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Synthesis and characterization of clinoptilolite-alginate beads for dye removal from water

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Abstract

The aim of this study is to synthesize a superior adsorbent by combining positive properties of alginate and natural zeolite (clinoptilolite). Electrostatic interactions between the negatively charged carboxyl groups in alginate, porous sites in clinoptilolite and positively charged cationic dye in wastewater make alginate and clinoptilolite superior for dye removal. A model wastewater was prepared with varying concentrations of methylene blue (MB). Effects of MB concentration, adsorption time, pH, and adsorbent concentration on adsorption performance were evaluated. Composite adsorbents were also characterized using Fourier transform infrared spectroscopy. While 97.0% of removal was achieved using 5 g/L adsorbent, 98.8% of removal was obtained using 15 g/L adsorbent dosage. When the dye concentrations were gradually decreased from 5 mg/L to 2 mg/L, dye removal of 96.9%, 97.7%, 97.9% and 98.4% were observed at the end of 180 minutes.

Key words: adsorbent, clinoptilolite, sodium alginate

INTRODUCTION

Dye is a component of the effluent of many chemical industries, including plastic, textile, paper and pharmaceutical. Dye molecules are generally toxic and degradation is difficult. Therefore, the dye component must be removed from the wastewater to prevent the hazardous effect of dye on the receiving water ecosystem and human health (Yagub *et al.* 2014). There are several batch and continuous methods for the removal of dyes from wastewater; such as membrane-based filtration, chemical precipitation, electrocoagulation, biological treatments, and adsorption. Adsorption is considered the most convenient technique for dye removal due to its cost effectiveness and ease of operation (Pathania *et al.* 2017).

Adsorption is a sludge-free and effective method to remove dyes, even the concentration of the dye is at the ppm level (Malik 2003). The efficiency of the adsorption is directly related to the performance of the adsorbents. Different types of adsorbents, such as activated carbon, can be used to remove dyes from the water. Conventional adsorbents may exhibit unstable adsorption capacity over the long-time (Chen *et al.* 2014). Regarding the environmental concerns and progress in sustainable material developments, it has become important to use cheaper, natural, reusable, recyclable, reconstructed from waste, and biodegradable adsorbents. Currently, natural zeolites such as clinoptilolite (Qiu *et al.* 2009; Tian *et al.* 2016), clays such as bentonite (Tahir & Rauf 2006; Anirudhan & Ramachandran 2015), biodegradable polymers such as cellulose (Zhou *et al.* 2013; Tu *et al.* 2017), alginate (Wu *et al.* 2017), chitosan (Moussout *et al.* 2016; Kyzas *et al.* 2017), and solid waste disposal such as fly ash (Li *et al.* 2006) are preferred as adsorbents. These materials can be used directly or can be functionalized based on the chemical-physical structure of the dye to be separated.

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In this study, natural zeolite (clinoptilolite)-doped alginate beads were prepared as a composite adsorbent in order to remove methylene blue (MB) from synthetic wastewater. Sodium alginate (SA) is a kind of polysaccharide synthesized from brown seaweed and is used as a bio-based polymer for different purposes. It is a water-soluble hydrophilic natural polymer that consists of mannuronic and guluronic acid. It contains carboxyl and hydroxyl groups, which are responsible for its structural functionally. Cationic dye removal from wastewater using alginate-based adsorbent has been studied several times (Rocher *et al.* 2010; Inal & Erduran 2015; Djebri *et al.* 2016). In its natural form, it is used as a thickening agent. To convert the alginate into an adsorbent, cationic agents are used. The transformation of the alginate into adsorbent is known as gelation or cross-linking. In the literature, Ca^{+2} has mostly been used for the gelation ion (Benhouria *et al.* 2015; Li *et al.* 2017).

Clinoptilolite is a natural zeolite used for industrial, agricultural, environmental and biomedical purposes. Owing to its porous structure, and the existence of the ionic sites on the surface, it is an appropriate material for cationic dye removal (Wang & Peng 2010). In particular, an acid treated form of zeolite generates more active sites, causes an increase in porosity, and reduces the mineral impurities; therefore, their affinity towards the cationic dyes increases (Shi *et al.* 2016). However, pure clinoptilolite can show a poor affinity towards dye or organic pollutants. Moreover, natural zeolite is present in powder form in nature and it is difficult to recover zeolite after adsorption. It dissolves in water and may cause turbidity in the treated water. Therefore, the main objective of this study to prepare a cheap, functional, regenerative adsorbent by combining the positive properties of the alginate and clinoptilolite.

