

UTILIZATION OF ACTIVATED CARBON FROM CANDLENUT SHELLS (*Aleurites Moluccana*) AS METHYLENE BLUE ADSORBENT

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ABSTRACT

Candlenut shell is a potential material to be used as activated carbon. This study aims to explore the kinetics and isotherm of adsorption of activated carbon from the shell of candlenut against the methylene blue (MBE) dye in the solution. Activation of carbon from the shell of candlenut was carried out physically for 1 h at 700 °C and proceeded with chemical activation using 10% zinc chloride (ZnCl₂) solution to produce each physical (ACp-CS) and chemically (ACc-CS) activated carbon. The presence of functional groups in ACp-CS and ACc-CS was identified by an infrared (IR) spectrometer, while the surface topography of the materials was analyzed by a Scanning Electron Microscope (SEM). Adsorption of MBE solution by ACp-CS and ACc-CS with a dosage amount of 0.1 g was optimum at an interaction time of 100 min and at pH of 10, resulting in the amount of adsorbed dye 44.269 and 45.932 mg g⁻¹, successively. The sorption of MBE dye by ACp-CS and ACc-CS tends to attend kinetics model of the pseudo-second-order (PSO) underrate constant (k_2) grades of 15.49×10^{-3} and 6.30×10^{-3} (g mg⁻¹ min⁻¹) and the isotherm model of the Freundlich (AIMF) by factor values of adsorption capacity (K_F) were 4.60 and 5.99×10^{-5} (mg g⁻¹) (L mg⁻¹)^{1/n}, successively. Activated carbon from the shell of the candlenut has the potential to be applied as an adsorbent to absorb dyes in liquid waste before being released to the surrounding.

Keywords: Candlenut Shell, Activated Carbon, Adsorption, Methylene Blue.

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INTRODUCTION

Currently, pollution from wastewater by organic dyes from industries such as textiles, paper, plastics, cosmetics, and printing has attracted a lot of attention.¹⁻³ The textile industry ranks first in the use of dyes for fiber coloring.⁴ The discharge of dyes into the environment poses major problems for many forms of life. One of the most common dyes is methylene blue (MBE). MBE with the chemical formula C₁₆H₁₈ClN₃S is one of the generally applied coloring agents for dyeing cotton, wood, and silk.⁵ In the staining process, only 5% of bound MBE and the remaining 95% will be wasted as dye waste.⁶ Methylene blue may induce various dangerous consequences for humans as vomiting, raised heart rate, cyanosis, shock, jaundice, formation of Heinz body (HzB), necrosis, and quadriplegia.⁷ Therefore, the dye from waste needs to be removed. Several methods as chemical, physical, and biological methods, including biosorption, adsorption, coagulation, high oxidation, flocculation, ozonation, liquid-liquid extraction technique, and membrane filtration, have been widely applied to remove dyestuffs in wastewater.⁸⁻¹¹ The disadvantages and advantages of each dye removal method have been reviewed extensively.^{5,12} Some of these techniques have weaknesses such as imperfect removal, the use of many reagents and causing toxic deposits or other waste products, high costs, intensive efforts, etc.^{13,14} One of the effective techniques for eliminating dye from wastes is the adsorption process.¹⁵⁻¹⁷ Adsorption technology using activated carbon (AC) is the most greatly applied technology to treat water purification, which is contaminated with toxic chemicals.^{18,19} The fruitfulness of the adsorption technique is mainly determined by the adsorbent used. AC is known as one of the greatly effective materials utilized as an adsorbent material for dye in solution. Several studies on the

manufacture of AC, both physically and chemically, have shown that AC has the characteristics of an effective adsorbent in absorbing toxic chemicals.²⁰⁻²²

Activated carbon was chosen for the reason that it has a big surface area, high adsorption ability, is simple to be utilized, and is relatively cheap cost.^{21,22} With the background of the application of activated carbon as an adsorbent, it is necessary to make efforts to produce activated carbon from the waste of candlenut shell, which has not been used optimally. Hence, the purposes of this research are to analyze the sorption ability of AC from the shell of the candlenut for MBe dye. The adsorption parameters of MBe on physically activated carbon (ACp-CS) and chemically (ACc-CS) were studied using kinetics and adsorption isotherm models. Information about the adsorption isotherm pattern is needed in the development of adsorbent material from candlenut shells to be applied in absorbing MBe dyes from industrial waste.

