REMOVAL OF DYES FROM TEXTILE EFFLUENT BY ADSORPTION ONTO OVEN DRIED ALUM SLUDGE

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ABSTRACT

The present study deals with the removal of dyes from the effluent of the state company for cotton textile industries located at Al-Khadmya by using oven dried alum sludge (ODS) as adsorbent. Two different dyes; Direct black and solar brown are studied. Alum sludge was collected from Al-Qadisiya water treatment plant; it was heated in an oven at 105°C for 24 hours, then cooled at room temperature and crushed to produce particle sizes of 1.18-2.36 and 4-4.75 mm. Batch and fixed bed mode were used. In batch experiments the effect of oven dried alum sludge weight on adsorption process and equilibrium isotherm were studied by using 15-125 g/l of oven dried alum sludge for direct black and 15-175 g/l for solar brown, with constant initial dyes concentration of 10 mg/l and constant particle size of 4-4.75 mm. Batch kinetics experiments showed that equilibrium time was about 12-14 days. The three models Freundlich, Langmuir and Freundlich-Langmuir gave good fitting for the adsorption capacity. In the fixed bed isothermal adsorption column, the effect of initial dye concentration (C_o), particle size, influent flow rate (Q) and bed depth (H) were studied. The results showed that the oven dried alum sludge was effective in adsorbing dyes with removal efficiency ranged between 90% to 92%.

الخلاصة:

تم في هذا البحث دراسة قابلية أطيان الشب المعالجة حراريا على أمتزاز وتقليل اللون من المياه المطروحة من الشركة العامة للصناعات القطنية في مدينة الكاظمية. الأصباغ التي تم استخدامها في الدراسة هي direct black و solar brown. أطيان الشب التي تم استخدامها قد جمعت من مشروع القادسية لمعالجة المياه في بغداد. تم معالجة أطيان الشب حرارياً في فرن بدرجة حرارة 105 م^{o} ولمدة 24 ساعة وترك ليبرد الى درجة حرارة الغرفة ثم تكسيره الى حجوم 2.36-1.18 و4-4.75ملم. تم استخدام نمطين من التشغيل في هذا البحث وهي تجارب النمط الدفعي وتجارب النمط المستمر. في تجارب النمط الدفعي تم دراسة تأثير كمية أطيان الشب المعالجة حرارياً على عملية الأمتزاز باستخدام 125-15 غم/لتر من المادة الممتزة لصبغة direct black و15- 175 غم/لتر لصبغة solar brown بثبوت تركيز الصبغة الابتدائي 10 ملغم/ لتر وحجم ثابت لجزيئات المادة الممتزة 4-4.75 ملم ، أظهرت النتائج ان نسبة إزالة الأصباغ تزداد بزيادة كمية أطيان الشب المعالجة حرارياً. كذلك أظهرت النتائج ان الوصول الى حالة التعادل تستتغرق تقريباً 12 الى 14 يوم، تم تحليل النتائج باستخدام موديلات (Langmuir, Freundlich and Langmuir-Freundlich) وأظهرت النتائج ان جميع الموديلات ذات تقارب جيد. في تجارب النمط المستمر تم دراسة تأثير تركيز الأصباغ الابتدائي وحجم جزيئات المادة الممتزة ومعدل الجريان وارتفاع عمود الأمتزاز على عملية الأمتزاز. لقد أظهرت النتائج ان أطيان الشب المعالج حرارياً فعال في امتزاز الاصباغ من مياه الصرف وكانت نسبة ازالة الأصباغ تتراوح بين 90% الى 92%.

KEYWORDS: Wastewater treatment, Adsorption, Alum sludge, dyes removal.

INTRODUCTION

Textile industries use large amount of water and chemicals for the finishing and dying processes. The chemical structures of dyes vary enormously and some have complicated aromatic structures that resist degradation in conventional wastewater treatment processes because of their stability to sunlight, oxidizing agents, and microorganisms. Dye 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 (Chu, 2001). Wastewater from textile and tannery effluents attracts attention of environmental protection agencies all over the world. Many methods have been used to treat wastewaters from effluents. Physical and chemical methods are considered very expensive in terms of energy and reagents consumption. Another account that limits their use is the excessive sludge they generate (Yakubu et al., 2008). 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 (Yavuz and Aydin, 2006). Alum sludge is a waste material generated during the coagulation / sedimentation process in drinking water treatment plant. This sludge contains precipitated alum hydroxides and the some contaminants related to the raw water chemistry (Galarneau and Gehr, 1997). The adsorbents are usually used in the fixed bed process because of the ease of operation. To design and operate a fixed bed adsorption process successfully, the column dynamics must be understood, that is the breakthrough curves under specific operating conditions must be predictable (Markovska and Meshko, 2001).

Abbas H. (2005) investigated the capability of activated alumina from bauxite compared with activated carbon adsorption capability to reduce the color from wastewater of textile company (Al- Hilla- Babel). The results showed that the adsorption process which using activated carbon insuring a good degree of reduction of color (99.7%) and is better than activated bauxite which reach (95%) removal percentage. Also, the capacity of adsorption increased with increase of bed depth and decrease in flow rate.

Ibtehal K. (2002) reported the treatment and recycling of industrial wastewater from cotton textile industry in Iraq which contains three different dyes namely, direct blue, sulphur black and vat yellow. Two dyes removal methods were used, chemical coagulation and adsorption onto activated carbon. The results showed that the best chemical coagulant for complete dye removal was found to be aluminum sulphate. Also adsorption onto granular activated carbon was found to be very effective for dyes removal.

Sarmad A. (2009) investigated the removal of phosphorous from wastewater by using oven dried alum sludge. The results showed that the oven dried alum sludge were effective for adsorbing phosphorous and the removal percentage was up to 85%.

The present study deals with the removal of dyes from the effluent of textile company (Al-Khadmya- Baghdad) using oven dried alum sludge (ODS) as adsorbent. Two dyes, direct black and solar brown which are mainly used in this industry will be tested to study the different variables affecting the adsorption behavior.

