ABSORPTION CHARACTERISTICS OF NAPA SOIL AS CONGO RED DYE ADSORBENT IN SOLUTION WITH CONTINUOUS SYSTEM

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ABSTRACT

Waste dyes such as Congo red at certain levels can damage the environment because of toxicity and may cause malfunctioning of the liver, kidneys, and nerves. Therefore, this study aims to analyze optimum pH, concentration, particle size of the adsorbent, and the eluent flow rate on the adsorption of Congo red by Napa soil (NS). The results showed optimum pH of 6, an initial concentration of 20 mg/L, and a particle size of 75 µm and the optimum flow rate of the eluent of 40 drops/minute. Furthermore, the determination of adsorption at the optimum condition of the NS as adsorbent without treatment (fresh) has a higher capacity than the purified Napa soil. The absorption capacity was 0.37 mg/g and 0.25 mg/g, and desorption at the optimum condition (recovery column) showed that the highest percentage is by using ethanol. Besides reducing the concentration of the Congo red dye and determining the absorption capacity of the adsorbent, the other aim of the adsorbent application is for pre-concentration. The results showed that the number of concentrated Congo red dye is equal to 0.11 mg/g.

Keywords: Napa Soil, Congo Red, Adsorption, Adsorbent, Pre-concentration

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INTRODUCTION

Napa Soil (NS) is the name given by the natives of West Sumatra province to this natural substance. It is used as a medicine for stomach aches and diarrhea when taken orally. Previous studies showed that NS minerals are aluminosilicate mineral groups, mainly in the form of kaolin minerals. In addition, preliminary data also reported that alumina, zeolite, and quartz are found in some locations in West Sumatra.¹ Kaolin is a clay product formed from the decomposition of feldspar rocks, which is a silicate of hydrate of aluminum. The main component is kaolinite, with the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, and it is widely used in a variety of technological applications.²⁻⁴ Several studies have reported data on unusual and low-cost adsorbents such as waste and natural minerals, as well as biosorbents from industry and agriculture. Adsorbents remove dyes from aqueous solution and are in the form of clay materials (bentonite, kaolinite), zeolite, silica materials, and agricultural waste.

The need for Kaolin depends on its use, and it is mostly consumed by the paper industry (as a filler). Furthermore, it is consumed as a traditional raw material in the ceramic industry, as a filler in the production of rubber, plastics, and pigments, in refractory materials, cosmetics, pharmaceuticals, food industry for the production of synthetic zeolites and as adsorbents.^{5,6} Kaolin has received considerable recognition as an adsorbent because of its high adsorption capacity. Generally, it is composed of kaolinite and a lower amount of minerals such as quartz and zeolite, etc. It is the most abundant mineral present in soils and sediments and interacts with other elements to contribute to the mechanical stability of the soil column.⁷ The application of kaolinite as an adsorbent to remove toxic pollutants from polluted waters has

been widely studied. It is used because of its specific surface, availability, stability, and strong structural characteristics.⁸⁻¹⁰ The adsorption process, which occurs on solid surfaces, involves its potential counter ions that provide a positive or negative charge surface concerning those produced from the crystal lattice. Dye-bearing effluent causes water pollution in textile, paper, rubber, leather, printing, carpet, plastics, food and cosmetic industries, etc. Dyes are mainly classified into cationic, anionic, and non-ionic dyes. The molecules consist of chromophores and auxochromes components. The chromophores (OH, NH₂, NHR, NR₂, Cl, and COOH) are responsible for producing colors, while auxochromes (NO₂, NO, N=N) enhance the affinity of the dye toward the fibers,¹¹⁻¹³ Congo red [1-naphthalene sulfonic acid, 3, 30-(4, 40-biphenylenebis (azo)) bis (4-amino-) disodium salt, CR] (Fig.-1), is a benzidine-based anionic diazo dye, which contains two azo groups within each molecule. This compound is toxic to many living organisms and is a suspected carcinogen substance and mutagen. Benzidine is a human carcinogen and CR is banned in many countries due to health care requirements. However, there are still several countries that allow their use widely. Since they are synthetic dyes, it is difficult to biodegrade because of complex aromatic structures which contribute to their physicochemical, thermal, and optical stability.¹⁴⁻¹⁶

