Competitive Adsorption of Three Reactive Dyes by Activated Carbon

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ABSTRACT

In this study three reactive dyes (blue B, red R and yellow Y) in single , binary and ternary solution were adsorbed by activated carbon AC in equilibrium and kinetic experiments. Surface area, Bulk and real density, and porosity were carried out for the activated carbon.

Batch Experiments of pH (2.5-8.5) and initial concentration (5-100) mg/l were carried out for single solution for each dye. Experiments of adsorbent dosage effect (0.1-1)g per 100 ml were studied as a variable to evaluate uptake% and adsorption capacity for single dyes(5, 10) ppm, binary and ternary (10) ppm of mixture solutions solution of dyes. Langmuir, and Freundlich, models were used as Equilibrium isotherm models for single solution. Extended Langmuir and Freundlich were used of multi-dyes solutions.

Kinetic (contact time) experiments carried out for single dyes (5, 10)ppm, binary and ternary(10) ppm of mixture solutions at dosage of adsorbent 5 g/l and pH(6.2-6.7) in order to investigate the fitting with the kinetic models (pseudo first and second order) and intrapartical to determine the mechanism of transfer the molecules of dye from bulk phase to solid phase.

Beer law principle and modified method Multi linear Regression (MLR) was used for single, binary and ternary dyes solutions

KEY WORDS: adsorption. Reactive dyes, activated carbon, single binary and ternary dyes

الامتزاز التنافسي لثلاثة صبغات فعالة بواسطة الكاربون المنشط

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الخلاصة

في هذه الدراسة تم استخدام الفحم المنشط لغرض امتزاز ثلاثة أنواع من الصبغات الفعالة (الزرقاء ، الحمراء والصفراء) من محاليلها المفردة والثنائية والثلاثية بعد ان تم إجراء فحوصات المساحة السطحية والكثافة والمسامية للفحم.

التجارب وجبية تمت من خلال تغير الدالة الحامضية (8.5-2.5) و التركيز الأولي (5-100) ملغم/لتر و وزن المادة المازة لغرض احتساب نسبة الإزالة و اختيار أفضل موديل توازن (لانكمير و فراندليش) للصبغات المفردة و (لانكمير و فراندلش المعدلين) للصبغات المتعددة.

تم أجراء تجارب وجبية بتغير زمن التلامس لغرض تحديد ميكانيكية انتقال المادة وفق موديلات سيدو درجة أولى و ثانية وموديل الانتشار داخل الجسيمات.

تم أجراء الفحوصات بالمطياف الضوئي باستخدام مبدا قانون بيير و والقانون المتعدد الانحدار للصبغات المفردة والمتعددة.

الكلمات المفتاحية: ألأمتزاز ، الصبغات الفعالة ، الكاربون المنشط ، الصبغات المفردة والثنائية والثلاثية.

INTRODUCTION

Water is one of most important commodities which man has exploited then other resources for sustenance of his life. Water can be regarded polluted when it changes its quality or composition either or as a result human activities (Goal, 1997).

Many materials can cause pollution like inorganic salts, acids, alkaline, organic matter, suspended solid, floating (solid or liquid), heat, color, toxic material, microorganisms, radioactive material and foam-reducing matter. (Nemerow, 1971).

Pure water is colorless, but water in nature often colored by foreign substances. Color contributed by dissolved solid that remain after removal of suspended matter is known true color. Highly colored water is unsuitable for laundry, dying, paper making, dairy production and other industries. Thus the color water effect its marketability for both domestic and industrial use. (Peavy et al., 1986).

The azo dyes are by far the most important class, accounting for over 50% of all commercial dyes, and having been studied more than any other class. The most important distinguishing characteristic of reactive dyes is that they form covalent bonds with the substrate that is to be colored during the application process. Thus, the dye molecule contains specific functional groups that can undergo addition or substitution reactions with the OH, SO_3, and NH2 groups present in textile fibers. Most reactive dyes fall in the category of azo dyes. Virtually every hue in the dye spectrum can be achieved by appropriate structural modifications (mono- and di-azo dyes, combinations involving either single or multiple aromatic and heterocyclic ring systems). (Hunger, 2003). Currently reactive dyes one of the mostly used of dyes in textile industries because these dyes have high bond with fibers (El-Barghouthi et al., 2007). Conventional biological and coagulation/ flocculation treatment methods are insufficient in discoloring of such waste water due to the nature of synthetic of reactive dyes since they are stable to light and resistant to aerobic treatment (Shaker, 2002).

Adsorption process has been considered as one of the efficient methods for removing dyes pollution from waste water. Activated carbon is the most widely used as adsorbent in this process but it is costly (Chiou et al., 2003) 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. (Barka et al. 2011).

Adsorption involves the inter-phase accumulation or concentration of substance at surface or interface. the process can occur at an interface between two phases, such as liquid-liquid, gas–liquid, gas-solid, or liquid- solid interfaces. The material being concentrated or adsorbed is the adsorbate and the adsorbing phase is termed adsorbent. Adsorption is integral to abroad of physical, biological and chemical process and operations in the environmental field. Purification of gases by adsorption has played a major role in air pollution control, and adsorption of dissolved impurities from solution has been widely employed for water purification. Adsorption is now viewed as a superior method for waste water treatment and water reclamation. (Walter and Weber, 1972).

The aim of study to investigate the ability of activated carbon for removing of reactive dyes in single, binary and ternary system and fitting the results with isotherm and kinetic models.

EQUILIBRIUM ISOTHERM MODELS

- Langmuir isotherm

Considered sorption as a chemical phenomenon by assuming that the forces that are exerted by chemically unsaturated surface atom (total number of binding sites) do not extend further then diameter of one sorbet molecules and there for sorption is restricted to a monolayer.

The Langmuir isotherm relationship is shown in eq.(1) :

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

Where q_e adsorption capacity mg adsorbate/ g adsorbent

C_e final concentration at equilibrium mg/l.

q_m is maximum adsorption capacity in forming complete monolayer on the surface mg/g.