EXPERIMENTAL WORK

Materials:

- Adsorbent: In this research alum sludge was collected from Al-Qadisiya treatment plant, Baghdad, Iraq. The alum sludge was tested in Ibn Sina State Company to determine the inorganic contents. Table 1 represents the combination of this sludge.

Table 1: Inorganic materials in alum sludge

Constituent	Weight percent,%	Constituent	Weight percent,%
Aluminum	3.38	Zinc	0.0098
Iron	0.819	Lead	0.0001
Manganese	0.16	Barium	0.0001
Chromium	0.013	Arsenic	0.0002
Vanadium	0.002	-	-

Alum sludge was heated in an oven at 105^o C for 24 hours, and then dried sludge was cooled to room temperature, crushed to produce particle sizes of 1.18-2.36 and 4-4.75 mm. The physical properties of these particles are listed in Table 2.

Table 2: Physical properties of oven dried alum sludge

Property	Oven dried alum sludge
Bulk density (kg/m^3)	786.7
Particle porosity	0.7
Bed porosity	0.65
BET surface area (m^2/g)	191

Tests for Characterizing Oven Dried Alum Sludge

(A) IR Spectroscopy: The samples for infrared spectra (Bruker Vector FT-IR spectrometers) were prepared with methylene chloride (CH_2C_{l2}) mulls on CsI plates. Vibrational spectra were reported in wavelengths (cm^{-1}) against ranked infrared absorption, values of wavelengths at peak correspond to the characteristics of active groups present on the surface of the sludge. This test was done in University of Baghdad/ College of science / Chemistry dept. and the results are shown in Fig. 1.

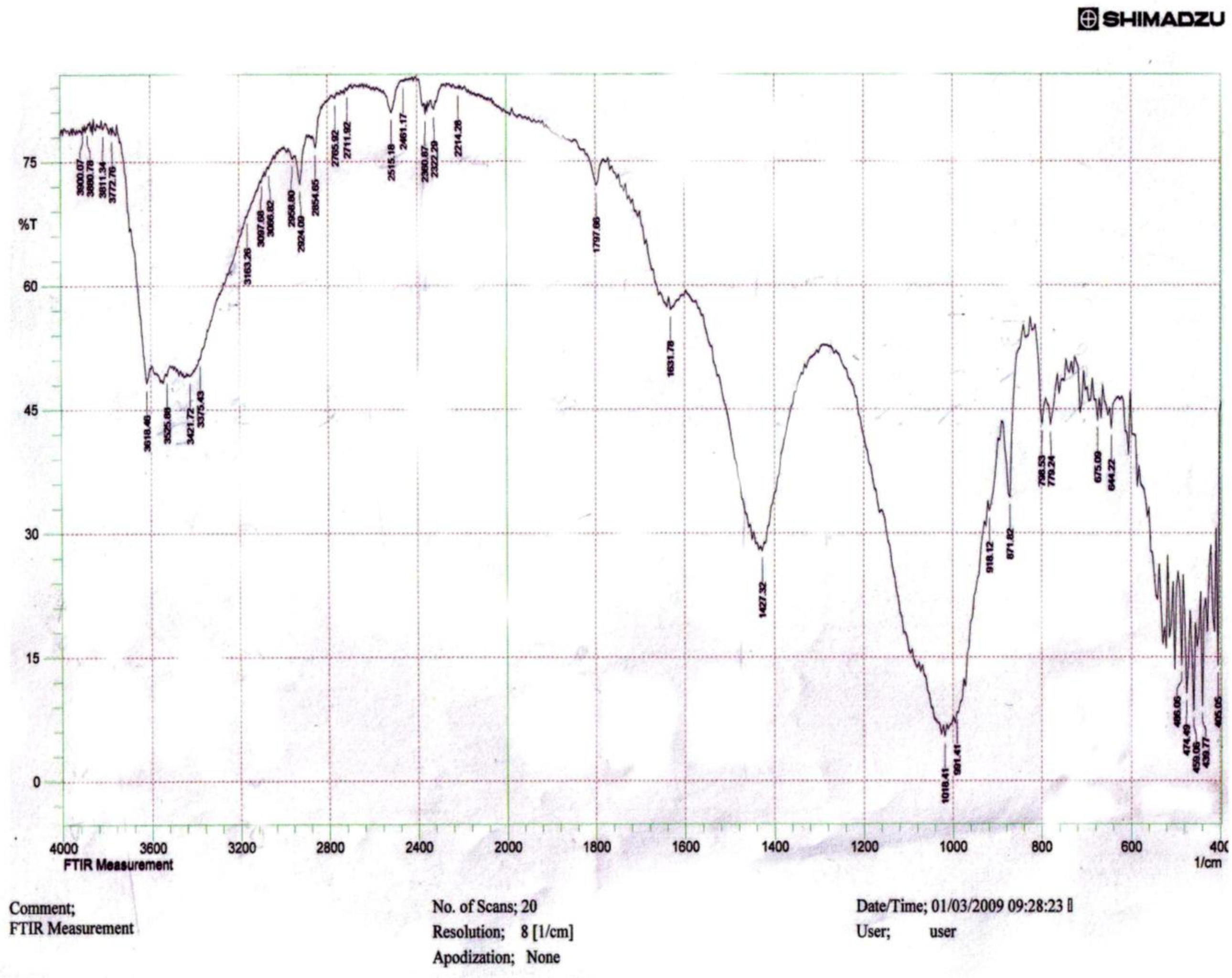

Fig. 1: IR Spectroscopy of ODS

(B) X-Ray Diffraction: X-Ray powder diffraction patterns of oven dried alum sludge (ODS) were obtained from gently pressed specimens of random powder particles that are less than 0.45 µm. Powder X-ray diffraction data were collected from 10 to 60° 2δ with a Nicolet X-ray powder diffract meter (graphite monoachromatized Cu KR radiation, 0.05° 2δ step size, and 2-s count time per steps), this test was performed also in University of Baghdad/ College of science / Chemistry dept. and the results obtained are shown in Fig. 2.

