Synthesis and characterization of carboxymethyl cellulose derived from office paper waste for methylene blue dye removal

N A Yusoff, L Y Yee, N I Iberahim, N A Zainol, S Abdullah and S N Zailani

Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.

Email: aidayusoff@unimap.edu.my

Abstract. The aim of this research was to extract cellulose from office paper waste and converted into carboxymethyl cellulose (CMC) based flocculant to treat methylene blue (MB) dye solution. The yield of extracted cellulose obtained was 62.17%. Three different CMC samples were prepared. Degree of substitution (DS) for CMC-1 is 0.6585, CMC-2 is 0.8124 and CMC-3 is 0.8946. This proved that CMC are substituted into cellulose structure due to the DS of the commercial CMC are in the range of 0.4 to 1.5. The coagulation flocculation process of the MB dye shows that the CMC-3 was effective for methylene blue dye removal with highest percentage (98.14%) at pH 9.0, flocculant dosage of 210 ppm with 100 ppm MB concentration solution.

1. Introduction
Wastewater are the liquid waste discharged from residences, institutions, commercial and industrial establishment come along with groundwater, surface water and storm water [1]. One of the foremost problematic causes of water pollution is dye effluent from dye manufacturing and dye consuming industries like food, paper, plastic and textile. In addition, most of the dyes are resistant to biodegradation and effluent discharged to the aquatic medium increase the biological load. Thus, releasing of these effluents to environment cause serious health problems as some dyes are carcinogenic effects on the living organisms. Dyes in surface water has a barrier effect on the penetration of sunlight and water body aeration, thereby reducing photosynthetic activity [2]. Methylene blue (MB) is one of the cationic dye which can lead to some harmful effects such as increase of heartbeat, vomiting and shock in humans [3].

To overcome this, there are several types of method in treatment technologies including physical, chemical and biological. Coagulation-flocculation is by far the most commonly used physical-chemical treatment technology. In water treatment, coagulation-flocculation has been found to be a cost-effective, can be handle easily and energy saving operation in various industrial applications. Coagulation is defined as a process occurring when adding a coagulant to water to destabilize the colloidal suspensions. It is a chemical process involving neutralization of charge. In contrast, the process of flocculation involves adding polymers to cluster small, destabilized particles into large particles so that they can be easily separated by water. Flocculation is a physical process that does not involve neutralization of charge [4]. Therefore, they have the application in removing turbidity, suspended and dissolved solids, colours and dye, and chemical oxygen demand (COD) [5].

Coagulation flocculation is one of the method in removing dye through extraction of cellulose by waste paper due to there would result in a decrease in the various kind of socioeconomic issues by the
conversion of waste materials into helpful products like providing a greener approach for manufacturing. Thus, recycling of waste has huge benefits in environmental and economical as recycling of one ton of waste paper saves 17 trees and 7000 gallons of water [6]. Some waste papers such as chemical pulp, napkins, blotting paper, hygiene paper, office paper are characterized by increased cellulose content and negligible lignin content [7]. Paper waste is rich in cellulose, has the advantages of low price, easy extraction and biodegradability. Thus, it has the potential towards the reutilization of paper waste to obtain cellulose as value-added product [8].

Carboxymethyl cellulose (CMC) is an anionic polyelectrolyte prepared by reaction of sodium chloroacetate with alkali cellulose. CMC is non-toxic and due to wide application regard to volume demand, carboxymethyl cellulose (CMC) is manufactured in significant for different industrial applications such as food ingredients, pharmaceuticals, cosmetics, paper products, adhesive, lithography, ceramics, detergents, and materials [6]. In this study, CMC is derived from the office paper waste and to study the CMC based flocculant for MB dye removal.

2. Material and method

2.1. Raw materials
The office paper waste were collected from different offices of University Malaysia Perlis. Non-paper objects such as stickers, staplers, rubber bands and others were removed from the paper waste. The materials were cut, soaked in the water, dried and blended.

