

Removal of Dyes from Wastewater of Textile Industries Using Activated Carbon and Activated Alumina

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Abstract

This work was carried to study the capability of activated alumina from bauxite compared with activated carbon adsorption capability to reduce the color content from Al-Hilla Textile Company wastewater. Six dyes were studied from two types (reactive and dispersed) namely (blue, red, yellow) from wastewater and aqueous solutions.

Forty eight experiments were carried out to study the effect of various initial conditions (bed height, flow rate, initial concentration, pH value, temperature, and competitive adsorption) on adsorption process.

The results showed that the adsorption process using activated carbon insured a good degree of color reduction reaching (99.7%) and was better than activated bauxite which reached (95%).

Introduction

Wastewater from the textile industry can contain a variety of polluting substances including dyes. The pollution problem is different for the various types of fibers (1). Color is the first contaminant to be recognized in the wastewater and has to be removed before discharging into water bodies or on land. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and affects the aesthetic merit, water transparency and gas solubility in lakes, rivers and other water bodies. The removal of color from water is often more important than the removal of the soluble colorless organic substances, which usually contribute the major fraction of the biochemical oxygen demand (BOD). Dyes, however, are more difficult to treat because of their synthetic origin and mainly complex aromatic molecular structures (2). Sorption has been involved into one of the most effective physical processes for decolorization of textile wastewaters. The most commonly used adsorbent for color removal is activated carbon, because of its capability for efficiently adsorbing a broad range of different types of adsorbates. However, its use is limited because of its high cost. Several researchers have been

studying the use of alternative materials: agricultural, forest, animal and several low cost industrial by products such as peat, wood, tree barks, chitin, silica gel, bauxite, bentonite clay, certain synthetic adsorbents, etc. (3) Activated carbon adsorption systems though widely used are very expensive and the regeneration cost is also very high. Therefore, their use in wastewater treatment may be economically not feasible. There is, therefore, a need to identify and study the adsorptive characteristics of low cost alternatives. (4)

The use of non-conventional adsorbents, particularly those that can be easily regenerated, to replace activated carbon in the removal of color from dye wastewater has been recently proposed. (5)

Textile wastewaters are usually complex. The composition is very variable and can change quickly. Wastewaters from dyeing and subsequent rising steps are one of the largest contributions to wastewater generation in the textile industry. (6)

In the fixed bed adsorption operation, the waste water to be treated is passed through a stationary bed of adsorbent. A fixed bed adsorber offers the advantage of simple operation plus the ability to serve as a filter for simultaneous suspended solids removal. Fixed bed

adsorber is used when the mass transfer zone is short (saturation of the adsorbent occurs shortly after initial breakthrough), two or more beds are used in series to increase the contact time, (i.e., increasing the efficiency of adsorbent utilization).

Two or more beds also can be combined in parallel to increase the capacity of adsorbent (i.e., when a high flow rate must be divided into a number of columns, each column will treat a specific amount of influent). (7&8)

In the application of adsorption for purification of water and wastewater, the material to be adsorbed commonly will be a mixture of many compounds rather than a single one. It is readily apparent that the presence of other solutes in the mixture adversely affects the adsorption of the first, leading to a much more rapid breakthrough of this material. (9)

There are many factors affecting the adsorption process including the packed bed height, temperature, pH, influent concentration, flowrate, adsorbate molecular weight and mixing of more than one adsorbate. (1)

Experimental Work

The adsorbents used in the experimental work were activated carbon and activated alumina with the physical properties shown in tables 1 and 2.

Table (1) Physical Properties of AC

Bulk Density (kg/m ³)	350		
Particle Density (kg/m ³)	1800		
Surface Area(m ² /kg)	680*10 ³		
Void Fraction	0.4		
Internal Porosity	0.2		
Sieve Opening (mm)	0.4	0.9	1.4

Activated Alumina (AA).

Table (2) Physical Properties of AA

Bulk Density (kg/m ³)	665			
Average Particle Size (mm)	4.1			
Pore Volume (cc/gm)	0.05			
Surface Area (m ² /kg)	345*10 ³			
Color	White			
Sieve Opening (mm)	2	3.2	4.8	6.4

Adsorbates:

Wastewater which was supplied by Al- Hilla Textile Company with six of the most commonly used dyes which are to be reactive and disperse classes, as listed in Table (3). The aquatic solutions used in the experiments contained R. Blue dye which was taken as a pattern. The solvent used was distilled water.

Table (3) Different Dyes Molecular Weights

Dye	Molecular Weight
Reactive Red	875.5
Reactive Yellow	716
Reactive Blue	562
Disperse Blue	420
Disperse Red	371.5
Disperse Yellow	289

Procedure and Equipments:

Packing

Four beds were packed with various heights by the two adsorbents as shown in Table (4).

