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Original research article

Adsorption of Direct Red 83 Using Cetyltrimethylammonium Bromide Modified Water Hyacinth

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ABSTRACT

As of present, water pollution that is caused by textile dyeing factories is one of the primary concerns in Thailand. Wastewater is contaminated with dyes, which results in an unpleasant watercolor. This research emphasized on the study of the adsorption of Direct Red 83 dye through the use of water hyacinths, which are abundant in number and can be easily obtained. Prior to the adsorption, water hyacinths were modified with cetyltrimetylammonium bromide (CTAB). The value of pH_{pzc} of the adsorbent was 5.15. The adsorption was most effective at the pH value of 3. After increasing the amount of adsorbent and the temperature for water treatment, the percentage of dye removal would increase. However, if the concentration of dye increases, the percentage of dye removal would decrease. Upon the addition of electrolytes into the Wastewater that contained this particular type of dye, it was found that calcium salts lowered the percentage of dye removal to a greater extent than sodium salts. The process of adsorption was in accordance with Langmuir adsorption model, with q_e value equals to 66.2252 milligrams per gram, K_L value equals to 1.6064 liters per milligram, and R_L value equals to 0.0062. Based on Dubinin-Radushkevich equation, the obtained E value represents physical adsorption. According to Redlich-Peterson equation, b_R equals to 1.0797, which supported the fact that adsorption conformed to Langmuir model. This adsorption was in accordance with the model of a second-order reaction. When the temperature of the Wastewater increases, K_2 value would increase. When the concentration of dye increases, q_e value would increase.

Keywords: Anionic dye; Biosorbent; CTAB; Direct dye; Textile wastewater

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1. Introduction

Currently, there are numerous industries in Thailand that are expanding, and the textile industry is amongst one of them. The textile industry is expected to grow in accordance with the global economic recovery. After 2015, the total value of exports was USD 2,700 million or approximately THB 8 billion, which resulted in the expansion of textile industry. The industrial factories were categorized dyes into 11 groups based on the used in the process, comprising: acid dye, direct dye, basic dye, disperse dye, reactive dye, azoic dye, vat dye, mordant dye, ingrain dye, oxidation dye, and sulfur dye. Each type of dye has different chemical structures, properties, and usage. If categorized according to the dissociation of dye into ions in the solvent, it can be separated into cationic, anionic, and nonionic dyes. Cationic dyes include basic dye, while anionic dyes include reactive dye, direct dye, and acid dye; and nonionic dyes include disperse dyes [1]. In the manufacturing process of each type of textile, a variety of dyes and chemicals are used. In particular, the processes of preparing, dyeing, printing, and decorating. As such, it is undoubted that water is an important factor in all of these processes, which consequently lead to polluted or Wastewater with higher temperature and unfavorable smell and color. Moreover, it was found that the dye in Wastewater is a colloid, which prevents sunlight from entering the water surface, therefore impeding water plants from photosynthesis. As a consequence, the amount of oxygen in water decreases, which further harms living organisms in water. Indeed, Wastewater also inhibits the activities of various microorganisms in the process of biological treatment. Water treatment can be performed in a variety of ways, such as membrane filtration [2], coagulation and flocculation [3], oxidation [4], and biological technology [5]. However, such methods are relatively complicated and expensive. Some even produce chemicals that are harmful to the environment. Hence, the process of adsorption through the use of natural materials is an alternative method of water treatment, which is not complicated and does not require the addition of chemicals into the water. Likewise, it requires low investment and less time for water treatment. It does not require a large space and can be processed at a temperature and pressure that are friendly to the ecosystem. Moreover, it is also regarded as one method of adding value to wastes.

Eichhornia crassipes, commonly known as water hyacinth, is a free-floating aquatic plant that can thrive in both still and flowing water. It reproduces rapidly through seeds and budding and has a high rate of growth. In addition, it has a high tolerance to the environment and is ranked in 8th place as the world's most aggressive weeds. According to the survey in Thailand, water hyacinths have spread to the river sources in 64 provinces, which is equivalent to a total of five million tons of biomass per year. Issues that arise from such spread include an obstruction in water transportation, hindering aquaculture and aquatic farming. It is apparent that water hyacinths do not only affect the environment, they also affect social and economic aspects. Thus, the issue of water hyacinths should be solved; whereby the appropriate solution to the problem is the collaboration between all related sectors to identify the best way to utilize benefits from water hyacinths.

