



Sulfhydryl functionalized hydrogel with magnetism: Synthesis, characterization, and adsorption behavior study for heavy metal removal



Rong Hua, Zhengkui Li*

State Key Laboratory of Pollutant Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, China
Institute of Oceanographic Research, Nanjing University, Nanjing 210023, China

HIGHLIGHTS

- A novel Fe₃O₄-poly(L-cysteine/2-hydroxyethyl acrylate) hydrogel was synthesized.
- The adsorption kinetics and isotherms of metal ions on the hydrogel were studied.
- The adsorption mechanisms were a combined reaction of chelation and ion-exchange.

ARTICLE INFO

Article history:

Received 23 January 2014
Received in revised form 19 March 2014
Accepted 22 March 2014
Available online 2 April 2014

Keywords:

Magnetic hydrogel
L-Cysteine
Heavy metal ions
Adsorption mechanism

ABSTRACT

In this study, functionalized hydrogel with sulfhydryl group was initially synthesized by ⁶⁰Co-γ induced copolymerization and then loaded with Fe₃O₄ nanoparticles by *in situ* coprecipitation method. The prepared magnetic hydrogel, Fe₃O₄-poly(L-cysteine/2-hydroxyethyl acrylate) (Fe₃O₄-P(Cys/HEA)), was used to remove Pb²⁺, Cd²⁺, Ni²⁺ and Cu²⁺ from aqueous solutions, and was characterized by various methods including scanning electron microscope, FTIR spectroscopy, X-ray diffraction, vibrating sample magnetometer, and X-ray photoelectron spectroscopy. The FTIR spectra analysis identified its functional groups featured of -NH₂ and -SH, indicating that the magnetic hydrogel was indeed a copolymer of 2-hydroxyethyl acrylate and L-cysteine. The saturation magnetization and superparamagnetic properties of the hydrogel were also measured, laying a foundation for the separation of Fe₃O₄-P(Cys/HEA) hydrogel from the environment when adsorption completed. The performance of the sulfhydryl modified magnetic hydrogel for heavy metal ions removal was evaluated by changing four process variables: pH, temperature, initial heavy metal concentration and the contact time of adsorbent and heavy metal solutions. Results showed that the hydrogel was pH sensitive but barely affected by temperature, and the adsorption process followed a pseudo-second-order rate equation and better fitted Langmuir monolayer adsorption. X-ray photoelectron spectroscopy analysis of the magnetic hydrogel further revealed that the adsorption mechanisms of Pb²⁺, Cd²⁺, Cu²⁺ and Cr³⁺ on Fe₃O₄-P(Cys/HEA) could be a combined reaction of chelation and ion-exchange between functional groups and metal ions. Moreover, Fe₃O₄-P(Cys/HEA) was regenerated with an efficiency of greater than 90% using 0.1 M ethylene diamine tetraacetic acid.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

During the past decades, humans have suffered a lot from exponential increase of using heavy metals in industrial processes, for instance, metal plating, mining activities and battery manufacture [1–3]. In view of the severe situation, techniques including chemical precipitation [4], adsorption [5], ion exchange [6], reverse osmosis [7], electrochemical treatments [8] and membrane separation [9]

are used to remove the heavy metal ions [10,11]. Among the methods, adsorption is regarded as the most reliable choice when both environmental and economic constraints are taken into consideration [12].

Hydrogels, which are three-dimensional networks composed of cross-linked hydrophilic polymer chains, can be cast into practically any shape, size, or form and can absorb water to reach thousands of times their dry weight due to the hydrophilic groups in their backbone [13]. As newly developing adsorbent materials, hydrogels have attracted particular attention because of their application advantages, like biocompatibility, biodegradability, lack of toxicity and facility of the incorporation of different chelating

* Corresponding author at: Institute of Oceanographic Research, Nanjing University, 163 Xianlin Avenue, Nanjing 210023, China. Tel./fax: +86 25 89680396.

E-mail address: zhkuili@nju.edu.cn (Z. Li).

groups into the polymeric networks [14]. Up to now, numerous monomers containing hydrophilic groups such as amino ($-\text{NH}_2$), carboxyl ($-\text{COOH}$), acylamino ($-\text{CONH}_2$) and sulfonic ($-\text{SO}_3\text{H}$) [15–18] that display complex ability towards metal ions have been used for the hydrogel synthesis. Whereas, most of the previous studies focused on the chelating ability of a specific functional group and rarely mentioned the coordination effect caused by multiple functional groups. L-cysteine is precisely a kind of monomer containing multiple functional groups. Furthermore, Among 20 kinds of amino acids constituting proteins, L-cysteine is the only one that contains a sulfhydryl group. Sulfhydryl group is an excellent ligand due to the strong affinity to a wide range of heavy metal ions as a result of Lewis acid-base interactions [19]. Najafi et al. [20] modified the silica gel with 3-trimethoxysilyl-1-propanethiol, and indicated that silica gel with a surface functionalization of sulfhydryl group was an effective adsorbent material for toxic soft metal ions such as Hg^{2+} , Pb^{2+} and Cd^{2+} . Chai et al. [21] functionalized spent grain with thioglycolic acid, and the sulfhydryl-functionalized spent grain showed significant improvement in terms of metal loading capacity. However, sulfhydryl-containing compounds including L-cysteine have seldom been used for one-step direct synthesis of hydrogels and mechanisms of metal adsorption by multiple functional groups of L-cysteine remains unknown, although great concerns are focused on the modification of materials with sulfhydryl-containing compounds.

