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Synthesis Activated Carbon/Chitosan/Pectin Composite as Methylene Blue Adsorbent

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Abstract. Composite of activated carbon/chitosan/pectin synthesized using $CaCl_2$ as a crosslinker and used for Methylene Blue (MB) adsorption. Activated carbon was prepared from water hyacinth, blended with pectin and chitosan to form a polyelectrolyte complex (PEC) composite. Composite beads have been synthesized by dissolving activated carbon and pectin in distilled water in the mass ratio of 0.5:2 then dripped in 2% (w/w) chitosan hydrosol with 2 % (v/v) acetic acid solution using $CaCl_2$ 0.5 M. The composite was characterized by FTIR spectrophotometer and MB concentration was measured by visible spectroscopy. Herein, the optimum pH adsorption, MB concentration, adsorption capacity were determined and the isotherm adsorption model was investigated. The adsorption of MB was optimum at pH 7 and concentration of 125 mg/L with the adsorption capacity of 83.4 mg/g (MB). The adsorption process tends to follow the Freundlich isotherm model. Therefore, the activated carbon/chitosan/pectin composite is promising to be utilized as the MB adsorbent.

INTRODUCTION

MB is a cationic dye (synthetic dye) that is widely applied in the dyeing process in industrial fields such as paper, cotton, wool, and textile industries [1]. The textile dyeing process produces about 24% of the dye and 6% of the salt used in the dyeing which then enters the aquatic environment as waste. The color of the waste appears due to the presence of chromophore groups in the textile dye. The dyed waste that is disposed of causes decreasing water quality then impacts on the degradation of environmental quality and human health [2]. Hence, efforts are needed to reduce the concentration of dye, one of which is by adsorption of dye with adsorbents [3].

Adsorption is an effective method of separating a particle of a substance, either in the form of ions, atoms, or molecules in an aqueous system. In the adsorption process, activated carbon is usually used because it has very good adsorption effectiveness for organic compounds [4]. This is because activated carbon has pores that can absorb dye [5]. The use of water hyacinth plant waste as activated carbon has been widely carried out and can be used as a dye adsorbent [6]. The weakness of activated carbon adsorbents is the low absorption of polar components [7]. It has triggered research to modify activated carbon by combining activated carbon with other materials.

Recently, it has been reported about the fabrication of a composite material consisting of activated carbon and a bio-composite for use as an adsorbent for the removal of cationic dye such as MB. Composite synthesis of activated carbon combined with chitosan and alginate can be used as adsorbents for MB and methyl violet 2B [8]. Chitosan is polycationic and alginate is polyanionic, based on the formation of a polyelectrolyte complex (PEC) the two polymers can interact through self-electrostatic interactions between the carboxyl group of alginate and the amino group of chitosan [9–11]. The presence of alginate in alginate-chitosan PEC could increase the swellability and physical instability in a high pH environment [12]. This limitation can be overcome by replacing alginate with other polyanionic such as pectin. Similarly, PEC can be formed by combining chitosan and pectin [13].

The utilization of chitosan-pectin PEC as a fabrication medium for activated carbon has never been reported. In this study, chitosan-pectin PEC will be fabricated with activated carbon using CaCl2 as a crosslinker to form a composite bead. Therefore, the main objective of this research was to explore the potential of activated carbon-chitosan-pectin composite beads as an adsorbent for MB dye. Optimization of adsorption conditions such as pH as well as dye concentration was carried out. Adsorption capacity and adsorption isotherm model were also determined.

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MATERIALS AND METHODS

Chemicals

Water hyacinth was obtained from Batujai dam in Lombok Tengah Indonesia. Chitosan was 95% deacetylated from crab shell and pectin was from citrus peel galacturonic acid ≥74.0 % (dried basis purchased from Sigma (St. Lois, USA). Other chemicals of analytical grade were supplied by Merck including MB, calcium chloride, sodium hydroxide, acetic acid, hydrochloric acid, and ethanol absolute.

Instrumentation

The equipment used in this research were pH meter (pH Smart Sensor AS218), magnetic stirrer (Memmert), centrifuge (Thermo Scientific SL 16R), and freeze dryer (Martin Christ Alpha 1-2 LDplus). Characterization of the functional groups of the activated carbon/chitosan/pectin composite beads was detected by Fourier transform infrared spectroscopy (FTIR) (FTIR-IR 1600 Perkin Elmer Co Japan) at 4000–500 cm^{-1} wavelength. The concentration of dye was analyzed by visible spectrophotometer (Thermo-scientific 20D).

