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Decolorization of basic and direct dyes by adsorption on chemically modified rice husk

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Abstract

Rice husks chemically modified with three different treatment methods; sodium hydroxide, nitric acid, and distilled water, were investigated to compare their color removal efficiencies for two dyes; Basic Red 4G (a cationic dye) and Direct Supra Red BWS (an anionic dye). The results revealed that the basic dye was adsorbed by these adsorbents better than the direct dye. The modified rice husk prepared using sodium hydroxide treatment showed the highest color removal efficiency (97% for Basic Red 4G) among the three modified rice husks. This modified rice husk was selected for further study of the adsorption equilibrium and adsorption isotherm. The results of adsorption equilibrium investigation fitted well with Langmuir model indicating that the dye adsorption takes place as a monolayer adsorption, based on the assumptions of the Langmuir model. The maximum adsorption capacity calculated from the Langmuir model was calculated to be 6.2 mg/g and 2.6 mg/g for Basic Red 4G and Direct Supra Red BWS, respectively. While the $1/n$ values from Freundlich model were calculated as 0.2702 and 0.5841 for Basic Red 4G and Direct Supra Red BWS, respectively, indicating favorable dye adsorption. This modified rice husk is a potential alternative adsorbent for color removal in the wastewater from dyeing process using cationic dyes.

Keywords: Dyeing wastewater, rice husk, color removal, adsorption

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1. Introduction

Textile industry is an important industry in Thailand. It can produce high income to the country every year. However, this industry generates pollutants during production process which can possible cause environmental problem if these pollutants are not controlled and treated properly. Wastewater from dyeing process is a major problem due to the residual color. This wastewater is normally drained to combine with wastewater from other parts of factory resulting in high volume of the undesirable color of wastewater which is difficult to be eliminated. When discharge outside, it is not only cause disgusting color in the receiving water source, this color can reduce penetration of light and then reduce the photosynthetic of algae and aquatic plants which effects to an ecosystem of other aquatic organisms. Moreover, the dyeing wastewater may be toxic and carcinogenic to some aquatic life [1, 2]. Therefore, color removal is a necessary treatment process for the dyeing waste water before discharge.

There are several treatment methods for textile and dyeing wastewater. Mostly, the effective color removal method is physical or chemical methods such as membrane filtration [3], ozonation [4] and coagulation-flocculation [5]. Adsorption with activated carbon is an effective method and easy to operate, but it is costly and require cost to regenerate. There were several researches about the adsorbent materials for color removal using agricultural wastes and residuals such as corn cobs [6], coconut shell [7], sugarcane bagasse [8], and other agricultures due to low-cost, eco-friendly, and available in Thailand.

Rice husk is an agricultural residue from rice mill process. It is an insoluble material with high mechanical strength which mainly contain cellulose (32%), hemicelluloses (21%), lignin (21%), silica (20%), and crude proteins (3%) [9]. Several studies reported the use of rice husk and modified rice husk as a good adsorbent for color removal from some dyes such as methylene blue [9], reactive yellow 15 [10], and direct red 23 [11]. This research aim to study the potential of rice husk as an adsorbent to remove color from two types of dye solution; basic dye (a cationic dye) and direct dye (an anionic dye). Three methods of the rice husk modification were compared. The adsorption isotherms with Langmuir and Freundlich equations were studied.

2. Materials and methods

2.1 Preparation of adsorbent

Rice husk was collected from a rice mill in Nongkheng District, Buengkan Province, Thailand. The material was washed three times with distilled water to remove dirt and dust, sun-dried, crushed, sieved to 30 - 40 mesh size, and dried in hot air oven at 105 ºC for 12 hours. The dried material was separated

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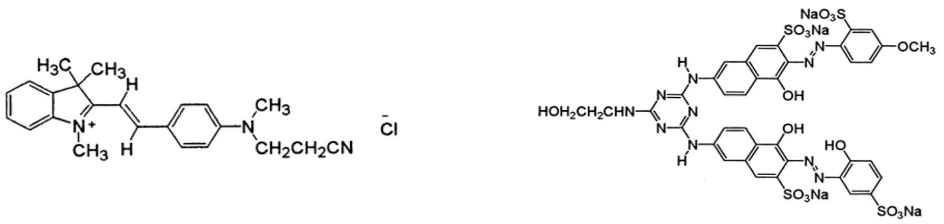