2.2. Extraction of cellulose from office paper waste
After the non-paper object was removed, the office paper waste was cut into smaller pieces and placed in the stagnant water for three days, during which time the water were changed frequently. Subsequently, the papers were boiled for about 15 minutes, and then washed several times in fresh water. Finally, the papers were dried in the oven. Instead of using a mill for grinding, the paper was blended by a blender. The blend papers were treated with 4% NaOH at 125℃ for 2 hours, after which bleaching treatment was carried out using 1.7w/v% NaClO₂ at pH 4.5 and 125℃ for 4 hour. The ratio of the paper to liquor is 5:100 (mg/L). The steps were repeated for two times, and the papers were washed with distilled water after each treatment [9]. The yield of cellulose extracted from office paper waste was measured based on the dry weight basis. The yield of cellulose was calculated based on the amount of office paper waste using and it is expressed in percentage as shown in equation (1) [10]:

\[
\text{Yield of cellulose (\%) = \frac{\text{weight of cellulose obtained (g)}}{\text{weight of office paper waste used (g)}} \times 100%}
\]

2.3. Synthesis of carboxymethyl cellulose (CMC)
Cellulose from office paper waste were converted to CMC in two steps which are alkalization and etherification of cellulose under heterogeneous conditions. In first step about 2.0 gram of office paper waste cellulose were weighed and added to 500 mL Schott bottle and followed by 120 mL of water: isopropyl alcohol solvent (1:4) in appropriate ratio. Then, 16 mL of 20% w/v of sodium hydroxide was added drop-wise and stirred for 2 hours. The cellulose-NaOH activation reaction is usually referred to as mercerization and it is commonly performed at approximately room temperature. The carboxymethylation reaction was started by adding various amounts of sodium monochloroacetic acid (MCA) (1g, 3g, 5g) to the reaction mixture place on magnetically stir hot plate. The reaction mixture was heated up at 50℃ with constant stirring for 3 hours. Then, the mixture was filtered and the residue was suspended in 100 mL of methanol for 40 minutes. The suspended slurry was neutralized using dilute glacial acetic acid. Again, the residue was filtered and washed with absolute methanol and the residue from the filtration was dried in hot air oven at 60℃ overnight and the powder obtained is carboxymethyl cellulose. Table 1 shows the experimental condition for the preparation of CMC from office paper waste[11]. The yield of carboxymethyl cellulose synthesized was measured based on the dry weight
basis. The yield of carboxymethyl cellulose was calculated by dividing the net dry weight of CMC with 2g of dry cellulose and it is expressed in percentage as shown in equation (2) [10]:

\[
\text{Yield of CMC (\%) = \frac{\text{weight of dry CMC (g)}}{\text{dry weight of cellulose (g)}} \times 100\%}
\]  

(2)

Table 1. Experimental condition for the preparation of CMC from office paper waste.

| Sample ID | Sodium monochloroacetic acid (MCA) concentration (gram) | Sodium hydroxide (NaOH) concentration (w/v %) | Temperature (°C) | Reaction time (h) |
|-----------|------------------------------------------------------|---------------------------------------------|------------------|-----------------|
| CMC-1     | 1                                                    | 20                                          | 50               | 3               |
| CMC-2     | 3                                                    | 20                                          | 50               | 3               |
| CMC-3     | 5                                                    | 20                                          | 50               | 3               |

