Optimal conditions of Dye Removal from Textile Dyeing Industrial Wastewater by Adsorption Process

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Abstract

The study was focused on optimal condition (pH, dosage and contact time), kinetic, and adsorption isotherm of dye removal from textile dyeing industrial wastewater by rice husk and water hyacinth as adsorbents. The results revealed that the maximum dye removals in both of rice husk and water hyacinth were occurred at initial pH 2.0 with the percentages of 95% and 93%, respectively. Optimal dosages of rice husk (50 g/L) and water hyacinth (10 g/L) were suitable contact time interval for adsorption equilibrium at 360 min. The kinetics followed a pseudo second-order. Correlation coefficient (R^2) of rice husk adsorbent used in both Langmuir's equation isotherm and Freundlich's equation isotherm (0.9946, 0.9445) were higher than R^2 of water hyacinth adsorbent (0.8043, 0.8109). Rice husk was the best adsorbent followed Langmuir’s equation isotherm and adsorption mechanism was a chemisorption. Moreover, the characteristics of textile dyeing industrial wastewater using rice husk adsorbent were decreased from 178 to 85 mg/L (TSS), 1,883 to 1,430 mg/L (TDS), 95 to 48 mg/L (BOD) and 445 to 292 mg/L (COD), respectively. Hence, rice husk and water hyacinth could be applied for dye removal in wastewater treatment.

Keywords: Adsorption, Dye removal, Industrial wastewater, Rick husk, Water hyacinth (*Eichhornia crassipe* (C.Mart) Solms)

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1. Introduction

Textile dyeing industry is one of the industries that consume a lot of water and chemical substances, which cause a number of problems to the society. One of the main problems caused the water pollution, which was reported that it was from the drainage. The discharged wastewater was composed of color, biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, suspended solid (SS), heat and others. Moreover, the artificial coloring provided for the procedure also affects the natural resources or the water resources [1]. Reactive dyes are widely used in dyeing processes for coloring yarn or fabric due to their high reactivity and good color resilience. Even though there are a number of different dyes, it seems that the reactive dye causes far more problems than other types [2]. They contain the chromophoric groups and reactive groups that come from covalent bonds of fibers. Substance named azo is let into the environment somehow from the textile dyeing industry and it has a huge effect on the environment. Besides limitations previously discussed, the regeneration of activated carbon, such as the high expense of regeneration and loss of carbon in the process, led to problem that could be a carcinogen [3]. For previous researches, there were various manners involving with the solutions of color problems in the wastewater. The method was called as adsorption that was widely used in many companies with the purpose of removing the color from the wastewater [4]. Other researches were reported that synthetic adsorbents such as activated carbon or known as the porous material had the ability to absorb various organic compounds in the fluid or gas due to the micro porosity and its high efficiency [5]. Moreover, activated carbon was the one of the excellent materials, however; it was the higher expenses as well. Also, after the treatment was finished, the ability of further procedure was denied. The waste materials (natural sorbents) such as rice husk and water hyacinth (*Eichhornia crassipe* (C.Mart) Solms) as adsorption media were applied for dye removal [6-7]. After the existing problems in textile dyeing industry were toward the society in Thailand, they necessarily happened to investigate the procedure to remove the mix color for specific reaction dye (reactive blue 19 and reactive blue 160). Hence, this study was focused on the feasibility of waste materials; rice husk and water hyacinth (*Eichhornia crassipe* (C.Mart) Solms) as adsorption media for dye removal from textile dyeing industrial wastewater. The optimal conditions for adsorption capacity of waste materials; initial pH (2.0-10.0), dosage (1-50 g/L) and contact time (30-1,440 min) were investigated. Kinetic, adsorption isotherm and the efficiency of color removal from textile dyeing industrial wastewater were also carried out.

2. Materials and methods

2.1 Preparation of adsorbents and synthetic wastewater

The natural sorbents of rice husk (RH) and water hyacinth (WH) were washed cleanly by a distilled water, cut in the small pieces and dried with a hot air oven at 80ºC for 2 h. Then, they were screened with a sieve (600 μm) and were kept in a desiccator before using as sorbents.

