

Adsorption of Reactive Blue Dye onto Natural and Modified Wheat Straw

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Abstract

Conventional treatment of textile wastewater such as biological treatment discharges will no longer be tolerated and identified as non-biodegradable. Advanced processes such as adsorption and advanced oxidation hold great promise to provide alternative for better treatment and protection of environment. In this study, adsorption process is carried out for both batch (kinetic and isotherm) studies using natural wheat straw (NWS) as low cost adsorbent, modified wheat straw (MWS) and Activated Carbon (AC) for comparing the results. Batch adsorption experiments were conducted on a shaker at 200 rpm, room temperature using 250 mL conical flasks contains 100 mL of dye solution to study the effects of adsorption conditions. The effect of pH was determined by adjusting pH values (2.5-10.5). To study the effect of initial dye concentration, six different concentrations of reactive blue dye (5, 20, 30, 50, 70 and 90) mg/L were prepared and used. Results showed that the removal percent using NWS, MWS and AC are; 68%, 92.17% and 90.5% respectively. Equilibrium isotherm experiment were carried at different dosages (0.1 – 1 g) to predict the isotherm model; Langmuir, Freundlich and BET. The experimental data showed that reactive blue is fitted with Freundlich isotherm ($1/n=1.25, 0.67$) for both (NWS) and (MWS) respectively, and for (AC) is fitted with Langmuir isotherm. Three kinetic models, were selected to fit the kinetic data; pseudo first, second order and intra-particle diffusion, reactive blue is fitted with intra-particle diffusion model with (NWS) and (MWS), and Pseudo second order for (AC).

Keywords: Adsorption; Modified wheat straw; Reactive blue dye

Introduction

The textile industry consumes a substantial amount of water in its manufacturing processes used mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition. In addition, the increased demand for textile products and the proportional increase in their production, and the use of synthetic dyes have together contributed to dye wastewater becoming one of the substantial sources of severe pollution problems in current times [1]. Dye wastewater usually consists of a number of contaminants, including acids, bases, dissolved solids, toxic compounds, and color. Color is the most noticeable contaminant even at very low concentrations, and it needs to be removed or decolorized before the wastewater can be discharged [2]. Reactive dyes which are usually characterized by azo-aromatic groups which are of extreme environmental concern due to their carcinogenic, mutagenic, and inert properties. The complex aromatic structures of the dyes result in physicochemical, thermal and optical stability and resistance to conventional wastewater treatment [3]. Various methods for dye removal were divided to three categories, which biological, physical and chemical methods such as oxidation, electrochemical destruction, adsorption by activated carbon, ion exchange, membrane filtration and coagulation [4]. Among the previous water treatment techniques, adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants, also does not result in the formation of harmful substances [5]. Since activated carbon is an expensive adsorbent, many researchers have been studied about the feasibility of using inexpensive alternative low cost adsorbents from agricultural by-product. Juang used Bagasse as a low cost biosorbent with basic red 22, Soldatkina showed that barley straw used in removing anionic acid red and cationic methylene blue from their aqueous solutions. Fiorentin used orange bagasse as an alternative adsorbent for removal of reactive blue 5G at pH=2. Robinson used low-cost, locally available, renewable biosorbents; apple pomace the results showed that 81% of dyes were removed from the synthetic effluent. Singh

2011 used Sawdust is a by-product of saw mills for removing acid dye (Orange G) from aqueous solutions. Agricultural wastes are renewable, available in large amounts and are less expensive as compared to other materials used as adsorbents. Agricultural wastes are better than other adsorbents because agricultural waste is usually used without or with a minimum of processing (washing, drying, grinding) and, thus, reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment [6]. The aim of this study is the removal of Reactive Blue dye (H_3R) that used in Al-Hilla textile factory (Iraq), using locally available low-cost adsorbent natural wheat straw (NWS), modified wheat straw (MWS) with cationic surfactant and comparing the performance of (NWS) and (MWS) with Activated carbon (AC) in decolorizing.