Water hyacinth is effective in adsorption and contains important elements that include cellulose (15% in leaf, 17% in stem, and 18% in all parts of the plant) and hemicellulose (30% in leaf, 22% in stem, and 28% in all parts of the plant), which have the functional group for exchanging ions or molecules of organic substances [6]. A previous research had experimented on water hyacinths by drying and processing them into powder, which was later used to adsorb dyes in the wastewater. Guerrero-Coronilla et al. (2015) used the leaves of water hyacinths to adsorb amaranth dye, which is an anionic dye [7]. It was found that the efficacy of water treatment per quantity of the adsorbent used (q_m) was 16.4 milligrams per gram, which was considerably low. Alternatively, Wanyonyi et al. (2014) ground the roots of water hyacinths into powder to adsorb Congo red dye [8]. The results indicated the q_m value to be at 1.6 milligrams per gram. Another group of researchers prepared the conditions of the adsorbent in various ways, such as modification water hyacinths with HCl, date seeds with $ZnCl_2$, rambutan shells with KOH, pineapple shells with KOH or K_2CO_3, tea residues with CH_3COOK, bamboos with H_3PO_4, HNO_3, $ZnCl_2$, or KOH, cocoa shells with CO_2, and barley straws with surfactant. Based on the results of experiments, it was found that the prepared adsorbents generally had higher efficacy than unprepared adsorbents [9]. Furthermore, Zhao (2014) improved rice straws with CTAB that were later taken to adsorb Congo red dye with a column system [10]. The results indicated that the improvement in the quality of the adsorbent increased the efficacy of adsorption.

This research has the objectives to study the physical properties of water hyacinths before and after modification with cetyltrimethylammonium bromide (CTAB), as well as to determine the value of pH that caused the charge value at the adsorbent surface to become zero and examine the effects of pH, amount of adsorbent, concentration of dye, temperature, and various electrolytes contained in wastewater. In addition, this research also aimed to study the activation energy, adsorption isotherms, kinetics, and thermodynamics. The success of this research can lead to the development of waste materials that can be utilized to the maximum benefit.

2. Materials and Methods

2.1 Preparation of adsorbent

Water hyacinth (WH) was collected at (13°46'54"N 100°37'43"N), a small fish pond without heavy metal and other toxic substances. The water hyacinth was washed with tap water several times to remove dirt, then sliced into small pieces and dried under sunlight for several days. The dried water hyacinth was ground into fine powder, sieved using 35 mesh sieve size and then put in an oven for 24 hours at 100°C. Preparation of the modified water hyacinth was carried out by mixing 75 grams of WH powder with 500 mL of 0.01 M CTAB [11]. A mixture was stirred continuously for 6 hours at room temperature and then filtered. The excess CTAB was removed by washing several times with deionized water. The modified water hyacinth (M-WH) was dried in the oven for 24 hours at 100° C and kept in a desiccator for further use.

2.2 Preparation of dye solutions

A dye used in the experiment was Direct Red 83 (C.I.29225). A stock solution of 1,000 ppm of Direct Red 83 was prepared. Various concentrations were prepared by diluting this stock solution with deionised water. All chemicals used in the experiments were AR grade.

2.3 Adsorbent characterisation

The unmodified water hyacinth, the modified water hyacinth before and after adsorption were analysed their physical characteristics. The FTIR spectra of the samples were scanned by placing KBr pellets in the Parkin Elmer (Spectrum GX model) spectrometer. The KBr pellets were prepared by mixing the samples with KBr powder, grinding it in an agate mortar and then shaping it into pellets under hydraulic pressure. SEM photograph of the samples was examined by scanning electron microscope (Leo 1455 VP). The analysis of a point of zero charges, pH_{PZC} was carried out by preparing 50 mL of 0.01 M NaCl. In 100 mL Erlenmeyer flask. The solution pH was adjusted to 2-12 by adding 0.01 M HCl or NaOH. The modified water hyacinth (0.15 g) was added to the solution. Shaking of the solution at 120 rpm for 24 hours was performed. The final solution pH was then measured. [12]

