



Removal of various cationic dyes from aqueous solutions using a kind of fully biodegradable magnetic composite microsphere

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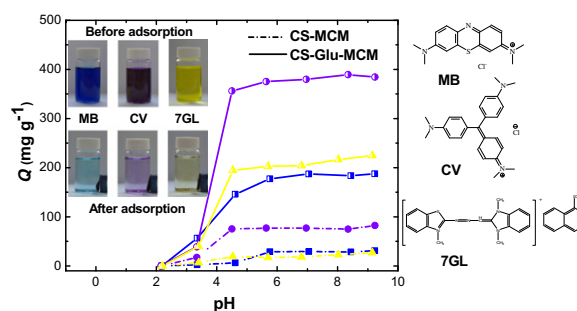
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HIGHLIGHTS

- Glutamic acid modified chitosan magnetic composite microspheres were prepared.
- This adsorbent is proven effective in adsorbing various cationic dyes.
- Glutamic acid plays a key role to improve the efficiency for dye removal.
- The adsorption mechanism is monolayer chemical adsorption.
- This adsorbent can be reused almost without any loss of adsorption capacity.

GRAPHICAL ABSTRACT

The glutamic acid modified chitosan magnetic composite microspheres (CS-Glu-MCMs) have been prepared and employed as adsorbents for removal of various cationic dyes from aqueous solutions.



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ABSTRACT

In this work, a kind of novel full biodegradable magnetic adsorbent based on glutamic acid modified chitosan and silica coated Fe_3O_4 nanoparticles was prepared successfully by a one-step method. The structure of the glutamic acid modified chitosan magnetic composite microspheres (CS-Glu-MCMs) was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG), vibrating-sample magnetometer (VSM), scanning electron microscope (SEM), and equilibrium swelling experiment. Then, CS-Glu-MCM was employed as adsorbent for removal of three different kinds of cationic dyes, methylene blue (MB), crystal violet (CV) and cationic light yellow 7GL (7GL), from aqueous solutions. Compared with chitosan magnetic composite microspheres (CS-MCMs) without modification, CS-Glu-MCM shows much higher dye uptakes. The fundamental adsorption experiments reveal that CS-Glu-MCM is more efficient in dye removal at pH higher than 5.0. Adsorption isotherms and adsorption kinetics of CS-Glu-MCM are all well described by Langmuir model and the pseudo-second order model, respectively, which indicates that the dyes adsorption behavior of CS-Glu-MCM is a homogeneous monolayer chemisorption process. Furthermore, the magnetic adsorbents could be easily regenerated at lower pH and reused with almost no loss of adsorption capacity.

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1. Introduction

Dye is one of the major pollutants found in the effluents of textile, paper, plastic, food and cosmetic industries [1]. Colored dye effluents may interfere with light penetration in the receiving

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water bodies, thereby disturbing the biological processes. Furthermore, many of the dyes are very toxic or strongly carcinogenic [2,3]. Removal of dyes is becoming a popular topic in controlling water pollution nowadays. Among the various techniques for dye removal from wastewater, such as adsorption, flocculation, oxidation and electrolysis [4,5], adsorption is an effective and economical method in low-concentration pollution treatment and operational convenience [6].

In recent years, adsorbents based on natural polymers, such as starch, cellulose and chitin, are gaining much more concerns in comparison with traditional adsorbents, since they bear advantages such as abundance, nontoxic, environment-friendly, low-cost and high-efficiency [7–9]. Among them, chitosan, which is derived from chitin, the second most abundant natural polymer [10], is one of the major raw materials of the polysaccharide-based adsorbents [11]. The abundant amino groups on the chitosan backbone make it easy to bind anionic species from aqueous solutions after being protonized [12]. But the adsorption efficiency of chitosan for cationic pollutants is usually unsatisfactory. Fortunately, chitosan can be conveniently chemically modified for bearing abundant free reactive groups such as hydroxyl and amino groups, and various functional groups can be grafted onto chitosan to enhance its affinity with various species containing different charge [13,14]. In recent years, numerous chitosan based adsorbents have been prepared by etherification, esterification and grafting methods, which showed great application potentials in removal of various pollutants such as heavy metals and dyes [8,11,15–17].

On the other hand, adsorbents are usually made into a very small size for improvement of the adsorption efficiency by increasing the surface area. But it would be very difficult to separate them from water after reaching saturated adsorption. Recently, magnetic separation technique is gaining wide use in water treatment due to its great significance in accelerating separation speed and improving water treating efficiency [18–20]. After being impregnated with magnetism, the adsorbents could be easily separated from solutions under an external magnetic fields. The separability of adsorbents is greatly enhanced. The impregnation of magnetism is usually achieved by combination of magnetic components into adsorbents, which are mainly Fe_3O_4 -based substances. However, Fe_3O_4 is susceptible to acidic corrosion and oxidation, which undoubtedly limits their application greatly. It is a frequently applied method to coat some of the inert substance on the surface of the magnetic matters for protection [21–23].

