Adsorption of Crystal Violet Dye Using Zeolite A Synthesized From Coal Fly Ash

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Abstract. Adsorption of Crystal Violet (CV) dye using zeolite A synthesized from coal fly ash (ZA) has been done. Effect of pH, contact time, and the initial concentration of dye adsorption was studied in this adsorption. Model experimental of adsorption isotherms and adsorption kinetics were also studied. The adsorption is done in a batch reactor at room temperature. A total of 0.01 g of zeolite A was added to the Erlenmeyer flask 50 mL containing 20 mL of the dye solution of Crystal Violet in a variety of conditions of pH, contact time and initial concentration. Furthermore, Erlenmeyer flask and its contents were shaken using an orbital shaker at a speed of 200 rpm. After a specified period of adsorption, the solution was centrifuged for 2 minutes so that the solids separated from the solution. The concentration of the dye after adsorption determined using Genesis-20 Spectrophotometer. The results showed that the Zeolite A synthesized from coal fly ash could be used as an effective sorbent for Crystal Violet dye. The optimum adsorption occurs at pH 6, and contact time 45 minutes. At the initial concentration of 2 to 6 mg/L, adsorption is reduced from 79 to 62.8%. Crystal Violet dye adsorption in zeolite A fulfilled kinetic model of pseudo-order 2 and model of Freundlich adsorption isotherm.

1. Introduction

The use of coal as a fuel in steam power plants continue to grow, as long with the increasing demand for electricity for various purposes. The burning of the coal not only to produce energy but also produce solid wastes such as fly ash and bottom ash. The amount of the generated fly ash from the coal burning to approximately 7.87% of the coal used [1]. The total coal consumption in Indonesia (new and existing power plant power plant) will reach 87.7 million tons in the year 2015 and 166.2 million tons in the year 2019. The fly ash and bottom ash production will attain 4.8 million tons in the year 2015 and 8.31 million tons in the year 2019 (assumptions 5% from fuel consumption) [2]. If the accumulated fly ash is not used, the waste would cause problems for the surrounding environment and have no economic value. That’s why the need for efforts to cultivate and utilize the fly ash in the various fields. The content of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} in the fly ash, allowing fly ash can be used as raw materials in the synthesis of zeolite A.

Meanwhile, the use of synthetics dyes for industry application continuously increases. The disposal of dye waste into the stream of water cause not only high color intensity but also disrupt aquatic life water accepts it. Waste water containing dye is very difficult to be processed because the dye is an organic compound that is stable, resistant to aerobic decomposition and stable to light [3]. The most
synthetic dye is an aromatic organic compound, soluble and dispersible in water [4]. The presence of dyes in the wastewater is undesirable and potentially inhibiting photosynthesis process [5]. The cationic dyes of Crystal Violet (CV), with C.I 42555, are widely used in the textile dyeing. The dye has a brightness and high color intensity, even at very low concentrations [6]. The disposal of CV into the hydrosphere can lead to environmental degradation. The CV is easily adsorbed fish tissue from the exposure water and reduced metabolism of fish due to leucomoiety, leucocrystal violet [7]. Some studies exhibited carcinogenic and mutagenic effects of the CV in rodents. Therefore the waste water containing dyestuff CV needs to be treated before it is discharged into water bodies.

The various methods have been used for removal of dyes in aqueous solution, either through ion exchange, activated carbon adsorption, membrane technology and coagulation, flocculation, and so on. Although the use of activated carbon obtained the most effective for the removal of dyes, but its use is limited due to high operating costs [8]. Adsorption is considered as the most effective method for the treatment of waste water. The effectiveness of alternative adsorbent to remove the dye has been studied. Zeolite is a once alternative material used as an adsorbent in treatment waste water of the heavy metals, dyes and other organic pollutants. Regarding with isomorphic substitution of Si by Al, the overall surface of the zeolite is negatively charged. The lower of Si/Al ratio of the zeolite, the higher negative charge of the zeolite surface. Zeolite A has a low Si/Al ratio, so that suitable for absorbing the cationic dye, CV. In this research, the adsorption of CV in zeolite A from coal fly ash has been studied. Adsorption was carried out in batch system with a variety of adsorption conditions, namely pH, contact time and initial concentration of the solution. Adsorption isotherms and kinetics models were also studied based on the experimental data obtained.