In the present study, clinoptilolite-doped sodium alginate adsorbent was prepared as a spherical bead shape by crosslinking the gel into a $CaCl_2$ solution. Beads were characterized using Fourier transform infrared spectroscopy (FTIR). Adsorption experiments were conducted to remove MB from the synthetic dye solution. Effects of contact time (0–210 min), dye concentration (2–5 mg/L), adsorbent concentration (5–15 g/L), and solvent pH (3.5–11 pH) on the dye removal were investigated. Adsorption isotherms were also studied at the different dye concentrations.

MATERIALS AND METHODS

The sodium salt of alginic acid, MB powders were purchased from Aldrich Chemicals, Turkey. Natural zeolite (clinoptilolite) with an average particle size $<1\,\mu m$ was kindly supplied from Rota Madencilik, Turkey. Calcium chloride was purchased from Across Chemical, Turkey. Deionized water was supplied from the Chemical Engineering Laboratory (Kocaeli University, Turkey).

Bead preparation

2.5 g of alginic acid sodium salt was dissolved in 100 ml deionized water until a homogeneous solution was obtained. Separately, 1 g of clinoptilolite was stirred in 10 ml water using an ultrasonic bath, then was added to the alginate-water solution. The mixture was stirred for three hours and added into the 2 wt% of $CaCl_2$-water solution by using a syringe and composite solid beads were formed. The beads were immersed in $CaCl_2$ for 24 hours. Following the bead formation, the beads were filtrated and washed several times with deionized water. Afterward, adsorbents were dried in a vacuum oven at 40 °C.

Dye solution preparation

The MB stock solution (1,000 mg/L) was prepared by dissolving 0.1 g of MB in 100 ml of deionized water. Different concentrations of synthetic dye solutions were prepared by diluting the stock

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solution. In order to evaluate the effect of dye concentration, varying concentrations of MB solution from 2 mg L^{-} to 5 mg L^{-} were prepared. The effect of pH on dye removal (%) was also studied by adjusting the pH of the dilute dye solution using 0.1 M of HCl and NaOH.

Batch adsorption

Batch adsorption experiments were conducted at room temperature. Experiments were also conducted using different amounts of beads (5–15 g beads/L dye solution). The beads were added to the different concentrations of MB-water solution (varying from 2 mg/L to 5 mg/L) prepared in a flask. The solution was shaken for the determined time period. At 30-minute intervals, synthetic solutions were collected, filtered, and the remaining amount of MB was determined using a UV-spectrophotometer (Thermo Spectronic) at the wavelength of 664 nm. Experiments were conducted for 210 minutes until the process reached the equilibrium adsorption capacity. Adsorption performances were evaluated as a function of dye removal (%), as is shown in Equation (1).

$$\text{Removal } (\%) = 100^{*}\left(\frac{C_0 - C_t}{C_0}\right) \tag{1}$$

Before the adsorption process, a standard calibration curve was plotted using the varying concentration of the dye solution. Figure 1(a) shows the calibration curve for MB adsorption. Figure 1(b) shows the MB solutions and the clinoptilolite-alginate adsorbent before and after the adsorption.

