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Preparation and properties of chitosan–metal complex: Some factors influencing the adsorption capacity for dyes in aqueous solution

Sadia Rashid[1], *Chensi Shen*[1,2,*], *Jing Yang*[1], *Jianshe Liu*[1,2], *Jing Li*[3]

1. *College of Environmental Science and Engineering, Donghua University, Shanghai 201620, China. E-mail:* sadiarashid@hotmail.com
2. *State Environmental Protection Engineering Center for Pollution Treatment and Control in Textile Industry, Shanghai 201620, China*
3. *Beijing Enterprises Water Group (China) Investment Limited, Beijing 100102, China*

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ABSTRACT

Chitosan–metal complexes have been widely studied in wastewater treatment, but there are still various factors in complex preparation which are collectively responsible for improving the adsorption capacity need to be further studied. Thus, this study investigates the factors affecting the adsorption ability of chitosan–metal complex adsorbents, including various kinds of metal centers, different metal salts and crosslinking degree. The results show that the chitosan–Fe(III) complex prepared by sulfate salts exhibited the best adsorption efficiency (100%) for various dyes in very short time duration (10 min), and its maximum adsorption capacity achieved 349.22 mg/g. The anion of the metal salt which was used in preparation played an important role to enhance the adsorption ability of chitosan–metal complex. SO_4^{2-} ions not only had the effect of crosslinking through electrostatic interaction with amine group of chitosan polymer, but also could facilitate the chelation of metal ions with chitosan polymer during the synthesis process. Additionally, the pH sensitivity and the sensitivity of ionic environment for chitosan–metal complex were analyzed. We hope that these factors affecting the adsorption of the chitosan–metal complex can help not only in optimizing its use but also in designing new chitosan–metal based complexes.

Introduction

Chitosan, a deacetylated form of chitin, has number of free amino and hydroxyl groups and thus it finds many applications that follow from its unique character such as depollution. The sorption properties of the polymer have been successfully utilized for environmental purposes such as the removal of toxic heavy metal ions and organic pollutants from waste water (Kumar, 2000; Synowiecki and Al-Khateeb, 2003). The mostly cited mechanism for the adsorption of anionic pollutants by chitosan is electrostatic interactions of the anionic pollutant with the protonated amino groups in the chitosan (Cheung et al., 2009b). The chitosan-based adsorbent often suffers from the disadvantage of pH-dependence, because the free amino groups of chitosan whose point of zero potential lies within 6.5–6.7 cannot be protonated under the alkaline conditions (Guibal, 2005).

To overcome this drawback, the advantage of polymer–metal complexes have been reported to enhance the adsorption efficiency *via* chelating interaction between pollutants

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[*] *Corresponding author*. E-mail: shencs@dhu.edu.cn (Chensi Shen).

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and metal center of the polymer–metal complex (Cheng et al., 2010; Shen et al., 2011; Wang et al., 2007). For instance, Cu(II) complex of dithiocarbamate modified starch was proposed to efficiently adsorb ionic dyes through strong chelating interactions (Cheng et al., 2010). Magnetic chitosan–Fe(III) hydrogel was used for the removal of dyes under strong alkaline conditions(Shen et al., 2011). Chitosan–Fe(III) complexes were used for the removal of Cr(VI) and As(III) from aqueous solution (Shen et al., 2013; Zimmermann et al., 2010). In addition, various other kinds of metals such as Zn(II), Cd(II), Ni(II), Co(II), Ca(II), Al(III), Eu(III), Nd(III), Pr(III), La(III), Mo(VI) and Zr(IV) have also been used to prepare the chitosan–metal complex and applied for the pollutant removal processes (Rhazi et al., 2002; Shinde et al., 2013).

Most recent studies for the chitosan–metal complexes have indicated that both NH_2 and OH groups are bonded to the metal ions and that more than one polymer chain is involved in the formation of such complexes (Crini and Badot, 2008; Guibal, 2004; Wan Ngah et al., 2011). And the water molecules or other ions in solution would complete the coordination sphere (Bhatia and Ravi, 2000). For example, chitosan–Fe(III) complex is proposed to be either penta or hexacoordinated, depending on the preparation conditions (Bhatia and Ravi, 2000; Shen et al., 2013). It was complexed through 2 atoms of O and N from the polymer and at least one water molecule in the coordination sphere of the metal ion (Dambies et al., 2001; Hernández et al., 2008; Klepka et al., 2008) and the adsorption was considered to occur *via* a ligand-exchange reaction between the coordinated water or other ions with the pollutant ions (Zimmermann et al., 2010).