The adsorbents were analyzed surface area, pore diameter, and pore volume by the Brunauer Emmett and Teller (BET) method [8] using BELSORP – mini, BEL, Japan. The averages of specific surface area, pore diameter, and pore volume of rice husk were 86.84 m^2/g, 3.35 nm, and 19.95 cm^3/g, respectively. While, that's of water hyacinth were 0.059 m^2/g, 190.12 nm, and 0.013 cm^3/g, respectively. It was apparent that the specific surface area of rice husk adsorbent was the larger and its pore size was smaller than water hyacinth.

Synthetic wastewater of mix reactive dye solution concentration at 1,000 mg/L were prepared by dissolving 0.5 g reactive blue 19 ($C_{22}H_{16}N_2S_3O_{11}.2Na$) with 0.5 g reactive dye 160 ($C_{38}H_{23}Cl_2N_{14}O_{18}S_5.5Na$) in 1 L of distilled water. Synthetic wastewater was prepared the concentration at 100 mg/L in all experiments. The concentrations of synthetic wastewater before and after the adsorption process were checked by a UV – Visible Spectrophotometer at wavelength 614 nm.

2.2 Experimental setup

The experiments were carried out in the batch test. Waste materials of rice husk and water hyacinth (*Eichhornia crassipe* (C.Mart) Solms) were applied for natural adsorbents in adsorption process of experiment. The synthetic wastewater at concentration 100 mg/L (100 mL) was agitated with 10 g/L of adsorbents, and was set in the range of initial pH from 2.0 to 10.0 with 0.1 N NaOH or 0.1 N HCl. The optimal dosages of adsorbents were varied weight (1, 5, 10, and 50 g/L) and were fixed with the optimum of initial pH. After that, the experiment was operated into the different contact times of 30, 60, 90, 120, 150, 240, 300, 360, 420, 480, 540, 720 and 1,440 min [9-10] with the optimum of initial pH and dosages of adsorbents. All batch tests were put into a shaker (200 rpm) for 24 h. and were performed in the triplicates. After the experiments have been completely finished, the liquid samples were collected and filtered to measure the absorbance of dye by a UV – Visible Spectrophotometer at wavelength 614 nm as well as were analyzed the final concentration of wastewater.

For an efficiency of dye removal from textile dyeing industrial wastewater, textile dyeing industrial effluent was obtained from the equalization tank (Wastewater from dyeing plant) of a textile industry at Nakhonpathom, Thailand. Effluent was collected by a grab sample and the physical and chemical characteristics were of pH (9.2), color (93 IAU), TSS (178 mg/L), TDS (1883 mg/L), BOD (95 mg/L), and

COD (445 mg/L) [11]. Moreover, analysis of initial dye concentration of effluent was determined by a UV – Visible Spectrophotometer. The best adsorbent (rice husk) was added 100 mL of effluent into flask (250 mL) at optimal conditions of initial pH (pH 2.0) and dosage (50 g/L) and then was put into the shaker at 200 rpm for a contact time equal to equilibrium (360 min) of adsorption. After water sample and adsorbent apart were filtrated and separated, measurement of absorbance was determined the final concentration for pH values and physical and chemical analysis of effluent.

2.3 Analytical method and data analysis

The efficiencies of color removal by rice husk and water hyacinth were expressed in the concentration of color (mg/L). The removal efficiency was calculated according to Equation (1) [12]:

$$\text{Removal efficiency (\%)} = [(C_0-C_e)/C_0]*100 \quad (1)$$

When, C_0 = Initial concentration (mg/L), C_e = Final concentration (mg/L)

The amount adsorbed (q_e) were calculated according to the Equation (2) [13]:

$$\text{The amount adsorbed } (q_e)(\text{mg/g}) = (C_0 - C_e)\ V/m \quad (2)$$

When, V= Volume of solution (L), m = Weight of adsorbent (g).

The adsorption kinetics was investigated by examining the influence of contact time on dye removal according to them, the period time required for the maximum of dye removal. Their kinetics were analyzed by the pseudo first-order and pseudo second-order equations to model.