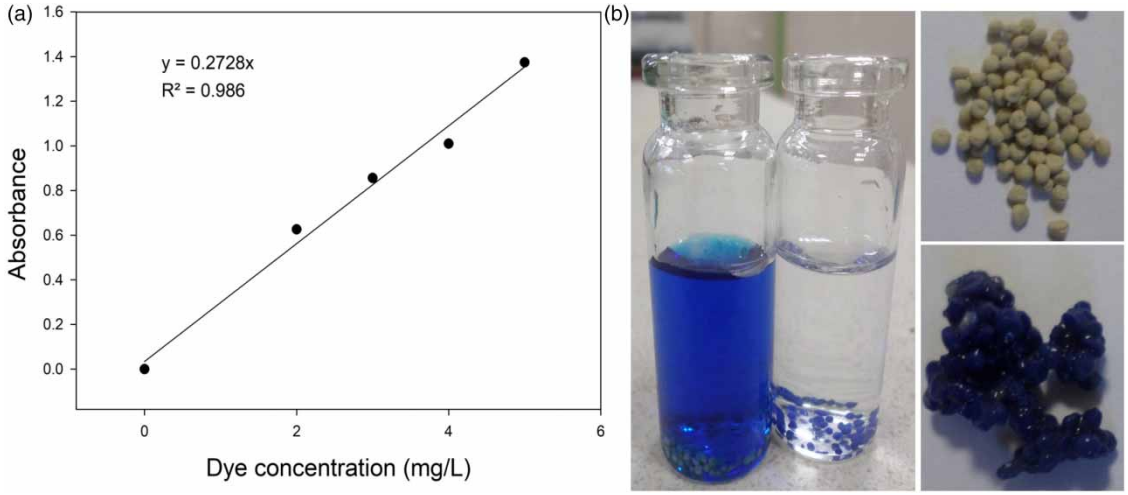

Figure 1 | (a) Calibration curve for methylene blue-water solution at 6.5 pH (b) MB solutions and adsorbents before and after the adsorption process.

Adsorption isotherm studies

The adsorption isotherm of MB was investigated at different dye concentrations (ranging from 5 mg/L to 30 mg/L) with the constant adsorbent dosage of 5 g/L. Langmuir isotherm and Freundlich isotherm were studied to determine the adsorption behavior of MB onto sodium alginate-clinoptilolite beads. The equilibrium adsorption capacity (at the end of 210 minutes) was calculated from the equation below:

$$q_e = \frac{(C_o - C_e)}{M} V \tag{2}$$

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where, q (mg/g) is the adsorption capacity of the adsorbent, C_o and C_e (mg/L) are the initial and equilibrium concentration of the dye solution, M is the amount of adsorbent (g), and V (L) is the volume of the dye solution. The linear forms of the isotherms are given in Equations (3) and (4) (Wu *et al.* 2017):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}.K_L} + \frac{C_e}{q_{max}} \tag{3}$$

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{4}$$

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

where q_{max} is the maximum monolayer adsorption capacity of the adsorbent (mg/g), K_L and K_f are Langmuir and Freundlich constants. Quantitative values of R_L (should be <1) (Equation (5)) and n (should be >1) determined which isotherm was appropriate for adsorption (Tu *et al.* 2017).

RESULTS AND DISCUSSION

The FTIR spectra of clinoptilolite-alginate bead is seen in Figure 2. An abroad absorption peak at 3,309 cm^{-1} is corresponding to the stretching of the O-H. The symmetric and asymmetric stretching of carboxyl bonds in alginate are seen in the bands of 1,415 cm^{-1} and 1,630 cm^{-1}, respectively. The peak at 1,030 cm^{-1} indicates the Si-O stretching in clinoptilolite.

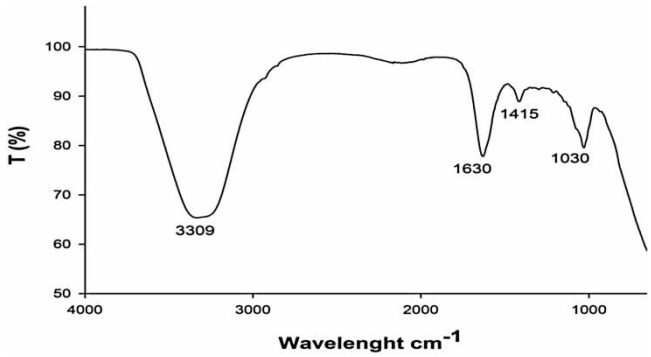

Figure 2 | FTIR spectra of alginate-clinoptilolite beads.