EXPERIMENTAL

Materials and Instruments

Candlenut shells employed as activated carbon material in this study came from Lampung Province, Indonesia. The chemicals used were AR grade, including methylene blue, sodium hydroxide, hydrochloric acid, and zinc chloride (European Pharmacopoeia, France).

The tools were used in this experiment consisted of an analytical balance (Airshwoth AA-160), glassware, crusher, sieve 600-micron mesh, centrifuge, magnetic stirrer, pH meter, scanning electron microscopy (JEOL-JSM-6510LA, Japan), and infrared (IR) spectroscopy Prestige-21 Shimadzu-Japan. The MBe concentration was analyzed by an ultra-violet visible (Agilent Cary 100, spectrophotometer) at 664.0 nm (wavelength).

Preparation of Activated Carbon from Candlenut Shell Charcoal

Candlenut shell charcoal which has been mashed with a size of 600 μm was activated physically and chemically. The physical activation was carried out by burning 50 grams of candlenut shell charcoal in a furnace at 700 $^{\circ}\text{C}$ for 1 h (ACp-CS). Then proceed with chemical activation, the activated carbon as a result of physical activation was soaked in 10% zinc chloride solution for 24 h. After that, the carbon obtained was filtered and washed using aquadest up to pH 6. This material was dried in an oven for 1 h at 100 $^{\circ}\text{C}$ (ACc-CS).

Adsorption Experiment

The MBe stock solution (1000 mg L^{-1}) was made by inserting MBe ($\text{C}_{16}\text{H}_{18}\text{C}_1\text{N}_3\text{S}$) in distilled water. All solutions utilized in the process of adsorption were obtained by diluting the mother liquor to the desired concentration. A series of adsorption tests with the batch method was performed to investigate the adsorption pattern of the MBe solution by ACp-CS and ACc-CS, including variety in diverse parameters, including interaction time, pH, and concentration of MBe solution. To achieve this goal, as much as 0.1 g of ACp-CS and ACc-CS adsorbents were interacted with 20 mL of MBe solution at varying pH of 2 - 12, interaction time of 20 - 120 min, and MBe solution concentration of 0 - 250 mg L^{-1} .

The amount of MBe adsorbed in % was determined using Eq.-1 while calculation of the total of MBe uptake per unit mass of material used Eq.-2 as follows:

$$\text{Adsorption (\%)} = \frac{([Co] - [Ce])}{[Co]} \times 100 \quad (1)$$

$$q = \frac{([Co] - [Ce])v}{w} \quad (2)$$

Where $[Co]$ and $[Ce]$ are beginning and following concentration of the adsorption process for MBe in mg L^{-1} , w is the adsorbent amount (g), q is an amount of the adsorbed MBe per mass unit (mg g^{-1}), and v belongs to the solution capacity (L).

RESULTS AND DISCUSSION

Characterization of ACp-CS and ACc-CS Adsorbent

Investigation of adsorbents from the shell of candlenut was carried out using an IR spectrometer to identify functional groups and SEM-EDX to analyze surface morphology and elemental composition. In Fig.-1, it may be investigated that the IR spectrum of the ACp-CS and ACc-CS adsorbents show a relatively similar

absorption band in the area of the wavenumber around $3397.93 - 3405.42 \text{ cm}^{-1}$, which comes from stretching vibrations of the hydroxyl groups (OH).^{23, 24} In addition, there is an absorption band around 1633.33 cm^{-1} which shows the bending vibration from the aromatic ring of the alkene ($\text{C} = \text{C}$).^{23,25}

