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RESEARCH PAPER

Cellulose/carrageenan/TiO_2 Nanocomposite for Adsorption and Photodegradation of Cationic Dye

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Abstract Cellulose/carrageenan/TiO_2 nanocomposites were simply prepared by the co-dissolution of cellulose and carrageenan, and the dispersion of TiO_2 in 1-ethyl-3-methylimidazolium acetate, followed by reconstitution with anti-solvents. The cellulose/carrageenan/TiO_2 composite showed a much higher adsorption capacity for methylene blue (MB) than the cellulose and cellulose/TiO_2 composite. The cellulose/carrageenan/TiO_2 composite also degraded MB more efficiently in aqueous solution than the cellulose/TiO_2 composite. The MB adsorption capacity of the cellulose/carrageenan/TiO_2 composite increased linearly with increasing carrageenan content in the composites.

Keywords: cellulose, titanium oxide, carrageenan, methylene blue, photodegradation

1. Introduction

Cellulose, a linear polysaccharide of D-glucose residues linked by β-(1→4)-glycosidic bonds, is the most abundant renewable biopolymer on earth. It has many industrial applications, such as paper-making, supports for catalysts, membranes for purification, and matrix for drug delivery, because of its excellent thermal and mechanical properties, biocompatibility, and biodegradability [1]. However, the insolubility of unmodified cellulose in most organic solvents has limited the applications of cellulose-based composites. Recently, ionic liquids (ILs) have been developed for the dissolution and reconstitution of cellulose. ILs are good solvents for various biopolymers and synthetic polymers, and are environmentally friendly. Therefore, they provide great opportunities for preparing various cellulose-based composites.

Introduction of nanomaterials as additives in the cellulose matrix has been used to give additional functionality. For example, Fe_2O_3, silver, and hydroxyapatite nanoparticles were added to cellulose-based composites in order to give magnetic, antibacterial, and biocompatible properties to cellulose-based composites, respectively [2-4]. Recently, unmodified cellulose/titanium dioxide (TiO_2) composite materials were prepared using ILs that can dissolve cellulose [5-7]. TiO_2 can degrade many aromatic compounds such as phenol, benzene, and chlorobenzene as well as various dyes such as methylene blue, Rhodamine B, and ethyl violet completely into carbon dioxide and water [8]. Cellulose/TiO_2 composites proved to have good catalytic activity for the photodegradation of organic dyes. However, the photodegradation of cationic dyes using cellulose/TiO_2 composites has limitations in the environmental applications such as the treatment of wastewater generated from the dyeing process, because of their very low adsorption capacity for cationic dyes.

Carrageenans are a family of linear sulfated polysaccharides extracted from red seaweeds. They have been used in the food and pharmaceutical industries because of their biocompatibility and gelling property. κ-Carrageenan has one negatively charged sulfonate group per disaccharide unit

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and possesses the best gelation properties in the carrageenan family. Therefore, κ-carrageenans have been studied as an interesting candidate for the adsorption of cationic dyes such as methylene blue, methylene green, fuchsine, toluidine blue, and thionine in wastewater treatment [9,10]. However, laborious desorption processes using ethanol or a high ionic strength medium is necessary to reuse the carrageenan adsorbent. In addition, carrageenan is unstable at acidic pH and high temperature.

In this work, cellulose/carrageenan/TiO_2 nanocomposite hydrogel films were simply prepared by the co-dissolution of cellulose and carrageenan, and the dispersion of TiO_2 in 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]), followed by reconstitution with an anti-solvent. Cellulose was used as the main supporting material for the nanocomposite because of its exceptional mechanical properties and chemical stability. Carrageenan was used to increase the adsorption capacity for cationic dyes because it has negatively charged sulfonate groups. TiO_2 nanoparticles were used to photocatalytically degrade cationic dyes in order to easily reuse the composites. The adsorption and photodegradation capacity of cellulose/carrageenan/TiO_2 nanocomposites for cationic dyes were investigated using methylene blue (MB) as a model compound. The influence of the carrageenan content in the nanocomposites on the adsorption capacity of MB was also studied.

2. Materials and Methods

2.1. Materials

Microcrystalline cellulose (Cat. No. 435236), carrageenan (Cat. No. C1013, predominantly κ and lesser amounts of λ), NaOH, HCl, titanium oxide (Cat. No. 718467, TiO_2, 21 nm nanopowder) were purchased from Sigma-Aldrich (St. Louis, MO, USA). MB and ethanol were obtained from J.T. Baker Chemical Co. (Philipsburg, PA, USA). [Emim][Ac] was obtained from IoLiTec Inc. (Tuscaloosa, AL, USA).