Mathematical Models

Adsorption isotherm

An adsorption isotherm is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium. It maps the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations [7]. Adsorption isotherms are important to describe the interaction of adsorbate molecules with adsorbent surface [8]. In this study, Langmuir, Freundlich and BET models were employed for the treatment of the

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Received November 12, 2015; Accepted November 20, 2015; Published November 25, 2015

Citation: Mousa KM, Taha AH (2015) Adsorption of Reactive Blue Dye onto Natural and Modified Wheat Straw. J Chem Eng Process Technol 6: 260. doi:10.4172/2157-7048.1000260

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equilibrium adsorption data. The applicability of the isotherm equation is compared by judging the correlation coefficients R^2 .

Langmuir Model

The Langmuir isotherm assumes adsorption is reversible and occurs only for the

monolayer on the adsorbent surface.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \dots \quad (\text{Eq. 1})$$

Where K_L (L/mg) is a constant and C_e is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed per gram of adsorbent (mg/g) at equilibrium concentration C_e , and q_m is the maximum amount of solute adsorbed per gram of sorbent (mg/g), which depends on the number of adsorption sites [9].

Freundlich Model

The Freundlich equation is one of the well-known models applicable for a single solute system. It is an empirical equation used to describe the distribution of solute between solid and aqueous phases at a point of saturation.

$$q_e = K_F C_e^{1/n} \dots \quad (\text{Eq. 2})$$

Where K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and $1/n$ are Freundlich constants depending on the temperature and the given adsorbent-adsorbate couple. The parameter n is related to the adsorption energy distribution, and K_F indicates the adsorption capacity (Madrakian et al.) [10].

BET Model

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.

$$q_e = \frac{q_m K_b C_o C_e}{(C_o - C_e)[C_o + C_e(K_b - 1)]} \dots \quad (\text{Eq. 3})$$

Where q_e and C_e as above C_o initial concentration of adsorbate mg/L. q_m maximum adsorption capacity in forming complete monolayer on the surface mg/g. and K_b is a constant relating to the energy of interaction with the surface (L/mg).

Adsorption kinetics

Study of adsorption kinetics is desirable because it provides information regarding the mechanisms of adsorption that is important for the efficiency of the process. Adsorption is a time dependent process. During removing contaminants from wastewater, it is important to know the rate of adsorption to optimize the design parameters [11].

In order to optimize the design of an adsorption to remove the dye, it is important to establish the most appropriate correlations for the equilibrium data for each system. Three kinetic models were applied for the experimental data, Pseudo first order, and second order and Intra-particle diffusion.

Pseudo First Order model

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \dots \quad (\text{Eq. 4})$$

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

Pseudo second order

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \dots \quad (\text{Eq. 5})$$

K_2 is the second order constant (g.min/mg).

Intra-particle diffusion

$$q_t = K_p t^{1/2} + C \dots \quad (\text{Eq. 6})$$

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 intra-particle diffusion rate constant ($\text{mg/g.s}^{1/2}$).

Experimental Work and Materials

Batch adsorption studies are performed to obtain the key parameters such as isotherm constants and pore diffusivity [12].