2.4. Degree of substitution (DS)

Absolute values of degree of substitution (DS) was determined by potentiometric titration. One gram of CMC was added to 250 mL beaker follow by 50 mL of 95% ethanol and stirred. Then, 5 mL of 2M nitric acid was added and the mixture was stirred for 10 min at room temperature. Then, the mixture was heated to boil by using magnetic hot plate for 5 minutes and stirred further for 20 minutes and left to settle. After solution is settle, the solution was filtered and the residue was washed with 100 mL 95% ethanol to removes the acid and salts. The precipitate was washed with methanol and transferred to beaker and was heated until it removes the alcohol. The beaker with the precipitate was dried in the oven at 90° C for 3 hours. CMC (0.5g) was weighed in 250 mL Erlenmeyer flask and 100 mL distilled water was added and stirred. 25 mL 0.5 M NaOH was added and boiled for about 20 min. Then, the heat solution was titrated with 0.3 M HCL by using phenolphthalein as an indicator to observe the colour change from Mexican pink (dark pink) to colourless. The DS of CMC are calculated using the equations (3) and (4).

\[
\text{Carboxymethyl content (%CM) = } \frac{[V_0 - V_n]}{M} \times 0.3 \times 0.058 \times 100
\]  

(3)

\[
\text{Degree of substitution} = \frac{162 \times \%CM}{100 \times 58 - (58 - 1) \times \%CM}
\]  

(4)

Where

\[ V_0 = \text{amount (ml) of HCl used to titrate the blank}; \]
\[ V_n = \text{amount (ml) of HCl used to titrate the sample}; \]
\[ M = \text{CMC in grams}; \]
\[ 0.3 \text{ is the normality of HCl used}; \]
\[ 162 \text{ is the molecular weight of the anhydrous glucose unit}; \]
\[ 58 \text{ is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group [12]}. \]

2.5. Coagulation and flocculation experiment

Jar test was carried to evaluate the coagulation flocculation performance of the prepared CMC. Each batch was involved rapid mixing, slow mixing and sedimentation process. In rapid mixing, the mixture was stirred at 200 rpm for 2 min. Then, the slow mixing phase was conducted at 30 rpm for 20 minutes to promote the collision particles and hence floc growth. Next, a 30 minutes settling period was applied [13]. First, the effect of DS of CMC on coagulation flocculation performance was carried out by 5
samples which are blank solution, CMC-1, CMC-2, CMC-3 and the other was compared with commercial flocculant, sodium alginate. The pH was fixed at original pH, flocculant dosage is 70 ppm and 100 ppm for MB concentration. The CMC that has the best value of flocculation performance was used to determine the effect of dosage, pH and MB concentration. The effect of flocculant dose was studied by using CMC-3, the best CMC that was obtained. In order to determine the optimum flocculant dosage, 30 - 270 ppm of CMC were added to a series of water samples with original pH of water and concentration of 100 ppm. The effect of pH on coagulation flocculation process was studied by adjusting the pH value of 3 - 13 using hydrochloric acid (HCL) or sodium hydroxide solution (NaOH). The test was carried out at optimum dosage determined previously and the concentration of 100 ppm. The experimental parameters are listed in table 2.

Table 2. Experimental parameters.

| Experimental parameters | Unit | Range         |
|-------------------------|------|---------------|
| Effect of DS on CMC     | -    | 0.6585, 0.8124, 0.8946 |
| Flocculant dosage       | Ppm  | 30, 50, 70, 90, 110, 130, 150, 170, 210, 230, 250, 270 |
| pH                      | -    | 3, 5, 7, 9, 11, 13 |

2.6. Determination of methylene blue dye removal
UV-visible spectrophotometer was used to determine the concentration of MB dye removal. The samples were collected and transferred into the cuvettes. It was placed into the UV-visible Spectrophotometer to determine the MB dye concentration at the λmax 664 nm. The calibration curve was prepared by recording the absorbance values for MB solution of known concentrations. The percentage removal of MB dye was calculated according to the equation (5):

\[
Dye\ removal\ (%) = \frac{C_0 - C}{C_0} \times 100
\]  

(5)

Where \(C_0\) and \(C\) are the MB dye concentrations before and after treatment (mg/L) respectively [14, 15]

