels, an incorporation of biodegradable, environmentally friendly polysaccharide, such as starch [11–13] cellulose [14,15] or chitosan [16,17], into the polymer

hydrogel has been focused on. Starch (St) is an abundant, inexpensive, renewable and fully biodegradable natural raw material. Considerable research and technical work have been reported so far, and the chemical modification of starch or modified starch via vinyl graft copolymerization constitutes the most important field for not only improving the properties of starch and enlarging the range of its utilization [18–20], but also affording corresponding hydrogels with biodegradability and biocompatibility.

Humic substances, a major component of organic matter, are some of the most abundant materials on earth. They are formed during the decomposition of plant and animal biomass in natural systems and usually include a skeleton of alkyl and aromatic units with functional groups such as carboxylic acid, phenolic hydroxyl, and quinone groups attached to them [21]. It was reported that the presence of humic acid/humates can benefit for the adsorption of heavy metals. Hizal and co-worker found that the clay mineral in the presence of humic acid probably behaved more like a chelating agent for heavy metal ions than a simple inorganic ion exchanger, since the stability of the dominating surface complexes in the presence of humic acid was higher than that of the corresponding binary metal ion complexes [22]. Arias et al. concluded that humic substances could be adsorbed on mineral particles by which they would promote the adsorption of some heavy metals [23]. Wang et al. reviewed that the presence of humic acid would result in the complexation of humic acid with metal ions, promoting the adsorption of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  on fly ash [24].

Recently, the humates had been introduced into the polymer hydrogels to enhance their water absorbencies [25–27]. However, only a few literatures were published on the adsorption performance of hydrogels with humates. In order to know whether these hydrogels

\* Corresponding author. Tel.: +86 931 4968118; fax: +86 931 8277088.  
E-mail address: [aqwang@lzb.ac.cn](mailto:aqwang@lzb.ac.cn) (A. Wang).

are also excellent adsorbents for  $\text{Cu}^{2+}$ , in this study, a series of starch-g-poly(acrylic acid)/sodium humate (St-g-PAA/SH) hydrogels were prepared and used as adsorbents for  $\text{Cu}^{2+}$  adsorption from aqueous solution. The parameters influencing the adsorption capacity of the hydrogel, such as SH content, initial pH values of solution, contact time and initial  $\text{Cu}^{2+}$  concentration were investigated. The effects of competitive cation of  $\text{Pb}^{2+}$  were evaluated and the adsorption mechanism of  $\text{Cu}^{2+}$  onto St-g-PAA/SH was also discussed.

## 2. Material and methods

### 2.1. Materials

Starch (St, Hua'ou Starch Co., Ltd., Inner Mongoulia, China) was derived from potato. Acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water before use. *N,N'*-methylenebisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Corp., Shanghai, China) was used as purchased. Sodium humate (SH, Shuanglong Humic Acid Co., Ltd., Xinjiang, China) was milled and passed through a 320-mesh screen prior to use. Other agents used were all analytical grade and all solutions were prepared with distilled water.

### 2.2. Preparation of St-g-PAA/SH hydrogels

St-g-PAA/SH hydrogels were prepared according to our previous reports [27]. 1.44 g St and 30 mL of distilled water were put in a 250 mL four-necked flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. The slurry was gelatinized at 95 °C for 30 min and cooled down to 60 °C, while 0.049 g of APS was added. After 15 min, the mixture containing 10 mL of distilled water, 10.08 g AA with 60% neutralization degree, 0.01 g MBA and a certain amount of SH was added dropwise into the flask. The reaction was performed at 70 °C for 3 h and the resulting product was put into 400 mL alcohol and then dried at 70 °C to a constant weight. The adsorbent used for test had a particle size in the range of 40–80 mesh.

### 2.3. Adsorption and analysis

Adsorption experiments were carried out by agitating 50 mg of hydrogel with 25 mL  $\text{Cu}^{2+}$  ion solution in a shaker at 30 °C/120 rpm. The samples were withdrawn from the flasks at predetermined time intervals and analyzed for  $\text{Cu}^{2+}$  content by atomic absorption spectrometry. The adsorption capacity of the hydrogel for  $\text{Cu}^{2+}$  was calculated through the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $q$  is the amount of  $\text{Cu}^{2+}$  adsorbed at time  $t$  or at equilibrium (mmol/g),  $C_0$  and  $C_e$  is the initial and final concentration of  $\text{Cu}^{2+}$  (mol/L),  $V$  is the volume of  $\text{Cu}^{2+}$  solution used (mL) and  $m$  is the mass of the hydrogel used (g). All assays were carried out in triplicate and the average was used in the analysis.