Adsorbents

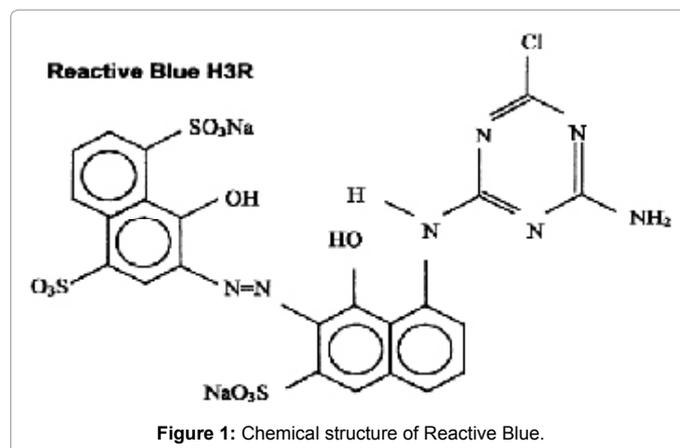
Three adsorbents are used Natural wheat straw (NWS) as a low-cost adsorbent, modified wheat straw (MWS) and Activated carbon (AC). Wheat straw is collected from countryside, washed with tap water several times to remove dust and unwanted parts, then washed with distilled water and dried at 70°C for 24 hr. the dried wheat straw then sieved to the desired size particle (1 mm), stored in a glass container and named (NWS). 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 before use, then stored and named (MWS) [3].

Adsorbate

Reactive Blue dyes with molecular weight (562) g/mol and wavelength (585 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 concentrations, Figure 1 shows the chemical structure of Reactive Blue [13].

Batch experiments

Batch adsorption experiments were conducted on a shaker at 200 rpm, room temperature using 250 mL conical flasks contains 100 mL of dye solution to study the effects of adsorption conditions. The effect of pH was determined by adjusting pH values (2.5 – 10.5). To study the effect



of initial dye concentration, six different concentrations of reactive blue dye (5, 20, 30, 50, 70 and 90) mg/L were prepared and used. The effect of adsorbent was carried out using amounts of adsorbents ranging (0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) g. After the biosorption process, the solution was centrifuged for 10 min at 8000 rpm and supernatants were analyzed for remaining dye concentration using a spectrophotometer (Shimadzu UV-1800) at each dye wavelength.

Results and Discussion

FTIR analysis and SEM

Fourier transform infrared spectroscopy (FTIR) was useful to examine the surface groups of the adsorbents and to identify some characteristic functional groups [14].

Figure 2 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 refer 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 [14-16]. The physical morphologies and surface properties of the Natural and Modified Wheat straw were examined by using scanning electron microscopy technique SEM. From Figures 3 and 4 it can be concluded that SEM images of NWS and MWS showed severe differences, surface of MWS contained more pores than NWS surface and this results in higher surface area.

Equilibrium experiments

pH effect: Reactive dyes are known to ionize to a high degree in aqueous solutions to form colored anions due to the sulfonate group(s) present in their structure [17]. Figure 5 shows the removal percentage of reactive blue dye. The removal percent was 68% using NWS, while the removal was 92.17% and 90.5% using MWS and AC respectively at pH=6.5. The increase in pH increases OH⁻ ions results in a competition with dye anions for biosorption sites, leading to a decrease in dye removal in the case of (NWS) and (AC) which is considered as positively-negatively charged adsorbent. As pH decreases, the number of positively charged sites on the adsorbent surface increases; therefore, dye removal also decreases due to the electrostatic repulsive force between positively charged dyes and positively charged adsorbent surface in the case of (MWS) [18].

Dosage effect: Adsorbent dose is an important parameter that strongly influences the adsorption process by affecting the adsorption

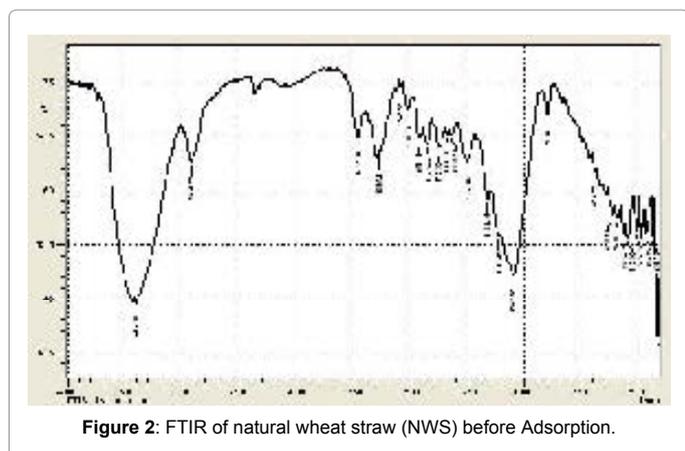


Figure 2: FTIR of natural wheat straw (NWS) before Adsorption.