3. Results and discussions

3.1. Extraction of cellulose from office paper waste.
According to Sheltami [9], there is an ester-type bond between the lignin of hydroxyl group and hemicellulose of carboxyl group and due to it is prone to the solutions of alkali, the linkage can be broken up with the alkali and bleaching treatment. Based on the measurements, the yield of the extracted cellulose obtained was 62.17 %. Alkali treatment responsible for destroying the linkage of ester bond between lignin and xylan (hemicellulose). It breaks the glycosidic ether bond which disrupt the structure of lignin. Thus, these lead to the swelling of cellulose, partial solvation of hemicellulose and solubilisation of hemicellulose and lignin. Lignin would not act as protective shield to cellulose therefore making extracted cellulose more vulnerable to synthesis of others cellulose derivatives [16]. Through bleaching treatment, the colour content such as ink present in the natural composition of fibre was simply removed. The surface adhesion between matrix and fibre was modified by this treatment thus it removes the residual lignin [17]. The permanent white cellulose fibres was obtained is due to the bleaching agent oxidised the colouring matter and destroyed it into simpler compound that are dissolved and washed out easily [18].
3.2. Synthesis of carboxymethyl cellulose

In this study, different amount of monochloroacetic acid was added in the etherification reaction gives variable effects on the percentage yield of CMC. Table 3 shows that the percentage yield and DS of CMC increased with increasing amount of monochloroacetic acid. It is due to the substitution of hydroxyl group of cellulose molecules with carboxymethyl group lead to a higher mass [19]. Table 3 shows that 5 grams of monochloroacetic acid obtained the highest percentage yield of CMC which is 100.5%.

| Sample ID | Monochloroacetic acid (g) | Yield of CMC (%) | Degree of substitution |
|-----------|--------------------------|------------------|-----------------------|
| CMC-1     | 1                        | 83.5             | 0.6585                |
| CMC-2     | 3                        | 95.0             | 0.8124                |
| CMC-3     | 5                        | 100.5            | 0.8946                |

Degree of substitution is an important parameter in determining the solubility in water. Based on the theoretical, the maximum value of DS for CMC is 3.0. The commercially CMC of DS are basically in the range of 0.4 to 1.5. It shows that the DS increased with increasing amount of monochloroacetic acid. The increasing trend is likely because of the greater availability of the acetate ions in the closeness of cellulose molecules at higher concentrations. The highest DS of 0.8946 was obtained with 5g of monochloroacetic acid added. Theoretically, DS above 0.6 are good solubility in water while DS below 0.2 is not soluble in water and increasing of DS improve the solubility of water [20].

3.3 Coagulation flocculation performance evaluation

3.3.1 Effect of DS on CMC. The effectiveness of synthesized flocculants which is carboxymethyl cellulose was determined and compared with the commercial flocculant which is sodium alginate using a standard jar test. The result of different DS of CMC were presented in Figure 1 with experimental condition of 70 ppm flocculant dosage, 100 ppm MB dye concentration and original pH value of 6. Based on the figure, the synthesized flocculant with higher DS lead to a high percentage removal of MB dye. CMC-1 with DS of 0.6585 had percentage removal of 26.47 %, CMC-2 with DS of 0.8124 had percentage removal of 53.59 % and CMC-3 with DS of 0.8946 had the highest percentage removal of 71.47 %. This evident that the CMC-3 had succeed in the substitution of carboxymethyl group towards the cellulose structure and act as an anionic polyelectrolyte flocculant to remove the cationic dye. CMC-3 shows the better flocculant efficiency than commercial flocculant, sodium alginate but sodium alginate had the second highest percentage removal of MB dye (66.14 %). This proved that the substitution of carboxymethyl group of CMC-1 and CMC-2 towards the cellulose structure were insufficient. Therefore, the flocculant efficiency in colour removal of MB dye solution is slightly lower than the sodium alginate. Since, CMC-3 has the best value of flocculation performance, it was used to determine the flocculant dosage and pH.
3.3.2 Effect of flocculant dosage. The coagulation flocculation performance of the carboxymethyl cellulose in treating the MB dye solution was shown in figure 2 with experimental condition of MB dye concentration 100 ppm and original pH value 6. It illustrates the increase of flocculant dosage lead to high percentage removal of MB dye solution. The percentage removal reached the highest point as 96.86% accompanied by flocculant dosage of 270 ppm. This indicated that during the flocculation process, charge neutralization mechanism played a major role due to the electrostatic adsorption between anionic carboxymethyl cellulose and cationic MB dye. Hence, it formed large flocs for settlement. In addition, 30 ppm had the lowest percentage (33.73%) of dye removal. This indicated that if the dosage is too low, the neutralization effect is insufficient. Thus, it had low efficiency in MB dye removal and formed little flocs for settlement. Moreover, the increase of percentage removal performed relatively mild and it reached constant when flocculant dosage was added beyond 210 ppm. Based on the principle of saving agents, the flocculant dosage of 210 ppm was selected for subsequent sections [21].