2.2. Preparation of cellulose/carrageenan/TiO_2 nanocomposite hydrogel film

For the preparation of gel forming solutions, 7% (w/w) of cellulose, 0.7% TiO_2, and carrageenan (0, 0.7, 1.4, 2.8, 4.2, or 5.6%) were mixed with 5 mL [Emim][Ac] and homogenized using a mortar. The mixtures were then incubated at 80°C with stirring until the cellulose and carrageenan were completely dissolved. The gel forming solution (0.2 mL) was cast on a cover glass (22 × 22 mm), and then, washed with ethanol after 1 h. The cast film was washed five more times using distilled water, and the resultant hydrogel film was stored in distilled water at room temperature until needed. The absence of [Emim][Ac] in the film was confirmed by measuring the optical density of the washing solution at 211 nm.

2.3. Adsorption and photodegradation of MB by nanocomposite hydrogel films

To investigate the adsorption efficiency, pieces of the hydrogel film (22 × 22 mm) were placed in 4 mL of MB solution (60 mg/L, pH 7.0) and stored in the dark for 5 h without stirring at room temperature until equilibrium was achieved. The amount of MB adsorbed on the hydrogel films was indirectly estimated by calculating the difference between the initial and final concentration of MB in the solution. The concentration of MB was spectrophotometrically determined by measuring the optical density at 664 nm. The extinction coefficient was 7.4×10^4 L/mol/cm. To investigate the photodegradation efficiency, the hydrogel films equilibrated with MB solution were exposed to UV light (254 nm) for a certain period. Periodically, samples were removed and the concentration of MB in solution was measured.

To investigate the effect of carrageenan on the adsorption capacity for MB of nanocomposite film, the pieces of the nanocomposite hydrogel films (22 × 22 mm) with various contents of carrageenan were placed in 4 mL of MB solution (1,000 mg/L, pH 7.0) and incubated in the dark for 6 h at 25°C under vigorous shaking. The adsorption capacity for MB (mg/g) of nanocomposite hydrogel films was calculated on the basis of dry weight of nanocomposite films.

2.4. Characterization of cellulose/carrageenan/TiO_2 nanocomposite film

To analyze the surface of nanocomposite films, hydrogel films were frozen overnight at -80°C, and were then freeze-dried under a vacuum for 12 h. All freeze-dried samples were sputter-coated with platinum prior to observation. The surfaces of the samples were examined using a scanning electron microscope (SUPRA 55VP, Carl Zeiss, Germany). To analyze the XRD patterns of nanocomposite films, freeze-dried nanocomposite films were ground using a homogenizer. The samples were scanned on a D8 Advance Diffractometer (Bruker, Madison, WI, USA) at 40 kV and 40 mA, and the 2 theta (θ) was scanned from 10 to 40° with a 0.1° width.

3. Results and Discussion

3.1. Adsorption of MB by nanocomposite hydrogel films

The amount of MB adsorbed on cellulose, cellulose/TiO_2, and cellulose/carrageenan/TiO_2 hydrogel films prepared with gel forming solutions containing 7% cellulose, 0.7% TiO_2,

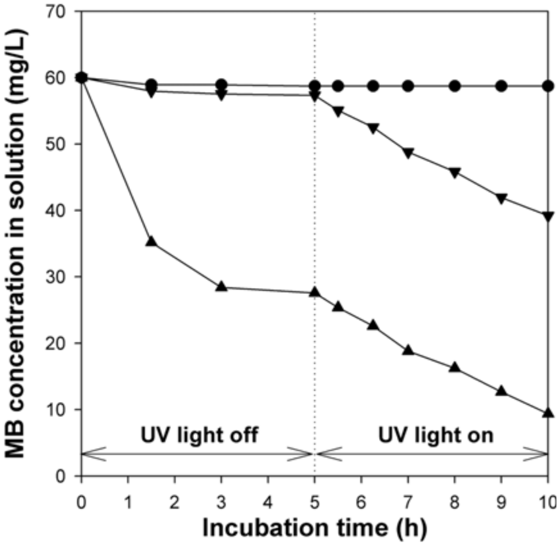

Fig. 1. Adsorption and photodegradation of MB by cellulose (●), cellulose/TiO_2 (▼), and cellulose/carrageenan/TiO_2 (▲) hydrogel film (22 × 22 mm) in MB solution (60 mg/L, pH 7.0) at room temperature. The contents of cellulose, carrageenan, and TiO_2 in gel forming solutions were 7, 0.7, and 0.7%, respectively.

