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## Modification of corn stalk using citric acid as biosorbent for methylene blue and malachite green

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**Abstract.** corn stalks are effective adsorbent for methylene blue (MB) and malachite green (MG). In this research, we modified corn stalks used citric acid. The adsorption process of MB and MG by corn stalks illustrates the suitability of pseudo second-order. The Langmuir isotherm is also describe in the data on adsorption of MG. MB and MG adsorption on corn stalks was confirmed by infra-red (IR) spectroscopy and showed that the intensity peak  $1734\text{ cm}^{-1}$  decreases. It indicated that the interaction between adsorbent and adsorbate involved the ester functional group.

### 1. Introduction

Dyestuffs produced from industry are generally non-biodegradable organic compounds. Dyestuffs can cause environmental damage especially the aquatic environment [1,2]. Dyes have been widely used in various industries such as textiles, leather, food, coloring and cosmetics [2,3]. Methylene blue (MB) is a difficult color to describe and this compound is toxic, causes genetic mutations and has an effect on reproduction [4]. Malachite green is the most widely used dye for coloring cotton, wool, fiber, jute and paper. Malachite green (MG) will attack human digestion if it consumes fish contaminated with these substances and has the potential to cause tumor [5]. In other mammals, malachite green are also carcinogenic and cytotoxic [6].

Corn in Indonesia is one of the staple foods in several regions of Indonesia. The average corn crop production in Indonesia based on data from the Central Statistics Agency (BPS) and the Directorate General of Food Crops reached 18.3 million tons / year. The biggest component in corn stalks is about 40% cellulose [7]. Increasing the adsorption capacity can be done by modifying the adsorbent. Citric acid is one of the modification materials which is expected to be able to increase the number of active groups that have an important role in the adsorption process. Ramos, et al., [8] in their research used citric acid to modify corncobs. The results point to an increase in the peak intensity of the ester group, followed by an increase in adsorption capacity. Several studies have suggested that the presence of modification can increase the adsorption capacity, such as corn stalks by NaOH and polyacrylic acid [9], cocoa pods by  $\text{HNO}_3$  [10], straw by acetic acid and citric acid. Based on the above study, in this study corn stalks modified using corn stalks and studied in (a) kinetics adsorption, and (b) isotherms adsorption. Besides that characterization of functional groups was carried out using infrared (IR) spectroscopy and morphological particle characterization using scanning electron microscopy (SEM) and optical microscopy.



## 2. Methods and Experiments

### 2.1. Preparation and Demineralization of corn stalk using 0.1 M HCl

Dried corn stalks was grinded and sieved to  $\pm 100$ -200 mesh. Then the cornstalk samples were immersed using 0.1 M HCl until completely submerged for 24 hours, and then samples washed with distilled water until it is free of  $\text{Cl}^-$  ions. The existing of  $\text{Cl}^-$  ions was detected with  $\text{AgNO}_3$ . Furthermore, the corn stalks are dried in an oven at  $60^\circ\text{C}$  for 24 hours.

### 2.2. Modification of Corn Stalks using Citric Acid

Corn stalks biosorbent is taken 13 grams and soaked in 250 mL of citric acid solution with variation concentration: 0.5, 1, 1.5, and 2 M and was heated for 2 hours at  $60^\circ\text{C}$ . Furthermore the solution is separated from the sample of corn stalks. Then the sample of corn stalks is dried in an oven at  $50^\circ\text{C}$  for 24 hours. Modified corn stalks are washed using distilled water to neutral pH. Furthermore, the corn stalks are dried in an oven at  $50^\circ\text{C}$  for 24 hours [8].

### 2.3. The characterization of corn stalk

Characterization of functional groups in corn stalks used IR spectroscopy and recorded at wavenumbers range  $4000 - 400\text{ cm}^{-1}$ .

