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Removal of Acid Yellow 25 from Aqueous Solution by Chitin Prepared from Waste Snow Crab Legs

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Abstract

Acid Yellow 25 (AY25) is used in the textile industry for dyeing of natural and synthetic fibers, and is also used as a coloring agent in paints, inks, plastics, and leathers. Effluents from such industries are major sources of water pollution. Hence, it is important to find simple, efficient, and inexpensive ways to remove these dyes from wastewater. Here, we determined the suitability of chitin extracted from waste crab legs as an adsorbent for removing AY25 dye. The adsorption kinetics was modeled using pseudo-first order, pseudo-second order, and intraparticle diffusion equations to determine the rate controlling step. Results showed that the pseudo-second order adsorption mechanism is predominant, and the overall rate of the dye adsorption process is therefore controlled by an adsorption reaction. Adsorption isotherms were analyzed by utilizing the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models at 23°C, with data collected by using various initial dye concentrations with different chitin dosages. Our results show the highest correlation with the Langmuir model, consistent with the fact that chitin contains both a monolayer and homogeneous adsorption sites. Based on the D-R model, the adsorption of AY25 dye onto chitin is via chemisorption. Furthermore, we have concluded that the rate constants of both pseudo-second order adsorption and film diffusion are correlated to the initial dye concentrations and chitin dosages. In conclusion, chitin from waste crab legs is a very suitable adsorbent material that is capable of rapidly removing up to 95% of the initial concentration of AY25 dye at a pH of 2 and room temperature.

Keywords

Acid Yellow 25, Chitin, Adsorption Kinetics, Adsorption Isotherm

1. Introduction

Dyes are widely used by textile, food, paper, paint, and pharmaceutical industries [1], producing tremendous amounts of wastewater. It has been reported that approximately 280,000 tons of textile dyes are dumped into the marine environment worldwide per year [2]. Textile wastewaters typically contain 10 - 200 mg/L of dyes. These industrial dyes are non-degradable and stable to light and oxidizing reagents. Therefore, the disposal of waste dyes into water streams creates an environmental problem. For example, the presence of dyes in rivers and lakes affects aquatic life directly and humans indirectly by 1) reducing light passage, 2) producing toxic breakdown products that eventually find their way into human food chains, and 3) causing skin allergies, cancer, and eye irritation [3]. Acid Yellow 25 (AY25) (Figure 1) is a commonly used dye in the textile industry for dyeing natural fibers like cotton, wool, and silk as well as synthetic fibers like polyesters, acrylic, and rayon in weak acid solutions (pH 2 to 6) [4], in which the name "acid" originates from the dyeing process. Acid dyes are mainly mono-azo compounds; but can also include diazo, nitro, 1-amino-anthraquinone, triphenyl methane, and other groups of compounds. They also carry one to three sulfonic groups, making them anionic.

Currently, there are many approaches for the treatment of dye wastes. Chemical methods like coagulation, precipitation, electrochemical destruction, electro-flocculation, irradiation, and oxidation, are used to treat wastewater dyes [5]. However, these methods are expensive and they generate toxic derivatives, such as primary aromatic amines and heavy metals, which persist in the treated wastewater. Using microorganisms for the removal of synthetic dyes is relatively
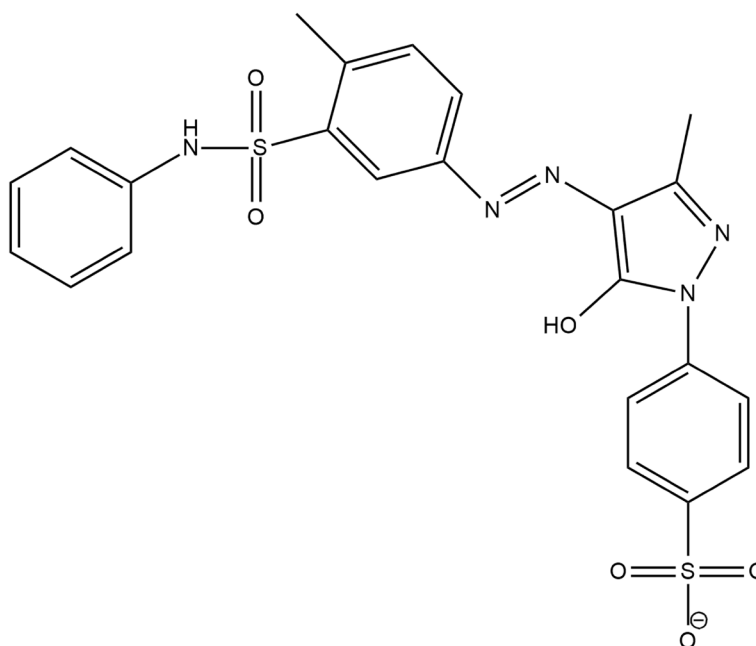

Figure 1. Chemical Structure of Acid Yellow 25 (AY25).

inexpensive and the breakdown products are completely mineralized. However, the microbiological approach needs a large land area due to the high volume of sludge generated, making this solution a challenge. Furthermore, some of the industrial dyes are resistant to aerobic digestion and thus may not be effectively removed due to their extremely slow oxidation rate [5]. Physical methods like membrane filtration and ion-exchangers have their own drawbacks in dye wastewater removal. For example, filtration membranes have a limited lifetime, are prone to pore clogging, and are costly to replace, while ion-exchangers are not effective for the removal of dyes with a neutral charge [5]. Therefore, biosorption appears to be a better method for the treatment of wastewater. This technology is easily adaptable and the materials used are inexpensive [6]. Various materials like shrimp shells [3] [7], ginger [4], and orange peels [6], have been investigated in the past, but there is still a need to develop cheap and effective biosorbent materials that are specific to dyes with different properties. Here, we used chitin prepared from waste snow crab legs as a sorbent for the removal of AY25 dye from an aqueous solution. The mechanism of adsorption, including the isotherm and kinetics, is reported.

