α-keratin/Alginate Biosorbent for Removal of Methylene Blue on Aqueous Solution in a Batch System

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Abstract. Methylene Blue (MB) is a cationic dye which is commonly used in textile industries for coloring agent. The presence of MB in water caused some negative effect on the environment and human health. Many common technologies such as membrane filtration, electrophoresis and adsorption have been widely employed for removal of MB in water, but the adsorption technique still has advantages than the others. In this study, removal of MB used a biosorbent α-keratin/alginate (KA). The biosorbent KA was prepared by using the encapsulation technique in CaCl2 2 % (w/v) solution. The biosorbent was characterized by Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM). The effect of composition of α-keratin and alginate, the pH of solution and contact time on the adsorption were investigated. The optimum adsorption of MB in aqueous solution was found at the composition of α-keratin and alginate of 1:2 (w/w), the pH at 5.0 and contact time at 4 hours. The adsorption of MB on KA biosorbent was comparatively higher than α-keratin and alginate only. Adsorption of MB dyes in aqueous solution followed the Langmuir adsorption isotherm, and the dynamic adsorption model could be described through a pseudo-second order kinetics.

1. Introduction
Methylene Blue (MB) is the most cationic dyes used for industrial applications such as a textile, printing, and plastics industries. This compound has complex aromatic molecular structure so the compound is stable and difficult to biodegradation in nature and dangerous for the environment [1,2]. Besides, the contamination of MB dyes is dangerous to the environment, the dye contaminants are also dangerous to human life. It can cause irritation of the gastrointestinal tract if ingested, causing cyanosis if inhaled, and irritation of the skin if touched by skin [3]. Therefore, it is necessary to remove the MB dyes from the industrial wastes. Many common methodologies such as membrane separation [4], flocculation-coagulation [5], aerobic or anaerobic treatment [6], ion exchange and adsorption have been widely used for removal these dyes from the industrial wastes. But, the remove dyes by the adsorption technique appeared to be an efficient, economical, simple and used for numerous years [7].
Various adsorbents such as activated clay and activated carbon [8], carbon nanotubes (CNT) [9], polymer and zeolite [9] have been reported for these dyes adsorption. But these adsorbent materials have deficiencies such as difficult preparation and availability of the raw materials. Therefore, in this study the adsorbent materials are used based on organic materials with the principle of waste for waste such as α-keratin. The α-keratin sources are as numerous as in chicken feathers and human hair, even the main chemical content of the hair is 88-96 % α-keratin protein [10]. This shows that α-keratin has the potential to be further developed. α-keratin is capable of acting as an adsorbent because it has a binding amino and hydroxyl functional group which causes the cation polyelectrolyte properties to act as ion exchangers and potentially developed as adsorbents such as for removal of cationic dyes [11]. Nevertheless, in very recent work, α-keratin is to difficulty of separating from the waste solution may result in the loss of the adsorbent. These advantages may limit its practical application of α-keratin as an adsorbent in the future.

The material that can be developed as a composite is alginate. Alginate is natural occurring carbohydrate polymer composed of α-L-gulurionate and β-D-mannurionate residues and has hydrophilic [12]. Some study has been reported that alginate can encapsulate activated carbon, CNT, maghemite nanoparticles to create adsorbent to remove dyes from aqueous solutions. However, to our knowledge, no study on preparing alginate encapsulated α-keratin (KA) for adsorption of dyes has been reported.

In this study, biosorbent was synthesized and used to develop new series of calcium alginate encapsulated α-keratin to increase the adsorption capacity and physical properties. Alginate with α-keratin will have cross-reactions in the group which results in the formation of amide bonds between carboxylates and amines so that their physical strength becomes better. The developed materials biosorbent were investigated as potential biosorbent for efficient removal of MB dyes from aqueous solutions.