2. Materials and Methods
In this study, the entire chemical used: the dye Crystal Violet, NaOH, and HCl, are analytical reagent grade, produced E Merck. The tools used include a set of glassware, analytical balance, orbital shaker, centrifuge, universal pH indicator sticks, and Genesis Spectrophotometer.

2.1. Adsorbent
The used adsorbent in this study is zeolite A from coal fly ash of PLTU Suralaya Banten Indonesia. The zeolite A (ZA) was hydrothermally synthesized through a modified alkaline fusion. The synthesis process and characterization of zeolite A has been described in our previous research. The synthesized zeolite A exhibited surface area of 18.998 m²/g and showed the similarity with the commercially zeolite A Wako produced Japan, in the diffraction patterns, SEM image, and IR spectra [9]. Figure 1 showed the diffraction patterns and SEM image of the zeolite A synthesized from fly ash.

![Diffraction patterns and SEM image of synthesized zeolite A](image_url)

Figure 1. Diffraction patterns (a) and SEM image (b) of the synthesized zeolite A [9]. ZA: zeolite A synthesized from fly ash, ZA Wako: zeolite A commercial Wako
2.2 Adsorbate
The used adsorbate in this study is the cationic dye of Crystal Violet (CV), having molecular formula C\textsubscript{25}H\textsubscript{30}N\textsubscript{3}Cl and molecular weight of 407.99 g/mol. Figure 2 shows the molecular structure of the Crystal Violet dye. The stock solution of CV was prepared by dissolving 1 g of CV in 1 liter of demineralized water and stored in glass jars for the further use.

2.3 Adsorption of dye Crystal Violet (CV)
The Crystal Violet adsorption on zeolite A (ZA) was conducted in a batch reactor at room temperature. A total of 0.01 g ZA was added to 20 ml of the dye solution of Crystal Violet in various conditions (pH, contact time and initial concentration) and shaken by using an orbital shaker at a speed of 200 rpm. After the adsorption in the given period is carried out, the solution was centrifuged for 2 minutes at 1000 rpm, so the solids separated from the solution. The concentration of the dye after adsorption was determined using Genesis-20 spectrophotometer, at wavelengths corresponding to the pH condition of each solution.

3. Result and Discussion
3.1 Effect of pH
Previously the adsorption is carried out, firstly determined the maximum wavelength of the CV solution at the different levels of acidity (pH). The results of the measurement of CV absorbance solution show the maximum absorbance occurred at pH 6 and wavelength (\(\lambda\)) 490 nm.

![Figure 3. Adsorption of CV dye at various pH.](image)

FA: fly ash, ZA: zeolite A synthesized from fly ash
The adsorption of CV dye in aqueous solution is performed in orbital shaker 200 rpm during 60 minutes, with the initial concentration of 3 mg/L. The adsorption used the adsorbents of fly ash (FA) 0.1 g and 0.01 g zeolite A (ZA). After the adsorption process, the CV concentration was determined using UV-VIS Spectrophotometer at wavelength 590 nm. The amount of CV dye adsorption at various pH is presented in figure 3. In this figure, it appears that the number of CV adsorbed by zeolite A increases with pH. The maximum adsorption of CV occurred at pH 6. This is in line with the maximum CV adsorption on acacia leaves adsorbent which occurs at pH 6 [7]. Figure 3 also shows that the amount of CV adsorption at the ZA adsorbent is greater than FA adsorbent. This occurs because of the zeolite A have greater electrostatic attraction than fly ash in their interaction with CV cationic dye.

The increase in pH, which means an increase in the concentration of OH⁻, causing the surface of the zeolite A more negatively charged and increasing the electrostatic interaction with cationic dye so that the adsorption of the dye CV increases. In general, for a cationic dye, the adsorption capacity and rate constants tend to increase with increasing pH of the solution [7]. For the subsequent experiments were performed at the optimum adsorption namely at pH 6 and the maximum wavelength of CV 490 nm.