Work Procedures

Synthesis Activated Carbon

Water hyacinth samples were cleaned and then dried. The sample was then oven-dried at 110 °C for 24 h and then blended. Samples that have been dried are then carbonized in a furnace at a temperature of 600 °C for 1 h. The carbon was then activated with 0.1 M HCl soaked for 24 h. The sample was filtered then the activated carbon was neutralized with 0.1 M NaOH then rinsed with distilled water. Then it was dried in an oven at 110 °C for 1 h.

Synthesis of the Activated Carbon/Chitosan/Pectin Bead

Composite beads have been synthesized by dissolving activated carbon and pectin in distilled water in the mass ratio of 0.5:2 with stirring at 400 rpm using a magnetic stirrer for 24 h to form a homogeneous mixture. Then dripped in 2% (w/w) chitosan hydrosol with 2 % (v/v) acetic acid solution using $CaCl_2$ 0.5 M by stirring at 400 rpm and allowing it to dissolve overnight (12 h) to form beads. The activated carbon/chitosan/pectin bead was neutralized with 0.1 M NaOH and rinsed with distilled water. The composite bead was placed in a freeze dryer for 24 h then further use.

Effect of pH

A series of dye solutions containing 20 mg/L MB in buffer solutions were prepared with pH range of 4–11. Immediately, 10 mL of series dye solution was put into erlenmeyer and added 0.001 g of activated carbon/chitosan/pectin bead powder. Shaking at a speed of 200 rpm was conducted for 30 min at room temperature. The solid material was filtered and the filtrate dye solution was analyzed with a visible spectrophotometer at 630 nm.

Effect of Dye Concentration

The effect of dye concentrations was investigated in 50, 75, 100, and 125 mg/L. Into the series of dye solution, 0.001 g of activated carbon/chitosan/pectin bead powder with optimum pH was added as obtained from the previous experiment. Shaking at a speed of 200 rpm was conducted for 30 min at room temperature. The solid material was filtered and the filtrate dye solution was analyzed with a visible spectrophotometer at 630 nm.

Isotherm Model for the Adsorption of MB Dye

Determination of the isotherm model for MB is used adsorption data based on differences in concentration at the optimum pH. In this study, the Langmuir adsorption isotherm and the Freundlich adsorption isotherm were used. The Langmuir equation is based on the assumption that adsorption occurs in a monolayer, reversible manner and is expressed in Eq. 1 and 2.

$$Q_e = \frac{Q_m \times K_L \times C_e}{(1 + K_L C_e)} \quad (1)$$

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (2)$$

Where Qe is the amount of adsorbed substance (mg/g), Ce is the adsorbate concentration (mg/L), Qm is the maximum adsorption capacity (mg/g) and K is the Langmuir constant. The Freundlich equation assumes that adsorption occurs in a multilayer and heterogeneous adsorbent surface. Ratio x/m, represent the amount of adsorbate by the adsorbent per gram (unit mass). The Freundlich isotherm equation is expressed in Eq. 3 and 4

$$Q_e = \frac{x}{m} = K_f \times C_e^{1/n} \quad (3)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

RESULTS AND DISCUSSION

FTIR Spectra of Activated Carbon/Chitosan/Pectin

FTIR analysis was used to identify several characteristic functional groups of the activated carbon/chitosan/pectin composite beads. The FTIR spectra of the activated carbon/chitosan/pectin composite beads are shown in FIGURE 1.

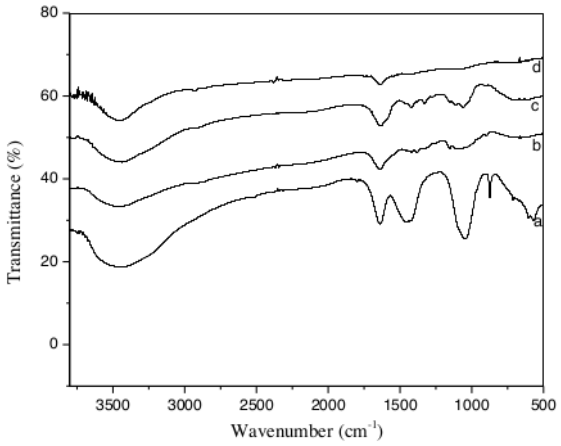


FIGURE 1. FTIR spectra for (a) activated carbon, (b) chitosan, (c) pectin, and (d) activated carbon/chitosan/pectin composite bead

FIGURE 1. shows that there is absorption at the wavenumber (cm^{-1}): 3449 (OH group from activated carbon), 1642 (C = C), 1045 (CO), and an absorption band appears below 1000 cm^{-1} which indicates the presence of residual activator [14]. Modified activated carbon peaks shifted from 1642 to 1640 cm^{-1}. The appearance of the active group –OH and residual activator can indicate that the carbon has been activated. Interaction of carboxylic acid and amine groups in PEC composite may give absorption at the wavenumber (cm^{-1}): 1640 which shows the interaction of the $-NH_3^+$ group from chitosan and –COO from pectin [15]. The appearance of the absorption band in the formed activated carbon/chitosan/pectin composite bead and the decrease in the absorption intensity at the wavenumber indicates the electrostatic interaction between the carbon-carbon double bond group of activated carbon, the carboxylate group of pectin, and the protonated amine of chitosan.

