



Carboxylated Multi-walled Carbon Nanotubes/Calcium Alginate Composite for Methylene Blue Removal

Puguh Setyoprato¹, Restu Kartiko Widi¹, Rudy Agustriyanto¹, and Endang Srihari¹

¹ Chemical Engineering Department, University of Surabaya, Kampus Tenggiling, Surabaya 60292, Indonesia
puguh@staff.ubaya.ac.id

Abstract. In this research work, the adsorption of methylene blue (MB) on carboxylated poly-walled nanotubes carbon (PWNC)/calcium alginate composite was studied. The composite was synthesized by the impregnation method. The study was aimed to observe the impact of carbon nanotube dosage on the ability of the composite to adsorb MB. Kinetics investigation was carried out to observe the suitability of the kinetic model of diffusion in a pore on the adsorption system. Research results show that the multi-walled carbon nanotubes/calcium alginate composite, which had a ball-like shape with a size of approximately 1 mm, had been successfully synthesized with carbon nanotubes dosage up to 15.7 w%. It was found that if the dosage of carbon nanotubes is greater then it will be higher the percent dye removal and the adsorption capacity of the composite. The incorporation as much as 15.7 w% carbon nanotubes to the calcium alginate structure increased its adsorption capacity to almost 2 times higher. The kinetic study had shown that the diffusion through the pore of the composite controls the overall rate of diffusion of methylene blue to the surface of the composite.

Keywords: Adsorption, Carbon Nanotubes/Calcium Alginate Composite, Impregnation Method, Kinetic Study, Methylene Blue.

1 Introduction

One of the environmental problems faced worldwide today was the increasing content of organic compounds in liquid waste. One of the main sources of organic pollutants in liquid waste was dyes contained in the effluent of textile industry waste streams. Especially with increasing industrialization, the increasing content of dyes in liquid waste had caused environmental damage and disruption to human health. Dyes were a group of organic molecules that had pseudo-persistent properties due to their very complex structures [1]. It was reported that 10,000 tons/year of dyes were used in the cloth material industry worldwide and 100 MT of these dyes were streamed into the river stream yearly [2]. Exposure to dyes had carcinogenic and mutagenic effects, causes heart palpitations and vomiting and could causing some malfunctions and damages in the parts of the human body, such as a blood disorder and brain dysfunction [3].

Removing pollutants from wastewater was critical to ensuring a healthy and sustainable living environment for the entire world's population. The development of

wastewater treatment was a very strategic issue to ensure the effectiveness of removing various pollutants [4].

Therefore, developing the most superior method for the removal of organic dyes from wastewater was urgently needed in the context of environmental protection [5]. Among the various methods and technologies developed for the separation of dyes from waste stream, adsorption was seen as a method that is simple, inexpensive, and easy to operate [6].

Researchers had intensively developed various adsorbents for dye removal including metal-organic frameworks (MOFs), functionalized biomass, nanocomposite membranes, molecularly imprinted polymers, and hyper-crosslinked macrocycle polymers [7]. The development of composite-based adsorbents for dye removal was interesting to increase the effectiveness of adsorption both in terms of adsorption capacity and from economic considerations. In this study, carboxylated multi-walled carbon nanotube/calcium alginate composite was synthesized, and its effectiveness was observed for methylene blue removal. This study was intended for observing the impact of the dosage of PWNC in the composite on the effectiveness of dye removal by adsorption.

2 Material and Method

2.1 Material

The PWNC were synthesized using liquefied petroleum gas as a carbon precursor. Synthesis was carried out using the method of the deposition of chemical vapor. A series of equipment and procedures for the production of PWNC had been described in previous publications [8]. Methylene blue (C.I. 52015, Merck CAS:61-73-4), sodium alginate (Sigma-Aldrich, Chemical AS 9005-38-3), $\text{Ca}(\text{Cl})_2$ (Merck, Chemical AS 10043-52-4), HNO_3 69% acid, (Merck, Chemical AS 7697-37-2) and sulfuric acid 95-97% (Merck, Chemical AS 7664-93-9) were obtained from local suppliers.