2.4 Adsorption experiments

Adsorption experiments were carried out in a batch process. In each experiment, an accurately adsorbent dose was added to 500 mL of a certain concentration of dye solution with a certain pH in a 1L beaker. The solution pH was adjusted by adding 0.1 M HCl or NaOH solution. The mixture was agitated in a thermostatic shaker at a constant temperature. Five mL of dye solution was continuously collected and measured its concentration until 180 min. Dye concentrations were measured using a double beam UV-Vis spectrophotometer (Thermo Scientific, model Genesis 10S UV-Vis, England) at the wavelength of maximum absorbance (535 nm). Prior to the measurement, a calibration curve was obtained by using the standard dye solution with 5 known concentrations. In order to study the effect of electrolytes, 0.01 M NaCl, $CaCl_2$, Na_2SO_4, Na_3PO_4 and $Ca(NO_3)_2$ were added to solutions.

2.5 Study of Isotherm, kinetic and thermodynamic

Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich (D-R), Sips and Redlich-Peterson isotherm were considered in this study. The kinetic models were applied mainly by pseudo-first order, pseudo-second order, Elovich model, and intraparticle diffusion model. For thermodynamic study, the free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes during adsorption were evaluated
All equations used were concluded as followed
Langmuir equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L.q_m} \qquad (3.1)$$

$$R_L = \frac{1}{1 + K_L.C_0} \qquad (3.2)$$

C_e = the dye concentration at equilibrium (mg/L)
C_0 = the initial dye concentration in solution (mg/L)
q_e = the dye adsorbed amount at equilibrium (mg/g)
q_m = the maximum dye adsorbed amount per unit mass of sorbent (mg/g)
K_L = Langmuir constant (L/mg) [13]

Freundlich equation

$$log\ q_e = logK_F + \frac{1}{n}logC_e \qquad (3.3)$$

K_F = Freundlich constant (L/g)
1/n= the value related to the adsorption intensity [14]

Temkin equation

$$q_e = \frac{RT}{b_0}lnA + \frac{RT}{b_0}lnC_e \qquad (3.4)$$

b_0 = Temkin constant related to heat of sorption (J/mol)
A = Temkin isotherm constant related to the maximum binding energy (L/g) [15]

Dubinin-Radushkevich equation

$$lnq_e = lnq_D - K_{DR}\left[RT\ ln\left(1 + \frac{1}{C_e}\right)\right]^2 \qquad (3.5)$$

$$E = \frac{1}{\sqrt{2K_{DR}}} \qquad (3.6)$$

q_D = the adsorption capacity (mg/g)
K_{DR}= the constant related to mean free energy of adsorption per mole of the adsorbate (mol^2/ kJ^2)
E = Mean adsorption energy (kJ/mol) of the adsorbate [16]

Sips equation

$$\frac{1}{q_e} = \frac{1}{q_m K_s}.\sqrt[n]{\frac{1}{C_e}} + \frac{1}{q_m} \qquad (3.7)$$

K_s = Sips equilibrium constant (L/g)
n = Sips model exponent, limited from 0 to 1 [17]

Redlich-Peterson equation

$$\ln\left[K_R\left(\frac{C_e}{q_e}\right) - 1\right] = b_R \ln C_e + \ln a_R \qquad (3.8)$$

K_R = Redlich–Peterson model isotherm constant (L/g)
a_R = Redlich–Peterson model constant $(mg/L)^{-g}$
b_R = Redlich–Peterson model exponent [18]

Pseudo-first order kinetic model

$$log(q_e - q_t) = log q_e - K_1 \frac{t}{2.303} \quad (3.9)$$

K_1 = the rate constant for pseudo-first order adsorption (1/min) [19]

Pseudo-second order kinetic model

$$\frac{1}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \quad (3.10)$$

K_2 = the rate constant for pseudo-second order adsorption (g/(mg.min)) [20]

Elovich model

$$q_t = (1/\beta) ln(\alpha\beta) + (1/\beta) ln\, t \quad (3.11)$$

α = the initial adsorption rate (mg/g. min)
ß = the constant related to the exte surface coverage and the activation energy for chemisorptions (g/mg) [21]