Effect of pH

One important aspect in determining the optimum condition of the adsorption is the selection of pH. The effect of pH on the MB dye adsorption of the activated carbon/chitosan/pectin composite beads powder was studied at the pH range of 4–11. The relationship curve between the amount of MB dye adsorbed and various pH is shown in FIGURE 2.

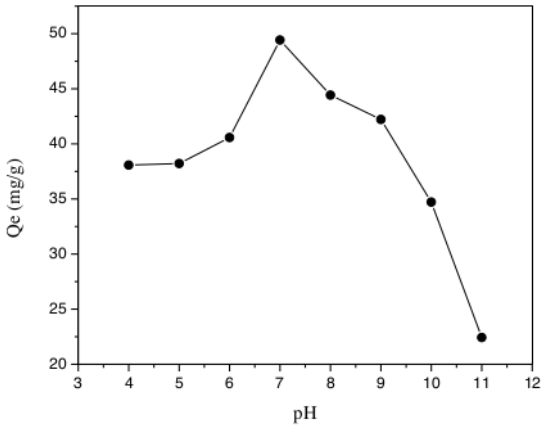


FIGURE 2. The relationship curve between pH and adsorption capacity

FIGURE 2 shows that the adsorption capacity increases with increasing pH solution. However, after pH 7, the adsorption capacity decreased, especially a significant decrease at pH 9–11 due to a decrease in the concentration of the solution due to the addition of excess NaOH solution to increase the pH of the solution. In a previous study [13] it was shown that the pectin-chitosan composite made in distilled water with a pH of zero net proton charge (pH_{zpc}) had a pH close to 4.7. The pH_{ZPC} value has an important effect in interpreting the interactions that occur on the surface of the adsorbate material, especially for charged adsorbate species when the adsorption mechanism tends to occur due to electrostatic interactions [16]. At a high pH value ($pH > pH_{ZPC}$), the surface of the adsorbent has a negative charge so that it can increase the adsorption of the dye molecules due to the electrostatic attraction between the cationic dye molecules and the surface of the adsorbent. At low pH values ($pH < pH_{ZPC}$), the adsorbent surface has a positive charge, the expected trend is a decrease in the adsorption of dye molecules due to electrostatic repulsion between the adsorbent surface and cationic dye molecules [17]. In this study, the optimal capacity of the activated carbon/chitosan/pectin composite beads powder at pH 7 was 49,429 mg/g (MB). At pH near neutral, chitosan has the dominant form $–NH_2$. Overall the increased interaction between composites and cationic dyes was due to the presence of $–NH_2$, -OH and –COO- groups on the surface of the activated carbon/chitosan/pectin composite beads powder [8].

Effect of Dye Concentration

The dye concentration of the solution is one of the factors that affect the adsorption process. The effect of dye concentration on the MB dye adsorption of the activated carbon/chitosan/pectin composite beads powder was studied at the concentrations of 50, 75, 100, and 125 mg/L. The relationship curve between the amount of MB dye adsorbed and various dye concentrations is shown in Fig. 3.

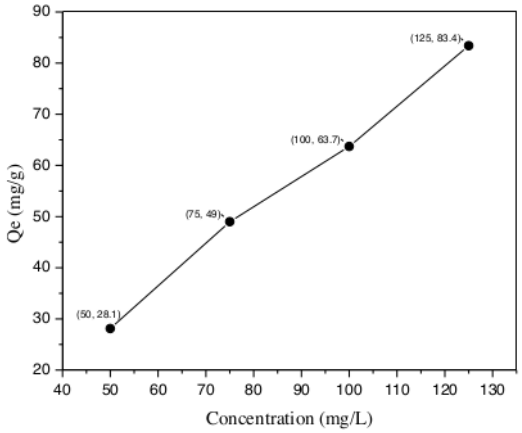
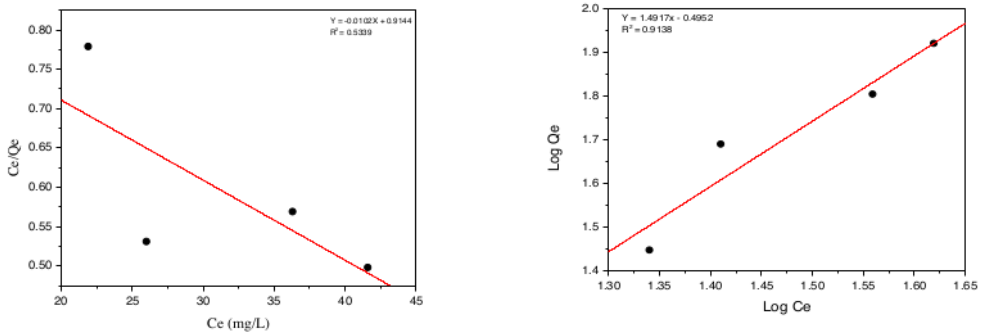


