Determination of the Optimal Condition of Direct Blue Dye Removal from Aqueous Solution Using Eggshell

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Eggshells was used as a natural adsorbent to remove direct blue(DB) dye from aqueous solution and investigating the four factors that affect the adsorption of DB dye ; amount of eggshell rang (0.1 - 1g), initial concentration (10 - 60 mg/L), time (5 - 45 min.) and pH (3 - 11). Central Composition Design with four variables and five levels coupled with response surface method was adopted to get a second order polynomial equation for dye removal percentage as the response, and to obtain the optimum conditions for maximum dye removal percentage ; which reach 84% with optimum point , eggshell (0.835 g) ,time (24min.) , initial dye concentration (10 mg/L) , pH (4.2). The most effecting factors on dye removal are pH and initial dye concentration. Langmuir, Freundich model gives good fitting with (R^2 >0.98). The process of adsorption of DB dye on eggshell fitted a pseudo-second order kinetic model.

Keywords: eggshells adsorbent, direct blue remove, second order polynomial equation, pseudo-second order kinetic model

Environmental pollution control has been a concerned issue in many countries; air and wastewater pollution are the most concerned environmental pollution [1].There are much than 100,000 different synthetic dyes parameter on the market, produced in over 700,000 tons annually worldwide[2] . Wastewater pollution gives bad effects on public water supplies which can cause health problems such as diarrhea [3]. Major pollutants in textile wastewater are high acidity, heat and other soluble substances main pollution in textile wastewater came from dyeing and finishing processes [4, 5]. Many treatment processes included physical, chemical, and biological have been employed to treat various municipal and industrial wastewaters for example chemical, biological, food, peanut hulls, maize bran, and others [6-9]. Many researchers suggested that the potential exists for the use of highly concentrated sunlight in the removal of dyes from wastewater. Industrial facilities take clean water from nature and re-contaminated water into water sources where these industrial pollutants affect the physical properties of natural water such as the intensity, color and taste, etc., have attracted the attention of several investigations for the removal of dyes [10-12].

In this work, we reuse waste eggshells as a dye sorbent.

The model of Design Expert was used to determine the optimum condition for dye removal from polluted aqueous solution.

The effect of four parameters in adsorption of dye including: sorbent dosage (eggshell), time, initial dye concentration, *p*H values and their interactions on dye removal were investigated.

A central composite design, (CCD) was used to obtain statistical model for dye removal percentage and then finding optimal conditions for the effective factors by response surface methodology was confirmed by the analysis of variance (ANOVA).

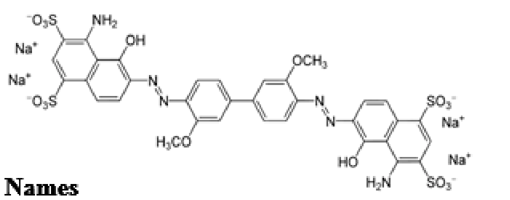
Experimental part

Materials and methods

Preparation and characterization of eggshell powder

Egg shells were collected from house, to remove impurity, the shells washed with distilled water followed by solar dried and ground into powder by using. The powdered egg shells were sieved to obtain particles of various size ranges and dried at 105 C° in an oven for 2 h. The particle sizes of (250μm) were taken for adsorption studies. The egg shell powder was stored in air tight container for further use. No other chemical treatment was used prior to adsorption experiments.

Table 1
THE CHEMICAL NAME AND PROPERTIES OF DIRECT BLUE DYE

Properties		Structure of dye
Chemical formula	$C_{34}H_{24}N_6Na_4O_{16}S_4$	
Molar mass	992.804	
Appearance	Amorphous, fine blue powder.	**Names** **tetrasodium (6*E*)-4-amino-6-[[4-[4-[*N'*-(8-amino-1-oxo-5,7-disulfonato-2-naphthylidene)hydrazino]-3-methoxy-phenyl]-2-methoxy-phenyl]hydrazono]-5-oxo-naphthalene-1,3-disulfonate**

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Direct Blue dye (DB): was used without further purification, (from textile factory in Baghdad) the properties of Direct Blue dye show in table (1). Direct Blue is an organic compound that is one of many azo dyes. It is used as a substantive dye for textiles with high contents of cellulose, i.e. cotton. It is prepared by the azo coupling of the amino naphthalene and diazotized derivative of o-dianisidine [13].