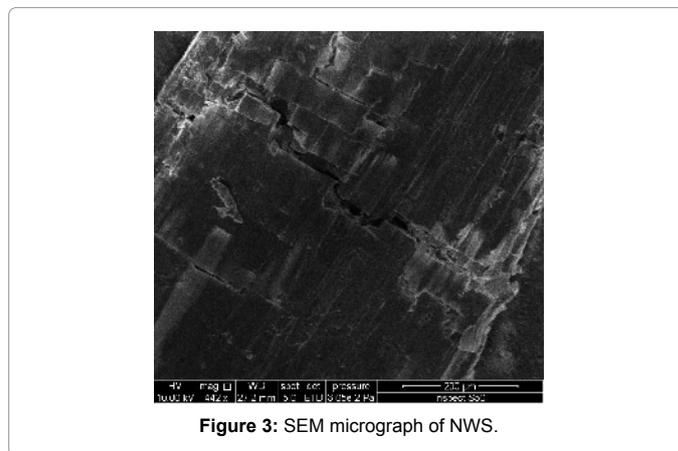


Figure 3: SEM micrograph of NWS.

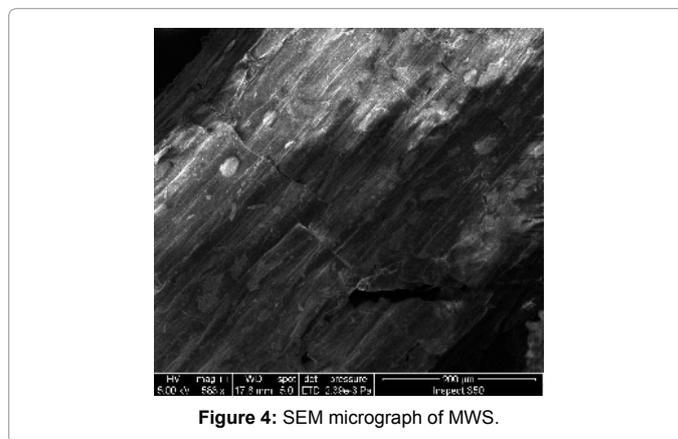


Figure 4: SEM micrograph of MWS.

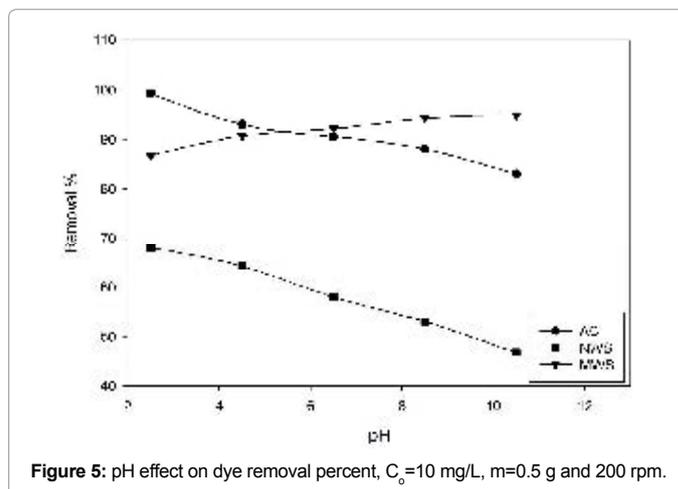


Figure 5: pH effect on dye removal percent, $C_0=10\text{ mg/L}$, $m=0.5\text{ g}$ and 200 rpm .

capacity of the adsorbent [16]. Results showed that the sorption capacity is decreases with increasing adsorbent amount at constant dye concentration and volume as shown in Figure 6, that may be attributed to saturation of adsorption sites on adsorbent surface due to particulate interaction such as aggregation, aggregation would lead to a decrease in total surface area of the adsorbent [14].