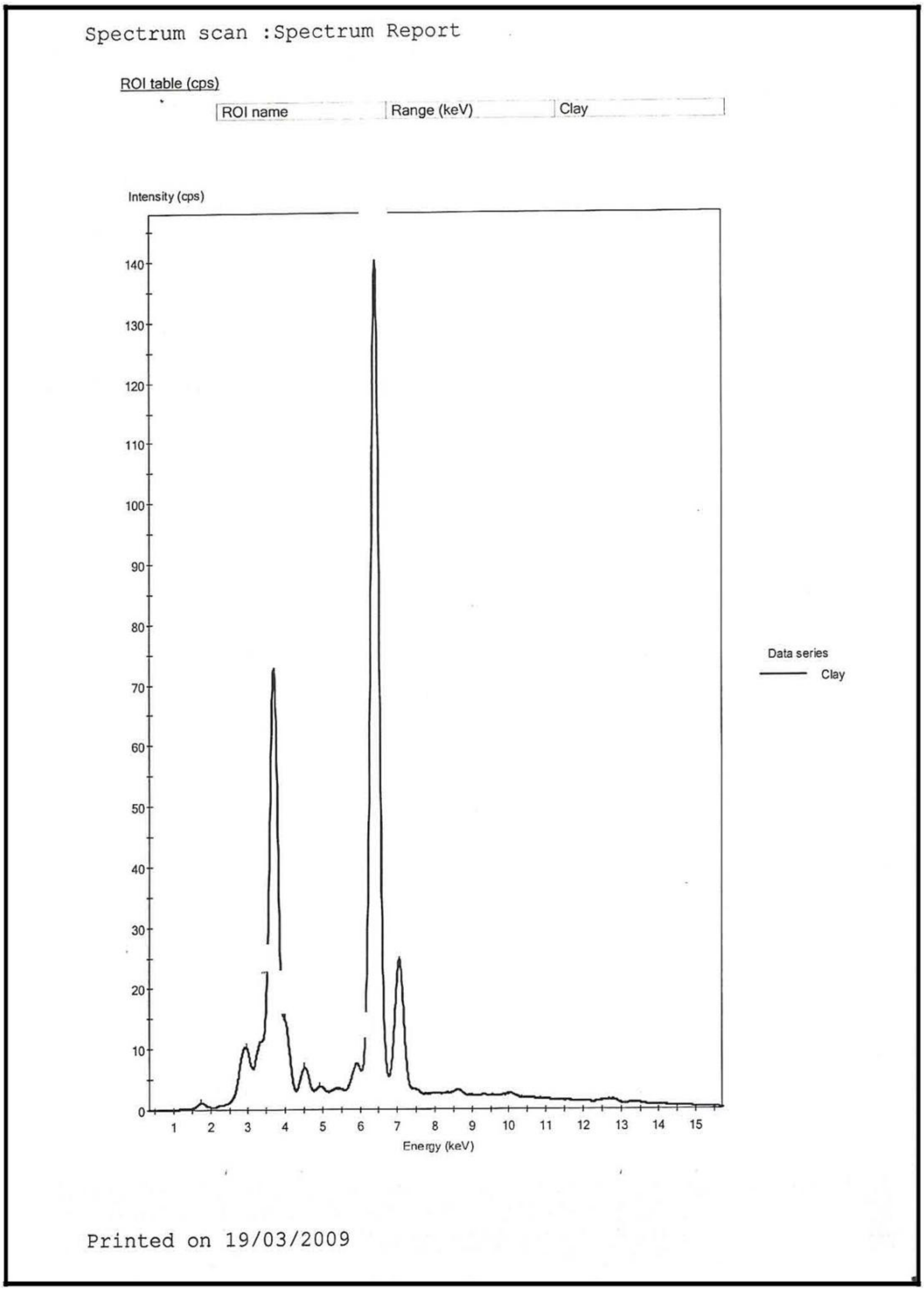

Fig. 2: X-ray diffraction of ODS

(C) Specific Surface Area: In practice, the method used for determining the specific surface area is the BET (Brunauer, Emmett and Teller) method based on the physical adsorption of an inert gas at constant temperature of liquid nitrogen. This test was done in the Research of oil and development center.

(2.1.3) Adsorbate: Two direct dyes were used as adsorbate; direct black and solar brown. The concentrations of the two dyes were measured with Shimatzu UV Spectrophotometer at wave length corresponding to the maximum absorbance for each dye, 566 nm for direct black and 419 nm for solar brown. According to the Lambert-Beer law, the absorbance was found to vary linearly with concentration.

Experimental Modes

- Batch Experiments

Batch experiments were used to obtain the equilibrium isotherm curves and then the equilibrium data. In batch mode the following experiments were carried out:

- Effect of oven dried alum sludge (ODS) weight on the adsorption process.
- Equilibrium isotherm experiments.

All experiments were carried out at 25^{o} C ±1. Six 1 L flasks were used for each dye. For experiments conducted with an initial dye concentration of 10 mg/L, alum sludge was used in concentration of 15, 35, 55, 75, 95 and 125 g/l for the direct black and 15, 55, 95, 125, 150 and 175 g/l for the solar brown. Samples were taken from the flasks and tested. Dye that was lost from the solution was assumed to be adsorbed onto the adsorbents. Data obtained from batch tests were conducted on deionized water fitted to Freundlich, Langmuir and Freundlich-Langmuir adsorption isotherm equations.

- Fixed Bed Column Experiments

Column experiments were carried out for various initial dye concentrations (C_o), particle size (dp), flow rate (Q) and bed depth (H) to measure the breakthrough curves for the systems.

