Cross-linked succinyl chitosan as an adsorbent for the removal of Methylene Blue from aqueous solution

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ABSTRACT

Removal of a basic dye (Methylene Blue) from aqueous solution was investigated using a cross-linked succinyl-chitosan (SCCS) as sorbent. The chemical structures of chitosan and its derivatives were testified by FT-IR. X-ray diffraction, DTG analysis and swelling measurements were conducted to clarify the characteristics of the chemically modified chitosan. The effect of process parameters, such as pH of the initial solution, and concentrations of dyes on the extent of Methylene Blue (MB) adsorption was investigated. The Langmuir isotherm model was used to fit the equilibrium experimental data, giving a maximum sorption capacity of 289.02 mg/g at 298 K. Kinetic studies showed that the kinetic data were well described by the pseudo-second-order kinetic model. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) were determined to be -25.32 kJ mol^{-1}, -6.76 kJ mol^{-1} and -62.36 J mol^{-1} K^{-1}, respectively, which leads to a conclusion that the adsorption process is spontaneous and exothermic.

1. Introduction

Water contamination from a wide range of toxic pollutants has posed a great threat to the environment due to their potential human toxicity. Dyes represent one of the problematic groups [1]. They are widely used in a substantial number of industries, such as dyestuffs, textile, paper making, printing, leather, plastic, paint, pharmaceutics, and cosmetics [2]. Dyes can be classified as follows: anionic/acidic, cationic/basic and non-ionic disperse dyes, and most dyes are aromatic azo type, which can cause health problems such as allergic dermatitis, skin irritation, cancer and mutation in human [3–5]. They are often stable to light, heat and oxidizing agents and resistant to degradation due to their complex aromatic molecular structure and synthetic origin [5,6]. Because of their intense colour, they reduce light penetration and seriously affect the photosynthetic activity in aquatic life [7]. Since dye pollution can lead to serious results, it is urgent to search for effective methods to remove dye from effluents before they are mixed up with unpolluted natural water bodies.

Conventional treatment methods such as coagulation and flocculation, precipitation, ozonation, photocatalytic oxidation, electrochemical destruction, membrane filtration, ion exchange, reverse osmosis, irradiation, biological treatment and adsorption, have been developed for water decontamination applications [4]. However, among these methods, few could achieve the discharge standards alone, and some of them even generated a large amount of secondary waste [8]. Relatively, adsorption is recognized as a more efficient treatment process since it has the advantage of simplicity in operation, low cost, flexibility and insensitivity to toxic pollutants [9].

Although commercial activated carbon is a preferred sorbent for colour removal, its widespread use is restricted due to high cost [9]. All these make the search for economic and effective adsorbents necessary and valuable. Recently, a large variety of non-conventional low-cost adsorbents, such as fly ash, clay minerals (kaolinite, montmorillonite, bentonite, zeolite, Metakaolin, etc.), wheat straw, sawdust, peat, hazelnut shell, duckweed and activated sludge [10–17], being available in large quantities worldwide and eco-friendly, have been proposed and examined for their ability for wastewater treatment. However, most of them still lack good adsorption capacity. In order to improve the efficiency of the adsorption processes, it is necessary to develop cheap and easily available adsorbents with high adsorption capacities.

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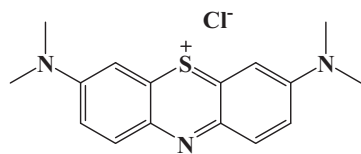
Fig. 1. Chemical structure of Methylene Blue.

The biopolymer chitin and its derivative chitosan have gained importance in environmental biotechnology due to their very good adsorption capacity toward dyes and metal ions [9,18]. Chitin is widely found in the exoskeleton of crustaceous, the cuticles of insects and the cell walls of fungi. Chitosan is a natural cationic polymer obtained by N-deacetylation of chitin [9,19]. It is more efficient than chitin in terms of adsorption capacity due to the presence of a large number of free amino ($-NH_2$) groups that can serve as the coordination and reaction sites. Chitosan has been reported with high potential for the adsorption of almost all classes of dyes, especially for anionic or reactive dyes [2,20,21]. Though perfect for adsorbing anionic or reactive dyes, chitosan presents poor sorption capacity for basic dyes [22,23], which limits its utilization as dye absorbent. To make it more suitable for adsorbing basic dyes, various functional groups, including carboxylate, sulfonate and phosphate groups have been used to modify chitosan [6,23,24].

