



Facile and green route to prepare magnetic and chitosan-crosslinked κ -carrageenan bionanocomposites for removal of methylene blue



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ABSTRACT

The objective of this investigation was to prepare magnetic bionanocomposite adsorbents based on κ -carrageenan using a simple and efficient method. The magnetic κ -carrageenan was prepared through *in situ* method and was crosslinked by chitosan polysaccharide through electrostatic attractions. The magnetic bionanocomposites were assessed as adsorbents to remove methylene blue (MB) from its aqueous solution. The effects of preparation conditions and operational terms including contact time, dye concentration, ion strength, pH, and temperature on removal of MB were investigated. The experimental adsorption isotherms of bionanocomposites for MB were described well by Langmuir model. According to the Langmuir constant (q_m), the maximum adsorption capacities of non-magnetic and magnetic adsorbents for MB were obtained 130.4 and 123.1 mg g⁻¹, respectively. Desorption experiments indicated that regeneration of the adsorbents can be made by using KCl solution in water/ethanol mixture. According to the data of the present work, it can be concluded that the magnetic κ -carrageenan bionanocomposites can be considered as an eco-friendly adsorbent for removal of cationic dye from aqueous solutions.

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1. Introduction

Water pollution with toxic organic dyes is a serious worldwide problem. The human life and aquatic biosystems are affected by these components and they must be removed from aqueous solutions before discharge them into environment [1]. Hence, some techniques such as chemical precipitation, filtration, electrochemical treatment, reverse osmosis, and adsorption have been used for removal of dyes from wastewaters [2,3]. Among mentioned methods of dye removal, adsorption process has suggested as an efficient, versatile, and low-cost choice [4]. In recent years, different adsorbents consisting of polymers have been extensively used for the removal of dyes from effluent of dye industries [5]. Polysaccharides, naturally occurring polymers with easy accessible resource, have been widely used for adsorption process due to their inexpensive and non-toxic properties [6]. The great adsorption behavior of these biopolymers is attributed to the hydrophilicity of reactive hydroxyl groups on polysaccharides [6] and also due to the presence of ionic functional groups including amine (in chitosan) [7], carboxylate (in alginate) [8], and sulfate pendants (in κ -carrageenan) [9].

κ -Carrageenan is one of the most abundant biopolymer that is found in cell wall and intercellular matrix of the seaweed plant tissue [10]. This natural polymer comprises anionic sulfate pendants ($-\text{OSO}_3^-$) with high affinity toward cationic dyes [11]. In our previous works, nanocomposite graft copolymers by combination of κ -carrageenan and nanoclays (including montmorillonite, sepiolite, and laponite RD) have been studied for removal of crystal violet and methylene blue (MB) dyes [12–14]. Also, adsorption of crystal violet on K⁺-crosslinked κ -carrageenan beads and film has been examined, and the results were favorable [9,15]. Each mentioned method has a few disadvantages. When the nanocomposites are prepared by grafting vinylic monomers on κ -carrageenan, the remained monomers and initiators can produce secondary pollution in aqueous solutions [16]. Thus, biosorption on biopolymers combined with nontoxic ingredients is an easy and efficient method to overcome the toxicity of adsorbents. Also, the K⁺-crosslinked κ -carrageenan beads [15] and κ -carrageenan/PVA films [9] indicated unfavorable behavior, which the adsorption efficiency showed a decrease during regeneration process. These results may be originated from disintegration of beads and films due to the low stability of K⁺ and κ -carrageenan complexes.

Chitosan/ κ -carrageenan complexes have been studied and utilized mainly for drug delivery [17,18]. The electrostatic interactions between positively charged amine groups on chitosan and negatively sulfate groups on κ -carrageenan can produce highly stable

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Table 1
Required amount of initial materials to prepare magnetic adsorbents.

	Chito0.4Car	LmChito0.4Car	HmChito0.4Car	LmChito0.1Car	LmChito0.2Car	LmChito0.6Car
κ -Carrageenan (g)	1	1	1	1	1	1
FeCl ₃ ·6H ₂ O (g)	0	1.35	2.70	1.35	1.35	1.35
FeCl ₂ ·4H ₂ O (g)	0	0.50	1	0.50	0.50	0.50
Chitosan (g)	0.40	0.40	0.40	0.10	0.20	0.60

ionic crosslinked materials [19]. According to literatures, there is no attempt to remove cationic dyes from wastewater by using crosslinked chitosan/ κ -carrageenan adsorbents. Due to the cationic pendants on chitosan ($-\text{NH}_3^+$) in acidic media, the removal of anionic dyes such as Reactive Black 5, Acid Red 37, and Reactive Red RB have been investigated by using epichlorohydrin- and H₂SO₄-crosslinked chitosan beads [20–22].

It has been reported that unlike the traditional adsorbents, the recovery of magnetic adsorbents from solutions can be performed by external magnetic field [23]. The co-precipitation of iron ions in the presence of biopolymers can be considered as a simple route to prepare magnetic adsorbents [24]. The objective of the present work was to establish new magnetic adsorbents by ionic complexing chitosan and κ -carrageenan. The iron ions were co-precipitated in the presence of κ -carrageenan, and the magnetic κ -carrageenan was crosslinked by chitosan biopolymer. The structure of adsorbents was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and vibrating sample magnetometer (VSM) techniques. The magnetic adsorbents were examined to remove MB cationic dye from aqueous solutions.