and 0.7% carrageenan were 0.4, 0.7, and 7.7 mg/(g of dried film), respectively, when these films were incubated in 60 mg/L MB solution of pH 7.0 for 5 h under the dark without stirring (Fig. 1). The MB adsorption capacity of cellulose hydrogel was very low and was slightly enhanced by adding TiO_2 nanoparticle, because of the high surface area of the nanoparticles. A significant enhancement in the MB adsorption capacity was achieved by adding carrageenan, owing to the ionic interactions between the negatively charged sulfate groups of carrageenan and the positively charged MB. The MB adsorption capacity of cellulose/carrageenan/TiO_2 nanocomposite film containing about 8 wt% carrageenan on the basis of total dry weight was about 19-folds higher than that of cellulose film. The gel strength of the cellulose/TiO_2 hydrogel film was weaker than that of the cellulose hydrogel film, but this could be enhanced by adding carrageenan because of its good gelation property.

The cellulose/carrageenan/TiO_2 nanocomposite hydrogel film as an adsorbent for MB removal could be easily prepared using [Emim][Ac], because [Emim][Ac] can dissolve both cellulose and carrageenan. In particular, complex chemical modifications of cellulose were not needed in order to increase the MB adsorption capacity of the cellulose/TiO_2 nanocomposite.

3.2. Photodegradation of MB by nanocomposite hydrogel films

The photocatalytic capacity of cellulose/carrageenan/TiO_2 film that have a high adsorption capacity for MB was also investigated. First, cellulose/TiO_2 and cellulose/carrageenan/TiO_2 hydrogel films were removed from the MB solution (60 mg/L) after 30 min incubation in the dark. The cellulose/carrageenan/TiO_2 hydrogel film adsorbed significantly higher content of MB than cellulose/TiO_2 film (The upper of Fig. 2). In order to photocatalytically degrade adsorbed MB, two films were placed in an open dish containing distilled water and exposed to UV radiation (254 nm). The adsorbed MB was completely decomposed after 3 h (The lower of Fig. 2). The simple recycling of adsorbents after adsorption process is very important for the commercial application of adsorbents. Both films could be successfully recovered using UV irradiation without any desorption processes of MB using ethanol or high ionic strength solutions.

Second, cellulose, cellulose/TiO_2, and cellulose/carrageenan/TiO_2 hydrogel films were incubated in MB solution (60 mg/L) under the dark until the adsorption processes were equilibrated, and then, exposed to UV radiation (Fig. 1). The MB concentration was not changed by the cellulose

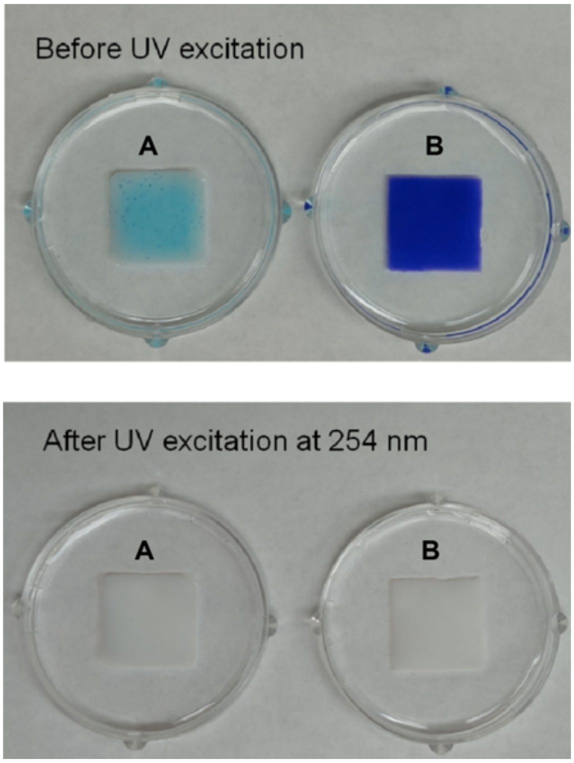

Fig. 2. UV-induced photocatalytic degradation of MB adsorbed on cellulose/TiO_2 (A) and cellulose/carrageenan/TiO_2 (B) hydrogel film. Two films were incubated in MB solution (60 mg/L, pH 7.0) at room temperature for 30 min in the dark, and then the films were exposed to UV radiation (254 nm) for 3 h. The contents of cellulose, carrageenan, and TiO_2 in gel forming solutions were 7, 0.7, and 0.7%, respectively.