2. Experimental
2.1 Preparation of α-keratin powder, biosorbents KA and characterization

Hair which obtained from some barbershop in Wonogiri and Surakarta, Indonesia, was washed with detergent in several times and dried in the sun to dry. Then, the hair was milled to fine at 180 mesh. The obtained hair powder was washed with acetone for 30 minutes and filtered through whatman filter paper. Then the residue was dried with an oven at 40 °C for 30 minutes. Cleaned hair powder and technical alginate were weighed with the variations of α-keratin:alginate weight composition are 1:1, 1:2, 1:3, 2:1, and 3:1. Then a mixture of hair and alginate with some composition, dissolved with aquadest of 50 mL. The obtained α-keratin-alginate solution, encapsulated with CaCl₂ 2 % (w/v) solution immersed in ice cubes. The result of the encapsulation of α-keratin-alginate (KA) composite was filtered and dried at 60 ºC for 8 hours. Then, the optimal composition was carried out by adsorption test on MB dyes in aqueous solution at the optimum condition of pH (5.0) and contact time (4 hours). The biosorbent was characterized using FTIR spectra and SEM micrograph. FTIR spectra of biosorbent were recorded in a Perkin-Elmer-238B FTIR spectrophotometer over the wave range 4000-400 cm⁻¹. SEM photographs were taken with JSM 6700F Scanning Microscope to examine the morphology of biosorbents.

2.2 Equilibrium adsorption and kinetics study

Adsorption isotherm, MB dyes solution with various designated concentrations and optimum pH (5.0) was prepared. The biosorbent KA (100 mg) was added into the MB dyes solutions. During the experiments, the mixtures were shaken on a shaker with stirred speed of 200 rpm for 60 minutes. The dye concentrations of final solutions (after 4 hours stirring) were analyzed by Spectrophotometer UV-Vis at λ_{max} 665 nm. All experiment were carried out at 298 K.

Adsorption kinetics, the biosorbent KA (100 mg) was added into the MB dyes solutions while being stirred with a speed of 200 rpm and optimum pH (5.0) at 298 K. The sample solutions were taken at various of time intervals and the concentrations of the dyes were measured by Spectrophotometer.
UV-Vis at $\lambda_{\text{max}}$ 665 nm. The common mathematical model used to describe adsorption kinetics included the Lagergen’s pseudo-first-order (Eq. 1) and pseudo-second-order (Eq. 2).

$$\ln \left( q_e - q_t \right) = \ln q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (1)

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

Where $q_e$ is the equilibrium capacity (mg/g), $q_t$ is the adsorption capacity at (mg/g)t, $k_1$ is the pseudo-first-order kinetic rate constant (min$^{-1}$), $k_2$ is the pseudo-second-order kinetic constant (g/(mg.min)).

3. Result and Discussion

3.1 Synthesis and Characterization

The synthesis of KA biosorbent was carried out by encapsulation method. Encapsulation method is carried out in CaCl$_2$ solution which serves as a crosslinking agent to form a $\alpha$-keratin-alginate composite. The principle of encapsulation is the exchange of Na$^+$ ions from Na-alginate with Ca$^{2+}$ from CaCl$_2$ when dropped into 2% CaCl$_2$ solution, forming a Ca-alginate gel. The illustration of synthesis biosorbent is shown in Figure 1.

![Figure 1. Illustration of synthesis of KA biosorbent](image)

The FTIR spectra of KA, alginate, and $\alpha$ are shown in Figure 2(a). The specific spectrum of $\alpha$-keratin-alginate (KA) biosorbent shows absorption bands at 3423 cm$^{-1}$ (OH stretching), 1639 cm$^{-1}$ (COO$^-$ symmetric stretching). In addition, there is a characteristic absorption of peptide bonds (-CONH-) with three absorption areas which are Amide I, Amide II, and Amide III. The absorption area of Amide I shows the absorption of C=O stretching vibrations at wave numbers 1600 and 1622 cm$^{-1}$, Amide area II shows the absorption of C-N stretching and N-H bending vibrations at wave numbers 1450 and 1420 cm$^{-1}$. Meanwhile, the amide III region indicates the absorption of N-H bending, C-N stretching on O=C-N bonds with wave numbers 1367 and 1300 cm$^{-1}$. In keratin and $\alpha$-keratin-alginate composites, there is also a disulfide group absorption (S=S) in the wave number 1074 and 1038 cm$^{-1}$. The specific of absorption wavenumber proves that the $\alpha$-keratin-alginate composite has been formed. The SEM morphology of KA (Figure 2(b)) shows that alginate is attached to the $\alpha$-keratin surface. This proves that $\alpha$-keratin has been protected by an alginate matrix so that $\alpha$-keratin has a stronger physical resistance to environmental damage and impact on the adsorption process of MB.
3.2 Influence of composition biosorbents, pH and contact time

The composition between α-keratin and alginate needs to be studied because it will affect the density of the resulting composite. The results of composition testing are shown in Table 1. The composition of α-keratin and alginate (1:2) was found optimum results.

