



Chelating magnetic copolymer composite modified by click reaction for removal of heavy metal ions from aqueous solution



Songwut Lapwanit, Thanida Trakulsujaritchok*, Piyaporn Na Nongkhai

Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Burapha University, Chonburi 20131, Thailand

HIGHLIGHTS

- Magnetic copolymer beads were functionalized by azide–alkyne click reaction.
- The chelating beads showed excellent adsorption capacity for heavy metal ions.
- The beads possessed a sensitive magnetic response and could be repeatedly used.

ARTICLE INFO

Article history:

Received 22 August 2015

Received in revised form 15 December 2015

Accepted 22 December 2015

Available online 29 December 2015

Keywords:

Chelating

Magnetic copolymer

Click reaction

Adsorption

Fe₃O₄ nanoparticles

Metal removal

ABSTRACT

Novel chelating magnetic copolymer beads in micron-size range were prepared by suspension polymerization and click reaction. The click chemistry was proposed as a tool for tuning the surface functionality of magnetic poly(vinylbenzyl chloride-co-styrene-co-divinyl benzene), M-PVBC, by a covalent attachment with propargyl alcohol via triazole formation. After click-coupling reaction, the changes in surface morphology and chemical functionality were examined by SEM–EDX and FT-IR, respectively. Adsorption characteristics for heavy metal were investigated by a batch adsorption in an aqueous system under different experimental conditions. The adsorption process was pH, concentration and time dependent. The maximum adsorption capacities of the chelating magnetic copolymer, M10-PVBC-C, for Zn(II), Cu(II) and Ni(II) in 500 ppm solutions were 67.29, 61.20 and 57.18 mg/g, respectively. Adsorption of Cu(II) ion, the model heavy metal ion, was well fitted to the Langmuir isotherm model. The magnetic chelating beads could be rapidly recovered from aqueous solution by an external magnetic field, regenerated and reused for 5 cycles without significant lost in adsorption capacity. The results of this work indicated that the surface functionalization by click reaction could be a simple and suitable method for the preparation of polymeric adsorbents for an effective removal of metal ions from aqueous solution.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Heavy metals are among the pollutants in aqueous waste effluents of many industries. Battery production, mining industry, oil refinery and paint production are just a number of examples. These toxic metals pose significant risks to the environment due to their non-biodegrading, carcinogenicity even at low concentration and tendency to accumulate, causing severe diseases in living organisms. Removal of heavy metals from wastewater has been a challenge in the field of environment protection and generally performed by traditional separation techniques including extraction, neutralization, precipitation/coagulation, membrane technology, biological treatment, and adsorption [1–5]. The application of adsorption technique has drawn enormous research attention over

the past years. Polymeric adsorbents have been used for this purpose because of their chemical functionality, adjustable surface area, dimension stability, easiness of handling and regeneration [6–8].

Recently, metal chelate adsorption combined with the use of magnetic nanoparticles is one of the promising techniques proposed due to its simplicity and fast separation in recovering adsorbent from wastewater under an appropriate magnetic field [9–12]. Several types of magnetic nanoparticles have been investigated including carbon-encapsulated magnetic, magnetite, maghemite and magnetic graphene nanoparticles [13–15]. These nanoparticles have attracted considerable attention because of their unique properties that make them very useful in different fields. They have at least one dimension smaller than 1 μm and are possible to be manipulated under an external magnetic field. Upon removal of the magnetic field, the superparamagnetic nanoparticles (usually diameter less than 15 nm) exhibit no

* Corresponding author. Tel.: +66 08 17234246.

E-mail address: thanida@buu.ac.th (T. Trakulsujaritchok).

magnetic properties and therefore have no attraction for each other, offering an advantage of reducing risk of particle aggregation and a possibility to be used for preparing polymeric composite [12,14]. The application of adsorption process based on the use of magnetic polymer composite involves the following steps: (i) adsorption, (ii) magnetic separation of the adsorbent from wastewater, (iii) adsorbent regeneration, and (iv) handling of the regeneration solution and the adsorbent. These magnetic polymer composites have been reported exhibiting good performance for the purpose of efficient removal owing to the choice of functionality and modification of the polymer matrix [16–18].

Different types of polymeric material have been chemically modified for the use of metal ion removal. The category of highly efficient organic reactions first described in 2001 by Sharpless and co-workers has emerged and become very popular in polymer chemistry [19]. The attention paid to the Cu-catalyzed “click” cycloaddition of azides and terminal alkynes has increased enormously in recent years as a useful and promising synthesis tool for functionalizing synthetic macromolecules and a wide range of polymer architectures [20–22]. These reactions proceed under mild conditions, generate inoffensive or no by products, and require simple purification techniques. One of the very important applications of the azide/alkyne click reaction is its high reactivity in heterogeneous reaction systems, which leads to the prospect of a high efficiency for the derivatization of surface and polymeric materials [23,24]. To the best of our knowledge, there has been no report on the preparation of chelating magnetic poly(vinylbenzyl chloride-co-styrene-co-divinyl benzene) by the effective click reaction for the application of heavy metal removal.

