Batch and Fixed-Bed Modeling of Adsorption Reactive Remazol Yellow Dye onto Granular Activated Carbon

Mohammed Sadeq Salman
Instructor
Computer Center
University of Baghdad
Iraqmas68@ yahoo.com

Waleed Mohammed Abood
Head of Engineering
Head of engineers
Ministry of industry-Iraq
Env_eng_waleed@yahoo.com

DhaferFaza Ali
Head of Chemists
Ministry of industry-Iraq
Dhaferali32@yahoo.com

ABSTRACT

In this work, the adsorption of reactive yellow dye (Remazol yellow FG dye) by granular activated carbon (GAC) was investigated using batch and continuous process. The batch process involved determination the equilibrium isotherm curve either favorable or unfavorable by estimation relation between adsorption capacity and concentration of dye at different dosage of activated carbon. The results were fitted with equilibrium isotherm models Langmuir and Freundlich models with R^2value (>0.97). Batch Kinetic study showed good fitting with pseudo second order model with R^2 (0.987) at contact time 5 h. which provesthat the adsorption is chemisorptions nature. Continuous study was done by fixed bed column where breakthrough time was increased at flow rates (21.67, 12.5 and 6 ml/min) and initial dye concentration (80, 40, 20 and 10 mg/l) were decreased and bed depth was increased (5, 10, 15 and 20 cm). The adsorption data were fitted to the fixed-bed adsorption mathematical models Thomas and Yoon-Nelson models. The results fitted well to the Thomas and Yoon-Nelson models with correlation coefficient, $R^2 \geq 0.944$. Average relative error ARE% was applied to examine the theoretical and experimental results.

Key Words: Adsorption, Reactive Yellow dye, Granular activated carbon, Fixed bed column

النمذجة الرياضية لامتزاز الصبغة الصفراء الفعالة باستخدام الفحم المنشط في تجارب الوجبة و تجارب الحشوة الثابتة

محمد صادق سلمان
مدرس
مركز الحاسبه الالكترونيه
جامعة بغداد

د. وليد محمد عبود
رئيس مهندسين
هيئة البحث والتطوير
وزارة الصناعه

ظافر فزع علي
رئيس كيميائيين
هيئة البحث والتطوير
وزارة الصناعه

الخلاصة

في هذا البحث تم امتزاز الصبغة الصفراء الفعالة باستخدام الفحم المنشط الحبيبي خلال تجارب وجبية و مستمرة حيث تضمنت التجربة الوجبية عملية تحديد منحني التوازن عند ثبوت درجة الحرارة وبيان هل نوعه مفضل ام غير مفضل من خلال احتساب علاقة مابين سعة الامتزاز وتركيز الصبغة المتبقية في المحلول بعد الامتزاز بعد استخدام اوزان مختلفة من الفحم المنشط حيث وضحت النتائج مطابقة مع موديل لانكمير بقيمة مربع معامل ارتباط اكثر من 97% في حين تطابقت تجارب تغيير زمن التلامس عند ثبوت الحجم مع موديل سيدو ذا المرتبة الثانية بقيمة مربع معامل الارتباط 98.7% في اقصى زمن تلامس مقداره 5 ساعات والذي يثبت ان طبيعة الامتزاز بين الصبغة والفحم المنشط هو امتزاز كيمياوي.

التجارب المستمرة من خلال استخدام حشوة ثابتة عند عدة متغيرات مثل معدل جريان محلول الصبغة من الاعلى الى الاسفل بمقدار (6 , 12.5 , 21.67) مل/دقيقة و عند تغيير تركيز الصبغة (10 , 20 , 40 ,80) ملغم/لتر وعند عمق حشوات (5 , 10 , 15 , 20) سم واحتساب منحني الانكسار ومقارنة النتائج مع موديلين ثوماس و يوون نيلسون و احتساب معدل الخطاء بين النتائج النظرية والعملية .

1- INTRODUCTION

Water is one of most important commodities which man has exploited a 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 as true color. Highly colored water is unsuitable for laundry, dying, paper making, dairy production and other industries. Thus the color water effects 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 NH_2 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.**

Wastewater effluent from the textile industries can be particularly problematic due to the presences of color in the final effluent. This color in the water system is highly visible and thus undesirable. Textile industries consist of multi-processes which produce wastewater which generally colored, different pH value, high chemical oxygen demand COD, high suspended solid and high temperature. **Nemerow, 1971.**

There are many technologies currently available for treating wastewater from textile industry which include Biological treatment,\Chemical precipitation, Ultra filtration, Adsorption and Advanced Oxidation. **Abood, 2012.**

Adsorption is a widely used method to treat industrial waste gas and effluent due to its low cost, high efficiency and easy operation. Particularly, the adsorption process is suitable for decontaminating those compounds of low concentration or high toxicity, which are not readily treated by biological processes. Based on the operation mode, adsorption can be generally classified into static adsorption and dynamic adsorption. Static adsorption, also called batch adsorption, occurs in a closed system containing a desired amount of adsorbent contacting with a certain volume of adsorbate solution, while dynamic adsorption usually occurs in an open system where adsorbate solution continuously passes through a column packed with adsorbent.