3.3.3 Effect of pH. The coagulation flocculation performance of the carboxymethyl cellulose in treating the MB dye solution was shown in figure 3 with experimental condition of MB dye concentration 100 ppm and flocculant dosage of 210 ppm. From figure 3, the experimental data shows that the percentage of methylene blue dye removal was minimum at pH 3.0 then sharp increase was observed at pH 5.0. Although the highest percentage MB dye removal was at pH 9.0 with 98.14%, the pH from 5.0 to 13.0 shows the trend of almost constant with percentage MB dye removal above 87%. This indicated that the
carboxylic groups of CMC tended to acquire a net positive charge at a lower pH of solution. The dissociation of carboxylic groups of CMC occurred when the solution of pH increased. Therefore, the overall charge on CMC surface became negative. This enhance the attraction between the positively charged MB and carboxylate anion. Thus, it results in an increase of sorption of MB and CMC surface [15]. Consequently, more flocs were formed during the coagulation and flocculation process. Thus, it concluded that CMC showed good performance in removing cationic dye at alkaline condition.

![Figure 3. Effect of pH on percentage MB dye removal.](image)

4. Conclusion
Cellulose was successfully extracted from office paper waste due to most of the non-cellulosic materials such as inks, wax and oils are removed. Percentage yield of extracted cellulose was 62.17 %. In synthesis of CMC, degree of substitution for CMC-1 is 0.6585, CMC-2 is 0.8124 and CMC-3 is 0.8946. CMC was successfully synthesized from the extracted cellulose. The experimental results in coagulation flocculation process indicate that CMC based flocculant were effective in removing MB dye solution. The result showed that the maximum DS of prepared CMC-3 (0.8946) had the highest percentage removal of MB dye solution (71.47 %) and it is better than commercial flocculant, sodium alginate (66.14 %). CMC-3 which shown to be the best CMC was used to determine the effect of flocculant dosage and pH. The highest percentage MB dye removal (98.14%) was at pH 9.0, flocculant dosage of 210 ppm with 100 ppm MB concentration solution and maximum DS of 0.8946. Hence, it may be suggested that carboxymethyl cellulose with higher degree of substitution value removes cationic dye more effectively from the aqueous solution at higher pH.

Acknowledgements
The author would like to acknowledge the support from Universiti Malaysia Perlis for the instrument used, laboratory equipment and chemicals.

