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The Capability of Mangrove Charcoal in Adsorption Process of Indigosol Substance in Wastewater of Batik Industry

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Abstract

The development of the textile industry has had a positive impact on economic growth in Indonesia. Batik is one of the products of the textile industry that is proliferating in Indonesia. Dyes are the main ingredients in the textile and batik industrial process. One of the dyes used is indigosol, and about 15% of the total dyes used will result in industrial liquid waste. The presence of these dyes can damage the water and soil ecosystems. Liquid sewage treatment is needed to minimize the amount of contamination against groundwater and surface water. A standard method used in the handling of liquid waste is by adsorption process with various adsorbents. Commonly used adsorbents are silica gel, activated alumina, zeolite, polymer, and activated carbon. Activated charcoal from mangroves becomes an alternative to natural adsorbents with a large surface area. The ability of activated charcoal as an adsorbent was the focus of this study, both by the activation process by Fe cations and the addition of hydrogen peroxide activators. Characterization using a UV-Vis spectrophotometer is performed to see changes in indigosol concentration during the adsorption process. Results have shown that charcoal with Fe and H_2O_2 give a better performance on adsorption of indigosol than pure charcoal. Removal of indigosol by charcoal + Fe and H2O2 can reach 51%.

INTRODUCTION

The textile and batik industry, both small and medium scale, is quite rapidly growing in Indonesia. The development of the textile and batik industry has a positive impact on economic growth, both from the producer sector and its marketing chain. In its development, the textile industry is in dire need of dyes as the primary material, especially in the manufacture of batik. Each knows about 70,000 tons of color substances are produced, and 15% of it becomes liquid waste from textile industry processes (Khataee & Kasiri, 2010). The content of dyes in liquid waste is estimated at 20-30 mg / mL (Widjajanti et al., 2011). Various color substances are used in the textile and batik industries, including methylene blue, naphthol, indigosol, and others (Maryudi et al., 2019; Herfiani et al., 2017). Excessive use of synthetic color substances can cause problems from the resulting waste (Mozammel et al., 2002). According to Aishwariya & Jaisri (2020) that liquid waste from the textile industry can cause problems with groundwater pollution, human health, and disruption of aquatic ecosystems. Sewage treatment units are needed to suppress environmental pollution that occurs (Mukimin et al., 2017).

There are many ways to treat wastewater i.e. filtration, flocculation, color removal (decolorization), and adsorption (Gürses et al., 2004). Adsorption is a method of liquid waste treatment that is often utilized. The benefits of adsorption technique are simple, easy to apply technology, diverse contaminant targets, and effective with rapid kinetics (Aishwariya & Jaisri, 2020). The adsorption process itself is proven to have high effectiveness in the removal of color substance content in the liquid waste of the textile

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and batik industry (Wanchanthuek & Thapol, 2011). Lately, there has been a lot of research on the processing of waste substances of textile and batik industry color with adsorption process with various adsorbents. Some types of adsorbents used in the liquid waste treatment process include zeolite, activated carbon, activated alumina, and active silica (Ali et al., 2020; Setyawati et al., 2015). Adsorbents that are widely used are activated charcoal because it has a porous structure with a surface area of up to 600 m2/gram (Sahara et al., 2019).

According to pore size, activated charcoal is classified into macropores (>50 nm), mesopore (2-50 nm), and micropore (<2 nm) (Ilomuanya et al., 2017). Generally, activated charcoal is grouped into Granular Activated Carbon (GAC) and Powdered Activated Carbon (PAC). GAC is more expensive than PAC and has a rate of 0.2-5 mm, while PAC ranges from 50-150 μm (Cao et al., 2017). Generally, activated charcoal is used by the sugar industry, oil industry and pharmaceutical industry (Bansal & Goyal, 2005). Activated charcoal can be obtained from various types of materials, one of which is mangrove charcoal. Mangrove charcoal will be utilized in the adsorption process of indigosol substances in the liquid waste of the textile industry. Indigosol itself is an anthraquinone synthetic color substance that has the bonds N-H and C = C. This waste has a strong chemical bond structure and is classified as non-degradable (Herfiani et al., 2017) and includes a type of cationic color substance (Derakhshan et al., 2013). Indigosol also has good wear-resistant properties, bright color, and is fairly evenly distributed. The use of indigosol is combined with hydrofluoric acid, sulfuric acid, and sodium nitrite to cause or evoke color (Nugroho et al., 2013). Observation of the process of liquid adsorption waste of the textile industry by mangrove charcoal needs to be done to find out the optimum conditions of its trapping.