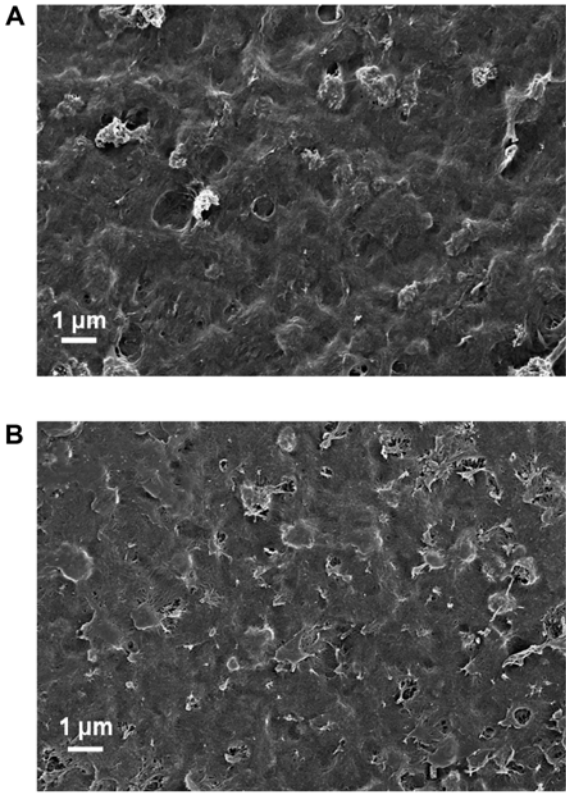

Fig. 3. SEM images of freeze-dried cellulose/TiO_2 (A) and cellulose/carrageenan/TiO_2 film. The contents of cellulose, carrageenan, and TiO_2 in gel forming solutions were 7, 0.7, and 0.7%, respectively.

hydrogel film. The photocatalytic activities of cellulose/TiO_2 and cellulose/carrgeenan/TiO_2 hydrogel film for the degradation of MB were very similar. Therefore, the cellulose/carrageenan/TiO_2 hydrogel film degraded MB more efficiently at a much lower initial MB concentration than the cellulose/TiO_2 film. These results clearly indicate that the cellulose/carrageenan/TiO_2 nanocomposites have a high adsorption and photodegradation capacity for MB.

3.3. Characterization of cellulose/carrageenan/TiO_2 nanocomposite film

The surface morphology of the cellulose/TiO_2 and cellulose/carrageenan/TiO_2 nanocomposite was investigated using scanning electron microscope (Fig. 3). A significant difference was not observed between the two composites. The viscosity of the gel-forming solution containing 7% cellulose and 0.7% TiO_2 increased slightly on adding 0.7% carrageenan. However, the increase in the viscosity did not induce a severe change in the surface morphology.

The XRD diagrams of cellulose, TiO_2, carrageenan, and composites are shown in Fig. 4. The diffraction patterns show the crystal structure type of TiO_2 and confirm the presence of TiO_2 in the cellulose/TiO_2 and cellulose/carrageenan/TiO_2 composite. TiO_2 nanoparticle can exist in two crystal forms of anatase and rutile. In Fig. 4C, the main peak at 25.3° shows the anatase form which has photocatalytic activity [6]. These peaks are also shown in the XRD patterns of cellulose/TiO_2 (Fig. 4A) and cellulose/carrageenan/TiO_2 composites (Fig. 4B). The XRD profiles of regenerated cellulose (Fig. 4D) and the cellulose-based composites (Figs. 4A and 4B) show broad amorphous peaks. These results mean that the crystalline nature of cellulose is disrupted in the composites because of the breakage of the internal hydrogen bonds. The XRD profile of the regenerated carrageenan (Fig. 4E) also exhibit a broad amorphous peak overlapping with cellulose [11].