Dye solution preparation

Dye solution was prepared by dissolving in volumetric flask an accurately weighted dye in distilled water at a concentration of (10,22.5,35,47.5,60) mg/L. Taking such concentrations of DB dye to determine the maximum absorbance wave length (λ max) with absorbance spectrum rang (200-800 nm) by using UV-visible spectrophotometer. The maximum absorbance (λ_{max}) of DB solution was in the visible region at 566nm, then using this λ max to prepare a calibration curve of absorbance and concentration of DB dye

Batch mode adsorption studies

The batch adsorption experiment were conducted in 250 mL capacity conical flask containing adsorbent (eggshell) (0.1-1) g and 50 mL of DB solution at various initial concentrations and agitated at 150 rpm in water bath shaker at predetermined time intervals (5-45) min at 24°C.

Dilute (0.1%) HCl or (0.1%) NaOH was used for *p*H adjustment in order not to increase the volume of samples too much and keep the error created by *p*H adjustment in a reasonable range. The adsorbate solution was centrifuge at (3000 rpm) and for (15min.). The residual concentration of the sample is measured by spectrophotometric at λ = 566 nm.

Equilibrium studies

Equilibrium data were obtained by adding 0.775 g of eggshell into a series of Erlenmeyer flasks each filled with 50 mL of dye solution. the initial dye concentration ranges from 10-60 mg/L then placed in water bath shaker for 90 min (take as equilibrium time) at 24°C and *p*H 5

The dye removal percentage was calculated from [14-15].

$$R_e\% = 100 \quad (C_o-C_e)/C_o \qquad (1)$$

where: C_o and C_e are the initial and the equilibrium concentrations (mg/ L) of Direct Blue in solution, respectively, R_e% percentage of dye removal at time of equilibrium.

The amount of sorption per gram of eggshell at time of equilibrium q_e and at any time t, q_t (mg/g) was calculated from

$$q_e = (C_o-C_e)\ 5ØÑÝ\ (V/m) \qquad (2)$$
$$q_t = (C_o-C_t)\ 5ØÑÝ\ (V/m) \qquad (3)$$

C_t : dye concentration at any time , m (g) : weight of egg shells, and V (L), the solution of volume taken for experiment] 15].

Sorption kinetic

Contacting a volume of 50 mL of solution at 10 and 22.5 mg/L of dye at interval of definite time, using 0.775 g of eggshell at 24°C and *p*H 5.

Design of experiments

To obtain the largest amount of information from a small number of experiments we are using central composite design method (CCD). In this study four variables (factors) including sorbent dosage (Egg shell), contact time, initial dye concentration and *p*H. Each variable have 5 levels. These values were designated by the codes (-2,-1,0,1,2) and are given in table (2) . The percentage of dye removal for each experiment was calculated from eq. (4), which was spotted as the response.

$$R_t\% = 100 \quad (C_o - C_t)/C_o \qquad (4)$$

where: R_t% percentage of dye removal at any time.

According to experimental design of the four variables there was thirty one experiments .The model of design was the second-order polynomial response equation was used to make relation between the collected response and variables as in eq. (5) [16]:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 \qquad (5)$$

where: Y is the predicted response (dye removal %). (b_0, b_1,b_2,b_3,b_4 ...) are regression coefficients. (X_1, X_2, X_3, X_4) are coded levels of the variables.

By using the Multi -Variable Least Squares to fitted the experimental data and estimate regression coefficients in the eq. (5).