Fig.-1: Molecular Structure of Congo Red (CR) Dye

Earlier applications of technologies, namely membrane separation, coagulation/ flocculation, filtration, microbial degradation, chemical oxidation, and biosorption, have been successful. However, they have shown some limitations in treating dye-containing wastewaters.¹⁵⁻¹⁷ Adsorption has been regarded as the most efficient method to deal with water and wastewater treatment, particularly due to its simplicity, low-cost, ease of operation, and high efficiency.¹⁸ This study investigated the potential use of NS (Napa Soil, Kaoline of West Sumatera) as an adsorbent to eliminate CR dye from an aqueous solution. The data included optimization of adsorption parameters, namely pH, the concentration of dye solution, particle size, and flow rate.¹⁹⁻²¹ This study aims to determine CR adsorption using NS as an adsorbent. CR concentrations have been measured using a UV-Vis spectrophotometer over the wavelength range of 400-700 nm. It can be utilized for further functional purposes in adsorbent while overcoming the environmental pollution precisely caused by CR on a laboratory scale.

EXPERIMENTAL

Materials and Instruments

The materials used are NS from Situjuah sub-district, 50 Kota district West Sumatera, NaOH (E. Merck), HCl (E. Merck), *CR dye*, and distilled water. The instruments used are glass equipment, analytical scale, column, evaporating dish, sieving 50, 75, 150 μ m, pH meter, magnetic stirrer, oven, dan Spectrofotometer UV-Vis (T70-Model).

Preparation of Napa Soil

The chunk of NS was crushed into a fine powder and then sieved using 50 μ m, 75 μ m, 150 μ m, and 250 μ m sieving. Furthermore, the fine powder was refluxed using distilled water for 4 hours and dried using an oven for 3 hours with a temperature of 105°C.

Adsorbent Preparation and Column Packing

Two grams of NS powder were packed into a column that was covered with glass wool. Before usage, the column was saturated using distilled water and ready to be contacted with the dye solution using a continuous system.¹

The Effect of Initial pH

To analyze the initial pH, 25 ml of Congo red solution was prepared with variations in 1, 2, 3, 4, 5, 6, 7, and 8. The solution was then eluted into a column which has been packed with 2 grams, and the adsorbed dye was specified using UV-Vis. Spectrophotometer at the wavelength range of 400-700 nm.

The Effect of Initial Concentration

To analyze the initial concentration, 25 ml of CR solution was prepared with 5, 10, 15, 20, and 25 dan 30 mg/L concentrations. Furthermore, it was eluted to the column and packed with 2 grams. The determination of adsorbed dye was conducted using UV-Vis. spectrophotometer.

The Effect of Particle Size

To discover the effect of particle size, 25 ml of CR solution was prepared and eluted into the column. It was then packed with 2 grams of different sizes 75, 100 and 150 μm . The determination of adsorbed dye was conducted using a UV-Vis spectrophotometer.

The Effect of Flow Rate

To determine the effect of the flow rate, 25 ml of CR solution with the optimum concentration and particle size were eluted into the column with different flow rates of 30, 40, 50, and 60 drops/minute. Then the determination of the adsorbed dye was conducted using a UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Napa Soil Composition and Characterization

Table-1 shows chemical composition (wt %) obtained from XRF analysis (PAN analytical, Epsilon) of natural NS sample. The results showed that the main oxides are alumina (23.313 %) and silicate (68.70%), as well as a small amount of potassium (4.295%), and ferric oxides (1.335%)

Table-1: Chemical Analysis of NS Sample

Constituent	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₂ O ₃
Wt %	23.313	70.067	0.316	4.295	0.525	0.02	0.009	0.002	1.335

XRD diffractogram spectra pattern of raw NS is shown in Fig.-2, and the main reflections were the highest intensity found at $2\theta = 12^\circ$ ($D = 22.32$ nm), 21° ($D = 33.83$ nm), 24° ($D = 28.60$ nm), 26° ($D = 28.23$ nm), 37° ($D = 38.24$ nm) and 50° ($D = 31.51$ nm), which confirmed with the JCPDS database file (PDF-00-058-2028). These findings are consistent with the characteristic peaks of Al₂Si₂O₅(OH)₄ (Aluminum Silicate Hydroxide). Therefore, NS demonstrated a predominant phase as kaolinite 1, and quartz as a minor impurity. Similar diffraction peaks were also reported by Mustapha *et al.*²⁴

The morphology of NS observed in the SEM image (Fig-3) showed that the particles presented irregular shapes, rough surfaces, different particle sizes, and the main pore diameter of 1.5 μm . This was measured by 2/3rd of the pore volume between 1.27-2.04 μm .