Table 1. Influence of composition KA biosorbents to adsorption MB dyes

| α-keratin : alginate | C_i (mg/L) | C_e (mg/L) | mass of biosorbents (mg) | adsorption capacity (mg/g) |
|---------------------|------------|------------|--------------------------|---------------------------|
| 1 : 1               |            | 90.52      |                          | 409.48                    |
| 1 : 2               |            | 30.67      |                          | 469.33                    |
| 1 : 3               | 500        | 140.89     | 50                       | 359.11                    |
| 2 : 1               |            | 170.08     |                          | 329.92                    |
| 3 : 1               |            | 200.28     |                          | 299.72                    |

In addition, the comparison of composition biosorbent, the other parameters influencing the adsorption capacity are the pH of solution and contact time of adsorption process. The result of the influence of pH and contact time to adsorption MB are shown in Figure 3. The optimum pH for KA biosorbent was found to be 6.0 with the maximum contact time at 5 hours for MB dyes adsorption. The effect of pH on adsorption capacity may be discussed on the basis of the nature of the chemical interactions of MB dyes with the biosorbent. The carboxylic (–COOH) from alginate and amino (–NH₂) groups present from α-keratin on the biosorbent are responsible for the binding of MB dyes. At lower pH, may be due to the protons competition with the MB dyes molecules for the adsorption sites. While at the optimum pH, it may be due to the more binding sites formed on the surface KA biosorbent to increase its surface complexation capability.
3.3 Adsorption isotherms and Adsorption kinetics

For the adsorption isotherms study, the Freundlich and Langmuir isotherms were used to fit the experimental data. The results from adsorption isotherms study are given in Table 2. From the experimental results showed that the adsorption process of MB dyes by KA biosorbent follows Langmuir isotherm. This is because the value of $R^2$ obtained is greater than Freundlich isotherm and the value of $q_e$ calculated near the $q_e$ experiment. Langmuir isotherm model assumes that adsorption occurs monolayer on a homogeneous surface. If one side of active adsorption has been filled by the adsorbate then there is no further absorption on the active side so that the adsorbent will reach saturation point when maximum adsorption has been reached.

Table 2. Langmuir and Freundlich isotherm constants for adsorption of MB dyes

| Adsorbent | $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_F$ (L/mg) | $n$ | $R^2$ | $q_e$ experiment (mg/g) |
|-----------|--------------|--------------|-------|--------------|-----|-------|------------------------|
| KA        | 426.68       | 0.0612       | 0.9991| 89.85        | 3.8712 | 0.8714 | 400.58                 |
| Alginate  | 312.83       | 0.0246       | 0.9755| 35.87        | 2.6123 | 0.7143 | 342.15                 |

The reaction kinetics model which studied in this research is the pseudo-first order and pseudo-second order kinetics model. The model of adsorption kinetics is given in Table 3. From the calculation results show that the adsorption of MB dyes follows the pseudo-second order. the second order kinetic model assumes that the rate-limiting step may be chemical adsorption [13].

Table 3. Pseudo-first order and second order rate constants for adsorption of MB dyes

| Adsorbent | $q_e$ (mg/g) | $k_1$ (hour$^{-1}$) | $R^2$ | $q_e$ (mg/g) | $k_2$ (hour$^{-1}$) | $R^2$ | $q_e$ experiment (mg/g) |
|-----------|--------------|---------------------|-------|--------------|---------------------|-------|------------------------|
| KA        | 33754.02     | 3.7353              | 0.7930| 460.54       | 0.0182              | 0.9977| 459.75                 |
| Alginate  | 3214.45      | 2.7634              | 0.5339| 316.23       | 0.0099              | 0.9925| 306.27                 |

4. Conclusion

In this study, α-keratin-alginate (KA) were developed as biosorbent and characterized using FTIR spectra and SEM micrograph. Adsorption of MB dyes on KA was investigated using batch systems. The data demonstrated that the biomaterials are effective adsorbents for the removal of MB dyes from aqueous solution. The adsorption of MB dyes depended on the composition of α-keratin and alginate,
pH of the solution and contact time of adsorption process. The equilibrium adsorption data were correlated well by Langmuir isotherm equations the adsorption kinetics followed pseudo-second order kinetics model. So, the biomaterial has potential to be developed as a biosorbent material of MB dyes adsorption.

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