Journal of Water Process Engineering 13 (2016) 143–152

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Removal of Cu(II) ions from water by ion-imprinted magnetic and non-magnetic cryogels: A comparison of their selective Cu(II) removal performances

Mitra Jalilzadeh, Serap Şenel*

Hacettepe University, Department of Chemistry, Postal Code:06800, Beytepe, Ankara 06800, Turkey

ARTICLE INFO

Article history:
Received 15 April 2016
Received in revised form 1 July 2016
Accepted 17 July 2016

Keywords:
IIP
MAH
Cu(II)
Cryogel
Magnetite

ABSTRACT

2-Hydroxyethylmethacrylate (HEMA) based ion-imprinted cryogel membranes (IIP) were synthesized using histidine containing functional monomer, *N*-methacryloyl-L-histidine (MAH) as complexing/chelating agent, Cu(II) ions as template, methylene bisacrylamide as cross-linker, TEMED and APS as redox pair in both magnetic and non-magnetic forms through free radical polymerization method for selective Cu(II) ion removal. A control non-imprinted cryogel (NIP) was also prepared for comparison. The matrices were characterized by swelling tests, scanning electron microscopy (SEM), BET, and FTIR. Effect of several parameters (pH, temperature, contact time, etc.) on adsorption capacities was examined in batch mode.

The maximum adsorption capacities of cryogel membranes under optimized conditions were 77.2 mg/g and 182.7 mg/g for non-magnetic and magnetic IIP cryogels, respectively. The adsorption process best fitted to Langmuir isotherm while pseudo-second-order kinetic model was well suited to explain controlling step in adsorption kinetics. The reusability of matrices was tested for three successive cycles. Competitive adsorption studies were finally performed to prove the selectivity of resulting matrices for Cu(II) ions in binary and multi-ion containing synthetic water samples.

1. Introduction

Copper is essential to all living organisms as a trace element, a component of several enzymes mainly participating in electron flow and a catalyst in redox reactions. The US Environmental Protection Agency's Maximum Contaminant Level in drinking water for copper is 1.3 mg/L. At higher level, copper poisoning causes hemostasis, hypotension, melena, coma, jaundice, and gastrointestinal distress. Long-term exposure to copper can also damage the liver and kidney [1,2]. Due to the harmful effects on human beings and ecological system, the wastewater containing heavy metal ions like copper at high levels should be treated properly. Amongst the available techniques for treatment, chemical precipitation, flotation, ion-exchange, electrochemical process, adsorption and membrane processes are frequently used [3–7]. Modified natural materials, industrial inorganic substances, by-products, synthetic polymers or biopolymers were treated as potential adsorbents for heavy metal removal purposes [8–12]. Due to the advantages such as macroporous highly cross-linked polymeric network, ease of synthesis, and chemical and structural stability, cryogel format for the polymeric adsorbent is a priority for the choice [13–15]. The advantages may be enhanced by including the ion-imprinting approach in synthesis to get ion-imprinted cryogels (IIPs) for selective heavy metal ion removal. IIPs are similar to molecularly imprinted polymers (MIPs) except that they recognize metal ions after imprinting while retaining all the virtues of MIPs. The preparation and use of IIPs in aqueous solutions have been limited since the water strongly interferences with the system. Overcoming this difficulty is to use organic solvents or to use interaction between template and functional monomer that are enhanced in water such as hydrophobic and metal coordination interactions [16].

Metal chelating chromatography [17,18] method in removal of heavy metal ions from environmental waters is the best approach because of its higher selectivity and sensitivity.

Chelate forming polymeric sorbent could be prepared through chemical modification of the ligand or synthesis of sorbent by monomeric ligands. Peptides, macrocyclic chelating ligands and nucleic acids can be used as biological ligands.

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* Corresponding author.
E-mail address: senel@hacettepe.edu.tr (S. Şenel).

http://dx.doi.org/10.1016/j.jwpe.2016.08.010

Due to the easy separation of sorbent from adsorption medium, the synthesis of sorbent in magnetic form is also preferable. Functionalized silica gel adsorbent [19], chitosan (CS), microsphere [20], composite adsorbent [Cu(II)-MICA] in magnetic form [21], amino-functionalized activated carbon sorbent [22], EDTA-modified chitosan/SiO_2/Fe_3O_4 [23], p(HEMA-*co*-VIM) composite cryogel [24], shell of lentil [25], p(EGDMA-*co*-MAH) microbeads [26] and p(HEMA-*co*-MAPA) [27] membrane were treated for Cu(II) ion removal.

In this study, Cu(II) ion-imprinted p(HEMA-*co*-MAH) cryogel membranes were synthesized in magnetic and nonmagnetic forms, characterized, and their Cu(II) removal performances were examined. The adsorption capacity of IIP cryogels was also tested for multi-ions containing sample as artificial wastewater simulation. The adsorption isotherm models and kinetics were studied as well.

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA), *N*, *N*'-methylene bisacrylamide (MBAA), L-histidine, hydroquinone, triethylamine and nitrate of copper were purchased from Sigma (St. Louis, MO, USA). *N*,*N*,*N*,*N*-Tetramethylethylenediamine (TEMED) and ammonium persulfate(APS) were from Bio Rad (Hercules, CA, USA). The Fe_3O_4 nanoparticles with diameters less than 5 nm were purchased from Sigma as well. All water used in the experiments was purified using a Barnsstead (Dubuque, IA) RO pure LP reverse osmosis unit.