Table (4): Adsorbents Weights and Packed Heights

Column Length (m)	Adsorbent Weight (g)	
	Activated Carbon	Activated Bauxite
0.1	13.2	21.8
0.15	19.8	32.7
0.2	26.4	43.6
0.25	33	54.5

Twenty six experiments were carried out on wastewater containing 0.05 kg/m³ of R. Blue dye as the initial influent concentration; eight for bed heights (0.1, 0.15, 0.2, 0.25) m, six for flow rates of wastewater (1.66, 2.55, 5)*10⁻⁵ (m³/min), six for pH values (4, 6, 8) and six for influent temperatures (290, 300, 310) (K).

Twenty two experiments were carried out on aquatic solutions; six for influent concentrations (0.03, 0.04, 0.05 kg/m³) of R. Blue color, twelve for color types (six types), one for R. Blue dye pure solution, and two for pure solutions mixture of the dyes. Half of the above experiments were carried out for every adsorbent in the same conditions.

Equipments

Two cylindrical columns (QVF) of (0.3) m in length, and internal diameter of (0.02) m. were used. One was packed with activated carbon and the second with activated bauxite. The columns were packed with adsorbents particles which were confined with a very fine screen to prevent losses of the particles.

Experiment Procedure:

The wastewater or aqueous solution was passed through the adsorbent column in the down flow direction with the different experimental conditions (flowrates, solution pH and solution temperatures) through different packed bed heights.

For each run of experiments the column was replaced by another bed with the same specifications. A sample of (5 ml) was taken every (5 minutes) duration and kept in a sample tube and then tested.

Analysis

A Cintra -5 GBC Scientific Equipment UV- Visible Spectrometer (computerized) and CECIL- CE 1011 UV- Visible Spectrometer were used to determine the solutions concentration of the dye in the samples taken from the tests performing

Results and Discussion

Effect of Packed Bed Height

The experiments were carried out on wastewater solution on different adsorbent beds with heights of (0.1, 0.15, 0.2, 0.25 m) . keeping other conditions constant (influent conc, =0.05 kg/m³ , temp. =290 K , flow rate = 1.66*10⁻⁵ m³ /min ,pH=6).

The main effect of the bed height in the adsorption process is on the capacity of adsorbent. Since increasing the bed height will provide extra particles and additional surface area, there will be a remarkable increase in the adsorbent capacity. In addition increasing in the bed height will increase the contact time between the pollutant and adsorbent particles that will provide enough time for pollutants to penetrate into the particles of the adsorbent(10).

Figs.(1) and (2) indicate that the increase in bed height will increase the breakthrough point value in each adsorbents bed. For activated carbon this value was higher due to the difference in surface area.

Fig.(3) shows the adsorption quantities for both adsorbents. It can be seen that the adsorption capacity increased as the packed bed height increased. The total quantity of dye removed by activated carbon was greater than that removed by activated bauxite because the rate of adsorption is proportional to adsorbent surface.

Fig.(4) shows the effect of packed bed height on both adsorbents mass transfer rates. This was directly influenced with the bed height and also in activated carbon this rate was greater than in bauxite.

Effect of Flow Rate

The experiments were carried out on wastewater solution at different flow rates (1.66, 2.55, 5)*10⁻⁵ m³/min. keeping other conditions constant (Temp. = 290 (K), C (inf) = 0.05 (kg/m³), h=0.2m, pH = 6, R. Blue Dye).

The effect of flow rate on the adsorption process is very important .This effect is based on the assumption that

film diffusion is the rate limiting in early portion of the column. Increasing the flowrate in this region may be expected to make a compression or reduction of the surface film. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate. Also, because the reduction in the surface film is due to disturbance created when the flow of the influent increases resulting from the easy passage of pollutants through the particles and entering easily to the pores(10).

Fig.(5) and Fig.(6) show that the variable flowrates (in the range used) had a small effect on the adsorption capacity and adsorption mass rate, but the breakthrough point was inversely related with the flowrate as shown in Fig.(7).

Also activated carbon had the greater adsorption capacity and mass rate, which was due to its greater surface area.

Effect of Solution pH

The experiments were carried out on wastewater solution with different solution pH (4, 6, 8). The other initial conditions were kept constant ($h = 0.15\text{m}$, $T = 290\text{ (K)}$, $f = 1.66 \times 10^{-5}\text{ (m}^3/\text{min)}$, $C(\text{inf}) = 0.05\text{ (kg/m}^3)$, R. Blue Dye).

pH strongly influences the adsorption as hydrogen and hydroxide ions are adsorbed and the charge of the other ions are also influenced by pH of the solution. For typical organic pollutants from industrial wastewater the adsorption increases with decreasing pH. (1)

Fig.(8) shows that the breakthrough point is inversely related with pH value. And Fig.(9) shows that the total amount of dye removed from the solution at any period of time increases with decreasing pH values for both adsorbents and activated carbon removed greater amounts. This can be explained on the basis of formation of a positively charged surface on the adsorbent. A low pH value quite probably results in a lowering of the decrease of the negative charge on the adsorbent, thus changing the adsorption of the negatively charged adsorbate. (5)

Fig.(10) indicates the effect of pH value on the adsorption mass rate, it can be seen that this rate is inversely related with pH values.