2.2 Preparation of carboxylated PWNC

Carboxylated PWNC were prepared by suspending PWNC in a liquor containing a concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture (1:3 v/v). Afterward, the suspension was sonicated at 40°C for 3 hours. The solid was then separated from the liquor and washed with purified water until it reached a neutral pH. The washed solids were then lowered the water content in an oven at 50°C overnight.

2.3 Preparation of Carboxylated PWNC/Calcium Alginate composite

The carboxylated PWNC/calcium alginate composite was synthesized by the impregnation method, following the method developed by Wang et al. [9]. The composites were prepared by dispersing carboxylated PWNC in deionized water (1% weight/volume) and sonicated at 25°C for 2 hours. The suspension was then mixed with sodium alginate solution (1% weight/volume) at a weight ratio of 0.25 g PMNC/g alginate to form a colloid. After that, 50 mL of this colloidal liquor was added drop by drop into

250 mL of 0.1 M CaCl_2 while stirring. The alginate composite that was produced was left 24 hours to achieve stability. The composite was then washed with purified water several times to separate the sodium, residual carbon nanotube, and un-cross-linked calcium ions. Finally, the composite was put in an oven drier at 50°C for 24 hours. The mass of PWNC used was varied to obtain PWNC dosage 6.9, 10.0, 12.9, dan 15.7 weight percent. The synthesis procedure of this composite schematically is shown in Fig. 1.

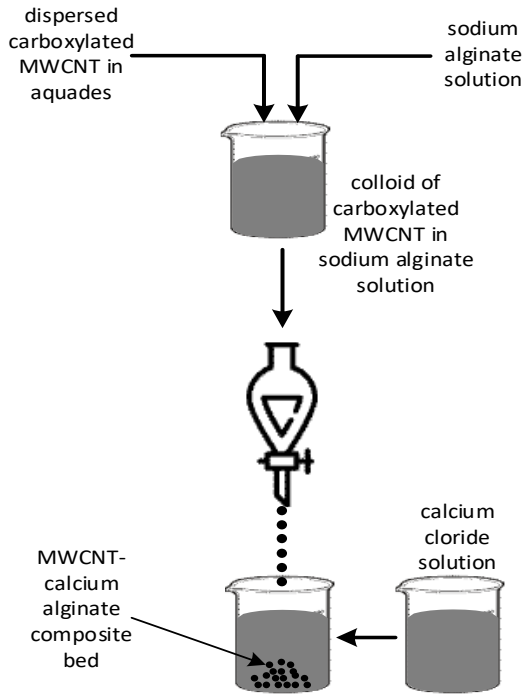


Fig. 1. Illustration of the process of synthesis of a composite of PWNC/ calcium alginate using the impregnation method.

2.4 Dyes Adsorption Procedure

As much as 0.1 g of carboxylated PWNC/calcium alginate composite was put into 100 ml of 100 ppm methylene blue solution in a 300 ml beaker glass while stirring at a constant rotational rate of 60 rpm. Sampling of the solution was done to monitor the concentration of MB in the solution from time to time up to the equilibrium point. The MB content in liquid phase was measured by the spectrophotometric method using a GENESYS 150 Spektrofotometer UV-vis Thermo Fisher Scientific. Experiments were carried out for all composites, calcium alginate, and multi-walled carbon nanotubes.

The dye removal and the adsorption capacity of the adsorbent was formulated in equations (1) and (2), respectively.

$$\text{Dye removal} = \frac{(C_i - C_f)}{C_f} \times 100\% \quad (1)$$

$$\text{Adsorption capacity} = \frac{(C_i - C_f)}{M} \times V \quad (2)$$

where C_i was the MB content in liquor at the start and C_f was the MB content in liquor at the end, V was the liquor volume and M was the weight of the solid adsorbent.