Table 2

RANG OF CODED AND THEIR REAL EXPERIMENTAL VALUES OF VARIABLES USED IN THE CENTRAL COMPOSITE DESIGN

Coded Level	Eggshell (g) X_1	Time (min) X_2	Dye con. (mg/L) X_3	*p*H X_4
-2	0.1	5	10	3
-1	0.3250	15	22.5	5
0	0.55	25	35	7
1	0.775	35	47.5	9
2	1	45	60	11

Results and discussions

Response surface of dye removal

The experimental design results of dye removal % is given in table (3) includes 31 runs, real data obtained from experiments and the fitted values of the developed model. These results were subjected to analysis of variance (ANOVA); in table (4) shows the regression coefficients for the response function (removal % of dye) and P- value lower than 0.05 was considered significant in surface response analysis. The p-value of the coefficient for linear effect of the factors : contact time , initial dye concentration and *p*H are less than 0.05; so for the response is significant except for amount of eggshell (absorbent) (P=0.144) is less significant ,and the interaction effect of the variables as show in table (4) some of it significant other non-significant depending on P- value .

In table (4) the R^2 values (R^2, R^2 (prediction), R^2 (adjusted)) shows no large difference this means good fit to the model. So the model of design was in eq. 6 as follow:

$$Y = 70.06 + 1.284*X_1 + 2.329*X_2 - 4.889*X_3 - 10.054*X_4 + 0.1498*X_1*X_2 + 1.038*X_1*X_3 - 1.324*X_1*X_4 + 2.661*X_2*X_3 - 1.535*X_2*X_4 + 0.72*X_3*X_4 - 0.419*X_1^2 - 3.439*X_2^2 - 1.148*X_3^2 - 4.616*X_4^2 \qquad (6)$$

Optimum condition

Equation (6) was used to determine the optimum condition of variables that give the higher percentage removal of dye. An experiment was then conducted on these variables to obtain the percentage of dye removal, and whether it is close to the value obtained from optimization. The result was as follows

X1: eggshell (g) = 0.835

X2: time (mint.) =24

X3: initial dye concentration mg/l =10

X4: *p*H = 4.2

The optimal values for dye removal, both expected and experimental (real), were 83% and 84.323%, respectively; It shows that they are convergent values.

Effect of variables on dye removal:

Figure 1 shows the relation between the percentage of dye removal and the effective variables (amount of eggshell, contact time, initial concentration of DB and *p*H). All these relationships were drawn together at the level of the 0 code for the variables values figure 1a shows that if the time increases the percentage of removal of dye increases to a certain extent and then starts to decrease slightly. On the other hand, the amount of egg shells has little effect on the removal of the dye.

The effect of increasing the initial concentration of the dye does not lead to an improvement in the percentage of dye removal as shown in figure 1b.

Figure 1c shows that increasing the *p*H reduces the dye removal, which reduces the absorbance of the dye. Therefore, the adsorption environment should preferably be acidic, not base, and the best *p*H values should be between 3 and 5.

