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Combination of carboxymethyl chitosan-coated magnetic nanoparticles and chitosan-citrate complex gel beads as a novel magnetic adsorbent

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ABSTRACT

Magnetic chitosan beads were synthesized by incorporating N,O-carboxymethyl chitosan-coated magnetic nanoparticles (NOCC-MNPs) into chitosan-citrate gel beads (CCGBs) for adsorbing Cu(II) ions. An increase of Cu(II) adsorption capacity was due to the combined chelation effects from the electron-donating functional groups in the CCGBs and NOCC-MNPs. Moreover, the paramagnetic susceptibility of Cu(II) citrate chelates could further improve the Cu(II) adsorption efficiency through the force of magnetic attraction. The adsorption data of the magnetic CCGBs fitted well with the Freundlich model, whereas the adsorption kinetics followed the pseudo-second-order kinetic model. The maximal adsorption capacity as estimated by the Langmuir model was 294.11 mg/g. The adsorption thermodynamic parameters indicated that the involved process should be spontaneous and exothermic.

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1. Introduction

Heavy metals are the primary pollutants in industrial waste water that may directly or indirectly enter the food chain. The most harmful aspect of heavy metals is that they cannot be excreted from the body following catabolism in the liver and easily accumulate in organs such as the brain and kidneys, thus gradually damaging and obliterating normal bodily functions. Heavy metals in human body would both inhibit enzyme activities and genetic mutations (Kawata, Yokoo, Shimazaki, & Okabe, 2007; Kim, Shin, & Warrant, 1985). Copper, the metal considered in this study, is extensively used in the electrical industry. Copper can accumulate in living microorganism, through consumption or uptake and may be hazardous to human health or the environment. Adsorbing metal ions using biosorbents demonstrates the advantage of being low-cost and highly efficient compared with alternative techniques such as extraction, precipitation, ion exchange, filtration, and electrolytic methods.

Chitosan contains a substantial number of amino and hydroxyl groups, which can adsorb a variety of metal ions (Liu et al., 2012; Ngah, Teong, & Hanafiah, 2011). However, a disadvantage of this

adsorbent is its weak acid resistance properties. Cross-linking methods are commonly employed to reduce the solubility of chitosan in acids (Mi, Kuan, Shyu, Lee, & Chang, 2000; Mi, Shyu, & Peng, 2005), thereby extending the applicability of this adsorbent (Boamah et al., 2014; Laus, Costa, Szpoganicz, & Favere, 2010; Osifo et al., 2008). However, the traditionally-used cross-linking agent, glutaraldehyde, is extremely toxic and can easily cause substantial environmental damage (Ballantyne, Myers, & Blaszcak, 1997). Tripolyphosphate has been used to cross-link chitosan for enhancing its acid resistance (Laus et al., 2010; Lee, Mi, Shen, & Shyu, 2001; Mi, Sung, Shyu, Su, & Peng, 2003; Ngah & Fatinathan, 2010; Wu, Liou, & Mi, 2009). Polyanion possess electron pairs without bonding (i.e., lone pairs), that can act as a multidentate to bind strongly to metal cations. Although sodium tripolyphosphate causes less environmental toxicity than glutaraldehyde does, it may generate phosphate-containing compounds when dissolved in water, leading to eutrophication. Thus, the development of chitosan-based adsorbents by using an environmentally friendly, cross-linking reagent that generates minimal environmental damage is critical. Polycarboxylic acids used in food processing, such as citrate, can provide lone pairs similar to those present in sodium tripolyphosphate to enhance the metal ion-chelating capability and increase the acid resistance of chitosan (Freitas, Nascimento, Souza, & Silva, 2013). Recently, the application of magnetic bioadsorbent for the removal of heavy metals has gained increasing attention and

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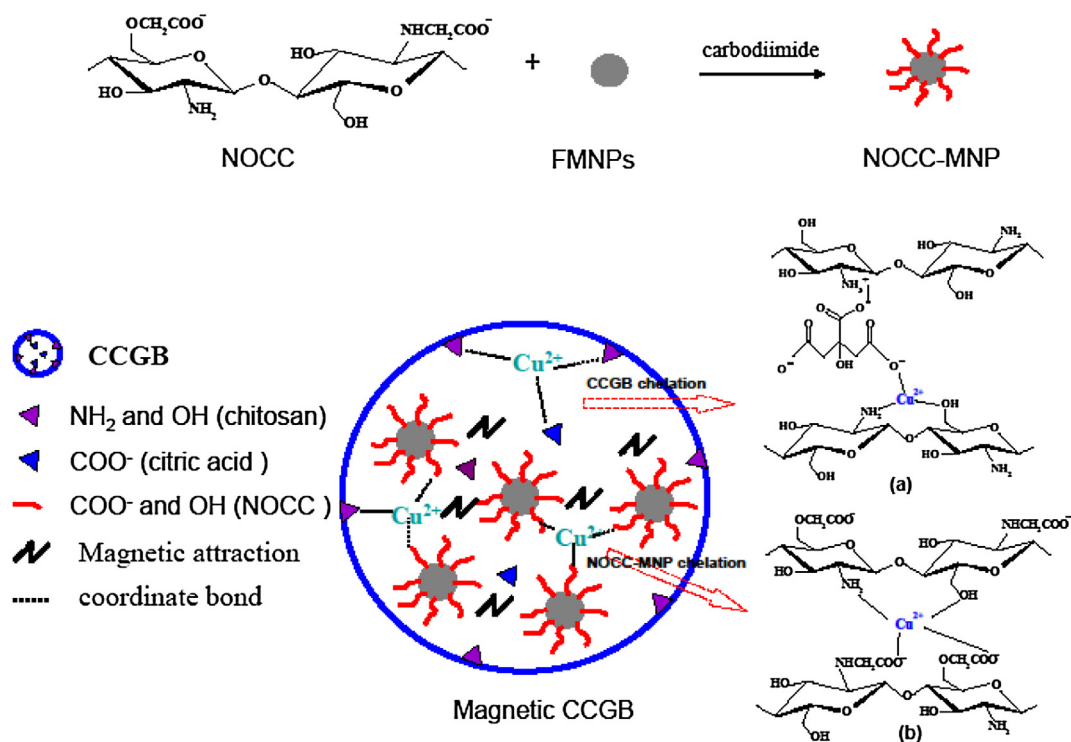
Scheme 1. (a) Binding sites of CCGB adsorbent, and (b) NOCC-MNPs for the adsorption of Cu(II) ions.

