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Microfluidic synthesis of thiourea modified chitosan microsphere of high specific surface area for heavy metal wastewater treatment

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ABSTRACT

An improved biosorbent of thiourea modified chitosan microsphere (TMCM) with high specific surface, favorable mechanical strength and excellent adsorption performance had been synthesized via microfluidic technology. Polyethylene glycol was used as a significant component added in aqueous solution of chitosan to produce such microspheres through droplets forming, chemical crosslinking and pores creating. For the improvement of adsorption capacity, thiourea was considered as an excellent choice in increasing amino functional group by graft modification. The SEM, FTIR and EDS were employed to detect distinct features of TMCM. Copper(II) was used to test the adsorption performance of TMCM. The experimental results indicated that TMCM exhibited higher adsorption capacity ($q_e = 60.6 \text{ mg g}^{-1}$) and faster adsorption rate than that non-modified chitosan microsphere (NMCM). The adsorption kinetic was described well by the *pseudo*-second order kinetic model, which suggested that chemical adsorption along with electrons transferring was dominant in adsorption process.

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1. Introduction

In recent years, amounts of heavy metal wastewater have been produced in metallurgy, electroplating, chemical engineering, mining and metal machining industries, and threatened human health and ecosystem seriously [1]. For the purpose of removing heavy metal contaminant from aquatic system, pioneers carried out many beneficial explorations, including coagulation, flotation, biological treatment, chemical precipitation, membrane osmosis, evaporation and adsorption [2,3]. Among these methods, adsorbent is a significant choice for its high efficiency, easy operating, renewability and favorable selectivity [4]. Srivastava and Majumder [5] found ion exchange resin adsorbent could remove toxic metal ions (Cu(II), As(III), Pb(II)) out of wastewater efficiently. Shafaei et al. [6] adopted activated carbon prepared by eucalyptus bark to adsorb Cu(II) and Pb(II), whose maximum adsorbance could reach 0.45 mmol g^{-1} and 0.53 mmol g^{-1} respectively. Sangvanich et al. [7] discovered that modified regular mesoporous material had adsorption selectivity for Cu(II), Cs(I) and Tl(I).

Chitosan is a unique natural alkaline polysaccharide synthesized by chitin hydrolyzing and deacetylation at alkaline condition [8]. There are plentiful amino functional groups which are able to chelate metal ions on molecular chain of chitosan with complicated double helix structure [9]. According to Gamage and Shahidi [10], the biopolymer chitosan presented an excellent capability of removing metal ion pollutant of Pb(II), Cu(II), Zn(II) and so on. Chitosan, a natural macromolecule material regarded as a metal ion adsorbent, has attracted much attention due to its extensive sources, nontoxicity, biocompatibility and degradability [11,12]. For the convenient recovery and separation, chitosan was prepared as microsphere or particle generally. Besides, chitosan in itself can carry out various reactions with other substances, which makes it an ideal material for graft modification so as to improve its adsorption performance. Zhou et al. [13] used ethylenediamine as modification agent, and prepared ethylenediamine-modified magnetic crosslinking chitosan microspheres for adsorption of Hg(II). Fujiwara et al. [14] synthesized crosslinked chitosan which was chemically modified with L-lysine to investigate the adsorption of Pt(IV), Pd(II) and Au(III) from aqueous solutions. In addition, glutaraldehyde, thiourea, rubeanic acid and epichlorohydrin all could be employed for graft modification [15-17].

Microfluidic technology, a facile microsphere synthesis approach, points out a new direction in producing functional material

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of controllable size, morphology, component and structure [18]. Some researchers have developed various chitosan microspheres via microfluidic method. Xu et al. explored uniform and high monodispersed spherical particles which were applied in catalysis, biomedical sciences and medicine field [19-21]. Besides, they also prepared composite chitosan/silica microspheres used in adsorption [22]. Lu et al. [23] synthesized Pb(II) imprinted chitosan (Pb(II)-CS) bead with uniform size and porous morphology for selective adsorption of Pb(II). However, there are few attempts to combine microfluidic technology with graft modification in preparing chitosan microspheres of high performance used in environment protection field. The situation does not permit any delay of exploring the potential benefits of utilizing microfluidic synthesized material in heavy metals treatment. The present work was aimed at exploiting a biosorbent of thiourea modified chitosan microspheres (TMCM) with high specific surface area as a model adsorption material for heavy metal. TMCM were prepared by a combination of facial microfluidic technology with nature adsorbent of chitosan. Through droplets forming, chemical crosslinking and pores creating, chitosan microspheres with high specific surface area were obtained. Then on this basis, amounts of amino functional group were grafted on chitosan through thiourea modification. In final, stoving was considered as a fast and efficient method to dry this biosorbent for the enhancement of mechanical property and peculiar surface structure. The adsorption behavior of TMCM toward copper(II) had been investigated by batch experiments. TMCM exhibited higher adsorption capacity ($q_e = 60.6 \text{ mg g}^{-1}$) and faster adsorption rate than that non-modified chitosan microsphere (NMCM). The adsorption kinetic was described well by the *pseudo*-second order kinetic model.