### 2.4. Adsorption methylene blue and malachite green by biosorbent of cornstalks modified citric acid

The adsorption power of corn stalks biosorbents on methylene blue was determined by inserting 100 mL of 350 mg/L MB or MG into a 250 mL Erlenmeyer containing 0.5 gram of corn stalks biosorbent, then covered with Aluminum foil and then shake sample with a speed of 120 rpm for 24 hours. After that, filtering and centrifugation were carried out for  $\pm 2$  minutes to obtain supernatant solution. The concentration MB or MG was measured using a UV-Vis spectrophotometer at a wavelength of 665 nm for MB and 617 nm for MG. Adsorption capacity can be calculated by the following equation [9] :

$$Q_e = (C_o - C_e) \frac{V}{m} \quad (1)$$

### 2.5. Determination of Adsorption Kinetics

A solution of methylene blue and malachite green was prepared for 350 mg/L each of 100 mL in a 250 mL erlenmeyer. 0.5 gram corn stalks added. Erlenmeyer was covered with aluminum foil and then shake with a speed of 120 rpm with time variations of 1, 2, 3, 4, 5, 18, 20, 24, 48, and 50 hours for MB and 2, 3, 4, 19, 24, and 28 hours for MG at room temperature and repeated three times. Then filtered and the filtrate obtained is adjusted to the optimum pH measurement and dilution is carried out. The empirical model approach used to determine adsorption kinetics is a Lagergen model expressed in equations 2 and 3 [9].

Pseudo-first-order

$$\log(q_e - q_t) = \frac{-k_1 \cdot t}{2.303} \quad (2)$$

Pseudo-second-order

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

Where  $q_t$  is the adsorption capacity at  $x$  time,  $q_e$  is the capacity of adsorption at equilibrium point,  $K_1$  and  $K_2$  are constants and  $t$  is the time.

### 2.6. Determination of Isoterms Adsorption

In this research the isotherms adsorption of MG by modified corn stalk was studied. A solution of 100 mL of MG solution was prepared with various concentrations of 50, 100, 150, 200, 250, 300, 350, and 400 mg/L with the pH set to pH 7 and 12 mL buffer of pH 7 added to 250 mL erlenmeyer. Then put 0.5 gram corn stalks. Erlenmeyer is covered with aluminum foil, then a 120 rpm dish with room temperature and is repeated three times. Then filtered and the filtrate obtained is adjusted to the optimum pH measurement and dilution is carried out.

The Langmuir and Freundlich isotherms adsorption equation were used in this research Langmuir isothermic is determined by following the equation 3 [9] [10] :

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

The Freundlich Isotherms is determined by following the equation 4<sup>th</sup> [9] :

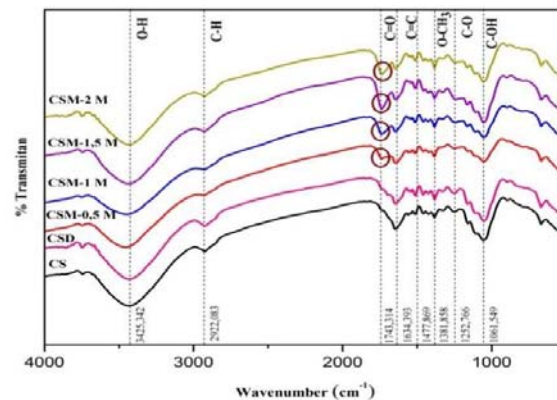
$$Q_e = K_F C_e^{1/n} \quad (5)$$

Where  $Q_e$  is a number of substances that are absorbed at the time of equilibrium (mg/g),  $C_e$  is the concentration of adsorbate at the time of equilibrium (mg/L),  $q_m$  is the maximum adsorption capacity (mg/g), and  $K_L$  is a constant Langmuir (L/mg).  $K_F$  is the Freundlich constant (mg/g),  $n$  is the maximum adsorption capacity (g/L) [9,12].