The consumption rate of snow crabs in the United States is nearly 50,000 tons per year [8]. Due to the large consumption rate, waste crab shell management has become another environmental issue. It has been reported that Maryland's Eastern Shore, one of the waste crab shell processing plants in the United States, processes up to 8 million pounds of waste crab shells per year. Thus, using waste crab legs as the raw material for the preparation of chitin, the second most abundant organic resource on the Earth, provides an eco-friendly method that would make use of one waste material to clean up another. Chitin, the major polymer component of the exoskeletons of crustaceans, mollusks, insects and certain fungi, consists of long chain of N-acetyl-D-glucosamine (GlcNAc or 2-acetamido-2-deoxy-D-glucopyranose) units linked through β-1,4-glycosidic linkages. Naturally, chitin associates with proteins, organic pigments, and minerals [9].

This crab-waste recycling method will benefit both the food industry and the textile industry by saving on their waste management expenses and their effluent treatment cost, respectively. The objective of this research is to study the suitability of using chitin prepared from waste snow crab legs to remove AY25 dye from aqueous solutions.

2. Experimental Procedure

2.1. Chemicals

Acid Yellow Dye AY25 (CAS 6353-85-9) was purchased from Sigma-Aldrich (St. Louis, MO) without further purification. Waste snow crab (*Chionoecetes opilio*) legs were obtained from Dierbergs Market (Edwardsville, IL). All other reagents were purchased from Fisher Scientific.

2.2. Chitin Preparation

The preparation of chitin was carried out as stated in previous reports. Briefly, loose tissues inside the crab legs were scraped out and the shells were washed thoroughly with tap water and finally with deionized water. The shells were dried at room temperature for 2 to 3 days and were ground to a fine powder, followed by demineralization as described previously [10] by using a 0.25 M HCl solution with a solution to solid ratio of 40 mL/g at room temperature. The resulting mixture was filtered through a filter paper (Whatman No. 8). The retained solid powder was washed with deionized water until the filtrate became neutral. Deproteinization was performed using 1.0 M NaOH at 70˚C with the ratio of solution to solid of 20 mL/g [9]. The deproteinized mixture was then washed with 100 mL of hot ethanol (60˚C) followed by boiling in 100 mL acetone for 10 - 15 minutes. The solution was suction filtered and the solid particles were then air dried. The dried chitin was passed through a No. 50 U.S. Standard Sieve followed by a No. 80 Sieve to select particles that were retained on the mesh, with their sizes ranging from 297 to 177 μm. The purified α-chitin was confirmed by the characteristics of the C=O stretching at 1655 and 1623 cm^{-1} and N-H stretching at 3265 and 3100 cm^{-1} using the Nicolet iS5 FT-IR spectrometer (Thermo Scientific), as well as X-Ray Power Diffractometry (XRD) [10]. The XRD measurements on powdered chitin samples were carried out using a model Rigaku MiniFlex+ X-ray diffractometer equipped with Ni-filtered Cu K$_\beta$ radiation (λ = 1.5406 Å). The relative intensities were recorded between 5º-40° (2θ = 5˚ - 40˚) at room temperature. The X-ray diffractometer was operated with 1˚ diverging and receiving slits at 50 kV and 40 mA and a continuous scan was carried out with a step size of 0.015˚ and a step time of 0.2 seconds. Peaks were compared with the α-chitin peaks obtained from the MDI JADE data base. Five reflections at angles of 9.3˚, 19.3˚, 23˚, 26˚, and 36.6˚ were detected.

2.3. AY25 Dye Adsorption by Chitin

The effects of chitin dosage, pH, and temperature were determined using batch experiments, in which the different amounts of chitin were placed in Erlenmeyer flasks containing different dye concentrations at varying pH and temperatures. A calibration curve of absorbance at 392 nm versus the known concentration of AY25 was obtained in order to determine the dye concentration that remained in the solutions for the characterization below. The total volume for each flask was 25 mL and the flasks were placed on a water-bath shaker (New Brunskwick Scientific, Edison NJ) at 70 rpm. Approximately 1 mL of dye solution from each flask was removed at different time intervals for 150 minutes. The samples were centrifuged at 13,000 rpm for 1 minute using a Brinkmann 5412 centrifuge. The absorbance values of the resulting supernatants after dilution were measured at 392 nm using a UV-1800 double-beam spectrometer (Shimadzu, Kyoto, Japan). The dye concentrations remaining in each solution (after correction for dilution factor if necessary) were determined. The dye removal efficiency (*E*%) was cal-

culated as:

$$E\% = \frac{C_i - C_f}{C_i} \times 100\% \quad \text{or} \quad \frac{A_i - A_f}{A_i} \times 100\% \tag{1}$$

where C_i (or A_i) and C_f (or A_f) are the initial and final concentrations in mg/L (or absorbance at 392 nm) of AY25 in liquid, respectively. The adsorption capacity at time t (q_t in unit of mg/g) was determined by Equation (2).

$$q_t = \frac{(C_o - C_t)V}{m} \tag{2}$$

where C_o and C_t are the initial dye concentration and the concentration at time t in the liquid phase (mg/L), respectively, m is the mass of chitin (g), and V is the volume of the aqueous phase (L). Adsorptive capacity at equilibrium (q_e) is a measurement of how well a certain adsorbent adsorbs the adsorbate in solution. This term is utilized for a better comparison and is important to judge the performance of an adsorbent. The value of q_e can be calculated by the equation below.

$$\text{Adsorptive Capacity}(q_e) = \frac{\text{Amount of dye adsorbed}(\text{mg})}{\text{Amount of Chitin}(\text{g})} \tag{3}$$

The data presented in the results section are reproducible and are from at least four separated trials using at least two different batches of chitin.