K_L is coefficient related to the affinity between the

Adsorbate and adsorbent (L/mg)

Langmuir relationship can be linearized by plotting ($1/q_e$) vs. ($1/C_e$) or (C_e/q_e) vs. (C_e).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (2)$$

Where $1/q_m$ is slope

$1/q_m K_L$ is intercept.

-Freundlich Model.

The Freundlich equation has been widely used for many years. This equation is special case for heterogeneous surface energies in which the energy term (K) in Langmuir equation varies as a function of surface coverage (q_e) strictly due to variation in heat of adsorption. This relationship is an empirical eq.(3) it doesn't not indicate a finite uptake capacity of the adsorbent and can thus only be reasonably for low and intermediate concentration range.

$$q_e = K_F C_e^{1/n} \qquad (3)$$

Where qe and Ce as above and K_F and n are constants. n larger then zero.
The linearization equation of Freundlich can be eq.(4):

$$\text{Log } q_e = \log K_F + 1/n \log C_e \qquad (4)$$

Where 1/n is slope
Log K_F is intercept

-Extended Langmuir Model

The Langmuir model can be extended for multi-component (binary & ternary) system to give the following two forms eq.(5) (Thomas and Crittenden, 1998;Vijayaraghavan and Yun, 2008;Dastgheb and Rockstraw 2002).

$$q_{e,i} = \frac{q_{mi} K_{L}{}_{i} C_{e,i}}{1 + \sum_{k=1}^{N} K_k C_{e,k}} \text{.....(a)}$$

$$q_{e,i} = \frac{q_{mi} K_{L}{}_{i} (C_{e,i} / \eta_i)}{1 + \sum_{k=1}^{N} K_k (C_{e,k} / \eta_k)} \text{.....(b)} \qquad (5)$$

Where q_{ei} and C_{ei} are the equilibrium capacity of the component 1 and C_{ei} is equilibrium concentration of component 1 in the multi-component solution respectively
K_{Li} is the single component Langmuir parameter for component 1 multi-component solution.
K_k is the single component Langmuir parameter of component 1 and others in the multi-component solution.
η is interaction factor between solutes.
Vijayaraghavan and Yun (2008) show for multi-component modeling an extended Langmuir equation with a constant interaction factor was used. The traditional extended Langmuir equation assumes no interaction between solute; which is not valid in real condition.

-Sheindrof-Rebhun-Sheintuch(SRS) model

This model can be represented for binary mixture as follow eq.(6) (Vijayaraghavan and Yun, 2008; Sheindorf et al., 1983; and Dastgheb and Rockstraw 2002).

$$(q_e)_{ij} = K_{Fi} C_{ei} \left(Cei + \theta i_j C_{ej}\right)^{[(1/n)-1]} \qquad (6)$$

Where $(qe)_{ij}$ is the amount of solute i which adsorbed per unit mass of adsorbent at presence of adsorbate j.
K_{Fi} is the single – component Freundlich constant for adsorbate i.
n the Freundlich exponent for solute i.
θ is the competitive coefficients represent effect of binary solutes.

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KINETIC MODEL

The transport and subsequent adsorption of adsorbate onto an adsorbent particle is usually described by one of the following transport mechanism or by combination of them film diffusion and intrapartical diffusion (Thomas and Crettinden, 1998; and Walter and Weber, 1972).

-Pseudo First Order model (Largergren Model)

Largergren model, proposed in 1898, assumes a first order adsorption kinetic and can be represented by the eq.(7):

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \qquad (7)$$

Where: q_e and q_t are adsorption capacity at equilibrium and at time t, respectively (mg.g-^{1}), k_1 is the rate constant of pseudo first order adsorption (min^{-1}).

After integration and applying boundary conditions:
q_t=0 at t=0 and q_t=q_e at t=t.
The integrated form becomes eq.(8):

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \qquad (8)$$

The values of log ($q_e - q_t$) were linearly correlated with *t*. The plot of log ($q_e - q_t$) versus t should give a linear relationship from which k_1 and q_e can be determined from the slop and intercept of the plot, respectively. The applicability of the pseudo-first order equation to experimental data generally, differs in two ways; the parameter $K_1(q_e-q_t)$ does not represent the number of available sites and the parameter log (q_e) is an adjustable parameter and often found not equal to the intercept of the plot log ($q_e - q_t$) versus t, whereas in true first order, log (q_e) should be equal to the intercept.

- Pseudo second order model.

The pseudo second-order adsorption kinetic rate equation is expressed as eq.(9):

$$\frac{dq_t}{dt} = K_1(q_e - q_t)^2 \qquad (9)$$

Where:

k_2 is the rate constant of the pseudo second order adsorption ($g.mg^{-1}.min^{-1}$).

For the boundary conditions:

q_t=0 at t=0 and q_t=q_e at t=t

the integrated form of the eq.(9) which can be rearranged to the linear form as eq.(10):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\;2}} + \frac{1}{q_e} t \qquad (10)$$

The plot of (t/q_t) and t of eq.(10) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

-The Intra-Particle Diffusion Model

The possibility of intra-particle diffusion of adsorbate onto the adsorbent by using the intra-particle diffusion model eq.(11).

$$q_t = K_p t^{1/2} + C \qquad (11)$$

Where: qt is the amount of dye adsorbed (mgg^{-1}) at time t; C is the boundary layer thickness and K_p

is the intra-particle diffusion rate constant (mgg^{-1} $min^{-1/2}$). The plots of the amount adsorbed, qt versus $t^{1/2}$. (Walter an Weber, 1972;)

EXPERMENTAL WORK

Materials

Adsorbent

Granular activated carbon with Surface area 911.581 m^2/g, Bulk density 711.8 and particle size (0.5-0.75)mm was washed with distilled water and dried in electrical oven at 100 ^oC

Adsorbate

Three reactive dyes(Blue B, Red R, Yellow Y) had been supplied from AL-Hilla textile factory south of Baghdad, (department of dying and printing). Simulated stock solutions had been prepared by dissolving 1 gm of each dye in one litter distilled water then diluted to the desired solutions concentration of single dyes (B, R and Y), binary dyes (BR, BY and RY) and ternary dye (BRY). (Issa and Al-Degs, 2009 Al-Gouti et al., 2007).