### 3. Result and Discussion

#### 3.1. IR Spectra Modified Corn Stalks

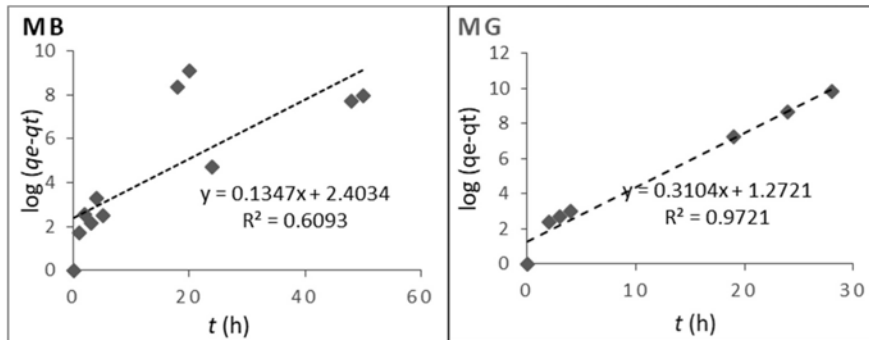
IR spectra of corn stalks (see in Figure 1) shows that corn stalks have OH stretching ( $3425 \text{ cm}^{-1}$ ), CH stretching ( $2922 \text{ cm}^{-1}$ ), aromatic C = C ( $1634$  and  $1477 \text{ cm}^{-1}$ ), O-CH<sub>3</sub> bending ( $1381 \text{ cm}^{-1}$ ), CO stretching ( $1252 \text{ cm}^{-1}$ ), and C-OH ( $1061 \text{ cm}^{-1}$ ). Corn stalks modified with citric acid 0.5; 1; 1,5; and 2 M has a new peak at wave number  $1743 \text{ cm}^{-1}$  indicated the presence of C = O esters in the biosorbent. It related to the interaction between cellulose in corn stalks with citric acid produces ester groups [8,9]



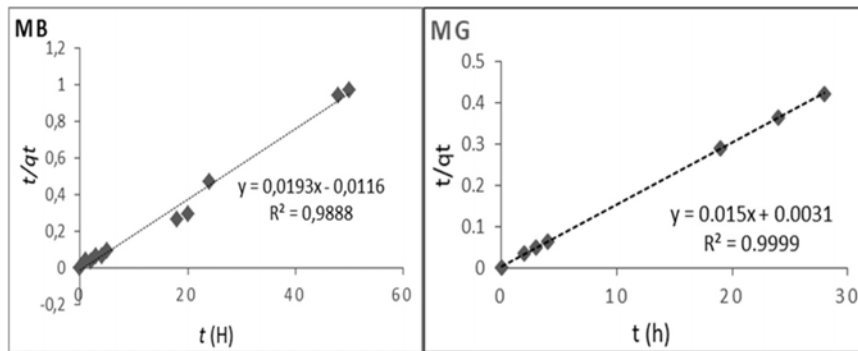
**Figure 1.** Infrared spectra of corn stalk (CS), after demineralization (CSD), corn stalk modified citric acid 0,5 M (CSM-0,5 M); modified citric acid 1 M (CSM- 1 M); modified citric acid 1,5 M (CSM-1,5 M); modified citric acid 2 M (CSM-2 M).

#### 3.2. Adsorption Kinetic

The results of kinetic model test was shown in Figure 2 and 3. For MB adsorption, The R value of pseudo-second-order (0,988) is higher than pseudo-first-order (0.6093). It was indicated that the adsorption kinetic for MB adsorption follow pseudo-second-order. For MG adsorption, The R value of pseudo-second-order (0,999) is higher than pseudo-first-order (0.9721). But the difference of R value is very slightly.