The fixed bed adsorber studies were carried out in Q.V.F. glass column of 2 in. (50.8 mm) I.D. and 700 mm in height. The oven dried alum sludge (ODS) was confined in the column by fine stainless steel screen at the bottom and a glass cylindrical packing at the top of the bed to ensure a uniform distribution of influent through the adsorbent. The influent solution was introduced to the column through a perforated plate, fixed at the top of the column.

The experimental procedure was as follow:

- The oven dried alum sludge was placed in the adsorption column for the desired bed depth and particle size.
- The wastewater with the desired concentration of dye was prepared in the feed container, using distilled water.
- The wastewater was pumped to the adsorption column through the calibrated rota meter at the desired flow rate.
- Samples were taken periodically and the concentration of dye in these samples was measured using an UV spectrophotometer.
- The breakthrough curves were determined by plotting effluent concentrations (C/Co) against time (t). The schematic diagram of the experimental set-up is shown in Fig. 3.

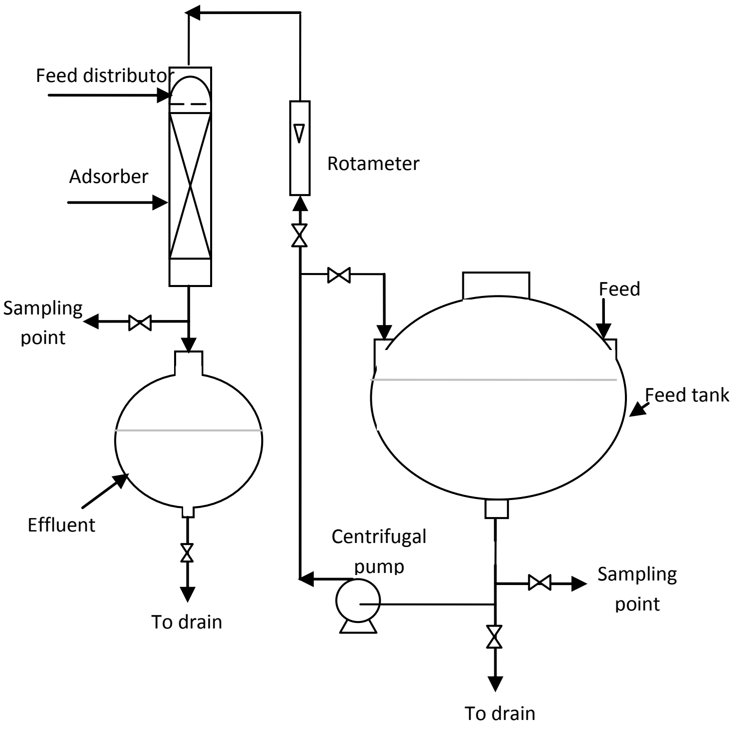

Fig. 3: Schematic diagram of experimental set-up

RESULTS AND DISCUSSION

Batch experiments

(i) Adsorption isotherms: Adsorption isotherm studies were performed to obtain equilibrium isotherm curves and data required for the design and operation of the fixed bed adsorber. The adsorption isotherm curves were obtained by plotting the weight of the solute adsorbed per unit weight of the adsorbent (q_e) against the equilibrium concentration of the solute (C_e). **Figs. 4** and **5** show the adsorption isotherm curves for adsorption of direct black and solar brown dyes onto oven dried alum sludge at 25^o C respectively.

The obtained data of both dyes were fitted with Langmuir, Freundlich and Langmuir-Freundlich models. The Langmuir model describing adsorption can be described as (Weber and Walter, 1972):

$$\frac{x}{m} = \frac{a\,b\,C_e}{1 + a\,C_e} \tag{1}$$

The Freundlich adsorption model is of the form (Weber and Walter, 1972):

$$\frac{x}{m} = K\,C_e^{1/n} \tag{2}$$

Combination of Langmuir-Freundlich Isotherm Model, i.e. the Sips model for single component adsorption (Sips, 1984) is:

$$q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}} \tag{3}$$

The parameters for each model were obtained from a non-linear statistical fit of the experimental data. All parameters with their correlation coefficients are summarized in Table 3.

Table 3: **Isotherm parameters for dyes adsorption onto ODS.**

Direct black			Solar brown		
Model	**Parameters**	**Values**	**Model**	**Parameters**	**Values**
Langmuir (1)	a	0.002305	Langmuir (1)	a	0.000716
	b	33546.28		b	68852.21
	Correlation coefficient (R)	0.9921		Correlation coefficient (R)	0.9869
Freundlich (2)	K	146.3275	Freundlich (2)	K	230.243
	n	0.899925		n	0.782
	Correlation coefficient (R)	0.9941		Correlation coefficient (R)	0.9948
Combination of Langmuir-Freundlich (3)	q_m	16817.88	Combination of Langmuir-Freundlich (3)	q_m	12605.77
	b	0.008702		b	0.018267
	n	0.899915		n	0.7819
	Correlation coefficient (R)	0.9942		Correlation coefficient (R)	0.9973

From the statistical analysis, high values of the correlation coefficients were found. Indicating that adsorption of dyes by oven dried alum sludge could be well described by the three isotherm models. The correlation coefficients were in the range 99.21-99.42% for direct black and 98.69-99.73% for solar brown at 10 mg/l initial dye concentration. The three models Freundlich, Langmuir and Freundlich-Langmuir gave good fitting for the adsorption capacity.

(ii) Effect of Mass of Oven Dried Alum Sludge on the Adsorption Process: The effect of mass of oven dried alum sludge on adsorption of dyes at constant adsorbate concentration was studied. The results of the dependence of dyes on the mass of oven dried alum sludge of size 4-4.75 mm at 25^{o} C are shown in Figs. 6 to 9. These figures show that the removal percentage of each dye increased with increasing the weight of the oven dried alum sludge. The increase in the removal percentage of each dye is due to the greater availability of adsorption sites or surface area of adsorbent. An identical trend was observed by other investigations (Kim et al., 2003a and Maruf et al., 2006).

To reach 90% removal of direct black dye a mass of 125 g/l of ODS should be used, as for solar brown, 175 g/l is required.

