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Adsorption of Textile Dye by Activated Carbon Made from Rice Straw and Palm Oil Midrib

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Abstract – Synthetic dye wastewater from textile industries is characterized by strong color, high temperature, variable pH and high chemical oxygen demand (COD). The strong color of wastewater affects aesthetic and water transparency of water bodies. One of method that has advantages in term of simplicity to remove synthetic dyes is adsorption. Two different biomaterial wastes of rice straw and palm oil midrib were used in this study to develop activated carbon adsorbents. These adsorbents were applied for the removal of Naphtol AS-G dye in aqueous solution. The effects of solution pH, adsorbents masses and contact time on dye adsorption were evaluated based on batch experiments. Removal of dye can be achieved within 60 minutes at a wide pH range starting from 4 to 8. At lower pH, synthetic dye removal was decreasing probably due to protonation of adsorbent's active sites. The adsorption isotherms based on Langmuir and Freundlich models were analyzed. The isotherms analysis indicated that the adsorption by rice straw and palm oil can be represented by Langmuir and Freundlich isotherm model, respectively. Adsorption isotherms of Naphtol AS-G onto activated carbon are favorable with high adsorption capacity for both biomaterials. The mechanisms of color removal by activated carbon involved chemical and physical adsorption, in accordance with both the Langmuir and Freundlich models. The calculated maximum dye adsorption capacities onto rice straw and palm oil midrib activated carbon were 55.86 and 69.44 mg/g, respectively. Adsorption using biomass-based activated carbon offers a good technique for textile wastewater treatment as it could remove up to 95% of the color intensity besides reducing other pollutants such as COD, nitrate and phosphate.

Keywords: Activated carbon, rice straw, palm oil midrib, Naphtol dyes, adsorption isotherms.

Introduction

Synthetic dyes are widely used in various industries such as colorings agents for textiles (Clark 2011), leather (Chatwal 2009), paper (Mahapatra 2016), pharmaceuticals and food (Erkurt 2010; Sharma 2015) due to its efficient synthesis process and economic price (Lim et al. 2010; Sulak & Yatmaz 2012). Compared to natural dyes, synthetic dyes are more stable, photo and chemical resistant. Many dyes are toxic and carcinogenic leading to severe ecological problems (Kooh et al. 2016; Rajamanickam & Shanthi 2015). The metabolites could be more toxic to aquatic biota and posing a potential hazard to human health. Eventually, it will cause severe environmental problems. Therefore, it is important to protect freshwater resources by applying pretreatment processes of dyes wastewater before its discharge to water bodies or municipal sewerage system.

Physicochemical methods such as filtration, coagulation, precipitation, photochemical reactions and oxidation have been used to treat dyes wastewater (Ali & Jain 2005). Whereas those of biochemical methods include activated sludge (Bromley-Challenor et al. 2000), aerobic and anaerobic treatment

(Kamaruddin et al. 2013; Santos et al. 2007). However, these methods have high operational cost, complicated procedure and produce toxic derivative chemical substances.

The potential of alternative methods for removal of synthetic dyes have been explored, and the adsorption process has been found to be effective compared to other methods. Various biomasses have been used for synthetic dyes adsorption which includes wheat bran (Sulak & Yatmaz 2012), rice husk (Chuah et al. 2005; Sarkar 2010), walnut shell (Dahri et al. 2014), sawdust (Malik 2004) and sugarcane bagasse (Amin 2008). Adsorbents with higher adsorption capacity may include activated carbon made from those biomasses. Here we report the use of biomass wastes from rice straw and palm oil midrib to prepare activated carbon for textile dye adsorption. Naphtol AS-G that is widely used as synthetic dye in textile industries was applied as a target adsorbate. To the best of our knowledge, it is the first paper reporting Naphtol AS-G decolorization using activated carbon from rice straw and palm oil midrib.

Materials and Methods

Sodium hydroxide, phosphoric acid, and all other chemicals were supplied by Merck Ltd (Darmstadt, Germany). Naphthol AS-G with PubChem ID 66686 has a chemical formula $C_{22}H_{24}N_2O_4$, MW=380.44 with chemical structure as shown at Figure 1. Stock solutions were prepared by dissolving accurately weighed Naphthol AS-G in distilled water to give a concentration of 1000 mg/L and diluting when necessary.