The linear pseudo first-order equation of Lagergren is expressed as Equation (3) [14-15]:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t \quad (3)$$

Where q_e and q_t are the amount of dye adsorbed onto the adsorbent (mg/g) at equilibrium and at t, respectively. K_1 is the rate constant of first-order adsorption (min^{-1}) was obtained from linear slope and q_e (cal) was obtained from intercept.

By contrast, the pseudo second-order kinetic model is based on the experimental data of solid phase adsorption [16]. The linear pseudo second-order equation is expressed as Equation (4) [16]:

$$t/q_t = (1/K_2q_e^2) + (t/q_e) \quad (4)$$

Where, K_2 is the rate constant of second-order adsorption (g mg^{-1} min^{-1}). It was obtained from intercept. q_e (cal) was obtained from a linear slope.

In the present study isotherm models, namely, Langmuir and Freundlich were fitted with the experimental equilibrium data for adsorption. These isotherm models in linear form are represented by the Equation (5) and (7) [17-19].

Langmuir adsorption isotherm model:

$$q = q_m bC/1+bC \quad (5)$$

When, q is x/m, the amount of dye adsorbed on adsorbent (mg/g) at equilibrium, C is the equilibrium concentration of solute (mg/L), q_m is monolayer adsorption capacity (mg/g), and b is adsorption equilibrium constant (L/mg) [20-24].

For the isotherm, it was showed that absorbing the experimental results were good or bad. It was also used for the calculation of the constant isotherm of Langmuir and showed in a fixed value of the separation R_L (Dimensionless Constant Separation Factor). R_L value ($0 < R_L < 1$) indicates the vacuum. Linear can be obtained from the relationship of Equation (6) [20-24].

$$R_L = 1 / (1+bC_0) \quad (6)$$

When, b = Adsorption coefficient, C_0 = Initial concentration (mg/L)

Freundlich adsorption isotherm model:

$$q = KC^{1/n} \quad (7)$$

When, q is x/m, the amount of dye adsorbed on adsorbent (mg/g) at equilibrium, C is the equilibrium concentration of solute (mg/L), K is related to adsorption capacity, and n is the measure of adsorption intensity or surface heterogeneity. The value of n ranges between 0 and 1, the adsorption becomes more heterogeneous as its value gets closer to zero [20-24].

3. Results and discussion

3.1 Optimal conditions of initial pH, dosage and contact time to equilibrium of adsorbent for dye removal

The results showed that initial pH significantly affected dye removal ($p < 0.05$) (Fig. 1). The percentage removals of all sorbents were increased at the lower pH and declined at the higher pH. Two types of adsorbents were recorded the maximum uptakes of dye at initial pH 2.0 by rice husk (RH) (95%) and water hyacinth (WH) (93%) (Fig. 1(a)), which were consistent with the amount of dye adsorb at 9 and 9 mg/g, respectively (Fig. 1(b)). It indicated that the amount of dye uptake decreased suddenly with an increase in the pH of the solutions similar to previous reports. The maximum adsorption was recorded for pH value in the range of 1.5 – 2.0 [25]. The experiments were also performed at pH 2.0 to avoid disruption of the fiber structure of the adsorbents [26-27]. As the pH value decreased, it was possible for the adsorbent surface to become positively charged, thereby allowing electrostatic attraction forced to enhance the dye anions, which were negatively charged. Thus, the increasing quantity of dye was adsorbed and also raised the dye removal percentage. When the pH values were raised, however, the surface may become negatively charged. These results were in hydroxide (OH^-) ions competing with dye anions and caused the quantity of dye adsorbed or the percentage removal of dye to drop [5].