Effect of Temperature

The experiments were carried out on wastewater solution at different temperatures of (290, 300, 310) (K). All other conditions were kept constant ($h = 0.2\text{ m}$, $\text{pH} = 6$, $\text{flowrate} = 2.5 \times 10^{-5}\text{ (m}^3/\text{min)}$, R. Blue Dye).

Normally the adsorption reactions are exothermic, which means that the adsorption will increase with decreasing temperature, although small variations in temperature do not tend to alter the adsorption process to a significant extent.(1&11)

The adsorption capacity and adsorption mass rate were inversely related with temperature as shown in Figs.(11) and (12), due to the fact that the adsorption reactions are exothermic, then high temperatures would inhibit or slow down the adsorption process.

Effect of Influent Concentration

The experiments were carried out on aqueous solution at different pure dye initial concentrations (0.03, 0.04, 0.05) (kg/m³). Keeping other conditions constant at ($h = 0.2\text{ m}$, $\text{pH} = 6$, $T = 290\text{ K}$, $f = 2.5 \times 10^{-5}\text{ (m}^3/\text{min)}$, R. Blue Dye).

Figure (13) Shows that the adsorption quantity at any period increases with increasing the dye influent concentration.

Figure (14) shows that the adsorption mass transfer rate also increases with increasing the influent concentration or the dye for both adsorbents where it was greater in activated carbon due to the difference in its surface area.

The initial concentration is inversely related to the adsorption equilibrium time. This may be explained by the fact that since the rate of diffusion is controlled by the concentration gradient, it takes a longer contact time to reach adsorption equilibrium for the case of low initial solute concentration values. Because adsorption rate is limited by diffusion, variables that influence diffusion have a significant effect on the adsorption rate. For example, a higher concentration gradient across the surface of the adsorbent particle will increase the rate of adsorption (10&11).

Effect of Dye Type

Molecular size is of significance if the adsorption rate is controlled by antiparticle transport, in which the reaction generally proceeds more rapidly with the smaller adsorbate molecule. Large molecules of one chemical

class sorb more rapidly than smaller ones of another if higher energies (driving forces) are involved (1&11&12).

To study the effect of the dye type on the adsorption behavior twelve experiments were carried out on the six types of dyes from their pure aqueous solutions separately, under constant conditions (pH=6, T=290 K, h=0.15m, f= 1.66*10⁻⁵ (m³/min) and C(inf)=0.05(kg/m³)).

Different dyes (reactive; red, blue, yellow, and dispersed; red, blue, yellow) with molecular weights of (875.5, 562, 716, 371.5, 420, and 289) respectively were tested.

From Fig.(15) It can be seen that the higher molecular weight dye the higher adsorption quantity.

The tendency of higher molecular weight to adsorption was due to two reasons: the first was the decrease of solubility with the increase in molecular weight, and the second was the higher affinity to adsorbent surface by the larger molecular weight dye (9).

Figure (16) shows the effect of molecular weight in pure dye solution on the mass transfer rate of adsorption. It can be seen that the molar rate of uptake decreases with increasing molecular weight and the activated carbon has more mass transfer rate than the activated bauxite for the same packed bed. This is due to the larger surface area of the first.

Effect of Competitive Adsorption

When adsorption occurs from a mixture of substances there is a competition between the various adsorptive for the interface. The presence of other solutes in the mixture adversely affects the adsorption of the first, leading to a much more rapid breakthrough of this material (9).

To study the competitive adsorption of the dyes, two experiments were carried on R. Blue dye from its pure solution at conditions (h=0.15m, pH=6, T=290 K, f=1.66*10⁻⁵ m³/min, C=0.05 kg/m³), and compared with wastewater solution at the same conditions as illustrated in Figures (17) and (18). Those Figures indicate the difference between the breakthrough curves (C/Co vs. t) on the two adsorbents. It is readily apparent that the presence of other solutes in the mixture adversely affects the adsorption of the first, leading to a much more rapid breakthrough of the dye.

Effect of Pure Mixtures Solution

Two experiments on two adsorbents separately were carried to study the effect of a competitive adsorption resulting from a mixture of pure dyes solutions at a concentration of (0.03) (kg/m³) for every dye and the other initial conditions were kept constant (pH=6, T = 290 K, h = 0.15m, f = 1.66*10⁻⁵ (m³/min), C(inf) = 0.03 (kg/m³)).

The comparison between adsorption from mixture solution and pure dye solution was shown in Figs.(19) and (20), the same effect in the previous section can be seen.

The effect of competitive adsorption on adsorption capacity is shown in Fig. (21). It can be seen that the adsorption capacity increases as the molecular weight increases, and in activated carbon it is greater

Figure (22) Shows the effect of molecular weight in the mixture of pure dye solutions on the mass transfer rate of adsorption where it can decrease as the molecular weight increases. It can be seen that the activated carbon had more mass transfer rate than the bauxite for the same packed bed; due to its larger surface area.