The ability of charcoal in the adsorption process will improved by activation process. The activation process can involve cations such as Fe, which is generally activated charcoal is used to treat liquid waste with the content of methylene blue color substances (Amelia, Rahmadani, et al., 2019; Amelia, Sediawan, et al., 2019). In addition, absorption ability by activated charcoal can be improved by the addition of activators such as hydrogen peroxide. Activated charcoal with Fe activation and the addition of hydrogen peroxide has been used to treat liquid waste containing dyes with fairly good results. Activated charcoal has been widely utilized for liquid waste processing with various combinations with fairly good results (Maryudi et al., 2019). The adsorption process that occurs can be physical and chemical adsorption. Physical adsorption occurs due to the Van Der Waals force, while chemical adsorption occurs due to a reaction between solute and the surface of porous solids (Lavrenko et al., 2018). The adsorption process is said to be effective when it can absorb the content of impurities well. Therefore, the characteristics of activated charcoal and its ability to absorb indigosol waste are the focus of this study. So, it is expected that the adsorption process of mangrove activated charcoal can be a solution in overcoming the liquid waste pollution of the textile and batik industries.

MATERIALS AND METHODS

Materials

The materials used for the study were mangrove charcoal which prepared from mangrove wood that obtained in Samas Beach, Yogyakarta, indigosol as artificial batik wastewater, $Fe(NO_3)_3.9H_2O$ 98% (Sigma Aldrich), and hydrogen peroxide 35% (Sigma Aldrich).

Methods

Adsorption Process

The mangrove charcoal was prepared in size of 40 mesh. The charcoal was then heated in a 60°C oven for 5 hours. Charcoal activation was done by adding 50 gr mangrove charcoal and 200 mL solutiion of $Fe(NO_3)_3.9H_2O$ 4% that has been dissolved with isopropyl alcohol in a beaker glass and then stirred with an ultrasonicator for 1 hour. The charcoal was then dried for 24 hours and calcined at 300 °C for 3 hours. Characterization of mangrove charcoal was done before and after activation with BET analysis to determine its surface area. The adsorption process was performed by mixing 25 mg of mangrove charcoal with 200 ml of indigosol solution volume of 25 and 45 ppm and stirring speed of 450 rpm. Sampling was done periodically to find out changes in the concentration of the solution. The effect of hydrogen peroxide was studied by adding five mL of H_2O_2 in indigosol solution before the adsorption process takes place.

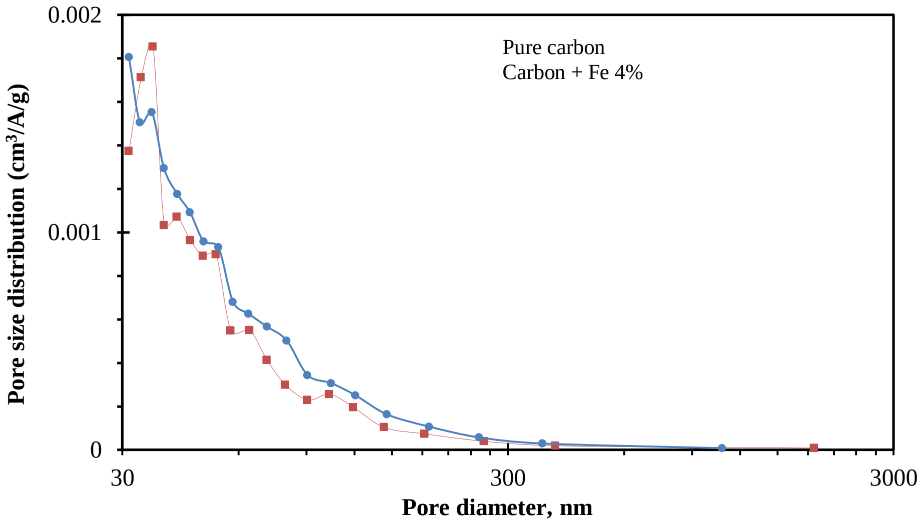

Figure 1. Size distribution of mangrove charcoal.