Intra-particle diffusion

$$q_t = K_{id} (t)^{\frac{1}{2}} + C \quad (3.12)$$

k_{id} = the intraparticle diffusion rate constant (mg/g $min^{1/2}$) [22]

Arrhenius equation

$$ln\, k = ln\, A - \frac{Ea}{RT} \quad (3.13)$$

Ea= the activation energy (kJ/mol)

Thermodynamic equation

$$K_c = \frac{q_e}{C_e} \quad (3.14)$$

$$lnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (3.15)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (3.16)$$

K_c = the equilibrium constant represents the ability of the adsorbent to retain the adsorbate and extent of movement of the adsorbate within the solution

2.6 Statistical analysis

All experiments were conducted with three replicates. Variability in the data was expressed as the standard deviation. To conduct a test with three or more variables, an analysis of variance (ANOVA) was used.

3. Results and Discussion

3.1 Adsorbent characterization

Blend the water hyacinths –both before and after the modification with CTAB –into powder at the size of 500 microns or 35 mesh. After that, examine the characteristics of the surface with a scanning electron microscope (SEM). Take pictures of the surface of the adsorbents before the modification, after the modification, and also after the modification and the adsorption of Direct Red 83. The results are illustrated in Fig. 1.

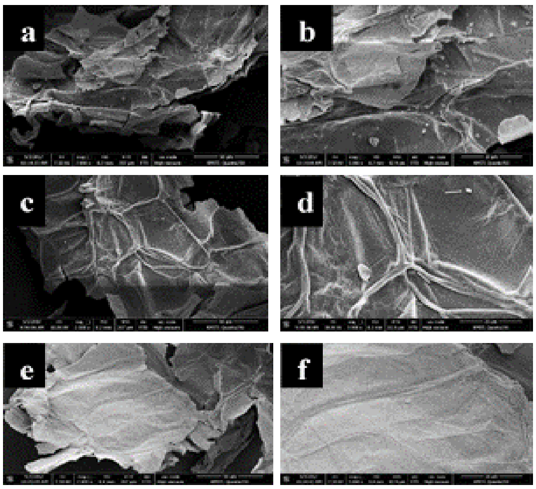

Fig. 1. SEM photograph of
(a) WH before modification (x 2,000)
(b) WH before modification (x 5,000)
(c) Modified WH before adsorption (x 2,000)
(d) Modified WH before adsorption (x 5,000)
(e) Modified WH after adsorption (x 2,000)
(f) Modified WH after adsorption (x 5,000)

Based on Fig. 1, it was found that the water hyacinths without modification (WH) had a rough texture. Upon the modification with CTAB (CTAB-WH), the surface became smoother, which might be due to the CTAB being attached to the surface of the adsorbent. After the adsorption of Direct Red 83, the surface became smoother than before adsorption, which might be caused by some molecules of the dye that penetrated into the pores and some that attracted to the surface of the adsorbent through covalent binding and Vander Waals Forces, which was the result of the combination of London dispersion force and electrostatic force [11].

Upon the study of the adsorbent characteristics using FTIR, the results were presented in Fig. 2.

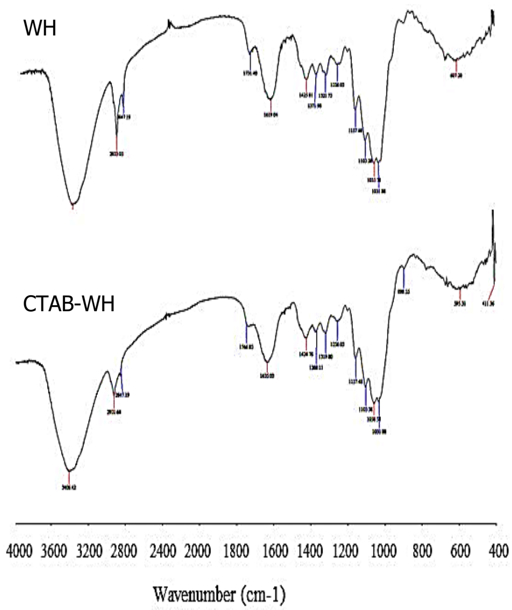

Fig. 2. FTIR spectrum.

