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Water hyacinth stems a potential natural adsorbent for the adsorption of acid green 20 dye

Mahmoud S.Aboul-Fetouh[1], Taha M.Elmorsi[1,2]*, Jamal M.El-Kady[1], Hassan A.El-Adawi[1]

[1]Chemistry Department, Faculty of Science, Al-Azhar University, 11884, Cairo, (EGYPT)

[2]Chemistry Department, Faculty of Science, Jazan University, Jazan, 706, (KSA)

E-mail : taha_elmorsi@yahoo.com

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ABSTRACT

The aim of this research was to investigate the potential of low- cost locally available stem water hyacinth (SWH) as an adsorbent for removal of acid green 20 (AG20) as an anionic dye from aqueous solution. Equilibrium behavior of SWH was investigated by performing batch adsorption experiments. The effect of initial dye concentration, pH, contact time and adsorbent dose on the adsorption process were evaluated. Adsorption isotherm models, Langmuir (four different forms), Freundlich and Temkin were used to simulate the equilibrium data at different experimental parameters (pH and adsorbent particle size). For Langmuir isotherm model, the four linear equations were discussed and used to obtain the isotherm parameters. Langmuir-II form was found to have the highest coefficient of determination ($R^2 = 0.999$) compared with the other Langmuir linear equations. Also, it was found that SWH has a high adsorptive capacity towards MB dye (200 mg/g) as determined by Langmuir-II model. SWH show favorable adsorption of AG2o dye with $0 < R_L < 1$. The intraparticle diffusion was also determined for the AG20-SWH system. The mechanism of the adsorption of AG20 dye onto SWH involved more than one process as indicating by the low value of Temkin constant b_T (0.285 kJ/mol). Also, it was found that intraparticle diffusion was not the limiting step.

KEYWORDS

Water hyacinth;
Acid green 20;
Adsorption isotherms;
Intraparticle diffusion.

INTRODUCTION

Presence of different pollutants in water and wastewater increased recently due to high increase in different industrial activities. Dyes used in textile, paper, plastics, leather, food and cosmetic industries[1] represent a large and important group of chemicals that get mixed in wastewater among the different aqueous pollutants. In recent years there is a dramatic increase in the annual production of different synthetic dyes representing more than 10,000 dyes[2]. Many dyes including azo dyes and their intermediates have toxic effects on environment and human health due to their carcinogenicity and visibility[3]. It was reported that incomplete degradation of dyes by bacteria in the sediment resulted in production of some carcinogenic and toxic amines are often

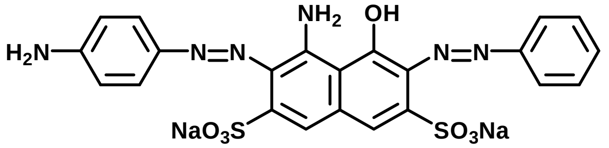

Figure 1 : Chemical structure of acid green 20 (AG20)

produced[4]. In addition, presences of colour substances in water body may decrease the light transmission which decreasing the photosynthesis activity, leading to decrease the growth of bacteria and hence decreasing the biodegradation of impurities in water[5]. Acid green 20 (AG 20), is an azo dye, has been extensively used in textiles and printing industry and it has been found as non-biodegradable azo dye. Therefore it is essential that wastewater contaminated with AG 20 dye be given some treatments before discharge. There are many treatment techniques have been applied to a broad range of water and wastewater contaminated with dyes including physical- or chemical-treatment processes[6]. These include chemical coagulation/flocculation[7], ozonation, oxidation, photodegradation[8], ion exchange, irradiation, precipitation and adsorption. Several critical reviews on current treatment technologies were reported[9]. These various techniques require different tools and various costs and have limitations. It has been reported that the adsorption onto activated carbon, have proved to be the most efficient and reliable method for the removal many pollutants including different dyes[7]. Although commercial activated carbon is very effective adsorbent, its high cost requires the search for alternatives and low-cost adsorbents[10]. To overcome the high coast of activated carbon, many researchers have focused to develop both cheaper precursors for activated carbon and another low-cost adsorbents. Several low-cost adsorbents have been tested for removing dyes[1] including peat, pith, Orange peel, Indian Rosewood[11], cellulose based wastes, giant duckweed, banana pith and other agricultural by-products[12]. On the other hand, water hyacinth (WH) is the most productive aquatic plant found widely in different water bodies in Egypt in addition to other countries. The high growth rate and availability of WH led to the presence of many aquatic and environmental problems[13,14]. Several trials have been proposed to use this aquatic plant in the production of biogas to solve its environmental problems[13]. Also, water hyacinth was reported to be very effective in removal of organic pollutants including dyes[13,15,16]. To make better use of this abundant plant, the present study, an attempt to use water hyacinth stems, as nonconventional low-cost adsorbent for removal of AG20 dye from aqueous solution. The capacity of adsorbent for adsorbate (such as SWH for AG20) is obtained by adsorption isotherm model which is the equilibrium relationships between adsorbent/adsorbate systems. It is important to select the best isotherm model representing the experimental data and could be used for the design purposes. In this study three two-parameter equations (Langmuir, Freundlich[17,18] and Temkin[19,20] have been used to describe the sorption process of AG20 onto SWH. Also, linear regression analysis method was used to determining the most fitted model and finding its parameters[21].