For column adsorption, how to determine the breakthrough curve is a very important issue because it provides the basic but predominant information for the design of a column adsorption system. Without the information of the breakthrough curve one cannot determine a rational scale of a column adsorption for practical application. There are two widely used approaches to obtain the breakthrough curve of a given adsorption system: direct experimentation or mathematical modeling. The experimental method could provide a direct and concise breakthrough curve of a given system. **Zhe, 2013.**

Reactive yellow dye was investigated as an adsorbate to be removed onto activated carbon during batch and the result shows good removal of dyes when increasing adsorption capacity at increasing initial concentration and temperature and the adsorption is considered as an endothermic**. Sulyamon and Abood 2013.**

The aim of this study is examining the reactive yellow dye as adsorbate and granular activated carbon as adsorbent in batch process using Langmuir and Freundlich models as equilibrium isotherm models and for kinetic study tested pseudo first and second order models were applied to investigate mechanism of adsorption, while for the continuous adsorption the fixed bed column was used with different condition (initial dye concentration , bed depth and flow rates)and the results were tested with most widely used models (Thomas and Yoon- Nelson) and the validity of results were approved according to the average relative error (ARE%) as a error function.

2- ADSORPTION ISOTHERMS MODELS

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration.

Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration**. Foo and Ahmed 2010**

2-1 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 than diameter of one sorbet molecules and therefore sorption is restricted to a monolayer.

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

$$q_e = q_m \frac{K_L \ C_e}{1 + K_L \ C_e} \tag{1}$$

Where q_e adsorption capacity mg adsorbate / g adsorbent, C_e final concentration at Equilibrium mg/l. q_m 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. ($1/C_e$) where $1/q_m$ is intercept ($1/q_m K_L$) is slope in Eq.(2).

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \tag{2}$$

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following Eq. (3)

$$R_L = 1/\,(1+ K_L \, C_o) \tag{3}$$

where C_o (mg/l) is the initial concentration of adsorbate, and K_L (L/mg) is Langmuir constant. The value of R_L indicates the shape of the isotherm which is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$)

2-2 Freundlich Model .

The Freundlich's Equation has been widely used for many years. This Equation is special case for heterogeneous surface energies in which the energy term (K_F) in Langmuir's Equation varies as a function of surface coverage (q_e) strictly due to variation in heat of adsorption. This relationship is empirical Eq. (4). It doesn't indicate a finite uptake capacity of the adsorbent and can thus only be reasonably for low and intermediate concentration range.

$$q_e = K_F C_e^{1/n} \tag{4}$$

Where q_e and C_e are as above and K_F and n are constants. n is larger than zero.
The linearization equation of Freundlich can be Eq.(5):

$$\log q_e = \log K_F + 1/n \log C_e \tag{5}$$

Where 1/n is slope and log K_F is intercept

3- ADSORPTION KINETICS

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 Crittenden, 1998**). Variations among such models are distinguished according to the rate limiting mass transport step. Examples of those kinetic models include; the linear driving force model, the surface diffusion model, the pore diffusion model, and the film pore and surface diffusion model. **Ho et al., 2000**

kinetic modeling was examined by researchers to investigate the mechanism of adsorption and potential rate–controlling process such us mass transfer and chemical reaction. The pseudo-first order and pseudo-second order kinetics models were used to analyze the adsorption kinetic of textile dyes**. Isa, et al., 2007**

3-1- Pseudo first order model

This model assumes a first order adsorption kinetic and can be represented by the Equation (6):

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{6}$$

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 (7):

$$\ln(q_e - q_t) = \ln(q_e) - Kt \tag{7}$$

The values of ln (q_e– q_t) were linearly correlated with *t*. The plot of ln (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.

3-2 Pseudo second order model.

The pseudo second-order adsorption kinetic rate Equation is expressed as Eq (8):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{8}$$

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_e

The integrated form of the Eq (8) which can be rearranged to the linear form as Eq (9):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{2}} + \frac{1}{q_e} t \tag{9}$$

The plot of (t/q_t) and t of Eq (9) should give a linear relationship from which q_e and K_2 can be determined from the slope and intercept of the plot, respectively.