Upon the spectrum analysis on the water hyacinths without modification, there were peaks that represented O-H stretching at the wavelength of 3406.42 cm^{-1}, C-H stretching at the wavelength of 2921.64 cm^{-1}, C=C stretching at the wavelength of 1635.00 cm^{-1}, C-O stretching at the wavelength of 1424.76 cm^{-1}, which was the elements of cellulose [23], and C-O functional group (stretching of primary alcohol) at the wavelength of 1058.54 cm^{-1}. Upon the modification with CTAB, there was an increase in C-N stretching of amine at the wavelength of 1163.28 cm^{-1}. The differences were most apparent at the wavelength of 3400 cm^{-1}, where the peaks had different widths, and at the wavelength of 2900 cm^{-1}, where the peaks became sharper and shorter. The peaks were shortened due to the decrease in C-H of aliphatic functional group and replacement of CTAB cations [24]. While the peak at 1600 cm^{-1} was shorter due to the decrease in water molecules of the adsorbent and the replacement of hydrate cations with the positive charge of CTAB [25].

Upon identification of the point of zero charge (pH_{PZC}) of water hyacinths that had been modified with CTAB, it was found that the value of pH_{PZC} was equal to 5.15.

3.2 Factors that affect adsorption

It was evident in Fig. 3 that the percentage of adsorption was at the highest at the pH of 3. If calculated in the percentage of adsorption, the value was 98.49%. Based on the point of zero charges of 5.15, it can be observed that there were a lot of positive charges at the surface of the adsorbent at the pH value of 3, which resulted in higher rate of adsorption. However, at the pH value of 4, the number of pos itive charges at the surface of the adsorbent was inadequate to create a difference in the ability of adsorption, relative to the pH value of 5. Similarly, at the pH value of 7, the number of negative charges at the surface of the adsorbent was inadequate, which resulted in no difference in the ability of adsorption as compared to the pH value of 5.

The effect of the amount of adsorbent was demonstrated in Fig. 4. The increase in the amount of adsorbent caused the ability of adsorption ($g_{dye}/kg_{adsorbent}$) to be reduced. If calculated in percentage of adsorption, it can be found that when the ratio of w/v increased from 0.5 kg/m^3 to 1, 1.5, and 2.0 kg/m^3, the rate of adsorption would gradually increase from 52.19% to 86.16%, 93.87%, and 98.84% respectively. This was due to the fact that the increase in the amount of water hyacinths resulted in a larger surface area for adsorption.

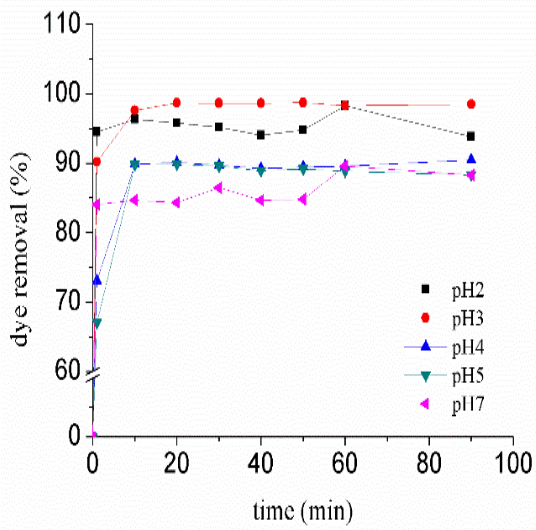

Fig. 3. Adsorption percentage at various pHs.

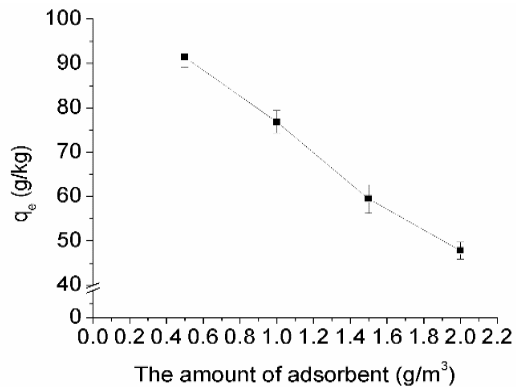

Fig. 4. Adsorption capacity at various amounts of an adsorbent.