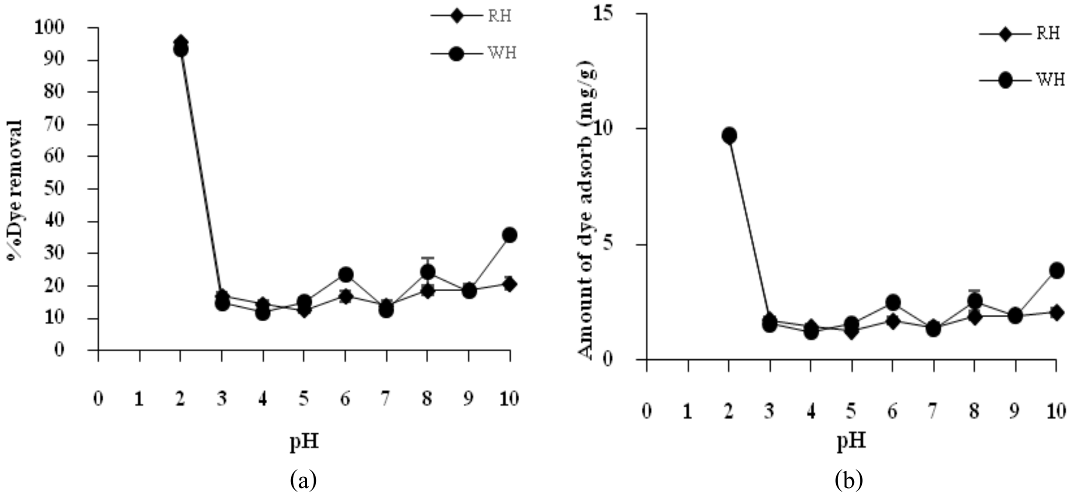
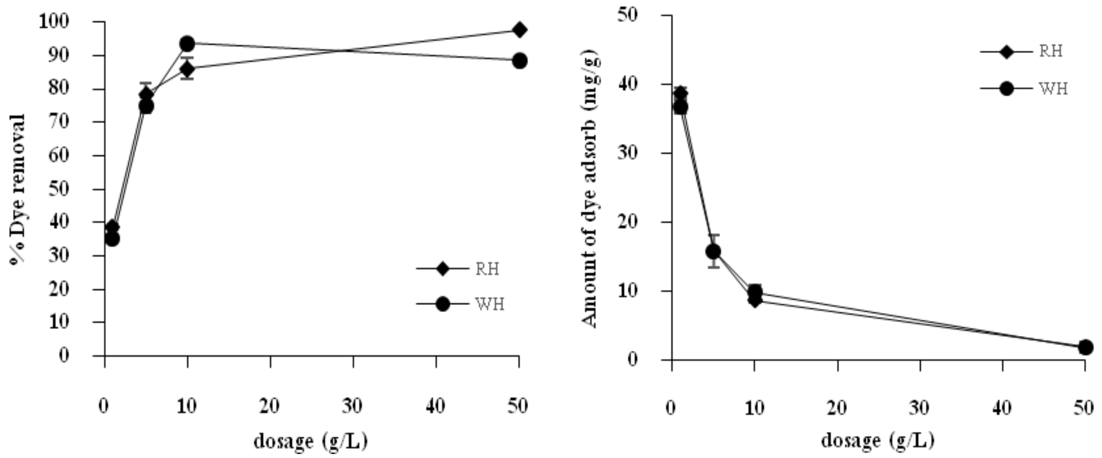


Fig. 1. Effect of initial pH for dye removal; (a) Percentage of dye removal and (b) Amount of dye adsorbed

The adsorbent dosages were significant ($p< 0.05$) for dye removal (Fig. 2). For quantitative removal of dye, a minimum RH dosage of 50 g/L, whereas WH dosage was at least 10 g/L were required. Similar results were reported with optimal adsorbent dosage at 1.0 g/100 mL [6]. For the higher values of sorbent dosage, the removal of dye remained almost constant or decreased slightly. An increase in adsorbent dosage was resulted in the higher percentage removal of dye. It was due to the available surface area of the adsorbent increased and more potential sites existed to facilitate bio-sorption [28]. The percentages of dye removal increased from 38% to 97% for RH and 35% to 85% for WH (Fig. 2. (a)). On the other hand, the amounts of dye adsorbed were decreased from 38 to 1 mg/g for RH and 36 to 1 mg/g for WH (Fig. 2 (b)).

