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# Synthesis of Partially Carboxymethyl Cellulose Derived from Rice Straw and Its Utilization as Dye Adsorbent

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## Abstract

Two samples of partially carboxymethyl cellulose derivatives of different D.S. values were prepared from Egyptian rice straw via pulping followed etherification using different concentrations of monochloro acetic acid under the catalytic action of sodium hydroxide. The prepared derivatives were assessed for D.S. and evaluated as dye adsorbent for different classes of dyestuff. The results obtained indicate that, the D.S. increases from 0.09 to 0.14 by increasing monochloro acetic acid from 5 to 10 g/100g cellulose pulp. The rate of dye absorbance increases by increasing the amount of adsorbent as well as the time of adsorption. While as the dye concentration increases from 0.01 to 0.5 the percent dye absorption decrease regularly. However, the magnitude of the percent decrease in the colour depends on : (a) the nature of the dyestuff used , (b) the D.S. of the adsorbent, and (c) on the technique applied . The magnitude of colour removal in case of using ultrasonic technique is relatively higher than the mechanical shaking irrespective of the nature of the dye used and/or the conditions of adsorbance. The percent colour removal follows the order Basic green> Basic yellow> Acid green> Acid blue respectively.

**Keywords:** rice straw- colour removal-ultrasonic- adsorption-carboxymethylation

## 1. Introduction

Rice is the largest cereal crop in the world. Rice straw represents around 45% of the volume in rice production, producing the largest quantity of crop residue. As rice straw is a marginal feed compared to other cereal grain straw and a problematic fuel source due to high ash generation, exploring more viable options to utilize rice straw is pressing, particularly as an environmental concern. With its compositions of cellulose (38.3%), hemicellulose (31.6%), lignin (11.8%) and silica (18.3%) [1] rice straw is the most available cellulose source from agricultural crop residues in the world[2] In recent years, many biological materials, such as orange bagasse [3], plant leaves [4], saw dust [5] and maize cob [6], have been applied as adsorbents to adsorb dyes from wastewaters. Researchers have been trying to find ways to take advantages of straw [7,8]. One of the promising ways to use this precious bioresource is to produce straw-based adsorbents

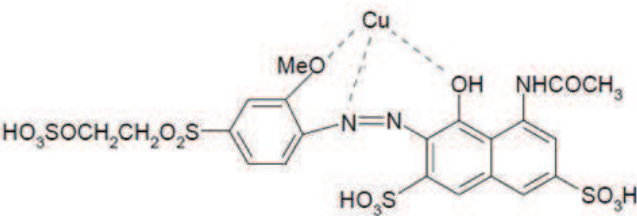
[9-13]. However, the adsorption capacity of unmodified straw is insignificant, since straw materials are deficient in free ionic groups, which would play an important role in removal of ionic dyes. Therefore, it could improve the adsorption capacity of straw by introducing some ionic functional groups through chemical modification [14]. Lilienfeld [15,16], was the first to affect the partial carboxymethylation of cotton. Two main methods for the preparation of partially carboxymethylated cellulose are known:(a)The aqueous carboxymethylation and (b)The non aqueous carboxymethylation. Partially carboxymethylated cellulose with a D.S. of about 0.05 to 0.15 retains the original fibrous nature and exhibits a number of potentially valuable properties. The objective of this paper is to synthesize two different partially carboxymethylated derivatives from Egyptian rice straw pulp and to investigate their suitability to be utilized these derivatives as adsorbent substrates for different reactive dyes under a variety of conditions.

2. Materials and Methods

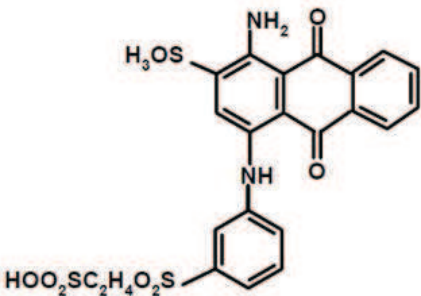
2.1. Native rice straw supplied by Racta Co. For Paper Manufacture, Alexandria, was used

The following different dyes selected from the most dyestuffs which are used in the Egyptian Textile Industry.