Fixed bed experiments:

(i) Effect of initial dye concentration: The initial dye concentration of the influent is important since a given mass of adsorbent can only adsorb a fixed amount of the dye. Therefore, the more concentrated the influent is, the smaller is the volume of effluent that a fixed mass of adsorbent can purify. So experiments were undertaken to study the effect of varying the initial dye concentration on the rate of dye adsorption and are shown in Figs. 10 and 11. The initial dye concentration in the inlet flow is one of the limitation factors and a main process parameter. Increasing the inlet dye concentration increases the slope of the breakthrough curve and makes it much steeper, reducing the volume of the effluent treated and reducing the throughput until breakthrough. This may be caused by saturation of adsorbent more quickly with high dye concentrations; there by decreasing the breakthrough time, the rate of diffusion is controlled by the concentration gradient, so a longer contact time is required to reach saturation for the case of low values of initial solute concentration. Wastewater treatment is limited by the breakthrough point or the dynamics of reaching that point. These systems have a small time delay with higher concentrations in the inlet, so the dye solutions have to be diluted before separation for better removal. The same conclusions were obtained by (Markovska and Meshko, 2001 and Maruf et al., 2006).

(ii) Effect of volumetric flow rate: In the design of a fixed bed adsorption column, the contact time is the most significant variable. Therefore, the bed depth and the dye flow rate are the major design parameters (Markovska and Meshko, 2001). The effect of volumetric flow rate was investigated for both dyes and the breakthrough curves are presented in Figs. 12 and 13. Increasing the flow rate from 1 to 3 l/h caused a reduction in the breakthrough time to about the half. It decreased from 800 to 400 min for the direct black and 1200 to 600 min for solar brown. It is obvious that increasing the flow rate decreases the treated volume reaching the breakthrough point and therefore the service time of the bed. This is due to the decreased contact time between the dye and the adsorbent at higher flow rate. Increasing the flow rates may be expected to make reduction of the surface film. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate, resulting of easy passage of the adsorbate molecules through the particles and entering easily to the pores. These results agree with that obtained by (Kim et al., 2003a; Maruf et al., 2006, Sarmad, 2009).

(iii) Effect of bed height: The effect of bed depths were investigated for dyes adsorption onto the oven dried alum sludge; the experimental breakthrough curves are presented in Figs. 14 and 15 for both dyes. The breakthrough curves were obtained for different bed depths 15 30 40 and 50 cm at a constant flow rate 1 l/h and constant dye concentration of 10 mg/l. It is clear that increasing the bed depth increases the breakthrough time and the residence time of the solute in the column, providing greater surface area for adsorption (Malkoc and Nugoglu, 2006).

Increasing the depth from 15 to 40 cm for direct black and 15 to 50 cm for solar brown as shown in Figs. 14 and 15 increased the breakthrough time from 400 to 800 min for the two dyes.

A comparison in Figs. 16 and 17 for the two dyes, where bed depths are different but the residence time was kept constant by changing the flow rate. These results show that increasing the fluid velocity had no significant effect. Thus, the residence time in the column is more effective in improving the removal efficiency.

(iiii) Effect of particle size: Using adsorbent particles of smaller sizes will eliminate interparticle mass transfer resistance, so that the rate determining step is diffusion through the film around each particle. The effect of varying the particle size was investigated and the experimental breakthrough curves are presented in Figs. 18 and 19 for both dyes. The breakthrough curves were obtained for different particle sizes 1.18-2.36, 4-4.75 mm at a constant initial concentration of the dyes 10 mg/l, bed depth and constant flow rate 1 l/h. The experimental results showed that fine particle sizes 1.18-2.36 mm showed a higher dye removal than the coarse particle sizes 4-4.75 mm. This was due to the large surface area available for adsorption when using fine particles.

CONCLUSIONS:

The present study has led to the following conclusions:

- Oven dried alum sludge was effective in adsorbing dyes from deionized water.
- In batch experiment the removal percentage of dyes increases 90-92 % with increasing in the oven dried alum sludge dose 125-175 gm/l.

- Batch kinetics experiments showed that equilibrium time was about 12-14 days without mechanical mixing at an initial concentration 10 mg/l and adsorbent weight 125 g/l for direct black and 175g/l for solar brown.
- The isotherm models, Langmiur, Freundlich and Langmiur- Freundlich gave good fitting for the adsorption of oven dried alum sludge versus equilibrium concentration of dyes. The correlation coefficients (R) obtained from “Satistica Program” for these models were in the range of 99.21-99.42% for direct black and 98.69-99.73% for solar brown.
- In fixed bed experiment, the removal percentage of dyes increased with increasing contact time, adsorbent surface area, bed height and decreasing flow rate.

NOMENCLATURE:

a	Langmiur constant (l/mg)
b	Langmiur constant (mg/g)
B	The Brunauer, Emmett and Teller
C	Concentration of solute in solution at any time (mg/l)
C_e	Concentration of solute in solution at equilibrium (mg/l)
C_0	Initial concentration of adsorbate (mg/l)
dp	Adsorbent particle size
K	Freundlich equilibrium constant indicative of adsorption capacity
m	Mass of solute adsorbent (g)
n	Freundlich constant indicative of adsorption intensity
ODS	Oven dried alum sludge
H	Bed depth (cm)
Q	Flow rate (l/h)
q_e	Amount of metal ion adsorbed at equilibrium (mg/g)
q_m	The maximum adsorption density in Langmiur equation
QVF	Quality vessels fabrication
R	Correlation coefficient
t	Time (min)
UV	Ultra violet
x	Mass of solute adsorbed (mg)