(a) (b)

Figure 1 Chemical structures of (a) Basic Red 4G and (b) Direct Supra Red BWS

to prepare 3 types of modified rice husk adsorbent; (1) RHB, the dried material was pre-treated with 10% sodium hydroxide (NaOH) solution for 12 hours, washed with distilled water several times until the pH of washed water become 6 - 7 [12]. (2) RHA, the dried material was pre-treated with 40% nitric acid (HNO_3) solution for 12 hours, washed with distilled water several times until the pH of washed water become 6-7 [13]. (3) RH, the dried material was pre-treated with distilled water several times until the pH of washed water become 6 - 7. All types of modified rice hush adsorbent were dried again in hot air oven at 110ºC for 24 hours and kept in desiccators before used in experiment.

2.2 Scanning electron microscope (SEM) analysis

This analysis aimed to study the characteristics such as surface morphology, pore size, and structure of the rice husk which was modified by different methods (RH, RHA, and RHB). The samples of modified rice husk were analyzed by using the scanning electron microscope (Model JSM-5410LV) at an electron acceleration voltage of 20kV.

2.3 Preparation of dye solutions

Two commercial dyes, Basic Red 4G (C.I.48016, Molecular weight = 379.93 g/mol, Molecular formula = $C_{23}H_{26}ClN_3$, λ_{max} at 515 nm) and Direct Supra Red BWS (C.I.29315, Molecular weight = 1116.91 g/mol, Molecular formula = $C_{38}H_{28}N_{10}Na_4O_{17}S_4$, λ_{max} at 523 nm) were obtained from a dye supplier company in Thailand. Their chemical structures are shown in Figure 1. The 1000 mg/l stock solution of both dyes was prepared by dilution with distilled water. The dye solution of Basic Red 4G at 5, 10, 20, 30, 40, 50, and 60 mg/l and Direct Supra Red BWS at 5, 10, 20, 40, 60, 80, and 100 mg/l were prepared from each dye stock solution and used to draw standard curve. The concentration of each dye was calculated from absorbance value which was measured by UV/Visible Spectrophotometer (Model HELOS OMEGA) at maximum wavelength of 515 nm for Basic Red 4G and 523 nm for Direct Supra Red BWS, respectively.

2.4 Color adsorption experiment

The experimental research was conducted in laboratory at Department of Environmental Health Sciences, Faculty of Public Health, Mahidol University. The color adsorption experiment consisted of three main factors including types of modified rice husk (RH, RHA, and RHB), types of dye solution (Basic Red 4G and Direct Supra Red BWS), and initial concentrations of dye solution. The experimental unit contained 1 g of adsorbent and 100 ml of dye solution at pH of 7 in 250 ml Erlenmeyer flask, run on the shaker machine at 120 rpm with 3 replications. Due to the limitation in color analysis by spectrophotometer, the difference of over-dark colors cannot be sorted out by the machine, thus the range of initial concentrations for both dye solutions in this study was different within limitation of the spectrophotometer. For Basic red 4G, the initial concentrations were 5, 10, 20, 30, 40, 50, and 60 mg/l, the sample was collected at adsorption durations of 0, 5, 10, 20, and every 20 minutes until reach equilibrium point of adsorption. For Direct supra red BWS, the initial concentrations were 5, 10, 20, 40, 60, 80, and 100 mg/l, the sample was collected at adsorption durations of 0, 5, 10, 20, 30, 40, 60, 80, and every 40 minutes until reach equilibrium point of adsorption. The collected samples were centrifuged at 6000 rpm for 10 minutes and analyzed for the dye concentration by UV/Visible Spectrophotometer (Model HELOS OMEGA). The color removal efficiencies from each modified rice husk were compared by percentage of color removal with calculated from Eq. (1).

$$\%\text{ Color removal } = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e (mg/l) are the initial concentration of dye solution and final concentration at equilibrium, respectively.