The sample was analyzed with a UV-Vis spectrophotometer at a wavelength of 465 nm to determine the levels of indigosol in the solution at various sampling times. Percentage of removal was calculated based on rasio of the concentration of absorbed indigosol and the initial concentration of indigosol.

RESULTS AND DISCUSSION

Characterization of Mangrove Charcoal

The initial characteristic of mangrove charcoal is the size distribution of mangrove charcoal pores. The purpose of this characterization is to find out the classification of activated charcoal whether included in macropores, mesopores, or micropores. The distribution of mangrove charcoal pore size can be seen in Figure 1.

Based on Figure 1, we can see that mangrove charcoal pore size distribution is between 30-300 nm. Based on Figure 1 we can also see that activated mangrove charcoal has a more uniform pore size distribution. Meanwhile, inactivated mangrove charcoal provides an up and down pore size distribution for each detected pore diameter. Therefore, with the activation process can maximize the surface area of activated charcoal. It is supported by Sivachidambaram et al. (2017) that activated carbon (in this case with H_3PO_4) provides a greater surface area. An increase in surface area can lead to a decrease in the average diameter of the pore. The results of the analysis of average pore size with the BET method can be seen in Table 1.

Table 1. Characterization of mangrove charcoal using BET analyzed after and before activation.

No	Parameters	Mangrove charcoal	Mangrove charcoal + Fe 4%
1	Surface area (m^2/gram)	41.0050	43.5480
2	Total volume of pores (cm^3/gram)	0.0830	0.0780
3	Diameter of the pore (nm)	3.6077	3.5869

Data in Table 1 reveals that activated mangrove charcoal that has been activated using Fe 4% cations has a slightly different surface area than before activation. Different conditions occur in the total volume of the pore, which after the activation process, the total volume of the pore obtained is slightly smaller than before activation. The diameter of activated charcoal pores with activation is smaller than before activation, which is 3.5869 nm compared to 3.6077 nm. Impurities on the surface of adsorbents cause the increased surface area of mangrove charcoal.

Effect of Mangrove Charcoal and Adsorption Time Variations on Indigosol Concentration

The adsorption process had been conducted using pure mangrove charcoal, Fe 4% activated mangrove charcoal, and Fe 4% activated mangrove charcoal 4% + H_2O_2. The adsorption process is carried out on indigosol liquid waste with an initial concentration of 25 ppm to study the influence of all three types of mangrove charcoal. Calibration standards are used to determine the final concentration of waste after the adsorption process. The results of observations for the adsorption process with all three variations of adsorbents can be shown in Figure 2.

Figure 2 shows changes in indigosol liquid waste concentrations over time with different types of mangrove charcoal. The concentration of waste over time continues to decrease for various variations of mangrove charcoal. After 10 minutes of adsorption, there is an insignificant decrease in waste concentration. The change in indigosol concentration with pure charcoal adsorbent from 10-60 minutes of adsorption is 19.5421 to 16.7255 ppm. The same is true of the 4% activated pure charcoal variation, a change in concentration from 19.1437 to 15.2336 ppm. Meanwhile, the addition of hydrogen peroxide obtained a change in concentration from 14.0546 to 12.0657 ppm.

Based on Figure 2, we can see that after ten minutes of the adsorption process, the decrease in indigosol concentration in various variations of mangrove charcoal is tiny. The phenomenon indicates that the effectiveness of adsorbents continues to decline over time. At any given time, there will be a state of fixed waste concentration value. It is due to the adsorbents that have saturated and reached maximum absorption conditions. To research conducted by Cano (2015), the adsorption of Pb (II) ions continues to increase over time. After 1800 minutes, the absorption of ions is prolonged and looks almost constant (Cano, 2015). It indicates that contact time is an essential parameter in its adsorption and kinetic process (Wang et al., 2007). According to Ndi Nsami & Ketcha (2013), the phenomenon of increasing concentration and then near-constant during the adsorption process is described in two stages. The first stage is the process of adsorption of waste to the surface of the adsorbent. The second stage is the intraparticle transfer from the bulk of the liquid to the external surface of the porous adsorbent.

Based on Figure 2, we can see that charcoal activated with Fe 4% and hydrogen peroxide have better waste absorption than pure mangrove charcoal and without the addition of an oxidizer. It is because activated adsorbents have a larger surface area (Ma et al., 2013). Activated mangrove charcoal has a surface area of 43,548 m^2/gr, and non-activated mangrove charcoal has 41,005 m^2/gr. It also suggests that the addition of activators may improve the chemisorption absorption process (Ademiluyi &David-West, 2012). So that the absorption of waste with activated mangrove charcoal is better because absorption takes place physically and chemically.