The effect of adsorbent contact time on MB dye removal is shown in Figure 3. The figure shows that the adsorption rate of the dye onto alginate-clinoptilolite beads showed a rapid increase initially, and

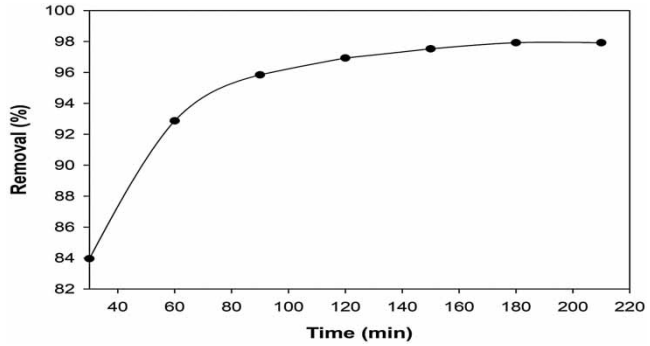

Figure 3 | Effect of contact time on adsorption performance (4 mg/L dye concentration, pH = 6.5, 10 g/L adsorbent dosage).

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then gradually reached the equilibrium adsorption capacity. The saturation time was detected as 150 minutes. After that time, increasing contact time did not affect the dye removal percentage. At the end of 180 minutes, 97.7% of dye removal was obtained when the dye concentration was 4 mg/L, with the adsorbent concentration of 10 g/L without pH adjustment.

The influence of the MB concentration on dye removal is illustrated in Figure 4. MB concentration was changed from 2 mg/L to 5 mg/L when the pH was 6.5, and adsorbent concentration was 10 g/L. As indicated in Figure 4, in the first 30 minutes, the highest removal of 87.7% was observed at the dye concentration of 2 mg/L, and 75.5% of dye removal was observed at the dye concentration of 5 mg/L. Because the dye concentrations were close to each other, the final concentrations of dye in the solutions were almost similar near the equilibrium state. When the dye concentrations were gradually decreased from 5 mg/L to 2 mg/L, dye removal of 96.9%, 97.7%, 97.9% and 98.4% were observed at the end of 180 minutes.

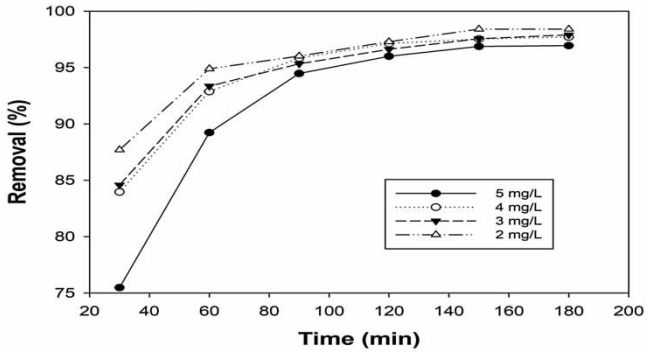

Figure 4 | Effect of dye concentration (180 min. 10 g/L adsorbent dosage, pH = 6.5).

The effect of the adsorbent concentration on MB dye removal is shown in Figure 5 when the dye concentration was 4 g/L and the pH was 6.5. In the first 30 minutes of the adsorption, the removal difference between the 5 g/L and 15 g/L adsorbent concentration was remarkable. Within 30 minutes, while 67.1% of removal was recorded using 5 g/L adsorbent concentration, 89% of removal was achieved using 15 g/L of adsorbent concentration. The increasing concentration of adsorbent enhanced the dye removal percentage depending on the increasing active adsorption site in the solution. At the end of 180 minutes, the removal difference between the lowest and the highest adsorbent concentration was very small. While 97.0% of removal was achieved using 5 g/L adsorbent,

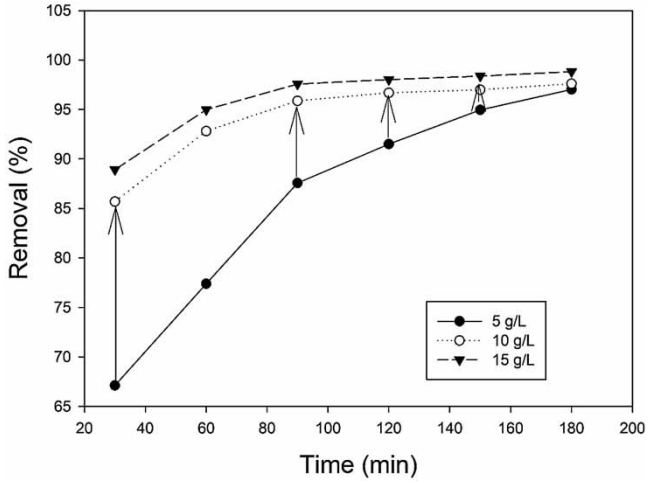

Figure 5 | Effect of adsorbent dosage on MB removal (4 g/L MB, pH = 6.5).