For the adsorption kinetic studies, a series of solutions containing 0.02 mol/L  $\text{Cu}^{2+}$  were allowed to contact with 0.05 g hydrogel with different amounts of SH. At different intervals (1–90 min), 2 mL aliquot was sampled and analyzed for residual  $\text{Cu}^{2+}$  concentration. When the adsorption equilibrium was achieved, the equilibrium pH values were also recorded. To investigate the adsorption isotherms, a series of  $\text{Cu}^{2+}$  solutions with different concentrations (0.003–0.02 mol/L) were kept in contact with 0.05 g hydrogel with different amounts of SH for 60 min. The effects of pH on  $\text{Cu}^{2+}$  adsorption were studied with an initial  $\text{Cu}^{2+}$  concentration of 0.02 mol/L and different

pH values (2.0–5.0) for 60 min. The pH values were adjusted with 0.1 mol/L HCl or NaOH solutions. During the adsorption process, the influences of ion strength on the adsorption capacity were investigated in the solution containing 0.02 mol/L  $\text{Cu}^{2+}$  and different concentrations of NaCl (5, and 10 mmol/L), and the effects of competitive cation,  $\text{Pb}^{2+}$  in this study, were also evaluated at different  $\text{Pb}^{2+}$  concentrations (5 and 10 mmol/L  $\text{Pb}(\text{NO}_3)_2$ ).

### 2.4. Desorption and regeneration

The desorption of  $\text{Cu}^{2+}$ -loaded hydrogel was done using 0.1 mol/L HCl as the desorbing agent. A fixed amount (50 mg) of each adsorbent was contacted separately with 30 mL 0.1 mol/L HCl solution. The bottle was placed in a thermostatic shaker and shaken for 60 min at 120 rpm. At the end of the experiment, the supernatant was discarded and the solid was washed with distilled water for several times. The obtained sample was regenerated with 0.1 mol/L NaOH for 30 min and then washed with distilled water for several times. The recovered hydrogel was employed for another adsorption. The water adsorbed during the regeneration process was taken into account when the adsorption capacity was calculated.

### 2.5. Characterization

As-prepared hydrogels were characterized and the adsorption mechanism of  $\text{Cu}^{2+}$  onto these hydrogels was analyzed on a Thermo Nicolet NEXUS TM spectrophotometer using KBr pellets.

## 3. Results and discussion

### 3.1. Adsorption kinetics for $\text{Cu}^{2+}$

The effects of contact time on the adsorption capacities of the hydrogels with different amounts of SH were studied, as shown in Fig. 1. To make a convenient comparison, all the adsorption capacities were represented based on per gram of polymer St-g-PAA. The results suggest that the time to adsorption equilibrium is measured to be 30, 10, 30, 30, 60 min for St-g-PAA, St-g-PAA/5% SH, St-g-PAA/10% SH, St-g-PAA/15% SH and St-g-PAA/20% SH, respectively, indicating a faster adsorption kinetics, particularly for St-g-PAA/5% SH. When the adsorption equilibrium is achieved, the adsorption capacities are found to be 2.80, 2.72, 2.69 and 2.61 mmol/g when 5% SH, 10% SH, 15% SH and 20% SH is introduced, while the controlled sample without SH shows an adsorption capacity of 2.76 mmol/g for

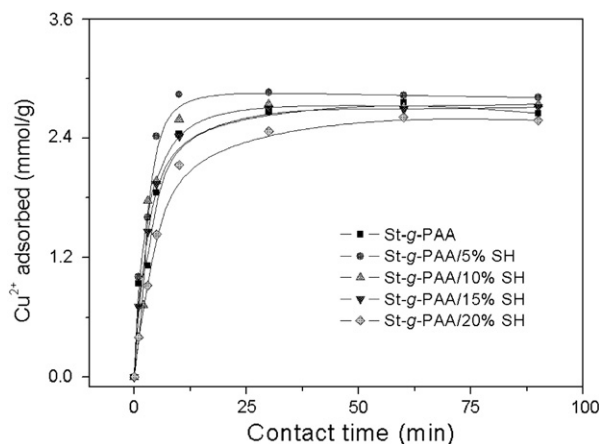


Fig. 1. Influences of contact time on the adsorption capacities of hydrogels with different amount of SH (initial  $\text{Cu}^{2+}$  concentration, 0.02 mol/L; pH, original; temperature, 303 K; agitation speed, 120 rpm; and adsorbent dose, 50 mg/25 mL).

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