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Efficient adsorption of both methyl orange and chromium from their aqueous mixtures using a quaternary ammonium salt modified chitosan magnetic composite adsorbent

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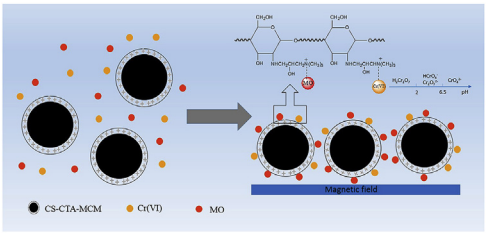
HIGHLIGHTS

- A quaternary ammonium salt modified chitosan magnetic adsorbent has been prepared.
- This adsorbent can be efficient removal of methyl orange (MO) and Cr(VI) from water.
- MO bears more affinity to this adsorbent than Cr(VI).
- This adsorbent has short adsorption time and rapid separation speed from water.
- This adsorbent can be efficient regenerated and reused after saturated adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

A quaternary ammonium salt modified chitosan magnetic composite adsorbent (CS-CTA-MCM) was prepared by combination of Fe_3O_4 nanoparticles. Various techniques were used to characterize the molecular structure, surface morphology, and magnetic feature of this composite adsorbent. CS-CTA-MCM was employed for the removal of Cr(VI) and methyl orange (MO), an anionic dye, from water in respective single and binary systems. Compared with chitosan magnetic adsorbent (CS-MCM) without modification, CS-CTA-MCM shows evidently improved adsorption capacities for both pollutants ascribed to the additional quaternary ammonium salt groups. Based on the adsorption equilibrium study, MO bears more affinity to CS-CTA-MCM than Cr(VI) causing a considerable extent of preferential adsorption of dye over metal ions in their aqueous mixture. However, at weak acidic solutions, Cr(VI) adsorption is evidently improved due to more efficient Cr(VI) forms, i.e. dichromate and monovalent chromate, binding to this chitosan-based adsorbent. Thus chromium could be efficient removal together with MO at suitable pH conditions. The adsorption isotherms and kinetics indicate that adsorptions of Cr(VI) and MO by CS-CTA-MCM both follow a homogeneous monolayer chemisorption process. This magnetic adsorbent after saturated adsorption could be rapidly separated from water and easily regenerated using dilute NaOH aqueous solutions then virtually reused with little adsorption capacity loss.

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1. Introduction

Water pollution are becoming more and more serious with the rapid development of industries in the world. Many kinds of industrial wastewaters have been produced and discharged in recent years (Fu and Wang, 2011). Among them, dyeing effluents generated in the dyestuffs, textile, papermaking, leather and plastics (Pokhrel and Viraraghavan, 2004) pose a significant threat to the human beings, animals and plants. They not only contain high toxicity and color the water body, but also seriously retard photosynthesis and inhibit normal growth of aquatic organisms (Yu et al., 2013; Lazar, 2005). Various techniques have been tried to treat with those wastewaters contained dyes including adsorption (Gupta and Suhas, 2009; Qiao et al., 2015), electrolytic chemical treatment (Xing et al., 2007), membrane separation (Dasgupta et al., 2015), chemical reduction (Rakhunde et al., 2012), and biological treatment (Herrero and Stuckey, 2015). Considering the cost, effectiveness and other effects, adsorption is an effective and versatile method to reduce or minimize the dyes from water (Yagub et al., 2014).

Moreover, many heavy metal ions such as Cr(VI), a highly toxic pollutant causing liver damage, pulmonary congestions and severe diarrhea, usually exist in many dyeing effluents discharged from leather tanning and dyestuff industries also (Owlad et al., 2009; Dima et al., 2015). Coexisted metal ions have significantly enhanced the harmfulness to the environment and the difficulty to efficient treatment. It is well known that adsorption is also one of effective techniques to deal with those wastewaters contained heavy metal ions (Wan Ngah et al., 2011; Reddy and Lee, 2013; Wang et al., 2015). However, until now little work has focused on removal of both dyes and heavy metal ions together from their aqueous mixtures through adsorption (Hernández-Montoya et al., 2013; Kyzas et al., 2015).

