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Adsorption of C.I. Reactive Blue 19 from aqueous solutions by porous particles of the grafted chitosan

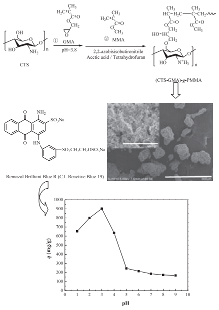
Xue Jiang *, Yongmei Sun, Lin Liu, Shugen Wang, Xiuzhi Tian *

School of Textiles & Clothing, Key Laboratory of Eco-Textile, Ministry of Education, Jiangnan University, Wuxi 214122, PR China

HIGHLIGHTS

- Chitosan was modified by graft copolymerization with Poly(methyl methacrylate).
- The grafted chitosan remains the C_2-NH_2 groups and is almost amorphous.
- Porous particles of the grafted chitosan were prepared.
- They have strong affinities for the C.I. Reactive Blue 19 dissolved in water.
- The adsorption process is pH controlled.

GRAPHICAL ABSTRACT



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ABSTRACT

Chitosan (CTS) was modified by graft copolymerization with Poly(methyl methacrylate) on the premise that its C_2-NH_2 groups were remained. Porous particles of the grafted CTS were prepared by emulsification together with wet phase inversion and evaluated as a new adsorbent for decolorizing the C.I. Reactive Blue 19 solutions. The chemical composition, thermal stability and amorphous structure of the grafted CTS were demonstrated by FT-IR, TGA and WXRD characterizations. Porous particles of the grafted CTS were observed in SEM images. For the given adsorbent/dye system, the data from equilibrium sorption experiments are well fitted to the Langmuir isotherm. The maximum dye uptake (1498 mg/g) is attained at 30 °C and pH 3. Besides, the pseudo-second-order sorption kinetics indicates that chemisorption controls the process. The dominant role for adsorption mechanism is electrostatic attraction. When the initial pH of dye solution is above 3, higher pH induces higher and faster dye uptake.

1. Introduction

Dyes have become one of the main sources of severe water pollution as a result of the rapid development of the textile industries. Dyes, especially those with good water solubility are difficult to be removed from their effluents due to their inert properties—anti-degradability by photos, oxidants and biological agents. Besides, their low amounts in the effluents always bring on high costs of treatment [1]. Recently, adsorption techniques using chitosan (CTS) derivatives, as an alternative to conventional treatment processes, have been developed to adsorb anionic dyes from aqueous solutions [2–7]. CTS has advantages over other adsorbents because of its special characteristics such as renewability, biocompatibility, biodegradability and non-toxicity. Besides, the primary amino groups of CTS can be protonated by the hydrogen ions in solution and thus strongly adsorb anionic dyes by electrostatic attraction. Nevertheless, CTS cannot be used directly to adsorb dyes from their effluents because it lacks not only good chemical, mechanical stabilities but also high adsorption capacity and efficiency. The products by means of cross-linking and graft modification present improved mechanical and chemical properties [8–12], but their adsorption capacities or adsorption rates are simultaneously depressed due to an obvious reduction of free amine groups and

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* Corresponding authors. Tel./fax: +86 510 85919920 (X. Jiang), tel.: +86 510 85912007; fax: +86 510 85912009 (X. Tian).

E-mail addresses: jiangx@jiangnan.edu.cn (X. Jiang), tianxz@jiangnan.edu.cn (X. Tian).

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accessible sites of dyes in the products. Accordingly, remaining free amine groups, increasing amorphous region as well as surface area are potential to prepare the CTS-related adsorbents with improved performances for the removal of anionic dyes from aqueous solutions.

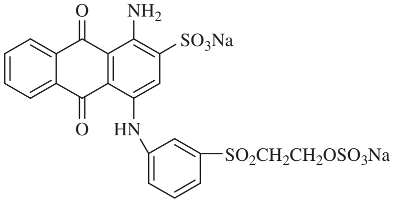
Poly(methyl methacrylate) (PMMA) is a polymer with an amorphous structure [13]. It has been reacted or blended with many synthetic and natural polymers with the purpose of increasing hydrophobicity, chemical and physical resistances of the new materials [11,12]. In the present study, CTS was modified by graft copolymerization with PMMA on the premise that the C_2-NH_2 groups of CTS are un-reacted. Concretely, glycidyl methacrylate (GMA)-modified CTS bearing double vinyl groups (CTS-GMA) was synthesized through ring-open reaction of GMA with the C_6-OH of CTS. Thereafter, CTS-GMA was radically copolymerized with methyl methacrylate (MMA) to obtain the graft copolymer—(CTS-GMA)-*g*-PMMA. Aside, emulsification together with wet phase inversion was used to prepare porous particles of (CTS-GMA)-*g*-PMMA. The obtained porous particles of (CTS-GMA)-*g*-PMMA were characterized by Fourier-transform infrared (FT-IR), wide-angle X-ray diffraction (WXRD), thermogravimetric analysis (TGA) and scanning electron microscope (SEM). They were used as a novel adsorbent for anionic dye's removal from aqueous solutions. C.I. Reactive Blue 19 (RB 19) as a representative of the anionic dyes was chosen for the dye adsorption bath experiments. Effect of the initial pH of dye solution on the dye's adsorption was evaluated. In addition, the experimental data were correlated by two generalized adsorption isotherm models namely, the Langmuir and Freundlich models. Kinetic experiments were also conducted to determine the rate at which RB 19 is adsorbed on the given adsorbent.