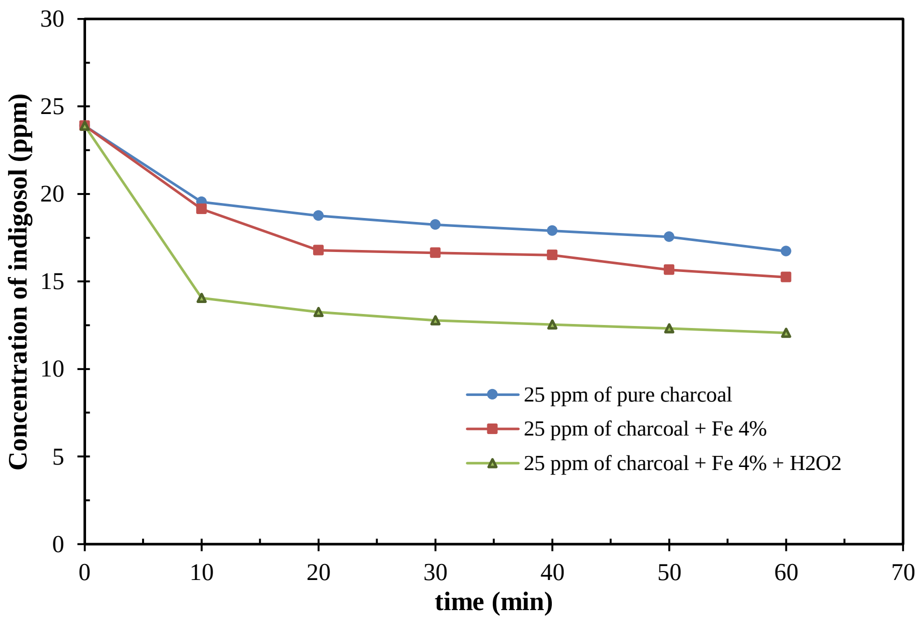

Figure 2. Changes in indigosol concentration during adsorption process with various types of mangrove charcoal.

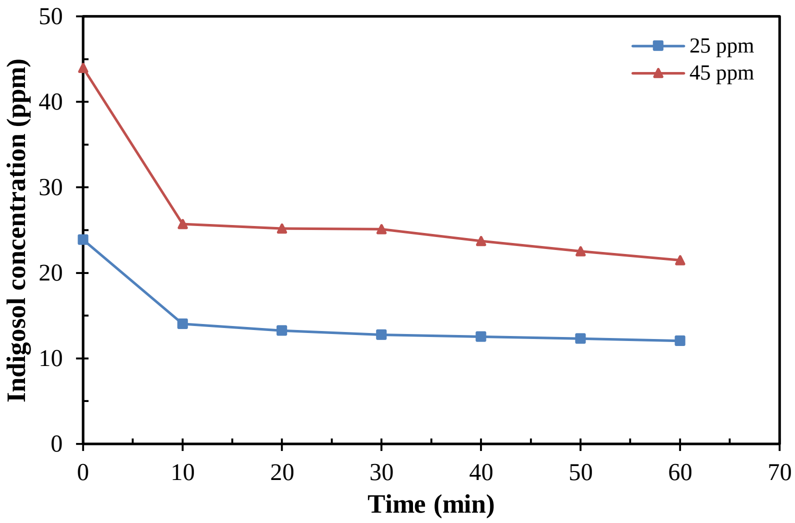

Figure 3. Concentration of indigosol over adsorption time with initial concentration variation of 25 ppm and 45 ppm using activated mangrove charcoal using Fe 4% + H_2O_2

Effect of Indigosol Concentration on The Adsorption Capability in Various Type of Mangrove Charcoal

In addition to studying the influence of mangrove charcoal types, adsorbent capabilities are also analyzed with variations in liquid waste concentrations. So, it is expected that we can learn how much capacity adsorbents in the absorption process. To determine the effect of waste concentration on adsorbent capabilities, we use activated charcoal Fe 4% + H_2O_2. Indigosol liquid waste concentrations used are 25 ppm and 45 ppm. The results of observations of waste concentrations at various times and variations in concentration can be seen in Figure 3.