Table 3

RESULTS OF EXPERIMENT PLANNED ACCORDING TO CENTRAL COMPOSITE DESIGN

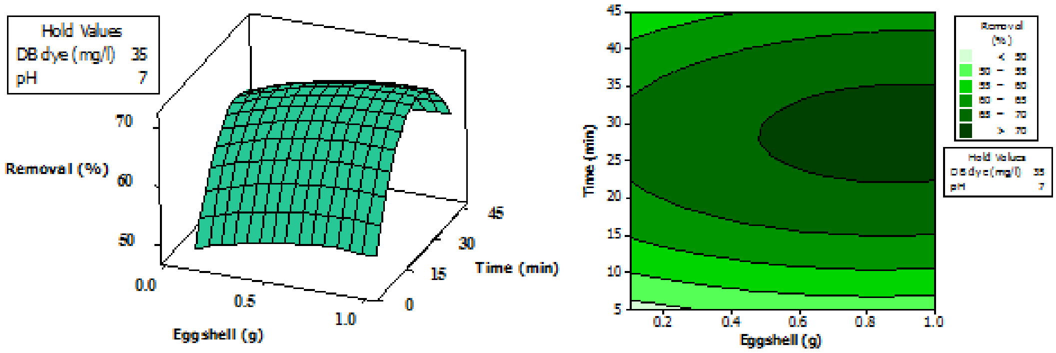
	Coded Variables				Real Variables				Dye removal % Y	
Exp. No.	X_1	X_2	X_3	X_4	Egg shell (g)	Time (min)	Dye con. (mg/L)	*p*H	Exp. values	Predicted values
1	-1	-1	-1	-1	0.325	15	22.5	5	72.25	73.478
2	1	-1	-1	-1	0.775	15	22.5	5	75.82	76.318
3	-1	1	-1	-1	0.325	35	22.5	5	74.084	75.584
4	1	1	-1	-1	0.775	35	22.5	5	79.89	79.023
5	-1	-1	1	-1	0.325	15	47.5	5	52.8	54.861
6	1	-1	1	-1	0.775	15	47.5	5	59.77	61.852
7	-1	1	1	-1	0.325	35	47.5	5	64.03	67.611
8	1	1	1	-1	0.775	35	47.5	5	70.5	75.201
9	-1	-1	-1	1	0.325	15	22.5	9	63.5	57.648
10	1	-1	-1	1	0.775	15	22.5	9	56.67	55.194
11	-1	1	-1	1	0.325	35	22.5	9	53.59	53.613
12	1	1	-1	1	0.775	35	22.5	9	54.97	51.758
13	-1	-1	1	1	0.325	15	47.5	9	38.94	41.912
14	1	-1	1	1	0.775	15	47.5	9	46.26	43.609
15	-1	1	1	1	0.325	35	47.5	9	50.17	48.521
16	1	1	1	1	0.775	35	47.5	9	49.94	50.817
17	-2	0	0	0	0.1	25	35	7	67.27	65.815
18	2	0	0	0	1	25	35	7	70.45	70.951
19	0	-2	0	0	0.55	5	35	7	50.6	51.646
20	0	2	0	0	0.55	45	35	7	62.96	60.96
21	0	0	-2	0	0.55	25	10	7	70.69	75.246
22	0	0	2	0	0.55	25	60	7	61.2	55.689
23	0	0	0	-2	0.55	25	35	3	78.62	71.705
24	0	0	0	2	0.55	25	35	11	25.53	31.491
25	0	0	0	0	0.55	25	35	7	69.71	70.06
26	0	0	0	0	0.55	25	35	7	67.6	70.06
27	0	0	0	0	0.55	25	35	7	69.5	70.06
28	0	0	0	0	0.55	25	35	7	72.15	70.06
29	0	0	0	0	0.55	25	35	7	71.16	70.06
30	0	0	0	0	0.55	25	35	7	70.2	70.06
31	0	0	0	0	0.55	25	35	7	70.1	70.06

Term	Coef	SE Coef	F- value	P- value
Constant	70.0600	1.5480	47.23	0.000
x1:amount Eggshell	1.2840	0.8360	2.36	0.144
x2 : Time	2.3285	0.8360	7.76	0.013
x3 : Dye concentration	-4.8893	0.8360	34.20	0.000
x4 : pH	-10.0535	0.8360	144.61	0.000
x1*x1	-0.4193	0.7659	0.30	0.592
x2*x2	-3.4393	0.7659	20.16	0.000
x3*x3	-1.1481	0.7659	2.25	0.153
x4*x4	-4.6156	0.7659	36.32	0.000
x1*x2	0.1497	1.0239	0.02	0.886
x1*x3	1.0378	1.0239	1.03	0.326
x1*x4	-1.3235	1.0239	1.67	0.215
x2*x3	2.6610	1.0239	6.75	0.019
x2*x4	-1.5353	1.0239	2.25	0.153
x3*x4	0.7202	1.0239	0.49	0.492