2.5 Adsorption equilibrium and adsorption isotherm

From the color adsorption results, the best adsorbent for each dye solution were selected with the highest percentage of color removal. Their adsorption data were used to calculate the amount of adsorption at time t (Q_t, mg/g) as following equation Eq. (2). The equilibrium time for each dye adsorption was determined from the constant amount of adsorption per increasing time.

$$Q_t = \frac{(C_0 - C_t) \times V}{W} \quad (2)$$

where C_0 and C_t (mg/l) are the initial concentration of dye solution and the concentration at any time t, respectively, V (L) is volume of the dye solution, and W (g) is weight of the adsorbent.

Table 1 Langmuir and Freundlich isotherm equations

Isotherm Models	Equations	Linear equations	Parameters
Langmuir	$q_e = \frac{q_e K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$	q_e (mg/g): equilibrium adsorption capacity q_m (mg/g): maximum adsorption capacity K_L (mg/l): Langmuir constant C_e (mg/l): concentration of dye solution at equilibrium
Freundlich	$q_e = K_F C^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	K_F (g/mg)(l/mg)$^{1/n}$: Freundlich constant n : Heterogeneity factor

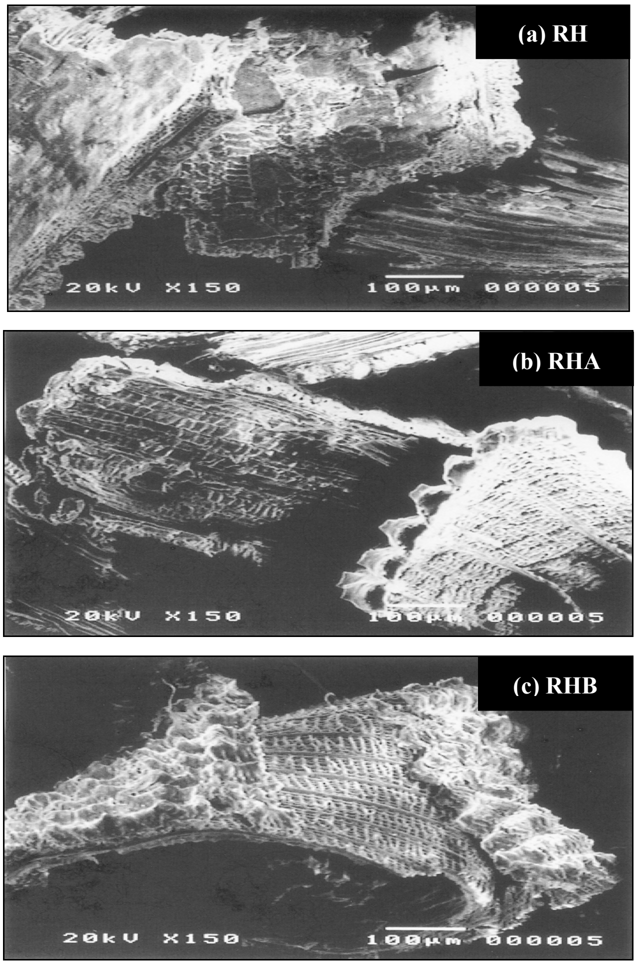

Figure 2 Scanning electron microscopic results of (a) RH, (b) RHA and (c) RHB at 150x-magnification

The adsorption data at equilibrium for each dye was used to fit with linear equations of two adsorption isotherm models, Langmuir and Freundlich isotherm, as shown in Table 1. These adsorption models were used to describe the correlation between the modified rice husk as the adsorbent and dye as the adsorbate.

3. Results and discussion

3.1 Scanning electron microscope (SEM) analysis

The surface area with 150x-magnification of all three modified rice husks (RH, RHA and RHB) were given in Figure 2. Irregular area and pores were usually found on the surface of RH (Figure 2(a)). While the complex structures with more roughness, cavities, and pores were found on the surface of RHA (Figure 2(b)) and RHB (Figure 2(c)) which resulted from erosion by the HNO_3 and NaOH modification, respectively. These more complex structures resulted in more surface area for adsorption. However, no obvious difference between surface area of RHA and RHB could be judged from the result.

