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Original Research Paper

Effective removal of dyes from aqueous solution using ultrafine silk fibroin powder

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ABSTRACT

Ultrafine silk fibroin powder was successfully produced using our developed machine and used as low-cost adsorbent to remove dyes in the printing and dyeing wastewater. The silk powder thus prepared was characterized by scanning electronic microscopy (SEM), laser particle analyzer and Fourier transform infrared (FTIR) spectrum. It showed that the silk powder with an average diameter of 3.8 μm was dominant in β-sheet structure. Dye adsorption experiments demonstrated that silk powder could effectively remove model dyes including direct orange (DO), disperse blue (DB) and methylene blue (MB) in particular. Factors influencing the adsorption of MB, e.g., solution pH, contact time, adsorption concentration and ionic strength were systematically investigated. Isotherm equilibrium studies demonstrated that MB adsorption process followed Langmuir model. The maximum adsorption capacity for MB dye was estimated to be 20.58 mg/g and the decoloration percentage could reach up to 95%. The batch experimental results suggested that silk fibroin powder could be used as an efficient sorbent to remove dyes in textile effluents.

1. Introduction

Water pollution due to the discharge of industrial effluents including textile, electroplating, chemical and other industry wastewaters is of major concern recently because of their toxicities and threat to the human life and environment [1–8]. In particular, textile effluents have gained increased attention because the extensive release of synthetic dyes has caused considerable environmental pollution (e.g., they produce unsightly color even at very low concentration, affect the photosynthetic activity of aquatic plants and raise the chemical oxygen demand) [9]. Importantly, the accumulation of dyes in water can seriously damage food chains of human and animals [10,11]. Therefore, elimination of dyes in textile effluents is of vital importance to textile industries. Various technologies have been explored for decolorizing the dyeing wastewater, including physical adsorption [12–14], chemical degradation [15–17], and biological treatment [18]. Among these technologies tested so far, physical adsorption using low-cost and eco-friendly adsorbents such as natural clays [19], orange peel [20], biological sludge [21–24], powdered peanut hull [25] and waste materials [26–30] has been extensively investigated as a promising approach for the removal of dyes in the wastewater.

Silk, a kind of natural protein fibers, has long been used as high quality textile material for its moderate moisture absorption and retention property, and used as sutures and other biomedical materials for its good mechanical properties and biocompatibility [31,32]. However, a large number of leftovers during silk fiber manufacturing have been wasted due to limited fiber reprocessing technology. In order to take full advantage of silk fibroin, silk protein has been processed into various forms such as nanofibrous mats, hydrogels, films, microspheres and powders for various applications through electrospinning, sol–gel approach, casting, spray-dying and milling, respectively [33–35]. In particular, powdered silk fibroin has evoked great attention as an additive of cosmetic and pharmaceutical products because of their good physicochemical properties.

As a popular and low-cost technology, milling-based approach assisted with pre-treatment processes is commonly selected to produce silk powders [36–38]. For example, Takeshita et al. [36] produced a water-soluble silk fibroin powder with a minimum particle size of 10 μm by pulverizing the irradiated silk fibers using a ball mill. In that study, raw silk fibers were firstly treated with enzyme to remove the sericin, and then silk fibroin powder was obtained by irradiating the degummed samples at room temperature with 1 MeV electron beam and the following pulverization. The silk powder thus produced exhibited remarkably water-soluble properties. Researchers in X. Wang's [37,38] group

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manufactured kinds of silk fibroin powders using combined milling technologies. The volume based particle size could be 700 nm. In our previous studies, ultrafine wool protein [32] and down powders [39] were successfully produced using our developed powder instrument at room temperature. The formed protein powders could preserve the native physicochemical properties of correspondent fibers and their average sizes were in the range of 1.56–2.0 μm. In addition, superfine down powder could positively promote the dyeing property of viscose casting film with the increase of down powder content because of its excellent dye adsorptive property [40]. Inspired by these studies and the good behavior of protein powder in dye adsorption, we hypothesized that ultrafine silk fibroin powder could be a kind of effective and economical absorbent to remove dyes in textile effluents.