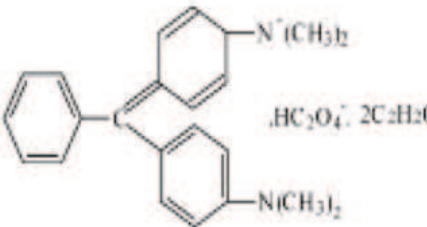
- Sunzol Brilliant Violet 5 R (C.I. Reactive Violet 5) (scheme 1).
- Sunzole Blue 19 (C.I. Reactive Blue 19) scheme 2.
- Ginacryl M alachite Green M (C.I. Basic. Green 4) scheme 3
- Ginacryl G . yellow GLE 200% (C.I. Basic yellow 28) scheme 4
- Dystar. Green BW (C.I. Acid Green 27) scheme 5
- Dystar. Sup ralan.Blue 22 R (C.I. Acid blue 225)



Scheme 1 -Reactive Violet 5

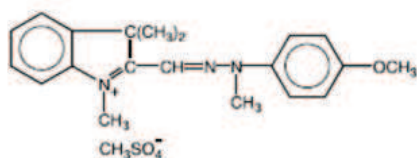


Scheme 2 -Reactive Blue 19

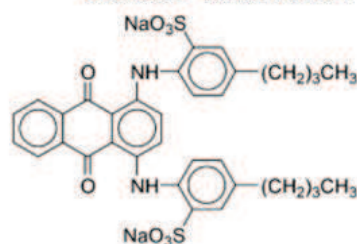


Scheme 3- Basic. Green 4

Scheme 2 -Reactive Blue 19



Scheme 3- Basic. Green 4



Sodium hydroxide and Sodium hypochlorite both of laboratory grade chemicals were also used.

## 2.2. Methods:

### 2.2.1. Preparation of bleached rice straw:

The alkali treated sample were subjected to sodium hypochlorite (NaOCl) bleaching (4g/l active chlorine) for two hours at room temperature, liquor ratio 10:1 followed by washing thoroughly with running water and finally air dried.

### 2.2.2. Preparation of partially carboxymethyl rice straw derivatives:

Two different substituted partially carboxymethylated rice straw derivatives were prepared from bleached rice straw via using different concentrations of the etherifying agents, i.e. monochloro acetic acid and sodium hydroxide. The procedure adopted was carried out as follows:

Alkali cellulose was prepared by treating 100g of dry bleached rice straw with 200 ml of 5% aqueous sodium hydroxide solution, and mixed well, a solution of 5g monochloro acetic acid in 100ml distilled water was added gradually to the alkali cellulose with continuous agitation for two hours, and the reaction mixture was left at room temperature overnight. The excess alkali was neutralized with glacial acetic acid using phenolphthalein as indicator. At this end the product was filtrated washed well with water and finally air dried at ambient conditions. Another sample was also prepared by the same technique using 10% sodium hydroxide solution and 10g monochloro acetic acid dissolved in 100ml water

## 2.3. Procedure of Dye Adsorption

Different amount of different substrate (rice straw, alkali treated and rice straw pulp) were added to aqueous solutions of the selected dyes (0.01g) dissolved in 1 liter of distilled water. The suspension was treated using either mechanical shaking or ultrasonic technique for different periods of time (5, 15, 30, 45, 60 minutes) and temperatures (30, 40, 50, 60°C). At the end of the run of aliquot was centrifuged at 5000 rpm for 30 min and the dye concentration in the clear solution was evaluated colourimetrically at the maximum wavelength for every dyestuff. The absorbance was measured using a double-beam spectrophotometer Thermo Electron Corporation Unicam 300, England.

The percent dye absorption was calculated by equation 1 :

% Colour removal =  $\frac{C A \text{ of original sample} - C A \text{ of treated sample}}{C A \text{ for the origin}} \times 100$

Where CA is the colour absorbance

2.3.1. Determination of degree of substitution (D.S.)

The D.S. was determined according to a standard method [17]. Where The water soluble sodium carboxymethyl cellulose is converted to the insoluble acid form, purified by washing, dried and then a weight sample is reconverted to the sodium salt with a measured excess of sodium hydroxide from which the D.S was calculated.