Table (1) shows some of specifications of these dyes.

The maximum wave length λ(nm) for each dye was measured using double beam spectrophotometer (Labomed, UVD. 3500 USA) and single beam spectrophotometer type (APEL PD- 303 UV JAPAN) (Karmo, 2007;Ong, 2010).

The analytical dyes concentration technique.

There are number of analytical methods that may be used for quantitative analysis of dyes solution like; first, chemical oxygen demand COD to characterize the content of organics which can be oxidize to inorganic .Second, UV-visible absorption spectrophotometer method. (Ekrami and Okazi, 2010) .

UV-visible absorption spectrophotometer method is the common procedure in determination of colorant concentration in their mixture.

The main principle in quantitative UV-visible spectrophotometer technique is linear relation between absorbance A and concentration of dissolved sample C (mg/l) which given by Beer-Lambert law eq.(12) (Al-Degs et al., 2008 and Ekrami and Okazi, 2010) .

$$A = K\,C + E \qquad (12)$$

Where A is absorbance of light at wave length λ.

K is absorbance coefficient (slope of linear relation).

C is Conc. of dye in solution (mg/l).

E is intercept of linear relation.

For multi-components (binary and ternary dyes) solution the absorptive (absorbance-coefficient for each dye is determined from absorbance measurement of dye at specific dye concentration when absorbance linear relation are constructed by plotting absorbance of each single dye against dye concentration at its wave length λ and re-plot at wave lengths of other dyes in the mixture of dyes solution. These determined coefficients are then used to determine the value of unknown dye concentration by using 2q. (13) which can be solving simultaneously by forming matrix which is called multiple linear regression (MLR) analysis. (Kang, 2007;De-Alba et al., 1997).

$$\begin{bmatrix} A_1 \\ A_2 \\ . \\ . \\ A_n \end{bmatrix} = \begin{bmatrix} K_{11} & K_{12} & . & . & K_{1m} \\ K_{21} & K_{22} & . & . & K_{2m} \\ . & . & . & . & . \\ . & . & . & . & . \\ K_{n1} & K_{n2} & . & . & K_{nm} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ . \\ . \\ C^m \end{bmatrix} \oplus \begin{bmatrix} E_1 \\ E_2 \\ . \\ . \\ E_n \end{bmatrix} \quad (13)$$

Where

A_i is the absorbance of at λ_i wave length. K_{ij} is absorbance coefficient of component (i) at wavelength of component (j). C_j Concentration of j^{th} component.

E_I is error of measurement (intercept value of linear relation) which can be ignored.

Calibration curves for analyses single and multi-dyes:

Four solution of single dyes (B, R and Y) with concentration (5, 10, 25 and 50 mg/l) were prepared. Absorbance at its wave lengths (585, 540 and 420 nm) were determinate then a linear relation was plotted between absorbance and each dye concentration at each wave length λ and repeat the process respectively in order to get absorbance coefficients for estimating the concentration of unknown dyes.

Adsorption capacity.

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. The characteristics of the adsorbate that are important include; solubility in the sense of chemical compatibility between the water and solute, the more hydrophilic a substance the less likely it is to be adsorbed. Conversely, a hydrophobic substance the will more likely be adsorbed , molecular structure affect the ease with which the molecule attach to the surface of adsorbent; aromatic being conducive to adsorption, molecular weight affect ease of adsorption through two effects- solubility and surface attraction higher molecular weight compound are generally less soluble and easily to adsorb so as to surface attraction, polarity affect the ease of adsorption because high polarity mean high soluble, and hydrocarbon saturation (Walter an Weber, 1972; and Tchohanoglous et al. 2003), the adsorption capacity is the adsorbent phase concentration which is computed using eq.(14) to determine type of equilibrium isotherm model:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (14)$$

Where q_e adsorbent (i.e., solid) phase concentration after equilibrium mg adsorbed /g adsorbent. C_o initial concentration of adsorbate.

C_e final concentration of adsorbate after adsorption has occurred mg/l.

V volume of liquid in the reactor.

m mass of adsorbent/g.

pH experiment.

The influence of pH on adsorption (i.e. the surface charged of adsorbent), the experiments were carried out by prepared samples of 10 ppm of each single dye (B , R and Y) at different pH (2.5, 4.5, 6.5 and 8.5) by adding HCl and NaOH to get the desired pH by using pH-meter type (Jenway, Model 3510, U.K).

Adding 0.5 g of AC in all sampling and shaking by shaker at 200 rpm for 12 h. The results where plotted as uptake% vs. pH, where uptake is :

$$\text{Uptake\%} = \frac{C_o - C_e}{C_o}\%$$

Where C_o and C_e are initial and equilibrium concentration. (Ong et al., 2010).

Initial dye concentration experiment.

Effect of initial concentration had been studied to determine the change of uptake% or adsorption capacity (q_e). (Suteu and Bilba, 2005).

Seven solutions of 100 ml for each single dye (B, R and Y) were prepared with different initial concentration (5, 10, 25, 40, 50, 75 and 100)ppm

and 0.5 g of adsorbent AC add to each sample and shaked for 12 hr at 200 rpm. The results were plotted as a relation between the adsorption capacity eq.(14) q_e vs. initial concentration (C_o).

Equilibrium isotherm experiment.

Adsorption equilibrium experiments were carried out by contacting different adsorbent (AC) dosage (0.1, 0.2, 0.3 ... 1) g with 10 samples of 100 solution for each dyes (single, binary and ternary). Each was placed in 300ml glass

Containers at pH 6.5 ± 0.3, Temperature 30 ± 3 C^o and agitated in the shaker at speed 200 rpm for 12 h.

Table (2) shows the concentration of solution (single, binary and ternary). Adsorption capacities q_e were obtained after equilibriums were obtained in order to plot equilibrium isotherm, adsorbed dye (C_o-C_e) vs. adsorbent dosage, where C_e is dye concentration (mg/ l) at equilibrium, to evaluate the type of curve comparing with the isotherm models. (Schimmel et al., 2010; Walker et al., 2007).