4- DYNAMIC ADSORPTION

The adsorption equipment is the heart of the system. Three types of adsorber are generally used in wastewater application: down flow fixed bed, packed moving bed an up flow expanded – bed **Cavaseno, 1980**. Down flow fixed bed adsorbers offer the advantage of simple operation plus the ability to serve as a filter and can be operated either under pressure or by gravity flow. Typical superficial linear velocity for liquid in bed is 0.3 (m/min) in vertical direction to prevent settling **Tchohanoglous et al., 2003.** Empirical or short cut models are still used extensively for the design of fixed beds. This is not only due to their simplicity and reliability but also because of the formidable nature of more rigorous alternative. **Thomas and Crittenden, 1999**

4-1 Thomas Model was developed for adsorption processes in which external and internal diffusion limitations are not present. The linearized form of the Thomas model can be expressed as in Eq. (10) . **Sachin et al., 2010**

$$\ln\left(\frac{C_o}{C} - 1\right) = \frac{K_T q_{cal} m}{Q} - \frac{K_T C_o}{Q} V_{eff} \tag{10}$$

where K_T is the Thomas rate constant (mL/min.mg), q_e is the equilibrium of reactive yellow dye uptake (mg/g), C_o is the inlet reactive yellow dye concentration (mg/L), C_t is the effluent reactive yellow dye concentration at time t (mg/L), W is the mass of adsorbent (g), Q is the inlet flow rate (mL/min) and t is the flow time (min). The value of Co/Ct is the ratio of inlet to outlet reactive yellow dye concentrations. A linear plot of ln [(C_o/C_t) − 1] against time (t) was drawn to determine the values of qe and K_T from the interception point and slope of the plot, respectively.

4-2 The Yoon–Nelson model was developed model to describe the adsorption behavior in the continuous column adsorption. The linearized form of the Yoon-Nelson model is given in Eq.(11). **Yahaya et al., 2011**

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = K_{YN} t - K_{YN} T \tag{11}$$

where, K_{YN} is the rate velocity constant(L/min) and T is the time in (min) required for 50% adsorbate breakthrough. A linear plot of ln [C_t / (C_o −C_t)] against sampling time (t) was used to determine the values of K_{YN} and τ from the slope and intercept of the plot. q_e is the amount of adsorbate being adsorbed in a fixed bed is half of the total adsorbate entering the adsorption bed within 2Tperiod. Hence, the following Equation (12) can be obtained for a given bed**. Sotelo, et al, 2012.**

$$q_e = \frac{q_{adsorbed}}{m} = \frac{C_o[(Q/1000)t]}{2m} = \frac{C_o.Q.T}{1000.m} \qquad (12)$$

The validity of the adsorption model was further determined by using normalizedaverage relative error (ARE%) Eq.(13) for experimental and theoretical results of (C_t/C_o**). Foo and Hameed, 2010**

$$ARE\% = \frac{100}{N}\sum\left[\frac{\left|X_{\exp} - X_{cal}\right|}{X_{\exp}}\right] \qquad (13)$$

Where X represent the result and N number testing time.

5- EXPERIMENTAL MATERIALS AND METHOD

5-1-Adsorbent

Granular activated carbon GAC was used as adsorbent with particle size (0.5–0.75 mm), bulk density 711.8 kg/m^3, porosity 53.44%, and surface area 911.56m^2/g.

AC was washed with distilled water to remove dust and fine particles then dried at 100°C.

5-2-Adsorbate

A yellow FG reactive dye (Remazol yellow 42) was obtained from Iraqi textile factory as a powder with solubility 150 g/l (manufacture companies). A stock of dye solution was prepared by dissolving the required amount of dye in distilled water. The dye was measured at a maximum wave length 420 (nm) using double beam spectrophotometer (Labomed, UVD. 3, 500 USA) and single beam spectrophotometer type (APEL PD- 303 UV JAPAN) which was used for the analyzing of samples. **Al-Degs, et al, 2009**

5-3 Isotherm Experiments

The batch adsorption isotherm experiments were carried out by varying adsorbent dosage m (0.05,0.1, 0.15, 0.2, 0.3and 0.4) g of activated carbon GAC which were added to 50cm^3 of aqueous dye solution with initial yellow concentrations C_o 10 mg/l in a 100 cm^{3}conical flask. The mixture was agitated at 200 rpm in a shaker at a constant temperature and pH for 5 h. The suspensions were decanted and the solutions were analyzed for yellow reactive dye concentrations C_e at equilibrium while adsorption capacity q_e at equilibrium is calculated for each using Eq.(14)

$$q_e=(C_o-C_e)*50/1000*m \qquad (14)$$

5-4 Kinetic Experiments

Effect of contact time was determined by the “limited bath” technique. A 5 g sample of GAC (m) was added to 500 ml volume of reactive dye solution with initial dye concentration 10 mg/l, under stirring for 5 h. The temperature was room temperature. After different time intervals (5, 15, 30,60,90,120,180,240 and 300 minutes) volumes of 5 ml of each sample analyzed for yellow reactive dye concentrations C_t at time t then adsorption capacity were estimated using Eq.(15) for each sample.

$$q_t=(C_o-C_t)*50/1000*m \qquad (15)$$

5-5 Fixed Bed Column Experiments

Removal of yellow dye in continuous process was investigated using fixed- bed of GAC in Perspex column with internal diameter 1.25 cm and length 50 cm **Fig. 1** at different conditions, bed height (5, 10, 15 and 20 cm), dye concentration (10, 20,40 and 80 mg/l), and flow rate (21.67, 12.5 and 6) ml/min. At the top of the fixed-bed, a layer of glass bed was used to provide uniform inlet flow to the column and the same layer was placed at the bottom to prevent discharging any AC particles during sampling. Dye solution was introduced into the top column and was controlled by perstatic pump range (1-10) ml/min which is adjusted for desired flow rates. Samples were collected at regular time intervals for analyzing.