3. Results and Discussion

3.1. The pH, Temperature, and Dosage Effect of AY25 Dye Adsorption to Chitin

We isolated chitin from waste crab legs by the demineralization and deproteinization processes as described previously [10]. The IR spectrum and X-ray diffraction data (data not shown) of the resulting purified chitin indicate that the α form of chitin was obtained, which was consistent with a previous report [10]. To determine the optimal pH for the AY25 adsorption by chitin, the measurements were conducted in a solution containing 58 mg/L AY25 and 3 g/L of chitin (particle size of 297 to 177 μm) at pH values ranging from 1 to 12 at room temperature (**Figure 2(a)**). The dye concentration in the liquid phase was determined after 0.5, 1, and 2 hour incubation periods. Our results show that the dye adsorption increased over time (data not shown). The dye removal efficiency was more than 50% for pH values ranging from 2 to 7 with the highest adsorption at pH 2. A pH higher than 8 resulted in less than 30% of dye removal. These observations suggest that the positively charged chitin, resulting from the protonation of the amino group of chitin under acidic conditions [11], interacts with the negatively charged sulfonic group of the dye. Such ionic interactions are diminished at pH 1, possibly due to the conversion of the sulfonic salt to sulfonic acid in very acidic conditions. AY25 is considered to be a strong acid due to its sulfonic group with a low pK$_a$, as seen in P-toluenesulfonic acid with its pK$_a$ = −2.1. Similarly, the solutions with a higher pH resulted in less protonation of the
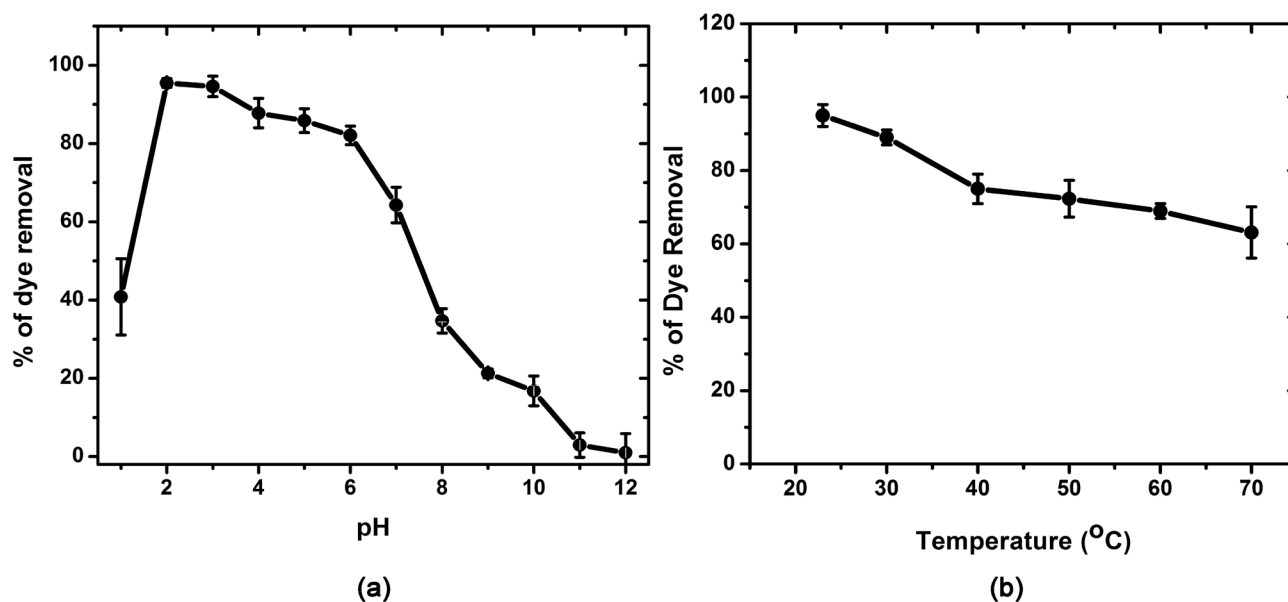
Figure 2. The Effects of pH and Temperature. The initial dye and total chitin concentrations were 385 mg/L and 3 g/L, which were incubated in the different pH solutions (a) or at specific temperatures (b) at a speed of 70 rpm.

amino group in chitin that weakens the ionic interaction as well. We also determined the effect of temperature on dye adsorption by chitin by utilizing 58 mg/L AY25 with 3 g/L chitin at pH 2 and 70 rpm. Our results revealed that higher temperatures have a lower efficiency of dye removal (**Figure 2(b)**), and the efficiency at room temperature (23˚C) appears to be optimal for dye removal.

We then determined the dosage effect of chitin at 23˚C. At a low initial dye concentration (58 mg/L), the adsorption of dye onto chitin is very effective and reaches equilibrium quickly. For example, the dye removal reaches 90% within 15 min of contact time with the exception of the chitin dosage of 1 g/L, which reaches equilibrium in ~1 hr (**Figure 3(a)**). Following the maximum adsorption, the system reaches a state of dynamic equilibrium between dye being adsorbed onto and desorbed from chitin. When the initial dye concentration was increased, more chitin was required (**Figure 3(b)**). When the initial dye concentration was 385 mg/L, at least 3 g/L of chitin was required to remove 90% of the dye within 1 hr. This observation was expected, as the increase in adsorption with higher adsorbent dosage is attributed to an increased adsorbent surface and the availability of more adsorption sites. Thus we chose the chitin dosages of 3, 4, and 5 g/L and initial dye concentrations of 58, 165, 284, and 385 mg/L for our adsorption kinetics and isotherm studies.