UV–Visible absorption spectra of the Naphthol AS-G concentration were measured using a BioSpectrometer (Eppendorf, Germany) at 480 nm wavelength. Rice straw (*Oryza sativa*) and palm oil midrib (*Elaeis guineensis*) were collected from the rice field and palm oil plantation in Bengkulu province, Indonesia. The biomasses were cut into small pieces and washed with water to remove sand and dust. The biomasses were then dried under sunlight irradiation to remove moisture. Carbonization was done by heating at 300°C for 30 minutes in a muffle furnace. Activation was done by soaking the 0.25 μm size carbons into 10% H_3PO_4 for 24 hours which was followed by gradual heating up to 450°C for 30 minutes. Besides Fourier Transform Infrared, water and ash content tests were done to characterize activated carbon. FTIR measurements were obtained on a Prestige 21 (Shimadzu, Japan).

Batch adsorption experiments were conducted for adsorption isotherm studies. The effect of pH on Naphtol AS-G adsorbed by activated carbon was investigated by adding 0.1 g of adsorbent into 50 ml of each dye solution with 100 mg/L concentration, and the solutions were adjusted to desired pH from 3.0 to 8.0 with 0.1 M HCl or 0.1 M NaOH. The mixtures were agitated at 100 rpm for 60 minutes at 25°C. The effect of contact time on dyes adsorbed by activated carbon were conducted by adding dye concentration of 100 mg/L at pH 5.0 and agitated for varying contact times from 5 to 90 min. The effect of the initial Naphtol AS-G concentration was investigated by adding 0.1 g of adsorbent into 50 ml of each dye solution, and the solutions were adjusted to pH 5.0. The final concentrations of Naphtol AS-G solutions were analyzed using a UV–VIS spectrophotometer.

Percentage of dye removal that adsorbed by activated carbon was calculated using the following equation:

$$\frac{C_0 - C_t}{C_0} x100\%$$

where C_0 and C_t (mg/l) are the initial and final concentration of dye solutions. Adsorption capacity of the activated carbon was calculated using the following equation:

$$q = \frac{(C_0 - C_e)xV}{W}$$

where q (mg/g) is the amount of dye adsorbed by activated carbon, V (l) is the initial volume of dye solution and W (g) is the weight of activated carbon.

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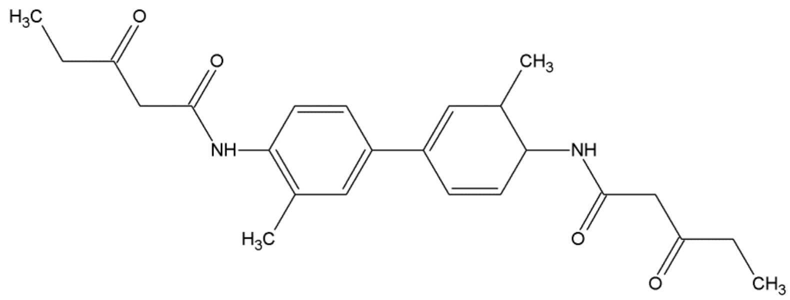

Figure 1. Chemical structure of Naphthol AS-G.

Results and Discussion

Water and ash content for both rice straw and palm oil midrib activated carbon were lower than 5.6% and 9.0%, respectively. These low water and ash content were fitted the criteria determined by SNI 06-3730-1995. Figure 2 shows FTIR spectra of rice straw and its corresponding activated carbon. The broad band that falls in the range of 3600–3200 cm^{-1} is attributed to the stretching –OH group. The peaks at 1639 cm^{-1} could be associated with the C=C stretching vibration. The peak observed at 1382 cm^{-1} is related to the bending –OH group. The peaks at the regions 1100 cm–1000 cm^{-1} correspond to the C–O stretching. These peaks suggested that the rice straw contains a lot of cellulose and hemicelluloses. After being carbonized, the absorption peaks at 3600–1500 cm^{-1} vanished indicating that the crystal structure of cellulose molecular chain has been destroyed. The as-prepared activated carbon has a mesoporous structure with hydroxyl and carbonyl hydrophilic functional groups, which might be responsible for the adsorption of Naphtol AS-G. The activated carbon spectra is similar to the reported values (Li et al. 2013).

