Effect of DVB on Adsorption of Methylene Blue using Coply(Eugenol-Strearyl acrylate-DVB)

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Abstract. This research aims to study the effect of divinylbenzene (DVB) on copoly(Eugenol-Strearyl Acrylate-Dvinylbenzene)/Copoly (Eg-SA-DVB) on the adsorption of methylene blue dyes. Variations of DVB ware added as much as 2%, 4% and 6% to the weight of eugenol. Adsorption was carried out by batch method in variations of acidity (pH), contact time and initial concentration of methylene blue. The results showed that the optimum pH of methylene blue dye adsorption ware pH 5.0 for copoly(Eg-DVB-SA) 2% and 6%; while for 4% was pH 3. The optimum adsorption contact time was 60 minutes for copoly(Eg-DVB-SA) 2% and 6%, while for 4% at 50 minutes. Study of adsorption kinetic presented the adsorption of methylene blue dyes using 2%, 4% and 6% copoly (Eg-DVB-SA) adsorbents followed the Langregen kinetic model, pseudo-first order. Study of isotherm revealed the adsorption of methylene blue dyes tends to follow the Langmuir isotherm. The maximum capacity of methylene dyes adsorption using copoly(Eg-DVB-SA) 2%, 4% and 6% were 31.2; 36.2 and 14.7 mg/g, with the adsorption energy 31.1; 33.6 and 31.3 KJ/mol respectively.

1. Introduction

Since the 19th century, synthetic dyes began to take over the role of natural dyes because their production is easier, the price is cheaper, the range of color variations is more high and the ability and stability of coloring is higher [1]. Dyes are organic compounds. The structure of the compound is designed to have resistance to time, exposure to sunlight, water, soap, microbial invasion and oxidizing agents so that it cannot be treated with conventional wastewater treatment processes [2]. Dyes can be classified into several types based on their use namely, acidic (anionic), basic (cationic), dispersive, direct, reactive, solvent, sulfur and vat [3].

Methylene blue (MB) is a synthetic cationic dyestuff with an aromatic amine structure that is often used in the textile industry for coloring leather, mori, cotton and wool fabrics [4]. Prolonged direct contact with MB can cause vomiting, nausea, anemia and hypertension [5]. The increasing level of contamination of dyes in water bodies requires the development of exploration methods of wastewater treatment that can reduce and eliminate levels of contaminants either physically, biologically or chemically [6]. The study of the method of handling waste containing cationic methylene blue (MB) in Indonesia that has been developed is by Susilawati [4] with the adsorption method using active bentonite clay. Dwiasi et al. [7] carried out MB photodegradation in batik waste using the Fe₂O₃-UV-H₂O₂ system. Is Fatimah et.al. [8] adsorbs MB using activated carbon from the melinjo shell. Badriyah and Putri [9] performed MB adsorption with eggsheells. Rizqi and Purnomo [10] tested the biodegradation activity of Daedalea
dickinsii fungi against MB dyes. Saadon et al. [11] used palm ash as an MB dye adsorbent. Latupeirissa et al. [12] carried out MB adsorption using activated carbon from the pecan skin.

Adsorption method is a method that has been widely explored to reduce levels of dyes from water bodies. The study of adsorption in Indonesia is prioritized in the search for adsorbents that are economical, effective, efficient and can be made using natural resources or modified waste [13]. One of these adsorbents can be made from eugenol modifications. Eugenol is a major component of clove oil which is one of the leading products with large commodities in Indonesia [14]. Eugenol has a vinyl functional group that allows it to be modified with other compounds through a polymerization reaction. Previous studies that have been carried out regarding the use of eugenol-based polymers as adsorbents were carried out by Silvianti et al. [13] the event of adsorption of dyes with polieugenol-derived adsorbents can occur because there is the formation of hydrogen bonds between [Fe (OH)]^{2+} with the ─OH group of eugenol.