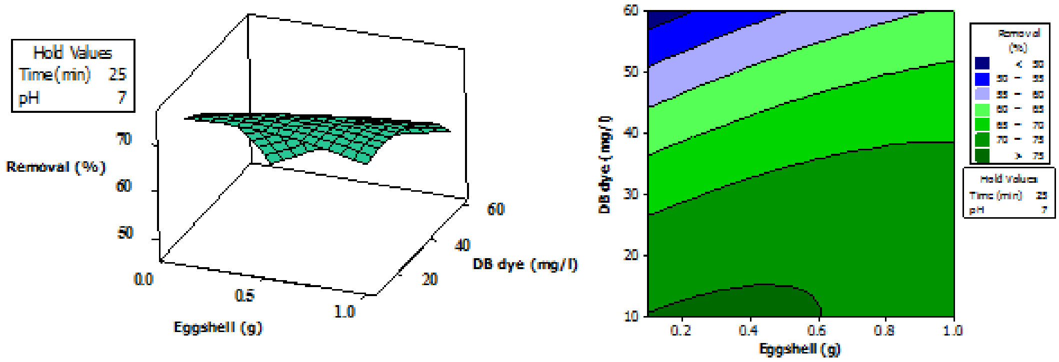
STD. Deviation = 4.09569 Average error % = 4.05118 PRESS = 1492.79

R^2 = 94.05% R^2(pred) = 66.91% R^2(adj) = 88.85%

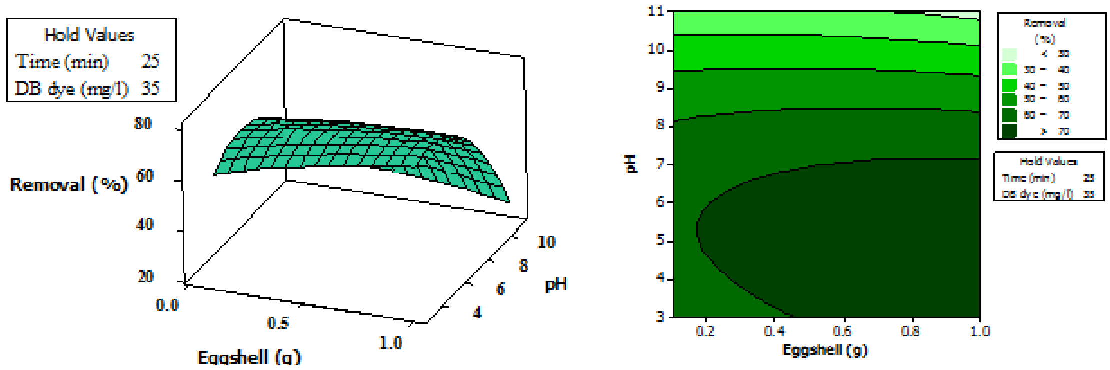
Table 4
ANALYSIS OF VARIANCE FOR DYE REMOVAL, THE ANALYSIS WAS DONE USING CODED UNITS. ESTIMATED REGRESSION COEFFICIENTS FOR Y IN EQ. (5)



(a)



(b)



(c)

Fig.1. Response surface and contour plots for variables and its effect on DB dye removal efficiency (a) eggshell and time (b) eggshell and initial concentration of DB (c) eggshell and *p*H

Adsorption isotherms modeling:

The isothermal curves describe the relationship at the adsorption equilibrium between eggshell and dye solution at constant temperature. Several models were analyzed such as Langmuir , Freundlich, and Temkin isotherm. The constant parameters of the isotherm equations were calculated. These model equations are expressed as follow. [15].