Examine **Table (2)** it can be seen that the final concentration is 10 mg/l for binary and ternary to keep the initial concentration equal for all solutions. (Al-Deg et al., 2007).

-Kinetic experiments

Ten samples with 100 ml volume of dyes solutions (single, binary and ternary) with concentration show in **Table (2)** had bean contact with 0.5g of adsorbent (AC) individually for each set of dyes solution at pH 6.5±0.5 and temperature 30 ±5 C^o and shaking at speed 200 rpm. At the desired time interval the samples were analyzed to determine the amount of adsorbed dye per mass of adsorbent (q_t) at time (t) eq.(16) below.

$$q_t = \frac{(C_o - C_t)}{m} V \qquad (16)$$

Where C_t is concentration of dye (mg/l) at time (t), V volume of sample 100 ml and m mass of adsorbent (g).

All above samples were filtrated before analyses using glass filter and paper filter .The first part of the filtrated liquor was discarded to eliminate the effect of the adsorption on the filter media. (Poots et al., 1976)

Plotting q_t vs. t to find the model to fit the experimental data (Pseudo first and second order and interapartical models) and to investigate the type of mass transfer mechanism (external, internal mass transfer or/and intraparticle diffusion). (Elass et al., 2010).

RESULTS and DISCUSSION

-Effect of pH (Single system).

Figure (1) show the decrease of pH (< 7, i.e increase H^+) leads to increase adsorbed dye (uptake %) (increase pH > 7 i.e increase OH^-).

The hydrogen and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the Adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process.

The pH value of the solution is an important parameter in the adsorption study since it determines the surface charged of adsorbent (Ong et al.2012). At low pH, the surface of adsorbent was surrounded by (H^+) which decrease the effect of negative functional groups on adsorbent surface and adsorption also increases due to increasing of the positive surface charge of adsorbents. (Abdul El-Latif et al. 2010).

Figure (1) shows that AC can be consider negatively –positively charges which are suitable for any adsorbate. The Y dye which is classified as an vinyl sulfone type which tends to longer lasting in water due to its high solubility and the result show the adsorption can be considered physical adsorption with AC and not chemical reaction which causes the binding which can be shown later more then other adsorbent and this is in agreement with adsorption of yellow reactive dyes (Fitria and Pranoto, 2003).

Effect of initial dye concentration (Single system).

Changing the single dye concentration (5, 10, 25, 40, 50,75 and 100 mg/l) has clear effects on adsorption capacity of activated carbon especially with yellow dye **Figure(2)**.

The AC shows the increase of initial concentration plays a role of driving force which enhance the process of mass transfer. (EL-Latif et al., 2010). With increasing initial concentration of dye solutions, the percent uptake decreased. This indicates that the saturation and quick exhaustion of the binding sites on the adsorbent reached as the number of dye molecules per unit volume increased. At low initial concentration, dye molecules are adsorbed on a specific binding site, however, when the concentration increases, there exist reductions in immediate solute adsorption due to the lack of available binding sites (Ong et al. 2010)

Effect of adsorbent dose (Single system).

Adsorbent dosage is representing an important parameter due to its strong effect on the adsorbent capacity at a given initial concentration of the adsorbate. **Figures.(3a, b and c)** show the plot of (C_o-C_e) against adsorbent mass at given type of adsorbent for single, binary and ternary respectively. These figures show that an increase in adsorbent dosage from 1 to 10 g/l resulted in an increase in the amount of adsorbed dye (C_o-C_e)

with (1-11 mg/l).The effect of adsorbent dosage on adsorption capacity (B, R and Y) in single and competitive dyes solution with adsorbent decrease with increase dosage. This can be explained in terms of depletion of dye in solution and accumulation of dye molecules on the surface of substrate giving rise to hindering the rest of dye to adsorb. (Ong et al.2010) (Mumins et al., 2007).

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-Equilibrium isotherms models (single system).

Two equilibrium isotherm models (Langmuir, Freundlich,) eq.(1, and 3) respectively were used to determine the constants by using the program (Statistics 10) for concentration 5 and 10 ppm single dyes (B, R and Y) with AC.

Fitting the experiment data with Langmuir model the constants K_L(l/mg) and q_m(mg/g)) for different single dyes were found and listed in **Table (3**).

Examining **Table(3)** it can be seen that the adsorption onto AC can fit Langmuir model for all single type dyes with R^2(0.93-0.975) except with yellow dye at 5 ppm R^2 (0.78) due to physical adsorption of yellow dyes and low concentration, knowing that an increase in an initial concentration will lead to an increase adsorbent capacity this is in agreement with (Fitria and Pranoto, 2003).

The experiments data were fitted with Freundlich model the constants of model K_F and n for different single dyes are tabulated in **Table (4).**

All values of n and R^2 are (1.2-1.7)and(0.85-0.97) respectively for AC therefore these values are accepted due to high surface area of AC which can form multi-layers of dye.

Equilibrium isotherms for(binary and ternary system).

Extended Langmuir model eq.(5) was used for the determination of an interaction factor)η) for the mixture of dye in binary and ternary system (η=1 there is effect of dye to other and η>>>1 no effect. Sheindrof- Rebhun- Sheintuch (SRS) model eq.(6) was used for binary system only for determination of competitive coefficientθ (θ=0 no effect) as shown in **Table (5) .**

Examining **Table (5)** it can be seen that the values of R^2 for Y dye are lower than others in binary and ternary systems dye with no effect of interaction factor (η) between dyes in Extended Langmuir model whileθ values show clear effect in (SRS) model where θ equal to zero represent no effect on difference for the dye to adsorbed as single or with other dyes in binary system. (Dastgheb and Rockstraw, 2002)

Kinetic models (effect of contact time)

The experimental adsorption capacity (q_t) was estimated at interval times (t) for single (5, 10 ppm), binary (10 ppm) and ternary (10ppm) systems by using eq.(16) and **Table (2)** for dyes solution with constant mass of (AC) graphs of plotting (q_t vs. t) are shown in **Figures (4a, b and c)** for single, binary and ternary B, R, and Y onto AC.