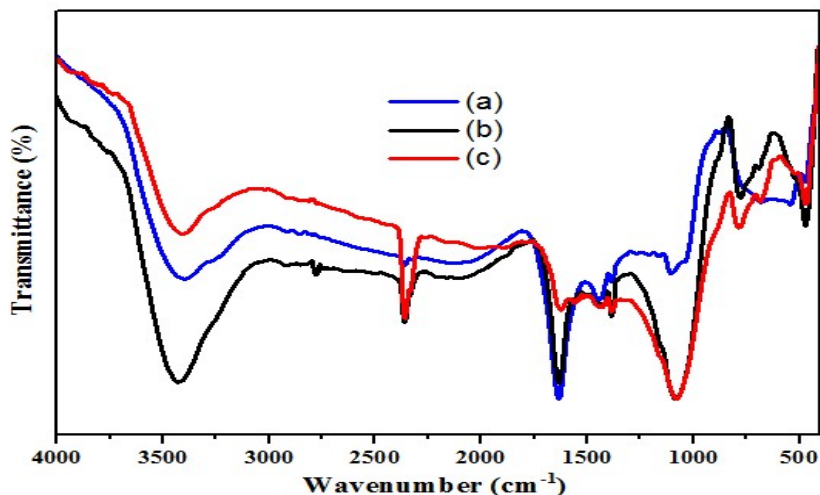


Fig.-1: Spectrum of IR from (a) Candlenut Shell Carbon, (b) ACp-CS, and (c) ACC-PS

From Fig.-2(a to c) may be indicated differences in surface morphology between inactivated candlenut carbon material (Fig.-2a), ACp-CS (Fig.-2b), and ACC-CS (Fig.-2c) at a magnification of 3000x. Changes in the surface morphology of the candlenut carbon after being activated physically and chemically looked different. In ACp-CS and ACC-CS (Fig.-2b and c), there are more pores with a more regular shape when compared to unactivated carbon (Fig.-2a). In addition, the activation process has also increased the percentage of atomic weight C and lowered the percentage of atomic weight O, as seen in the EDX spectra data (Fig.-2e to f) for weight percent C in the material before activation and after activation both physically and chemically (ACp-CS and ACC-CS) of 85.82, 95.78, 96.58%, respectively. This occurs because the physical and chemical activation processes open pores on the surface of the carbon material and increase the C content in the activated material.

Impact of pH

The degree of acidity (pH) is the main indicator that influences the MBe adsorption process in a solution because the solution pH will affect the charge contained in the ACp-CS and ACC-CS adsorbents, besides that the presence of H^+ ions is going to contend with the cations in MBe to interact with the adsorbent. It may be analyzed from Fig.-3 that the percentage of MBe adsorbed by the ACp-CS and ACC-CS adsorbents has an increase which is directly proportional to the increase in pH.

It is able to be stated from Fig.-3 that at $\text{pH} < 7$, the adsorption of MBe by ACp-CS and ACC-CS is relatively low. This happens because in an acidic atmosphere, the existence of excess H^+ ions will contend with MBe which tends to be positively charged so that electrostatic repulsion occurs between the MBe and the adsorbent surface, which can also be a partial positive charge. At high pH ($\text{pH} > 7$) there is an increase in adsorption due to electrostatic attraction between the adsorbent surface, which is partial negative charged and the adsorbate, which is partial positive charged.^{26,27} In addition, the rise in MBe adsorption at high pH can also be linked to the lowering of ions (H^+) that contend with cations of MBe at low pH to interact with the adsorbent surface.²⁸ However, at $\text{pH} > 12$ the adsorption decreased due to the increased level of free OH^- ions in the solution that would contend with MBe to occupy the adsorbent surface.¹⁶

Adsorption Kinetics

During the process of uptake, the interaction time among adsorbents and adsorbate is the main indicator that needs to be known because it will affect the planning of an economical adsorption procedure in industrial waste treatment.^{29,30} In this study, the contact time between MBe and ACp-CS and ACC-Cs was evaluated at various times from 0 to 120 min (Fig.-4).