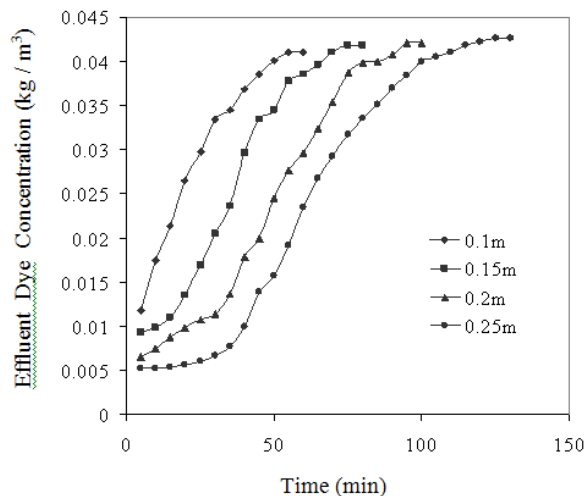


Fig (1): Breakthrough Curves of Isothermal Adsorption for Different Packed Bed Heights (R.Blue, Bauxite)

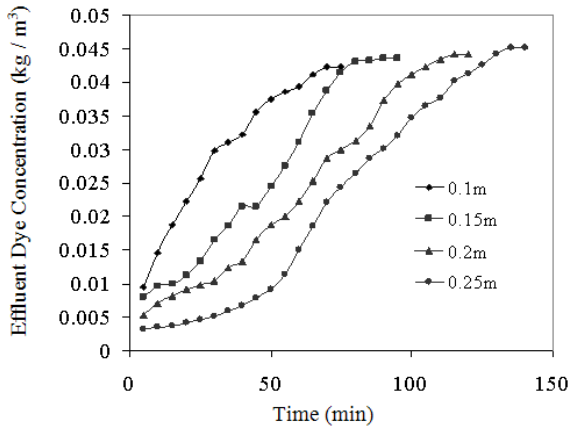


Fig (2): Breakthrough Curves of Isothermal Adsorption for Different Packed Bed Heights (R. Blue, Carbon)

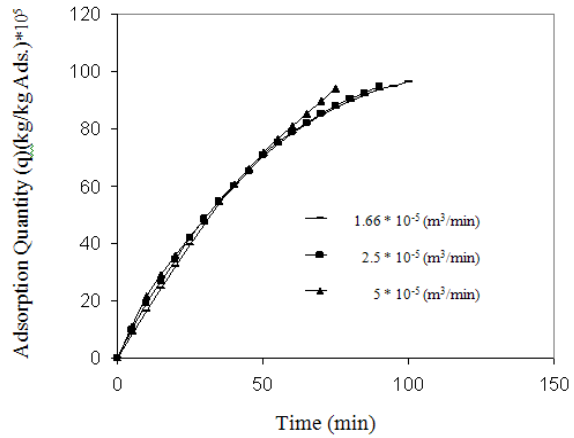


Fig (5): Adsorption Quantity for Different Flowrates (R. Blue, Bauxite)

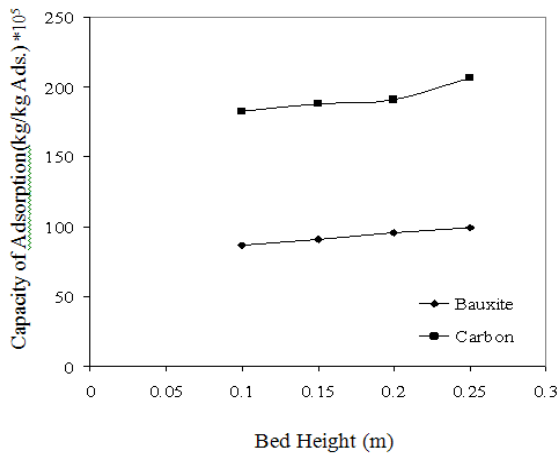


Fig (3): Effect of Packed Bed Height on Adsorption Capacity on Both Adsorbents (R. Blue)