EXPERIMENTAL

Chemicals

Acid green 20 (AG20) is an anionic dye with a molecular formula of $C_{22}H_{16}N_6Na_2O_7S_2$ (M.Wt. 586.50 g/mol), was provided by Dyeing company, Egypt and used in this study without further purification to evaluate the efficiency of Stem of water hyacinth (SWH) as a natural adsorbent. The chemical structure of AG20 is shown in figure 1. Hydrochloric acid, sodium hydroxide were used to adjust the pH were purchased from BDH.

Adsorbent

Stem of water hyacinth (SWH) was used as an adsorbent in this study. SWH was collected from fields around Manzala leak beach in Egypt. Adsorbent was air dried and washed several times with distilled water, dried again then ground well and the size distribution was determined using a sieve. Two different mesh sizes of SWH were used in this study 20-30 and 30-40.

Preparation of dye solutions

Acid green 20 (AG20) was used in this study as an environmental pollutant. Stock solutions (500 mg/L) of AG20 dye were prepared by dissolving the required amount in distilled water. Calibration curves and batch experimental solutions were obtained by diluting the dye stock solutions in accurate different initial concentrations (5.0 to 30.0 mg/L).

Adsorption studies

In batch adsorption experiments, certain amounts of SWH were added into several 20 mL bottles, each containing 20 mL solution of AG20 dye with an initial concentration of 20 mg/L. Then the bottles were stirred at 450 rpm for 9 hrs using a magnetic stirrer at room temperature. SWH in the samples was separated by centrifugation and the concentrations of dye at any time (C_t) were determined in the supernatant solutions. Adsorption isotherms were determined by introducing 0.02g (1.0g/L) SWH to respective 20 mL of different dye concentrations (5-30 mg/L) at room temperature.

Effect of adsorbent mass

To investigate the effect of adsorbent mass, different mass of SWH 0.004 to 0.04 g (0.2 - 2 g/L) was introduced to a number of glass tubes containing a specific volume (20 mL) of a fixed initial concentration (20 mg/L) dyes solution at the same pH and room temperature. Concentrations of AG20 were measured at equilibrium.

Effect of mesh size

To study the effect of mesh size adsorbent, various mesh sizes were ground ranging from 20 to 40 mesh size and were added to the sample solution in different tubes with the same initial concentration (20 mg/L) of AG20 dye. After stirring the solutions to the specific time, samples were centrifuged to remove the adsorbent and analyzed.

Effects of initial dye concentration (C_0) and contact time

To evaluate the effect of both contact time and adsorption kinetic, experiments were conducted at different periods using same system.

Analytical methods

Standard solution of AG20 dye was used to obtain calibration curves. A double beam UV–vis spectrophotometer Perkin Elmer was used for determining the concentrations of dye solutions. For each adsorption experiment, samples were withdrawn at interval times and the adsorbate (SWH) was separated by the centrifuge. Then concentrations of residual dye solutions were measured at its maximum absorption (λ_{max}) corresponding to the maximum absorption for AG20 dye solution (λ_{max} = 636 nm).

The amount of dye sorbed at any time, q_t, was calculated from

$$q_t = \frac{V(C_o - C_t)}{W} \qquad (1a)$$

At equilibrium, $q_t = q_e$ and $C_t = C_e$; therefore the amount of sorbed dye, q_e, was calculated from

$$q_e = \frac{V(C_o - C_e)}{W} \qquad (1b)$$

where C_o, C_t and C_e are the initial concentration, concentration at any time and equilibrium concentrations of dye solution (mg/L), respectively, V is the volume of the solution (L), and W is the mass of adsorbent (g). The dye removal percentage can be calculated as follows:

$$\text{Removal \%} = \frac{(C_o - C_t)}{C_o} \times 100 \qquad (2)$$

Equilibrium isotherm modeling

Study the adsorption equilibrium of the dye on the adsorbent materials are described by isotherm models. The experimental data at equilibrium between the amount of adsorbed dye (q_e) on the adsorbent (SWH) and the concentration of dye in solution (C_e) at constant temperature and pH were used to describe the optimum isotherm model. In this study different isotherm models namely; Langmuir (four isotherm forms), Freundlich and Temkin were used to describe the equilibrium data. The linear and nonlinear forms of these models are shown in TABLE 1.