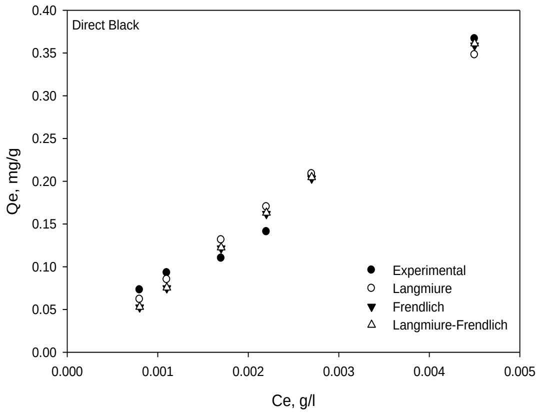

Fig. 4: Adsorption isotherm for direct black onto oven dried alum sludge (C_o=10 ppm, Temp. =25^o C)

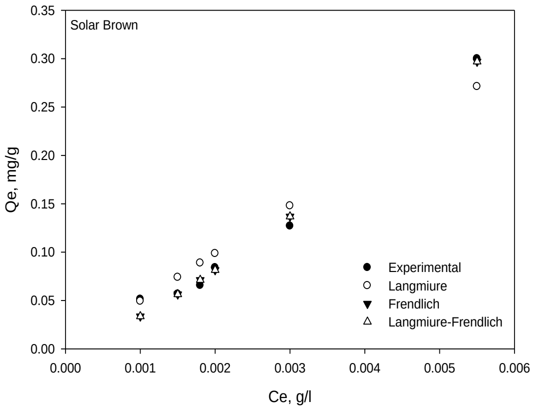

Fig. 5: Adsorption isotherm for solar brown onto oven dried alum sludge (C_o=10 ppm, Temp. =25^o C)

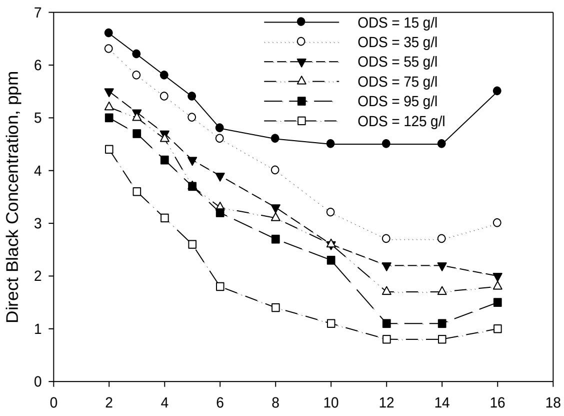

Fig. 6: Variation of direct black concentrations with time of batch tests (C_o=10 ppm, Temp. =25^o C, particle size=4 mm)

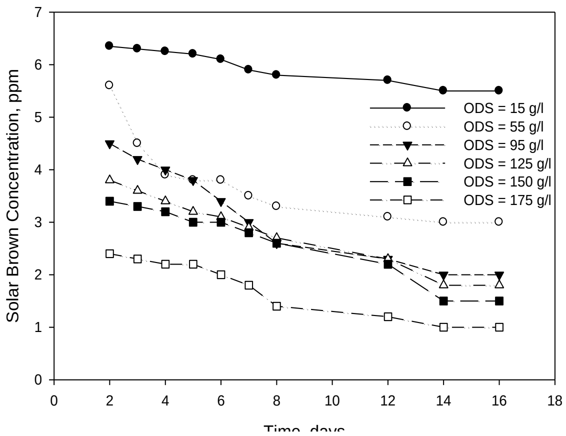

Fig. 7: Variation of solar brown concentrations with time of batch tests (C_o=10 ppm, Temp. =25^o C, particle size=4 mm)

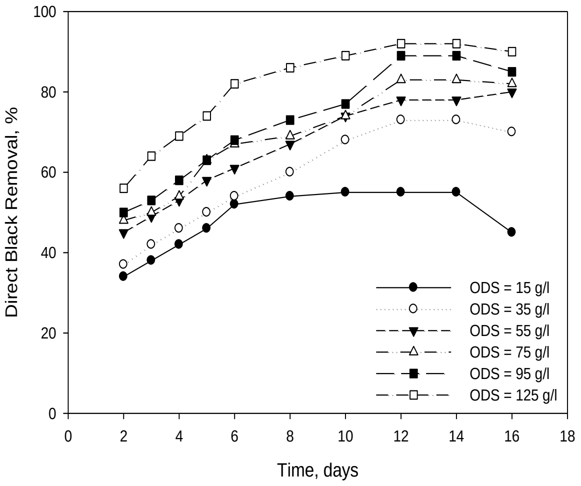

Fig. 8: the effect of ODS on direct black removal (C_o=10 ppm, Temp. =25^o C, particle size=4 mm)

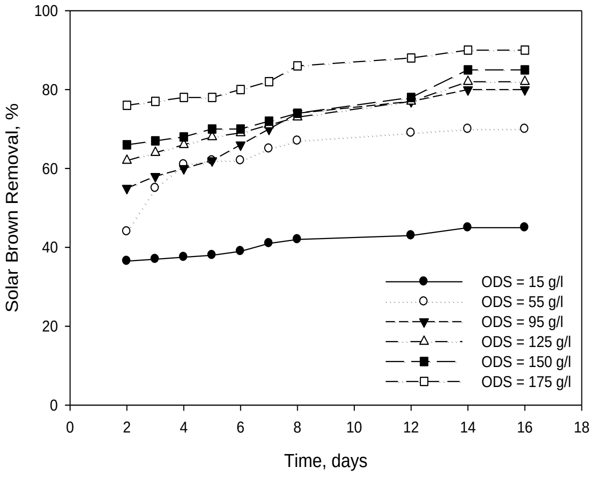

Fig. 9: the effect of ODS on solar brown removal (C_o=10 ppm, Temp. =25^o C, particle size=4 mm)