In this study copoly(Eugenol-Stearil Acrylate-Divinylbenzene) or copoly (Eg-SA-DVB) as adsorbent for methylene blue dye. Eugenol compounds are modified with stearyl acrylate (SA) and divinylbenzene crosslinking agents (DVB), where the addition of DVB crosslinking agents directs the formation of 3-dimensional structured polymers such as nets allowing particles of a size corresponding to the size of the net to be trapped [15]. In addition, the anion carbonyl as active group from the SA monomer and the ─OH group from the eugenol monomer allow copoly (Eg-SA-DVB) to be used as an adsorbent for methylene blue cationic dyes through the formation of hydrogen bonds and electrostatic interactions.

This research studies the adsorption parameters of coply (Eg-SA-DVB) are the influence of pH, contact time and adsorbate concentration; besides also studying the kinetics and isotherms adsorption.

2. Experimental
2.1. Ingredient
All chemical used in research were procured fram E Merck, expect special ones, Copoly(Eg-SA-DVB) 2 %, 4 % and 6 % (synthesis product), NaOH, HCl

2.2. Instrument
Spectrophotometer UV Visible Shimadzu, Spectrometer Fourier Transform Infra Red (FTIR) Shimadzu Type FTIR-8201 PC KBr, Scanning Electron Analysis (SEM) (JEOL JSM 6360 EDX (JED-2200))

2.3. Procedure
2.3.1. Adsorbent Stability Test
A total of 10 mL Copoly (Eg-SA-DVB) was put into the solution with a pH variation at 2, 4, 6, 8 and 10. The mixture was stirred for 2 hours, then filtered. The final mass of the adsorbent is weighed and compared to the initial mass.

2.3.2. Effect of pH on adsorption of methylene blue
Methylene blue with a concentration of 10 ppm of 10 mL each was adjusted to pH 1, 2, 3, 4, 5 and 6 using HCl and NaOH. Then copoly (Eg-SA-DVB) of 5 mg was added to each solution and stirred for 30 minutes. Sample concentrations before and after adsorption were analyzed by UV Vis spectrophotometer at maximum wavelength. The analysis results are used to determine the optimum pH.

3. Results And Discussion
The concentration of Methylene blue (MB) adsorbed was determined by UV Vis spectrophotometer at a wavelength of 664 nm. Adsorption of MB dye using copoly(Eg-SA-DVB) at 2%, 4% and 6% DVB variations was assessed based on several adsorption parameters including pH, contact time and initial concentration of the dye.
Effect of pH on Adsorption

The acidity (pH) of the solution is one of the factors that influence the adsorption process of MB cationic dyes using copoly(Eg-SA-DVB) in the variation of DVB. The effect of the pH of the MB solution on the adsorption capacity was shown in Figure 1.

![Figure 1. Effect of pH on adsorption of MB dyes](image)

Copoly (Eg-SA-DVB) at variation of DVB 2% and 6% had an optimum pH of 5 with adsorption capacities at 15.18 and 8.21 mg/g, whereas MB Adsorption with copoly(Eg-SA-DVB) the variation of DVB 4% had an optimum pH of 3 with an adsorption capacity of 19.45 mg/g. The negatively charged active group on the surface of copoly(Eg-SA-DVB) can be protonated at low pH so that it can cause electrostatic repulsion between MB cation and the adsorbent surface which are both positively charged. This was demonstrated in MB adsorption by copoly(Eg-SA-DVB) at 6% DVB variation, where the adsorption capacity was higher with increasing pH. In addition, it is possible that MB can also be protonated at low pH to colorless leuco-methylene blue (LMB).

The copoly adsorption capacity (Eg-SA-DVB) at variations of DVB 2% and 4% was higher than 6%, this indicates that the higher DVB composition of the adsorbent leads to the formation of copolymer structures with the number of negatively charged active groups on the surface, so the MB dyed adsorption decreases.

Effect of Contact Time on Adsorption

The effect of contact time on adsorption of methylene blue (MB) dyes is shown in Figure 2. The adsorption rate is higher at the initial adsorption time because the surface area of the adsorbent available for MB adsorption is still large. After reaching a certain time, the adsorption rate decreases as the surface active side of the adsorbent decreases.
Adsorption of MB using copoly(Eg-SA-DVB) at a variation of 4% DVB had an optimum contact time at 50 minutes with an adsorption capacity of 36.84 mg/g. As for copoly(Eg-SA-DVB) at variations of 2% and 6% DVB showed an optimum contact time of 60 minutes with adsorption capacities of 14.92 and 19.95 mg/g. The adsorption rate decreased at the end of the experiment because the adsorbent was saturated after equilibrium was reached.

