

Effectiveness of Carboxymethyl Cellulose for the Removal of Methylene Blue from Aqueous Solution

Hosne Ara Begum* and Mohammad Khalid Bin Mahbub

Department of Chemistry, Dhaka University, Dhaka-1000, Bangladesh

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Abstract

The adsorptive properties of carboxymethyl cellulose (CMC) prepared from sugarcane bagasse (SB) for the removal of methylene blue (MB) from aqueous solution was investigated. Two batches of CMC, CTSB-CMC-B1 and CTSB-CMC-B2, were prepared from chlorite treated sugarcane bagasse (CTSB). The prepared CMCs were characterized by FT-IR spectral analysis. Degree of substitution (DS) value of prepared CMCs was estimated. Batch adsorption experiments show that the adsorption of MB on CMCs reaches equilibrium within 30 minutes. The MB adsorption capacity of CTSB-CMC-B1 and CTSB-CMC-B2 were found to be 652.0 and 369.0 mg g⁻¹, respectively. CMC with the higher DS value (CTSB-CMC-B1) shows higher adsorption capacity than the CMC having lower DS value (CTSB-CMC-B2). The uptake of MB was minimum at pH 2 and gradually increases with the increase of pH. From the desorption studies, it was found that large amount of MB was released in strong acidic (pH 3.0) conditions.

Key words: CMC, DS value, batch adsorption experiments, adsorption capacity.

I. Introduction

Waterways have been used as dumping grounds for industrial effluent since the time of the industrial revolution. However today, because of the sheer volume of waste dumped into our waterways, the natural regeneration capacities of these waterways are being overwhelmed. This poses an environmental threat which directly affects humankind's ability to build a sustainable habitat. Therefore, wastewater decolourisation processes have been the subject of recent research. Dye removal is a complex and expensive process. Methods such as chemical and electrochemical oxidation, membrane filtration, coagulation-flocculation, adsorption and ion exchange are recommended¹. Amongst the several dye removal techniques, adsorption is considered to give the best results as it can be used to remove different types of coloring materials and organic pollutants. Nowadays, a good number of low cost, commercially available adsorbents have been used for the removal of dyes from coloured wastewater². However, the adsorption capacities of these adsorbents are not satisfactory. The new effective adsorbents which are low-cost and biodegradable are highly demanded.

Sugarcane bagasse is the fibrous residual material of the sugarcane stems left after the crushing and extraction process from sugar mills, which normally accounts for 20–24% of the cane³. In Bangladesh, about 21 million metric tons of bagasse is produced per year as by-product of sugar mills⁴. Sugar cane bagasse contains about 30–50% of cellulose and 20–24% of lignin. Some studies on adsorption of different dyes onto sugarcane bagasse have been reported recently⁵⁻⁹. To improve the adsorptive properties of cellulose, its structure is modified to increase its active sites for adsorption of dyes. Currently the most widely adopted methods for modification of cellulose based materials include etherification, esterification, grafting, amination, etc. Carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups (-CH₂-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone (Fig. 1). A number of

reports have been published on the adsorption of dye from aqueous solution on CMC¹⁰⁻¹².

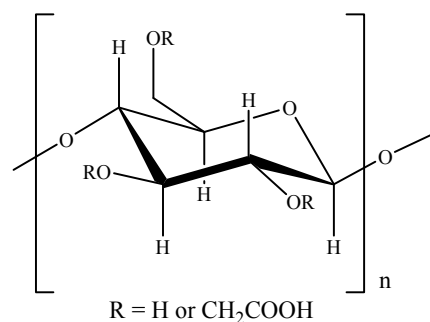


Fig. 1. Structure of carboxymethyl cellulose

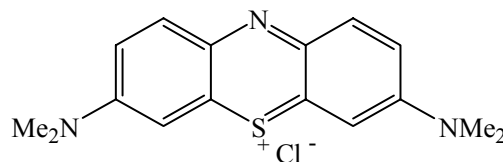


Fig. 2. Structure of methylene blue (MB)

Keeping all these in mind, the aim the present work was to study the effectiveness of partially carboxymethylated cellulose as a biosorbent for the removal of meythlene blue (MB) from aqueous solution. Meythlene blue, a cationic dye, was selected as a model pollutant (Fig. 2). Sorption experiments included effect of pH, sorption equilibrium, effect of initial concentration and desorption study of MB from MB-adsorbed carboxymethyl cellulose under different pH conditions.