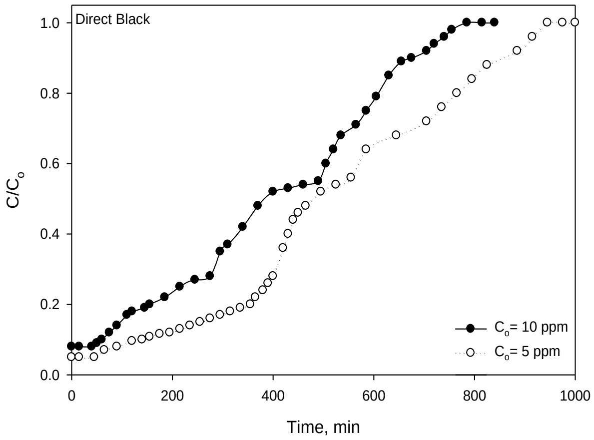

Fig. 10: Experimental breakthrough curves for adsorption of direct black onto ODS at different initial concentration

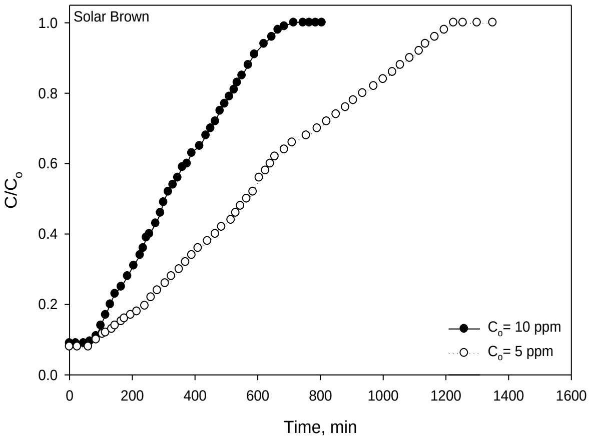

Fig. 11: Experimental breakthrough curves for adsorption of solar brown onto ODS at different initial concentration

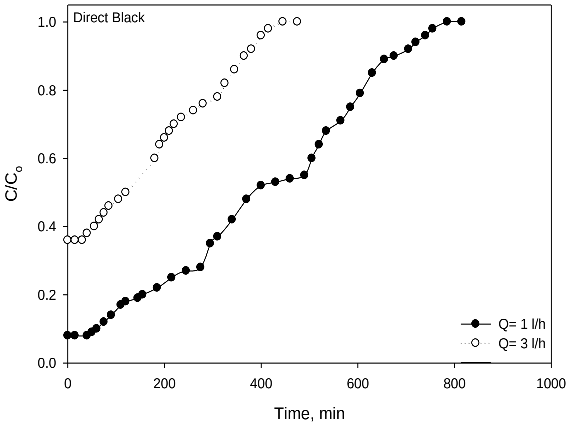

Fig. 12: Experimental breakthrough curves for adsorption of direct black onto ODS at different flow rates

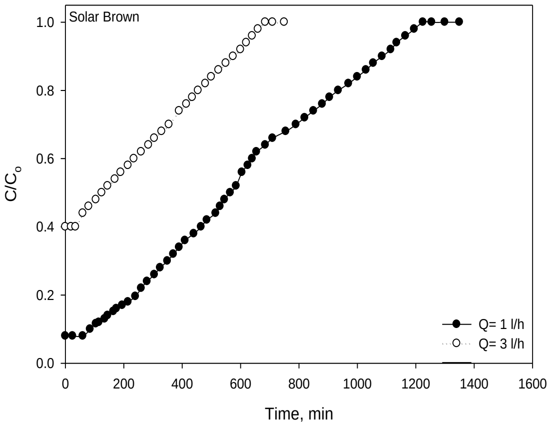

Fig 13: Experimental breakthrough curves for adsorption of solar brown onto ODS at different flow rates

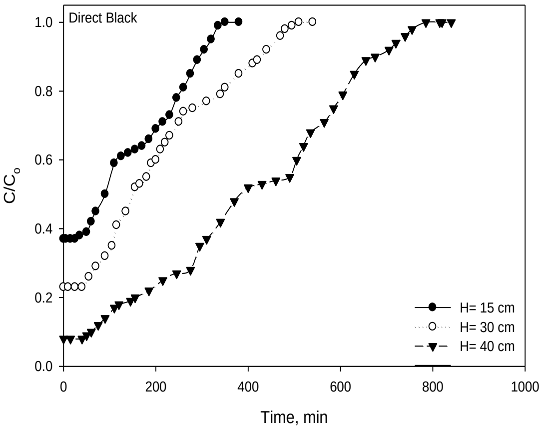

Fig. 14: Experimental breakthrough curves for adsorption of direct black onto ODS at different bed depth

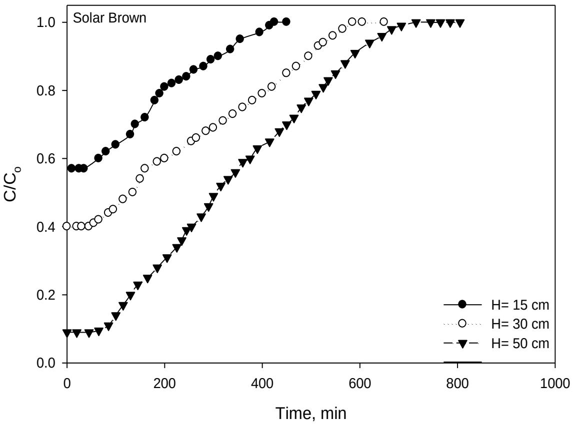

Fig. 15: Experimental breakthrough curves for adsorption of solar brown onto ODS at different bed depth

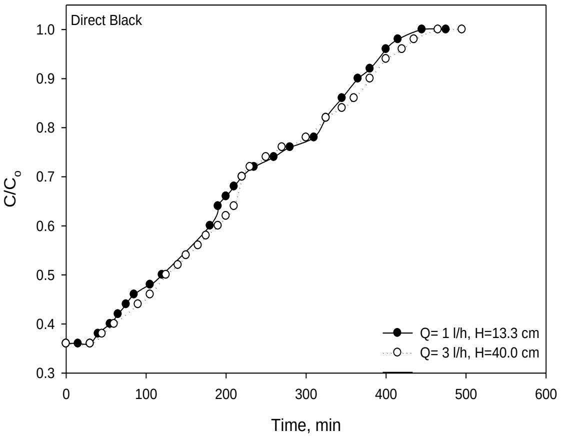

Fig. 16: Experimental breakthrough curves for adsorption of direct black onto ODS at constant residence time

