



Study of Adsorption Isotherm and Kinetics of Reactive Yellow Dye on Modified Wheat Straw

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Abstract: In this study, the adsorption of reactive yellow dye which is one of the most commonly used soluble dyes in textile industries was studied using modified wheat straw, the surface of raw wheat straw was modified with a cationic surfactant CTAB. to understand the adsorption behavior of the reactive yellow, dye the adsorption kinetics and the adsorption isotherm studies have been investigated. Batch experiments was carried out with an initial concentration of 10 mg/L with 0.5 gm of adsorbent to study the contact time of equilibrium and then the adsorption mechanism process using three kinetic models; Pseudo-first, second order and intra-particle model. Isotherm studies was carried out at three different adsorbent amounts (0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) gm to predict the type of adsorption process on the surface (chemical or physical) using three isotherm models; Langmuir, Freundlich and BET models. The results showed that the pseudo-second order is best fitted, intra-particle diffusion kinetic model fitted well to experimental data and is not the only controlling step of adsorption rate, and the adsorption isotherm follows both Langmuir and Freundlich models referring to the chemical adsorption.

Keywords: Kinetics, Isotherm, Modified Wheat Straw

1. Introduction

The production of textiles represents one of the big consumers of high water quality. As a result of various processes, considerable amounts of polluted water are released. Representative magnitudes for water consumption are 100–200 L of water per kilogram of textile product. Considering an annual production of 40 million tons of textile fibers, the release of wasted water can be estimated to exceed 4–8 billion cubic meters per year [1]. Textile wastewater usually consists many of contaminants, including acids, bases, dissolved solids, toxic compounds and color. Color is the most noticeable contaminant even at low concentrations, and it needs to be removed or decolorized before the discharging the wastewater [2]. Colors are easily visible to human eyes even at very low concentrations. Hence, color from textile wastes carries significant aesthetic importance. Most of the dyes are stable and include no effect of light or oxidizing agents [3]. Reactive dyes are widely used in the textile industry which link to fibers through chemical combining by react with OH group in fiber [4]. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity

of design, ease of operation and insensitivity to toxic substances. At the present time, there is a growing interest in using low-cost, commercially available materials for the adsorption of dyes [5]

2. Mathematical Models

2.1. Adsorption Kinetics Models

Various adsorption kinetic models have been adopted to describe the behavior of batch biosorption processes under different experimental conditions, among which we have the intra-particle diffusion model. Kinetics of adsorption is one of the important characteristics defining the efficiency of adsorption, the study of adsorption dynamics describes the solute uptake rate and evidently the rate control the resident time of adsorbate uptake at the solid-solution interface. The adsorption rate constant can be used to compare the performance of activated carbons [6]

2.1.1. Pseudo First Order Model

The Lagergren rate equation may have been the first rate equation for the sorption in liquid /solid systems based on solid capacity, the linearized form of pseudo first order as following:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (1)$$

Where: q_e and q_t are adsorption capacity at Equilibrium and at time t , respectively (mg/g), K_1 is the pseudo first order rate constant (1/min).

2.1.2. Pseudo Second Order Model

The integrated form of pseudo-second order chemisorption kinetics may be expressed as:

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

Where K_2 is the second order constant (g.min/mg). The plot of (t/q_t) and t of Eq. (2) should give a linear relationship from which q_e and K_2 can be determined from the intercept and slope of the plot, respectively [7]

2.1.3. Intra-particle Diffusion model

The possibility of intra-particle diffusion of adsorbate onto the adsorbent by using the intra-particle diffusion model as shown in the following equation:

$$q_t = K_p t^{1/2} + C \quad (3)$$

q_t is the amount of dye adsorbed (mg/g) at time t ; C (mg/g) is the boundary layer thickness and K_p is the rate constant of intra-particle diffusion model (mg/g.s^{1/2}).