II. Experimental

All chemicals and solvents used in the present work were analytical grades (Merck and BDH). All solvents were distilled before use. Different solutions and reagents were

*Author for Correspondence, e-mail: hosnearabegum@yahoo.com

prepared using analytical procedure. Sugarcane bagasse was procured from a sugarcane mill of Bangladesh. The sample was dried in the oven at 45°C for 72 hours. After drying, the dried materials were grinded with grinder mill and sieved to a size between 0.500 to 0.212 mm.

Pretreatment of sugarcane bagasse with sodium chlorite

Raw sugarcane bagasse powder (SB) was treated with acidified sodium chlorite to remove lignin¹³. The resultant delignified powder obtained was designated as sodium chlorite treated sugar cane bagasse (CTSB).

Preparation of carboxymethyl cellulose (CMC)

Sodium chlorite treated sugarcane bagasse (CTSB) was partially chemically modified into a carboxymethylated derivative of cellulose (CTSB-CMC) according to the method described elsewhere¹⁴. CTSB was steeped in aqueous alcoholic sodium hydroxide solution (18%, water : alcohol = 1:4) and the reaction mixture was continuously stirred for 2 hours at 30°C. The cellulose alkali mixture was placed in a thermostatic water bath and the temperature was maintained at 58°C. Monochloroacetic acid solution (80% in ethanol) was added drop wise to the reaction mixture with occasional stirring. The reaction was then allowed to proceed for the desired length of time. Two batches of CTSB-CMC were prepared and they were labeled as CTSB-CMC-B1 and CTSB-CMC-B2. The reaction time was 3.5 and 2.0 hours for CTSB-CMC-B1 and CTSB-CMC-B2, respectively. The yield of CTSB-CMC-B1 and CTSB-CMC-B2 was found to be 50 and 60%, respectively.

FT-IR spectral analysis

The FT-IR spectra of the prepared CMCs were recorded using a FT-IR spectrometer (Shimadzu, FT-IR 8400S, Japan) using KBr pallets in the range of 400–4000 cm⁻¹ with 2 cm⁻¹ resolution.

Determination of degree of substitution (DS) value of CMC

Degree of substitution (DS) of the prepared CMC samples was determined by pH titration¹⁵. pH vs. volume of sodium hydroxide titration curves (smoothing 1st derivative & 2nd derivative) were obtained from experimental data and analyzed by using software CurTipot (pH and acid base titration curve: Analysis and simulation) version 3.3.1 (2008) for MS Excel¹⁶.

Sorption experiments for removal of MB

The stock solution of MB was prepared by dissolving accurately weighed dye in deionized double distilled water (DDW). The experimental solutions were obtained by diluting the stock solution (1000 mg L⁻¹) in appropriate proportions to the required concentrations (2–700 mg L⁻¹). A calibration curve was prepared by recording the absorbance values for MB solutions of known concentrations (2–10 mg L⁻¹) at λ_{max} 664 nm, using a UV-visible spectrophotometer (Shimadzu UV-1650, Japan) at 30°C.

To determine the adsorptive properties of the prepared adsorbents, CTSB-CMC-B1 and CTSB-CMC-B2, batch sorption experiments were conducted. 0.03 g of adsorbent and 40 mL of MB solution of definite concentration were added in each of the experimental bottles. The bottles were shaken in a thermostatic mechanical shaker at 30°C with constant speed (110 rpm). For blank, 0.03 g of adsorbent and 40 mL of deionised double distilled water (DDW) were added in a bottle and was shaken for 5 hours at 30°C. pH adjustments were made using HCl and NaOH solutions and was measured using a digital pH meter. After a definite interval of time each bottle was withdrawn from the shaker. The supernatant of the bottle was transferred and was centrifuged repeatedly until a clear liquid was obtained. Absorption spectrum of the clear solution was then recorded at λ_{max} 664 nm, using the UV-visible spectrophotometer indicated above. Finally the amount of MB adsorbed for each experiment, *q* (mg g⁻¹), was calculated according to the following equation:

$$q = \frac{(C_0 - C_e)V}{m}$$

Where, *C*₀ and *C*_e (mg L⁻¹) are the initial and final concentrations of solute in solution, respectively; *V* (L) is the volume of solution; and *m* (g) is the mass of the adsorbent.