The fast adsorption at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the adsorbent and the following slower adsorption due to intraparticle diffusion. The initial rapid phase may also be due to the increased number of vacant sites available at the initial stage, consequently exists an increase in driving force of the concentration gradient between adsorbate in solution and adsorbate in the adsorbent (Ong et al.2010)

Pseudo -first order model was obtained by plotting log(qe-qt) vs. time (t) eq.(8) for AC with all dye (single , binary and ternary) to estimate the model constant K_1 and calculated q_{cal} and compared with experimental q_{exp} **Table(6).**

Pseudo -second order model had been achieved by plotting t/q_t vs. time (t) eq.(10) for AC with all dye (single , binary and ternary) to estimate the model constant K_2 and calculated q_{cal} and compared with experimental q_{exp} **Table (6).**

Intraparticle diffusion model had been achieved by plotting (q_t) vs. time (t) eq.(11) for AC with all dye (single , binary and ternary) to estimate the model constant K_p and calculated q_{cal} and compared with experimental q_{exp} **Table (6),**

Examining the results in **Table (6)** it can be seen that the data fitting with pseudo first order model with R^2 (0.767-0.985)for dyes all, with pseudo second order model R^2(0.84-0.998) for all dyes except for (BR) system R^2 is very low and with intrapartical diffusion model R^2(0.8-0.987) for B and R dyes systems while for Y dye system is (0.69-0.818).

The data show there are good fitting with all models except for yellow due to the physical adsorption by AC lead to accumulate the yellow dye and clogging the micro pores. The K_p increases with increases of initial concentration and decreases at presence of other dyes due to concentration gradient between the solution and porous adsorbent (Suteu and Bilba, 2005).

CONCLUSIONS

The study showed numbers of conclusions during batch experiments for adsorption of single, binary and ternary dyes solutions by Activated carbon.

-Blue, Red and Yellow reactive dyes play an anionic species in their solutions due to decrease the pH of distilled water from (7.5-7.7) to (6.3-6.6) during preparation of solutions

- Decreasing pH increase removal of three dye in single solutions due to effect of proton (H^+) on the surface of Activated Carbon which lead to decrease the effect of repulsive force between the molecules of dye and the negative surface.
- Effect of initial concentration was clear to increase uptake at increase initial concentration for AC.
- AC show good fitting with Langmuir and Freundlich for binary and ternary systems without interaction of presence more one dye.

-AC show follow all models of kinetic with different acceptable correlation with calculated adsorption capacity by pseudo first model more closed the experimental.

Intrapartical diffusion curve for AC show the external diffusion is important stage

REFFERENCES

- Al-Degs, Y. S., Khraisheh, M. A., Allen, S. J., Ahmed, M., and Walker, G. M., 2007, Chemical Engineering Journal, vol. 128, pp. 163-167.
- AL-Degs Y., El-Sheikh, A. H, Al-Gouti, M. A. and Sunjuk, M. S., 2008, Jordan Journal of Chemistry, vol. 3, No. 3, pp. 321-336.
- Abdul El-Latif(1), M. M., Ibrahim, A. M., El-kady, M. F. and Ossman, M. E., 2010, Journal of American Science, vol. 6, No. 5, pp. 280-292.
- Al-Gouti, M. A., Khraisheh, M. A., Allen, S. J. and Ahmed, M., 2007, Journal of Hazardous Materials, vol. 146, pp. 316-327
- Barka N.,Qourzal,S. , Assabbane, A., Nounah,A., and AitIchou,Y.,2011,Journal of Saudi Chemical Society,vol.15, pp.263–267.
- Chiou, M. S., Kuo, W., and Li, H. Y., 2003, J. Environmental Science and Health, vol. A38, No. 11, pp. 2621-2631.
- Dastgheib, S. A. and Rockstraw, D. A., 2002, J. Carbon, vol. 40, pp. 1853-1861.
- De-Alba, P. L., Martinze, L. L., Rodriguez, L. I., and Hernandez, J. A., 1997, J. The Analyst, December, vol. 122, pp. 1575-1579.
- Ekrami, E. and Okazi, M., 2010, World App. lied Science Journal, vol. 11, No. 8, pp. 1025-1034.
- El-Barghouthi, M. I., El-Sheikh, A. H., and Al-Degs, Y. S., 2007, J., Separation Science and Technology, vol. 42, pp. 2195-2220.
- Fitria, R. and Pranoto, N., 2003, J. Alchemy, September, vol. 2, No. 2, pp. 10-18.

-Goel, P. K., 1997, "Water Pollution- causes, effects and control", New Age International Publishers, New Delhi, India.

-Hunger, K. 2003, "Industrial Dyes Chemistry, Properties, Applications " WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

- Issa, A. A. and Al-Degs, Y. S., 2009, Jordan Journal of Chemistry, vol. 4, No. 1, pp. 89-101.
- Kang, Q., 2007, Separation Purification Technology, vol. 57, pp. 356-365.
- Karmo, O., 2007, Al-Assad Journal of engineering Science, University of Damascus No. 23.
- Mumin, M. A., Khan, M. M. and Uddin, M. j., 2007, International J. of Environmental Science and Tech. vol. 4, No. 4, pp. 525-532
- Nemerow, N. L., 1971, "Industrial Water Pollution- Origins, Characteristics and Treatment", Addison-Wesley publishing company, Canada.

. - Ong, S. T., Keng, P. S. and Lee, C. K., 2010, American Journal of App. lied Science, vol. 7, No. 4, pp. 447-452.