Initial concentration: The initial dye concentration provides an important driving force to overcome resistant encountered when molecules are transferred between aqueous and solid phases [19]. Figure 7 shows that the capacity of the adsorbent material gets

exhausted with increase in initial dye concentration; this may be probably as a result of the fact that for a fixed adsorbent dose, the total available adsorption sites remain invariable for all the concentrations checked. With increasing concentration, the available adsorption sites become fewer and hence the percent removal of dye is dependent upon the initial concentration [20].

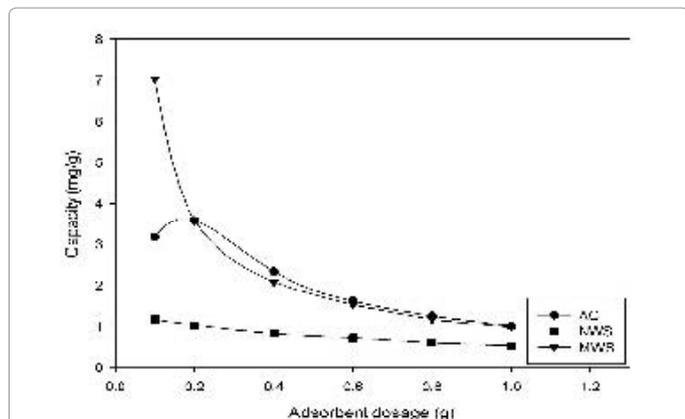


Figure 6: Effect of dosage on adsorption dosage, $C_0=10$ mg/L, pH = 6.8 and 200 rpm.

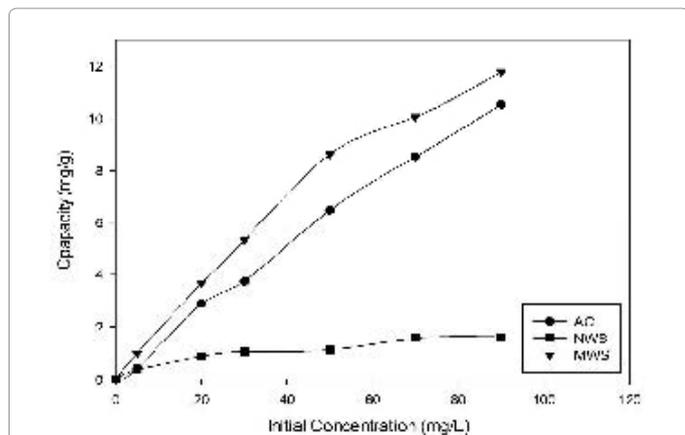


Figure 7: Initial concentration effect on adsorption capacity, pH = 6.8, m=0.5 g, 200 rpm.

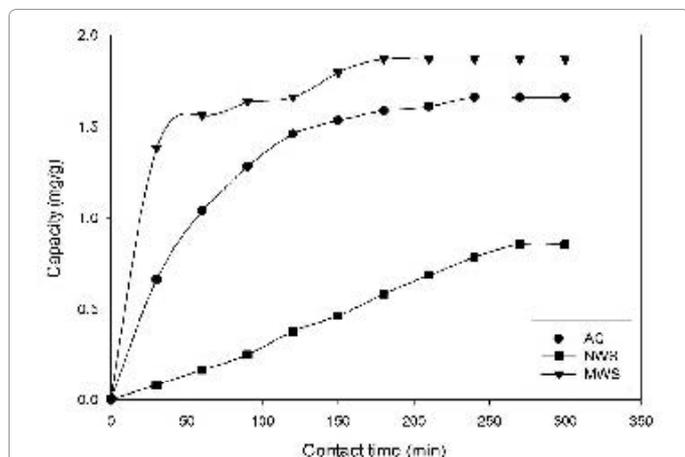


Figure 8: Contact time effect, $C_0=10$ mg/L, m=0.5 g, pH=6.8, 200 rpm.