3.2. Adsorption Kinetics

Adsorption kinetics provides information about the interactions between the adsorbent and adsorbate, which are important to understand the adsorption process conditions. Typically, dye adsorption kinetics is influenced by the adsorption and mass transfer steps, including external- and intra-particle diffusions that are related to the structure of the absorbent (e.g. particle size and
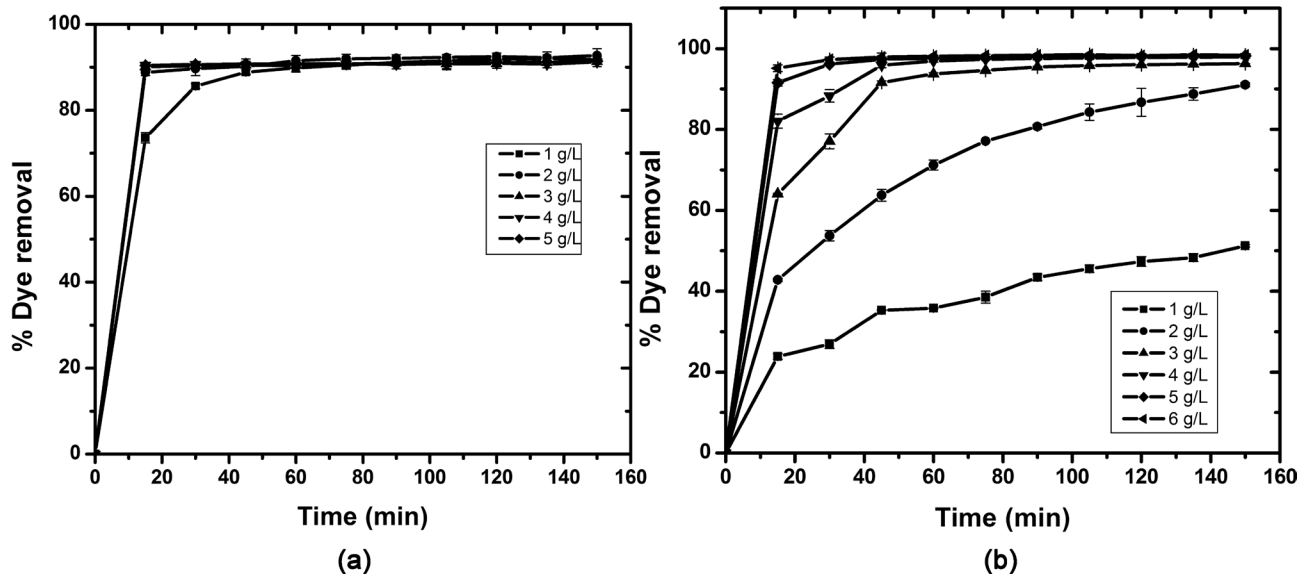
Figure 3. Effect of Initial Dye Concentration on Adsorptive Capacity. The batch experiments were conducted at 23˚C and pH = 2 using 58 mg/L (a) and 385 mg/L (b) of AY25.

intrinsic property), the nature of adsorbate, and the process conditions such as temperature, pH, and mixing speed. Many models, including pseudo-first order, pseudo-second order, and intra-particle diffusion models, have been employed to describe the kinetic processes.

The pseudo-first order kinetic model is expressed as:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \qquad (4)$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at time t, and k_1 is the equilibrium rate constant for pseudo-first order kinetics (min^{-1}). The pseudo-first order model is based on the rate of adsorption being related to the concentration difference of adsorbate between the solution and the surface of adsorbent. In such a process, the adsorption process is primarily controlled by the external mass transfer coefficient. For this model, a linear plot of $\log\left(q_e - q_t\right)$ versus t (Equation (4)) is anticipated and the resulting slope corresponds to the value of k_1. However, the pseudo-first order equation cannot be applied well for a slow adsorption process and, therefore, is generally limited for the adsorption with a short contact time [12]. The adsorption of AY25 onto chitin cannot be described by the pseudo-first order model (data not shown) as its application at different initial dye concentrations (58, 165, 284, and 385 mg/L) resulted in very low R^2 values (Table 1).

We then fit our data with a pseudo-second order model, which includes the same equation for both internal and external mass transfer mechanisms as expressed by the following formula:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (5)$$

where k_2 is the pseudo-second order rate constant (g·mg^{-1}·min^{-1}). An example showing a linear fit of t/q_t versus contact time (t) for 165 mg/L initial dye concentration with 3, 4, and 5 g/L of chitin is shown in **Figure 4(a)**, and the fitting results for other initial dye concentrations are listed in **Table 1**. The fitting with $R^2 > 0.9993$ yields the pseudo-second order rate constant k_2 and the calculated q_e ($q_{e,cal}$) agrees with the experimental ones ($q_{e,exp}$) derived from the experiments

Table 1. Kinetic parameters for AY25 dye adsorption onto chitin at different initial dye concentrations and different adsorbent dosages at 23˚C and pH = 2.

Initial Conc. (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
		$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2 (g·mg^{-1}·min^{-1})	R^2
58[a]	17.73	0.097	0.002	0.0427	17.67	0.3027	0.9999
58[b]	13.54	0.124	0.008	0.7734	13.49	0.4210	0.9999
58[c]	10.85	0.163	0.016	0.7404	10.82	0.6668	0.9999
165[a]	53.88	1.16	0.031	0.8454	54.35	0.0385	1.0000
165[b]	35.87	0.434	0.014	0.5338	35.97	0.1137	1.0000
165[c]	28.82	0.113	0.008	0.6067	28.82	0.5016	1.0000
284[a]	92.07	17.29	0.040	0.9437	92.94	0.0070	0.9999
284[b]	69.32	2.354	0.027	0.8829	69.64	0.0277	1.0000
284[c]	55.58	0.719	0.013	0.5887	55.56	0.0562	0.9999
385[a]	127.17	65.90	0.045	0.9818	130.72	0.0021	0.9993
385[b]	98.08	25.55	0.047	0.9656	99.90	0.0049	0.9997
385[c]	78.64	4.61	0.032	0.8775	79.18	0.0137	0.9999