Given that adsorbents mainly count to the final performance during an adsorption process (Dąbrowski, 2001), researchers have taken considerable effects in development of novel and high-efficient adsorbents in recent years (Yagub et al., 2014). Chitosan, an amino polysaccharide extracted by a deacetylation procedure from chitin, is a kind of high-performance natural polymers with advantages of widespread availability, environmental friendliness and low cost (Wan Ngah et al., 2011; Rinaudo, 2006). Moreover, chitosan has been also considered as an ideal adsorbent because of abundant free amino and hydroxyl groups on its backbone (Bhatnagar and Sillanpaa, 2009). Numerous metal ions could be easily bound to these groups due to chelating effects (Reddy and Lee, 2013; Li et al., 2005, 2015), and various dyes could be also attracted through some specific interactions such as electrostatic attraction (Sakkayawong et al., 2005). Moreover, on the basis of structure-activity relationship of materials, various functional groups could be flexibly grafted onto chitosan for effective adsorption of target pollutants, thus it is possible that a variety of different pollutants such as metal ions and dyes could be efficient removal simultaneously.

In this work, methyl orange (MO) and Cr(VI) have been selected as target pollutants, since MO is a kind of normal anionic dyes and Cr(VI) usually coexists in dyeing effluents (Elasser, 2005). Accordingly, 3-chloro-2-hydroxypropyl trimethyl ammonium (CTA), a low toxic quaternary ammonium salt reagent with strong positive charge in water (Cai et al., 2007), was selected to modify chitosan for improvement of its adsorption affinity to aforementioned two anionic pollutants. Moreover, in order to achieve fast separation from water after its saturated adsorption, magnetic Fe_3O_4 nanoparticles were embedded into chitosan, since the magnetic separation technique has been recently proven to be an effective method to accelerate the separation process and widely applied in water treatment (Linh et al., 2011; Tang and Lo, 2013). Thus a novel CTA modified chitosan magnetic composite adsorbent (CS-CTA-MCM) was obtained through a simple method. Then various characterization techniques were conducted to characterize its structure and magnetic property. Aside from the fundamental adsorption behaviors of CS-CTA-MCM for the removal of Cr(VI) and MO from their respective single pollutant system, i.e., the pH effects, adsorption equilibrium and kinetics, the simultaneous and selective adsorption for Cr(VI) and MO in their binary system was also investigated systematically. Adsorption and competitive adsorption mechanisms were discussed in detail. In addition, a pure chitosan magnetic adsorbent (CS-MCM) without CTA modification was also prepared for comparison. Moreover, the recycling and reuse of this chitosan-based adsorbent were carried out too for its precious importance in real applications.

2. Experimental

2.1. Materials

Chitosan (CS) with deacetylation degree of 90.5% and viscosity-average molecular weight of 3.0×10^5 g mol^{-1} was purchased from Shandong Aokang Biological Co. Ltd. CTA from Wuhan Yuancheng Technology Development Co. Ltd. was used without further purification. $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, glutaraldehyde (GLA) solution (25%,w/w), cyclohexane, and $Na_2SiO_3 \cdot 9H_2O$ were supplied by Sinopharm Chemical Reagent Co. Ltd. Span 80 (sorbitan monooleate) was obtained from Shenyu Chemical Reagent Co. Ltd. Methyl orange (MO), $K_2Cr_2O_7$, hydrochloric acid (HCl), sodium hydrate (NaOH), acetic acid, and other reagents used in this work were purchased from Nanjing Chemical Reagent Co. Ltd. All chemicals are of analytical grade, and distilled water was used in all experiments.

2.2. Preparation of adsorbents

Magnetic Fe_3O_4 nanoparticles were obtained by co-precipitation method and then silica-coated Fe_3O_4 particles (Fe_3O_4@SiO_2) was prepared to improve its acidic duration (Yan et al., 2012). CTA modified chitosan (CS-CTA) has been also prepared by etherification reaction according to previous work (Huang et al., 2013). The aforementioned detailed preparation processes are described in Supplementary Materials Text S1.

CS-CTA-MCM was prepared by combining CS-CTA and silica-coated Fe_3O_4 nanoparticles by a very simple method. Briefly, a desired amount of CS-CTA powder was dissolved in Fe_3O_4@SiO_2 suspension under vigorously stirring. The mixture was then dispersed evenly in cyclohexane containing a small amount of Span 80, and the volume ratio of cyclohexane to the aforementioned aqueous mixture was 10:1. Glutaraldehyde was selected as crosslinker and added dropwise into the water–cyclohexane emulsion. After 3.0 h crosslinking reaction at 318 K, the mixture was adjusted by a dilute NaOH aqueous solution to pH around 8.0. The resultant product was then filtered and washed with ethanol and distilled water in succession. Finally, CS-CTA-MCM was obtained and kept in distilled water for further use. The degree of CTA substitution on this chitosan-based composite was ~0.92 per glucosamine unit of chitosan, estimated from the integrated area of the corresponding characteristic peak in its ^{1}H nuclear magnetic resonance spectrum (Bruker AVANCE Model DRX-500).

Besides, CS-MCM was also prepared by the same method as a control sample except that pure chitosan was directly used instead of CS-CTA.