In this work, Fe_3O_4 nanoparticles were prepared and coated with a layer of silica at the beginning for improvement of its acidic durability. The silica coated magnetic particles are hydrophilic and compatible with chitosan, on which the silanol groups would also improve affinity with cationic adsorbates. Then, glutamic acid, which is an amino acid compositing protein, was chosen as the modifying agent to improve the adsorption capacity of chitosan for cationic pollutants further. It could be easily obtained from monosodium glutamate, which is an inexpensive flavoring agent commonly used in Asian cuisines. The magnetic composite adsorbents combination of glutamic acid modified chitosan and SiO_2 coated Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) were prepared by a one-step method, and applied to adsorptive removal of three kinds of cationic dyes, namely methylene blue (MB), crystal violet (CV) and cationic light yellow 7GL (7GL), from aqueous solutions. The fundamental adsorption behavior of magnetic composite adsorbents including the effect of the initial solution pH, isothermal adsorption equilibrium and adsorption kinetics have been investigated to explore the adsorption mechanism further. Moreover, the recycling and reuse of the used adsorbents was also performed for its great importance in practical applications.

2. Experimental section

2.1. Materials

Chitosan, whose deacetylation degree is 90.5% and viscosity average molecular weight is $3.0 \times 10^5 \text{ g mol}^{-1}$, was purchased from Shandong Aokang Biological Co. Ltd., China. Glutamic acid was prepared from monosodium glutamate, which was made in

Lotus Co. Ltd., China and available from local supermarket, using hydrochloric acid as the neutralizer. Ammonium iron(II) sulfate hexahydrate $((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$, iron(III) chloride hexahydrate $(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$, glutaraldehyde (GLA) solution (25%, w/w), cyclohexane and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ were supplied by Sinopharm Chemical Reagent Co. Ltd., China. Span 80 (Sorbitan Monooleate) was purchased from Shenyu Chemical Reagent Co. Ltd., Shanghai, China. MB and CV were both purchased from Tianjin Institute of Chemical Reagents, and 7GL was from Xingwu Chemical Co. Ltd., China. Hydrochloric acid (HCl), sodium hydrate (NaOH), acetic acid and other reagents used in this work were all A.R. grade reagents. Distilled water was used in all experiments.

2.2. Preparation of adsorbents

2.2.1. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$

The magnetic nanoparticles, $\text{Fe}_3\text{O}_4@\text{SiO}_2$, were prepared via precipitation method proposed by Wang et al. [21]. Briefly, 3.1 g of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 4.3 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water together; then the mixture of the ferric compounds was added into excessive NaOH aqueous solution dropwisely under vigorous stirring and N_2 atmosphere; finally Fe_3O_4 nanoparticles with average diameter approximately 90 nm were obtained. The magnetic nanoparticles were washed and suspended in water. Then 8.0 g of Na_2SiO_3 aqueous solution was added into the Fe_3O_4 suspension. The silica coated nanoparticles were obtained by subsequent neutralization using HCl aqueous solution. At last, the prepared $\text{Fe}_3\text{O}_4@\text{SiO}_2$ were washed and kept in water for further use.

2.2.2. Preparation of CS-MCM and CS-Glu-MCM

2.2.2.1. Preparation of CS-MCM. 1.6 g of chitosan powder and 0.9 g of acetic acid was dissolved in 100 cm^3 of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ suspension under vigorous stirring at 50°C ; then the mixture of chitosan and magnetic nanoparticles were dispersed evenly in cyclohexane containing a small amount of Span 80, and the volume ratio of cyclohexane to the aforementioned aqueous mixture is 5:1; then glutaraldehyde was chosen as crosslinker and added into the water–cyclohexane suspension system dropwisely. Subsequently, the crosslinking reaction was kept at 50°C for 45 min. After completion of the reaction, the mixture was neutralized by dilute NaOH aqueous solution to pH approximately 8.0. Then, the microspheres were filtered and washed with ethanol and distilled water. Finally the chitosan magnetic microspheres were obtained and kept in water for further use.

2.2.2.2. Preparation of CS-Glu-MCM. CS-Glu-MCM was prepared using the same method as CS-MCM, except that acetic acid was replaced by equivalent amount of glutamic acid in the first step. However, glutaraldehyde was employed here as not only the crosslinker but also the reagent for grafting glutamic acid. The simultaneous chemical reactions of glutamic acid grafting onto chitosan and crosslinking for preparation of CS-Glu-MCM was described in Scheme 1.

2.3. Characterization of adsorbents

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of CS-MCM and CS-Glu-MCM were recorded using a Fourier transform infrared spectrometer (Type TENSOR 27; Bruker Co.; Germany). Since they were obtained after neutralization to pH approximately 8.0 by sodium hydrate solution, the carboxyl groups in CS-Glu-MCM were deprotonized and formed Na-form microspheres. For further comparison, CS-Glu-MCM was also treated in acidic solution to be H-form one for another FTIR

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