



Granular hydrogel initiated by Fenton reagent and their performance on Cu(II) and Ni(II) removal

Yian Zheng^{a,b}, Aiqin Wang^{a,*}

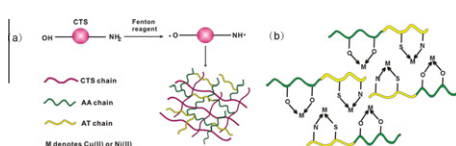
^a Center of Eco-materials and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

^b Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- ▶ Granular hydrogel was formed using Fenton reagent in air atmosphere.
- ▶ Allylthiourea was used to decrease the swelling degree during the adsorption.
- ▶ The hydrogel can interact with Cu(II) and Ni(II) via different functional groups.
- ▶ The hydrogel can work as effective adsorbent for treatment of a real wastewater.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 May 2012

Received in revised form 22 June 2012

Accepted 26 June 2012

Available online 5 July 2012

Keywords:

Granular hydrogel
Fenton reagent
Allylthiourea
Heavy metals
Removal

ABSTRACT

With acrylic acid (AA) and allylthiourea (AT) as the monomers, an “instantaneous” granular hydrogel was prepared using Fenton reagent as redox initiator under an ambient temperature in air atmosphere, and then characterized by means of Fourier transform infrared spectroscopy and scanning electron microscope. The obtained hydrogels were investigated as the adsorbents to remove Cu(II) and Ni(II) from the aqueous solution. The effects of operating parameters on the adsorption capacity were studied, including the composition ratio (AT:AA), contact time, pH and initial concentrations of heavy metal ions. The results indicate that the introduction of allylthiourea into the hydrogel can reduce greatly the swelling ratio, but with no significant variation in the adsorption capacity as the initial Cu(II) and Ni(II) concentrations lower than 400 and 200 mg/L, respectively. In addition, the adsorption capacity shows a pH-independence at $\text{pH} \geq 4.0$, and the adsorbed Cu(II) and Ni(II) can be partially desorbed using 0.01 mol/L HCl as the desorbent, rendering the as-prepared hydrogel good re-adsorption ability, especially for Cu(II). The applicability in real electroplating wastewater demonstrates that the as-prepared hydrogel with AT is promising for the removal of Cu(II) and Ni(II) for its comparable adsorption capacity with the hydrogel without AT.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Chitosan (CTS), poly- $\beta(1 \rightarrow 4)$ -2-amino-2-deoxy-D-glucose, is the deacetylated product of chitin, poly- $\beta(1 \rightarrow 4)$ -N-acetyl-D-glucosamine, which is the second most abundant polysaccharide in nature forming the principal constituent of shells of crustaceans such as crabs, lobsters, prawns and Antarctic krill. Due to its

biocompatibility and biodegradability, CTS is now receiving increasing attention and has shown prospective applications in many fields. However, CTS can only be dissolved in few diluted acid solutions, a major drawback for its further exploitation. To improve its solubility and widen its applications, there has been a growing interest in chemical modification of CTS. Among various methods, graft copolymerization is the most attractive because it is a useful technique for modifying the physical and chemical properties of natural polymers [1].

CTS bears two types of reactive groups that can be grafted: the free amino groups on deacetylated units and the hydroxyl groups

* Corresponding author. Tel.: +86 931 4968118; fax: +86 931 8277088.

E-mail address: aqwang@licp.cas.cn (A. Wang).

on acetylated or deacetylated units. Graft copolymerization of synthetic polymers onto CTS can introduce desired properties and enlarge the field of the potential applications by choosing various types of side chains [2]. In recent years, the graft copolymerization of vinyl monomers onto CTS backbone in water in the presence of crosslinker has been used to obtain a three-dimensional structured product, i.e. hydrogel with the properties of variable flexibility and swelling to a predictable volume in a fluid medium [3–5]. Different from the bulk hydrogel, the graft copolymerization of typical vinyl monomer, acrylic acid, onto CTS can obtain a well known granular hydrogel via a grafting reaction in homogeneous phase, with tunable particle size [6,7], while the standard method used for preparation of granular hydrogel is heterogeneous polymerization such as emulsion and dispersion polymerization. Sahiner and Singh obtained the hydrogel particles in lecithin organogel using microemulsion polymerization and the novelty of that work was the synthesis of completely charged hydrogel micro/nano-particles in w/o microemulsion of a biocompatible phospholipids [8]. In addition to this, it was shown that a cationic hydrogel can be prepared in a variety of sizes utilizing inverse microemulsion polymerization technique [9]. By dispersion polymerization, a granular hydrogel from *N*-isopropylacrylamide had been obtained by atom transfer radical polymerization using hydrophilic poly(ethylene glycol) methyl ether as a macro-initiator [10].