Langmuir isotherm

The Langmuir isotherm model (derived by Irvin Langmuir, 1916) is used to predict the sorption of aqueous compounds onto a solid phase[17,18]. This mechanistic model assumes that a monolayer of adsorbed material (in liquid phase) is adsorbed over a uniform adsorbent surface (a flat surface of solid phase) at constant temperature and that the distribution of the compounds between the two phases is controlled by equilibrium constant. Thus, in this case, it is describing the relationship between the amount of adsorbed AG20 dye at equilibrium (q_e) and its equilibrium solution concentration (C_e) over a uniform adsorbent surface (SWH) at constant temperature according to equation (3). The model assumed that when AG20 dye molecule adsorbed to a specific site on SWH surface, no other molecule can attach to that site. Hence at equilibrium both rates of adsorption and desorption are equal, the Langmuir equation is derived by some mathematical manipulation as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where, q_m (the maximum capacity of adsorption, mg/g,) and K_L (a constant related to the affinity of the binding sites, L/mg,) are the Langmuir isotherm constants. Both q_m and K_L will greatly impact the conclusions made about the experimental data. It is known that the isotherm constants can be determined by a simple method of equation optimization by linear regression[21,22]. That is to transform the isotherm variables to a linear form and then to apply the linear regression analysis of known C_e and q_e values. There are four common linear regression methods used for optimizing Langmuir equation, called; Langmuir (Langmuir-1), Lineweaver-Burk (Langmuir-II), Eadie-Hofstee (Langmuir-III), and Scatchard (Langmuir-IV)[23]. Langmuir-I linear regression (proposed by Langmuir, 1918), has very little sensitivity to data error and has some bias toward fitting the data in the middle and high concentration range. The linear form of these four different equation will be used to fit the equilibrium data as will be discussed later on.

Freundlich isotherm

Freundlich isotherm model is assuming that the adsorption process takes place on a heterogeneous surface. The Freundlich exponential equation[17,18], is given as:

$$q_e = K_F C^{1/n} \quad (4)$$

where, K_F (mg/g, dry weight, $(L/mg)^{1/n}$) is an indicator of the adsorption capacity and 1/n is the adsorption intensity and indicates both the relative distribution of energy and the heterogeneity of the adsorbent sites. The linear form is derived by taking the log of the terms as shown in TABLE 1.

Temkin isotherm

Temkin isotherm model[19,20] was used also to test the adsorption potential of SWH to AG20 dye. This model is taking into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process. Also, the model is assuming that the heat of adsorption (ΔH_{ads}) of all molecules in the layer decreased linearly by increase the coverage. The linear form of Temkin is given as follow:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \quad (5)$$

where, R is common gas constant (0.0083 kJ/mol K), T is the absolute temperature (K), $1/b_T$ is the Temkin constant related to heat of sorption (kJ/mol) which indicates the adsorption potential (intensity) of the adsorbent and K_T (L/g) is Temkin constants related to adsorption capacity. The liner plots of q_e versus $\ln C_e$ according to Eq.(5) enable to determine the constants $1/b_T$ and K_T from the slope and intercept respectively.

It should be noted that the constant $\frac{RT}{b_T}$ is represented as $B = \frac{RT}{b_T}$.

RESULTS AND DISCUSSION

Effects of initial dye concentration (C_0) and contact time

A 0.02 g (1.0 g/L) of SWH was added to 0.020 L of different concentrations (5-30 mg/L) of AG20 dye solution and experiments conduct at room temperature for 9.0 h to test the effect of initial concentration and contact time on the adsorption of AG20 dye. From the six different initial concentrations of AG20 dye studied, the results of two concentrations, the lowest (5 mg/L) and highest (30 mg/L), are shown in figure 2. It is indicated that the adsorption of AG20 dye onto SWH increase as the initial concentrations of the dye and contact time increased. At the first hour of the adsorption process, as the initial concentrations of the dye increased 6 times (from 5 to 30 mg/L), the adsorbed amount onto SWH increased more than four times (from 1.88 to 7.9 mg/g). Also, as the contact time increased to 9.00 hr, the adsorbed amount (q_e) increased more than five times (from 3.54 to 19.17 mg/g). The results showed that the uptake of the dye by the adsorbent (SWH) depends on the initial concentrations and contact time. This is because the initial dye concentrations act as the driving force that increases the mass transfer of AG20 dye from

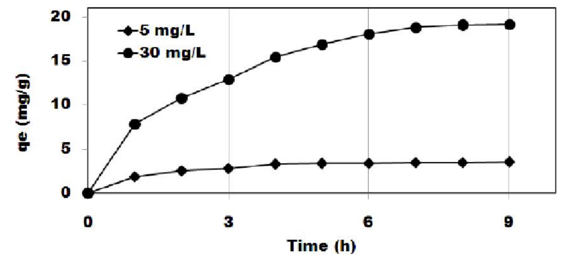

Figure 2 : Effect of initial concentration and contact time on AG20 dye adsorption (T = 293 K, pHi = 3.0 SWH dosage = 1.0 g/L, [AG20]i = 5, 30 mg/L, V = 0.020 L)