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98.8% of removal was obtained using 15 g/L adsorbent dosage. This observation clarified that the highest adsorbent concentration shortened the adsorption time.

The effect of the pH of dye solution ranging from 3.5 pH to 11.5 pH was also studied at the constant dye concentration of 4 mg/L with the constant adsorbent concentration of 10 g/L. Results are shown in Figure 6. From the initial to the final periods of the experiments, pH = 6.5 appeared to the most appropriate pH value for MB removal. In the first 30 minutes, the MB removal increased from 78.7% to 85.7% when the pH of the solution was increased from 3.5 to 6.5. When the pH value continued to increase to 9.5, MB removal decreased to 83.2%. The lowest removal was observed when the pH was 11.5. This situation was related to the surface ion density of the adsorbent and ion repulsive effect between the adsorbent and dye solution. Sodium alginate has anionic carboxylate groups ($-COO^-$) which creates a charge affinity to the cationic MB. With increasing H+ ions resulted by the increase in pH of the dye solution, the active groups on the alginic adsorbent collected H+ ions instead of the positive groups on MB, consequently, adsorption performance decreased as expected. In the literature, MB removal generally increased with increasing pH. However, increasing pH affected the surface charge of the adsorbent and decreased the attraction of the beads to MB. Only a few studies have been reported related to decreasing with pH. Similar decrement trend was also reported by Ahmed *et al.* (2015).

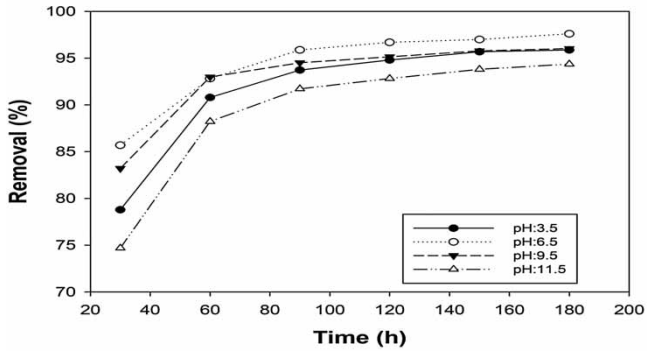

Figure 6 | Effect of pH (4 g/L dye 10 g/L adsorbent dosage).

Table 1 | Isotherm findings

	Isotherms	
Values	**Langmuir**	**Freundlich**
R^2	96.95	99.8
q_{max}	10.4	–
K_L	4.3	–
K_f	–	7.3
R_L	0.188	–
n	–	3.06

According to the isotherm study, the calculated and fitted data have been given in Table 1. The fitted equilibrium data show that the Freundlich isotherm was well adapted to the experimental results with a R^2 value of 99.8. The favorable adsorption was confirmed with the *n* value of 3.06 (>1). Results showed that the multilayer adsorption occurred with the interaction between adsorbed molecules and adsorbent.

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CONCLUSIONS

In the present study, a sodium alginate-clinoptilolite-based composite adsorbent was synthesized and used for MB removal from a synthetic wastewater. Influences of the dye concentration, adsorbent dosage, pH, and contact time on MB removal were evaluated.

- In the first 30 minutes, greater than 84% removal was achieved when the dye concentration was 4 mg/L, at a pH of 6.5, and the adsorbent dosage was 10 g/L. The saturation time was detected as 150 minute.
- From the initial to the final period of the experiment, pH = 6.5 appeared to be the most appropriate pH value for MB removal.
- The increasing adsorbent dosage enhanced the dye removal. The highest removal of 98.8% was obtained using 15 g/L adsorbent dosage.
- The decreasing dye concentration increased the removal. When the dye concentrations were gradually decreased from 5 mg/L to 2 mg/L, dye removal of 96.9%, 97.7%, 97.9% and 98.4% were observed.
- Freundlich isotherm was appropriate to define the adsorption behavior with a R^2 of 99.8.

As a result, sodium alginate-clinoptilolite beads appeared to be an appropriate adsorbent for effective removal of dye from the wastewater.

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