6-RESULTS and DISSCUSSION

6-1 -Equlibruim Isothrm

Fig. 2 shows q_e vs. C_e as a favaroble curve for reactive yellow dye adsorption by activated carbon due to the separation factor R_L vlaue (0.69) when the standard range is ($0<R_L<1$).
Using q_e and C_e values of equilibrium isotherm were applied in Eqs. (2) and (5) to estimate Langmuir and Freundlich models constants and regression coefficients as shown in **Table 1**.
R^2 values show good fitting for both models with slightly larger for Freundlich than Langmuir, while deviation by average relative error shows good fitting with Freundlich model.

6-2 Contact Time Effect

The objective of adsorption kinetic study is to investigate the possible mechanisms for the adsorption process and to determine the time required to attain equilibrium. **Fig. 3** show the decrease of dye concentration C_t and adsorption capacity at each sampling time were calculate by Eq. (15) and adsorption capacity at equilibrium q_e equal to 0.865 mg/g at end of contact time (300 min).

The kinetics data of **Fig. 3** were analyzed using the linearized pseudo first and second order models presented in Eqs. (7) and (9). The parameters of the models are listed in **Table 2**

Results in **Table 2** show good correlation coefficients R^2 (0.978 and 0.987) by fitting the experimental data to pseudo-first and second order kinetic models. Comparing ARE% value shows low value for calculated q_e by pseudo second order model Therefore, the adsorption is more favorably by pseudo second order kinetic model which is based on the assumption that the rate limiting step may be chemisorptions involving valence forces through sharing or exchange of electron between reactive yellow dye as asdorbate and activated carbon as adsorbent and these result with agreement conclusion by **(Ong et al. 2010)** and **(Sulyamon and Abood 2013**)

6-3 Fixed –Bed Column

6-3-1 Effect of flow rates

Fig. 4 shows low effect of flow rate higher than 12.5 ml/min even though increasing flow rate decrease breakthrough time (the position at $C/C_0 = 0.1$) which were (25.67 , 16 and 13 min) and contact time (volume of bed/ flow rate) (0.566 ,1 and 2.05 min) for flow rates (21.67,12.5 and 6ml/min) respectively. This is due to decreased contact time between the dye and the adsorbent at higher flow rates. When the flow-rate has smaller values, equilibrium correspondent with batch experimental data could be reached, and the shape of the curves is more like an ideal breakthrough curve, this result is in agreement explaining by **Liljana, 2001**

6-3-2 Effect of bed depth.

Fig. 5 shows the breakthrough curve obtained for reactive yellow dye adsorption on the GAC for different bed height at a constant flow rate of 21.67 ml/min and dye inlet concentration of 10 mg/l where the breakthrough time increased (0, 15, 40, and 120 min) and contact time increased (0.283, 0.566, 0.849 and 1.039 min) for bed depth (5, 10, 15 and 20 cm) respectively. Increasing bed depth will provide more binding sites will be available for the yellow reactive dye to be adsorbed which will eventually lead to the attainment of a higher bed capacity. Also, an increased bed height results in more contact time being available for the dye to interact with the adsorbent. This phenomenon has allowed the yellow dye molecules to diffuse deeper into the adsorbent. Subsequently, the percentage of dye removal increased (low C_t/C_o) when the bed height was increased. Faster breakthrough curves were observed for a bed height of 5 cm, while the slowest breakthrough curve was observed at a bed height of 20 cm. The bed capacity (q_e) increased from 4.74 to 17.14 mg/g when the bed height increased from 5 to 20 cm. This results are in agreement with conclusion by **Zulfadhly et al., 2001.**

6-3-3 Effect of initial dye concentration

The initial dye concentration of the effluent is important since a given mass of adsorbent can only adsorb a fixed amount of dye. Therefore, the more concentrated an effluent, the smaller is the volume of effluent that a fixed mass of adsorbent can purify.

