Efficiency of Reactive Black 5 dye removals and determination of Isotherm Models in aqueous solution by use of activated carbon made of walnut wood

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Abstract
Industrial textile colors and other industrial dying materials are one of the important organic materials that increase environmental impacts. There-fore, it is necessary to treat those effluents prior to discharge into environment. Various parameters including initial concentration of dye, effect of mass of adsorbent on color removal and pH were surveyed. For determina-tion of residual concentration of dye, a spectrometry set UV/VIS Lambda 25.UV/VIS (Perkin Elmer) at 599 wavelengths was used. Various parameters including initial concentration of dye, effect of mass of adsorbent on color removal and pH were surveyed. Results indicated that removal of Rea-ctive Black5 dye depend on Langmuir (R2>0.96), respectively. In the study kf was 1.47 and amount of adsorbed reactive black5 was qm(mg/g)=14.08 for mass unit of activated carbon. In general, the results of study showed that activated carbon made of walnut wood can be used as an effective adsorbent for the removal of Azo dyes.

Keywords: Isotherm, Aqueous solution, Active Carbon, Reactive Black 5.

Introduction
One of the oldest reactive dyes is Reactive Black 5 which is used widely in textile industries. Synthetic dyes are one of the major problems in environment because these kinds of dyes due to decomposition may convert in to toxic products. Industrial dyes are one of the main organic components that can increase environmental hazardous[1-3]. Around 1 to 20 percent of total world dye products is wasted in painting process and enters to textile wastewater streams. These colourful materials have diverse structures such as acidic, alkaline, reactive, disperse, azo, diazo, anthraquinone-based and metal complex dyes[4-5]. Most of the dyes which are used in these industries are synthetic dyes. Synthetic dyes are divided to different groups such as acidic, reactive, direct, alkaline dyes and others groups[2, 6]. Various painting dyes which are used in industries are usually azo groups.

Azo dyes are one of the largest groups of synthetic dyes which have one or more Azo bands –N-N- [3, 7.] Azo dyes often can be identified by one or some Azo bands (–N-N-) in their structures and they are used in textile, leather and food industries[8]. Painting materials often have one or more benzene circles. Due to their toxicity and resistance, they can cause irreparable damages to environment[9-11]. Various treatment process including Biological methods[1,12], Membrane process[13-14], Advanced Oxidation process[15] have been used for treatment of such effluents. Adsorption process is one of the procedures in water and wastewater treatment. The adsorption process is usually done on Activated Carbon (AC). Commercial AC is typically expensive and requires expert operators to make use of it. These days researchers utilize different natural adsorbents such as chitosan[3] oxihumolite[16] ash[12,17] TiO_2 nanopar-ticles[18] and other adsorbents for removing diverse organic and inorganic pollutants.

In this investigation, the efficiency of Activated Carbon made of walnut wood as adsorbent in adsorption of Reactive Black5 dye has been evaluated. Duo to AC structure and its proper porosity and density, it can be used as a good adsorbent for removing disturbing factors such as dye from water and wastewater. In this study the Reactive Black 5 was selected as indicator of azo group. Reactive Black 5's chemical structure is shown in figure 1. As shown in figure 1, the Reactive Black 5 has two sulfonate groups and two sulfatoethylsulfon groups in its molecular structure[12].

Materials and Methods
All chemicals used were obtained from Merck, Germany and were used without purification. In this investigation, the walnut wood was used to prepare the walnut wood adsorbent. At first the woods were cut in to 0.5 cm pieces and then were soaked with acid phosphoric which acts as an activator matter. After that the soaked woods were put in uncovered jugs and the jugs were closed by pottery mud and only one small hole was left for vapor withdrawal. Then the jugs were placed in furnace for 2 hours at 900 ^{0}C. After bring jugs out of furnace, the activated carbon was taken out and washed by Deionized water and placed in oven to get dry. Finally the AC was grinded by mortar and separated by 30 mesh sieve and was ready for utilization. Various parameters including initial concentration of dye, pH, contact time and effect of initial mass of adsorbent were surveyed in this study.