References
[1] Topare N, Topare NS, Attar SJ, Manfe MM 2011 Sewage/Wastewater Treatment Technologies : A Review Sci. Revs, Chem. Commun 18–24
[2] Fil BA, Özmetin C, Korkmaz M 2012 Cationic Dye (MB) Removal from Aqueous Solution by Montmorillonite Bull. Korean Chem. Soc. 33 3184–90
[3] Kushwaha AK, Gupta N, Chattopadhyaya MC 2011 Removal of Cationic MB and Malachite Green Dyes from Aqueous Solution by Waste Materials of Daucus Carota J. Saudi Chem. Soc. 200–207
[4] Khiari R, Dridi-Dhaouadi S, Aguir C, Mhenni MF 2010 Experimental Evaluation of Eco-Friendly
Flocculants Prepared from Date Palm Rachis Int. J. Environ. Sci. 22 1539–1543
[5] Salehizadeh H, Yan N, Farnood R 2018 Recent Advances in Polysaccharide Bio-Based Flocculants Biotechnol. Adv. 36 92–119
[6] Joshi G, Naithani S, Varshney VK, Bisht SS, Rana V, Gupta PK 2015 Synthesis and Characterization of Carboxymethyl Cellulose from Office Waste Paper: A Greener Approach towards Waste Management J. Waste Manag. 38 33–40
[7] Ioelovich M 2014 Waste Paper as Promising Feedstock for Production of Biofuel J. Scientific Research and Report 3 905–16
[8] He X, Wu S, Fu D, Ni J 2009 Preparation of Sodium Carboxymethyl Cellulose from Paper Sludge J. of Chem. Tech. and Biotech. 84 427–34
[9] Sheltami RM, Abdullah I, Ahmad I, Dufresne A, Kargarzadeh H 2012 Extraction of Cellulose Nanocrystals from Mengkuang Leaves (Pandanus Tectorius) Carbohydr. Polym. 88 772–9
[10] Hong KM 2013 Preparation and Characterization of Carboxymethyl Cellulose From Sugarcane Bagasse IEEE International Symposium on Applications of Ferroelectrics
[11] Haleem N, Arshad M, Shahid M, Tahir MA 2014 Synthesis of Carboxymethyl Cellulose from Waste of Cotton Ginning Industry Carbohydr. Polym. 113 249–55
[12] Huang CMY, Chia PX, Lim CSY, Nai JQ, Ding DY, Seow P bei, et al. 2017 Synthesis and Characterisation of Carboxymethyl Cellulose from Various Agricultural Wastes Cell Chem. Technol. 51 665–72
[13] Dong C, Chen W, Liu C 2014 Flocculation of Algal Cells by Amphoteric Chitosan-Based Flocculant Bioresour. Technol. 170 239–47
[14] Fang R, Cheng X, Xu X 2010 Synthesis of Lignin-Base Cationic Flocculant and Its Application in Removinganionic Azo-Dyes from Simulated Wastewater Bioresour. Technol. 101 7323–29
[15] Begum HA, Mahbub MK Bin 2013 Effectiveness of Carboxymethyl Cellulose for the Removal of MB from Aqueous Solution Dhaka Univ. J. Sci. 61 193–8
[16] Lee H V, Hamid SBA, Zain SK 2014 Conversion of Lignocellulosic Biomass to Nanocellulose: Structure and Chemical Process Sci. World J. 2014
[17] Ouahrhim W, Zari N 2019 Mechanical Performance of Natural Fibers-Based Thermosetting Composites Compos Sci Eng. 43-60
[18] E.S. Abdel-Halim 2014 Chemical Modification of Cellulose Extracted from Sugarcane Bagasse : Preparation of Hydroxyethyl Cellulose Arab. J. Chem. 7 362–71
[19] Tasaso P 2015 Optimization of Reaction Conditions for Synthesis of Carboxymethyl Cellulose from Oil Palm Fronds Int. J. Chem. Eng. 6 3–6
[20] Helène Amllöf Ambjörnsson, Karla Schenzel and UG 2013 Carboxymethyl Cellulose Produced at Different Mercerization Conditions and Characterized by NIR FT Raman Spectroscopy in Combination with Multivariate Analytical Methods Bioresources 8 1918–32
[21] Zhang Y, Yao J, Shao L, Liu H, Zhang X, Yang X, et al. 2015 One-Step Green Synthesis of Non-Hazardous Dicarboxyl Cellulose Flocculant and Its Flocculation Activity Evaluation J. Hazard. Mater. 296 1–8