Fig. 6 shows decreasing in breakthrough time (service time) (18, 5, 0, and 0) for increasing initial inlet reactive dye concentration (10, 20,40 and 80 mg/l) respectively due to initial dye concentration in the inlet constant flow (constant contact time) is one of the limitation factors and main process variables. An increase in the inlet dye concentration increased the slope of the breakthrough curve, reducing the efficiency of bed This may be caused by high yellow dye concentrations saturating the adsorbent more quickly, thereby decreasing the breakthrough time **Banat et al., 2007.** The dye concentration play driving force to mass transfer of dye from liquid phase (yellow dye solution) to solid phase (adsorbent GAC) therefore high concentration increase rate constant and rapid saturation of adsorbent.

6-4 Mathematical Mode

Constants of (Thomas and Yoon-Nilson) model were calculated using Eq.(10) and Eq.(11) at different variable flow rate ,reactive yellow dye initial concentration and bed depth as shown in **Table 3** while T_{exp} values (50% C_t/C_o) were calculated approximately by breakthrough curves.

Examining results of **Table 3** show accepted values of R^2 (>0.944) at all conditions for both mathematical models Thomas and Yoon-Nelson. Adsorption capacity q_o were approximately equal in both models which explain the harmony application of two models. The actual value shows fitting at low flow rate, initial yellow dye initial concentration and high bed depth T_{cal} values for Yoon-nelson model show increasing at decreasing flow rate and initial yellow dye concentration and increasing bed depth and this is in match with T_{exp}. This result is in agreement with **Nwabanne, 2012** and **Sotelo et al., 2012.** ARE% for calculated and experimental T (50% C_t/C_o) which show good fitting with most variables.

The calculated adsorption capacity q_o values were increased at increasing flow rate due to the larger mass transfer driving force at high flow rates where high velocity reduce resistance of molecule transfer of yellow dye from solution phase to solid phase. This is the same as at increasing inlet yellow dye concentration leading to the increasing of q_o by models due to the fact that the mass transfer driving force increases with increasing the feed concentration which is in agreement with results by **Banat et al., 2007**. Calculated and experimental q_e show increasing value at increasing bed depth (5-15 cm) and this disagrees with result at **Nwabanne, 2012** but was in agreement with results by **Sotelo et al., 2012**. This is may be due to more available adorable site will be provided at exact bed depth which lead to increasing mass of adsorbent then reduce q_o value at constant initial dye concentration and flow rate.

Eq.(16) and Eq.(17) are used for the theoretical breakthrough curves using Thomas and Yoon-Nelson models **Trgo et. al., 2011** and comparing them with experimental one as shown in Figs. 7 and 8 respectively according to obtained parameters in **table 3**.

Thomas breakthrough curve is shown in Eq. (16)

$$\frac{C_t}{C_o} = \frac{1}{1+\exp\left[K_T(\frac{q*m}{Q} - Co*t\right]} \tag{16}$$

Yoon-Nelson breakthrough curve is shown Eq. (17)

$$\frac{C_t}{C_o} = \frac{1}{1 + \exp\left[K_{YN} * (t - T)\right]} \tag{17}$$

The validity of models is shown in **Fig. 7 and 8** and Eq. (16) and Eq. (17) are used to estimate ARE% values at different flow rate, initial reactive yellow dye and bed depth.

Table 4 shows that ARE% value for Thomas model less than Yoon- Nelson model for flow rate (>6 ml/min) and initial dye concentration except 20 mg/l while ARE% values are lower by Yoon-Nelson model than Thomas model, generally both models are considered acceptable due to that Thomas model is widely used to predict adsorption in column study and Yoon –Nelson less complicated than the other models but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of the adsorption bed like Thomas model. **Mohammad, 2013**

7-CONCLUSIONS

- Adsorption of reactive yellow dye onto granular activated carbon show good fitting with Langmuir and Freundlich equilibrium isotherms as chemisorptions process.
- Kinetic study shows good fitting with first and second order models but the ARE % shows the best results for second order model.
- Increasing breakthrough time with decreasing flow rates and initial yellow dye concentration and increasing bed depth of activated carbon in fixed bed experiments due to slowly bed saturation and more contact time respectively.
- Shortcut breakthrough curves models (Thomas and Yoon-Nilson) show good fitting with all of experiment variables according to the ARE% values in fixed bed continuous process.
- Calculated adsorption capacity by (Thomas and Yoon -Nilson) models show increasing at increasing flow rate due to elimination of film thickness effect at high velocity.
- T_{cal} and T_{exp} by (Yoon –Nilson) model show good fitting at bed depth due to increasing contact time at constant velocity.

