Contents lists available at ScienceDirect

Carbohydrate Polymers

Experimental study of the removal of copper ions using hydrogels of xanthan, 2-acrylamido-2-methyl-1-propane sulfonic acid, montmorillonite: Kinetic and equilibrium study

Marzieh Aflaki Jalali [a], Ahmad Dadvand Koohi [a,*], Mehdi Sheykhan [b]

[a] Chemical Engineering Department, Engineering Faculty, University of Guilan, Rasht, Iran
[b] Chemistry Department, University of Guilan, Rasht, Iran

ABSTRACT

In this paper, removal of copper ions from aqueous solution using novel xanthan gum (XG) hydrogel, xanthan gum-*graft*-2-acrylamido-2-methyl-1-propane sulfonic acid (XG-*g*-P(AMPS)) hydrogel and xanthan gum-*graft*-2-acrylamido-2-methyl-1-propane sulfonic acid/montmorillonite (XG-*g*-P(AMPS)/MMT) hydrogel composite were studied. The structure and morphologies of the xanthan-based hydrogels were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). Adsorbents comprised a porous crosslink structure with side chains that carried carboxyl, hydroxyl and sulfonate. Maximum adsorption was observed in the pH = 5.2, initial concentrations of Cu^{2+} = 321.8 mg/L, Temperature = 45 °C, contact time = 5 h with 0.2 g/50 mL of the hydrogels. Adsorption process was found to follow Langmuir isotherm model with maximum adsorption capacity of 24.57, 39.06 and 29.49 mg/g for the XG, XG-*g*-P(AMPS) and XG-*g*-P(AMPS)/MMT, respectively. Adsorption kinetics data fitted well with pseudo second order model. The negative $\Delta G°$ values and the positive $\Delta S°$ confirmed that the adsorption was a spontaneous process. The positive $\Delta H°$ values suggested that the adsorption was endothermic in nature.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Heavy metals are one of the main sources of pollution, non-biodegradable, and they can accumulate throughout the food chain (Milosavljević et al., 2010). Copper is one of the heavy metals that is widely used in fertilizer manufacturing, paints and pigments, copper polishing, paper and pulp, etc. Several methods have been widely applied for removing excess of this element in industrial wastewater because of their hazardous and significant toxic effects in the environment (Milosavljević et al., 2011). Some of these methods are chemical precipitation, coagulation and flucculation, membrane filtration, adsorption, flotation, ion exchange, electrochemical treatment and coprecipitation/adsorption (Fu & Wang, 2011). Among all of treatment processes, the adsorption process has attracted great attention because of its flexibility in design and operation as well as producing superior effluent suitable for reuse without other pollutants. It has been proved recently that

polymeric adsorbents are more effective adsorbent for removal of Cu^{2+} ions from aqueous solution due to their structure, abundant resources, availability of different sorbents, chemical and mechanical strength, easy handling, low production cost and reusability (Milosavljević et al., 2010; Bao, Ma, & Li, 2011). XG is an anionic polysaccharide which contains a large number of COOH and OH groups, but its application as an adsorbent is limited due to their solubility in water (Mittal, Parashar, Mishra, & Mishra, 2014; Pandey & Mishra, 2012). Because of this limitation, recent polysaccharide based composites are used extensively for the removal of toxic metal ions from aqueous solution (Ghorai, Sinhamahpatra, Sarkar, Panda, & Pal, 2012; Zhang, Xu, Wang, Luo, & Wang, 2014; Ghorai, Sarkar, & Pal, 2014a). MMT is a layered aluminum silicate with exchangeable cations (e.g. Na^+, K^+, Ca^{2+} and Mg^{2+}) and reactive —OH groups on the surface (Bao et al., 2011; Kumar, Depan, Tomer, & Singh, 2009). MMT is environmentally friendly, and its incorporation of it in many polymer-layered silicate (PLS) nanocomposites systems improves the properties (such as swelling ability, gel strength, mechanical and thermal stability) of adsorbents, and also reduces production cost (Bao et al., 2011; Nguyen & Baird, 2006). AMPS is hydrophilic monomer containing nonionic

* Corresponding author. Tel.: +98 1333690274; fax: +98 1333690271.
E-mail address: dadvand@guilan.ac.ir (A. Dadvand Koohi).

and anionic functional groups. Therefore, introduction of AMPS on the hydrogels can increase the number of ionic groups and boosts their adsorption capacity (Bao et al., 2011). However, no studies have been done on the removal of Cu^{2+} by XG-g-AMPS hydrogel and XG-g-AMPS hydrogel composite. The objective of the present study is to synthesize XG hydrogel, XG-g-AMPS hydrogel and XG-g-AMPS hydrogel composite and investigate the removal efficiency of Cu^{2+} ions from aqueous solution by these novel hydrogels. The effect of initial pH value of the Cu^{2+} solution, adsorbent dosage, contact time, initial Cu^{2+} concentration and temperature on adsorption were investigated and the optimal conditions were determined to obtain maximum adsorption. The adsorption kinetics and isotherms for Cu^{2+} onto xanthan-based hydrogels were also studied.