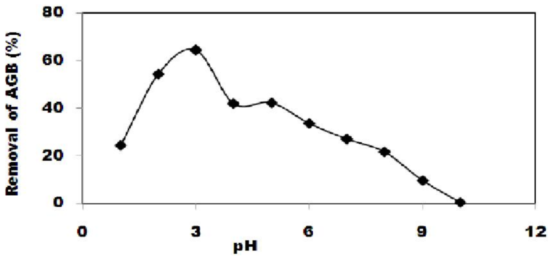

Figure 3 : Effect of solution pH on the adsorption of AG20 dye (T = 293 K, SWH dosage = 1.0 g/L, [AG20]i = 5, 30 mg/L, V = 0.020 L)

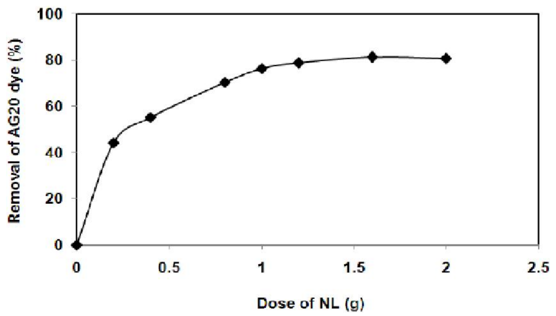

Figure 4 : Effect of adsorbent dose on the adsorption of AG20 dye by SWH (T = 293 K, SWH dosage = 0.5-2.0 g/L, [AG20]i = 20 mg/L, V = 0.020 L)

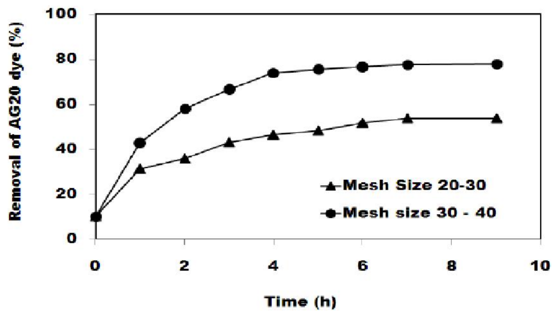

Figure 5 : Effect of adsorbent mesh size on the adsorption of AG20 (T = 293 K, SWH dosage = 1.0 g/L, [AG20]i = 20 mg/L, V = 0.020 L)

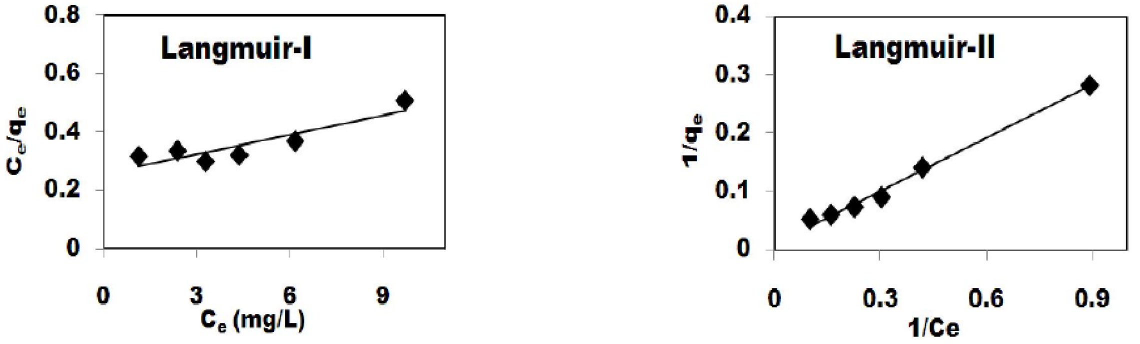

Figure 6a : Langmuir isotherm type (I) and type (II) for the adsorption AG20 onto SWH, (T = 293 K, SWH dosage = 1.0 g/L, [AG20]i = 5- 30 mg/L, V = 0.020 L)