Sorption of MB at different initial pH of solution

The effect of initial pH of MB solution on the adsorption on CTSB-CMC-B1 and CTSB-CMC-B2 were investigated, for a range of pH values between 2.0 to 11.0. The initial concentration of MB solutions was 100 mg L⁻¹. The adsorbents were weighed and immersed into 40 mL of MB solutions with different initial pH. The bottles were continuously shaken at 30°C for 6 hours. Final pH was measured and the optimum pH (Figs. 3 and 4) was determined. From the amount of MB adsorbed at each pH, the effect of pH on adsorption (Figs. 5 and 6) was investigated.

Estimation of equilibrium time

The time taken for maximum adsorption of MB on CTSB-CMC-B1 and CTSB-CMC-B2 adsorbents were investigated, using 9.6 and 50.0 mg L⁻¹ MB solutions. Adsorbents were weighed and immersed into bottles of specified concentration and continuously shaken at 30°C and pH 8. After a definite interval of time, ranging from 5 to 360 min, each bottle was withdrawn from the shaker. The initial and final concentrations of the adsorption experiments were determined by the method mentioned above and the extent of adsorption was calculated based on Eq. (1). Results are presented in Figs. 7 and 8.

Effect of initial MB concentration on sorption

Adsorption experiments were carried out as indicated above using raw sugarcane bagasse (SB), CTSB-CMC-B1 and CTSB-CMC-B2 for different concentrations of MB solutions

in the range of 10–663 mg L⁻¹ at pH 8 and 30°C with 6 hours continuous shaking. Results are presented in Fig. 9.

Desorption study

After saturated sorption of MB, the MB-adsorbed CTSB-CMC-B1 and CTSB-CMC-B2 were collected and washed by deionized double distilled water (DDW). Each of the MB-adsorbed CMC was then dried at 65°C in an oven. The effects of different initial pH on MB desorption from CMCs were studied at room temperature. The desorption medium of definite pH was prepared using HCl and NaOH solutions. Each of MB-adsorbed CMC (MB-CMC) was weighed, and then immersed into the desorption medium of definite pH, such as pH 3.0, 6.5 and 10.0 and was continuously stirred for 6 hours. The final MB concentration of each solution was analyzed spectrophotometrically to determine the amount of desorption. The results are presented in Table 1.

III. Results and Discussion

Characterization of prepared CMC

The prepared CMCs were characterized by FT-IR analyses. In the FT-IR spectra of CTSB-CMC-B1 and CTSB-CMC-B2, typical peaks for cellulose were observed. The wide peak at around 3000–3700 cm⁻¹ could be due to the stretching vibrations of –OH groups. Spectra showed C–H stretching vibrations in the range of 2850–2950 cm⁻¹. The peak around 1040 cm⁻¹ corresponded to C–O–C bonds. Besides the cellulose backbone, characteristic absorption bands for CMC were observed in the spectra. The presence of strong absorption bands at around 1600–1640 cm⁻¹ and 1400–1450 cm⁻¹ were observed due to symmetric and asymmetric vibrations of ionized –COO⁻ group. This indicated that carboxyl groups were grafted onto cellulose backbone when carboxymethylation reaction occurred, and CMC was prepared successfully.

The DS value of CTSB-CMC-B1 and CTSB-CMC-B2 were found to be 0.09 and 0.06, respectively. These values provide an idea on the extent of carboxymethyl substitution on the surface of the CTSB, and the subsequent adsorption characteristics based on this value. The DS values of CTSB-CMC-B1 and CTSB-CMC-B2 also provide us information on the amount –COOH group present in per gram of adsorbent. CMC having low DS value is water insoluble and suitable as adsorbent for dye removal from aqueous solution in a broader pH range.

