



# Microfluidic preparation of chitosan microspheres with enhanced adsorption performance of copper(II)

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## ABSTRACT

This article presents facile microfluidic methods to prepare different chitosan microspheres by combining chemical crosslinking and solvent extraction. And the enhancement of Cu(II) adsorption kinetics and capacity was realized. The effects of solidifying time, initial concentration of Cu(II) and initial pH on adsorption performance were systematically studied. The adsorption isotherms can be fitted with Langmuir equation. The adsorption capacity was about 50 mg/g, which is similar to that in references. To enhance the adsorption kinetics, porous chitosan microspheres were prepared by using poly(ethylene glycol) to form the pores. Many tiny pores were closely arranged on the surface, which resulted in accelerating the adsorption of Cu(II). And the adsorption time to reach equilibrium was reduced from 100 h to 20 h. To enhance the adsorption capacity, chitosan was crosslinked with another biocompatible polymer, poly(acrylic acid), and the blending microspheres were prepared with a two-step solidifying method. By adjusting the content of acrylic acid, the adsorption capacity could be increased to 66.3 mg/g. Finally, porous chitosan-poly(acrylic acid) composite microspheres were prepared by combining the above methods. Adsorption reached equilibrium after about 25 h and the adsorption capacity is about 72 mg/g. Both the adsorption kinetics and capacity of the composite microspheres were enhanced.

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## 1. Introduction

Chitin is the second most abundant polysaccharide after cellulose on earth. Chitosan (CS) is generally obtained by alkaline deacetylation of chitin and is the only alkaline cationic polysaccharide in nature. Chitosan is nontoxic, antibacterial, anticoagulant, biocompatible and biodegradable, which makes it an excellent natural polymer material. There are many hydroxyl and amino groups as well as some *N*-acetyl amino groups on chitosan molecular chains. Accordingly, chitosan can have a variety of chemical reactions such as acylation, esterification, etherification, *N*-alkylation, chelation, graft copolymerization and crosslinking. That makes chitosan a functional bio-material which can be applied in enzyme immobilization, drug controlled release, adsorption of protein and heavy metal ions, and so on [1–3].

Chitosan microspheres are widely applied in many fields on account of their special sizes and various structures. For instance, chitosan microspheres can react as micro-storer, micro-reactor, micro-separator, or just microstructural units, and they can also be applied in pharmaceutical engineering and biochemical engineering [3–5]. With the rapid development of microfluidic methods, preparation of functional materials with controllable

sizes, morphology and composition using microfluidic technique has been a research hotspot and an important direction. In recent years, some researchers have prepared chitosan microspheres with microfluidic methods successfully. Yang et al. [6] prepared monodispersed chitosan microspheres with a chemical crosslinking method, while Xu et al. [7] prepared highly spherical, uniformly distributed and highly monodispersed chitosan microspheres with a solvent extraction method. On these bases, Xu et al. [8] prepared monodispersed chitosan microspheres with controllable sizes and structures in a coaxial microfluidic device by combining chemical crosslinking and solvent extraction methods, and they also found that the longer the solidifying time is, the smaller and compacted the chitosan microspheres are.

Chitosan is an efficient adsorbent which can adsorb protein, heavy metal ions [9], halides and dyes. Considering that chitosan is nontoxic, antibacterial and biocompatible, chitosan is an ideal adsorbent in food industry and wastewater treatment. Amino groups on chitosan chains have strong chelation with metal ions, and then chitosan is applied in adsorbing heavy metal ions to achieve water purification and heavy metal recovery. In order to be convenient for recovery, chitosan is often prepared as hydrogel microspheres instead of flakes or powder. To protect chitosan microspheres from dissolving and enhance stability of microspheres, chitosan is usually crosslinked in the process of preparing the microspheres with the cross linker such as glutaraldehyde (GLA), epoxy chloropropane (ECH) and ethylene glycol diglycidyl

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ether (EGDE). The most widely used cross linker is glutaraldehyde. Xu et al. [8] prepared monodispersed chitosan-glutaraldehyde microspheres in a microfluidic device by adding 0.5 wt% glutaraldehyde into the solidification bath. Dai et al. [10] suspended as-prepared chitosan microspheres in glutaraldehyde solution to prepare chitosan-glutaraldehyde (CS-GLA) microspheres and obtained the adsorption isotherm which is fitted well with Langmuir equation.

In most researches reported, it takes a long time for the prepared chitosan microspheres to adsorb heavy metal ions completely. The adsorption rate is directly related to the mass transfer rate. Metal ions diffuse to the surface of a microsphere first, and then diffuse to the interior from the surface of the microsphere, and at last metal ions are adsorbed onto the chitosan molecular chains through chelation. While the initial concentration of copper ions in aqueous solution and the temperature of the solution are fixed, the adsorption rate is decided by the rate that ions diffusing from the surface to the interior. To enhance the absorption kinetics, the chitosan microspheres can be prepared with porous structure [11–13]. Zeng et al. [14] prepared porous chitosan microspheres by adding poly(ethylene glycol) (PEG) as the pores template. Since poly(ethylene glycol) in microspheres is dissolved in water when microspheres are washed by water, a lot of pores are formed on the surface and in the interior. As predicted, porous chitosan microspheres should have a higher adsorption rate.