[a,b,c]The concentrations of chitin are 3, 4, 5 g/L, respectively.
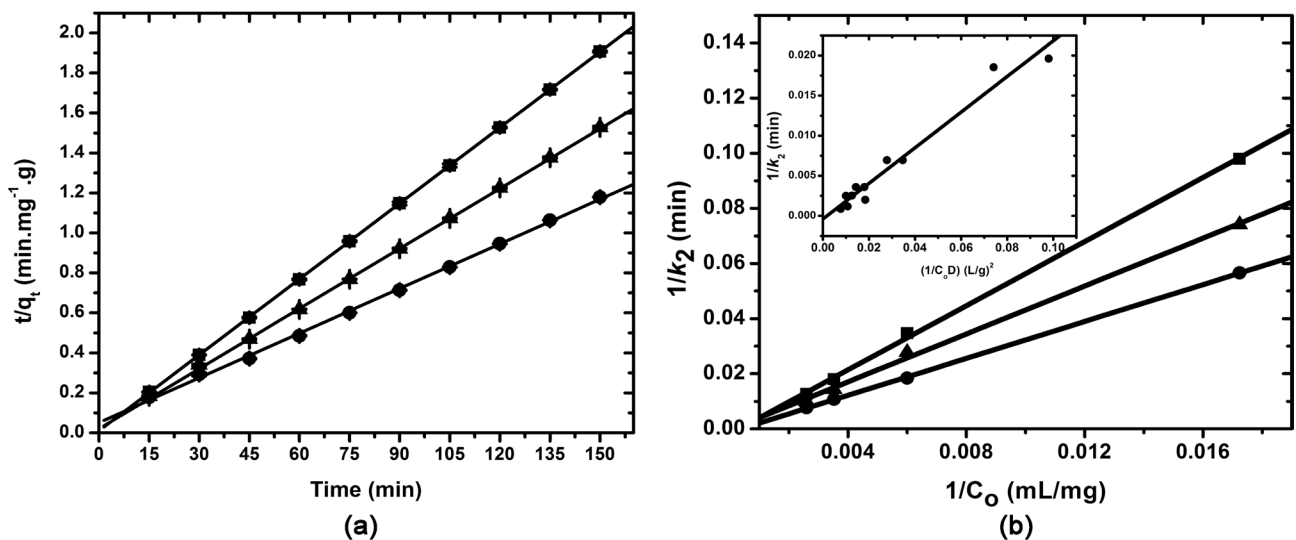

Figure 4. Adsorption Kinetics of AY25 onto Chitin. The pseudo-second order kinetics were conducted using 385 mg/L AY25 in the presence of 3 (circle), 4 (triangle), and 5 (square) g/L of chitin at pH 2 and 23˚C (a). The plots of $1/k_2$ versus $1/C_o$ (b) and C_oD (Insert) were analyzed using Equation (6) and Equation (7), respectively.

conducted shown in **Figure 2**. The results indicate the pseudo-second order model is adequate for describing the AY25/chitin adsorption process. The pseudo second-order model is consistent with a previous study showing that a higher k_2 is associated with a lower initial dye concentration for a fixed chitin dosage (see **Table 1**). It has been shown that k_2 is a complex function of initial concentration C_o [13], and their relationship can be expressed as the following based on the theoretical derivation by Aziaian [14].

$$k_2 = C_o \left(A_k C_o + B_k \right) \quad \text{and}$$

$$1/k_2 = A_k + B_k \left(1/C_o \right) \tag{6}$$

where A_k (mg·min·g^{-1}) and B_k (mg^2·min·g^{-1}·L^{-1}) are fitting constants, and can be determined by the plot of $1/k_2$ versus $1/C_o$. Our data shows the linearity for each plot at different chitin dosages (**Figure 4(b)**) with the B_k values of 3.346, 4.342, and 5.816 mg^2·min·g^{-1}·L^{-1} for 3, 4, and 5 g/L chitin, respectively. The values of B_k increase with the increase of dosage, indicating that k_2 is also dependent on chitin dosage. Interestingly, our data can be fit well when considering the amount of adsorbent into Equation (6), as shown in the following.

$$1/k_2 = A_k + B_k' \left(1/C_o D \right) \tag{7}$$

where D is the amount of chitin in g/L and B_k' (mg^2·min·L^{-2}) is the new fitting parameter. The values of A_k and B_k' obtained by the fitting with Equation (7) are 0 mg·min·g^{-1} and 0.222 mg^2·min·L^{-2}, respectively, with $R^2 = 0.9824$ (the insert in **Figure 4(b)**).

Our observations suggest an intra-particle diffusion that may be involved in this sorption phase. The possibility can be explored by plotting q_t versus $t^{1/2}$ (*i.e.* W-M plot) based on the Weber and Morris model [15]. Such intraparticle diffusion can be determined from the initial adsorption process via the following equation.