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NOMENCLATURES

C	Dye concentration in aqueous solution(mg/l) .
C_e	Dye concentration in liquid phase at equilibrium (mg/l).
C_t	Dye concentration in liquid phase at time of sampling (mg/l).
C_o	Initial dye concentration in aqueous solution(mg/l).
K_1	Pseudo-first-order rate constant (min^{-1}).
K_2	Pseudo-second order rate constant(g mg^{-1} min^{-1})
K_F	Freundlich constant (mg g^{-1})
K_L	Langmuir adsorption constant (l mg^{-1})
K_T	Thomas rate constant (mL/min.mg)
K_{YN}	Yoon-Nelson rate constant(1/min)
m	Adsorbent dosage (g)
n	Freundlich parameter
N	Number of tested sampling
Q	Flow rate (m^3/min)
q	Adsorption capacity mg/g
q_e	Aquilibrium dye concentration in solid phase(mg g^{-1}) .
q_o (cal	Adsorption capacity (calculated by model and estimated by experimental results) mg/g)
q_t	Amount of dye adsorbed per unit mass of adsorbent at time t *(*mg g^{-1})
q_m	Langmuir isotherm parameter, maximum dye adsorbed/unit mass of adsorbent (mg g^{-1})
R_L	Separation factor(favorability index of Langmuir isotherm model curve)
T	Time of (50% Ct/Co removal in fixed bed) Yoon model parameter. min
t	Time (min)
V	Treated water volume (ml)

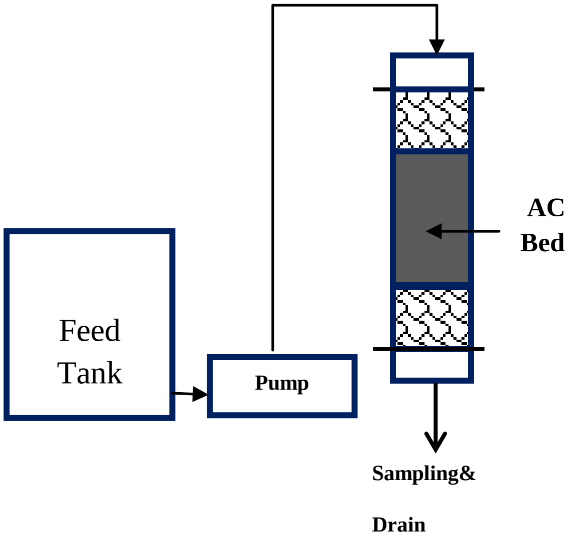


Figure 1. Fixed bed column diagram.

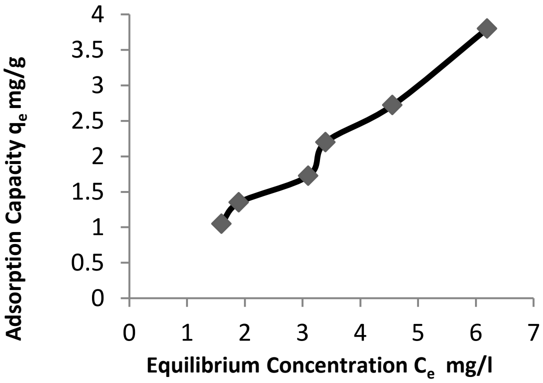


Figure 2. Equilibruim isotherm curve.