2. Results and discussion

2.1. Characteristic researches

2.1.1. SEM analysis

Droplets solidifying 30 min appeared golden yellow, which was different from that solidifying 5 min remarkably under an optical microscope, as shown in Fig. 1(a and b). These droplets were uniform and high monodispersed, which profited from the distinct feature of microfluidic technology in product control. After organic solvent cleaning and washing by deionized water, great changes have taken place.

A more meticulous observation with SEM is shown in Fig. 2. Fig. 2(a-d) and (e-h) shows the surface of NMCM whose mass ratio between PEG and chitosan was 1:1 and 2:1, respectively. Through SEM images, we found that there was an obvious difference on the surface of NMCM when mass ratio between PEG and chitosan changed. When mass ratio between PEG and chitosan was 1:1, the surface of NMCM represented wrinkling, whose situation was as like as ravines and gullies criss-cross. In the valley bottom, there were pieces of fish scale. The morphology

was so different from normal chitosan microspheres without PEG added in prepared by microfluidic technology, whose surface was highly smooth and spherical as seen in Fig. 3. When mass ratio between PEG and chitosan was 2:1, the situation on the surface of NMCM changed again. There were lots of curly strips which tangled together. Amounts of pores and spaces were produced on the surface, which increased the specific surface area greatly. Microspheres with high specific surface area would be beneficial for fast adsorption. Therefore, we adopted microspheres whose mass ratio between PEG and chitosan was 2:1 to make graft modification by thiourea. Fig. 2(i-l) shows the SEM images of TMCM. We found that the surface of TMCM was similar to that of NMCM. Besides, the curly strips on the surface seemed more compact. The pores and spaces became narrow and small. This phenomenon may be caused by the modification process. In the graft modification, reactions between microspheres and external agents occurred continuously. Reaction products and the state variation of microspheres would cause some differences with the comparison to NMCM. In order to verify the high specific surface area of TMCM, we adopted Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods to analyze specific surface area and pore volume of TMCM and NMCM. The specific surface area and pore volume of TMCM were $69.2 \text{ m}^2 \text{ g}^{-1}$ and $0.023 \text{ cm}^3 \text{ g}^{-1}$, while that of NMCM(w(PEG):w(CS) = 0:1) were $4.24 \text{ m}^2 \text{ g}^{-1}$ and $0.0011 \text{ cm}^3 \text{ g}^{-1}$. The specific surface area of TMCM increased greatly and it was beneficial for fast adsorption.

2.1.2. Preparation process

The peculiar surface structure of NMCM could be explained by the specific preparation process. PEG was added in chitosan solution as pore-foaming agent. In the microfluidic chip, uniform droplets with controllable component of PEG and chitosan were produced. Then, these droplets were led into a beaker filled with solidification bath for crosslinking. In the process of crosslinking, the chain structure of chitosan molecule previously turned into network structure on account of Schiff-base reaction as shown in Fig. 3. Unsolidified microspheres were fragile and easy to polymerize together. After solidification, microspheres became compact and stable. When microspheres were taken out solidification bath, they would be cleaned by *n*-octane, acetone and ethanol in turn for the elimination of unreacted glutaraldehyde and maintaining the existence of PEG. Then, microspheres were washed by deionized water for several times. PEG, as a pore-foaming agent, was easily dissolved in water. After organic solvents cleaning, PEG was preserved in microspheres. When washed by deionized water, PEG would dissolve in water quickly, but the network structure of chitosan still kept original state. Many pores could be left in microspheres. The absence of component resulted in the bone of microsphere instable.

When drying, these pores would shrink, and the instable bone also had a tendency to frap. Finally, NMCM with peculiar surface structure were prepared. In the formation process, the mass ratio

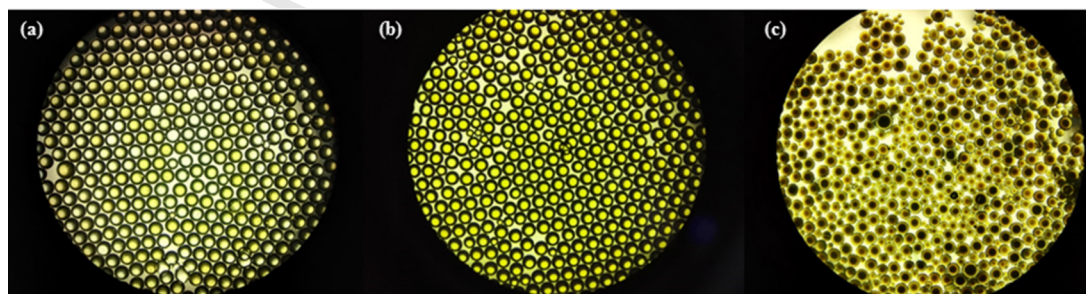


Fig. 1. Optical micrographs of droplets for (a) solidifying 5 min, (b) 30 min and (c) after cleaning and washing.

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