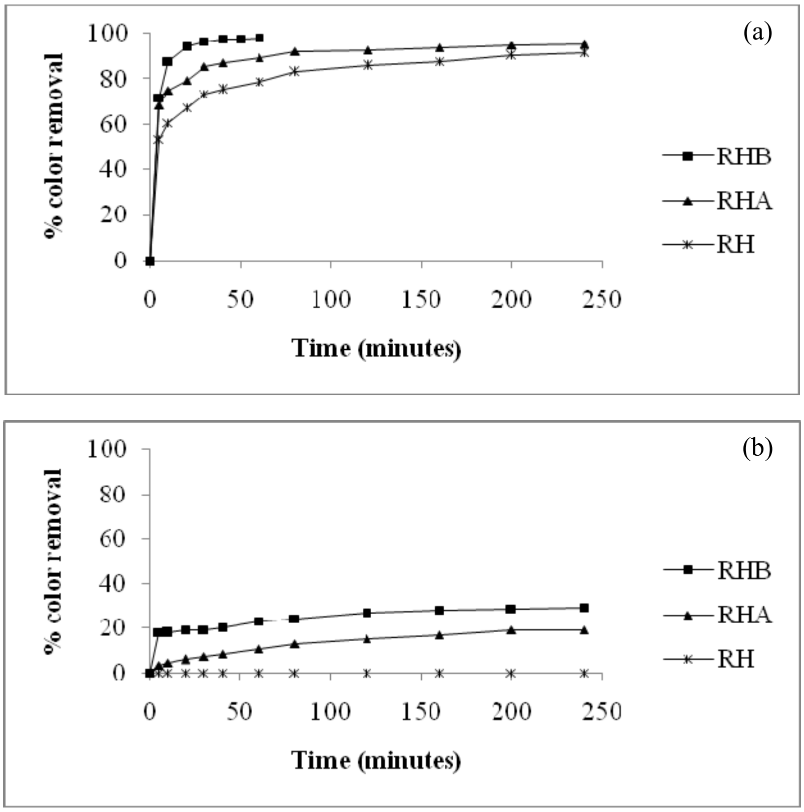

Figure 3 Comparison of the percentage of color removal of (a) Basic Red 4G and (b) Direct Supra Red BWS by modified rice husks; RHB, RHA, and RH

3.2 Comparison of the color removal efficiencies

The color adsorption at 60 mg/l of Basic Red 4G and Direct Supra Red BWS by each modified rice husk was compared by percentage of color removal as shown in Figure 3.

From the result, the Basic Red 4G was adsorbed well by all modified rice husks while the Direct Supra Red BWS was adsorbed partially. Because the rice husk has naturally anionic surface, the modification with acid and especial alkaline for this adsorbent can increase negative charge on the surface, the Basic Red 4G is a cationic dye thus it can be adsorbed well on the surface of these modified rice husks with electrostatic attraction force [14, 15]. While the Direct Supra Red BWS is an anionic dye thus it was hard to be adsorbed on those surfaces.

In case of Basic Red 4G adsorption, the RHB showed the highest color removal (97%) following by RHA (92%) and RH (86%). Because the main factors for dye adsorption were surface charge and surface area [16]. The chemical modification with NaOH (for RHB) and HNO_3 (for RHA) removed surface impurities such as natural fats, waxes, and low molecular weight lignin compounds from the rice husk surface which can improves the surface roughness and increase the surface area and adsorption properties [14], thus the color removal by RHB and RHA was more than RH. While the modification with NaOH increased more negative charge on the RHB surface which was favorable to the attraction between active sites and positive charge of the basic dye, resulting in the higher color removal comparing with the RHA.

3.3 Effect of contact time and initial dye concentration

The best modified rice husk from previous experiment, RHB, was selected to study the adsorption equilibrium. The data of color adsorption at different initial concentrations of both dyes were conducted to fit with Eq. (2) as the results showed in Figure 4.