According to the reported results, the adsorption ability of chitosan–metal complexes strongly depends on the chelated metals. It has been reported that chitosan polymers chelated with Fe(III), were suitable for the removal of Cr(VI) and As(V) (Shen et al., 2013; Shinde et al., 2012; Zimmermann et al., 2010) while the chitosan polymers chelated with Al(III), Zr(III) and Ca(II) were suitable for fluoride removal (Shen et al., 2016; Viswanathan and Meenakshi, 2009). Secondly, the crosslinking ratio of chitosan–metal complex might also play an important role in pollutants adsorption. As the published studies shown, increasing the crosslinking ratio of chitosan can initially increase the sorption capacity but higher glutaraldehyde (GLU) content beyond the optimal ratio will result in attenuated sorption capacity due to potential changes in surface chemistry and inaccessibility of the sorption sites (Kamari et al., 2009; Poon et al., 2014; Pratt et al., 2013). Additionally, it has been reported that the presence of sulfate ions in the solution can facilitate the metal ions to chelate with the chitosan polymer in addition to taking the role of crosslinking reagent (Mitani et al., 1991). Thus, despite the increasing research efforts focused towards the development of chitosan–metal complex, the important factors involved during the complex preparation such as the metal centers, the anion of the metal salts and the extent of crosslinking still need to be further investigated for the improvement of the adsorption ability of chitosan–metal complex for practical applications.

Wastewater from dyeing industries creates a great problem of pollution such as high chemical oxygen demand (COD), bad smells, toxicity and especially color. The kind of reactive dye is one of the most widely used dyes in the present textile industry, which is known to be resistant to aerobic digestion and stable to oxidizing agents. Therefore, the present work aims to extend the previous study (Shen et al., 2011) of chitosan–Fe complex used for the removal of various dyes in order to optimize the adsorption ability of chitosan–metal complex adsorbents. Various types of chitosan–metal complexes with different metal centers, different anion of the metal salt and different extent of crosslinking have been prepared and the effects of these factors on the adsorption ability of chitosan–metal complexes were examined.

1. Materials and methods

1.1. Chemicals

GLU, $MgSO_4$, $MgCl_2·6H_2O$, $Mg(NO_3)_2·6H_2O$, $Fe_2(SO_4)_3$, $FeCl_3·6H_2O$, $Fe(NO_3)_3·9H_2O$, $CuSO_4·5H_2O$, $CuCl_2$, $Cu(NO_3)_2·3H_2O$, $NiSO_4·6H_2O$, $NiCl_2·6H_2O$, $Ni(NO_3)_2·6H_2O$, $MnSO_4·H_2O$, $MnCl_2·2H_2O$, $Mn(NO_3)_2·4H_2O$ and ethanol were attained from National Medicines Corporation Ltd. of China. Chitosan was purchased from Zhejiang Golden-shell Biochemical Co., Ltd., Zhejiang, China (deacetylation degree = 91.04%). C. I. Reactive Black 5 (RB 5) and other dyes were bought from Sigma-Aldrich. During all experiments, doubly distilled water was used and other chemicals were of laboratory reagent grade which were used without any further purification.

1.2. Synthesis of chitosan–metal complexes

The typical chitosan–metal complex was synthesized by modifying the reported study procedure (Shen et al., 2011; Wilson and Xue, 2013). Chitosan powder (1.0 g) was dissolved in 50 mL water containing 0.1 mol/L acetic acid. Subsequently, the aqueous solution containing 0.1 mol/L metal ions (50 mL) were added into the chitosan solution and the mixture was stirred at room temperature for 4 hr. The pH of chitosan–metal solution was maintained around 2.0 by adding 1 mol/L HCl or 1 mol/L NaOH. Next, the chitosan–metal complex precipitation or hydrogel was obtained by adding the absolute ethanol (150 mL). The nonspecific binding metals were eluted with ethanol for several times till the concentration of metals in the eluent was lower than 0.01 mg/L which was measured by inductively coupled plasma mass spectrometry (ICP–MS). Then the solid or hydrogel was crosslinked in 50 mL ethanol solution containing different weight percentage of GLU (2 wt.%, 10 wt.% and 20 wt.%) for 12 hr and finally separated by centrifugation. At last, the crosslinked complexes were dried at 80°C and grounded into fine powders. For simplicity, here after these complexes are abbreviated as CS–Metal–SO_4 which were prepared by sulfate metal salts, CS–Metal–Cl which were prepared by chloride salts and CS–Metal–NO_3 which were prepared by nitrate salts. In addition, the normal crosslinked chitosan was also prepared to investigate its adsorption efficiency. Chitosan powder (1.0 g) was dissolved in 0.1 mol/L acetic acid solution (50 mL), and the mixture was stirred at room temperature for 4 hr. The pH of chitosan solution was maintained around 2.0 by adding 1 mol/L HCl. Subsequently, the chitosan was precipitated by adding the ethanol and then placed in ethanol solution in contact with GLU for 12 hr. At last, it was dried at 80°C and grounded into fine powders.

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