Based on Figure 3, we can see that activated mangrove charcoal can absorb indigosol liquid waste with concentrations greater than 25 ppm. At a variation of waste concentration, 25 ppm can be adsorbed up to a concentration of 12 ppm at the end of the process. Meanwhile, a variation of 45 ppm gives the final concentration of waste up to 21.47 ppm. It means that activated mangrove charcoal is more effective in lowering indigosol levels with higher initial concentrations. It is due to more significant mass transfer, and at any given time, adsorbent efficiency decreases because the active site of the surface has been covered by adsorbate/saturation (Derakhshan et al., 2013). In addition, other factors that must be considered are process temperature, stirring speed, adsorbent mass, solution pH, and activator concentration.

%Removal of Indigosol with Variations of Mangrove Charcoal and Initial Concentration of Solution

The percentage of indigosol removal means how many adsorbents can decrease the concentration of impurities in a waste/solution. The greater the %removal means, the better the adsorbent in adsorption waste. The percentage results of indigosol solution removal on various variations of mangrove charcoal and the initial concentration of the solution can be seen in Figure 4. Based on Figure 4, we can see that the %removal of indigosol solution continues to increase over time. The increase in %removal is seen significantly in the first 10 minutes of the adsorption process. The adsorbent surface has not been tied to waste, and there are still many active sites so that mass transfer takes place quickly.

When the adsorbent surface has absorbed the impurities, the presence of impurities can inhibit the mass transfer process. In addition, the number of active sites is also reduced to reduce the capacity of adsorbents in absorbing waste. Decreased absorption capacity by saturated active side absorption can be caused by the considerable interaction of particulates and the presence of aggregation (Aljeboree et al., 2015). Meanwhile, mangrove charcoal on variations of pure and activated charcoal using Fe 4% and H_2O_2 has a slightly higher %removal in a 25-ppm solution than a 45-ppm solution. At low indigosol concentrations, a more significant number of active surfaces are empty. As the concentration of the solution increases, many active sides will be used to absorb

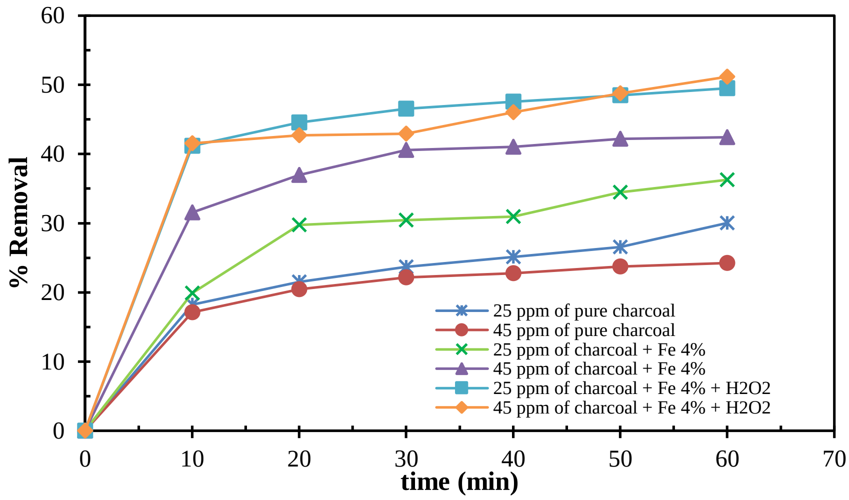

Figure 4. %Removal of indigosol solution with any variations of initial concentration of idigosol and type of mangrove charcoal.

the dye molecules to lower the %removal (Ramesh et al., 2018). Meanwhile, the increase in concentration will increase the concentration of indigosol that is successfully absorbed. It is due to higher driving force during the mass transfer process (Bulut &Aydin, 2006).

CONCLUSION

Activated charcoal from mangrove wood can be an alternative adsorbent for dyes wastewater treatment. Mangrove charcoal shows a good capability in removing indigosol in the wastewater. The longer the adsorption time, the greater the pollutants adsorbed, and adsorption will be constant when equilibrium is reached. The higher the concentration of the solution, the smaller the mangrove charcoal adsorption capacity. The contact time is directly proportional to the %removal obtained. The Fe activator dan H_2O_2 improve the adsorption capability of mangrove charcoal.

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