2. Materials and methods

2.1. Materials

A high molecular weight chitosan with 800–2000 cp viscosity (1 wt% of chitosan in 1 wt% of acetic acid solution) supplied from Sigma–Aldrich Co., USA; and degree of deacetylation (DD) was 85%. κ -Carrageenan was obtained from Condinson Co. (Denmark, molecular weight: 90,000 Da; purity: 96%). All other chemicals were analytical grade and used as received.

2.2. Preparation of magnetic bionanocomposites

The magnetic adsorbents were prepared through *in situ* co-precipitation of Fe²⁺/Fe³⁺ ions in the presence of κ -carrageenan. Aqueous solutions of chitosan with different concentrations were used for crosslinking the obtained κ -carrageenan/Fe₃O₄ solutions. The required amount of initial materials for preparing magnetic bionanocomposites is summarized in Table 1. In brief, κ -carrageenan solution was prepared by dissolving 1 g of this biopolymer in 100 mL distilled water at 60 °C for 2 h. The desired amount of iron salts were poured to κ -carrageenan solution ($n\text{Fe}^{3+}/n\text{Fe}^{2+}=2$) and the solution purged with N₂ inert gas for 30 min. The ammonia solution (3 M) was slowly dropped into (Fe²⁺/Fe³⁺)-loaded κ -carrageenan solution with vigorously stirring (800 rpm). The dark color belongs to the magnetic Fe₃O₄ nanoparticles was gradually appeared and the pH of solution was adjusted to 11. The magnetic solution was allowed to stir at 60 °C for 1 h. Chitosan solution was individually prepared by pouring required content of chitosan in 100 mL acetic acid solution (1%wt) and allowed to dissolve completely. The temperature of chitosan solution was set at 60 °C. Finally, the magnetic κ -carrageenan solution was slowly added in chitosan solution and stirred at 800 rpm at 60 °C for 20 min. The produced magnetic bionanocomposites were

separated from solution and washed with fresh distilled water for three times. The adsorbents were dried in an oven at 40 °C for overnight. The dried bionanocomposites were ground and sieved to the nominal sizes of 40–60 mesh. The adsorbents were designated as LmChito y Car, where the “Lm” is “low magnetic” and “y” is the content of chitosan used. In HmChito0.4Car, “Hm” shows “high magnetic”. The non-magnetic sample (Chito0.4Car) was prepared similar to magnetic ones without using iron ions or adding ammonia solution.

2.3. Swelling measurements

Degree of swelling (DS) of bionanocomposites determined by immersing 0.1 g of samples in 100 mL distilled water or solutions with different pHs (adjusted by 0.1 M of HCl/NaOH) and allowed to swell for overnight. The swollen adsorbents removed from water and blotted by filter paper to remove surface water, and the amount of absorbed water was calculated using Eq. (1).

$$DS = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_s and W_d are weights of the samples swollen in water and in dry state, respectively. All swelling experiments repeated for three times and the mean of data reported in graphs (mean \pm 3%).

2.4. Dye adsorption measurements

All adsorption experiments were done through batch method on a shaker with rate of 90 rpm. The adsorption kinetics of MB by bionanocomposites was studied by immersing 0.05 g (m , g) of adsorbents (60–80 mesh) in 25 mL dye solution (V , L) with initial concentration of 50 mg L⁻¹ (C_0 , mg L⁻¹; T 26 °C; pH 5.5). At different time intervals, 0.5 mL of dye solution withdrawn and the concentration of dye at time t (C_t , mg L⁻¹) was determined using UV–vis spectrophotometer at $\lambda_{\text{max}} = 664$ nm. The content of adsorbed dye on adsorbents (q_t , mg g⁻¹) was calculated according to Eq. (2):

$$q_t = \frac{(C_0 - C_t)}{m} \times V \quad (2)$$

The adsorption isotherms were carried out by varying the initial dye concentration in a range from 10 to 250 mg L⁻¹. The adsorbent dosage and volume of dye solutions was 0.05 g and 25 mL, respectively. The effects of pH (2–12) and NaCl concentration (0–0.5 M) on adsorption process were studied by immersing 0.05 g of bionanocomposites in 25 mL of dye solution with initial concentration of 50 mg L⁻¹. The equilibrium dye adsorption capacity (q_e , mg L⁻¹) was determined using Eq. (2); where the C_t was replaced with C_e (mg L⁻¹, residual dye concentration at equilibrium time). To investigate the effect of temperature on adsorption process, the adsorption isotherm of LmChito0.4Car was performed at three temperatures 16, 26, and 36 °C.

2.5. Desorption studies

Desorption study was carried out via bath method. The desorption solutions in this study were ethanol, water/ethanol (50/50, V/V), 0.5 M KCl in water, 0.5 M KCl in water/ethanol (50/50 m V/V), and 0.2 M acetic acid solutions. The dye loaded LmChito0.1Car

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