Fig.-2. XRD Pattern of Raw Napa Soil

Fig.-3: Morphological Characteristics of Napa soil, especially from Situjuh sub-district Kota district West Sumatera

The Effect of Initial Solution pH To Congo Red Adsorption by Napa Soil

The CR dye is a base-acid indicator because its colors significantly change in the solution. The initial pH is very influential in the adsorption process and specifically on the capacity. The natural pH is around 5.0 and it was stated that the color changes from red to dark blue when set to 2. In the pH range of 10-12, the red color is different from the original.⁵ Therefore, the pH range for the CR adsorption experiments is maintained in the range 1-8. Figure-3 shows the effect of pH CR solution on adsorption by NS.

Figure-4 shows that the optimum adsorption (0.23 mg/g) occurs at pH 6 with an initial concentration of 20 mg/L CR solution. At low pH, the absorption of CR by NS is small, because the high concentration of H^+ ions will cause protonation of the O atom on the silanol group (Si-O-) and the Al-O and O and N groups on the neutral molecule CR. This argument is reinforced by FT-IR spectra (Fig.-5) of the change in bandwidth at $3355.91\text{--}3346.28\text{ cm}^{-1}$ OH in the Si-OH group (silanol) or the Al-OH group, which is thought due to protonation of the O atom at low pH. In addition, CR, which is a benzidine-based anionic diazo dye, will mostly be present in neutral molecular form at low pH. This condition causes the push-pull force between the adsorbent and the adsorbate to reduce the adsorption of CR.¹¹

Fig.-4: The Influence of pH to Congo red ads (mg/g) by NS (for 2 g of napa soil, 25 ml of Congo red 20 mg/L, adsorbent particle size 150 μm).

Fig.-5: FTIR Spectra Soils as an adsorbent NS for dyes at various pH

In addition, decreased absorption occurs at higher pH, alkaline solutions, because at high pH the loss of protons in alkaline solutions will cause the adsorbent surface to become neutral or negatively charged. In alkaline conditions, the CR molecule has an -SO_3^- group with a negative charge, so an increase in the level of OH^- ions in the alkaline solution makes the environment competitive with the anionic CR molecule for the adsorption site. This condition causes the push-pull force between the adsorbent and the adsorbate to reduce the adsorption of CR.¹¹ A similar trend of pH effect was observed for the adsorption of CR dye by Algerian kaolin.⁷ Based on the data on the effect of pH and the above discussion, it shows that absorption of CR dye by napa soil involves chemical absorption.

Figure-5 is the results of the FTIR spectrum of NS as an adsorbent for dyes at various pH. FTIR test of NS with broadband at $3355.91\text{-}3346.28\text{ cm}^{-1}$ from OH in the Si-OH group (silanol) or Al-OH group. Furthermore, there was a sharp absorption band at the wave number $1639.44\text{-}1640.41\text{ cm}^{-1}$, which is the bending vibration of the OH group from Al-OH / Si-OH (silanol). Strong absorption bands were also found at $990.39\text{-}992.44\text{ cm}^{-1}$ with symmetrical stretching bands of the Si-O group in the siloxane (Si-O-Si) group or the Al-O group of Al-O-Al. Wavenumber $773.32\text{-}684.31\text{ cm}^{-1}$ showed the absorption band for stretching vibrations of the silanol group (Si-O), and this is typical of the kaolinite mineral spectrum.³

The Influence of Solution Initial Concentration to Congo red Adsorption by Napa Soil

The effect of the initial concentration of CR on its adsorption in an aqueous solution was investigated under 30 mg/L of adsorbate concentration, pH 6, flow rate 30 drops/minute. The results are shown in Fig-6a, which depict that dye uptake increases with high initial CR concentration from 5 to 20 mg/L. The optimum concentration is 20 mg/L at pH 6, with adsorption of Congo red 0.23 mg/g. At the concentration of 25 mg/L, the adsorption of CR is decreased due to the maximum point of NS to CR. After reaching this point, the adsorption is not increased. This is because the side of the NS surface has been saturated with CR and has reached an equilibrium system. The increased concentration causes more particles to be adsorbed due to high collision frequency.^{7,23,24,25}

Adsorption Isotherm

Analysis of isothermal data is essential. To predict the adsorption capacity of adsorbent, analysis of isothermal data needs to be conducted. This is one of the most important parameters needed to design the system. Furthermore, isothermal equilibrium studies were performed with different initial concentrations

of CR (5-30 mg/L) at 25 °C and pH 6.0. The Langmuir isotherm model analyzed the equilibrium adsorption data following the physical hypothesis that the maximum capacity consists of a monolayer on an active site and can be written as:¹⁴

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

C_e is the equilibrium concentration of the CR (mg/L), q_e is the amount adsorbed per unit mass of adsorbent (mg/g). At equilibrium concentration, C_e , and K_L (L/g) constitute the Langmuir constants. Also, q_m , which is the maximum adsorption capacity (mg/g) depends on the number of sites.