These results were consistent with previous study. The fall in the quantity of adsorbed dye when the adsorbent mass increased was attributed to the split in the flux, or to the concentration gradient measuring the relationship between the concentration of the solute in the solution and the concentration of the solute at the adsorbent surface. When the adsorbent mass increased, the quantity of dye adsorbed per unit weight of adsorbent decreased. Thus, the dye adsorbed value was lowered by raising the adsorbent dosage [5].



(a) (b)

Fig. 2. Effect of optimal dosage for dye removal; (a) Percentage of dye removal and (b) Amount of dye adsorbed

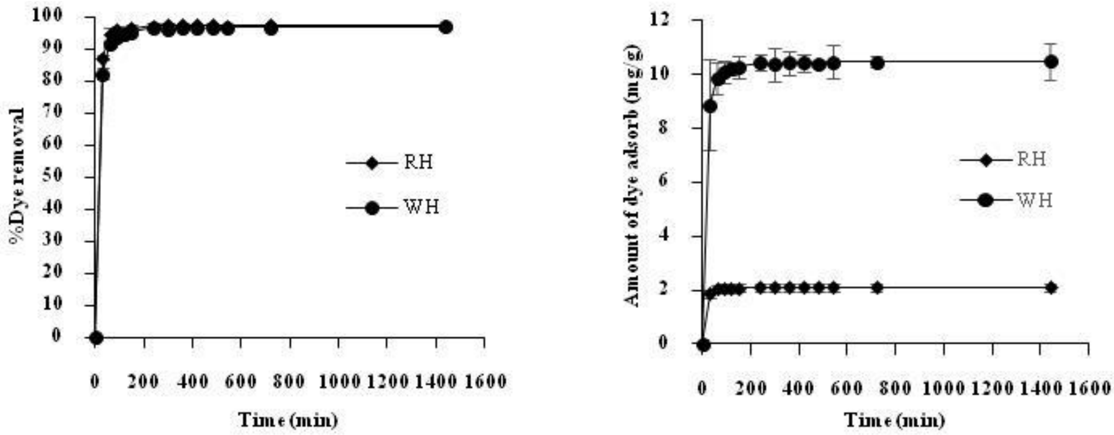
The effect of contact time was investigated at 100 mL of synthetic wastewater at concentration 100 mg/L. The adsorbent dosages were fixed in 50 g/L of RH and 10 g/L of WH. They were carried out at the optimum of initial pH 2.0 and put into the shaker (200 rpm) for different contact times. Results showed that adsorption was very fast at the beginning, whereas the time was required to reach equilibrium increased with the significant ($p < 0.05$) [29]. Also, the contact time period of 360 min was suitable time interval for adsorption equilibrium. The percentage of dye removal increased with contact time for all sorbents. Furthermore, after a contact time of 360 min, the curves exhibited a flat plateau. The adsorption yields of sorbents for dye removal were 97% (RH) and 96% (WH) (Fig. 3 (a)), and the amounts of dye adsorbed were 2 and 10 mg/g for RH and WH, respectively (Fig. 3 (b)).

3.2 Kinetic adsorption of dye removal

The adsorption kinetics was investigated by examining the influence of contact time on dye removal. The applicability of pseudo first-order and pseudo second-order kinetic models was determined by measuring the coefficients of determination (R^2). High values of R^2 indicated that the model was appropriate for the data [25]. The results of the kinetic parameters are displayed in Table 1.

The R^2 values of pseudo first order kinetic were relatively low. The calculated q_e values were obtained from these models and failed to match the q_e (exp). The first-order kinetic model did not match well with the whole range of contact times. However, this model could be used for the preparatory stage of the mechanism of adsorption [31].

The high correlation coefficients obtained for the pseudo second-order kinetic model were predicted that dye adsorptions of both rice husk (0.9999) and water hyacinth (0.9998) were fitted to this model and the rate-limiting step may be chemical adsorption involving valence forces through sharing of electrons between adsorbent and adsorbate, or covalent forces [30, 32-35]. The kinetics of dye adsorption onto the adsorbents could be explained by a pseudo second-order kinetic equation.



(a) (b)

Fig. 3. Effect of contact time to equilibrium; (a) Percentage of dye removal and (b) Amount of dye adsorbed.