Determination of optimum pH

Prior to the determination of the equilibrium time for the adsorption of MB on CTSB-CMC-B1 and CTSB-CMC-B2, the optimum pH of the solution used for adsorption experiments was determined. The results of optimum pH determination are shown in Figs. 3 and 4. To determine the optimum pH for adsorption of MB on CTSB-CMC-B1 and CTSB-CMC-B2, pH of the solution was varied from 2.0 to 11.0 keeping other experimental conditions same. Change of

pH of the solution before and after the adsorption was found to be negligible at pH 8.2 for CTSB-CMC-B1 and pH 7.5 for CTSB-CMC-B2. For this reason, pH 8 was selected as working pH for the adsorption experiments.

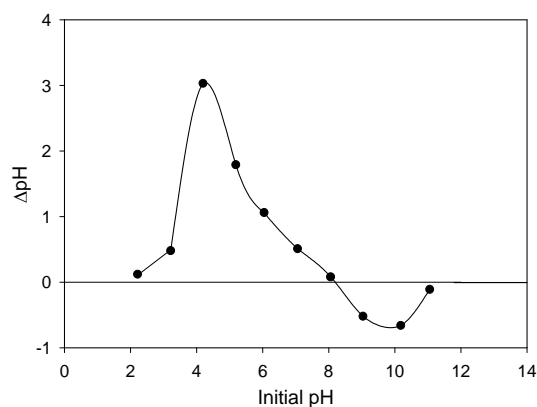


Fig. 3. Determination of optimum pH of CTSB-CMC-B1 for the adsorption of MB.

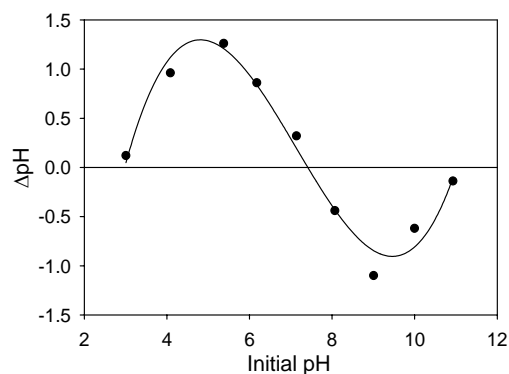


Fig. 4. Determination of optimum pH of CTSB-CMC-B2 for the adsorption of MB.

Effect of initial pH on MB sorption

The initial pH of the solution is an important parameter for controlling the adsorption process. The experimental results for the effect of pH on adsorption of MB on CTSB-CMC-B1 and CTSB-CMC-B2 are shown in Figs. 5 and 6, respectively. The experimental data shows that the uptake of MB was minimum at around pH 2.0 then gradually increased with the increase of pH. For CTSB-CMC-B1, the uptake gradually reached to maxima near about pH 6, and then remained almost constant over the pH range of 6.0 to 11.0. Whereas for CTSB-CMC-B2, sharp increase was observed at pH 4.0 and adsorption reached to maxima when pH exceeds 4.0 and then remained almost constant over the pH range of 5.0 to 11.0. At a lower solution pH, the carboxylic groups of CMC tended to acquire a net positive charge. As the solution pH increased, dissociation of carboxylic groups of CMC occurred and overall charge on CMC surface became negative. This caused an enhancement of attraction between positively charged MB

and carboxylate anion, resulting in an increase of sorption of MB onto CMC surface.

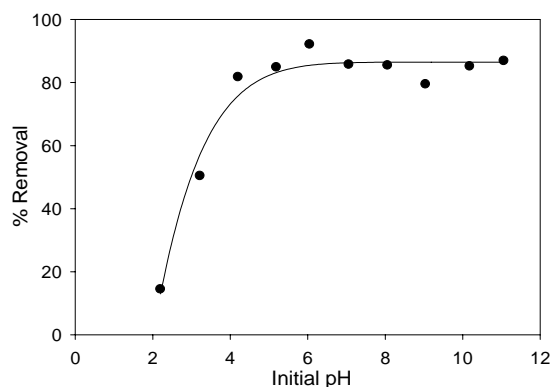


Fig. 5. % Removal versus Initial pH of CTSB-CMC-B1.