$$q_t = k t^{1/2} + C \tag{8}$$

where k is the intra particle diffusion rate constant (mg·g^{-1}·min$^{1/2}$). While k provides information for the diffusion process, the value of C carries profound information, such as the thickness of the boundary layer that controls the process. For $C = 0$ (*i.e.* the fitting line passes through the origin), the intraparticle diffusion is the rate controlling step. Multilinearity of W-M plots has been reported. Typically for adsorption, the first linear sorption process involves the fastest dye migration to external surfaces of chitin via either external surface adsorption or boundary layer diffusion. The second linear adsorption phase is attributed to a slower intra-particle diffusion followed by a third linear final equilibrium stage, in which the diffusion is very slow due to very low dye concentration left in the solution. We only observed two linear portions of the adsorption in our case. The adsorption process is very rapid such that the adsorption kinetics cannot be determined precisely during the onset of the adsorption. **Figure 5** shows the plot of q_t versus $t^{1/2}$ for 385 mg/mL dye and 3, 4, and 5 g/L chitin, in which the first
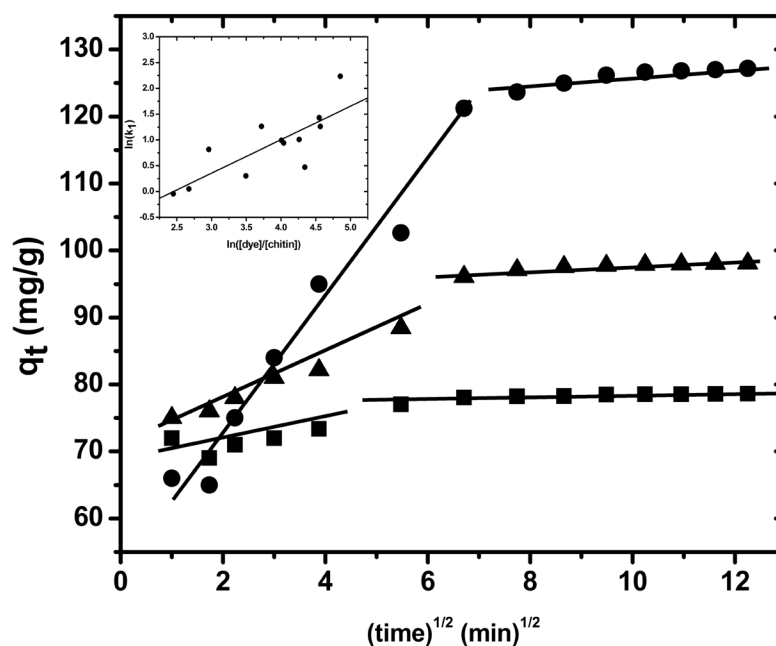
Figure 5. Weber-Morris Plot of AY25 Adsorption onto Chitin and the Correlation to the Amounts of AY25 and Chitin. The experiments were conducted using 385 mg/L AY25 in the presence of 3 (circle), 4 (triangle), and 5 (square) g/L of chitin at pH 2 and 23°C. Two linear portions of the adsorption were fitted with the W-M equation and the rate constants are summarized in **Table 2**. The insert shows the correlation between $\ln k_1$ and $\ln([AY25]/[chitin])$.

linear region corresponds to the boundary layer diffusion with the k_1 values of 9.3235, 3.5211, and 1.4478 min^{-1}. The second linear portions can be explained by the intraparticle diffusion, a slow process giving k_2 values of 0.3457, 0.1582, and 0.0972 mg·g^{-1}·min$^{1/2}$ (**Table 2**). The lines do not pass through the origin, indicating that intraparticle diffusion is only a part of the rate determining step while the boundary layer diffusion controls the adsorption to some degree. The assignments for the individual adsorption processes are reasonable given that chitin's structure is typically rigid and nonporous which renders a slower intraparticle diffusion [1]. Similarly, we performed the dye adsorption using lower initial concentrations of dye against 3, 4, and 5 g/L of chitin. The results were consistent with the previous observation, indicating both the boundary layer and intraparticle diffusion rates are inversely proportional to the dosages of chitin. Interestingly, Cheung *et al.* [15] studied the adsorption of several acid dyes onto chitosan and showed that k_1 (the uptake process) is more significantly affected by the initial concentration (C_o), but not by the mass of chitosan. They obtained straight lines from the plot of $\ln k_1$ versus $\ln C_o$ and demonstrated that the first phase of adsorption can be fitted by:

$$k_1 = A_n C_o^{B_n} \tag{9}$$

where A_n and B_n are the fitting parameters. However, our study showed that the first phase of the adsorption of AY25 onto chitin is also affected by the amount of adsorbent (D). The plot of $\ln(k_1)$ versus $\ln([dye]/[chitin])$ in our study suggests

Table 2. Film and Intra-particle diffusions for AY25 dye adsorption onto chitin at different initial dye concentrations and different adsorbent dosages at 23°C and pH = 2.

Initial Conc. (mg/L) (dye/chitin: mg/g) ———	Film and Intra-particle diffusion models			
	k_1 (mg·g^{-1}·min$^{1/2}$)	R^2	k_2 (mg·g^{-1}·min$^{1/2}$)	R^2
58 (19.33)[a]	2.2595	0.9798	0.0253	0.8761
58 (14.50)[b]	1.0496	0.5875	0.001	0.5875
58 (11.60)[c]	0.9553	0.8717	0.011	0.7828
165 (55.00)[a]	2.6921	0.7421	0.1855	0.9827
165 (41.25)[b]	3.5274	0.9617	0.0461	0.7548
165 (33.00)[c]	1.352	0.7226	0.017	0.9663
284 (94.67)[a]	4.1732	0.8276	0.1719	0.9397
284 (71.00)[b]	2.7384	0.9189	0.0991	0.9799
284 (56.80)[c]	2.5635	0.9614	0.0704	0.8624
385 (128.33)[a]	9.3235	0.9749	0.3457	0.9628
385 (96.25)[b]	3.5211	0.9795	0.1583	0.9669
385 (77.00)[c]	1.4478	0.8432	0.0972	0.8584

[a,b,c]The concentrations of chitin are 3, 4, 5 g/L, respectively.

a correlation among the film diffusion rate, the dye and chitin concentrations. Thus, Equation (9) can be modified as:

$$k_1 = A_n \left(\frac{C_0}{D} \right)^{B_n} \tag{10}$$

Note that the poor fitting (R^2 = 0.7945) is mainly due to the experimental errors associated with the measurements for the rapid adsorption of this phase. Though the basis of the correlation is not known, our results indicate that the mass transfer process of AY25 adsorption onto the chitin surface from the onset of the process is very quick, followed by a slower intraparticle diffusion, and both processes are controlled by the "availability" of dye to the surface of chitin.