2.2. Adsorption Isotherm Models

Numerous mathematical models attempt to characterize the adsorption process. The three most widely accepted isotherm models are Langmuir, Freundlich, and BET models. Langmuir and BET isotherms are based on theoretical developments. The Langmuir isotherm is based on the concept of monolayer adsorption, while the BET isotherm assumes multilayer adsorption. Freundlich isotherm is an empirical relationship [1]

2.2.1. Langmuir Model

The Langmuir isotherm assumes that the adsorption process takes place as the surface of adsorbent pellets or each adsorption site is homogeneous. This model is more usually appropriate for the description of chemisorption (when an ionic or covalent chemical bond is formed between adsorbent and adsorbate) [8], [9]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

Where q_e is the adsorption capacity (mg/g), C_e equilibrium concentration of adsorbate (mg/L), K_L constant

(mg/L), and q_m is the maximum capacity (mg/g). The essential features of the Langmuir isotherm can be shown in terms of a dimensionless constant is the separation factor R_L that is given by the following Equation:

$$R_L = \frac{1}{1 + K_L C_o} \quad (5)$$

Where C_o (mg/L) is the initial concentration of adsorbate, and K_L (L/mg) is Langmuir constant. The value of R_L indicates the shape of the isotherm which is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

2.2.2. Freundlich Model

Freundlich isotherm is another most widely used model. Comparing with Langmuir, the Freundlich isotherm do not have much constraint, i.e., it can deal with both heterogeneous and homogeneous surfaces, and both chemical and physical adsorption [8]

$$q_e = K_F C_e^{1/n} \quad (6)$$

By taking the logarithm of both sides of Eq. (6), the following linearized equation is obtained:

$$\log(q_e) = \frac{1}{n} \log C_e + \log K_F \quad (7)$$

The constant, K_F in the Freundlich expression and $1/n$ is a function of the strength of the adsorption.

2.2.3. Brunauer–Emmett–Teller Model (BET)

The BET model assumes that layers of molecules are adsorbed on top of previously adsorbed molecules. Each layer adsorbs according to the Langmuir adsorption model. The BET equation has the following formula for adsorption from a liquid solution:

$$q_e = \frac{q_m K_B C_e}{(C_o - C_e)[1 + (K_B - 1)(C_e/C_o)]} \quad (8)$$

Where q_m is the maximum adsorption capacity (mg/mg); C_o initial concentration of adsorbate at saturation of all layers; and K_B constant related to energy of interaction between adsorbent and adsorbate [1]. The BET equation can be linearized as follows:

$$\frac{C_e}{(C_o - C_e)q_m} = \frac{(K_B - 1)}{K_B q_m} \left(\frac{C_e}{C_o} \right) + \frac{1}{K_B q_m} \quad (9)$$

3. Materials and Experimental Works

3.1. Adsorbate

Reactive yellow dyes with molecular weight 716 g/mol and wavelength 420 nm, is supplied from Al-Hilla textile factory south of Baghdad. A stock solution of 1000 mg/L is prepared by dissolving 1.0 g of dye in 1.0 L of distilled water and then the solution is diluted the desired concentration of 10 mg/L.

3.2. Adsorbent

Raw wheat straw is collected from countryside, washed with tap water several times to remove dust and unwanted parts, then washed with distilled water and dried at 70°C for 24 hr. 35 g of wheat straw was weighed and mixed with 500 mL of CTAB solution having a concentration of 4.0 g/L. The mixture was shaken for 5 h at room temperature. washed with distilled water in order to remove any loosely adsorbed surfactant, dried about 70°C and sieved to 1 mm size particle before use [10]

4. Results and Discussions

4.1. FTIR Analysis

FTIR refers to Fourier Transform Infrared, the favorite

method of infrared spectroscopy, it can identify unknown materials, determine the consistency or quality of a sample and determine the amount of components in a mixture. Figures 1 shows the FTIR analysis of RWS before adsorption process. Figure 1 shows the peaks that indicates the complex structure of wheat straw. The strong peak around 3414 cm^{-1} represents the hydroxyl groups -OH, the bond at 2916 cm^{-1} is attributed to the presence of the C-H bond. The peaks of 1732 and 1655 cm^{-1} are referring to the carbonyl group -C=O, 1508 cm^{-1} represents the aromatic rings, while 1427 and 1373 cm^{-1} associated with the C-O in phenols and -CH₃ respectively [11], [12]. The components of the MWS are not necessary differ from RWS because the change occurred only on the surface by changing the surface's charge.