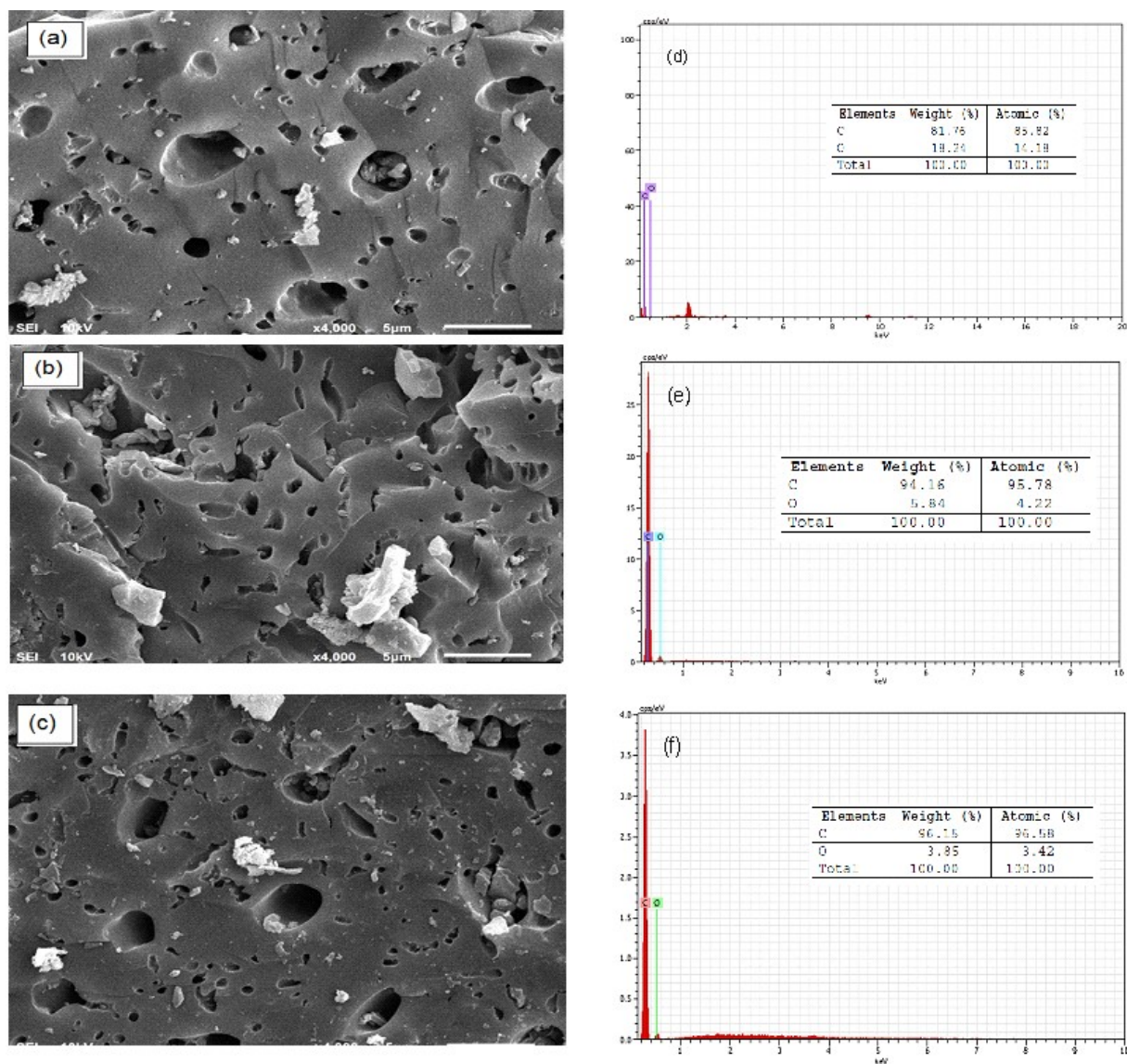


Fig.-2: SEM-EDX of (a,d) Candlenut Shell Carbon, (b,e) ACp-CS , and (c,f) ACC-PS

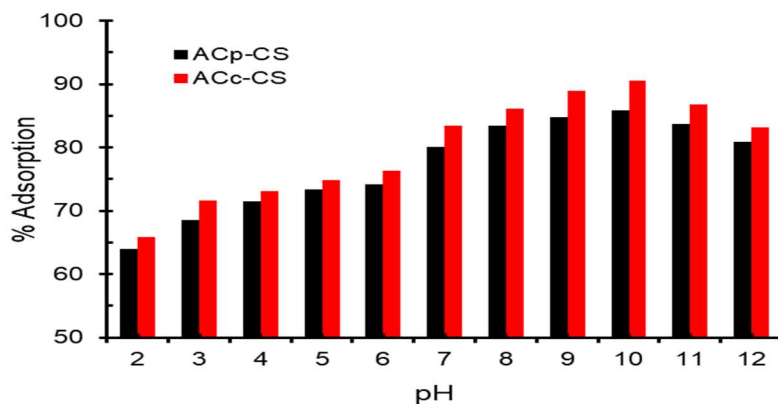


Fig.-3: Impact of pH on the Percentage of MBe adsorbed by ACp-CS and ACC-CS

It may be stated from Fig.-4 that the MBe adsorption by the ACp-CS and ACc-CS adsorbents occurred quite rapidly from the first 20 min to reach the optimum time in the range of 80-100 min. After going through 100 min the adsorption began to decline because the adsorbent pores were fully filled so that the adsorbed MBe was released again.

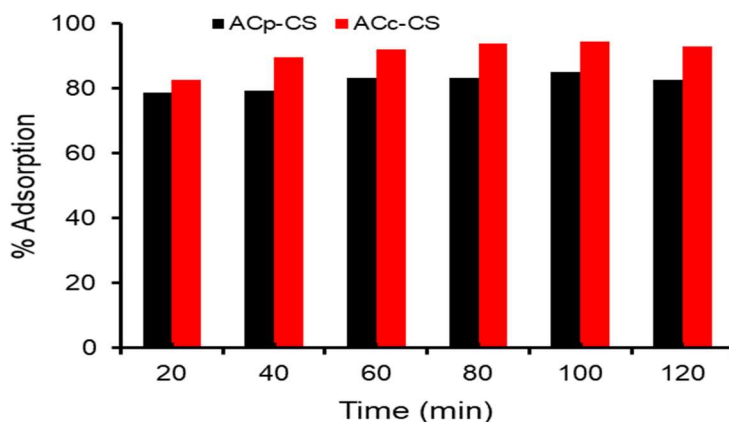


Fig.-4: Influence of Interaction Time in MBe Adsorption (%) to ACp-CS and ACc-CS