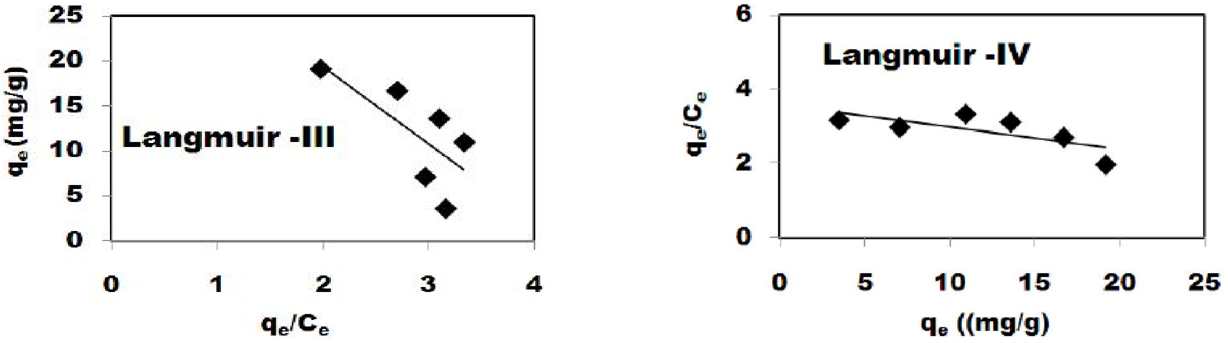

Figure 6b : Langmuir isotherm type (III) and type (IV) for the adsorption of AG20 onto SWH, (T= 293 K, SWH dosage = 1.0 g/L, [AG20]i = 5 - 30 mg/L, V = 0.020 L)

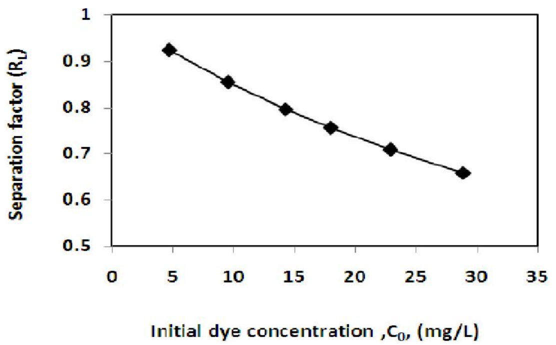

Figure 7 : Plot of separation factor versus initial AG20 concentration, (T = 293 K, SWH dosage = 1.0 g/L, [AG20]i = 5 - 30 mg/L, V = 0.020 L)

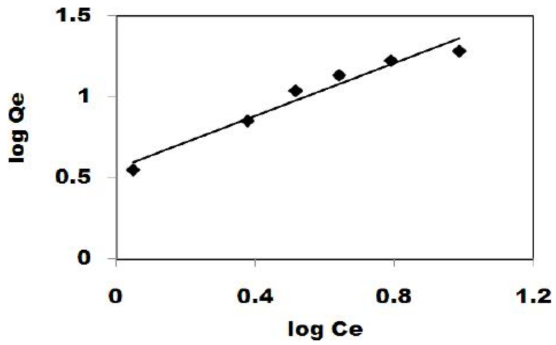

Figure 8 : Freundlich isotherm data for the adsorption of AG20 onto SWH, (T = 293 K, SWH dosage = 1.0 g/L, [AG20]i = 5 - 30 mg/L, V = 0.020 L)

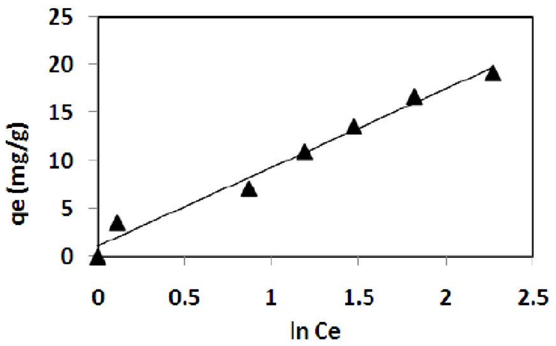

Figure 9 : Temkin isotherm data for the adsorption of AG20 onto SWH, (T = 293 K, SWH dosage = 1.0 g/L, [AG20]i = 5 - 30 mg/L, V = 0.020 L)

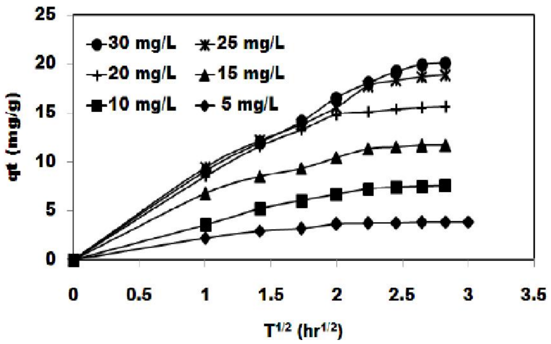

Figure 10 : Intraparticle diffusion plot for adsorption of AGB20 dye onto SWH for different initial dye concentrations; (T = 293 K, pHi = 3.0, SWH dosage = 1.0 g/L, V = 0.020 L)