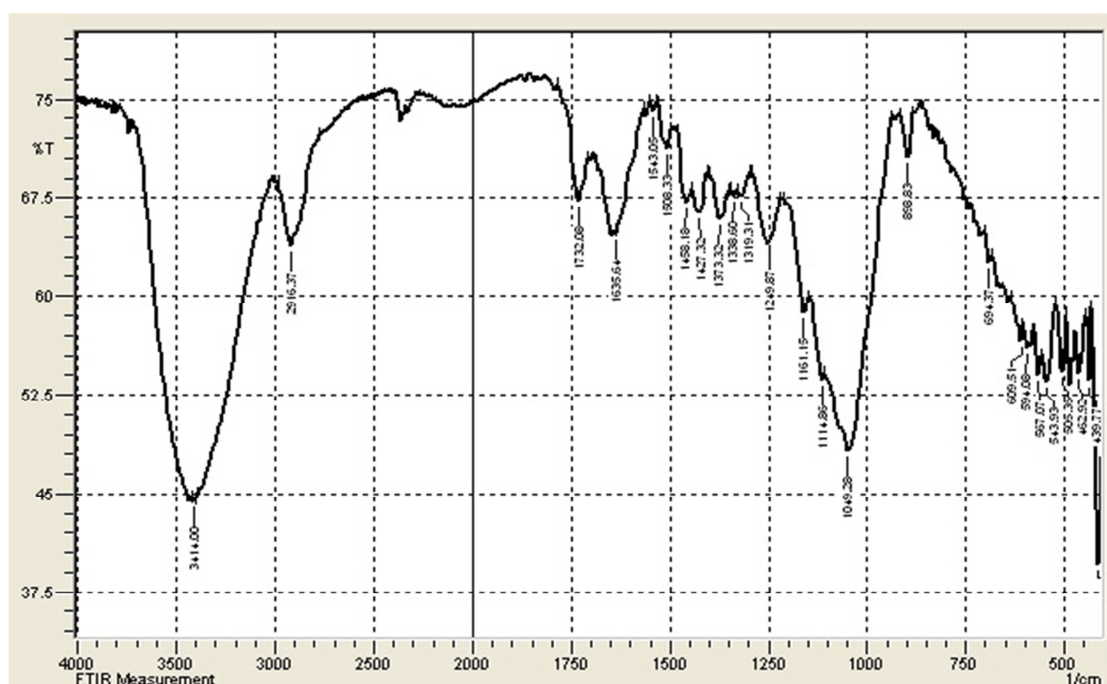


Figure 1. FTIR analysis of raw wheat straw before adsorption process.

4.2. Scanning Electron Microscope Analysis (SEM)

SEM is commonly used to study the morphological structures and surface features of the adsorbent material. It also reveals the porosity and surface texture of adsorbent [13]. Figures 2 and 3 are shown the textural structure investigation of RWS and MWS particles from SEM micrograph. It can be concluded that SEM images of RWS and MWS showed severe differences. It is clear that there are good pores enhancements at the surface of MWS. The modification process involves changing original surface texture of RWS, the main modification is changing the charge of the surface to increase the interaction between the dye molecule and the MWS surface which has a different charge.

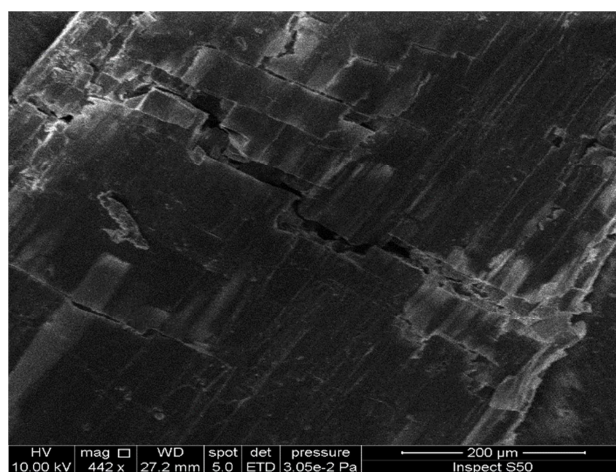


Figure 2. SEM micrograph of Raw wheat straw RWS.