In this study, chitosan was first coupled with succinyl to form succinyl chitosan (SCCS) by introducing the carboxyl group, the SCCS was then crosslinked with epichlorohydrin (ECH). The adsorption of a model basic dye, Methylene Blue (MB) from basic solution by as-prepared cross-linked SCCS was investigated. The adsorption kinetics was testified by fitting adsorption curve with pseudo-first-order and pseudo-second-order models, through which the adsorption rates were determined quantitatively. The equilibrium isotherms at different temperatures were fitted by Langmuir equation, and the thermodynamics of MB adsorption was clarified as well. In addition, the chemical structures of the original chitosan and modified chitosan have been verified by FT-IR spectra, XRD and thermal analysis have been applied to testify the structure change induced by modification. By comparing the swelling behavior of chitosan and cross-linked SCCS as well as their MB uptaking at different pH values, the efficiency of chitosan modification has been verified.

2. Materials and methods

2.1. Materials

Chitosan was obtained from Sanland Chemical Co., Ltd. (Los Angeles, CA, USA). According to the specifications from the manufacturer, it has a molecular weight of 450 kDa, and the degree of deacetylation is above 95%.

Methylene Blue (MB) was a basic dye purchased from Alfa Aesar Co. (Tianjin, China), its chemical structure is shown in Fig. 1.

Succinic anhydride, epichlorohydrin, and other reagents used in this experiment were of analytical grade and used without further purification.

2.2. Preparation of succinyl chitosan (SCCS) beads

Chitosan solution was prepared by dissolving 2.0 g of chitosan powder in 100 ml of 2 vol.% acetic acid solution. The mixture was kept stirring at room temperature for at least 6 h. To the as-prepared homogeneous viscous solution, 120 mL of methanol was added, followed by the addition of 2.48 g of succinic anhydride in 10 min. The mixture was kept stirring under room temperature for 24 h to com-

plete the reaction between succinic anhydride and chitosan, SCCS gel was obtained thereafter. To prepare succinyl chitosan bead, the SCCS gel was dripped into a precipitation bath containing 240 mL of 5% (m/V) KOH ethanol solution by a disposable syringe. The SCCS gel thereby coagulated to uniform beads. The obtained SCCS beads were thoroughly rinsed with distilled water to remove any KOH, afterwards were filtered and finally dried under vacuum. The dry beads were then ground by a laboratory mill and sieved, the beads with size of 80–100 mesh were used in this study.

2.3. Preparation of cross-linked SCCS beads

Fresh prepared wet SCCS beads were added to the 300 mL of ethanol solution containing 5% (m/V) KOH and 8 mL epichlorohydrin under constant stirring at 50 °C. After 4 h, the beads were collected by filtration and washed with ethanol solution and dried under vacuum. The cross-linked beads were ground and fractionalized with sieve, the beads with size of 80–100 mesh were used.

The synthesis route was illustrated in Scheme 1.

2.4. Characterization

2.4.1. Swelling degree of cross-linked SCCS beads

The swelling studies of cross-linked SCCS were done according to the method proposed by Lazaridis [24]. 0.0500 g of cross-linked SCCS beads was placed in 50 mL aqueous solutions of hydrochloride acid or sodium hydroxide, which has various pH values between 2 and 10. After immersion for 24 h at room temperature, the material was visually judged to have finished swelling. Then the material was removed from the solvent by filtration, and excess solvent was removed by blotting with filter paper. The weight of the swollen sample was measured, and the degree of swelling S (g/g) was calculated using the following equation:

$$S = \frac{W_S - W_o}{W_o} \tag{1}$$

where W_S and W_o are the weights of the swollen and dry beads, respectively. Duplicate measurements were carried out for each initial pH condition, and the mean values are presented.

2.4.2. FT-IR spectrum

FT-IR spectra of pure chitosan, SCCS, virginal and dye-loaded cross-linked SCCS, were recorded with a FT-IR spectrometer (Thermo FTIR-6700, Nicolet Instrument Co., USA) in the range of 4000–400 cm^{-1} using KBr pellets containing the prepared materials.

2.4.3. X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of pure chitosan, SCCS and cross-linked SCCS were performed via an X-ray diffractometer (Purkinje General, China) using Cu Kα characteristic radiation ($\lambda = 1.5406$ Å at 36 kV, 30 mA in the 2θ range of 2–40°).

2.4.4. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA)

To examine the thermal properties of pure chitosan, SCCS and cross-linked SCCS, differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were performed using a thermal analyzer DTG-60. The scans were carried out at a heating rate of 15 °C/min in a temperature range of 50–300 °C. A nitrogen flow was applied with a flowing rate of 20.0 mL/min to maintain an inert atmosphere.