3.3. Adsorption Isotherms

Adsorption isotherms can be used to explain the adsorption in equilibrium at a specific temperature, which provides a better understanding of the surface properties of the adsorbent and the adsorption behavior. Thus we analyzed our data using several established adsorption isotherm models, including Langmuir, Freundlich, and Dubinin-Radushkevich (D-R). To do so, we studied the effect of chitin dosage on equilibrium dye concentration (C_{eq}) by using an initial dye concentration of 385 mg/L and chitin dosages from 1 to 5 g/L, shown in **Figure 6**. First, we obtained isotherm parameters using the Langmuir adsorption model, which assumes that 1) the surface contains a homogeneous monolayer and 2) the adsorption sites are identical and independent [16]. The Langmuir equation
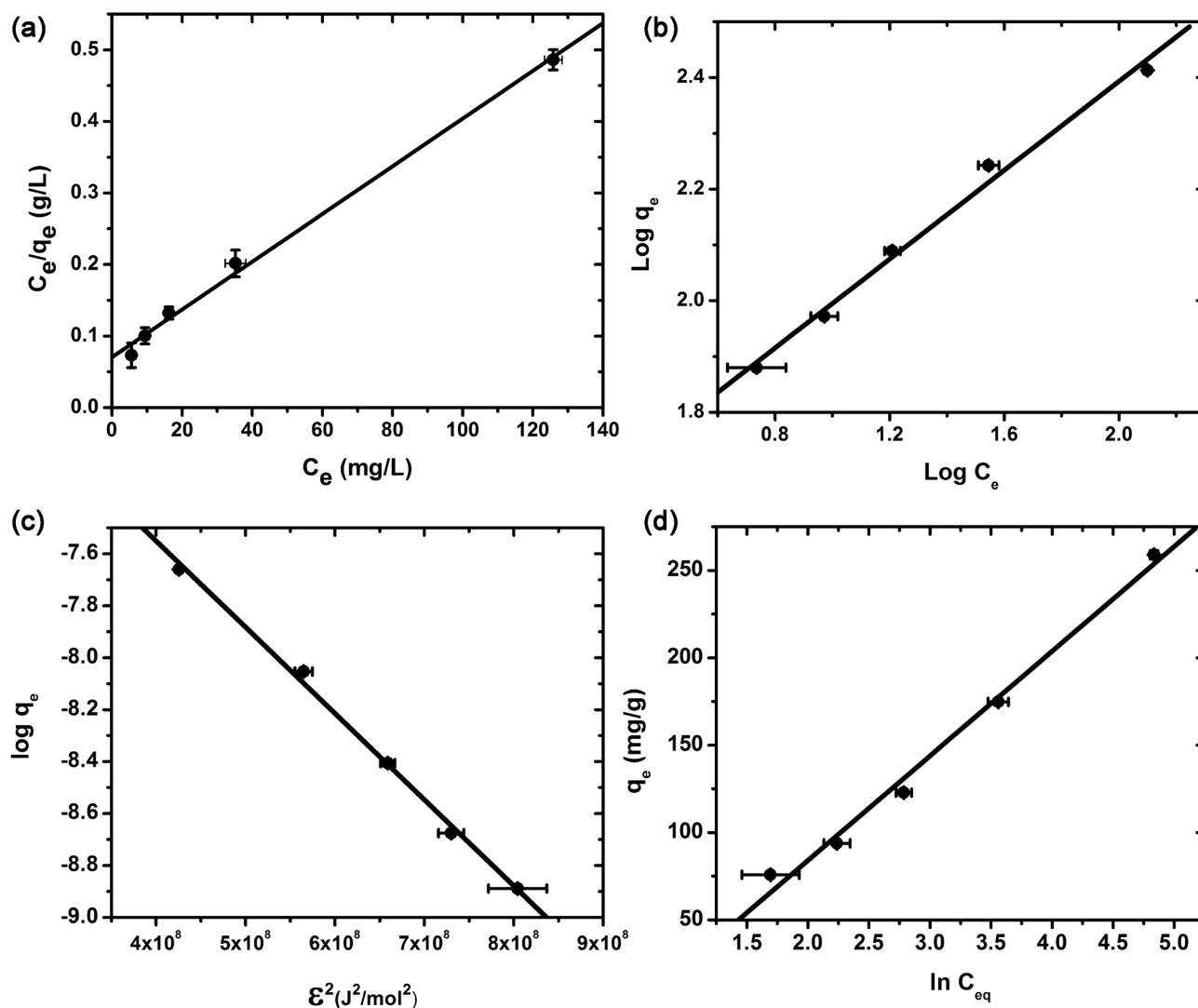
Figure 6. Isotherm Parameters Obtained from Different Models. The experiments were conducted with the initial dye concentration of 385 mg/L and chitin dosages of 1, 2, 3, 4, and 5 g/L at 23°C and pH = 2. Four different isotherm models were used for analysis: Langmuir (a), Freundlich (b), D-R (c), and Temkin (d). The parameters obtained from fitting were summarized in Table 3.

is shown in the following.

$$\frac{q_e}{q_{\max}} = \frac{bC_e}{1 + bC_e} \tag{11}$$

where q_e and $q_{\max}$ are the equilibrium concentration of adsorbate adsorbed per adsorbent (mg/g) and saturation capacity of adsorbent (mg/g) forming the monolayer, respectively; C_e is equilibrium concentration of the adsorbate (mg/L) and b is the Langmuir adsorption constant (L/mg) that is related to the heat of adsorption. The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called the equilibrium parameter (separation factor), R_L, as defined below.

$$R_L = \frac{1}{1 + bC_o}$$

where C_o is the initial dye concentration (mg/L).

Our results reveal that the dye adsorption process fits the Langmuir adsorption model well (Table 3), indicating that the adsorption process takes place at the binding sites of chitin near the monolayer of the chitin surface, in which there is no further adsorption at that particular site when that site is occupied by a dye molecule. R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linearly adsorptive ($R_L = 1$), or unfavorable ($R_L > 1$) [17]. The R_L value for the adsorption of AY25 dye onto chitin is 0.045 (Table 3), which indicates that the adsorption is favorable. The behavior is consistent with the Type I Langmuir isotherm, suggesting a unimolecular adsorption that applies to microporous adsorbents with small pore sizes.