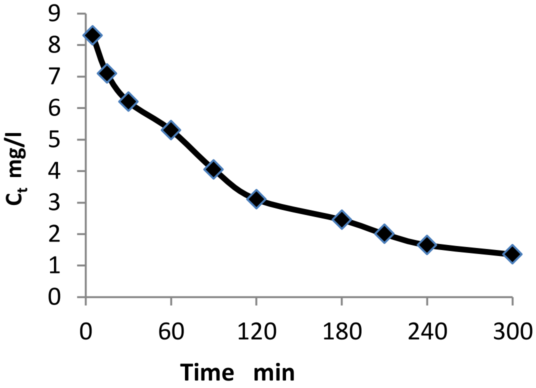


Figure 3. kinetic curve

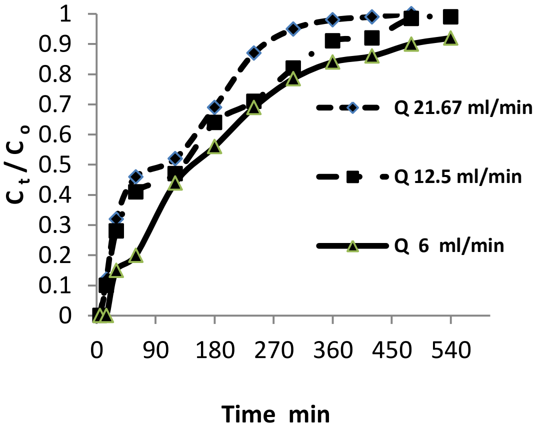


Figure 4. Effect flow rate in fixed bed column

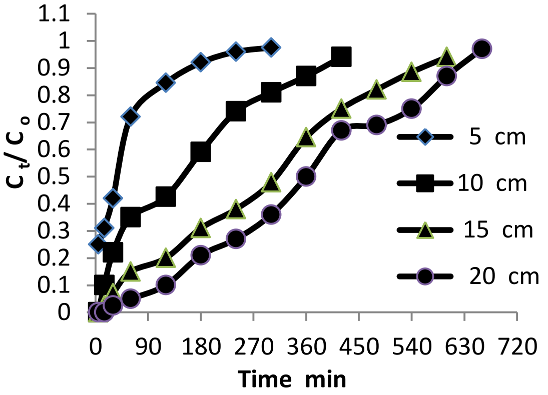


Figure 5. Effect bed depth column

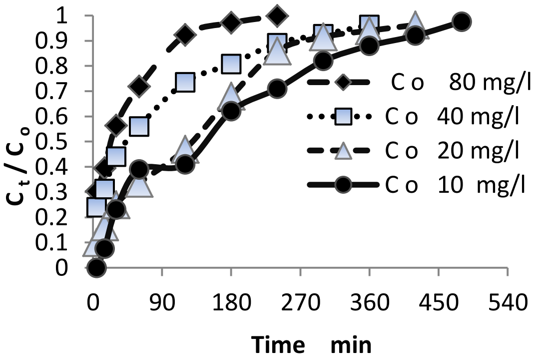
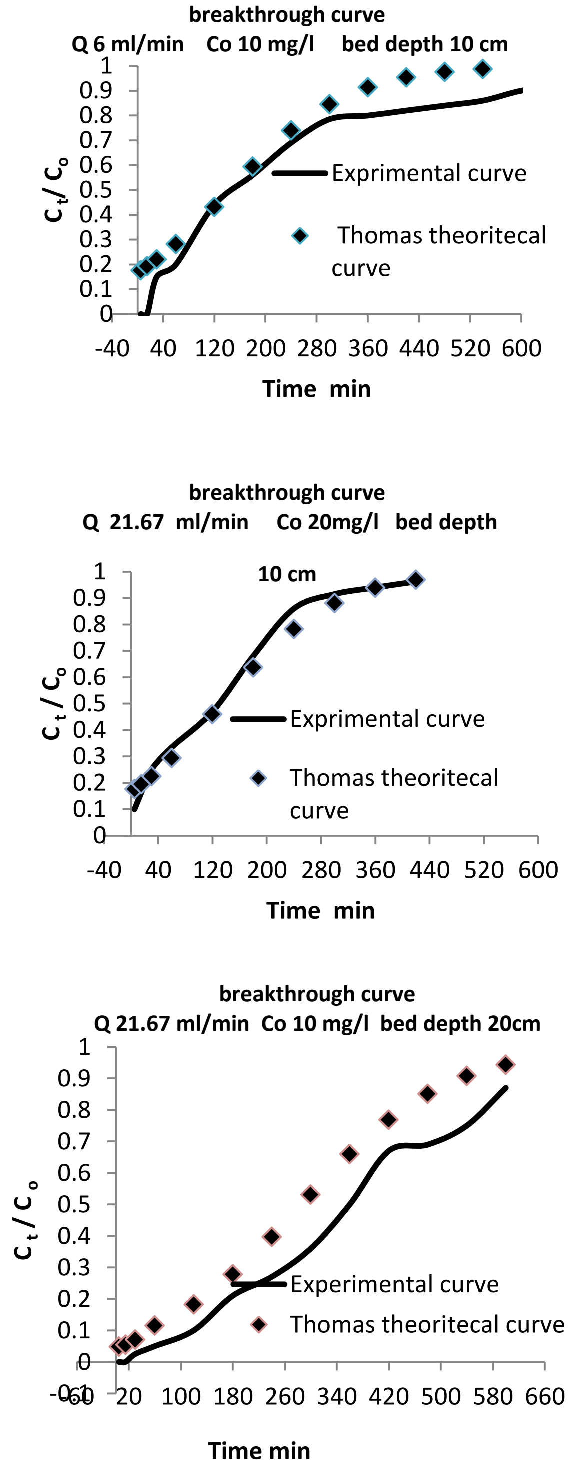
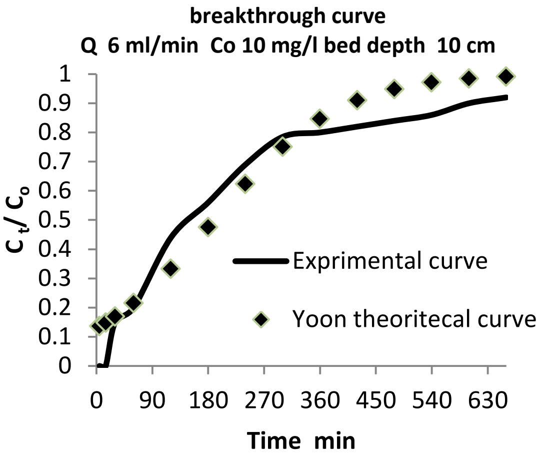
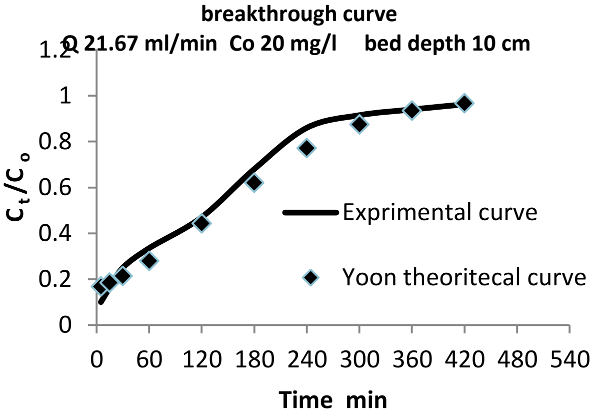