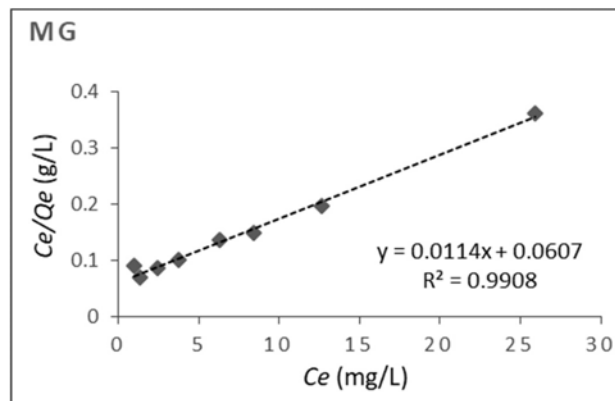
**Figure 2.** Pseudo-first-order model



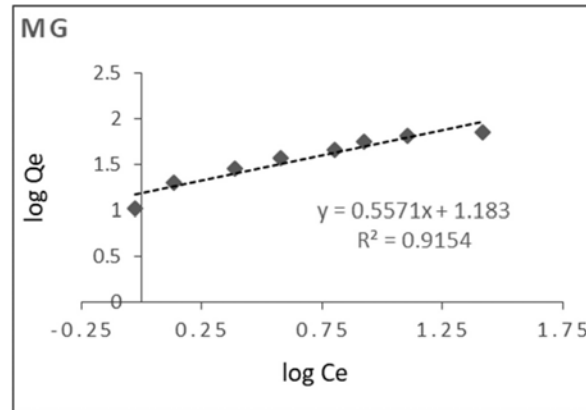
**Figure 3.** Pseudo-second-order model

3.3. Adsorption Isotherm

The type of MG adsorption was studied using Langmuir and Freundlich isotherm equation (see in Figure 4 and 5). Based on the result *R* in Figure 4 and 5 that *R* value for Langmuir isotherm model (0,9908) is higher. It indicated that the MG adsorption follows the Langmuir adsorption isotherm. The Langmuir isotherm assumes that the adsorbent has a monolayer surface to adsorb the adsorbate [11]. So the adsorbent only have one active side on the surface that adsorb just only one adsorbate molecule. The type of adsorption on Langmuir isotherm adsorption can be classified as chemical adsorption (chemisorption).



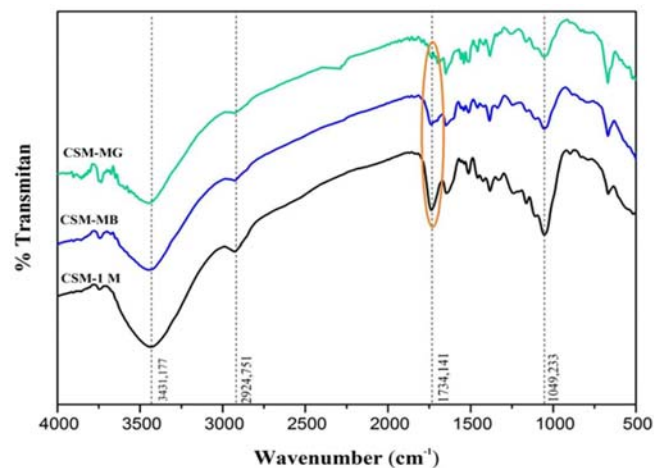
**Figure 4.** Plot the Langmuir Isotherm for MG adsorption



**Figure 5.** Plot the Freundlich Isotherm for MG adsorption

#### 3.4. IR Spectra Before and After Adsorption

Figure 6 shows the IR spectra of corn stalks before and after adsorption. As can be seen that the intensity of peak at wave number  $1734\text{ cm}^{-1}$  (peak ester group) decreases after the adsorption process. It corresponded to the interaction between the ester groups on the adsorbent with the cation on the adsorbate [8]. Interactions that occur on the surface of corn stalks are assumed to be covalent bond interactions and Van der Waals force interactions.



**Figure 6.** Infrared spectra of corn stalk (CS), after adsorption Methylene Blue (CSM-MB), after adsorption Malachite Green (CSM-MG)

#### 4. Conclusion

Corn stalk has the potential as a natural adsorbent that can reduce the pollution of colored liquid waste. The MB and MG adsorption kinetics are more in line with the second order equation. MG adsorption follow the Langmuir isotherm that indicated that the adsorption process is chemisorption.

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