In this study the dye adsorption kinetic was investigated by observed the suitability the experiment results with the kinetic model of diffusion in a pore. The model was shown in Eq. 3, where q_t : dye uptake (mg/g), t : adsorption time (min), k_{id} : intra particle diffusion kinetic constant and C : constant.

$$q_t = k_{id}t^{0.5} + C \quad (3)$$

3 Results and Discussion

3.1 The Morphology of Carboxylated PWNC/Calcium Alginate Composite

To observe the morphology of the composite, image of an electron microscope was taken and the the result is presented in Fig. 2.

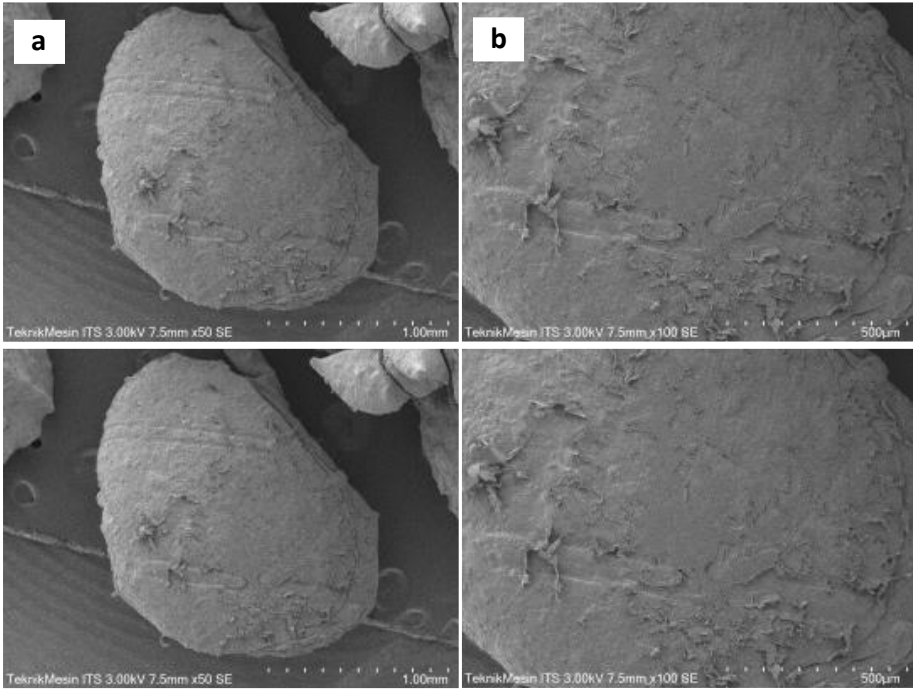


Fig. 2. The electron microscope image of the carboxylated PWNC/calcium alginate composite at carbon nanotubes dosage 15.7%. (a) the individual composite particle; (b) the surface captured at a higher magnification.

It could be seen that the individual composite had a ball-like shape with a size of approximately 1 mm. The particle size of this composite was close to the size of the same composite synthesized by Ulu et al. [10]. For large-scale continuous adsorption applications, a particle size of 1 mm was sufficient to avoid excessive pressure drop without granulating.

3.2 The Effect of Multi-walled Carbon Nanotubes Dosage

Methylene blue adsorption profile using PWNC/calcium alginate composite on all variations of carbon nanotubes dosage was shown in Fig. 3. As a comparison, adsorption was also carried out using adsorbent PWNC (in the figure labeled as CNT) which were used as material to synthesize the composites and calcium alginate (in the figure labeled as CA) which was synthesized with the same method as the method used for synthesizing the composites but without the addition of carbon nanotubes. All experimental runs were conducted with concentration of MB in a solution of 100 ppm at the start. In this profile, the MB content in the solution was expressed as C/C_0 , which was the ratio of the concentration of MB in the solution at a certain time to its initial concentration.