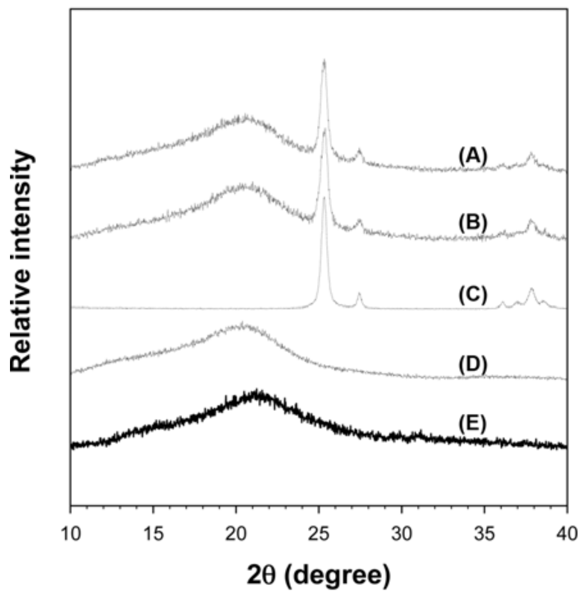

Fig. 4. Powder XRD patterns of cellulose/TiO_2 film (A), cellulose/carrageenan/TiO_2 film (B), TiO_2 (C), regenerated cellulose film (D), regenerated carrageenan film (E). The contents of cellulose, carrageenan, and TiO_2 in gel forming solutions were 7, 0.7, and 0.7%, respectively.

3.4. Influence of carrageenan content on the adsorption capacity of MB

The adsorption capacity of the nanocomposite films for MB was highly dependent on the carrageenan content in the gel-forming solution (Fig. 5). The MB adsorption capacity of the cellulose/carrageenan/TiO_2 film prepared with 7/5.6/0.7 wt% in [Emim][Ac] was 115.3 mg/g, whereas that of the cellulose/TiO_2 film was only 0.8 mg/g. When the cellulose and TiO_2 content were fixed at 7 and 0.7%, respectively, the MB adsorption capacity (q_e; mg/g) of the cellulose/carrageenan/TiO_2 film increased linearly with increasing the weight ratio of carrageenan in the composite film ($x_{\text{carrageenan}}$). The MB adsorption capacity of nano-

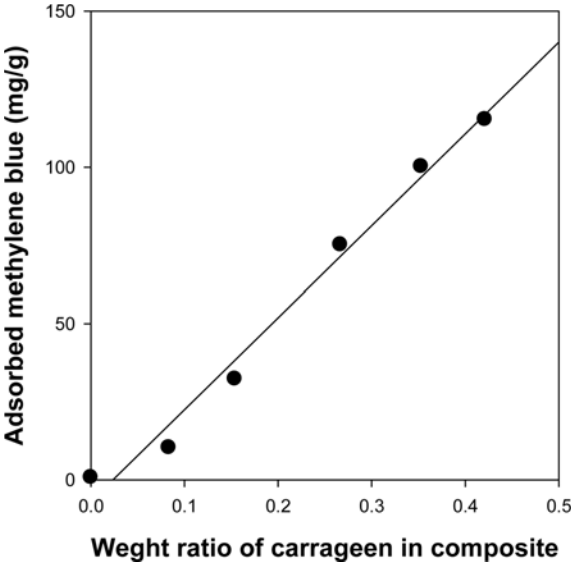

Fig. 5. Influence of carrageenan content in various cellulose/carrageenan/TiO_2 hydrogel films on the adsorption capacity for MB. The contents of carrageenan in gel forming solutions were changed from 0 to 5.6%, while the contents of cellulose and TiO_2 were fixed at 7 and 0.7%, respectively.

composites was predicted well with high coefficient of determination value (eq. 1).

$$q_e = 293x_{\text{carrageenan}} - 6.91 \text{ (number of sample} = 6, r^2 = 0.985) \quad (1)$$

4. Conclusion

Cellulose/carrageenan/TiO_2 nanocomposite films were simply prepared using [Emim][Ac]. The advantages of each component for the adsorption and photodegradation of MB were preserved. These negatively charged composites may have a high adsorption capacity for various cationic dyes, and can easily be recovered by UV irradiation without laborious desorption processes. In addition, the fabrication process of the cellulose/carrageenan/TiO_2 nanocomposite film using [Emim][Ac] can also be used to make various forms of composites such as beads, fibers, and molded shape. Therefore, biocompatible cellulose/carrageenan/TiO_2 nanocomposites have many potential applications in the environmental fields to treat cationic dyes in wastewater.

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