In a standard approach, the polymerization of vinyl monomer-based hydrogels is initiated by a water-soluble free-radical initiator. The most commonly used initiator is potassium persulfate (PPS)/ammonium persulfate (APS), which can be used alone at higher temperature (>60 °C) [11–13], or in combination with *N,N,N,N'*-tetramethylethylenediamine (TEMED) to decrease the triggering temperature [14–16]. In addition to APS/TEMED, other water-soluble redox initiators have also been examined for hydrogel synthesis, such as APS/sodium pyrosulfite [17,18], APS/ascorbic acid [19,20], APS/sodium bisulfite (SBS) [21,22] and PPS/ferrous ammonium sulfate (FAS) [2,3]. Through an electron transfer mechanism, free radicals can be easily generated under mild conditions (lower temperature), which can reduce the unpredictable self cross-linking using an initiator at higher temperature, and is more appropriate for the encapsulation of enzymes, antibodies, or any other thermally unstable moieties. Additionally, these initiators have the advantage of being soluble in water, circumventing any use of organic solvents.

With acrylic acid as a typical vinyl monomer, the resulting CTS-grafted hydrogel contains a number of anionic carboxyl groups, and accordingly, these ionotropic hydrogels are capable of interacting with polyvalent metal cations [23]. Also, the unique structure of three-dimensional networks is favorable for the convective mass transport of an adsorbate, making CTS-grafted hydrogel an attractive material for the removal of many pollutants from the aqueous solution [24]. The higher swelling ratio of the hydrogel is responsible for their fast adsorption kinetics for the heavy metal ions, whereas it is the major problem when a low-level concentration is applied for these heavy metal ions. We have tried to modify the three-dimensional networks with hydrophobic moieties, but the results are not so satisfactory, i.e. lower swelling ratio but at the expense of adsorption capacity.

In this work, we demonstrate a very simple route to obtain a series of CTS-grafted hydrogels at room temperature using Fenton reagent, i.e., a redox initiator pair, with acrylic acid as the main monomer and allylthiourea as the co-monomer. As well known, thiourea group can easily form coordination linkage with the heavy metals [25–27], and after *in situ* polymerization, abundant thiourea and amino groups are trapped within the three-dimensional networks, by which the swelling ratio of the hydrogel will be reduced whereas the higher affinity to the heavy metal ions is expected to be retained.

2. Materials and methods

2.1. Materials

Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Chitosan (CTS, with an degree of deacetylation of 0.90 and average molecular weight of 3.0×10^5 , Zhejiang Yuhuan Ocean Biology Co., Ltd., Zhejiang, China) and *N,N'*-methylene-bisacrylamide (MBA, chemically pure, Shanghai Yuanfan additives plant, Shanghai, China) were used as received. Allylthiourea (AT, analytical grade), ferrous ammonium sulfate (FAS, analytical grade) and hydrogen peroxide solution (H₂O₂, analytical grade) were provided by Shanghai Reagent Factory (Shanghai, China), Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and Jiangsu Sanmu Group Co. Ltd. (Jiangsu, China), respectively. The complexing reagents, 2,9-dimethyl-1,10-phenanthroline and dimethylglyoxime, were received from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

The stock solutions containing 1000 mg/L Cu(II) or Ni(II) were prepared by dissolving a known quantity of copper acetate or nickel chloride in 1000 ml of distilled water. This stock solution was diluted as required to obtain a series of working solutions containing 100–800 mg/L Cu(II) or Ni(II). The solution pH was adjusted by adding 0.1 and 1.0 mol/L HCl or NaOH solutions (Mettler Toledo FE20 pH-meter). All other chemicals used were of analytical reagent grade, and all solutions were prepared with distilled water unless stated otherwise.

2.2. Preparation of hydrogels

A series of hydrogels from CTS, AA, and AT were prepared according to the following procedure. Typically, 0.3 g CTS was dissolved in 45 ml distilled water containing 3.6 g AA and 0.15 g MBA, while an appropriate amount of AT was added according to the weight ratio of AT:AA. When the above mixture was stirred at room temperature (18 ± 2 °C) for 30 min, the required quantities of FAS and freshly prepared H₂O₂ solution (3%) were added. Immediately, the granular hydrogel was observed, and by then the reaction was carried out for 1 h at room temperature in atmospheric oxygen. The resulting granular hydrogel was neutralized with 2.0 mol/L NaOH solution to neutral pH, dehydrated with industrial alcohol and dried at room temperature. The as-prepared hydrogel with and without AT was denoted as CTS-g-PAA and CTS-g-P(AA-co-AT), respectively. The digital photographs of them were shown in Fig. 1. All hydrogel samples used for adsorption had a particle size in the range of 40–80 mesh.

2.3. Swelling degree

In 25 mL solution containing 200 mg/L Cu(II) or Ni(II), an accurately weighed hydrogel (50 mg) was immersed until the swelling equilibrium was reached (4 h). These hydrogels were then separated from the solutes by filtrating with a 100-mesh stainless screen and hanging up for 10 min. The swelling degree (SD) was calculated from the following equation:

$$SD = (m_s - m_d)/m_d \quad (1)$$

where m_s and m_d were the swollen and dry weight of each hydrogel, respectively.

2.4. Adsorption experiments

Adsorption experiments were performed in a series of 50 mL conical flasks containing 50 mg hydrogel and 25 mL Cu(II) or Ni(II)

Download English Version:

<https://daneshyari.com/en/article/149577>

Download Persian Version:

<https://daneshyari.com/article/149577>

[Daneshyari.com](https://daneshyari.com)