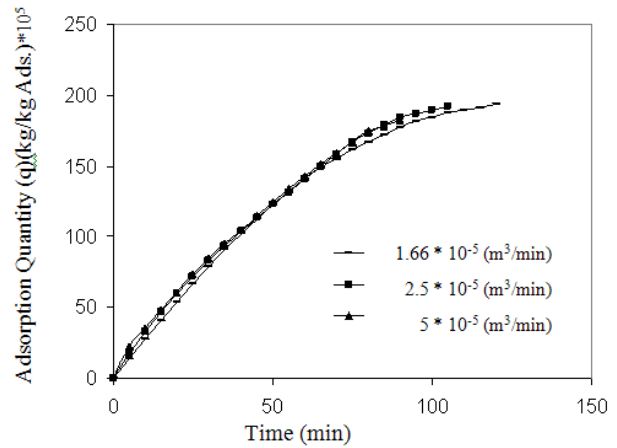
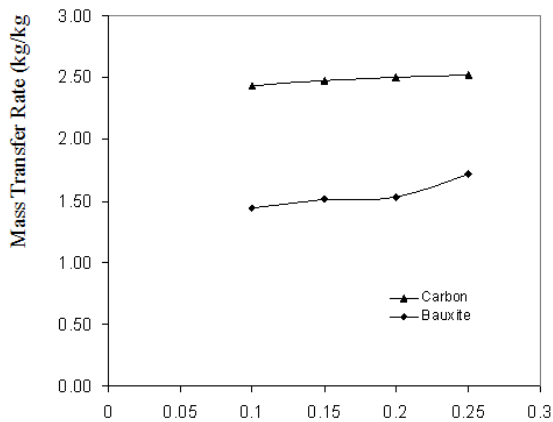


Fig (6): Adsorption Quantity for Different Flow rates (R. Blue, Carbon)



Fig(4) :Effect of Bed Height on The Rate of Mass Transfer on Both Adsorbents (R. Blue)

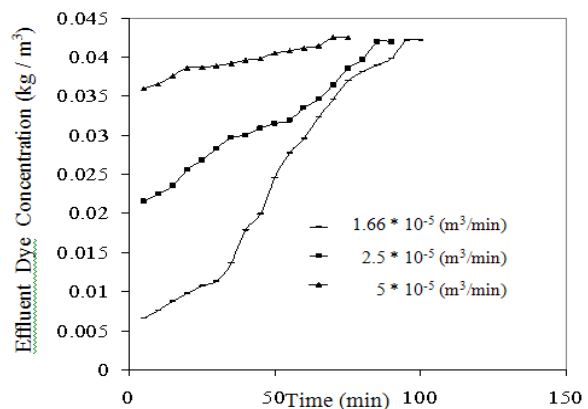


Fig (7): Breakthrough Curves of Isothermal Adsorption for Different Flow rates (R. Blue, Bauxite)

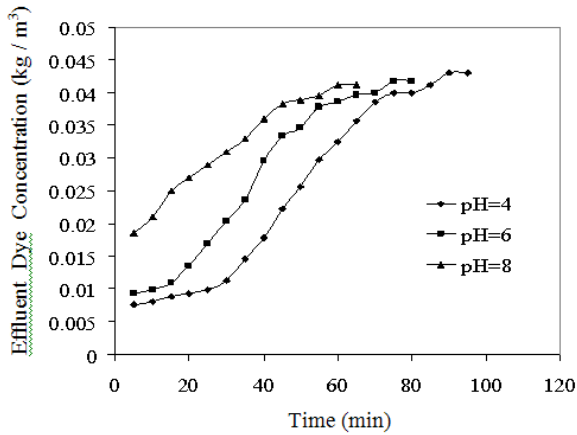


Fig (8): Breakthrough Curves for Different pH Values (R. Blue, Bauxite)

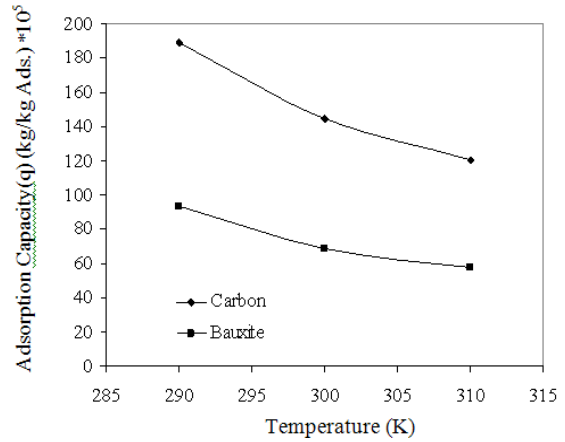


Fig (11): Effect of Influent Temperature on Adsorption Capacity on Both Adsorbents (R. Blue)

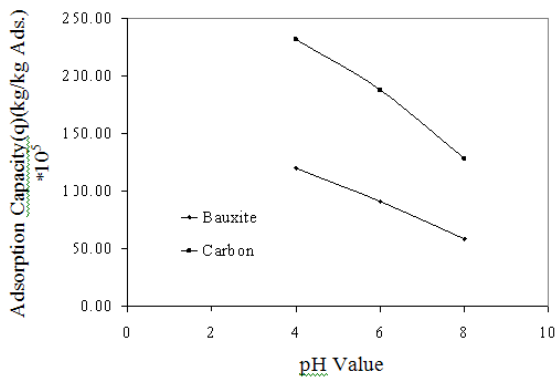


Fig (9): Effect of pH Value on Adsorption Capacity on Both Adsorbents (R. Blue)