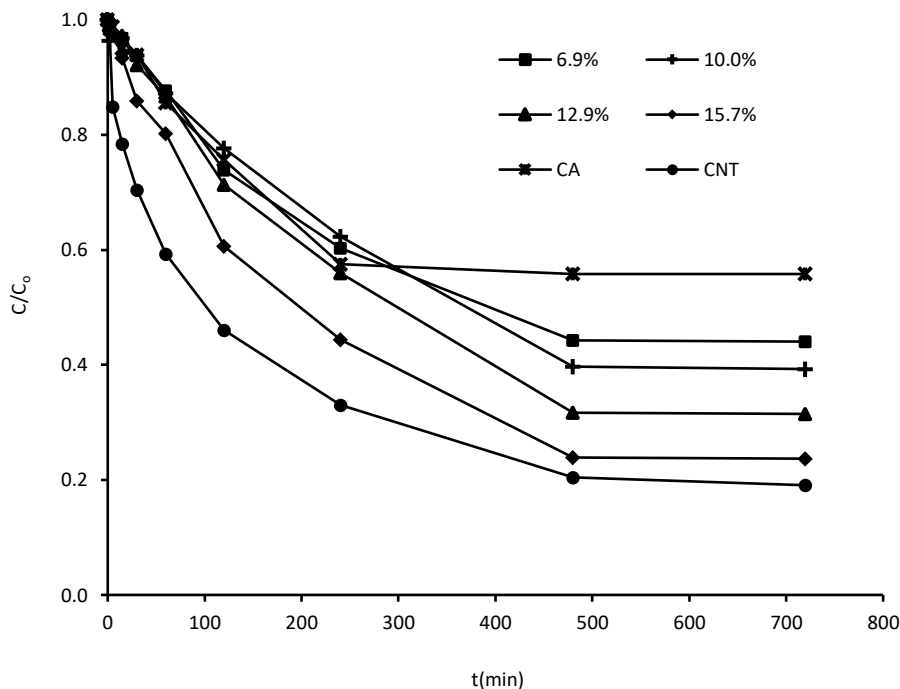


Fig. 3. Adsorption profile of MB on PWNC/calcium alginate composite with variations in carbon nanotube dosage.

The adsorption profile showed that the concentration of MB in the solution did not decrease significantly after 480 minutes and the equilibrium phase/condition was obtained at the time of 720 minutes.

The profile also showed that the higher the dosage of carbon nanotubes in the composite, the lower MB content in liquor at the equilibrium point. The lowest equilibrium concentration of methylene blue in solution was achieved with a C/C_0 value of 0.24 which was achieved when the dosage of carbon nanotubes in the composite was 15.7%. Experimental results also showed that calcium alginate itself also had the ability to adsorb the methylene blue, which was shown to be able to reduce the concentration of methylene blue in the solution until the C/C_0 equilibrium reaches 0.56.

The ability of the composite to adsorb methylene blue was also indicated by the value of its percent dye removal and adsorption capacity, and both values were presented in Table 1.

It could be seen with certainty that when the dosage of carbon nanotubes increased, then the percent dye removal and the adsorption capacity of the composite would increase. The highest value for the percent dye removal was 76.3% and the ability of composite in adsorbing MB was 83.8 mg/g which was achieved when the carbon nanotubes dosage was 15.7 w%.

From the experiment, it was also found that the adsorption capacity of calcium alginate on methylene blue was 46.8 mg/g. This showed that the addition of 15.7 w% carbon nanotubes to the calcium alginate structure would increase its adsorption capacity to almost 2 times higher from 46.8 mg/g to 83.8 mg/g. This means that the composite with 15.7 w% carbon nanotubes dosage had an ability in adsorbing MB almost the same as the ability of the PWNC themselves which was 87.0 mg/g. This showed that by using this composite the adsorption capacity per unit mass of carbon nanotubes was significantly increased so that it was more economically profitable.

Table 1. The dye removal and the adsorption capacity.

Parameter	Adsorbent					
	Percent carbon nanotubes dosage in carbon nanotube/calcium alginate composite				Calcium alginate	Multi-walled carbon nanotubes
	6.9%	10.0%	12.9%	15.7%		
Dye removal (%)	56.0	60.7	68.5	76.3	44.2	80.9
Adsorption capacity (mg/g)	61.0	66.5	73.5	83.8	46.8	87.0

3.3 The Adsorption Kinetic Model

In this study, the suitability of the kinetic model of diffusion in a pore was observed. The diffusion kinetic model observed iedapplies the same formula used by Masinga et al. [11].