The result revealed that the amount of adsorption increased with the longer contact times, this could be found obviously at the high initial concentrations for both dyes. Also, the amount of adsorption and the contact time to reach equilibrium of both dyes increased with the increased initial dye concentration. The amount of adsorption increased from 0.500 to 5.848 mg/g and 0.268 to 2.046 mg/g, while the required contact time to reach equilibrium increased from 5 to 40 minutes and 160 to 200 minutes, when the initial concentration increased from 5 to 60 mg/l and 5 to 100 mg/l for Basic Red 4G and Direct Supra Red BWS, respectively. Similarly, Hameed *et al.* [17] explained that the increased initial dye concentration results in an increase of the adsorption capacity because it enhance driving force to overcome the mass transfer resistance of dyes between the aqueous and solid phase. While the contact time to reach equilibrium increase with

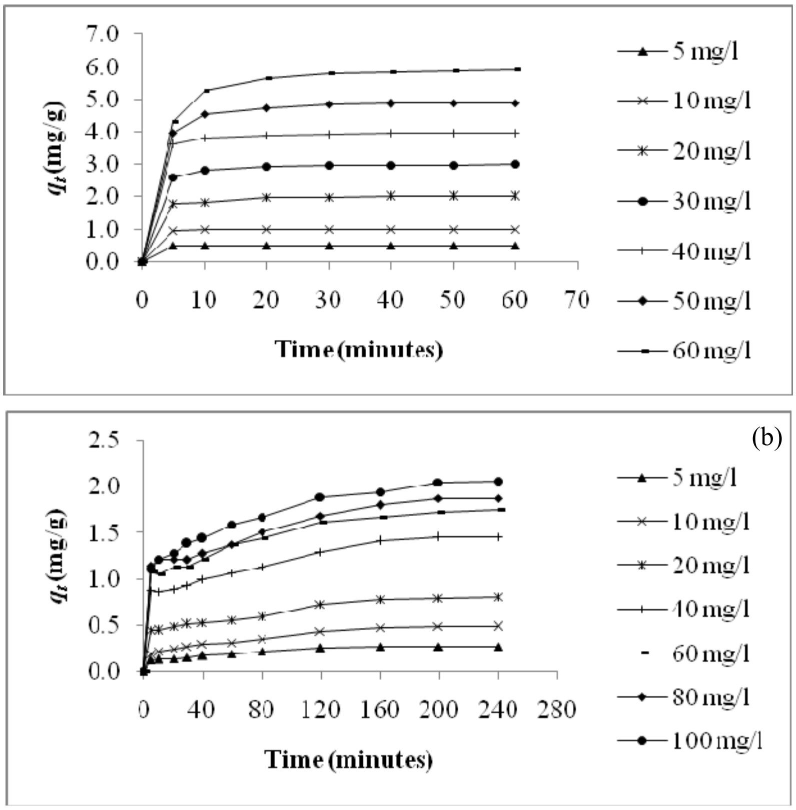

Figure 4 The adsorption at different contact times and initial concentrations of (a) Basic Red 4G and (b) Direct Supra Red BWS by RHB

Table 2 The parameters from Langmuir and Freundlich equations

Dyes	**Langmuir isotherm**			**Freundlich isotherm**		
	Q_{max} (mg/g)	**K_L (mg/l)**	**R^2**	**1/n**	**K_F (mg/g) (l/mg)$^{1/n}$**	**R^2**
Basic Red 4G	6.1996	0.0057	0.9719	0.2702	4.8831	0.9566
Direct Supra Red BWS	2.6021	3.3463	0.9932	0.5841	01807	0.9796

the increased initial dye concentration because the high initial concentration, the binding sites for adsorption onto the exterior surface less available and become saturated, thus the residual dye molecules were adsorbed by entering into pores (interior surface) with the slower rate [14]. The maximum amount of adsorption at equilibrium was found at 5.848 mg/g within 40 minutes and 2.046 mg/g within 200 minutes for 60 mg/l of Basic Red 4G and 100 mg/l of Direct Supra Red BWS, respectively. Some researcher reported the similar result, Suttanan and Piyamongkala [13], found that their rice husk-adsorbent can adsorb methylene blue (Basic dye) at 3.46 mg/g within 40 minutes. While Chowdhury et al. [14] found that their pretreated rice husk can adsorb malachite green (a cationic dye) at adsorption capacity of 17.98 mg/g within 30 minutes. While, Safa and Bhatti [18] found that the pretreated rice husk can adsorb Direct Red 31 and Direct Orange26 at adsorption capacity of 129.87 and 66.67 mg/g within180 minutes.