Contact Time: Figure 8 shows that the dye concentration reduced from an initial value to an equilibrium value provided the contact time is sufficient. According to results, 300 min was obtained as equilibrium contact time for NWS which is longer than the equilibrium time of both MWS and AC. at this time, therefore, 300 min of contact time was chosen as the adsorption time for further experiments to ensure that the equilibrium was achieved, due to saturation of absorption sites on adsorbent; dye removal efficiency will not have any changes [21,22].

Kinetics study

The controlling mechanisms of adsorption process such as chemical reaction, diffusion control or mass transfer coefficient are used to determine kinetic models using Equations (2.4, 2.5 and 2.6). The kinetics of dye adsorption onto adsorbent materials is prerequisite for choosing the best operating conditions for the full-scale batch process. 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 [23]. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model as shown in Tables 1 and 2 [24]. Figure 9 shows the intra-particle model regression, the first stage is the external surface adsorption or instantaneous adsorption stage which is less apparent or absent than because the completion of this stage before 8 min. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate-controlled. The third portion is final equilibrium stage where the intra-particle diffusion starts to slow down due to extremely low solute concentrations in the solution [25]. The intercept of stage kp , gives an idea about the thickness of boundary layer, i.e., the larger the intercept, the greater the boundary layer effect. The fact that the plots did not pass through the origin indicated that although intra-particle diffusion was involved in the dye adsorption process, it was not the only rate control step [26].

Isotherm study

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 [25]. Figures 10 and 11 shows the Freundlich isotherm for AC, NWS and MWS respectively. The Freundlich equation yielded the

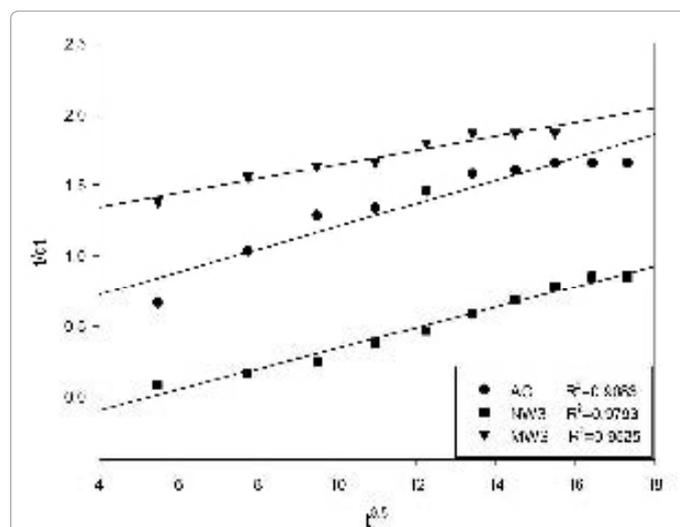


Figure 9: Intra-particle diffusion, reactive blue for AC, NWS and MWS.

Adsorbent	q_{exp}	Pseudo 1 st order			Pseudo 2 nd 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
NWS	0.852	1.14	10.34	0.9402	5.83	0.135	0.3509	0.3888	12.15	0.9793
MWS	0.67	0.771	23.4	0.8912	2	46.9	0.9374	1.147	8.3	0.9535
AC	1.66	1.3	14.9	0.9873	2.01	14.7	0.9971	0.3968	13.5	0.9083

Table 1: Kinetics parameters.

Adsorbent	Langmuir			Freundlich			BET		
	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F	R^2	q_m (mg/g)	K_B	R^2
NWS	3.2	0.03	0.9919	0.8	0.08	0.9944	0.2	1.72	0.8537
MWS	4.22	1.44	0.8859	1.49	2.5	0.9218	5.69	6.18	0.6613
AC	3.7	2.35	0.9742	4.2	2.34	0.8082	1.0	32.3	0.9372

Table 2: Adsorption isotherm models.