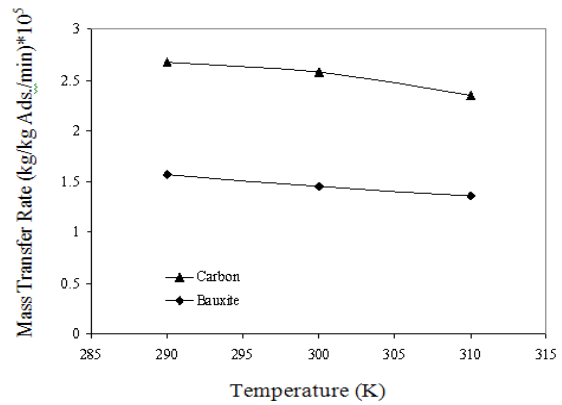


Fig (12): Effect of Influent Temperature on the Rate of Mass Transfer on Both Adsorbents (R. Blue)

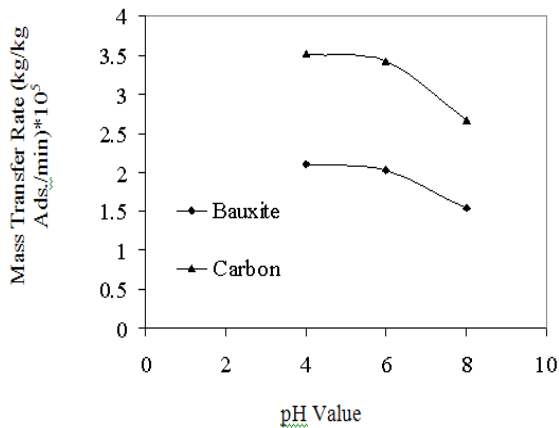


Fig (10): Effect of pH Value on The Rate of Mass Transfer on Both Adsorbents (R. Blue)

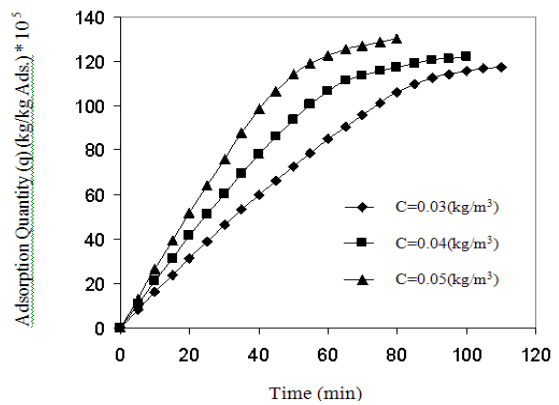


Fig (13): Adsorption Quantity for Different Influent Initial Concentrations (R. Blue, Bauxite)

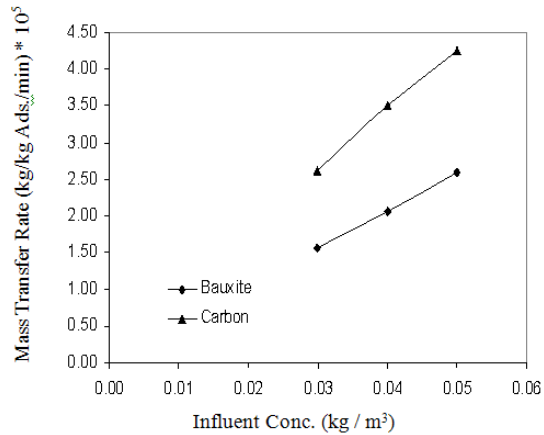


Fig (14): Effect of Influent Concentration on Mass Transfer Rate on Both Adsorbents (R. Blue)

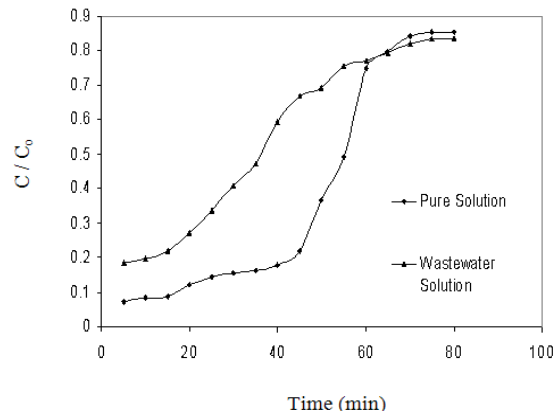


Fig (17): Comparison between Breakthrough Curves for Adsorption of R. Blue Dye from Its Pure Solution and from Waste water Dyes Solution (Bauxite)

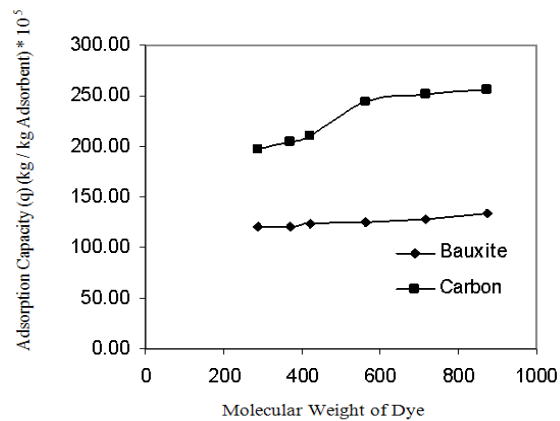


Fig (15): Effect of Molecular Weight on the Capacity of Adsorption on Both Adsorbents