aqueous solution onto the surface of SWH. Also, it can be seen from figure 2 that the adsorption of AG20 dye was very rapid during the first three hour, and increased gradually during the second three hour until reached equilibrium. During the adsorption process, solutions with different initial concentrations possibly will reach equilibrium at different times. This may be due to the time required for the dye molecules to encounter the boundary layer effect, then diffuse to the surface of the of the adsorbent and finally diffuse to the porous structure of the adsorbent[24]. Therefore, solution with initial concentration of 5 mg/L (lower amount of dye) reached equilibrium first at about 4 h, while solution with initial concentration of 30 mg/L (highest amount of dye) takes longer time and reached equilibrium at about 6 h. To ensure complete equilibrium of the data, adsorption samples were collected at 9.0 h. It was noted that as the initial concentration of AG20 increased from 5 to 30 mg/L, the removal of AG20 at equilibrium decreased by about 13% (from 75.97 to 66.38%). This may be because the mass transfer driving force increases by increase the initial concentration which would lead to increase the adsorption of AG20. Similar trend for other dyes was reported by researchers[25,26].

Effect of solution pH on dye removal

Experiments were conducted at 20 mg/L initial dye concentration, 1.0 g/L SWH dose, and 9.0 h contact time at room temperature to study the effect of solution pH on the % removal of AG20 dye as shown in figure 3. It is indicated that removal of AG20 dye reaching a maximum in acidic medium and decreased by increasing the pH values in alkaline medium. The % removal of AG20 dye in acidic medium (pH3) reached 64.44% and become less than 1% at pH 10. The variations in the pH values from acidic to alkaline medium would affect the adsorption rate because both the degree of ionization of dye molecules and the surface properties of the adsorbent (SWH) would vary. It is previously reported that the adsorption process increased by increasing the electrostatic attraction. Thus anions are favorably by the adsorbent at lower pH values due to presence of H^+ ions, while adsorption of cations are favorably at higher pH values which led to increase the

TABLE 1 : Different isotherm models used in this study and their linear forms

Isotherm	Nonlinear form	Linear form	Plot
Langmuir –I(Langmuir 1918)	$q_e = \frac{K_L\,C_e}{1 + K_L\,C_e}$	$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right)C_e + \left(\frac{1}{K_L\,q_m}\right)$	$\frac{C_e}{q_e}$ VS C_e
Langmuir –II(Lineweaver-Burk 1934)		$\frac{1}{q_e} = \left(\frac{1}{K_L\,q_m}\right)\frac{1}{C_e} + \left(\frac{1}{q_m}\right)$	$\frac{1}{q_e}$ VS. $\frac{1}{C_e}$
Langmuir –III(Eadie-Hofstee 1942,1952)		$q_e = q_m - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e}$	q_e VS. $\frac{q_e}{C_e}$
Langmuir –IV(Scatchard 1949)		$\frac{q_e}{C_e} = K_L\,q_m - K_L\,q_e$	$\frac{q_e}{C_e}$ VS. q_e
Freundlich	$q_e = K_F\,C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	$\log q_e$ VS. $\log C_e$
Temkin	$q_e = \frac{RT}{b_T}\ln(K_T\,C_e)$	$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e$	q_e VS. $\ln C_e$

presence of OH^- ions as a result of increase the electrostatic attraction in each case[1]. Thus performing the adsorption in acidic medium, at pH 3, would increase the positive charge on the adsorbent surface causing increase in the electrostatic attraction between anionic dye molecules (AG20 dye^-) and the surface of SWH, hence increasing the adsorption rate of AG20 dye. On the other hand, the negative charge on the surface of the adsorbent (the amount of OH^- ions) would increase by increase the pH in alkaline medium. Presence of high concentration of OH^- ions would make them compete effectively with anionic dye molecules (AG20 dye^-) causing a decrease in the amount of dye adsorbed. This result can be further proven by opposite behavior shown for the adsorption of cationic dyes such as methylene blue (MB)[1]. It was found that the high adsorption yield was obtained at pH 8-10. This because performing the adsorption in alkaline medium, at pH 8-10, would increase the negative charge on the adsorbent surface causing increase in the electrostatic attraction between cationic dye molecules (MB+) and the surface of the adsorbent, tripoli, hence increasing the adsorption rate. Also, similar trend was shown by the adsorption of some metals onto different adsorbents[27,28].

Effect of adsorbed dose

At constant initial concentration of AG20 dye (20 mg/L), different doses of SWH (0.5 to 2 g/L) were added to dye solutions (0.020 L) to study the effect of SWH dose on AG20 dye adsorption. Results in figure 4 shows that the % removal of AG20 dye in the first stage increased rapidly with the increase in adsorbent dose then increased slowly with further increase in adsorbent dose. It can be seen that at 1.0 g/L of adsorbent dose the color removal of dye reached the most at 76.34%, then increase the dose of SWH from 1.0 to 2.0 g/L resulted only in about 4.9 % more to reach 81,21%. Thus 1.0 g/L of SWH was chosen as the optimum dose and used in the further experiments. The increase in % removal of AG20 dye with the increase in the amount of SWH up to 1.0 g can be assigned to increase in both the surface area and the adsorption sites to AG20 dye molecules[29,30]. The adsorption of different dyes[11] such as indigo carmine dye and methylene blue onto rice husk ash, grass waste and onto bamboo-based activated carbon[30] respectively was reported with similar trend.