If the experimental data plot agrees with the kinetic model of diffusion in a pore, then it meant that the molecular diffusion step inside the particle pores controls the entire adsorption step.

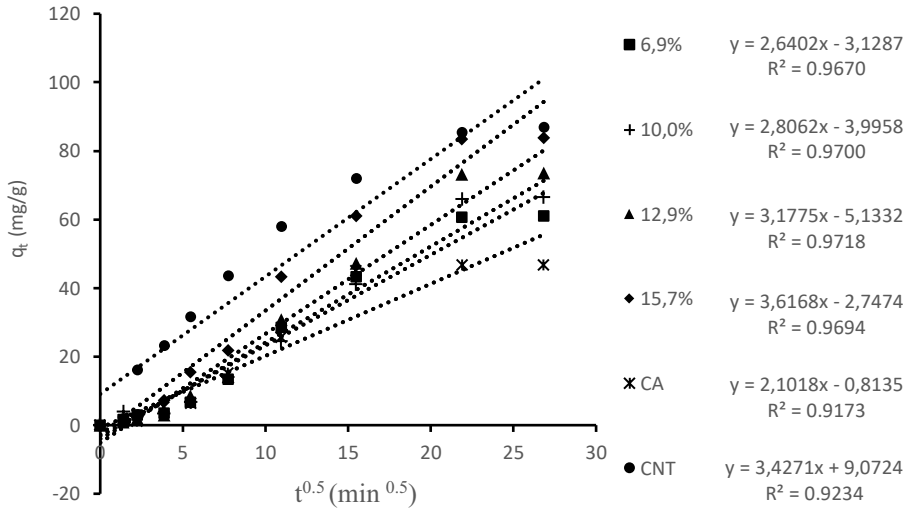


Fig. 4. Plot of the kinetic model of diffusion in a pore.

Table 2. The diffusion in pore kinetic model parameters and correlation coefficient.

Parameter	Adsorbent					
	Percent carbon nanotubes dosage in carbon nanotube/calcium alginate composite				Calcium alginate	Multi-walled carbon nanotubes
	6.9%	10.0%	12.9%	15.7%		
k_{id}	2.6402	2.8062	3.1775	3.6168	2.1018	3.4271
C	3.1287	3.9958	5.1332	-2.7474	0.8135	9.0724
R ²	0.9670	0.9700	0.9718	0.9694	0.9173	0.9234

The plot of the kinetic model of diffusion in a pore to the experimental data obtained in this study is presented in Fig. 4. From the plot it could be seen with certainty that all the adsorption data followed the kinetic model of diffusion in a pore for all composite adsorbents as well as calcium alginate and PWNC. This was indicated by the high value of the correlation coefficient. Thus, this study had proven that the overall adsorption rate of MB blue on the PWNC/calcium alginate composite was controlled by the molecular diffusion rate of MB through the pores network of the composite and then the external diffusion resistance in the liquid film was small compared to the overall resistance of MB transfer from the body of the liquid to the outer surface of the solid adsorbent. The kinetic model of diffusion in a pore parameters, which include the

kinetic model of diffusion in a pore constant and the correlation coefficient is tabulated in Table 2.

4 Conclusions

In this research work, the multi-walled carbon nanotubes/calcium alginate composite had been successfully synthesized with carbon nanotubes dosage up to 15.7 w%. It was found that the individual composite had a ball-like shape with a size of approximately 1 mm. Varying the dosage of carbon nanotubes in the composite had shown that if the dosage of carbon nanotubes was increased, then the the percent dye removal and the adsorption capacity of the composite would increased. It was also found that the addition of 15.7 w% carbon nanotubes to the calcium alginate structure would increase its adsorption capacity to almost 2 times higher. The kinetic study had shown that the diffusion through the pore of the composite controls the overall rate of diffusion of methylene blue to the surface of the composite.

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