3.3 Adsorption isotherm for dye removal

Regarding to Table 2, the dosage of RH and WH were used at various weights (0.1, 0.5, 1, 5 g) under the optimal conditions of initial pH 2.0, initial concentration 100 mg/L, contact time 360 min and agitated on shaker at 200 rpm.

The correlation coefficients (R^2) of rice husk adsorbent for both the Langmuir (0.9946) and the Freundlich equation isotherms (0.9445) were higher than that of water hyacinth adsorbent (i.e. 0.8043 and 0.8109). The adsorption capacity (q_m) of rice husk was 0.418 mg/g, while that's of water hyacinth was 0.3623. As well as the R_L value of rice husk (0.3131) was higher than the R_L value of water hyacinth (0.1943). It was indicated that rice husk adsorbent had a high capacity for dye adsorption in solution.

Table 1 Kinetic parameters of dye adsorption onto the rice husk and water hyacinth

Adsorbents	q_e (exp)	Pseudo first order kinetic			Pseudo second order kinetic		
		q_e (cal)	K_1 (min^{-1})	R^2	q_e (cal)	K_2 (g mg^{-1} min^{-1})	R^2
Rice husk	2.1048	0.4104	0.0068	0.8592	2.1133	0.3012	0.9999
Water hyacinth	10.4352	0.3394	0.0063	0.7848	10.4932	1.0265	0.9998

Table 2 Adsorption isotherms data of rice husk and water hyacinth

Types of adsorbent	Langmuir's equation isotherm				Freundlich's equation Isotherm		
	R^2	$q_{m\ (mg/g)}$	b	R_L	R^2	K	n
RH	0.9946	0.418	0.0215	0.3131	0.9445	$8.73x10^{-3}$	1.1143
WH	0.8043	0.3623	0.0393	0.1943	0.8109	$1.78x10^{-2}$	1.3963

Table 3 The efficiency of dye removal from synthetic wastewater and textile dyeing wastewater

Type of adsorbents	Initial dye concentration (mg/L)	Final dye concentration (mg/L)	% Dye removal	Initial color intensity (IAU)	Final color intensity (IAU)	% Color intensity removal
Synthetic wastewater	108.33	2.90	97%	103	15	85.44
Wastewater (adjusted pH 2.0)	102.32	16.41	83%	93	46	50.54
Wastewater (no adjusted pH)	102.32	63.79	37%	93	76	18.28

Thus, the results of rice husk adsorbent were only focused and were more discussion in this part. The experimental data for rice husk adsorbent was described accurately by the Langmuir model. The linear regression curve obtained from the Langmuir model gave a better fit than the Freundlich model. It was suggested that the mechanism of adsorption was monolayer and the surface area of the adsorbent was the major factor in the adsorption process. These results were similar to previous studies regarding the use of agricultural waste as adsorbent for removal of direct blue 199 [33], reactive orange dye 16 [35], direct blue 86 [36], direct yellow 12 [37], direct red 23 and direct red 80 [38] from solution by following the Langmuir isotherm. These results also indicated that the best adsorbent was rice husk (R^2= 0.9946), which was fitted to the Langmuir equation isotherm with a chemisorption mechanism involving the adsorption. The value of R_L (0.3131) was obtained in the range of 0–1, which suggested that the adsorption process was favorable. It was also confirmed that the surface of the rice husk was a significant parameter for dye removal efficiency as the smaller particles provided more available sites for dye adsorption. Due to the specific surface area of rice husk adsorbent was the larger and its pore size was smaller than that of water hyacinth.

Therefore, the surface of rice husk was an important factor for efficiency of dye removal because an increase of surface area with decreasing in pore diameter of rice husk can provide a favorable adsorption process with more available site for dye adsorption than the larger particles. In the process of dye removal, the surface area is critical because when adsorption takes place, the molecules become attached to the active regions of the sorbent surface before diffusing into the pores to provide coloration. The extent to the pore volume influences adsorption depends upon the level of steric hindrance, which is related to the dye molecule size. Thus, it can penetrate the structure of the pores. However, adsorption is increased with the greater surface area and the greater sorbent pore volume [39].