The percentage of adsorption when using the dye concentration 100, 150 and 200 g/m^3 was 98.84, 93.44 and 82.54, respectively. However, the ability of adsorption ($g_{dye}/kg_{adsorbent}$) increased when the concentration of the wastewater increased, which was due to the fact that an increase in concentration stimulated the mass transfer (Fig. 5). This occurred from the difference between the amount of dye on the adsorbent and the concentration of wastewater, which consequently increased the ability of adsorption.

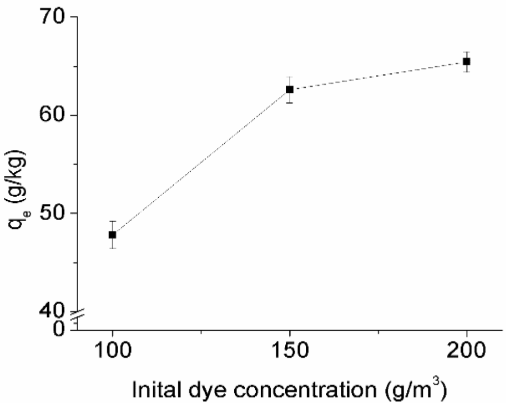

Fig. 5. Adsorption capacity at various dye concentrations.

The effect of temperature was illustrated in Fig. 6. The ability of adsorption ($g_{dye}/kg_{adsorbent}$) increased to a small extent after the temperature was increased from 33°C to 45°C and 55°C. All three data, when tested by an analysis of variance (ANOVA), were significantly different.

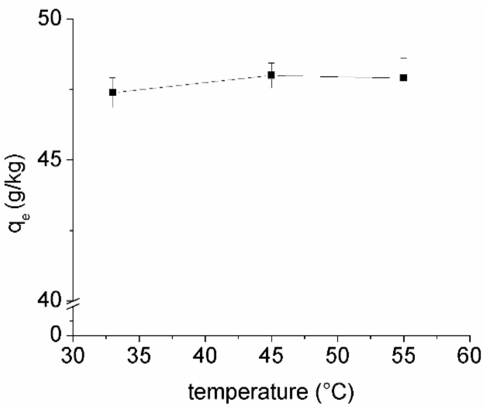

Fig. 6. Adsorption capacity at various temperatures.

The effect of electrolytes was represented in Table 1. Without an addition of electrolytes, the percentage of adsorption was at 98.77%. In the presence of electrolytes, the percentage of adsorption decreased, which was due to the fact that electrolytes caused the negative charges of Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^- to compete with anionic dye in order to attract to the positive charges of the adsorbent. As a result, the adsorption of Direct Red 83 was reduced. In addition, the experimental results further indicated that calcium salts had more effect in obstructing adsorption than sodium salts. Accordingly, the ability of adsorption reduced by a greater extent in the presence of calcium salts relative to sodium salts. The ratio of Na: Cl (for NaCl) and Ca: Cl (for $CaCl_2$) are 1:1 and 1:2, respectively. This can be a reason why calcium salt had a higher impact to the adsorption. Maurya et.al (2006) conducted a study on the adsorption using fungi [26]. They found that after adding electrolytes, which include sodium chloride (NaCl) and calcium chloride ($CaCl_2$), into the waste water, the percentage of adsorption reduced by a greater extent with $CaCl_2$ as compared to NaCl.

3.3 Isotherms

The six adsorption isotherms were studied, which include Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Sips and Redlich-Peterson. The results were shown in Table 2.

Upon consideration of the correlation coefficient (R^2) according to Langmuir and Freundlich adsorption models, it can be seen from Table 2 that the value of R^2 obtained from Langmuir equation was higher than that of Freundlich equation. This illustrated the adsorption was in accordance with Langmuir model, which hypothesized that each molecule of the adsorbent can only adsorb one molecule of dye. The adsorbent molecules that are located within close proximity from one another would have no intermolecular forces between each other or would not react with each other. The adsorbent molecules that had already been adsorbed cannot be relocated for adsorption. Hence, the number of adsorbent molecules is finite and adsorption will occur in a fixed position. The heat and energy values of the adsorption in each position are all equal and constant. With such hypothesis, it can be inferred that adsorption can occur in only single layer, with the highest ability of adsorption at 66.22 milligrams per gram, K_L value at 1.60 liters per milligram, and R_L value at 0.01, which clearly reflected Langmuir model.