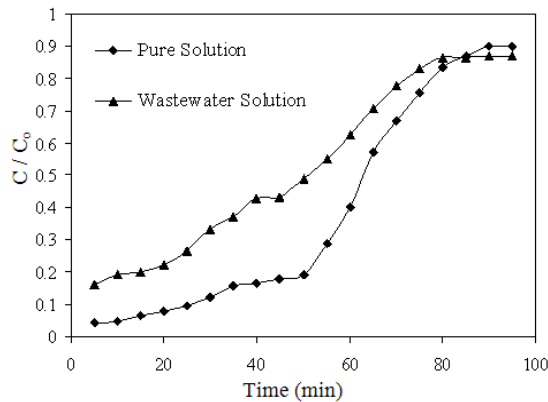


Fig (18): Comparison between Breakthrough Curves for Adsorption of R. Blue Dye from Its Pure Solution and from Waste water Dyes Solution (Carbon)

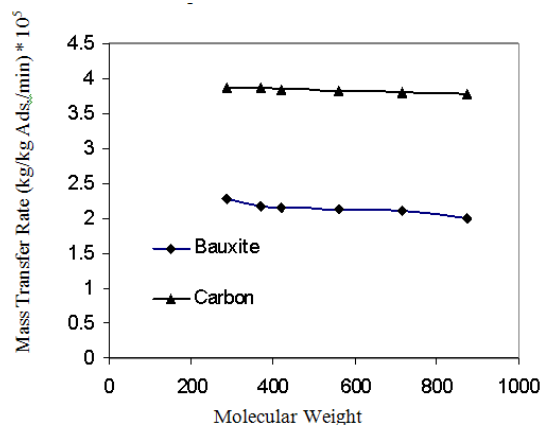


Fig (16): Effect of Molecular Weight of Dye from Pure Solution on Mass Transfer Rate of Adsorption for Both Adsorbent

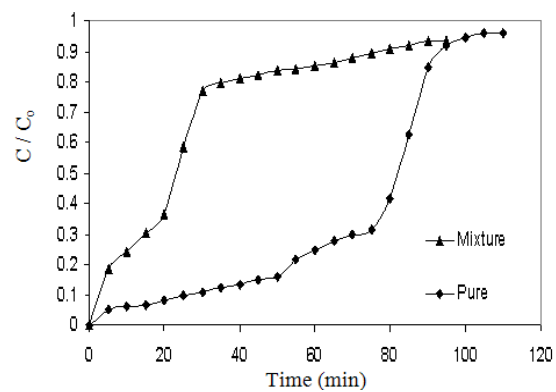


Fig (19): Comparison between Breakthrough Curves for Adsorption of R. Blue Dye from Its Pure Solution and from Mixture Pure Dyes Solution (Bauxite)

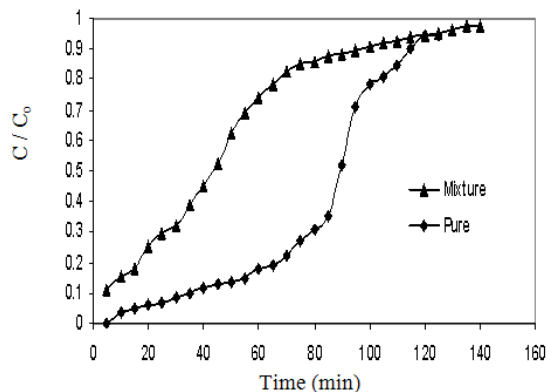


Fig (20): Comparison between Breakthrough Curves for Adsorption of R. Blue Dye from Its Pure Solution and from Mixture Dyes Solution (Carbon)

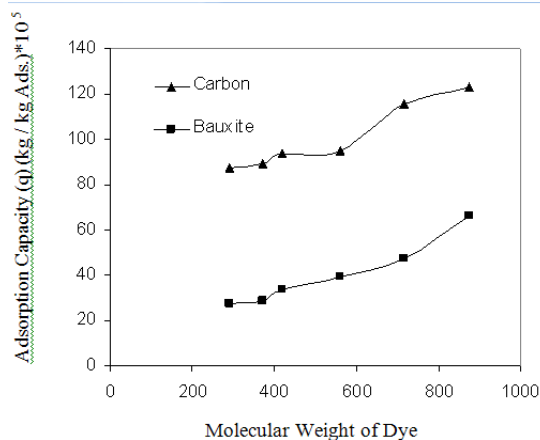


Fig (21): Effect of Pure Mixture Dyes Solution on Adsorption Capacity on Both Adsorbent