Fig.-6: (a) The influence of concentration to CR adsorption by Napa soil (for 2 g of Napa Soil, (b) Curve of Langmuir curve of Congo red adsorption by Napa soil. (25 ml of solution with concentration 5, 10, 15, 20, 25 and 30 mg/L in pH 6)

The Langmuir isotherm showed that the number of anions adsorbed increased with the concentration up to a saturation point. Provided the sites are available, adsorption will increase with high CR concentrations. However, when they are occupied, a further increase in concentrations does not increase the amount of CR on adsorbents.^{21,22} The plot C_e/q_e versus C_e is a straight line, (Fig.-6b), and the data obtained meets the Langmuir Isotherm Adsorption equation. Furthermore, between the absorbed substance and the active absorbent center, a single layer on the absorbent surface (monolayer adsorption) was formed. When a linear line is obtained when C_e/q_e is plotted against C_e , the absorption affinity is constant (K_L) and maximum absorption capacity (q_m) are calculated using the slope and the intercept. The amount of CR adsorbed (mg/g) at equilibrium per unit mass of sample were calculated with the following equation:^{5, 26}

$$q_m = \frac{V(C_o - C_e)}{m} \quad (2)$$

In the equation, C_o is the initial concentration of CR in mg/L, V is the volume of experimental solution in L, and m is the dry weight of nanoparticles in g. The data showed that CR adsorption by NS fulfilled the Langmuir isotherm adsorption equation, with a correlation coefficient (R^2) 0.9878. Therefore, CR adsorption by purified NS is chemically running with K_L and q_m value of 0.163 and 0.271 mg/g.

The Effect of Particle Size and Solution Flow Rate to CR Adsorption by Napa Soil

The capacity in the adsorption process depends on the surface area, and the smaller the particle size, the more amount of substance to be adsorbed.²⁷ Figure-7(a) showed that the particle size of 75 μm has optimum adsorption of 0.24 mg/g. This finding is consistent with the theory, which explains that the smaller the particle size the larger the surface area of material and the capacity to adsorb. Therefore, smaller kaolin particles can increase the specific surface area, number of pores, and volume to improve the CR removal rate by adsorbent.²⁶ Figure-7(b) led to a conclusion that when the flow rate of solution

was faster, the adsorption of CR by NS decreased, and vice versa. When the flow rate was slower, the adsorption of CR by NS increased. This finding showed that the flow rate of 40 drops/minute is optimum with 20 mg/L initial concentration and 75 μm particle size. This condition has 0.25 mg/g as optimum adsorption. This is because, at a slower rate, the residual time of the adsorbate in the column is long enough. Therefore, the adsorption equilibrium is reached at a slow flow rate. Increasing this rate creates a shorter time for saturation.²⁸ The time required to reach saturation increased significantly with a decrease in flow rate.^{29, 30}

Fig.-7: (a) The effect of particle size and (b) The effect of flow rate on CR adsorption by NS to CR ads (mg/g) (2 g of NS with 25 mL of CR solution 20 mg/L in pH 6)

CONCLUSION

Based on the results of the research that has been carried out, it can be concluded as follows: Napa soil, which is silica alumina, has the potential to be used as an adsorbent material for CR dye. Most likely, it can be used as an adsorbent for other dyes. The absorption of CR by the adsorbent is influenced by several variables, namely the effect of the pH of the solution, the initial concentration of the solution, the particle size and the flow rate of the solution. The optimum conditions of NS were purified as an adsorbent for pH, 20mg / L for solution concentration, 75 μm for particle size and 40 drops / minute for flow rate. In addition, fresh NS used as adsorbent had a higher adsorption capacity compared to purified Napa soil. Based on the result, it is reasonable to conclude that the optimum condition of purified NS as adsorbent is 6 for pH, 20mg/L for solution concentration, 75 μm for particle size and 40 drops/minutes for flow rate. In addition, fresh NS used as an adsorbent has a higher adsorption capacity than purified Napa soil. The data showed that CR adsorption by NS fulfilled the Langmuir isotherm adsorption equation, with a correlation coefficient (R^2) 0.9878. Therefore, CR adsorption by purified NS is chemically running with K_L and q_m value of 0.163 and 0.271 mg/g.

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