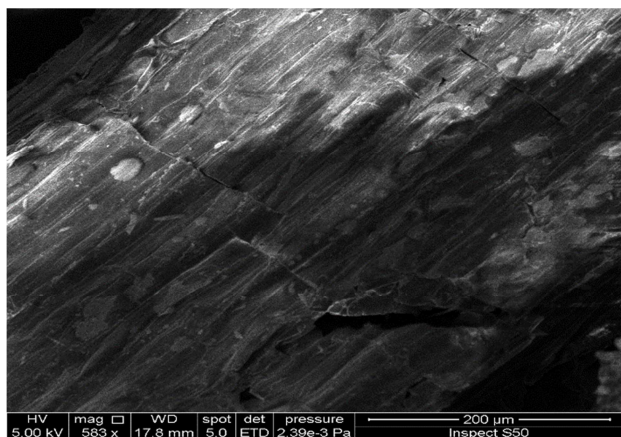


Figure 3. SEM micrograph of Modified wheat straw MWS.

4.3. Adsorption Kinetics

The study of adsorption kinetics illustrates how the solute uptake rate and obviously this rate control the residence time of the adsorbate at the solution interface. This rate is most important when designing the adsorption system and this rate can be calculated from kinetic study [14]. Figure 4 shows the application of Pseudo-first order with high fit, figure 5 illustrates Pseudo-second order with best fit of (0.999) which refers to the chemisorption kinetics [15]. Intra-particle diffusion model shown in figure 6, the fast uptake at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the sorbent and the following

slower sorption to intra-particle diffusion [16]. For intra-particle diffusion plots, the first, sharper region is the instantaneous adsorption or external surface adsorption, the value of K_p gives an indication about the boundary layer thickness as shown in table 1. The second region is the gradual adsorption stage where intra-particle diffusion [17]. The intra-particle diffusion plots for adsorption of reactive yellow were linear but did not pass through the origin, indicated that the intra-particle diffusion is not the rate limiting step of the studied adsorption process [10]. Figure 4 shows the application of Pseudo-first order with high fit, figure 5 illustrates Pseudo-second order with best fit of (0.999) which refers to the chemisorption kinetics [15]. Intra-particle diffusion model shown in figure 6, the fast uptake at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the sorbent and the following slower sorption to intra-particle diffusion [16]. For intra-particle diffusion plots, the first, sharper region is the instantaneous adsorption or external surface adsorption, the value of K_p gives an indication about the boundary layer thickness as shown in table 1. The second region is the gradual adsorption stage where intra-particle diffusion [17]. The intra-particle diffusion plots for adsorption of reactive yellow were linear but did not pass through the origin, indicated that the intra-particle diffusion is not the rate limiting step of the studied adsorption process [10].

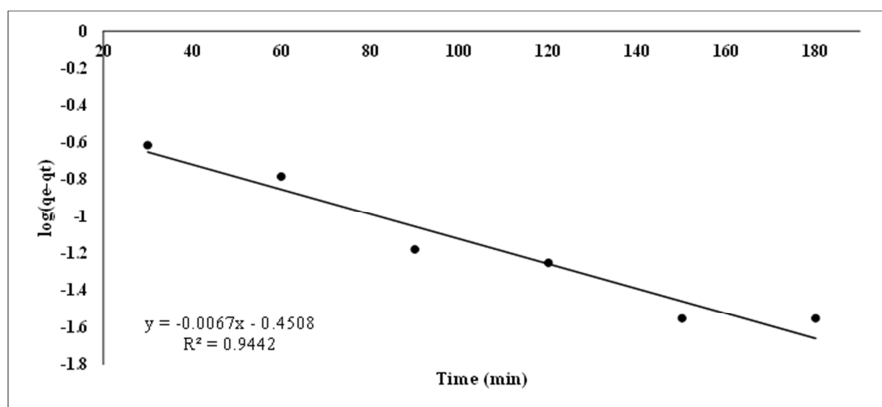


Figure 4. Pseudo-first order model of reactive yellow using modified wheat straw.