Effect of mesh size

Results in figure 5 indicated that using different mesh sizes of SWH adsorbent lead to rapid removal of AG20 dyte up to the first 4.0 h of the experiment. However, the data obtained at 4.0 h, show that using mesh size of 30 -40 mesh resulted in the higest uptake of the dye with 74.17% color removal compared to 46.55 % colore removal by using mesh size of 20-30 mesh. Thus mesh size 30-40 mesh was as the optimum for further experiments. Increase the removal of AG20 dye with increase the mesh size may be due to increase the binding active sites for dye molecules. Percentage removal of some cationic dyes from aqueous solution by bioadsorption onto granular cucumis sativa was also

TABLE 2 : Summary of the value of langmuir, freundlich and temkin isotherm constants for the equilibrium adsorption of AG20 dye onto SWH

Isotherm model	q_m(mg/g)	Parameters K_L (L/mg)	R^2
Langmuir-I	45.45	0.09	0.809
Langmuir-II	200	0.016	0.999
Langmuir-III	36.527	0.117	0.511
Langmuir-IV	60.09	0.060	0.511
	K_F (L/mg)	**N**	**R^2**
Freundlich	3.597	1.23	0.957
	b_T(kJ/mol)	**K_T (L/mg)**	**R^2**
Temkin	0.285	1.556	0.980

increased by increasing the adsorbent dose[4].

Isotherms for the sorption of AG20 dye onto SWH

In this study the best-fitting isotherm model to describe the adsorption data of AG20 dye at equilibrium has been determined by common two parameters models such as Langmuir, Freundlich and Temkin equations (TABLE 1) using linear and nonlinear regression methods. Applicability of these equations was compared by judging the correlation coefficients (R^2).

Langmuir isotherms

The four different forms of Langmuir isotherm model may result in different parameter estimates as reported previously[31]. The typical results for the linear forms of Langmuir-I and Langmuir-II (more popular equations) are shown in figure 6a, while other two linear forms ((Langmuir-III and Langmuir-IV) are shown in figure 6b. The values of Langmuir constants, the maximum sorption capacity (q_m), the adsorption equilibrium constant (K_L) and the value of the coefficient of determination (R^2), are presented in TABLE 2. The results indicated that linear form of Langmuir-II model shows the minimal deviation from the fitted equation as indicated by the value of R^2 as 0.999. However, the value of R^2 for Langmuir-I model is equal to 0.809. Also, the value of R^2 for both Langmuir-III and Langmuir -IV is almost the same and equal to 0.511. It was proposed by Jaynes and Boyd[32] that when the value of the correlation coefficient (R^2) is greater than 0.89, the adsorption data would follow the Langmuir model. Furthermore, the sorption capacity, q_m which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage is reported in TABLE 2 as calculated from the plots of the four different forms of Langmuir model. Linear form of Langmuir-II provided the highest mass capacity (200 mg/g) of SWH for AG20 dye. Thus comparing the correlation coefficient (R^2) values of the four forms of Langmuir and the maximum adsorption capacity, Langmuir-II model was the most satisfactory model to describe the equilibrium data for the adsorption of AG20 dye onto SWH as indicated by the value of R^2 ($R^2 = 0.999 > .89$). It should be noted that the four different linear forms of Langmuir isotherm resulted different values for Langmuir constants (q_m and K_L) and the coefficient of determination (R^2) as shown in TABLE 2. This is because the linearizations of Langmuir nonlinear equation affect the calculations by altering the error structure and violate both the error variance and normality assumptions of least square method[33].

TABLE 3 : Weber-Morris parameters

[dye],mg/L	K_{1d}	R^2	K_{2d}	R^2
5	1.542	0.945	0.203	0.999
10	3.297	0.992	0.571	0.999
15	4.992	0.97	0.479	0.905
20	6.951	0.975	0.67	0.951
25	7.709	0.988	1.436	0.942
30	7.858	0.995	3.642	0.858

Separation factor

Separation factor (R_L), is a dimensionless constant[20], and it is a good characteristics of the Langmuir isotherm. R_L, can be expressed in the following equation:

$$R_L = \frac{1}{1+K_L C_o} \qquad (6)$$

where, C_o (mg/L) is the highest initial concentration of adsorbate, and K_L (L/mg) is Langmuir constant which it is related to the energy of adsorption. The value of R_L indicates the shape of the isotherm to be either linear ($R_L = 1$), unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Thus the R_L values between 0 and 1 indicate favorable adsorption. For adsorption of AG20 dye onto SWH, R_L values obtained as shown in figure 7 are in the range of 0.658-0.923 (less than unity), indicating that the adsorption of AG20 onto SWH is a favorable process and the data fits Langmuir isotherm model. Thus SWH is a good adsorbent for AG20 dye.