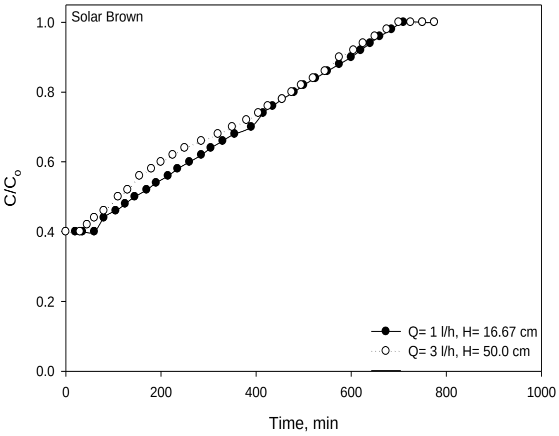

Fig. 17: Experimental breakthrough curves for adsorption of solar brown onto ODS at constant residence time

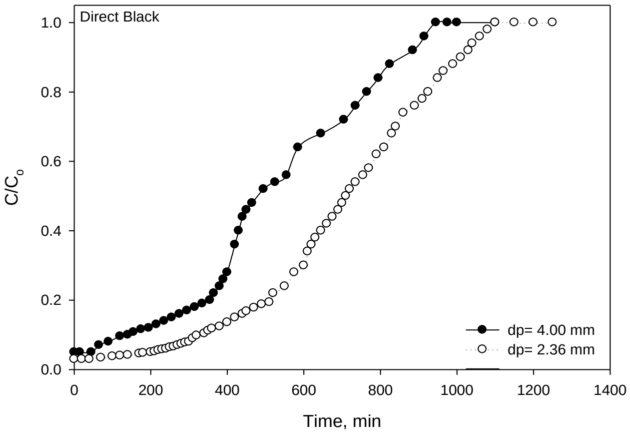

Fig. 18: Experimental breakthrough curves for adsorption of direct black onto ODS at different particle size

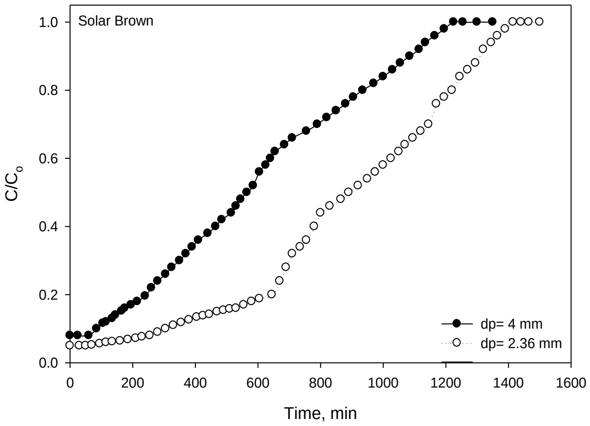

Fig. 19: Experimental breakthrough curves for adsorption of solar brown onto ODS at different particle size

REFERENCES

- Abbas H.B., 2005, "Removal of Dyes from Wastewater of Textile Industries Using Activated Carbon and Activated Alumina", M.Sc. Thesis, Chem. Eng. Dept., Collage of Eng., University of Baghdad.

- Chu, W., 2001,"Dye Removal from Textile Dye Wastewater Using Recycled Alum Sludge", Water Researches, 35(13), pp. 3147-3152.

- Galarneau, E. and Gehr, R., 1997, "Phosphorus Removal from Wastewaters: Experimental and Theoretical Support for Alternative Mechanisms", Water Research, 31 (2), pp 328-338.

- Ibtehal K.SH., 2002, "Study of Industrial Wastewater Treatment and Recycling Process For Cotton- Textile Industry", Ph.D. Thesis, Chem. Eng. Dept.,Collage of Eng., University of Baghdad.

- Kim, J.G., Kim, J.H., Moon, H.S., Chon, C.M. and Ahn, J.S., 2003a, "Removal Capacity of Water Plant Alum Sludge for Phosphorus in Aqueous Solutions", Chemical Speciation and Bioavailability, 14, pp 67-73.

- Malkoc, E. and Nuhoglu, Y., 2006, "Fixed Bed Studies for the Sorption of Chromium (VI) onto Tea Factory Waste", Chemical Engineering Science, V.61, pp 4363-4372.

- Markovska, L. and Meshko, V., 2001, "Solid Diffusion Control of The Adsorption of Basic Dyes onto Granular Activated Carbon and Natural Zeolite in Fixed Bed Column", J. Serb. Chem. Soc., 66 (7), pp 463-475.

- Maruf Mortula, Meaghan Gibbons and Graham, A. Gagnon, 2006, "Phosphorus Adsorption by Naturally-Occurring Materials and Industrial by-Products", J. Environ. Eng. Sci., 6, pp 157-164.

- Sarmad A. R., 2009," Phosphorous Removal from Wastewater using Alum", M.Sc. Thesis, Chem. Eng. Dept., Collage of Eng., University of Baghdad.

- Sips, R., 1984, Journal Of Chemical Physics, 16, pp 490-495.

- Weber, J. R. and Walter, J., 1972, "Physicochemical Processes for Water Quality Control", Wiley-Interscience, New York.

- Yakubu, M.K., Gumel M.S. and abdullahi A.M., 2008, "Use of activated carbon from date seeds to treat textile and tannery effluents", African Journal of science and technology (AJST), Science and Eng. Series, 9(1), pp.39-49.

- Yavuz, O. and Aydin, A.H., 2006, "Removal of Direct Dyes from Aqueous Solution using Various Adsorbents', Polish Journal of environmental studies, 15(1), pp.155-161.