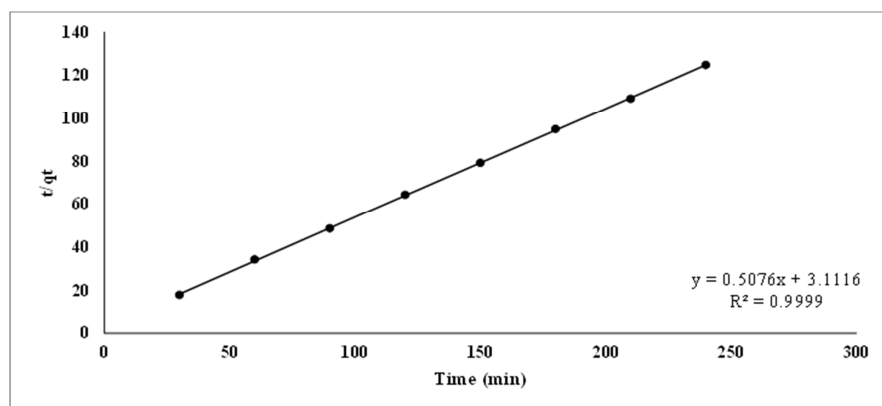


Figure 5. Pseudo-second order model of reactive yellow using modified wheat straw.

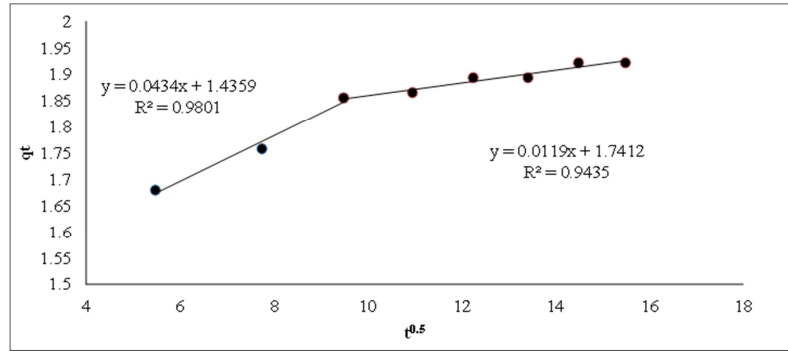


Figure 6. Intra-particle diffusion model of reactive yellow using modified wheat straw.

4.4. Adsorption Isotherm

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent. Distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir and Freundlich [18]. Figures 7, 8 and 9 show the adsorption isotherm models using Langmuir, Freundlich and BET, figures 7 and 8 show a

good fit using both Langmuir and Freundlich models which indicates that the adsorption is chemical and forming only monolayer on the surface. BET model application shows poor fitting with the adsorption process, referring that the BET model is not applicable as shown in figure 9. Table 2 illustrates the parameters and the separation factor of three models with reactive yellow dye using modified wheat straw.

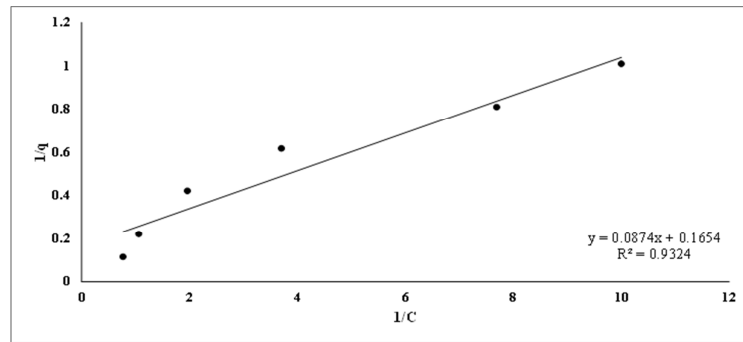


Figure 7. Langmuir isotherm model for reactive yellow using modified wheat straw.