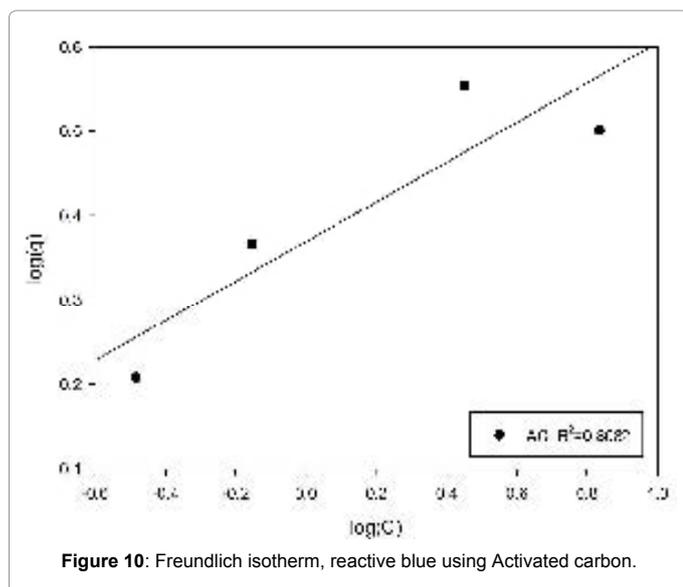


Figure 10: Freundlich isotherm, reactive blue using Activated carbon.

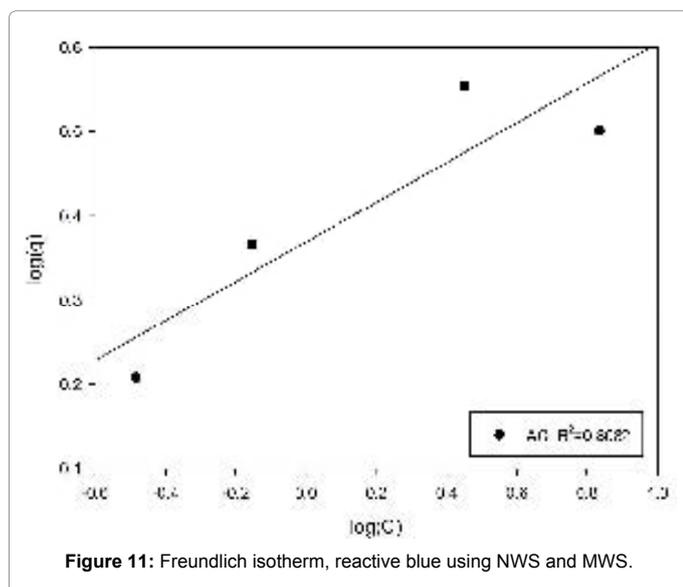


Figure 11: Freundlich isotherm, reactive blue using NWS and MWS.

best fit to the experimental data in comparison to the other equations in this study. The Freundlich equation is suitable for homogeneous and heterogeneous surfaces, indicating a multi-layer adsorption. The magnitude of the Freundlich constant n gives a measure of favorability of adsorption. Values of $n > 1$ represent a favorable adsorption process [16].

Conclusion

The following conclusions may be drawn from the present investigation:

1. A surfactant modified wheat straw MWS produces a good adsorption for reactive blue dye and remove the dye at a faster rate compared to NWS.
2. MWS and AC had a greater capacity to adsorb reactive blue 11.79 mg/g and 10.53 mg/g respectively, and 1.63 mg/g for NWS at the experimental conditions.
3. NWS and AC shows higher removal percent at lower pH values, whereas MWS shows higher removal percent at higher pH values.
4. Kinetic process is well fitted with intra-particle diffusion using NWS and MWS are fitted with Pseudo first order using AC
5. Adsorption isotherm experiments is fitted with Freundlich isotherm model using both NWS and MWS, while Langmuir isotherm model is fitted with AC.

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