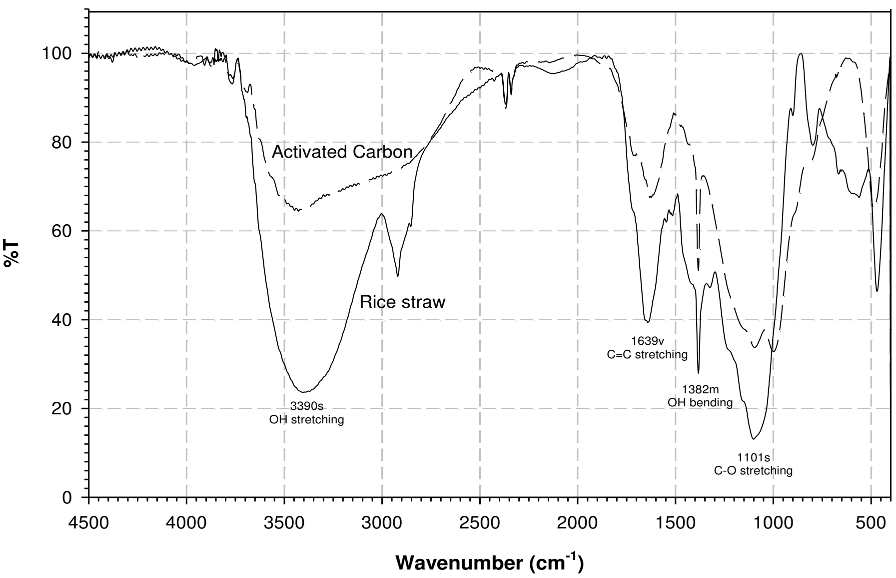

Figure 2. FTIR spectra of rice straw and its corresponding activated carbon.

Effects of initial pH on Naphtol AS-G adsorption onto activated carbon are shown in Figure 3. The adsorption behavior for both adsorbents was similar showing lower dye removal at low pH (i.e. pH = 3). At this acidic pH, adsorbent was positively charged due to protonation and dye molecules were either neutral or partially positively charged, thus decrease the dye adsorption onto activated carbon. Dye removal percentages at wide range of pH from 4.0 to 8.0 that are beneficial for real wastewater application were more than 95% and 80% for palm oil and rice straw activated carbon, respectively.

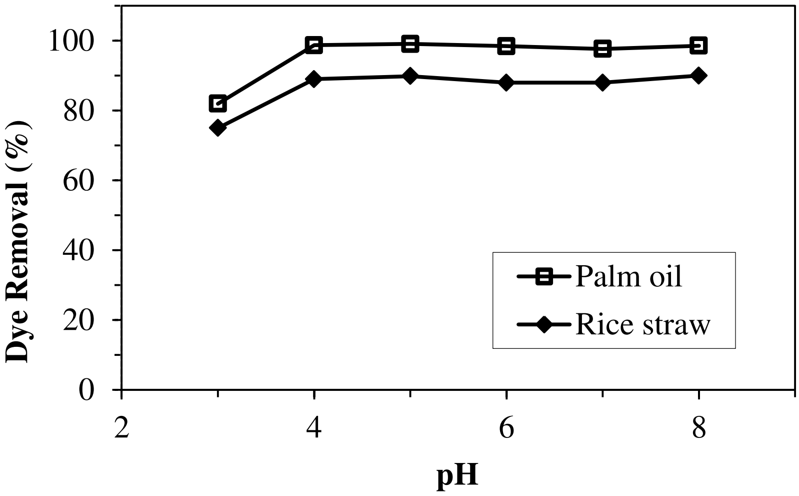

Figure 3. Effects of pH on Naphtol AS-G adsorbed by activated carbon made from rice straw and palm oil midrib. Experimental conditions: equilibrium time = 60 minutes, dye concentration = 100 mg/L, adsorbent mass = 0.1 g, temperature = 25°C).

As shown in Fig. 4, adsorption of dye onto activated carbon increased upon time and reached equilibrium after 60 minutes contact time. At initial stage from 0 to 15 minutes, dye adsorption is in its kinetic region showing a steep increase of dye removal percentage.

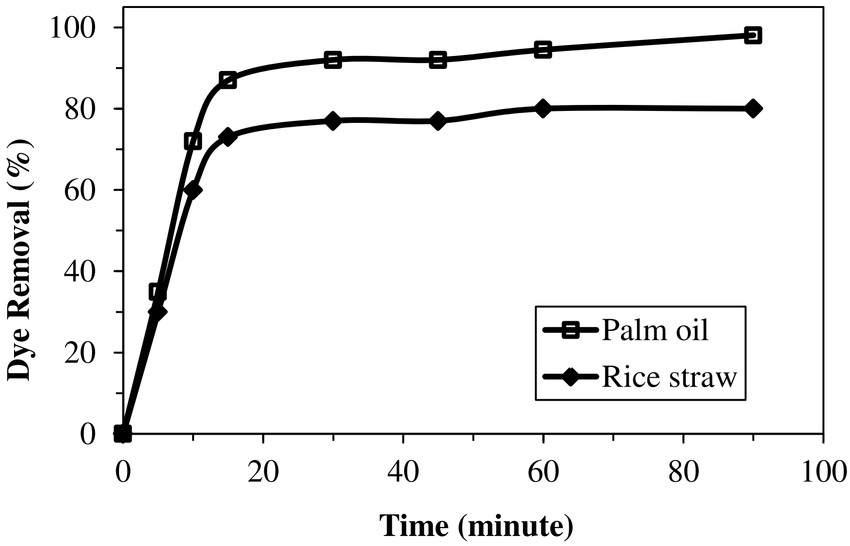

Figure 4. Effects of contact time on Naphtol AS-G adsorbed by activated carbon made from rice straw and palm oil midrib. Experimental conditions: dye concentration = 100 mg/L, adsorbent mass = 0.1 g, temperature = 25°C, pH = 5.0).