- Peavy, H.S., Rowe, D. R., and Techobanoglous, G., 1986, "Environmental Engineering", McGraw-Hill book company, New York, USA.
- Poots, V. J., McKay, G. and Healy, J., 1976, Water Research, vol. 10, pp. 1061-1066.
- Schimmel, D., Fagnani, K. and Silva, E. A., 2010, Brazilian Journal of Chemical Engineering, vol. 27, No. 2, pp. 289-298.
- Shakir, I. K., 2002, Ph.D., Thesis, University of Baghdad, College of engineering.
- Sheindorf, C., Rbhun, M. and Sheintuch, M., 1983, Chemical Engineering Science, vol. 38, No. 2, pp. 335-342.
- Suteu, D. and Bilba, D., 2005, J. Acta. Chim. Slov., vol. 52, pp. 73-79.
- Tchohanoglous, G., Burton F. L. and Stensel, D., 2003, "Waste Water Engineering- Treatment and reuse-", Mc-Craw-Hill Co., 4th edition, Hong Kong, China
- Thomas, W. J. and Crittenden, B., 1998, "Adsorption technology and Design", Butterworth Heinemann, Oxford, UK.
- Vijayaraghavan, K. and Yun, Y. S., 2008, Journal of Hazardous Material, vol. 153, pp. 478-486.
- Walker, G. M., Al-Degs, Y., El-Barghouthi, M. I. and El-Shiekh, A., 2007, Dyes and Pigments, vol. xx, pp. 1-8.

. - Walter, J. and Weber, JR., 1972, "Physicochemical Process for Water Quality Control", Wiley-Interscience, New York, USA

NOMENCLATUR

A Absorbance of light at wave length λ

C Conc. of dye in solution (mg /l)

C_o Initial concentration of adsorbate

C_{ei} Concentration of dye i at equilibrium in multi-dyes solution (mg /l)

C_e Concentration at equilibrium (mg /l)

C_t Concentration of dye (mg /l) at time t

E Intercept of linear relation of Absorbance equation

K Absorbance coefficient (slope of linear relation)

K_{Fi} The single-component Freundlich constant for adsorbate i l/mg

K_F Freundlich constant for adsorbate (l/mg)

K_1 The rate constant of pseudo first order adsorption (s^{-1})

K_2 The rate constant of the pseudo second order adsorption ($g.mg^{-1}. s^{-1}$)

K_{Li} The single component Langmuir parameter for component 1 multi-component solution.

K_L Coefficient related to the affinity between the adsorbate and adsorbent for Langmuir model (l/mg)

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

K_{xy} Absorbance coefficients(slope of line) where x represent used type of dye and y the used wave length

q_{cal} Predicted adsorption capacity(mg/g)

q_e Adsorbent (i.e., solid) phase concentration after equilibrium mg adsorbed/g adsorbent

q_{ei} The equilibrium capacity of the component 1 in multidyes (mg/g)

q_m Maximum adsorption capacity in for complete monolayer on the surface (mg/g)

q_t Adsorption capacity at equilibrium and at time t, ($mg.g^{-1}$)

m Mass of adsorbent (g)

n Freundlich Constant

β The competitive coefficient represent effect of binary solutes

η Interaction factor between solutes in extended Langmuir

ρ Density (kg/m^3)

Table (1) Main characteristics of the dyes used in this study

Item	Reactive blue B	Reactive Red R	Reactive Yellow Y
Trade name	Blue H3R	Red 3B	Yellow FG
Origin	India	China	Swiss
Phase	Solid/ Powder Package 25 kg	Solid/Powder Package 25kg	Solid/ Powder Package 25 kg
Wave length (nm)	585	540	420
Solubility g/l	90	100	150
pH	6.2-6.5	6.2-6.5	6.2-6.5

Table (2) Initial system concentrations for equilibrium adsorption isotherms.

Adsorption system	Dye initial conc. mg/l	Mixture dye initial conc.	Ratio of mixing
Single B	5 10	5 10	
Single R	5 10	5 10	
Single Y	5 10	5 10	
Binary (B+R)	B: 5, R:5	10	B:R (1:1)
Binary (B+Y)	B: 5, Y:5	10	B:Y (1:1)
Binary (R+Y)	R: 5, Y:5	10	R:Y (1:1)
Ternary (B+R+Y)	B: 3.33, R: 3.33 Y: 3.33	10	B:R:Y (1:1:1)

Table (3) Langmuir constants for different single dye.

Dye	Dye Concentration C_o	
B	**5 ppm**	**10 ppm**
K_L(l/mg)	0.4	0.187
q_m(mg/g)	2.98	10.56
R^2	0.93	0.95
R		
K_L(l/mg)	0.432	0.062
q_m(mg/g)	2.664	12.6
R^2	0.96	0.95
Y		
K_L(l/mg)	3.45	0.1406
q_m(mg/g)	6.06	28.25
R^2	0.78	0.975

Table (4) Freundlich constants for different single dye.

DYE	Dye Concentration	
B	**5 ppm**	**10 ppm**
K_F(mg/g)	0.831	0.965
n	1.6	1.238
R^2	0.92	0.96
R		
K_F(mg/g)	0.778	0.807
n	1.7	1.2
R^2	0.97	0.97
Y		
K_F(mg/g)	3.48	0.788
n	1.23	1.62
R^2	0.85	1

Table (5) Extended Langmuir model for binary and ternary system and SRS models for binary (AC) system.

Type of dyes solutions	Extended Langmuir model				Extended Freundlich model(SRS)	
	η_1	η_2	η_3	R^2	θ	R^2
B-R	2.73	40407		0.97	5.46	0.86
B-Y	2.736	189044		0.78	7.32	0.635
B-RY	5.2	520705	242577	0.8		
R-B	0.78	0.95		0.9	0.974	0.89
R-Y	2.7	347981		0.7	7.32	0.58
R-BY	0.017	0.088	0.16	0.39		
Y-B	19.28	35530		0.785	742	0.91
Y-R	19.3	83860		0.776	580	0.81
Y-BR	31.37	176	93	0.73		