3.4 Adsorption isotherm

The experimental equilibrium data of both dyes was conducted to fit with Langmuir and Freundlich equations. The results showed in Figure 5-6. These adsorption models were used to describe the correlation between the modified RH as the adsorbent and dye as the adsorbate. The parameters from both models were calculated as the result showed in Table 2.

From the results, the experimental equilibrium data of both dye adsorptions was fitted with Langmuir model (R^2 = 0.9719 and 0.9932 for Basic Red 4G and Direct Supra Red BWS, respectively) better than Freundlich model (R^2 = 0.9566 and 0.9796 for Basic Red 4G and Direct Supra Red BWS, respectively), this possibly indicated the occurrence of monolayer adsorption of the dyes molecules onto the internal and external surfaces of RHB as an adsorbent base on the assumption of Langmuir model.

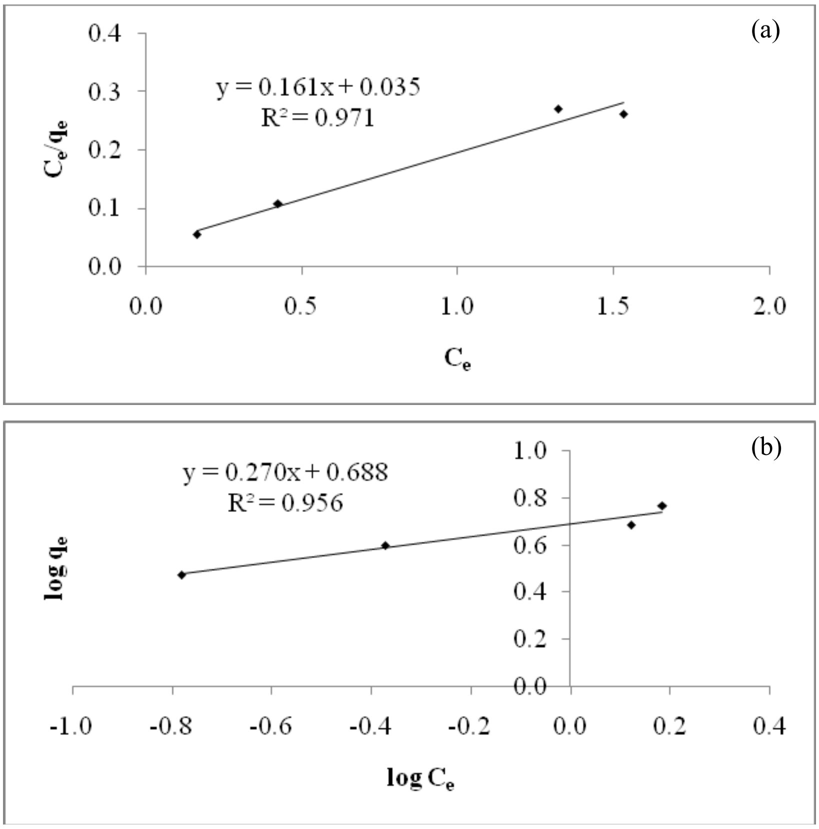

Figure 5 Adsorption isotherm of Basic Red 4G by RHB; (a) Langmuir and (b) Freundlich isotherm