The used dye was provided from Alvan Sabet Company with 99 percent purity. All dye concentrations were determined with a spectrometry set UV/VIS Lambda 25.UV/VI (PerkinElmer) according to maximum wave length (λ_{max}). The maximum wave length (λ_{max}) was at 599 nanometer for Reactive Black 5. To adjust the samples pH (Sartorius PP-50), a normal solution of NaOH or H_2SO_4 was used. The experiments were done in batch system and in beakers with 500 ml volume. To examine the effect of initial concentration of dye on removing Reactive Black 5 by AC made of walnut, the stock solution with 100 mg/l concentration in 1 liter volume was prepared. 10, 20, 40, 60 and 80mg/l of dye solutions were made by dilution of the stock solution (Deionized water was used for dilution). 250 cc of each above concentration were poured in to 500 cc flask and then 0.8g AC made of walnut was added to flask and pH was adjusted on 3.

Due to mixing, the samples were placed on agitator and sampling was done after 400 minutes. At all experiments, the agitator was fixed on 160 rpm. The effect of adsorbent dosage on dye removal to extract the adsor-ption isotherms, the equilibrium time was obtained through initial syntactic testing and then the equilibrium adsorption tests were done. The data obtained from equilibrium ex-periments are known as adsorption isotherms. These data are considered as basic data for the adsorption systems design. For this purpose, the classical adsorption models which are Langmuir and Freundlich were used. These mod-els indicate the concentration of adsorbent’s equilibrium relationships between adsorbent and solution.

The adsorption isotherm and capacity were determined. The following equation was utilized to determine the adsorption capacity[13, 19].

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

In this equation C_0 and C_e are initial and final concentration of dye solutions (mg/l), V is the volume of solution (L) and m is mass of adsorbent (g). To determine the isotherm models, 0.6g of adsorbent was added in to dye solutions (10, 20, 30, 40, 50 and 60mg/l). It must be mentioned that the solution's pH was adjusted at 7. These solutions were placed on agitator for 2 days with 160 rpm and then the samples were filtered. The adsorption isotherms are equations to describe equilibrium of sorbent between liquid and solid phase. In this study the experimental adsorption equi-librium data were surveyed by Langmuir and Freundlich isotherm models. The Langmuir isotherm equation is as follows:

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} c_e \tag{2}$$

where q_e is the amount of adsorbed adsorbate per adsorbent mass unit (mg/g), C_e is the equilibrium concentration of adsorbate in the solution after adsorption (mg/l), q_m indicates adsorption capacity and b shows Langmuir constant. One of the Langmuir equation characteristic is the dimensionless parameter of the separation factor (R_L) which is calculated as follows:

$$R_L = \frac{1}{(1 + bC_0)} \tag{3}$$

By utilizing this parameter, the type of adsorption process can be identified[9]. Freundlich isotherm equation (4) is as follows:

$$\log q_e = \log K_f + \frac{1}{n}(\log C_e) \tag{4}$$

where C_e is equilibrium concentration (mg/l), q_e is the equilibrium adsorption capacity (mg/l) and K and n are Freundlich constants which are obtained by plotting log q_e versus log Ce[20].

Results and Discussion

Effect of initial dye concentration: The results of initial dye concentrations 10, 20, 40, 60 and 80 mg/l at pH= 3 with 0.8g adsorbent dosage were shown in figure 2. By increasing initial dye concentration from 10mg/l to 80mg/l, the dye removal efficiency was decreased. According to figure 2, the Reactive Black 5 removal efficiency in initial con-centrations of 10, 20, 40, 60 and 80mg/l was respectively determined as 80, 79.55, 62, 52.7 and 51.68 percent. It could be said that Reactive Black 5 removal efficiency descents increasingly by increasing initial conce-ntration of dye from 10mg/l to 80mg/l. So by increasing initial concentration from 80mg/l, the removal efficiency is almost constant. According to figure 2, dye removal efficiency decreases with increasing initial concentration. Wang et al [17,23] found out that the adsorption of alkaline dyes on Zeolite MCM-22 reduces by rising initial dye concentration.