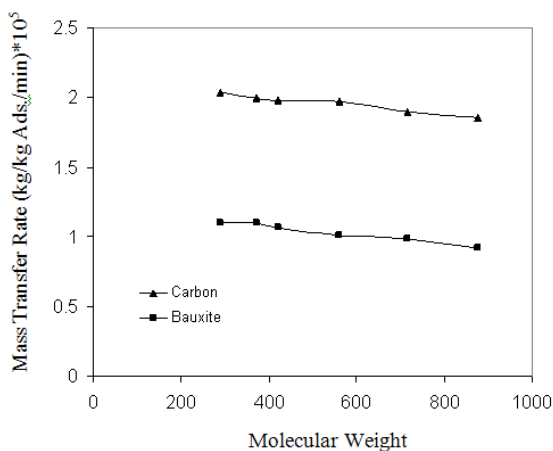


Fig (22): Effect of Molecular Weight in Dye Mixture Solution on Mass Transfer Rate of Adsorption for Both Adsorbents

Conclusions

1. Sorption was an effective process for decolorization of textile dyes. Although activated carbon was the most effective sorbent due to the high surface area, another low cost sorbent (activated bauxite) could be used for color removal.
2. The time to breakthrough point decreases with: The decrease in bed height, molecular weight of dye in both pure and mixture solution.
3. The increase in flow rate, pH value, initial concentration of dye in the influent, and temperature.
4. The capacity of adsorption increases with: The increase in bed height, influent concentration And dye molecular weight.
5. The decrease in flow rate, temperature, and pH value.
6. The rate of mass transfer for initial stage of adsorption increases with increasing in influent concentration, flow rate, and bed height and also with decreasing in pH value, molecular weight and temperature.
7. The adsorption rate and, therefore the adsorption capacity of the activated carbon are greater than that for the activated bauxite (255*10⁻⁵ kg color/kg carbon) and (133*10⁻⁵ kg color/kg bauxite) respectively. That is due to the fact that for the same bed height column the weight of the carbon was less than the bauxite because of its smaller bulk density; (bulk densities for the adsorbents used were (350 and 665) (kg/m³) for activated carbon and activated bauxite respectively).
8. The adsorption process using activated carbon had a good degree of color reduction, reaching 99.7%, and for activated bauxite it reached 95%.

References

1. Sven Erik Jorgenson, "Industrial Waste Water Management", Amsterdam, Oxford, New York (1979).
2. Yongjie Miao, "Biological Remediation of Dyes in Textile Effluent: A Review on Current Treatment Technologies", www. ccee. iastate.edu/ courses/ ce s21/yongjie.
3. E. Voudrias, K. Fytianos, E. Bozani, "Sorption and Desorption Isotherms of Dyes from Aqueous Solutions and Wastewaters with Different Sorbent Materials", Global Nest: the Int. J. , Vol.4, No.1, pp. 75-83,(Greece), 2002 (Internet).

4. Ajay Meena & Chitra Rajagopal, "Comparative Studies on Adsorptive Removal of Chromium from Contaminated water Using Different Adsorbents", Indian Journal of Chemical Technology, ISSN:0971-457X, Vol. 10 No.1, Jan.2003, pp.72-78 Activated Carbon, <http://www.activatedcarbonindia.com/powdered,granulated,AC.htm>.
5. R.F.P.M. Moreira & M.G. Peruch and N.C. Kuhnen, Brazil, "Adsorption of Textile Dyes on Alumina", Brazil J. Chem. Eng. Vol. 15, No. 1 San Paulo, (1998).
6. Prof. Dr. Ing. M.Jekel, Dr. Ing. Silke Karcher, "Sorption and Oxidation Processes for the Removal of Reactive Dyes in Partial Streams and Mixed Wastewaters", German Research Council (GFG), Corporate Research Center S FB 193, <http://itu107.ut.tu-berlin.de/wrh/english/research/proold/anion.htm>, (2004).
7. Hayder M.A.H.M.Sc. Thesis, "Reduction of Organic Content in Wastewater by Adsorption onto Activated Carbon", Env.Eng.Dept. Collage of Eng. Univ. of Baghdad,(1996).
8. Maisa M. AR. Thesis,"Adsorption of BTX Aromatics from Reformate by 13X Molecular Sieve",(2003).
9. Ibtehal K. Sh. Ph.D. Thesis ,"Study of Textile Industrial Wastewater Treatment and Recycling Process", Chem. Eng. Dept. Collage of Eng. Univ. of Baghdad,(2002).
10. Liangs S., "Dual Practice Diffusion Model in Fixed Bed", AICE Env. Prog., (1983).
11. Sorption with Activated Carbon, www.cee.vt.edu/program-areas/environmental/teach/gwprimer/group23/sorp-ac.
12. M. Bonnevie-Svendsen, "Sorption and Filtration Methods for Gas and Water Purification", Noordhoff- Leyden, pp(160), 1975.