Table (6) Kinetic models constants for AC adsorbent

Dyes solutions	q_{exp} mg/g	Pseudo -first order model			Pseudo -second order model			Intrapartical diffusion model	
		q_{cal} mg/g	K_1 (1/s) 10^{-4}	R^2	q_{cal} mg/g	K_2 (g/mg s) 10^{-4}	R^2	K_p (mg/g $s^{0.5}$) 10^{-4}	R^2
B 5	0.8	0.788	2.33	0.957	0.99	2.167	0.977	47.76	0.8
B 10	1.24	2.36	1.83	0.88	2.85	0.117	0.77	101	0.97
B-R	0.42	0.68	1.217	0.77	9.26	0.02	0.02	34.85	0.94
B-Y	0.3	0.24	1.117	0.93	0.4	3.08	0.94	18.72	0.9
B-RY	0.346	0.544	1.8	0.94	0.85	0.383	0.76	29.7	0.95
R 5	0.58	1	1.833	0.95	2.2	0.08	0.93	49.08	0.93
R 10	0.8	0.8	1.67	0.97	1.1	1.083	0.96	54.02	0.9
R-B	0.5	1.6	1.417	0.93	0.72	1.217	0.99	34.46	0.98
R-Y	0.44	0.38	0.767	0.96	0.61	1.24	0.91	28.35	0.96
R-BY	0.376	0.72	1.767	0.86	1.07	0.02	0.84	31.37	0.91
Y 5	1	0.87	2.08	0.99	1.16	2.67	0.97	52.9	0.81
Y 10	2	1.57	2.083	0.98	2.2	2.167	0.99	84.65	0.82
Y-B	0.77	0.4	1.8	0.93	0.85	5	0.98	34.34	0.69
Y-R	0.77	0.35	2.717	0.81	0.87	4.833	0.98	36.15	0.69
Y-BR	0.566	0.223	1.167	0.91	0.6	9.167	0.99	19.5	0.75

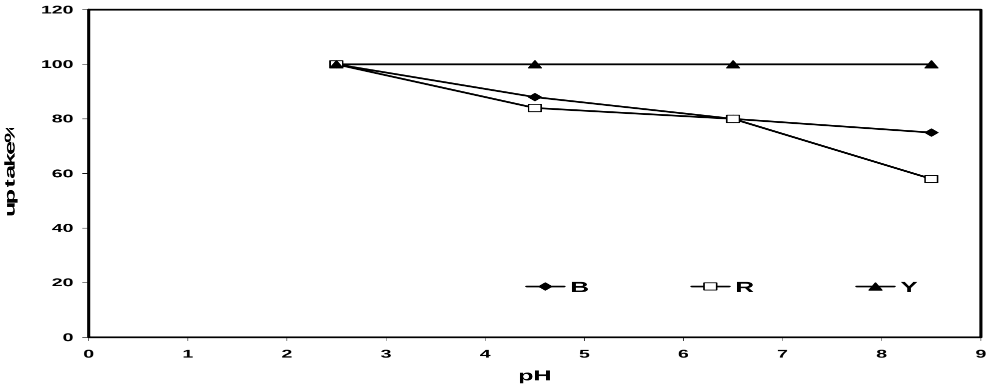

Figure (1) Effect of pH on uptake for AC at C_o 10ppm, adsorbent dosage 0.5 g per 100ml.

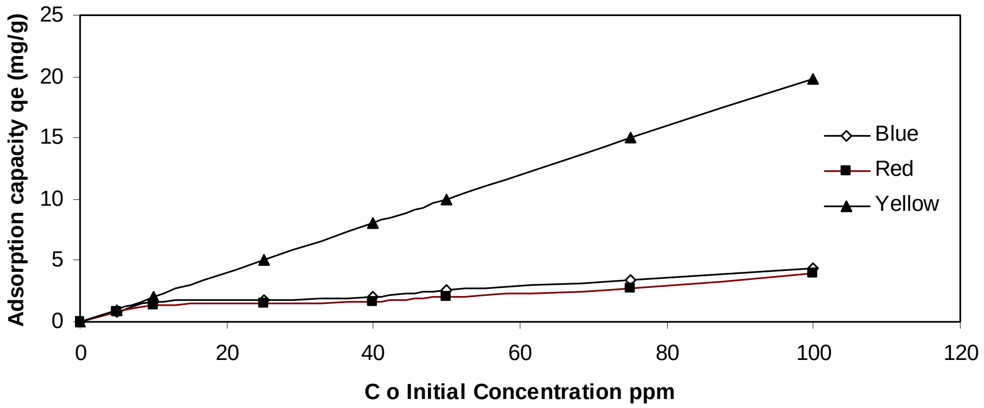

Figure (2) Effect of initial concentration dyesB , R and Y on adsorption capacity at constant dosage of adsorbents 0.5 g per 100ml (AC), pH 6.2-6.5.

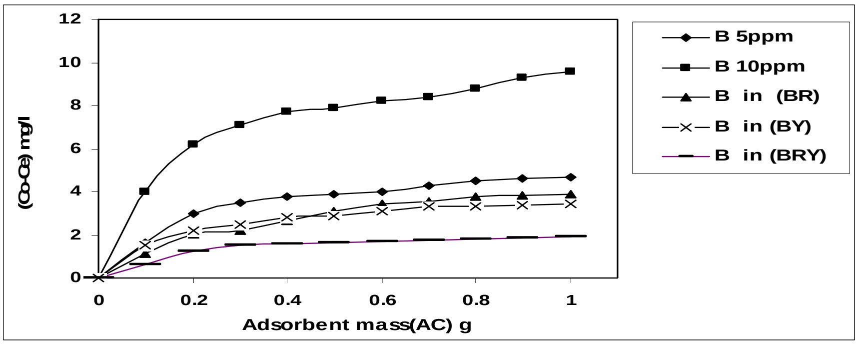

Figure (3a) Show the amount of adsorbed dye Blue (Single, binary and ternary) at different adsorbent dosage (AC) 0.5 g per 100ml, pH 6.2-6.5.