interest. However, to our knowledge, few reports have addressed the combination of chemically modified, chitosan-based Fe_3O_4 magnetic nanoparticles and chitosan beads as a biosorbent.

Magnetic adsorbents after adsorbing contaminants can be separated from a solution by using an external magnetic field (Ge, Li, Ye, & Zhao, 2012; Jung, Lee, & Shinkai, 2011; Tang, Su, Li, Gao, & Shang, 2013). Therefore, magnetite (Fe_3O_4) is considered a promising magnetic material because it possesses a large surface area and excellent magnetic properties. In recent years, Fe_3O_4 magnetic nanoparticles have been functionalized with various stabilizers, including organic or inorganic compounds (Hao, Man, & Hu, 2010; Kim, Lee, Chang, & Chang, 2013), polypeptides (Takahashi, Yoshino, & Matsunaga, 2010), polysaccharides (Chang, Yu, Ma, & Anderson, 2011; Zamora-Mora et al., 2014), activated carbon (Ai, Huang, Chen, Wei, & Jiang, 2010), silica or silanes (Badruddoza et al., 2013a; Zhang, Cheng, He, Chen, & Zhang, 2010), clay (Szabo et al., 2007), synthetic polymers (Sun et al., 2013), and β-cyclodextrin (Badruddoza et al., 2013b; Zhang, Wang, & Yang, 2014). Magnetic nanoparticles have attracted considerable attention because of their unique properties in the removal of several heavy metal or toxic ions (Lin, Zhang, Chen, & Qian, 2012; Wang et al., 2012). The surface-modified functional groups improve the dispersion stability of nanoparticles and act as chelating ligands. Such a high number of adsorption sites on nanoparticles are responsible for the successful adsorption of heavy metals (Pang et al., 2011).

Chitosan can be used to coat magnetic nanoparticles to prepare magnetic nano-adsorbents because the functional groups of chitosan, including amine and hydroxyl groups are effective in adsorbing heavy metal ions and dyes (Donia, Yousif, Atia, & Elsamalehy, 2014; Liu, Hu, Fang, Zhang, & Zhang, 2009). Moreover, chemical modification of chitosan successfully improved the adsorption efficiency of magnetic nanoparticles (Hritcu, Humelnicu, Dodi, & Popa, 2012; Kuang, Wang, Liu, & Wu, 2013; Ren, Abbood, He, Peng, & Huang, 2013; Wang, Peng, Yang, Liu, & Hu, 2011; Zhu, Hu, & Wang, 2012). In this study, magnetic nanoparticles functionalized with a polyanion were prepared. *N,O*-carboxymethyl chitosan (NOCC)

consisting of multiple chelating functional groups, such as carboxyl ($-COO^-$), amino ($-NH_2$) and hydroxyl ($-OH$) groups, was synthesized by chemically modifying chitosan with chloroacetic acid. NOCC-MNPs were incorporated into CCGBs, which were synthesized by employing citrate as the ionic cross-linking agent, and then lyophilized. The porous, magnetic CCGBs reduced the internal resistance during the process of heavy metal adsorption, and increased separation efficiency. The prepared magnetic CCGB adsorbents were then used to adsorb heavy metal, Cu(II) ions. We employed Cu(II) ions of various initial concentrations and pH values as experimental variables for the adsorption experiment to determine the effects of the variables on heavy metal ion adsorption. Furthermore, we investigated the adsorption kinetics, adsorption isotherm models, and thermodynamics in this experiment. Schematic diagrams of the synthesis, reaction and adsorption mechanism binding sites in CCGBs and NOCC-MNPs for Cu(II) are shown in Scheme 1.

2. Experimental methods

2.1. Materials

Chitosan was obtained from Challenge Bioproducts Co. (Taichung, Taiwan). The molecular weight was 400,000 Da, and the degree of deacetylation was 98%. Ferrous chloride tetrahydrate, ferric chloride hexahydrate, citric acid anhydrous and copper(II) sulfate pentahydrate were purchased from Showa Chemical Industry Co., Ltd. (Japan). Chloroacetic acid was purchased from Acros Organics. Carbodiimide (cyanamide, CH_2N_2) was purchased from Alfa-Aesar. Ethylenediaminetetraacetic acid (EDTA) was purchased from Merck. All the reagents used were analytical-reagent grade.

2.2. Preparation of magnetic Fe_3O_4 nanoparticles

In this study, free magnetic nanoparticles (FMNPs) were prepared using a coprecipitation procedure (Jiang et al., 2013). First, we