Langmuir $$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{k_l\, q_{max}} \quad (7)$$

Freundlich $$q_e = k_f \cdot C_e^{1/n} \quad (8)$$

$$\ln q_e = \ln k_f + 1/n \ln C_e \quad (9)$$

Temkin $$q_e = A + B \ln C_e \quad (10)$$

where q_e (mg/g) is the adsorption capacity of equilibrium, q_{max} is the maximum adsorption capacity and k_l (L/mg) is a constant related to the adsorption energy. C_e (mg/ L) is the concentration of DB solution at equilibrium. Both k_f, and n are Freundlich constants related to adsorption capacity and adsorption intensity. A, and B are constants. Table (5) shows the analysis of equilibrium data of the three models; as comparison the Langmuir, Freundlich models gave the greatest fit to the experimental data than Temkin model with R^2 = 0.9854, 0.9856, 0.9562 respectively. The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, and is applied to homogeneous sorption.

Freundlich isotherm model are an empirical adsorption isotherm used for non-ideal sorption and involves heterogeneous sorption. In table 5, value of n >1 that's means the adsorption of DB dye on eggshell is a favorable process [17].

The Temkin isotherm model assumes a uniform distribution of energies over of surface adsorption sites. [18].

Kinetic models and effect of contact time:

Figure 2 shows the amount of sorption of dye per gram of eggshell at any time of two different initial concentration 10, 22.5 mg/L of DB dye, increasing at the beginning till reached equilibrium at 90 min. for both concentration of dye. The increasing of initial concentration from 10 to 22.5 mg/L will increase the uptake of DB dye on the eggshell due to surface adsorption which is increase with increasing the sorbate quantity [5].

Adsorption kinetics and effect of contact give information on the adsorption process mechanisms. In the present work two of the most widely used kinetic models which are pseudo- second order, intra-particle diffusion.

pseudo-second order model : $$\frac{t}{q_t} = \frac{1}{k_2\, q_e^{2}} + \frac{t}{q_e} \quad (11)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_2 is the rate constant of pseudo- second order adsorption (g/mg·min).

$$h = k_2\, q_e^{2} \quad (12)$$

h: are the initial sorption rate (mg/g.min

Intraparticle diffusion model: $$q_t = k_t\, t^{0.5} + C \quad (13)$$

k_t : the intraparticle diffusion rate constant (mg /g·min$^{0.5}$), C : constant gives about the thickness of boundary layer . The results in figure 3 and table 6 shows that the pseudo-second order model have higher R^2 values (0.9999 for 10mg/L) and (0.9984 for 50 mg/L). This means the adsorption is controlled by chemisorption]19[.

The experimental value of q_e ($q_{e\ exp}$) Very close to value of calculated ($q_{e\ cal}$) for both initial concentration, and increase from 0.588 to1.329 as the initial concentration increase from 10 to 22.5mg/L also h increase, but k_2 decrease.

Intra-particle diffusion model have less R^2 values (0.9138, 0.8117) for both initial concentration (10, 22.5mg/L) respectively than pseudo- second order. k_t and C increase as the initial concentration increase this means; the greater is the boundary layer effect; when C not equal zero This gives an idea about the boundary layer thickness, i.e. the larger intercept; the greater is the boundary layer effect. The plot of qt versus t ½ with zero intercept determines the rate of adsorption. In this case intra-particle diffusion is not the only rate limiting step.

Table 5

CHARACTERISTICS OF ADSORPTION ISOTHERMS AT 24 C^O, *p*H=5, SORBENT (EGGSHELL) = 0.775G

Langmuir			Freundlich			Temkin		
q_{max} (mg/g)	K_l (l/mg)	R^2	k_f	n	R^2	A	B	R^2
3.879	0.179	0.9854	0.564	1.579	0.9856	0.7322	0.7328	0.9562