3. Results and discussion

Pure cellulose was prepared from rice straw wastes via alkali scouring and bleaching as previously mentioned. The prepared cellulose was subjected to carboxymethylation using two different amounts of the etherifying agents i.e. monochloro acetic acid and sodium hydroxide. The caroxymethelation reaction took place according to the following reaction:



Table 1 represent the effect of concentration of monochloro acetic acid on the D.S. of the prepared partially carboxymethyl cellulose derivatives.

Amount of ClCH <sub>2</sub> COOH/100g of cellulose	Amount of NaoH/100g of cellulose	D.S.	Solubility	
			Water	ethyl alcohol
5g	5g	0.09	Insoluble	Insoluble
10g	10g	0.14	Insoluble	Insoluble

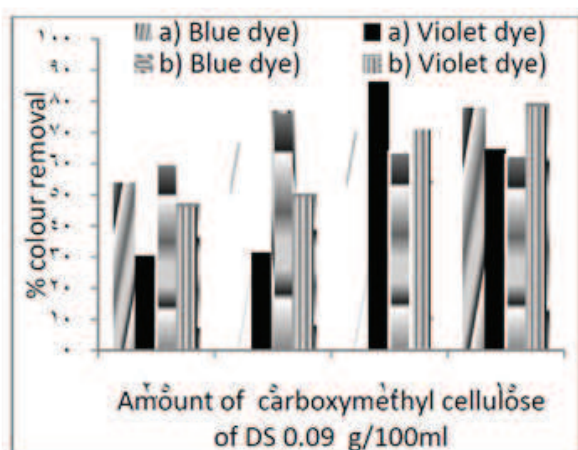
Table 1. The effect of the amount of monochloro acetic acid on the D.S. of the prepared derivatives

It is clear from the data of Table I that the degree of substitution (D.S.) depends on the concentration of the etherfying agent i.e. monochloro acetic acid.As the latter increases from 5 to 10 g/100 pure cellulose, the D.S. increases from 0.09 to 0.14 respectively.It is also clear from Table I that the prepared partially carboxymethylated bleached rice straw is insoluble in both water and ethyl alcohol.

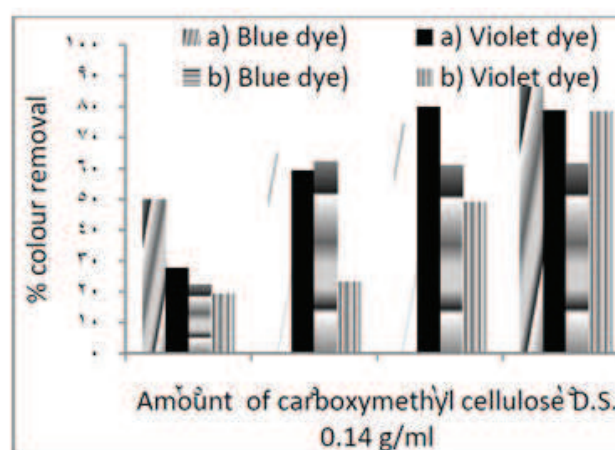
3.1. Effect of amount of partially carboxymethyl cellulose on dye adsorbents

The prepared two partially carboxymethylated cellulose derived from rice straw was utilized as dye adsorbent for both reactive blue19 and reactive violet5. Figure 1and 2 represent the data obtained on using the two partially carboxymethyl cellulose derivative of different D.S.values on conducting the adsorbance using mechanical shaking or ultrasonic technique.





**Fig 1.** Effect of amount of carboxymethyl cellulose derivative of D.S. 0.09 on % colour removal using different reactive dyes reactive dyes for (a) ultrasonic and (b) shaking treatment.