In contrast to the Langmuir isotherm, the empirical Freundlich isotherm is used to describe the adsorption onto a heterogeneous surface or surfaces containing binding sites with different binding affinities. In this model, the strong binding site is occupied first followed by a weaker binding. The Freundlich isotherm is given by Equation (12) [16].

$$q_e = K_F C_{eq}^{1/n}$$

$$\log q_e = \frac{1}{n} \log C_{eq} + \log K_F \tag{12}$$

where K_F and n are the Freundlich constant and heterogeneity factor (or adsorption intensity), and C_{eq} is the concentration of adsorbate remaining in solution. The $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), or unfavorable ($1/n > 1$). If $n = 1$ then the partition between the two phases are independent of the concentration. The calculated R^2 value ($R = 0.9884$) indicates that the equilibrium data in this study fairly agrees with the Freundlich model, presenting heterogeneous adsorption sites on the surface of chitin. This is probably because multiple interactions are present in this system where dye could interact with different sites of the adsorbent. Our results also show that the $1/n$ value (0.4195) for AY25 dye adsorption is between 1 and 0,

Table 3. Isotherm parameters obtained from different models with an initial dye concentration of 385 mg/mL and chitin dosages of 1, 2, 3, 4, and 5 g/L at 23°C and pH = 2.

Isotherm Model	Parameters			
Langmuir	q_{max} (mg/g)	b (L/mg)	R_L	R^2
	303	0.045	0.055	0.9951
Freundlich	K_F (L/g)	$1/n$		R^2
	37.35	0.4195		0.9884
D-R	q_D (mol/g)	β_D (mol²/J²)	E_{DR} (kJ/mol)	R^2
	0.00202	3.36×10^{-9}	12.20	0.9934
Temkin	A_T (L/mg)	B (mol²/kJ²)	b_T (J/mol)	R^2
	0.888	46.14	53.34	0.9467

and thus the adsorption process is favorable under the studied conditions.

We then used the Dubinin-Radushkevich (D-R) isotherm model to test the nature of the chemical and physical means of adsorption [18]. The D-R isotherm equations are shown below [19]:

$$q_e = q_D \exp\left(-\beta_D \varepsilon^2\right)$$

$$\ln q_e = \ln q_D - \beta_D \varepsilon^2 \tag{13}$$

where q_D is Dubinin-Radushkevich monolayer saturation capacity (mol/g); β_D is the constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2); and ε is the Polyani potential (J/mol) and defined as $\varepsilon = RT \ln\left(1 + 1/C_{eq}\right)$ (R is the gas constant and T is absolute temperature). By plotting $\ln q_e$ versus ε^2, q_D and β_D can be obtained. The constant β_D gives an idea about the mean free energy, where the mean free energy can be calculated using $E_{DR} = \dfrac{1}{\sqrt{2\beta_D}}$. All initial dye concentrations of AY25 dye tested show a good agreement to the D-R isotherm model. The correlation for this isotherm is higher when compared to the Freundlich isotherm. The fitted results indicate the E_{DR} value is 12.20 kJ/mol (**Table 3**), which is between 8 and 16 kJ/mol for chemisorption via ion-exchange [20]. The chemisorption appears to attribute from the electrostatic attraction between positively charged chitin [1] and negatively charged dye at pH 2 as described previously.

The Temkin adsorption isotherm is used to determine the interaction between adsorbate and adsorbent [21]. The model assumes that heat of adsorption of all molecules in the layer decreases linearly with surface coverage due to adsorbent-adsorbate interactions. Adsorption is thus characterized by a uniform distribution of binding energies. The Temkin adsorption isotherm is given in Equation 14 [22].

$$q_e = \frac{RT}{b_T} \ln\left(A_T C_e\right)$$

$$q_e = B \ln A_T + B \ln C_e \tag{14}$$

where A_T is the Temkin isotherm equilibrium binding constant (L/mg); b_T is the Temkin isotherm constant related to the heat of adsorption (J/mol), and $B = RT/b_T$ (R is 8.314 J mol^{-1} K^{-1} and T is absolute temperature in Kelvin). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B and A_T from the slope and the intercept, respectively. The calculated coefficient of determination (R^2) shows that the experimental data does not have a very good fit ($R^2 = 0.9471$) with the Temkin isotherm (**Table 3**), indicating that the binding energy is not uniformly distributed up to its maximal binding energy.

4. Conclusions

Here we have shown that the AY25 adsorption onto chitin (particle size of 297 to 177 μm) at pH 2 and room temperature with a shaking rate of 70 rpm can be

described best by a pseudo-second order model. The intraparticle study indicates that the adsorption is mainly controlled by a film adsorption process. By varying the amounts of AY25 and chitin, we have determined that the rates of pseudo-second order adsorption and boundary layer diffusion that are a complex function of both initial concenentration of AY25 (C_o) and the dosage of chitin (D) as defined in Equations (7) and (10).

The adsorption isotherms of AY25 onto chitin were also analyzed using different models, including the Langmuir, Freundlich, D-R, and Temkin isotherms. Our adsorption data showed a good correlation for all isothermal models except for the Temkin model. Among them, the Langmuir isotherm showed the highest correlation, suggesting that the surface of chitin contains a monolayer with heterogeneous adsorption sites. Additionally, the separation factor (R_L) from the Freundlich isotherm indicated that such an adsorption is favorable. The mean free energy of adsorption in D-R was 12.2 kJ/mol, which accounts for the adsorption of AY25 dye onto chitin being chemisorption, primarily through ion-exchange interactions. The maximum AY25 adsorption capacities of chitin (q_{max}) obtained from the Langmuir and Freundlich isotherm models were ~300 and 320 mg/g, which are comparable to those of chitin with other acidic dyes, such as Acid Blue 25 and 158 [23].

In summary, our study demonstrates that chitin can be effectively used for the removal of AY25 dye as shown by its high adsorption capacity and rapid adsorption via chemisorption and film mass transfer processes. Our study on the effects of pH and temperature also indicates that wide ranges of pH (2 - 7) and temperature (20˚C - 70˚C) are adequate for removal of the majority of the dye from solution, making chitin as an ideal adsorbent for AY25 in textile water.

Acknowledgements

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