3.2 Effect of contact time
Contact time is an important factor in the adsorption process. In general, the adsorption process runs quickly at the start of contact time and gradually decreases with increasing time of adsorption. In physical adsorption, the adsorbate species are adsorbed in a short contact time. Nevertheless, the adsorption equilibrium can often be achieved within a longer time. The adsorption of CV dye was performed on contact time of 0, 5, 10, 20, 30, 45, 60, 75 and 90 minutes, in the orbital shaker at 200 rpm. The adsorption was carried out at pH 6, the initial concentration of 3 mg/L and using adsorbent 0.1 g FA, 0.01 g ZA. The amount of the adsorption of CV at a variety of contact time (qt) was presented in figure 4.

![Figure 4. Adsorption of CV dye at contact times.](image)

qt FA: adsorption CV at fly ash, qt ZA: adsorption CV at ZA: zeolite A synthesized from fly ash

From figure 4, it appears that the amount of adsorbed CV is increasing with increasing contact time and gradually fixed and reaches a maximum at 60 and 45 minutes respectively to FA and ZA. The result exhibited that the equilibrium adsorption take place at 45 and 60 minutes respectively for zeolite A and fly ash. In the early research, the CV adsorption equilibrium time on BTEA-CTMA-bentonite and bentonite was obtained at 70 minutes [5], while the adsorption CV on acacia leaves at 120 minutes [7]. From figure 4 also appears that the maximum adsorption of Crystal Violet to the adsorbent FA and ZA each other 0.1134 mg/g (17.35%), and 4.2927 mg/g (65.68%). Adsorption CV runs quickly at the start of contact time and gradually reduced and the adsorption rate is relatively constant at the
optimum time (equilibrium). With increasing contact time the active sites present in adsorbent ZA were filled adsorbate CV and diminishing with the passage of the adsorption process. The CV dye adsorption in zeolite A is higher than in the fly ash adsorbent. This happens because the zeolite A have the higher electrostatics attraction than fly ash, due to the surface of the zeolite A more negatively charged.

### 3.3 Effect of initial concentration

To study the effect of the initial concentration, the adsorption of CV was done in orbital shaker at 200 rpm, pH 6, the contact time of 60 and 45 minutes respectively to adsorbent FA and ZA. The initial concentration solution of CV is 1, 2, 3, 4, 5 and 6 mg/L. Adsorption CV at the different initial concentrations was presented in figure 5.

![Figure 5. Adsorption of CV dye at various initial concentration.](image)

FA: fly ash, ZA: zeolite A synthesized from fly ash

Adsorption CV per unit mass of adsorbent increases with the initial concentration, although the percentage of adsorption decreases with increasing initial concentration. At the initial concentration of 1 to 6 mg/L adsorption CV increased from 0.043 becomes 0.2276, and 1.2045 becomes 7.5359 mg/g, respectively to adsorbent FA and ZA. This happens because there is an increase of the concentration gradient driving force with the increase in the initial concentration of the dye [11]. Similar results were obtained that the adsorption CV increased from 7 to 23 mg/g with increasing initial concentrations of 50 to 200 mg/L [7].

### 3.4 Adsorption isotherm of CV

Study of the adsorption isotherm is obtained by variation of the initial concentration of dye CV from 2 to 6 mg/L, at pH 6 and the optimum contact time for adsorbent FA and ZA. Langmuir and Freundlich isotherm models used to describe the color characteristics of adsorption equilibrium CV. Langmuir and Freundlich isotherm constants respectively can be calculated from the slope and intercept the plot between $Ce/qe$ vs $Ce$ and log $qe$ vs log $Ce$, each other from equation (1) and (2).

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]  \hspace{1cm} (1)

\[
q_e = K_F C_e^{1/n}
\]  \hspace{1cm} (2)
The linear curve of Langmuir and Freundlich isotherm models on dye adsorption CV in ZA were presented in Figure 6. Based on the value of slope and intercept in Figure 6, the adsorption isotherm parameters value CV in ZA were obtained, as listed in Table 1.