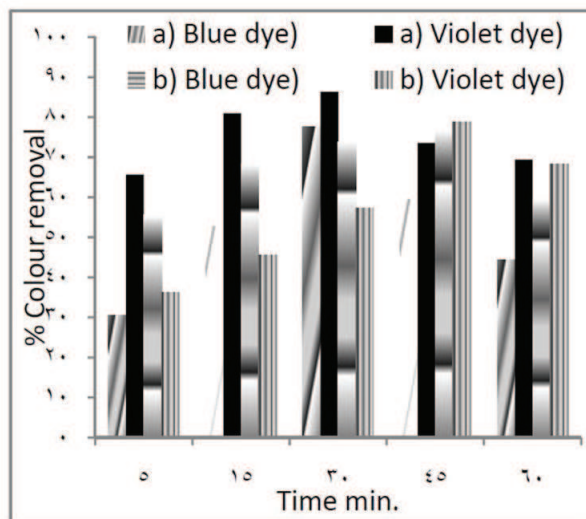
**Fig 2.** Effect of amount of carboxymethyl derivative of D.S. 0.14 on % colour removal using different reactive dyes for (a) ultrasonic and (b) shaking treatment

Generally speaking it is clear from the Figures 1 and 2 that increasing the amount of adsorbent, i.e. partially carboxymethyl derivatives, is accompanied by an increase in the % colour removal to reach to a maximum after which it either remain constant or decreases. This phenomenon holds true regardless of (a) the D.S., (b) the nature of the reactive dye used, or (c) the technique applied. It is also clear from the figures that in case of the samples conducted via mechanical shaking the % dye adsorption of the carboxymethyl derivative of relatively low D.S. (0.09) is higher than their corresponding samples acquire relatively higher D.S. (0.14) this phenomenon is true on using either reactive violet5 or reactive blue19. While, in case of ultrasonic, there is irregularity in the results. It seems that the sample of partially carboxymethylated derivative prepared using 5g monochloro acetic acid acquire the sufficient carboxymethyl groups to open the structure of cellulose and hence its absorbance reach to the maximum. Increasing the D.S. causes an increase of the COOH groups. The latter ionize in the solution into  $\text{COO}^-$  and  $\text{Na}^+$  which causes an increase in the negative charge on the substrate. Since the reactive dye acquire negative charge too hence the rate of dye adsorption decrease. It is also observed that ultrasonic technique increases the absorbance capacity of both carboxymethyl derivatives under investigation since they are higher than their corresponding samples conducted via mechanical stirring. For example the % colour removal for the relatively higher D.S. (0.14) derivative on using reactive blue19 was 86.6% against 62.2% for the sample conducted using ultrasonic and

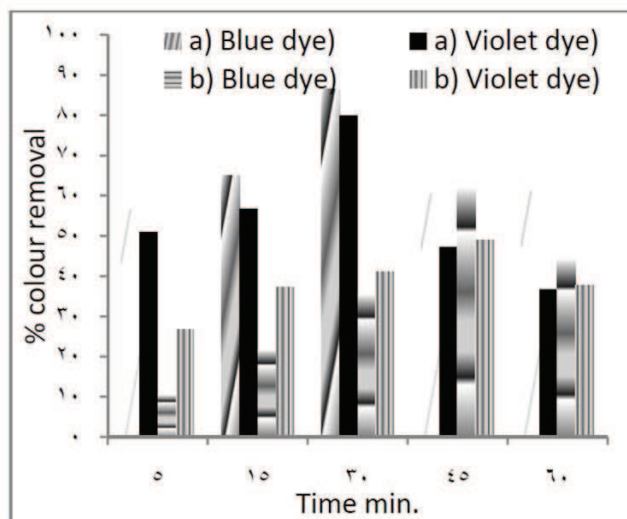
mechanical shaking respectively. Furthermore, it is clear from the data that, irrespective of the amount of the adsorbent or the technique applied, Partially carboxymethylated samples acquire higher % colour removal compared with the native, alkali treated and the pure cellulose, i.e. alkali treated and bleached samples.

### 3.2. Effect of Treatment Time

Figures 3 and 4 represent the data obtained on studying the effect of time of adsorption of different reactive dyes, on using two carboxymethylation derivatives of different D.S. values 0.09 and 0.14 respectively.