The pseudo-second-order (PSO) model (Eq.-3) has been utilized to identify the data contained in Fig.-4 as shown in Table-1 and Fig.-5.³¹

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

As described in Fig.-5, the products of the adsorption kinetics data investigation of MBe on ACp-CS and ACc-CS tended to attend the PSO kinetics model.

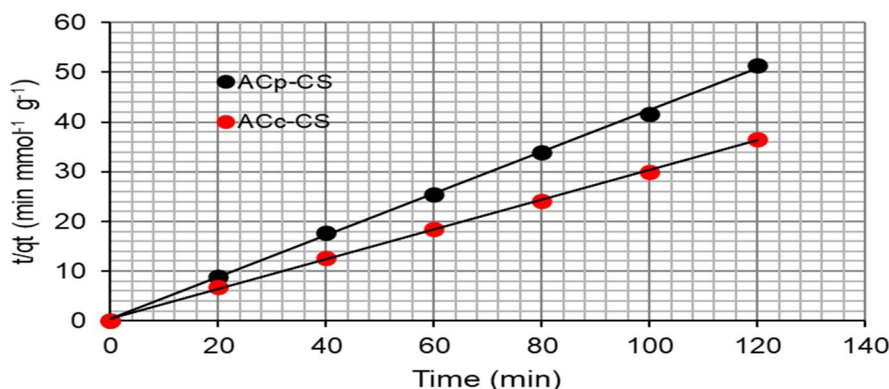


Fig.-5: PSO Kinetics Model of MBe Adsorption by ACp-CS and ACc-CS

Table-1: Kinetic Indicators of the MBe Adsorption upon ACp-CS and ACc-CS

Adsorbent	Kinetic parameters of PSO	
	$k_2 \times 10^{-3} \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	R^2
ACp-CS	15.490	0.999
ACc-CS	6.296	0.991