The values of R^2 derived from Temkin and Sips equations were not as high as when calculated using other models. The value of R^2 derived from Dubinin-Radushkevich equation was equal to 0.9902, which was relatively high. The equation of Dubinin-Radushkevich evaluated the adsorption mechanisms of the adsorbent, whether they were chemical or physical adsorption that occurred on the surface of heterogeneous adsorbent. Free energy (E) from isotherms was calculated. If E was between 8-16 kJ/mol, the adsorption mechanism was an ion exchange reaction. If $E < 8$ kJ/mol, the adsorption mechanism was a physical reaction, and if $E > 16$ kJ/mol, the adsorption mechanism was a chemical reaction. The value of E obtained from this experiment was 1.58 kJ/mol, which concluded that physical adsorption was the main mechanism. Sumanjit et.al. (2015) conducted a study on the adsorption using water hyacinths with quality improvement, the E value was found to be equal to 0.75 kJ/mol, which illustrated physical adsorption [11]. Meanwhile, q_D was equal to 56.74 mg/g, which was similar to the q_D value obtained from this research at 64.41 mg/g, which was also similar to the value obtained from the calculation using Langmuir equation.

The value of R^2 derived from Redlich-Peterson was equal to 0.9993. The adsorption equation of Redlich-Peterson combined the features of both Langmuir and Freundlich models. Many research studies stated that the adsorption isotherms of Redlich-Peterson were very accurate, since they comprised of three parameters. From the calculation, it was found that b_R = 1.08, which illustrated that the adsorption of Direct Red 83 was inclined towards the adsorption isotherms of Langmuir.

Table 1. Percentage of adsorption when adding electrolytes.

no electrolyte	NaCl	$CaCl_2$	Na2SO4	Na_3PO_4	$Ca(NO_3)_2$
98.77+0.98 %	97.64+0.79 %	93.99+1.94 %	97.98+0.88%	96.29+1.08 %	93.13+ 1.72 %

Table 2. Adsorption parameters of Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Sips and Redlich-Peterson isotherms.

	value		value
Langmuir isotherm		Dubinin-Radushkevich isotherm	
q_{max} (mg/g)	66.22	K_{Dr}	2×10^{-7}
K_L (L/mg)	1.60	q_D (mg/g)	64.41
R_L	0.01	E (kJ/mol)	1.58
R^2	0.9998	R^2	0.9902
Freundlich isotherm		Temkin isotherm	
K_F (L/g)	46.87	b_o (kJ/mol)	0.46
1/n	0.10	A (L/g)	1.01
R^2	0.8988	R^2	0.9103
Sips isotherm		Redlich-Peterson isotherm	
K_S (L/mg)	0.03	K_R (L/g)	66
q_m (mg/g)	1428.57	a_R $(mg/L)^{-g}$	1.33
n	0.19	b_R	1.08
R^2	0.9145	R^2	0.9993

3.4 Kinetics

The kinetic of adsorption was studied using four types of models: Pseudo-first order model, Pseudo-second order model, Elovich model, and Intra-particle diffusion model. The results were represented in Table 3.

The value of R^2 derived from Pseudo-second order model was closer to 1 than that of Pseudo-first order model, which can be explained as the result of chemical adsorption that occurred from the chemical exchange of ions or the sharing of electrons between the surface of water hyacinths that had been modified with CTAB and the molecules of dye. When the initial concentration of the dye increased, there would not be a significant change in K_2. When the temperature of the reaction increased, K_2 would also increase, suggesting that the adsorption mechanism was endothermic. When the initial concentration of dye increased, q_e would also increase. However, an increase in temperature did not affect q_e. According to the research of Sumanjit et.al. (2015) that used water hyacinths that had been modified with a surfactant (positive ions) as the absorbent, it was found that the adsorption followed Pseudo-second order model and K_2 was equal to 0.0034 g/mg.min, which was similar to the value obtained from this study [11]. Using Elovich equation, the constant value obtained from the experiment was similar to that of the research of Sumanjit et.al. (2015), with ß at 0.21 mg/g and α at 498 mg/g min. Meanwhile, the value of R^2 obtained from the intra-particle diffusion equation was not high, so it might not be an ideal equation to explain the kinetics of adsorption.