In this present study, we report the preparation, characterization and dye removal capacity of ultrafine silk fibroin powder. Ultrafine silk fibroin powder was prepared using home-made instruments. The effect of pH value, contact time, electrolytes, and the amount of silk powder on the dye removal capacity were systematically investigated. Isotherm adsorption experiment confirmed that the methylene blue removal fitted well with Langmuir model. To our knowledge, this is the first report related to the use of silk fibroin powder as an adsorbent to removal dyes in textile effluents.

2. Experimental

2.1. Materials

Raw Bombyx mori silk fiber was provided by Luotian Silk Co., Ltd. (Hubei, China). Methylene blue (MB), direct orange (DO), and dispersive blue (DB) were brought from Shanghai Jingchun Reagent Co., Ltd., and used without further purification. Sodium carbonate (Na_2CO_3), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. Water used in all experiments was purified using a Milli-Q Plus 185 water purification system (Millipore, Bedford, MA) with resistivity higher than 18 MΩ cm.

2.2. Fabrication of silk fibroin powder

The fabrication process of ultrafine silk fibroin powder was similar to our previous reports (Scheme 1) [32,41]. Briefly, raw silk filaments were boiled at 90 °C for 1 h in an aqueous solution of 0.3 M sodium carbonate to remove sericin. Degummed silk filaments were rinsed thoroughly in warm distilled water and dried at room temperature. Then, dried silk fibers were cut into short pieces (nearly 3 mm) with a rotary blade and ultimately pulverized with our home-made machine. The machine was mainly consisted of two special milling pans with low heat generation and high anti-abrasion properties. The structure of milling pans has been described in detail in our patent [42]. Under the mechanical action including pressure, drawing, torsion, and sheer action, short silk fiber pieces could be easily milled into a fine powder. The silk fibroin powder thus prepared was stored in a desiccator before characterization and application.

2.3. Dye removal

Three kinds of dyes usually used in textile and dyeing industries were chosen as model species to prepare the dye-contaminated water. The stock solution of each dye was prepared in a concentration of 200 mg/L by dissolving the dye in water and then diluted to predetermined concentrations for each test. The pH of dye solution was adjusted with 0.1 M HCl or 0.1 M NaOH. A series of batch experiments were performed to examine the removal of dyes from solutions under an array of varying conditions, including solution pH, contact time, adsorbent content, and solution ionic strength. For these experiments, 50-mL glass beakers were used as reactors and each reactor contained 30-mL of solution that was adjusted to a predetermined condition. A 1-mL aliquot of the solution was sampled at fixed sampling time to analyze the concentration of residual dye in the solution. For certain discussion, dye removal percentage was calculated using the following:

$$\text{Removal percentage}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1)$$

Experiments were also conducted at selected conditions to examine the sorption isotherm. 20-mL vials were used as reactors, and each reactor contained 10-mL dye solution and 2 mg/mL silk fibroin powders. The initial concentrations of dye varied from 10 mg/L to 120 mg/L, and the solution was mixed under magnetic stirring for 60 min, a period that has been verified in preliminary tests allowing for adsorption equilibrium. Then, 1 mL of the aqueous sample was taken and analyzed for residual dye concentration. The dye uptake by the powder at equilibration time was calculated following:

$$q_t = \frac{(C_0 - C_t)V}{M}, \qquad (2)$$

where q_t (mg/g) and C_t are the amount of dye uptake by silk powder and dye concentration at time t, respectively. C_0 is the initial dye solution concentration. V (L) is the solution volume, and M (g) denotes the mass of silk powder. All the experiments were carried out at room temperature and three parallel experiments were conducted for dye decoloration at each condition. The data presented were mean of three independent sample measurements.

2.4. Characterization

Morphologies of silk fibroin powder were observed using a scanning electron microscope (SEM) (JSM5600LV, JEOL Ltd., Japan) with an operating voltage of 10 kV. Prior to SEM observation, samples were first glued onto a conducting resin and then sputter-coated with Pt films with a thickness of 10 nm. Fourier transform infrared (FTIR) spectrum was recorded using a Nicolet 5700 FTIR spectrometer (Thermo Nicolet Corporation, United States) in a wavenumber range of 4000–500 cm^{-1} at ambient conditions. For FTIR testing, measured silk powder was mixed with KBr powders

Scheme 1. Schematic illustration of silk fibroin powder fabrication.