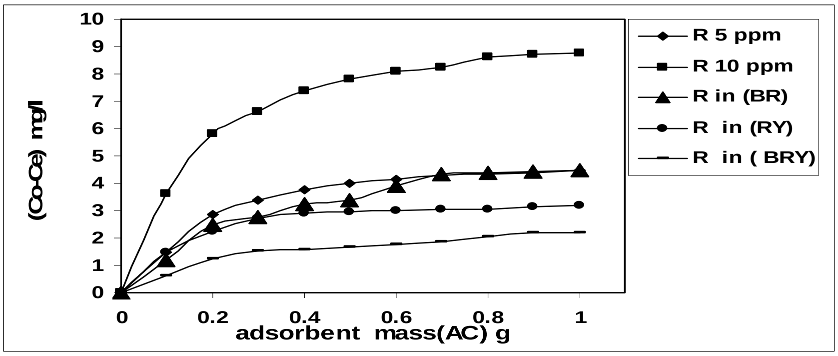

Figure (3b) Show the amount of adsorbed Red dye (Single, binary and ternary) at different adsorbent dosage (AC) 0.5 g per 100ml, pH 6.2-6.5.

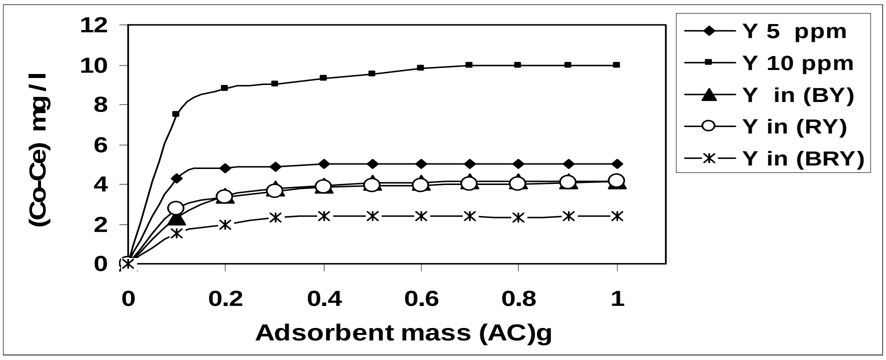

Figure (3c) Show the amount of adsorbed Yellow dye (Single, binary and ternary) at different adsorbent dosage (AC) 0.5 g per 100ml, pH 6.2-6.5.

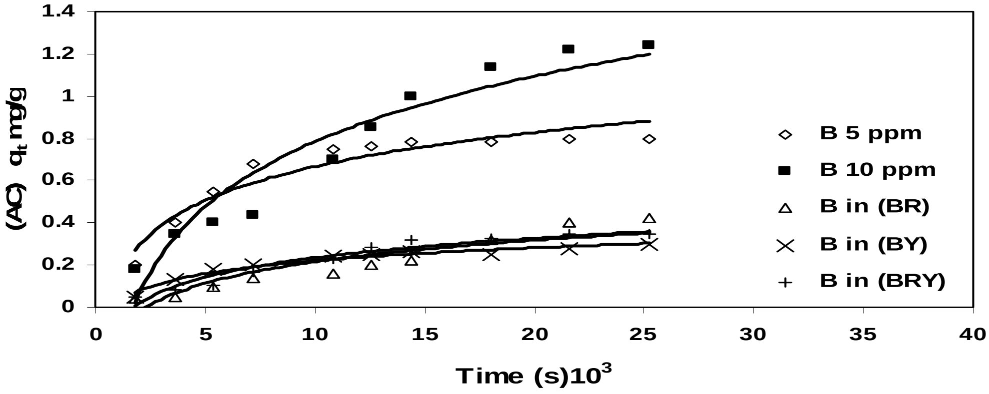

Figure (4 a) Adsorption capacity of AC for blue dye (Single, binary and ternary) for all dyes at interval time

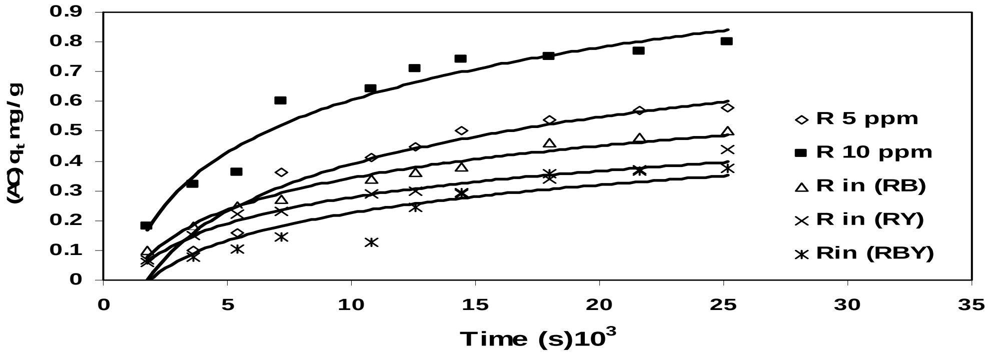

Figure (4 b) Adsorption capacity of AC for Red dye (Single, binary and ternary) for all dyes at interval time

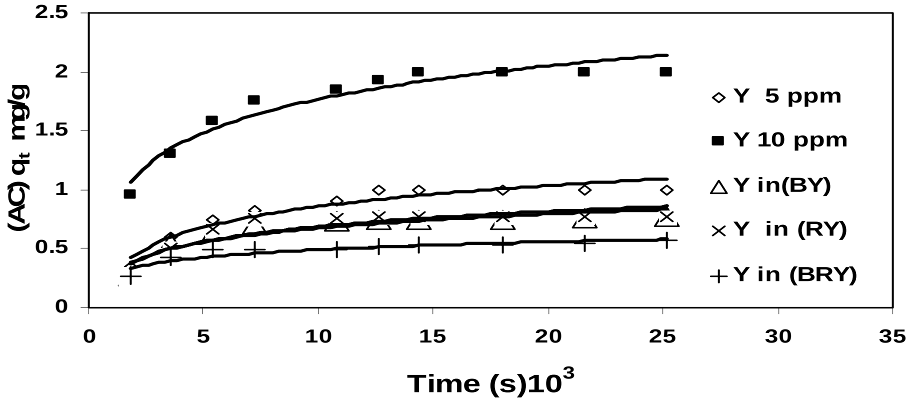

Figure (4 c) Adsorption capacity of AC for Yellow dye (Single, binary and ternary) for all dyes at interval time