Adsorption isotherm

The adsorption isotherm pattern of MBe dye absorbed by ACp-CS and ACc-CS was investigated by reacting MBe solution at various concentrations ranging from 0 - 250 mg L⁻¹. It may be stated that the absorbed MBe molecules have increased with the increasing concentration of the interacted MBe molecules (Fig.-7). The adsorption of MBe molecules raises harshly at poor equilibrium concentrations and slowly raises at upper concentrations, which indicates that ACp-CS and ACc-CS have a high adsorption affinity for MBe molecules. The models of adsorption isotherms were known to play an important role in representing the distribution between the solution and solid phases. In order to observe the models of

adsorption isotherms, the adsorption isotherm model of Langmuir (AIML) (Eq.-4) and Freundlich (AIMF) (Eq.-5) can be used to analyze the data displayed in Fig.-6 as follows:¹¹

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (4)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

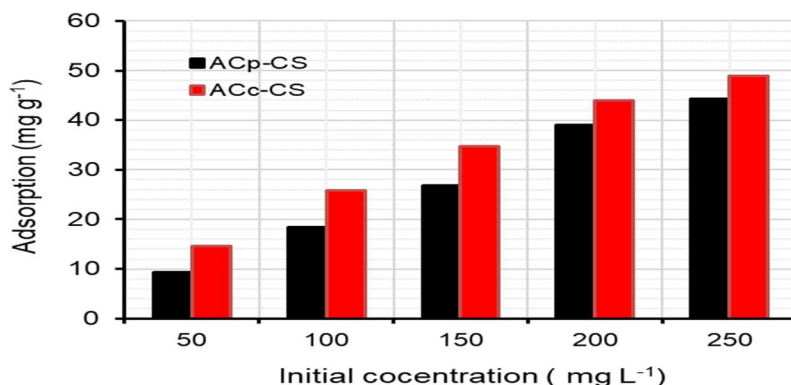


Fig.-6: Graph of the beginning concentration Versus Uptake of MBe dye by ACp-CS and ACC-CS

With C_e and q_e describe the MBe solution concentration and the uptake capacity of MBe under equilibrium conditions in mg L^{-1} and mg g^{-1} , serially. While q_m represents the uptake capacity of the adsorbent monolayer and K_L in L mg^{-1} represents the equilibrium constant for the affinity of the binding site. K_L and q_m are able to result by the plot of $\log 1/q_e$ against C_e as the linear equation, which will produce a straight line accompanied by $1/q_m K_L$ as the slope and $1/q_m$ as the intercept. K_F and n are the capacity factor and the intensity factor of adsorption, serially.³² Next, the plot of $\log q_e$ against $\log C_e$ is going to yield K_F and the exponent n .