2. Experimental

2.1. Chemicals

Xanthan gum polysaccharide (XG, molecular weight 2.5×106 to 3.0×106 g/mol, brookfield viscosity 1% solution 800–1200 cps) and montmorillonite (MMT) were purchased from Sigma, USA. 2-Acrylamido-2-methyl-1-propane sulfonic acid (AMPS), ammonium persulfate (APS) and N,N-methylenebisacrylamide (MBA) were supplied by Merck, Germany. For all the experiments, double distilled water was used. The aqueous solutions of Cu^{2+} were prepared by dissolving $CuCl_2 \cdot 2H_2O$ (Merck, Germany) in deionized distilled water.

2.2. Xanthan-based hydrogels preparation

The XG-g-P(AMPS)/MMT was synthesized by free radical polymerization technique in nitrogen atmosphere using APS as initiator and MBA as crosslinker. 0.7 g of XG polysaccharide was slowly dissolved into 50 mL of distilled water. Afterwards, 10 mL of MMT solution (2 wt%) was added to the XG solution, and it was homogenized with a constant stirring rate, for 1 h. At this stage, 0.02 g of APS, was added, and reaction was continued for another 1 h in an oil bath at a temperature of 70 °C. Afterwards, 1 g of AMPS and 0.2 g of MBA solution were added to above solution, and it was continued to heat at the same temperature (70 °C), for 3 h without any disturbance. During the whole reaction nitrogen gas was purged through reaction system. The hydrogels were dried at room temperature in 7 days, and in order to remove the unreacted monomers the hydrogels were immersed in water, which was changed daily in duration of one week.

XG hydrogel was prepared according to a similar procedure except without addition of MMT and AMPS. For preparing the XG-g-P(AMPS) hydrogel, MMT was eliminated of the previous preparation method.

2.3. Characterization

The hydrogels, were characterized using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analyses. FTIR (Bruker, United States of America, Alpha) of XG polysaccharide, MMT, XG hydrogel, XG-g-P(AMPS) hydrogel and XG-g-P(AMPS)/MMT hydrogel composite, before and after adsorption of Cu^{2+} ions, was done using KBR pallet method for determination of which functional groups were responsible for metal uptake, confirmation of the grafting of AMPS onto XG polysaccharide. The dried hydrogels were directly analyzed using FTIR, and the samples were scanned from wave number 550–4000 cm^{-1}.

The % grafting and % grafting efficiency were calculated using Eqs. (1) and (2) given by (Pandey & Mishra, 2012; Athawale & Lele, 1998):

$$precent\ grafting(\%G) = \frac{W_1 - W_0}{W_0} \times 100 \tag{1}$$

$$precent\ efficiency(\%GE) = \frac{W_1 - W_0}{W_2} \times 100 \tag{2}$$

where W_0, W_1 and W_2 are the weights of XG polysaccharide, purified graft copolymer and AMPS monomer, respectively.

The morphologies of the hydrogels were examined using a SEM instrument (Philips, Netherlands, XL 30) after coating the sample with gold film.

2.4. Adsorption studies

In all typical batch experiments, required amount of adsorbent was thoroughly mixed with 50 mL of Cu^{2+} ions solution, whose concentration was known previously. A 50 mL of Cu^{2+} solution of a desired concentration, adjusted to a desired pH, was taken in reaction bottles of 250 mL, and 0.1 g of hydrogels was added. The pH was carefully adjusted by adding dilute NaOH or HNO_3 in drops. The effect of adsorbent dosage on the Cu^{2+} ions adsorption was studied for different initial concentration of 0.05, 0.075, 0.1, 0.125, 0.15, 0.2 and 0.25 g/50 mL, at a pH value of 5.2 and 25 °C. The effect of temperature on the Cu^{2+} ions adsorption was conducted at 5, 15, 25, 35 and 45 °C, at pH 5.2 with initial concentration of Cu^{2+} being 70 mg/L, and 0.1 g of one of the hydrogels was added.

Adsorption isotherms were studied at three different temperatures (25, 35 and 45 °C). Optimized amount of hydrogels (0.2 g) was added in 50 mL Cu^{2+} ions solutions of different concentrations varying in the range of 18.16–321.8 mg/L in at pH 5.2. The amount of copper adsorbed at equilibrium (q_e) was calculated according to the following (Ghorai et al., 2012):

$$q_e = \frac{(C_0 - C_e)}{m} \times V \tag{3}$$

where C_0 (mg/L) and C_e (mg/L) are the initial and the final concentration of copper, respectively. V is the volume of the solution (L), and m is the weight of the adsorbent (g).

Adsorption kinetic experiments were performed using 0.1 g of hydrogels in 50 mL of Cu^{2+} aqueous solution with 50 mg/L of Cu^{2+} aqueous solution at 25 °C. The concentartion of Cu^{2+} in solution were analyzed by Atomic Adsorption Spectrometer (AA) (Make: YL Instrument, South Korea; Model: Younglin AAS 8020). Amount of Cu^{2+} adsorbed at different time intervals was calculated using the following equation (Mittal et al., 2014):

$$q_t = \frac{(C_0 - C_t)}{m} \times V \tag{4}$$

The percentage adsorption of Cu^{2+} ions was calculated using the following equation (Ghorai et al., 2012):

$$\%\ removal = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{5}$$

where q_t is amount of Cu^{2+} ions adsorbed per unit mass of adsorbent (mg/g) at time t, C_0 is the initial concentration of Cu^{2+} ions (mg/L), C_t is the concentration of Cu^{2+} ions (mg/L) at time t, V is the volume of the solution (L), and m is the weight of the adsorbent (g).