**Fig 3.** Effect of treatment time using carboxymethyl cellulose derivative of D.S. 0.09 on % colour removal using different reactive dyes for (a) ultrasonic and (b) shaking treatment

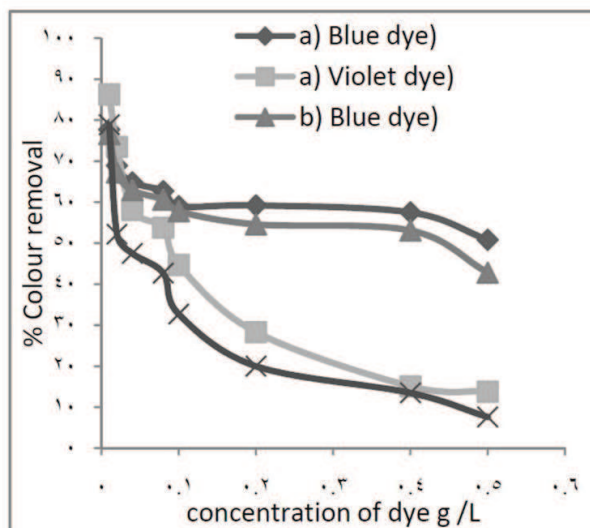


**Fig 4.** Effect of treatment time using carboxy- methyl cellulose derivative of D.S.0.14 on % colour removal using different reactive dyes for (a) ultrasonic and (b) shaking treatment

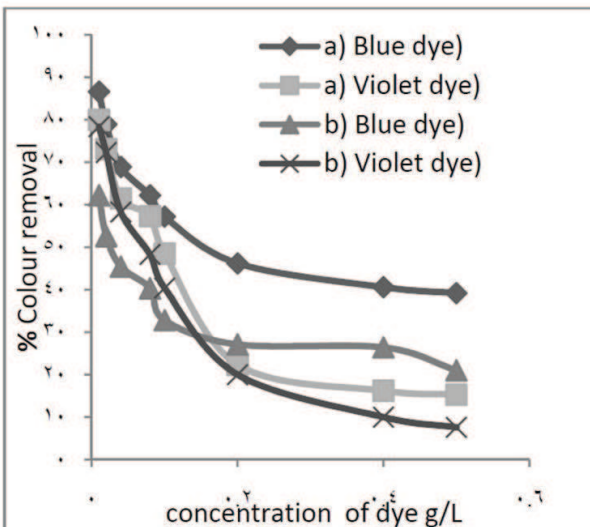
Generally speaking, it is clear from figures 3& 4 that in all cases the rate of dye adsorption increases by increasing the time of adsorption to reach to a maximum after which it shows slight decrease or remains constant. However, the time of adsorption to reach the maximum value and magnitude of the % colour removal at the maximum adsorption depends on the nature of the colour and the adsorbent used as well as the technique applied. It is clear that for the samples conducted via mechanical shaking the maximum dye adsorption was obtained after 45 minutes irrespective of the D.S. of carboxymethyl sample or the nature of the reactive dye used, where, it reaches to 78.9% and 48.9% on using reactive violet5 and 76.6% and 62.2% on using reactive blue19 for carboxymethyl samples of D.S. 0.09 and 0.14 respectively. In other words, the sample of low D.S. acquires a higher absorbance capacity than the sample which acquire relatively higher D.S. While, in case of using ultrasonic technique the maximum dye adsorption arrived at relatively lower time, i.e. 30 minutes only. However, the magnitude of the maximum dye adsorption was higher for carboxymethyl derivative of relatively low D.S. value only on using reactive violet5. While in case of using reactive blue19, the opposite holds true. The decreases in the % colour removal on using carboxymethyl derivative of relatively higher D.S. value may be due to the increase in the negatively charged ( $\text{-COO}^-$ ) groups on the polymer. The latter repel the reactive dye molecules which acquire the similar negative charge as previously explained. Hence, the numbers of the adsorbed dye molecules decreases.

3.3. Effect of Dye Concentration

Figures 5 and 6 represent the results obtained on using different concentrations of the aforementioned two different reactive dyes in case of carboxymethyl derivatives of D.S. 0.09 and 0.14 respectively.