Effect of pH: To survey the effect of pH, dye solutions with 50mg/l concentration at different pH (3, 5, 7, 9 and 11) were prepared. Then 0.6 AC was added in to 150cc dye solution (50mg/l) and after 400 minute of contact time, the remaining dye concentration was determined through spec-trophotometer. The results were shown in figure 3. The Reactive Black 5 removal effi-ciency at this pH 5, 3, 7, 9 and 11 were 80.64, 71, 51.86, 46 and 38.5 percent respectively. The reason of increasing removal dye efficiency at low pH could be explained by increase in H^+ ion and OH^- ion reduction in aquatic environment and raise of positive ions quantity on adsorbent surface[25]. In this work the used dye in aquatic solution will get negative charge, therefore the removal efficiency at low pH increases because at low pH the surface of AC will got positive charge[19]. Janos et al[16,19] worked on removing anionic and cationic dyes on ash. They found out the cationic dye removal increases with rising pH, however by pH reduction the ionic dyes removal increases.

Effect of adsorbent mass: In table 1 the calculated parameters from isotherm equations are shown. R^2 values of Freundlich and Langmuir isotherms for dye adsorption are respectively 0.922 and 0.908. By noticing these R^2 values it could be said that Reactive Black 5 adsorption follows Freundlich isotherm. The values of Freundlich and Langmuir isotherms parameters are given in table 1. Also in case of Freundlich isotherm the value of n is a scale of adsorption intensity. If this value is between 1 to 10, the isotherm function is mathematically desirable[9]. Also it was found out the Reactive Black 5 has great adhesion. According to table 1, the n value obtained from Reactive Black 5 adsorption by AC is equal to 1.64. Therefore the Freundlich isotherm model is mathematically ideal.

Moreover in this study as in table 1, the amount of Reactive Black 5 adsorbed per AC mass unite is equal to q_m(mg/g)=14.08 mg/g. The results showed Reactive Black 5 adsorption follows Freundlich isotherm model (R^2=0.922). Elwakeel[15] removed Reactive Black 5 by two types of chitosan resins. He found out K_f for the first and second type of chitosan respectively 0.8 and 1.6[15]. According to table 1, the K_f value in present study is obtained 1.47. This showed the Adhesion of AC made of walnut for Reactive Black 5 adsorption is more than the first type of chitosan. In addition the maximum adsorption values for first and second type of chitosan were respectively 0.7 and 0.8mg/g[15]. As seen in table 1, the maximum adsorption value in present study is 14.08mg/g. The relation between R_L and adsorption could be determined according to the studies which had been done. Based on equation 3, the R_L value for Reactive Black 5 adsorption on AC is calculated 0.15. This amount indicates a desirable adsorption of Reactive Black 5 on this adsorbent[12, 27].

Conclusion

In general, the results of this study showed that activated carbon made of walnut wood can be used as an effective adsorbent for the removal of azo dyes from industrial effluents.

Acknowledgement

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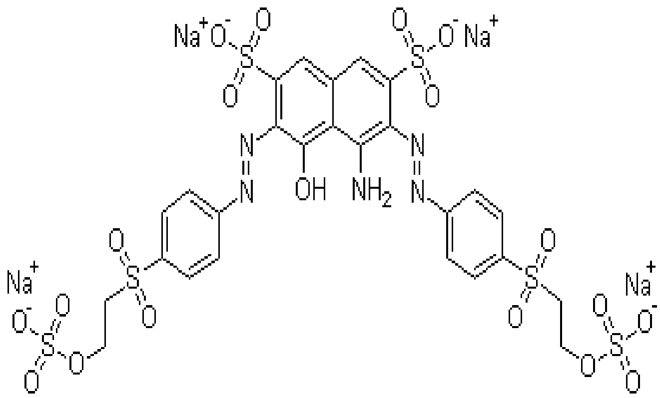

Figure 1: Chemical srtucture of RB5

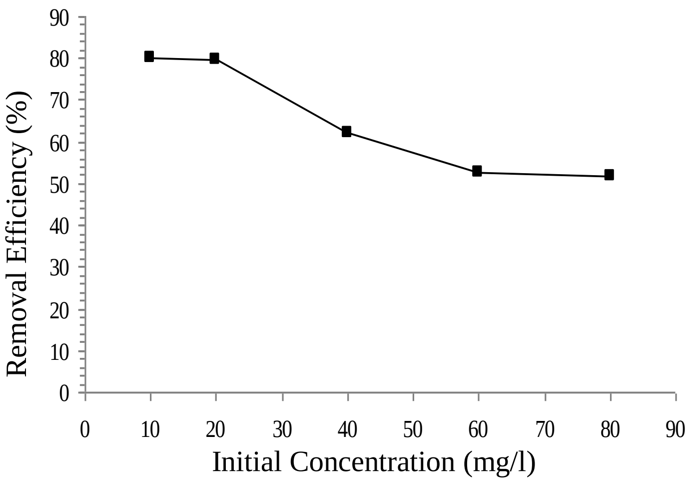

Figure 2: The impact of dye initial concentration on Reactive Black 5 removal efficiency (in presence of 0.8 g AC adsorbent in 250 cc sample at pH=3)