In this study, we reported the combination of facile suspension copolymerization between vinylbenzyl chloride, styrene and divinyl benzene in the presence of magnetic nanoparticles and the “click” 1, 3-dipolar cycloaddition reaction of azide and propargyl alcohol. Adsorption property and efficiency for the removal of Ni(II), Cu(II) and Zn(II) ions from aqueous solutions were investigated by a batch adsorption experiment. The influences of initial ion concentration, pH, and adsorption time on the adsorption capacity were studied. Adsorption isotherms, their parameters and correlation factors were also reported. Furthermore, the regeneration and reusability of these chelating magnetic beads were also studied to evaluate their effectiveness as an adsorbent.

2. Experimental

2.1. Materials

The materials used in organic phase for suspension polymerization, benzoyl peroxide (BPO), styrene (ST), vinylbenzyl chloride (VBC) and divinyl benzene (DVB) were purchased from Merck. The monomers were passed through activated alumina to remove inhibitors before use. Sodium azide, dimethylformamide, propargyl alcohol, dimethylsulfoxide, diethylenetriamine (99% grade) and chemicals used for nanoparticles preparation were purchased from Aldrich and used as received. Sodium chloride, sodium hydroxide, copper iodide and magnesium chloride were of reagent grade. The following chemicals, copper nitrate trihydrate, zinc chloride and nickel chloride hexahydrate (Ajax Finechem) were used for the adsorption study.

2.2. Synthesis of Fe_3O_4 nanoparticles

The magnetic Fe_3O_4 nanoparticles were synthesized via chemical co-precipitation between an aqueous mixture of ferric and ferrous salts. 4.00 g $FeCl_3 \cdot 6H_2O$ and 2.00 g $FeCl_2 \cdot 4H_2O$ were dissolved in 75 mL deionized water with a mechanical stirring

under nitrogen atmosphere at 50 °C for 30 min. 40 mL of ammonia was then added into the mixture and stirred for 3 h. The obtained nanoparticles were separated from the reaction mixture by a magnet, washed with deionized water for several times to neutrality, and dried in a vacuum oven.

2.3. Synthesis of magnetic copolymer beads

Poly(vinylbenzyl chloride-co-styrene-co-divinyl benzene), PVBC, and magnetic-PVBC, M-PVBC, beads were synthesized by a radical suspension polymerization from the reaction mixture given in Table 1. A three-necked glass reactor equipped with a mechanical stirrer and a reflux condenser was used. Dissolved oxygen in the reaction mixture was removed by bubbling nitrogen through a gas inlet tube and then the reactor content was covered with a nitrogen blanket. Suspension was achieved by stirring and sonication of the monomer mixture with magnetic nanoparticles. The mixture was added dropwise to an aqueous phase in the glass reactor with 250 rpm stirring. The contents of magnetic nanoparticles in monomer phase were varied at 1, 5, and 10% wt/v of monomer. The polymerization was carried out at 85 °C for 8 h using a thermostated water bath. The resulting copolymer beads were then washed, sequentially with water and methanol to remove any unreacted monomers. The beads were then dried under vacuum. Using this procedure, a series of magnetic copolymer beads was produced with a constant degree of crosslinking (10 mol% DVB). The obtained composite beads were named M1-PVBC, M5-PVBC and M10-PVBC according to the content of magnetic nanoparticles added into the monomer mixture.

2.4. Surface modification of the copolymer by click reaction

In order to run the reaction, the initial key procedure involves a covalently attachment of $-N_3$ onto the PVBC and M-PVBC beads. The copolymer beads (1.0 g) were agitated with NaN_3 (3.0 g) in DMF (30.0 mL) at 50 °C for 7 h. After cooling to room temperature, the obtained beads were rinsed with distilled water and methanol, and dried under vacuum. Next, clicking of propargyl alcohol onto the azide functionalized beads was performed. 1.0 g of PVBC- N_3 (or M-PVBC- N_3) was dispersed in a solution of DMSO (10.0 mL) and diethylenetriamine (0.5 mL) at room temperature for 10 min. Then, propargyl alcohol (2.5 mL) and CuI (0.05 g) were added and stirred in the reaction mixture at 50 °C for 1 h. At the end of reaction, the resulted chelating magnetic copolymers, M-PVBC-C, were washed several times with DMSO, distilled water and methanol, then dried under vacuum at 55 °C for 24 h.

2.5. Characterization

2.5.1. TEM analysis

Transmission electron micrographs of the magnetic nanoparticles were obtained using a transmission electron microscope, Phillip-Tecnai20.

Table 1
Standard recipe for M-PVBC microsphere preparation.

Monomer mixture	Aqueous phase
50% mole ST	8.6 g $MgCl_2 \cdot 6H_2O$
40% mole VBC	90 mL, 20% NaCl
10% mole DVB	40 mL, 2 M NaOH
1% mole BPO of monomer	
Total volume of monomers = 30 mL	
Magnetic nanoparticles at 1,5 and 10% wt/v of monomer	

Download English Version:

<https://daneshyari.com/en/article/145858>

Download Persian Version:

<https://daneshyari.com/article/145858>

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