By comparing the correlation coefficient between the Langmuir and Freundlich isotherm models can be concluded that the Freundlich isotherm models more suitable for adsorption CV in ZA. The maximum monolayer adsorption (qm) obtained is 10.753 mg/g and K_L 7.75 L/mg.

![Figure 6. Model of adsorption isotherm CV in ZA: Langmuir (a) and Freundlich (b)](image)

**Table 1. Parameter of adsorption isotherm model of CV.**

| Adsorbent | Langmuir | Freundlich |
|-----------|----------|------------|
|           | q_m (mg/g) | K_L (L/mg) | R^2 | n | K_f (mg/g) | R^2 |
| ZA        | 10.672 | 7.808 | 0.937 | 2.02 | 4.5 | 0.981 |

The obtained equilibrium factor value, R_L, is 0.06 to 0.02 in range, indicating a favorable adsorption of CV dyes on the adsorbent ZA. In the model of Freundlich isotherm parameters obtained K_f 4.5 and 1/n is 0.494 or n = 2.02. The quantity of 1/n indicate that the adsorption involves a heterogeneous surface and chemical adsorption.

### 3.5 Kinetics of Adsorption of Dyes CV

Kinetics of adsorption of the dye CV solution on the adsorbent zeolite A of fly ash were tested using kinetic model of pseudo-order first Lagergren, as in equation (3) and the pseudo-order second of Ho, as in equation (4).

\[
\log B(q_e - q_t) = \log B(q_e) - \frac{k_1}{2.303}t
\]  
(3)

\[
\frac{t}{q_t} = \left(\frac{1}{k_2 q_e}\right) + \left(\frac{1}{q_e}\right)t
\]  
(4)

The kinetic constants in the linear equation (3 and 4) can be computed from the slope and intercept of plot log (qe-qt) vs. t and t/qt vs. t respectively. The resulted adsorption kinetics curves of CV in ZA
were presented in figure 7. Figure 7 showed plot of \( \ln(qe-qt) \) against \( t \) and \( t/qt \) against \( t \) for adsorption CV in zeolite A, which resulted in a straight line, with \( R^2 \) 0.851 and 0.997 respectively. Of the value of the slope and intercept of figure 7 can be obtained constanta of \( k1, k2 \) and \( qe \) as listed in table 2.

![Figure 7](image)

**Figure 7.** Kinetics of pseudo-first-order (a) and pseudo-second order (b) of adsorption CV on ZA.

| Adsorbent | Pseudo-orde 1 | Pseudo-orde 2 |
|-----------|---------------|---------------|
|           | qe (mmol/g)   | \( k1 \) (min\(^{-1}\)) | \( R^2 \) | qe (mmol/g) | \( k2 \) (g/mmol.min) | \( R^2 \) |
| ZA        | 4.4x10^{-3}   | 0.046         | 0.851       | 10.3x10^{-3} | 38.51         | 0.997       |

Based on the obtained \( R^2 \), it can be concluded that the kinetic model of pseudo-order two is more appropriate to describe the process of adsorption CV dye in ZA. Similar results were obtained that the CV adsorption is best described by kinetics model of pseudo-second order [5, 7]. Although the mechanism of adsorption on zeolites are complex due to the pore structure, surface charge on inside and outside, heterogeneity and the crystal imperfect on its surface, but the zeolite adsorption properties mainly related to its ability as an exchanger ion [12]

### 4. Conclusion

Regarding on the adsorption of Crystal Violet, zeolite A synthesized from fly ash showed adsorption capacity much greater than the fly ash. The adsorption of Crystal Violet depending on the pH and the maximum adsorption occurred at pH 6. The adsorption process is best described by an equation pseudo-orde 2 kinetics. Furthermore, the adsorption equilibrium data fulfilled the Freundlich adsorption isotherm models. Based on these results, can be concluded that zeolite A synthesized from fly ash is an effective adsorbent for Crystal Violet dye in aqueous solution.

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**Acknowledgment**

The authors would like to thank Directorate General of Higher Education (DGHE), Department of National Education Republic of Indonesia for the financial support in Competitive Research Program (Contract Number: 1.5.5/UN37/PPK.3.112014).