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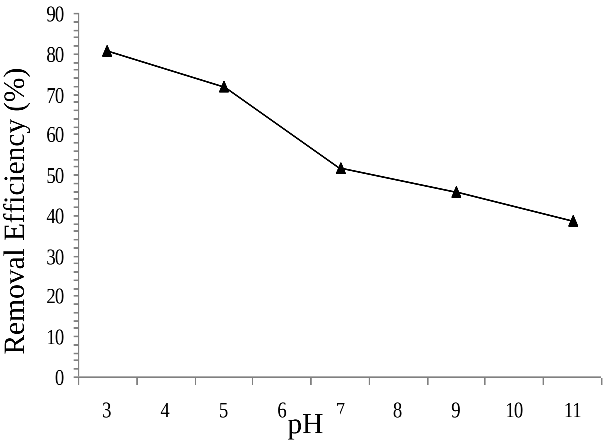

Figure 3: Impact of pH on removal efficiency of Reactive Black 5 (in presence of 0.8 g AC in 250cc sample with 50 mg/l dye concentration)

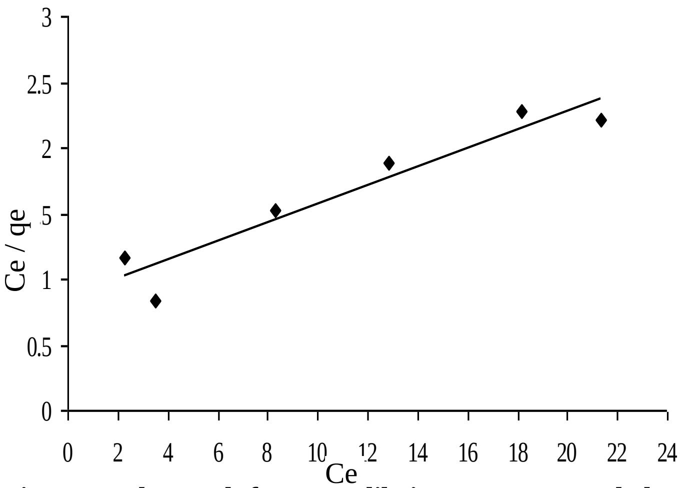

Figure 4: The result from equilibrium constant study by Langmuir model

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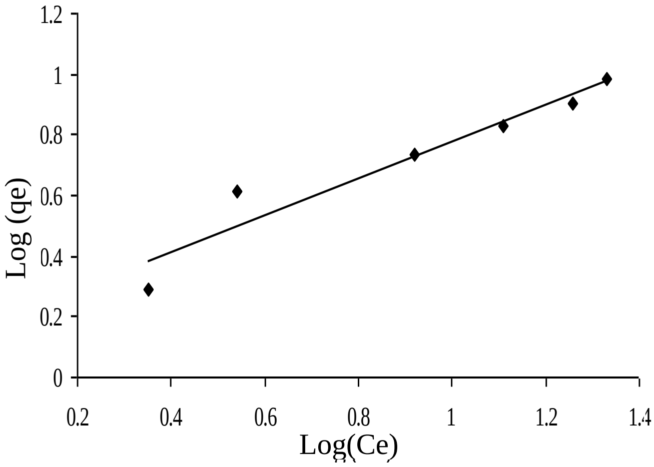

Figure 5: The result from equilibrium constant study by Freundlich model

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Table 1
Calculated parameters for isotherm models

Models	**Langmuir**			**Freundlich**		
Parameters	q_m(mg/g)	b(L/mg)	R^2	K_f	n	R^2
Values	14.08	1.15	0.908	1.47	1.641	0.922

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