The adsorption kinetics can be assessed from experimental data on the influence of contact time. The kinetics test was performed on the pseudo first order (lagergren) and pseudo second order (Ho) models. The results of the kinetics model of the adsorption of the three copoly(Eg-SA-DVB) against MB dyes are presented in Table 1.

| Adsorbent | Lagergren $K$ (g/mg.min) | Lagergren $R^2$ | Ho $K$ (g/mg.min) | Ho $R^2$ |
|-----------|--------------------------|-----------------|-------------------|---------|
| DVB 2%    | $5.78 \times 10^{-2}$    | 0.95            | $6.5 \times 10^{-3}$ | 0.68    |
| DVB 4%    | $5.64 \times 10^{-2}$    | 0.98            | $3.1 \times 10^{-3}$ | 0.84    |
| DVB 6%    | $2.40 \times 10^{-2}$    | 0.90            | $11 \times 10^{-3}$  | 0.77    |

The adsorption kinetics model was determined based on the higher coefficient of determination ($R^2$) between the Lagergren and Ho kinetics models. The three copoly(Eg-SA-DVB) at variations of DVB 2%, 4% and 6% have higher $R^2$ values in the Lagergren pseudo first order kinetics model. This shows that the adsorption process using the three copoly(Eg-SA-DVB) against MB dyes is more likely to follow the Lagergren kinetics model (first-order pseudo).

Effect of Initial Concentration on Adsorption

The effect of initial concentration of methylene blue (MB) dyes on adsorption with copoly(Eg-SA-DVB) on the variation of DVB 2%, 4% and 6% is shown in Figure 3.
Figure 3. Effect of initial concentration on adsorption of MB

Figure 3 shows that the adsorption capacity increases with the initial MB concentration increase. The adsorption capacity continues to increase until the optimum adsorption capacity was obtained, when the adsorption process has reached equilibrium. The decrease in MB adsorption at higher concentrations of concentration is likely due to MB cation monomers forming dimeric compounds or other aggregates. The results of determining the effect of the initial concentration of the dye were used to study the MB adsorption isotherm with copoly (Eg-SA-DVB). The results of the adsorption isotherm study are shown in Table 2.

| Tabel 2. Isoterm adsorption of MB with copoly(Eg-SA-DVB) |
|-----------------|-----------------|-----------------|
| Isoterm Adsorption | Copoly(Eg-SA-DVB) | DVB 2% | DVB 4% | DVB 6% |
| Langmuir : | | R² | 0.97 | 0.99 | 0.92 |
| | X_m (mg/g) | 31.20 | 36.22 | 14.66 |
| | K_L (L/mol) | 24.11 × 10⁴ | 64.94 × 10⁴ | 25.30 × 10⁴ |
| | E_ads (kJ/mol) | 31.12 | 33.60 | 31.28 |
| Freundlich : | | R² | 0.50 | 0.61 | 0.35 |
| | n | 3.11 | 3.80 | 2.93 |

Isotherms adsorption of MB using all three copoly(Eg-SA-DVB) tend to follow the Langmuir isotherm (higher R² value). The Langmuir model assumes that the monolayer layer is formed when adsorption takes place without interaction between the absorbed MB molecules. Adsorption energy can be used to estimate the type of adsorption, if the value is below 8 kJ / mol shows a tendency towards physical adsorption, while for 8-16 kJ / mol indicates adsorption can be explained through ion exchange reactions, and if> 16 kJ / mol shows more adsorption tends to occur more strongly by chemical adsorption than ion exchange reactions. It can be concluded that the three adsorbents show that the adsorption process occurs chemically.

4. Conclusion
Adsortion of MB using copoly(Eg-SA-DVB) in the variation of DVB 2%, 4% and 6% tends to follow the kinetics of Lagergren pseudo first-order and Langmuir isotherm.
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