Table 1. Kinetic models parameters of Reactive Yellow.

	q_{exp} (mg/g)	Pseudo first order			Pseudo second order			Intra-particle diffusion		
		q_{cal} (mg/g)	$K_1 \cdot 10^5$ (1/s)	R^2	q_{cal} (mg/g)	$K_2 \cdot 10^5$ (mg/g.s)	R^2	C (mg/g)	$K_P \cdot 10^4$ (mg/g.s ^{0.5})	R^2
MWS	1.92	0.354	25.7	0.944	1.97	13.8	0.999	1.584	3.95	0.898

Table 2. Isotherm models parameters of Reactive Yellow.

	Langmuir				Freundlich			BET		
	q_m (mg/g)	K_L (L/mg)	R_L	R^2	n	K_F	R^2	q_m (mg/g)	K_B	R^2
MWS	6.04	1.89	0.05	0.932	1.3	5.22	0.932	12.41	6.15	0.348

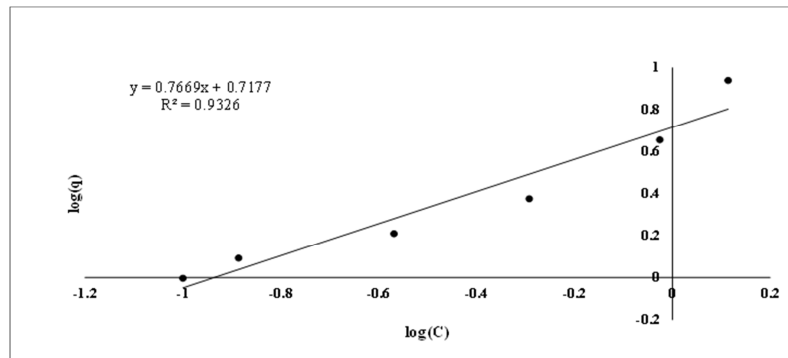


Figure 8. Freundlich isotherm model for reactive yellow using modified wheat straw.

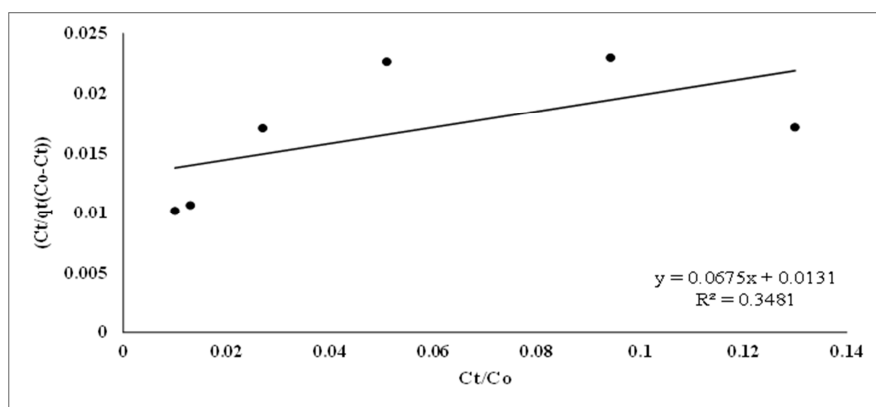


Figure 9. BET isotherm model for reactive yellow using modified wheat straw.

5. Conclusion

From the above studies it can be shown that modified wheat straw is a good adsorbent for a soluble reactive yellow dye and the adsorption process is a chemical adsorption on the surface of the adsorbent and follows the Langmuir and Freundlich isotherm models. The kinetics studies showed that the data are best fitted with the pseudo-second order model and well fitted with the intra-particle diffusion model and there are two adsorption mechanism controlling the adsorption process; the first on the surface and the second on the pores of the adsorbent as shown in the intra-particle diffusion model. Another isotherm models could be used to study the possibility of mono or multi-layer adsorption such as Elovich, Temkin and Anderson.

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