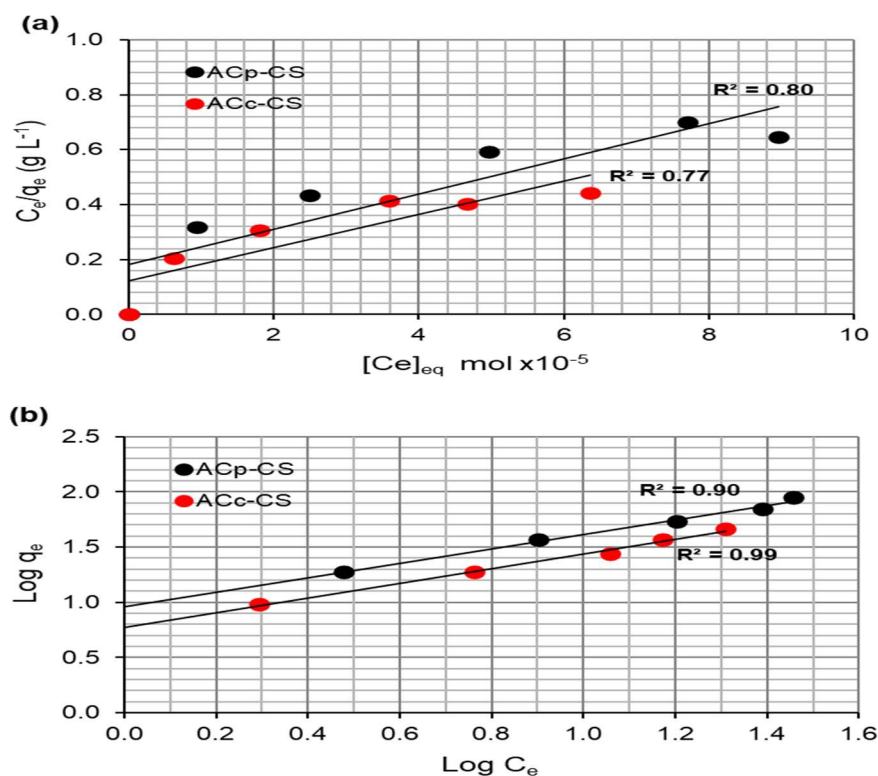


Fig.-7: Graph of MBe Adsorption Linear Equation by ACp-CS and ACC-CS with (a) AIML and (b) AIMF

Table-2: Parameters from AIML and AIMF to the uptake of MBe upon ACp-CS and ACC-CS

Adsorbent	q_{exp} (mg g ⁻¹)	AIML			AIMF		
		q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	K_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	n	R^2
ACp-CS	44.269	49.899	1.560 x 10 ⁻⁴	0.802	4.602 x 10 ⁻⁵	1.531	0.992
ACC-CS	45.932	53.043	1.658 x 10 ⁻⁴	0.774	5.980 x 10 ⁻⁵	1.508	0.993

From the results of the adsorption data analysis using the AIML and AIMF as described in Fig. 7 and presented in Table-2, it can be stated that the MBe adsorption parameters by ACp-CS and ACC-CS show the linear equation regression coefficient (R^2) of the AIMF is bigger than the AIML for MBe molecules adsorption. This indicates that the MBe adsorption isotherm by the two adsorbents is more in accordance with AIMF. The AIMF describes an empirical equation taken for multilayer adsorption and heterogeneous system.³³ The AIMF constant (n) of the MBe adsorption by ACp-CS and ACC-CS (Table-2) has a value more than 1, this denotes that MBe adsorption on ACp-CS and ACC-CS is favorable in this research.³³ The adsorption of MBe on both adsorbents not only occurs at the active site on the adsorbent surface, which is homogeneous (monolayer) but is more likely to occur reversibly on heterogeneous surfaces (multilayer layers), which originates from the pores or cavities of activated carbon from the shell of candlenut.³⁴ Thus, activated carbon from the candlenut shell is a very potential material to be applied as an adsorbent to absorb dyes such as MBe in liquid waste before being released into the surrounding.

CONCLUSION

The preparation of activated carbon from candlenut shells which was physically activated at 700 °C and followed by chemical activation using 10% zinc chloride solution, has been successfully carried out. The adsorption data investigation showed that the MBe dye solution adsorbed on the two activated carbons follows the adsorption isotherm model of the PSO and AIMF. Both adsorbents from the shells of candlenut, which were physically and chemically activated, were effective in absorbing MBe dye in solution under 0.1 g adsorbent at pH 10 and interaction time of 100 min with an initial concentration of MBe 250 mg L⁻¹, each absorbing MBe with an amount adsorbed 44.269 and 45.932 mg g⁻¹. Activated carbon from the candlenut shell is very potential to be applied as an adsorbent to absorb dyes in liquid waste before being discharged into the environment.

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