Freundlich isotherm

Equilibrium adsorption data of AG20 dye onto SWH was tested with Freundlich isotherm model. The linear plot of Freundlich isotherm (plot of log qe versus log Ce) is employed to determine the intercept value of K_F and the slope $1/n_F$ as shown in figure 8. The values of K_f and n_F along with R^2 calculated from the plot (Figure 8) are given in TABLE 2. The results showed that the correlation coefficient value (R^2 = 0.957) of Freundlich is lower than the R^2 value of Langmuir-II isotherm (R^2 = 0.999). In addition, the value of adsorption intensity parameter (1/n) is a measure of the deviation degree from linearity (favorability) of the adsorption[5] and the high value of 1/n indicates the favorability of the adsorption process. The results show the value of 1/n = 0.867, which is close to the unity. Therefore, Freundlich model is still a good model to describe the adsorption data as indicated by relative high value of both 1/n and R^2.

Temkin isotherms

Also, to evaluate the adsorption potential of SWH for AG20 dye, another model such as Temkin adsorption isotherm model was chosen to fit with the equilibrium adsorption data. The linear plot of the Temkin isotherm is illustrated in figure 9. The parameters, K_T and, b_T of the Temkin equation have been calculated for AG20 dye and are listed in TABLE 2. Analysis of Temkin constants for AG20 dye removal showed high value of both adsorption capacity, K_T, (1.556 L/g) and the value of R^2 (0.980). Thus although the data is better fitted by Langmuir, it can also be modeled by the Temkin isotherm, as indicated by the greater coefficient of correlation (R^2). Furthermore, the constant b_T reflects bonding energy which in turn dictates the type of interaction, was low value (0.285 kJ/mol) indicating that the interactions between the AG20 dye and SWH are neither purely through ion-exchange nor purely through physisorption. Similar trend was reported previously by other researchers[34].

Intraparticle diffusion study

In order to investigate the mechanism of the AG20 adsorption onto SWH, intra-particle diffusion based mechanism was studied. It is proposed that the uptake of the adsorbate (AG20 dye) by the adsorbent (SWH) varies almost proportionately with the square root of the contact time ($t^{1/2}$). Weber and Morris[35] proposed the most-widely applied intraparticle diffusion equation for sorption system as:

$$q_t = K_{id} t^{1/2} \qquad (7)$$

where, q_t is the amount of AG20 dye adsorbed per unit mass of adsorbent (mg/g) at time t and K_{id} the intraparticle diffusion rate constant ($mg/g.min^{-1/2}$). The rate parameter K_{id} of stage i, is obtained from the slope of the straight line of q_t versus $t^{1/2}$. If intraparticle diffusion is the mechanism of the adsorption process, then the plot of q_t versus $t^{1/2}$ will be line and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion[36]. Otherwise, some other mechanism along with intraparticle diffusion is also involved[1]. Figure 10 presented the intraparticle diffusion model. The results indicated that the plot of q_t versus $t^{1/2}$ were not linear over the whole time range. Furthermore, it may be seen that the intra-particle diffusion of AG20 dye occurred in 2 stages. The first straight portion is attributed to the macropore diffusion (phase I) and the second linear portion to micro-pore diffusion (phase II)[37]. The intra-particle diffusion constants for these 2 stages (K_{1d} and K_{2d}) are given in TABLE 3. Therefore, the adsorption of AG20 dye onto SWH involved more than one process and the intra-particle transport is not the rate-limiting step. Such finding is similar to that made in previous works on adsorption[1]. In addition, the rate constants of intra-particular diffusion on SWH were slow and increased by increase the initial dye concentration, hence AG20 dye, as a big molecule, diffused slowly among the particles during the adsorption process. Similarly, D.N.Jadhav et al.[38], reported slow rate of sorption in cases of larger molecular dyes such as acidic, basic and disperse dyes on sawdust, polymerized sawdust and sawdust carbon. On the other hand, the sorption rate was generally faster and was not affected and intraparticle diffusion was the rate-limiting step in cases of sorption of metal ions[39].

CONCLUSION

The adsorption of AG20 dye onto SWH was studied. Among the four different forms of Langmuir isotherm model, the equilibrium data was fitted very well with Langmuir-II equation. The equilibrium capacities based on the Langmuir analysis was 200 mg/g. Also, the equilibrium data can be modeled by Temkin as well as Freundlich isotherm models as indicated by indicated by the greater coefficient of correlation (R^2). The low value of the Temkin constant b_T (0.285 kJ/mol) indicating that the interactions between the AG20 dye and SWH are not controlled by one process. Intraparticle diffusion was not the rate-limiting step. However, AG20 dye diffused slowly among the particles during the adsorption process.

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