2.2. Synthesis of functional monomer

The synthesis method was given elsewhere [28]. The histidine amino acid containing imidazole side groups were chosen for complexing Cu(II) ions and obtaining good water compatibility. Histidine based functional monomer *N*-methacryloyl-L-histidine (MAH) was synthesized as given: 5.0 g of L-histidine methyl ester and 0.2 g of hydroquinone were dissolved in 100 mL of CH_2Cl_2 and resulting solution was cooled down to 0 °C. Then, after 5.0 mL of methacryloyl chloride was slowly poured into 12.7 g of triethylamine; the mixture was magnetically stirred under nitrogen atmosphere at room temperature for 2 h. The unreacted methacryloyl chloride was extracted with 10% NaOH solution. The aqueous phase was removed in rotary evaporator and MAH was obtained.

2.3. Synthesis of MAH-Cu(II) pre-complex

23.3 mg (0.1 mmol) of $Cu(NO_3)_2$. $2{\cdot}5H_2O$ was added to 5.0 mL of water containing 22.3 mg (0.1 mmol) of MAH monomer to form MAH-Cu(II) prepolymerization complex in 1 MAH:1 Cu(II) by mole ratio. The solution was magnetically stirred for 3 h, and MAH-Cu(II) pre-complex (blue crystals) was separated by filtration, cleaned by ethanol: water mixture (75:25, V:V) and dried under vacuum (12 h, 200 mmHg).

2.4. Synthesis of cryogels

The cryogel samples were synthesized by free radical polymerization method under partially frozen conditions. Three Cu(II) ion imprinted nonmagnetic cryogels having different compositions were prepared (Table 1). In general, 4.7 mL of HEMA was dissolved in 5.3 mL of water (Phase 1). N_2 gas was passed through solution for 5 min under vacuum (100 mmHg) to remove dissolved oxygen. The final monomer concentration was adjusted to 18.8% (w/v). Phase 2 contained 2.013 mg of MBAAm (crosslinker) dissolved in 20.0 mL of water.

Table 1
Composition of Cu(II) ion imprinted magnetic cryogels and non-magnetic cryogels.

Cryogel Codes	MAH-Cu(II) complex (mol)	Fe_3O_4 (mg)
Cu-1	0.050	–
Cu-2	0.100	–
Cu-3	0.200	–
Cu*-1	0.050	25
Cu*-2	0.100	25
Cu*-3	0.200	25
Cu*-4	0.050	50
Cu*-5	0.100	50
Cu*-6	0.200	50
Cu*-7	0.050	100
Cu*-8	0.100	100
Cu*-9	0.200	100

HEMA: 4.7 mL (in 5.3 mL of water), Methylenebisacrylamide: 2.013 mg (in 20 mL of water)*: Cu(II) ion imprinted magnetic cryogel.

The two phases were then mixed and the desired amount (50, 100, 200 mmol) of pre-complex was included. APS (100 mg), 1% w/v of total amount of monomer as initiator, was introduced to solution. Then, the solution was cooled in an ice bath for 5 min. Finally, TEMED (100 μL) was included as activator. The solution was placed between two electrophoresis glasses (25 × 25 cm) while the teflon plate (thickness 0.2 mm) was placed between the glasses as separator. Polymerization solution between the three-edge closed glass plates was kept at −12 °C for 24 h. The product was thawed at room temperature. The resulting membrane was cut by a perforator in circles having a diameter of 1.0 cm. An extensive cleaning process was applied to remove the unreacted monomers and initiator using diluted HCl solution and water: ethanol mixtures. Cryogel membranes were incubated by Na_2(EDTA) solution (100 mmol/20 mL) to desorb the imprinted Cu(II) ions. The membranes were finally stored in 0.02% sodium azide solution at 4 °C until use. The same experimental procedure was applied for non-imprinted cryogels, using only MAH monomer in the same amount instead of MAH-Cu(II) complex.

To evaluate magnetism effect on the ion recognition performance of cryogels, magnetic forms of cryogel samples were also prepared. The compositions of Cu(II) ion imprinted magnetic cryogels are given in Table 1 as well. In that case, before the addition of initiator into the polymerization mixture, Fe_3O_4 nanoparticles (<5 nm) were included into polymerization recipe. The experimental procedure was performed as same mentioned above for synthesis of ion-imprinted and non-imprinted (Cu-2N) magnetic and (Cu*-2N) non-magnetic cryogels. For the synthesis of non-imprinted magnetic cryogels, pre-complex was excluded in recipe as well.

2.5. Characterization studies

2.5.1. Swelling properties

The swollen membrane was dried in an oven at 50 °C until constant weight. After determining of the mass of dried sample (m_o,g), the mass of swollen sample (m_s,g) was also determined following an incubation period of 2 h in 20 mL of water at room temperature. The swelling degree was calculated as follows:

$$\text{Theswellingdegree} = (m_s - m_o)/m_o$$

where m_s and m_o are the masses (g) of swollen and dried cryogels, respectively.

2.5.2. FTIR studies

The cryogel samples dried until constant weight were crushed into fine powder. Then, powdered samples (2 mg) were mixed with KBr (IR-grade, 98 mg), and pressed into a pellet form to get