**Fig 5.** Effect of dye concentration on % colour removal using carboxymethyl derivative of D.S.0.09 (a) ultra-sonic and (b) shaking treatment

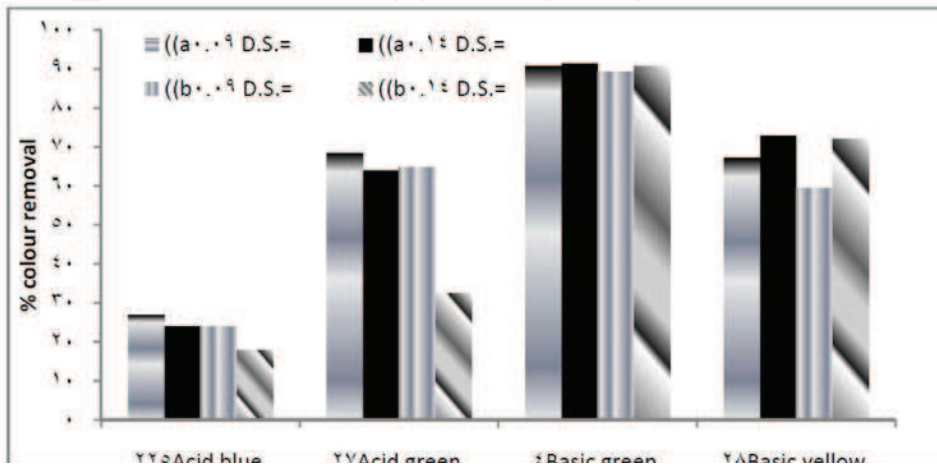


**Fig 6.** Effect of dye concentration on % colour removal using carboxymethyl derivative of D.S.0.14 (a) ultrasonic and (b) shaking treatment

It is clear from the data that in all cases as the dye concentration increases from 0.01 to 0.5gm, % the percent dye adsorption decreases regularly. This may be due to either: (a) aggregation of the dye molecules which increases as the concentration increases, or (b) the decrease in the mobility of the dye molecules as the concentration increases.

**3.4. Effect of nature of the dyestuff used**

At the end, it is of great interest to investigate the effect of the nature of the dyestuffs used on the percent colour removal on using carboxy methyl cellulose derivatives derived from rice straw of D.S. 0.09 and 0.14. Hence 4 different dyestuffs (two of them acid and the other are basic) were chosen and used with the mentioned carboxymethyl cellulose derivatives under identical conditions in case of either mechanical shaking or ultrasonic. The results obtained are illustrated in Figure 7 in case of using mechanical shaking and ultrasonic.



**Fig 7.** Effect of nature of dyestuff on the ability of carboxymethyl derivatives towards colour removal on using (a) ultrasonic and (b) shaking treatment



Generally speaking it is obvious from the figure 7 that the % decreases in colour depends on: (a) the nature of the dyestuff used, (b) the D.S. of the adsorbent and, (c) on the technique applied. It is also clear on using carboxymethyl derivative of D.S. (0.09) for the samples conducted under mechanical shaking the % colour removal in case of basic dyes is higher than that of acid dye. The percent colour removal

cellulose derivatives acquire (- ve) charges. Hence, it is expected that the capacity for dye adsorption of carboxymethyl cellulose derivatives is higher on using basic dyes than using acid dyes. It is clear from figure 7 that for basic dyestuffs used the % colour removal is higher on using carboxymethyl cellulose of relatively D.S. (0.14) values than their corresponding samples conducted using relatively D.S. (0.09) derivative. This due to the increases in the (- ve) charge of adsorbent as the D.S. increase. The same trend could be observed for the samples conducted via ultrasonic technique. Furthermore, it is clear that on using acid dyestuffs either blue or green the % colour removal decreases by increasing the D.S. of carboxymethyl derivatives from 0.09 to 0.14. As the D.S. increases the (- ve) charges increases and hence the adsorbed acid dye which acquire (- ve) charges decrease.

#### 4. Conclusion

The percent colour removal increases by increasing the time of treatment and / or the amount of substrate. While the opposite holds true by increasing the dye concentration. In all cases the magnitude of dye adsorption in case of ultrasonic is relatively higher than mechanical shaking. Increasing D.S of carboxymethyl derivatives decrease the % colour removal of reactive dye . The percent colour removal depends on the nature of dye used and follows the order Basic green> Basic yellow> Acid green> Acid blue respectively.

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