3.4 Comparison of the efficiencies of dye removal by rice husk between synthetic wastewater and textile dyeing industrial wastewater

The results of efficiencies of dye removal by rice husk between synthetic wastewater (pH 2.0) and textile dyeing industrial wastewater (adjusted or no adjusted pH 2.0) are shown in Table 3. The initial dye concentration of synthetic wastewater was 108.33 mg/L (color intensity 103 IAU). After a period of time, the dye removal was 97% with 2 mg/g dye adsorbed of rice husk. The final concentration of synthetic wastewater was 2.90 mg/L (color intensity 15 IAU). As, the initial dye concentration of textile dyeing industrial wastewater was 102.32 mg/L (color intensity 93 IAU). After a period of time, the dye removal at the optimal condition (adjusted pH 2.0) was 83%, the amount of dye adsorbed was 1.7181 mg/g of rice husk, and the final dye concentration of textile dyeing industrial wastewater was reduced to 16.4118 mg/L (color intensity 46 IAU). Meanwhile, the acidic conditions (pH 2.0) affected adversely to the ecosystem and environment and may not be appropriate for use in wastewater treatment plant. After a period of time was done, the percentage of dye removal, the amount of dye adsorbed and final concentration at the normal condition (no adjustment to pH) were 37%, 0.7706 mg/g, and 63.7882 mg/L (color intensity 76 IAU), respectively.

After the textile dyeing industrial wastewater was adsorbed by rice husk, the quality of wastewater was showed the better values. The physical and chemical characteristics of wastewater were BOD 48 mg/L, COD 292 mg/L, TSS 85 mg/L, and TDS 1,430 mg/L. These parameters were followed the standards of industrial effluent quality of the Department of Industrial Works, Thailand [40]. Consequently, application of rice husk could be reduction of TSS, TDS, BOD and COD values from wastewater and was effective for dye removal from textile dyeing industrial wastewater. Regarding an evaluation of approximate capital cost of using rice husk for dye removal, it was based on only the saturation capacity (q_m) of the adsorbent without other cost factors, for example cost for regeneration or disposal cost, in the evaluation. Rice husk was also a ready-to-use material with low-cost adsorbent for dye removal. In case of the adsorption system cost was estimated as the relative cost for 1 kg of adsorbent, the comparative assessment of cost and adsorption (saturation) capacity for dye removal with other adsorbents was showed in Table 4.

Table 4 Comparative assessment of cost and adsorption (saturation) capacity for dye removal with other adsorbents

Adsorbents	Adsorption capacity (mg/g)	Price/kg of adsorbent (Bath)	Reference
Activated carbon (powder)	222.22	150	[41]
Bentonite	151-175	43	[42]
Carbonaceous materials	75.1	17.28	[43, 44]
Fly ash (bagasse)	6.46	7	[44, 45]
Rice husk	0.478	5	This study

4. Conclusions

Waste materials of rice husk (RH) and water hyacinth (WH) as natural adsorbents could be applied effectively for dye removal from textile dyeing industrial wastewater. Both adsorbents were optimal recorded the maximum uptake of dye at initial pH 2.0. For quantitative of dye removal, the minimum dosages were found out at 50 g/L (RH) and 10 g/L (WH). A contact time period of 360 min for both adsorbents was considered to be a suitable time interval to attain adsorption equilibrium. Moreover, their kinetic adsorptions were fitted to the pseudo second-order model. The Langmuir (0.9946) and the Freundlich equation isotherms (0.9445) of RH adsorbent were higher than that of WH adsorbent (i.e. 0.8043 and 0.8109). Thus, the best adsorbent was rice husk (R^2=0.9946), which was also followed the Langmuir equation isotherm. The efficiencies of dye removal from textile dyeing industrial wastewater by RH adsorbent under the optimal condition were at 83%. The textile dyeing industrial wastewater after using adsorption of RH were reduction values of BOD (from 95 to 48 mg/L), COD (from 445 to 292 mg/L), TSS (from 178 to 85 mg/L), and TDS (from 2,243 to 1,430 mg/L).

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