Table 3. Results calculated from Pseudo-first order model, Pseudo-second order model, Elovich equation and Intra-particle diffusion.

	Dye concentration (g/m^3)			Temperature (˚C)		
	100	150	200	33	45	55
Pseudo first order						
K_1 (1/min)	0.03	0.05	0.03	0.03	0.10	0.07
q_e (mg/g)	47.82	62.60	65.44	47.39	46.45	47.12
R^2	0.9096	0.9830	0.9597	0.8688	0.9303	0.9995
Pseudo second order						
K_2 (g/mg min)	0.03	0.01	0.02	0.03	0.07	0.06
q_e (mg/g)	47.39	63.29	64.52	47.39	46.73	47.39
R^2	0.9993	0.9994	0.9973	0.9993	0.9992	0.9992
Elovich						
α (mg/g min)	1268.73	835.63	230.61	1268.73	2038.61	807.73
β (mg/g)	0.19	0.13	0.10	0.19	0.19	0.16
R^2	0.9415	0.9689	0.9867	0.9415	0.9889	0.9810
Intra particle diffusion						
K_{id} (mg/g min)	3.03	4.46	5.55	3.03	2.33	2.65
R^2	0.7715	0.8150	0.8676	0.7715	0.7196	0.7005

3.5 Activation energy (Ea)

Activation energy is the minimum energy required by the particles in order to result in a chemical reaction. A chemical reaction that requires a high level of activation energy is relatively less feasible. The value of Ea can also indicate the mechanisms of adsorption. If Ea is between 5-50 kJ/mol, the physical adsorption would be the main mechanism. On the other hand, if Ea is between 60-800 kJ/mol, the chemical adsorption would be the dominating mechanism [27]. In this experiment, the value of Ea was 30.31 kJ/mol, which suggested that the physical adsorption was the dominating mechanism and the reaction was spontaneous. Han et.al. (2010) conducted a research on the adsorption of Methylene blue using rice straws with modification [28]. The value of Ea was found to be at 24.24 kJ/mol, which was similar to the Ea obtained in this experiment.

3.6 Thermodynamics

The experimental results of thermodynamics of adsorption were illustrated in Table 4.

Table 4. Thermodynamic constant.

ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)	ΔG^0 (kJ/mol)		
		33ºC	45ºC	55ºC
38.84	152.25	-7.7	-9.5	-11.1

According to Van't Hoff equation, the standard enthalpy (ΔH^0) was found to be equal to 38.84 kJ/mol, which was positive (ΔH^0 = positive), suggesting that the adsorption involved the endothermic process. If the temperature in adsorption increased, the percentage of adsorption would also increase.

The entropy of adsorption (ΔS^0) was equal to 152.25 J/mol, which was positive (ΔS^0 = positive), suggesting that there was high disorder between the adsorbent and adsorbate. The molecules of dye bonded with the adsorbent, while the adsorbate was attached to the surface of the adsorbent.

The values of Gibbs free energy (ΔG^0) of the adsorption of dye using water hyacinths with modification at the temperatures of 33°C, 45°C, and 55°C were -7.7, -9.5, and -11.1 kJ/mol, respectively. In general, physical adsorption would have the value of Gibbs free energy between -20 and 0 kJ/mol. Meanwhile, chemical adsorption would have the value of between -80 and -400 kJ/mol [29]. The value of Gibbs free energy was negative, which suggested that the adsorption was a spontaneous and physical reaction.

4. Conclusion

Water hyacinths negatively affected the environment. Hence, it is appropriate to utilize water hyacinths and make them beneficial. By improving the quality of water hyacinths with CTAB, they can be used to adsorb Direct Red 83 dye in wastewater, with the highest ability of adsorption at 66.22 mg/g. Langmuir isotherm can be used to explain the process of adsorption effectively. Moreover, the dominating mechanism of adsorption is a physical process, and the reaction is spontaneous.

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