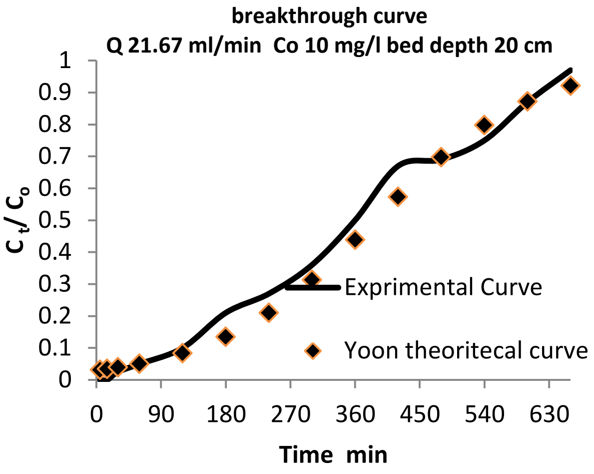
Figure 6. Effect of concentration dye



Figures 7 . Thomas model application of fixed bed column.


breakthrough curve
Q 6 ml/min Co 10 mg/l bed depth 10 cm
C t / C o
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
90
180
270
360
450
540
630
Time min
Exprimental curve
Yoon theoritecal curve


breakthrough curve
Q 21.67 ml/min Co 20 mg/l bed depth 10 cm
C t /C o
1.2
1
0.8
0.6
0.4
0.2
0
0
60
120
180
240
300
360
420
480
540
Time min
Exprimental curve
Yoon theoritecal curve



Figures 8. Yoon-Nelson model application of fixed bed column

Table 1. Equilibrium isotherm models constants.

Langmuir model	Freundlich model
K_L (l/mg)0.045 R_L0.69	K_F(mg/g) 0.699
q_m(mg/g)16.13	N1.1
$R^2$0.972	$R^2$0.977
ARE %4.7	ARE%2.15

Table 2. kinetic models parameters.

pseudo first order	Pseudo second order
K_1 (1/min)0.012	K_2(g/mgmin)0.023
$q_{e(cal)}$(mg/g)0.756	$q_{e(cal)}$ (mg/g) 0.97
$R^2$0.978	$R^2$0.987
ARE %12.2	ARE %12.1

Table 3. Calculated parameters of mathematical breakthrough models.

Models	Flow rates ml/min			Yellow dye Conc. mg/l				AC Bed depth cm		
	21.67	12.5	6	80	40	20	10	20	15	10
Thomas K_T (ml/min/mg)	1.1	1.1	1	0.275	0.325	0.6	1.05	0.9	0.9	1
q_{ocal} (mg/g)	4.137	2.03	1.15	6.87	6.7	6.42	4.168	4.168	4.85	4.04
R^2	0.952	0.959	0.989	0.985	0.967	0.972	0.947	0.968	0.962	0.96
Yoon- nelson										
K_{YN} (min^{-2})	0.011	0.011	0.01	0.026	0.012	0.011	0.0105	0.009	0.009	0.01
q_o (mg/g)	3.07	2.02	1.15	5.78	6.36	6.74	4.165	4.66	4.85	4.08
T_{cal}min (%50C_t/C_o)	127.2	145.7	172.7	30.2	66.4	140	165	387	313.4	168
R^2	0.95	0.96	0.988	0.985	0.967	0.972	0.965	0.968	0.96	0.96
$T_{exp\ min}$ (%50 C_t/C_o)	100	130	155	25	42	130	150	360	312	145
ARE% (T_{cal}&T_{exp})	27.2	12.	11.4	20.8	56	7	10	7.5	0.4	15
q_{oexp}.(mg/g)	2.85	1.89	1.05	5.99	7.03	5.51	3.48	4.03	4.25	3.44

Table 4. ARE Percentage

Model	Thomas	Yoon-Nelson
variable	ARE%	ARE%
Flow rates ml/min		
21.67	2,17	9.8
12.5	7.7	7.6
6	1.9	0.9
Initial dye Conc.mg/l		
80	0.2	1.7
40	2.7	4.4
20	1.9	6.6
10	11.1	11.6
Bed depth cm		
5	5.9	5.1
10	10.1	7.8
15	21.2	1.2
20	14.1	4.5