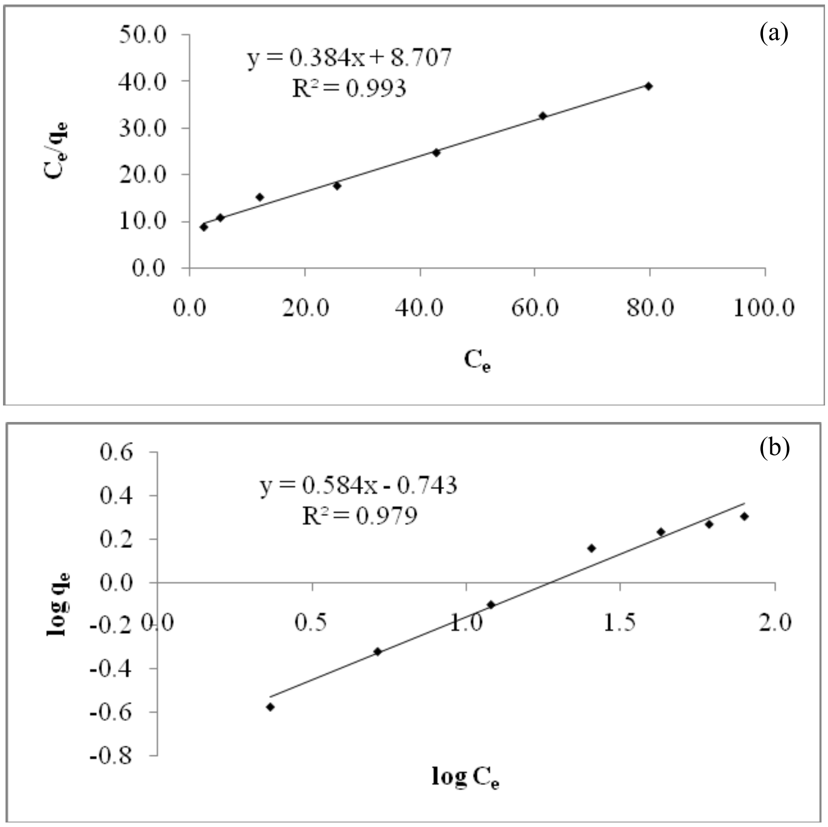

Figure 6 Adsorption isotherm of Direct Supra Red BWS by RHB; (a) Langmuir and (b) Freundlich isotherm

The maximum adsorption capacity (Q_{max}) was calculated from the slope and intercept of the plot between C_e/q_e and C_e (Table 2). The Q_{max} from dye adsorption by RHB showed rather less capacities as 6.2 mg/g and 2.6 mg/g for Basic Red 4G and Direct Supra Red BWS, respectively. Several researchers reported the higher maximum adsorption capacities from their modified adsorbents. Deniz and Karaman [19] reported the maximum adsorption capacity reaching 71.94 mg/g from Basic Red 46 adsorption by pine tree leaves. Consolin *et al.* [20] found that their sugarcane bagasse can adsorbed Methylene blue with the maximum adsorption capacity of 34.20 mg/g, and Arami *et al.* [21] studied the use of orange peel as adsorbent for removing color from Direct Red 23 (DR23) and Direct Red 80 (DR80) and reported the maximum adsorption capacity of 10.72 and 21.05 mg/g, respectively. However, some researchers reported less maximum adsorption capacity from their adsorbents. Khattri and Singh [22] studied the malachite green (a basic dye) adsorption by neem sawdust and reported the maximum adsorption capacity of 4.354 mg/g. While Kavitha and Namasivayam [23] reported the maximum adsorption capacity of 5.87 mg/g from methylene blue adsorption by coir pith carbon.

In addition, the 1/n value from Freundlich equation was calculated from the slope of the straight line of the plot log q_e versus log C_e (Table 2).This value is a measure of the adsorption intensity, the value of 1/n less than 1 represents a favorable adsorption [14]. Thus 1/n values of 0.2702 and 0.5841 for Basic Red 4G and Direct Supra Red BWS adsorption in this study indicated the favorable dye adsorption by RHB.

4. Conclusions

This study revealed the possibility of the modified rice husk for the textile dyeing wastewater treatment. Because this adsorbent had naturally negative charge on the surface, it can well adsorb the cationic dye as the basic dye more than the anionic direct dye with electrostatic attraction force. The modification of rice husk with sodium hydroxide can increase the surface area and negative charge on the surface thus it can increase the efficiency in the basic dye adsorption. The equilibrium time of Basic Red 4G and Direct Supra Red BWS adsorption was found at 40 and 200 minutes, respectively. The result of adsorption equilibrium fitted well with Langmuir model indicated that the adsorption of both basic and direct dyes was monolayer adsorption onto the internal and external surfaces of the modified rice husk. Although the maximum adsorption capacity from Langmuir model was calculated rather low as 6.2 mg/g and 2.6 mg/g for Basic Red 4G and Direct Supra Red BWS, respectively. However the 1/n value from Freundlich model was calculated as 0.2702 and 0.5841 for Basic Red 4G and Direct Supra Red BWS, respectively, indicating the favorable dye adsorption. Thus this modified rice husk may be an alternative adsorbent to treat color in wastewater from the particular dyeing process using cationic dye.

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