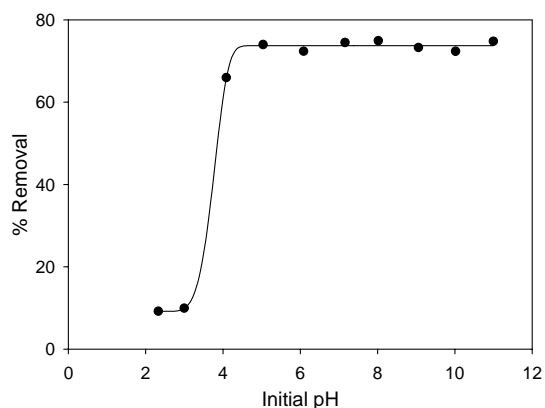


Fig. 6. % Removal versus Initial pH of CTSB-CMC-B2.

Equilibrium time for sorption

The sorption-time graph of CTSB-CMC-B1 and CTSB-CMC-B2 shown in Figs. 7 and 8, indicates that the adsorption of MB on CMC can be considered as a fast adsorption process because more than 70% of MB was adsorbed within 10 minutes. Within 30 minutes, adsorption reached to equilibrium. The adsorption process can be divided into three stages: (1) an initial stage with adsorption occurring instantly, (2) subsequently slow adsorption, and (3) a final stage with adsorption reaching equilibrium and remaining constant. The first stage can be attributed to the rapid attachment of MB to the surface of CMC by surface mass transfer. At this stage, more than 70% of CMC adsorption was found. The second stage was slower, possibly because many of the available external sites were already occupied and because of the slow diffusion of MB molecules into the pore spaces of CMC. At final stage, the amount adsorbed did not vary significantly at contact time longer than the equilibrium time. It is evident from Figs. 7 and 8 that the time required to reach an equilibrium concentration (C_e) increases with the increase of the initial MB concentration (C_0).

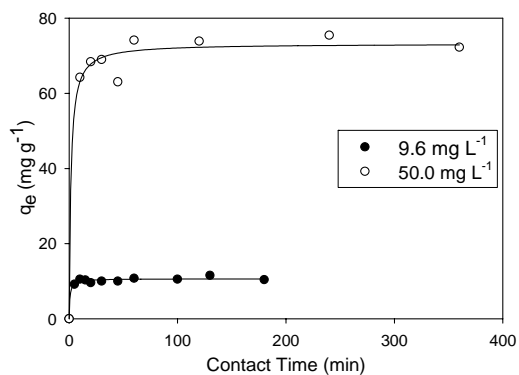


Fig. 7. Comparison of equilibrium time of CTSB-CMC-B1 in different concentrations of MB solutions at pH 8.0.

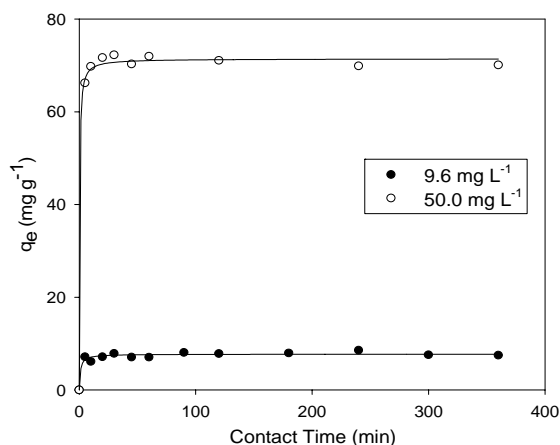


Fig. 8. Comparison of equilibrium time of CTSB-CMC-B2 in different concentrations of MB solutions at pH 8.0.

Effect of initial MB concentration

The influence of initial dye concentration on equilibrium uptake of MB by CTSB-CMC-B1 and CTSB-CMC-B2 is presented in Fig. 9. Results show that increased initial MB concentration led to increased MB adsorption. Apparently, the initial MB concentration plays an important role in affecting the capacity of CMC sample to adsorb MB. The higher the MB concentration, the stronger is the driving force of the concentration gradient, and therefore the higher is the adsorption capacity. The MB adsorption capacity of CTSB-CMC-B1 and CTSB-CMC-B2 were found to be 652.0 and 369.0 mg g^{-1} , respectively (at initial concentration of MB solution = 663 mg L^{-1} , pH = 8 and temperature = 30°C). It is observed that the CMC with the higher DS value, i.e. CTSB-CMC-B1 with DS = 0.09, shows higher adsorption capacity than CTSB-CMC-B2 with DS = 0.06, due to the presence of higher number of $-\text{COOH}$ group, as shown in Fig. 9. The adsorption capacity of MB on CTSB-CMC-B1 and CTSB-CMC-B2 was much greater than that of raw sugarcane bagasse (SB) (Fig. 9), which indicates that carboxyl groups on CMC enhanced the sorption capacity to a great extent. The amount of $-\text{COOH}$ group plays a vital role in adsorption process. A possible mode of MB binding on CMC due to