It is difficult to separate traditional (eg. zeolites) or newly developed (eg. hydrogels) adsorbent materials from aqueous environment, especially when adsorption surroundings is complex. Recently, adsorbents with magnetic properties have received growing concerns due to their readily separation with applied magnetic field [22]. Additionally, the large surface area and highly active surface sites caused by size-quantization effect of magnetic nanoparticles existing in adsorbents enable them to possess higher adsorption capacity compared with the previous adsorbents [23,24]. Hu et al. [25] developed a new method to combine nanoparticle adsorption with magnetic separation, and the synthesized maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles were utilized for removal of Cr(VI). Ozay et al. [26] synthesized hydrogels based on 2-acrylamido-2-methyl-1-propanesulfonic acid via photopolymerization technique and applied them to the preparation of magnetic responsive composite hydrogels. It was revealed that hydrogel networks with magnetic properties could effectively uptake toxic metal ions, and readily be removed with applied magnetic field upon completion of their mission. Lee et al. [27] prepared iron-oxide nanoparticles-immobilized sand (INS) by simple impregnation process before employing the magnetic material into the removal of several toxic heavy metal ions, and results showed that INS could be potentially applied in the remediation of wastewaters contaminated with heavy metal ions. Despite of a number of researches on magnetic adsorbents, the *in situ* combination of magnetite (Fe_3O_4) nanoparticles with a novel hydrogel has not been reported, and it would be of great importance to develop a novel adsorbent with both high adsorption capacity and fast separation ability from aqueous environment.

In this study, a novel poly (L-cysteine/2-hydroxyethyl acrylate/) (P(Cys/HEA)) hydrogel was developed via $^{60}\text{Co-}\gamma$ -induced copolymerization as a clean and environmentally friendly way of initiation and utilized for *in situ* Fe_3O_4 nanoparticles loading to induce magnetic field responsiveness. The material $\text{Fe}_3\text{O}_4\text{-P(Cys/HEA)}$ was then characterized by using scanning electron microscope (SEM), FTIR spectroscopy (FTIR), X-ray diffraction (XRD), vibrating sample magnetometer (VSM) and X-ray photoelectron spectroscopy (XPS) before its adsorption capacity were investigated. The Freundlich and Langmuir adsorption isotherm equations, as well as the pseudo-first-order and pseudo-second-order equations, were utilized to verify the mechanism and kinetics of the adsorption

process. Separation and regeneration studies were also carried out for further investigating the potential application of $\text{Fe}_3\text{O}_4\text{-P(Cys/HEA)}$ hydrogel for the removal of heavy metal ions from wastewater.

2. Materials and methods

2.1. Materials used in this study

HEA, 2-hydroxyethyl acrylate, molecular formula $\text{C}_5\text{H}_8\text{O}_3$, and Cys, L-cysteine, molecular formula $\text{C}_3\text{H}_7\text{NO}_2\text{S}$ were purchased from Sigma-Aldrich, USA. FeCl_3 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Ammonium hydroxide, $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and of analytical grade were purchased from SINOPHARM (Shanghai, China).

2.2. Preparation of P(Cys/HEA) hydrogel

Crosslinked P(Cys/HEA) hydrogel was prepared by irradiation solution polymerization in the presence of water as solvent. Firstly, Cys and HEA mixture was prepared in deionized water (v./v. = 3:7) at a fixed monomers ratio 9:1 (mol/mol). The solution was then purged with nitrogen gas for 15 min to eliminate any dissolved oxygen. Thirdly, the solution was transferred to a 125 ml brown bottle covered with a transparent 30 lumen thick teflon film to prevent oxygen inhibition. Then under a nitrogen atmosphere, the prepared mixture was irradiated with $^{60}\text{Co-}\gamma$ source for 30 h to a total dose of 30 kGy. The $^{60}\text{Co-}\gamma$ source is installed at the Nanjing Radiation Center. Finally, the obtained copolymer hydrogels were removed from the brown bottle and cut into pieces with $5 \times 5 \times 5$ mm dimension. The reaction occurring during radiation polymerization of Cys and HEA monomer has been presented in Fig. 1.

2.3. Preparation of $\text{Fe}_3\text{O}_4\text{-P(Cys/HEA)}$ hydrogel

After irradiation, the solid polymerized hydrogel was shifted out from the container and cut into cubes, and then washed with deionized water for 48 h to remove the unreacted components in the network. The *in situ* Fe_3O_4 nanoparticles loading process followed a modified procedures recommended by Jiang et al. [28]. Firstly, proper amount of swollen hydrogel cubes were transferred into a three-necked 1000 ml-bottle with condensing unit before

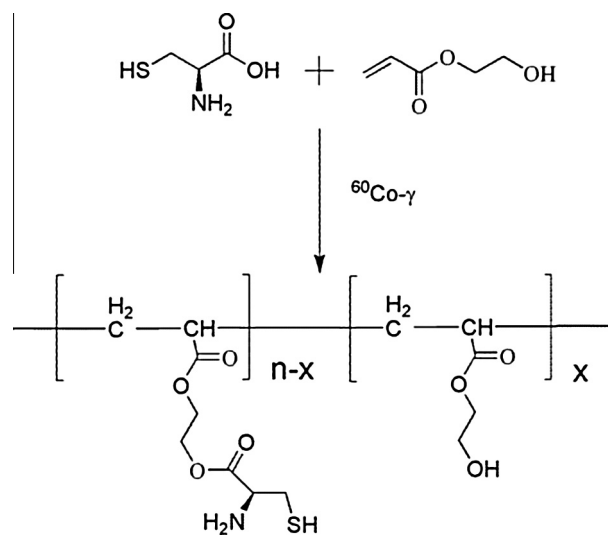


Fig. 1. Scheme for synthesis of p(Cys/HEA) hydrogel.

Download English Version:

<https://daneshyari.com/en/article/147406>

Download Persian Version:

<https://daneshyari.com/article/147406>

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