The effects of initial dye concentration to its removal from solution were studied under identical optimum conditions. The data are presented in Fig. 5, which indicate that the adsorption behavior of Naphtol AS-G reached a maximum dye removal at 100 mg/L. Increase of the dye concentration over 100 mg/L did not affect the adsorption capacity significantly.

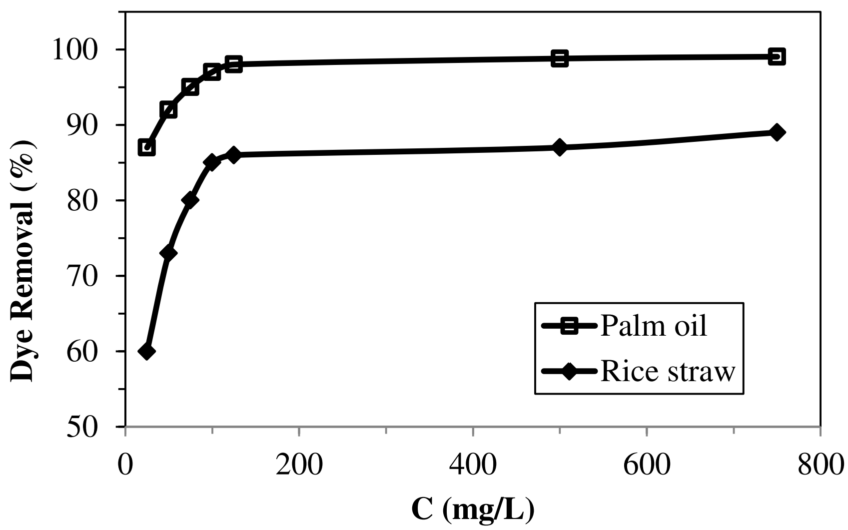

Figure 5. Adsorption isotherms of Naphtol AS-G adsorbed by activated carbon made from rice straw and palm oil midrib. Experimental conditions: equilibrium time = 60 minutes, adsorbent mass = 0.1 g, temperature = 25°C, pH = 5.0).

Adsorption isotherms are the most important information for analyzing the adsorption process. Two important isotherms, Langmuir and Freundlich, are selected in this study (Fig. 4 and Table 1). The theory of Langmuir is based on the assumption that adsorption is a chemical process as a monolayer adsorption. The Langmuir isotherm can be written by the following equation (Langmuir 1918):

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

where C_e is concentration of dye at equilibrium (mg/L), q_e is the amount of adsorbed dye at equilibrium (mg/g), q_m is maximum adsorption capacity (mg/g) and K_L is Langmuir constants (L/mg). The Freundlich adsorption model is an empirical equation employed to describe heterogeneous systems. The amount of dye adsorbed, q_e, is related to the equilibrium concentration of dye in solution, C_e. The Freundlich equations are as follow (Freundlich 1907):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F is a constant for the system, related to the bonding energy and 1/n is adsorption intensity that indicates the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1) and unfavorable (1/n > 1). As shown in Table 1, adsorptions of Naphtol AS-G onto activated carbon are favorable with high adsorption capacity for both biomaterials. The results of coefficient of determination show that rice straw tend to follow Freundlich isotherm model while those of palm oil follow Langmuir adsorption isotherm model.

Table 1. Parameters of Langmuir and Freundlich adsorption isotherm for dye adsorbed by activated carbon made from rice straw and palm oil

Activated carbon adsorbent	Langmuir			Freundlich		
	q_{max}	kL	r^2	1/n	kF	r^2
Rice straw	55.86	0.12	0.9316	0.85	5.01	0.9755
Palm oil	69.44	0.01	0.9708	0.95	0.61	0.9049

Conclusions

New activated carbon adsorbents were prepared from rice straw and palm oil midrib biomass and were successfully used for the removal of Naphtol AS-G dye. The FTIR spectra of the prepared adsorbent confirmed that it has hydroxyl and carbonyl hydrophilic functional groups that are responsible for dye adsorption. Freundlich and Langmuir adsorption isotherm model fitted the data well for rice straw and palm oil midrib, respectively. The Naphtol AS-G removal rates were up to 95% with high adsorption capacity for both activated carbon adsorbents. These results indicate that rice straw and palm oil midrib carbon could be employed as low-cost adsorbents in the removal of dyes from wastewater.

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