electrostatic attraction is shown in the Fig. 10. Ion exchanging mechanism of MB sorption on CMC is presented here.

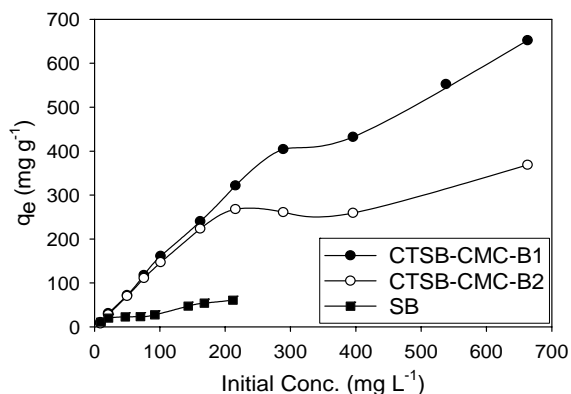


Fig. 9. Amount MB adsorbed on CTSB-CMC-B1, CTSB-CMC-B2 and SB at different initial concentrations

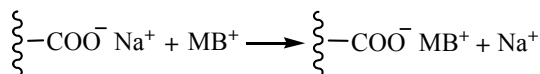


Fig. 10. A possible mode of MB binding on CMC. MB⁺ represents the cationic part of MB.

Desorption Study

It is very important to regenerate the used sorbents in practice applications. However, before this application, the stability of the new sorbents should be checked first. Desorption study of MB from MB-adsorbed CMCs (MB-CMC) in desorption medium of pH 3.0, 6.5 and 10.0 were carried out at room temperature. If the adsorbed dyes can be desorbed using pure water, the attachment of the dye to the adsorbent is due to weak bonds. If acid or alkaline water desorbs the dye then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the dye then the dye is held by the adsorbent through chemisorption. The pH dependence of MB desorption from MB-CMC is shown in Table 1. It was found that large amount of MB was released in strong acidic conditions, which was in accordance with previous MB sorption study¹¹. It was suggested that MB-CMC was stable enough in the medium having pH higher than 3.0. Under acidic condition, CMC with the higher DS value (CTSB-CMC-B1) showed higher desorption ability than that of the low DS value (CTSB-CMC-B2).

Table 1. Data for the determination of the amount of MB desorbed for CMC

No. of Obs.	pH of desorption Medium	% Desorption	
		CTSB-CMC-B1	CTSB-CMC-B2
1	3.0	72.4	54.0
2	6.5	4.5	8.1
3	10.0	3.8	4.5

IV. Conclusions

The experimental results in batch adsorption studies, indicate that carboxymethyl derivatives of cellulose (CMC) prepared from sugarcane bagasse were effective sorbents for removal of MB from aqueous solutions. The sorption rate of MB on CMCs was very fast and reaches to sorption equilibrium within 30 minutes. The MB adsorption capacity of CTSB-CMC-B1 and CTSB-CMC-B2 were found to be 652.0 and 369.0 mg g⁻¹, respectively. It was observed that CMC with the higher DS value showed higher adsorption capacity of the MB, due to the presence of higher number of -COOH group. Increased initial MB concentration led to increased MB adsorption. The experimental results showed that MB sorption was pH dependent. The uptake of MB was minimum at around pH 2.0 then gradually increased with the increase of pH. It was found that large amount of MB was released in strong acidic conditions. CMC with the higher DS value showed higher desorption ability under acidic condition. The ability of the CMC adsorbents to undergo desorption had given it the unique ability to be reused, thereby decreasing the cost of industrial effluent treatment. Finally, it may be suggested that CMC with higher DS value removes cationic dye more effectively from the aqueous solution at higher pH.

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