FIGURE 3. The relationship between dye concentration and adsorption capacity

Based on FIGURE 3, the results showed that the MB solution at a concentration of 125 ppm showed the results where the most adsorbed MB was 83.4 mg/g. The lower the concentration of the MB solution, the lower the adsorption rate of the adsorbent. In this case, the adsorption limit by the adsorbent which describes the saturation of the adsorbent of activated carbon/chitosan/pectin against the adsorbent of dye molecules in the solution is not visible. This is related to the molecular collision theory, which states that when the concentration of MB is increased, more molecules collide and interact with the adsorbent, thereby increasing the adsorption capacity value. The chance of the adsorbate interaction with the activated site of the adsorbent will increase with an increasing number of MB dye molecules in the solution [18].

Isotherm Model for the Adsorption of MB Dye

The adsorption isotherm was carried out to describe the process and the mechanism formed. The adsorption isotherm shows the state of the adsorption molecules distributed between the solid phase and the liquid phase when the adsorption process reaches an equilibrium state. The study of adsorption isotherms refers to the well-known model of two isotherms (Langmuir and Freundlich) carried out at different temperatures. The type of adsorption can be determined by testing the linear regression equation of the Langmuir adsorption isotherm and the Freundlich isotherm. The Langmuir isotherm was determined by following equations 1 and 2. The curve of the Langmuir adsorption isotherm equation in FIGURE 4a was obtained by plotting Ce (ppm) and Ce/Qe. The Freundlich equation was determined by equations 3 and 4. The curve of the Freundlich adsorption isotherm equation in FIGURE 4b was obtained by plotting the log Ce and log Qe.



(a) Langmuir isotherm model (b) Freundlich isotherm model

FIGURE 4. Isotherm model for the adsorption of MB dye solution

The adsorption isotherm Langmuir model supports the adsorption process occurring at certain homogeneous sites on the adsorbent surface and has been successfully used in monolayer adsorption processes. And the adsorption isotherm Freundlich model supports the adsorption process occurring at surface heterogeneity and the adsorption process occurring at sites with different adsorption energy levels [17]. The application of the isotherm equation is compared by assessing the correlation coefficient, R^2. Based on FIGURE 4a, the curve of the Langmuir isothermic equation above shows that the adsorption of MB dye on the composite gives a degree of linearity (R^2) of 0.5339, while in FIGURE 4b. the graph of the Freundlich adsorption isothermic equation shows a degree value (R^2) of 0.9138. The adsorption isotherms studied in this research are Langmuir and Freundlich isotherms. A summary of the adsorption isotherms (Langmuir and Freundlich model) calculation can be seen in Table 1.

TABLE 1. The Summary of Langmuir and Freundlich isotherm parameters for MB dye

Model	Persamaan	R^2	Q_m	K_L	K_f	N
Langmuir	Y = -0.0102x + 0.9144	0.5339	-98.039	-0.0111	-	-
Freundlich	Y = 1.4917x – 0.4952	0.9138	-	-	0.31974	0.67037

To determine the equilibrium model, it is possible to see the value of the degree of linearity (R^2) which is close to the value 1. So it can be assumed that the adsorption isotherm in this study follows the Freundlich isotherm model and same as the results of previous studies [8]. In Freudlich's model, the values of K_f and n show the balance between adsorbent and adsorbate. If the resulting value is positively charged, it indicates that equilibrium exists and occurs. However, if the value is negative, then there is no equilibrium between the adsorbent and the adsorbate. The K_f value obtained is 0.31974 L/g. While the value of the adsorption intensity (n) is 0.67037. The result is positive, so there is an equilibrium.

CONCLUSIONS

Based on the explanation above, it can be concluded that the complex polyelectrolyte composite made of activated carbon combined with chitosan and pectin has been characterized by FTIR and gives rise to absorption at a wavenumber of 1640 cm^{-1}. The ability of this composite as an optimum MB adsorbent at pH 7 and a concentration of 125 mg/L with an adsorption capacity of 83.4 mg/g. This composite adsorption isotherm model follows the Freundlich adsorption isotherm model. Hence, the activated carbon/chitosan/pectin composite is an efficient adsorbent for removing MB from wastewater.

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PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6

PAGE 7

PAGE 8