2. Experiments

2.1. Materials

Chitosan (CTS) with molecular weight of 700 kDa and deacetylation degree of 90% was purchased from Golden-Shell Biochemical Co., Ltd., China. Glycidyl methacrylate (GMA), methyl methacrylate (MMA), acetic acid (HOAc), potassium hydroxide (KOH) and 2,2-azobisisobutironitrile (AIBN) were purchased from Sigma–Aldrich Chemical Co., USA. MMA and GMA were purified with 5% NaOH to remove the inhibitor then washed twice with a 10% (w/v) aqueous $NaHCO_3$ and dried over $MgSO_4$. The solutions were finally distilled. AIBN was re-crystallized from methanol prior to use. Solvents of *n*-hexane, tetrahydrofuran (THF), acetone and ethanol were purchased from Refinary Mill, Hangzhou, China. They were of reagent grade (99% pure) and used without further purification.

C.I. Reactive Blue 19 (RB 19) used as the adsorbate was a gift from a dye manufacturing unit in China and was used as it is without further purification. Its chemical structure was schemed as follows.



C.I. Reactive Blue 19(RB 19)

2.2. Preparation of the absorbent

The route to modify CTS was schemed as in Fig. 1, which involved two processes: (1) functionalization of CTS with GMA in the acidic media (pH = 3.8) [14] and (2) synthesis of the copolymer—(CTS-GMA)-*g*-PMMA using the mixed solvent of HOAc and THF (v/v, 2/1). The mol ratio of CTS/GMA/MMA was 1/1/1.

Specifically, 0.5 g of CTS was dissolved in 100 mL of the acetic acid (HOAc) solution (0.4 M). The CTS solution was poured into a glass vial and its pH was regulated as 3.8 by using the KOH solution (0.05 M). Then the subscribed amount of GMA was added. The vial was closed and gaseous nitrogen was flowed through the system at 65 ± 1 °C with mechanical stirring. The reaction proceeded for 2 h. Thereafter, the subscribed amount of MMA dissolved in 50 mL THF and AIBN (0.002 M) were introduced into the reaction system. The graft co-copolymerization proceeded for 4 h and the final product was cooled in an ice bath for 15 min to stop the mixture from further reacting.

Thereafter, the solution from the graft co-polymerization was directly added into *n*-hexane. The volumetric ratio of water phase to oil phase is 1:1.5. The mixture was emulsified using Span-80 for 30 min. Then, $NaHCO_3$ solution (0.1 M) was slowly dropped into the latex till its pH reached at about 9. Obvious delamination was observed. The oil phase and the water phase were removed using separating funnel, respectively. The remnant phase was vacuum-extracted and vacuum-dried at 50 °C for 24 h. Finally, the crude product was extracted with ethanol and acetone, respectively in a soxhlet apparatus for 4 h to dissolve all the free monomers, homo-polymers and residual emulsifier. The colorless product was dried under vacuum at 50 °C for 24 h to a constant weight. The gravimetric analysis has been effectively used to determine the grafting percentage as Eq. (1) [12].

$$\%G = \frac{W_1 - W_0}{W_0} \times 100 \qquad (1)$$

where W_0 andW_1 are the weights of the initial CTS and grafted CTS after extraction and drying. According to Eq. (1), the grafting percentage was 72.4%.

2.3. Instrument analyses

FT-IR spectra were recorded on a Nicolet Nexus 470 spectrometer in the optical range of 400–4000 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1}. The wide-angle X-ray diffraction (WXRD) patterns were carried out on a Bruker AXS X-ray diffractometer (D8 Advance, Germany) equipped with graphite monochromatized high intensity Cu Kα radiation (λ = 1.54406 Å) with the 2θ ranging from 3° to 80°. Calorimetric analyses [weight loss and thermogravimetric analysis (TGA)] were carried out in a TA DSC Q100 (TA Co., Ltd., America) calorimeter at a heating rate of 10 °C/min in N_2. The surface morphologies were observed by scanning electron microscope (SEM; SU-1510, Hitachi, Japan).

2.4. Dye adsorption batch experiments

Adsorption experiments were carried out using the prepared (CTS-GMA)-*g*-PMMA absorbent on a temperature controlled incubator shaker set at 30 rpm maintained at 30 °C for 7 h. A known amount of adsorbent (5 mg) was thoroughly mixed with 50 mL of RB 19 solution, whose concentration and pH were previously known. The pH of the mixture was initially adjusted using either hydrochloric acid or sodium hydroxide (1 M). After the flasks were shaken for the desired time, the suspensions were filtered through Whatman 0.45 mm filter paper. The remnant solutions were