To enhance the adsorption capacity, chitosan microspheres are chemically modified. The most common chemical modification for chitosan is grafting new functional groups or polymer blending. By grafting new functional groups to chitosan chains, the number of adsorption sites is increased, the pH range in which metal ions can be adsorbed is varied and adsorption sites or adsorption mechanism is also changed. Carboxyl groups can chelate with many heavy metal ions. Carboxylates have two structures, monodentate and bidentate. Take copper ions for example, two carboxyl groups chelate with one copper ion in monodentate carboxylates, and it takes only one carboxyl group to chelate with one copper ion in bidentate carboxylates. As it is known, in chitosan microspheres without chemical modification, four amino groups chelate with one copper ion. Therefore, grafting carboxyl groups onto chitosan molecular chains can increase adsorption capacity of chitosan microspheres [10,14]. Poly(acrylic acid) (PAA) is a water-soluble polymer and possesses good biocompatibility. Each repeated unit in poly(acrylic acid) has a carboxyl group which can chelate with copper ions. The  $pK_a$  value of PAA is 4.75 to be an anionic polyelectrolyte. Electrostatic attraction between poly(acrylic acid) and copper ions is beneficial to adsorption of copper ions. Electrostatic interaction between ionized amino groups and ionized carboxyl groups brings about polyelectrolyte complexes of chitosan and poly(acrylic acid), so that chitosan is chemically modified. Dai et al. [10] prepared chitosan/poly(acrylic acid) (CS/PAA) microspheres and suspended the microspheres in glutaraldehyde solution to get chitosan/poly(acrylic acid)-glutaraldehyde (CS/PAA-GLA) microspheres. The adsorption capacity of CS/PAA-GLA is larger than that of CS-GLA.

In this work, with facile microfluidic methods, we used glutaraldehyde as crosslinking reagent and prepared various chitosan microspheres with different structures and composites by combining chemical crosslinking and solvent extraction. Firstly we prepared monodispersed chitosan microspheres and studied the Cu(II) adsorption performance of the chitosan microspheres. Then we studied the enhancement of adsorption kinetics by preparing porous chitosan microspheres. Furthermore, by preparing chitosan/poly(acrylic acid) microspheres, we studied the enhancement of adsorption capacity. Finally, porous chitosan-poly(acrylic acid) composite microspheres were prepared by combining the above

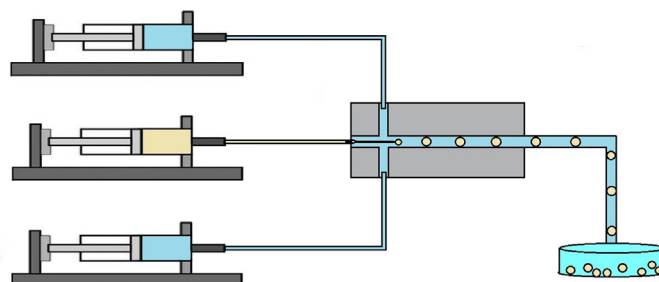


Fig. 1. The microfluidic device.

methods. And the adsorption kinetics and capacity of the composite microspheres was both enhanced.

## 2. Experimental

### 2.1. Materials

Chitosan with an average molecular weight of 180 kDa was purchased from Yuhuan Ocean Biochemical Co., Ltd., Zhejiang, PR China. Acetic acid was purchased from Beihua Fine Chemicals Co., Ltd., Beijing, PR China. Glutaraldehyde was purchased from VAS Chemical Co., Ltd., Tianjin, PR China. Poly(ethylene glycol) (PEG) with an average molecular weight of 20,000 was purchased from SIGMA-ALORICH, USA. Acrylic acid and n-octanol were purchased from Guangfu Institute of Fine Chemicals, Tianjin, PR China. Ammonium persulfate and Span 80 were purchased from Modern Eastern Fine Chemicals Co., Ltd., Beijing, PR China. n-Octane was purchased from Fuchen Chemical Co., Ltd., Tianjin, PR China.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , hydrochloric acid (HCl), sodium hydrate (NaOH), ethanol and other reagents used in this work were all A.R. grade reagents. Distilled water was used in all experiments.

### 2.2. Microfluidic device

The microfluidic device was fabricated on two  $40\text{ mm} \times 20\text{ mm} \times 5\text{ mm}$  polymethyl methacrylate (PMMA) plates using micromachining technology, as shown in Fig. 1. A Teflon (PTFE) tube with 0.5 mm inner diameter was inserted as the multiphase flow channel. A 30# stainless steel needle with inner diameter of 0.16 mm was inserted as the dispersed phase inlet, and two 8# stainless steel needles were inserted as the continuous phase inlet. The microfluidic device was obtained by sealing the two PMMA plates together. Three microsyringe pumps and three gastight microsyringes were used to pump the fluids into the microfluidic device. The droplets forming in the Teflon tube were collected with a solidification bath placed on a shaker.

### 2.3. Preparation of various microspheres

#### 2.3.1. CS-GLA microspheres

The dispersed phase is aqueous solution with 2 wt% chitosan and 2 wt% acetic acid, and the continuous phase is n-octane solution with 2 wt% Span80. The solidification bath is n-octane solution with 0.5 wt% glutaraldehyde and 2 wt% Span80. The dispersed flow is injected into the microchannel and separated into monodispersed droplets by the shearing force of the continuous flow. Droplets were collected in solidification bath that was shaken. Schiff's base reaction occurred between glutaraldehyde and chitosan, which made chitosan crosslinked. Meanwhile, water was extracted from the droplets by n-octanol. The solidification time was adjusted by controlling the time droplets shaken in the solidification bath. Finally,

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