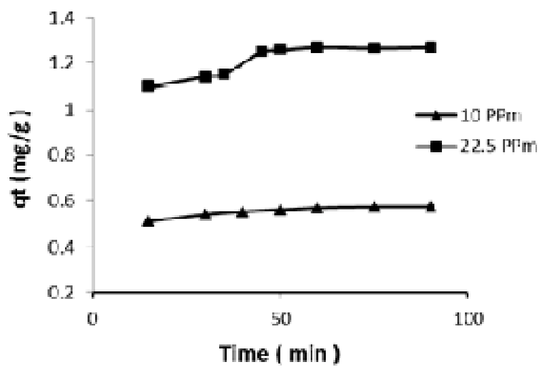


Fig. 2 . Effect of contact time on removal and adsorption of DB dye

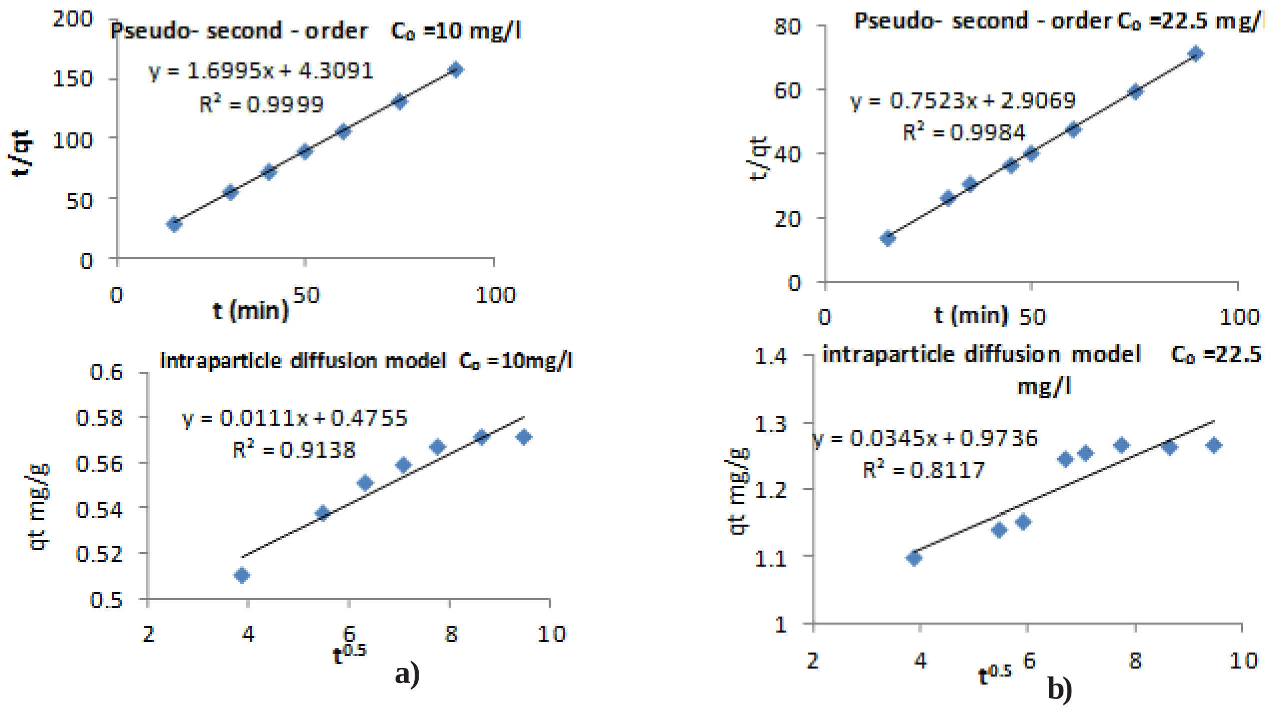


Fig. 3. Contact time effect on DB dye adsorption by eggshell and kinetics plots (a) 10 mg/L and (b) 22.5 mg/L

Table 6
KINETICS PARAMETERS FOR ADSORPTION OF DB DYE ONTO EGGSHELL POWDER

Models	Parameters	10 mg/L	22.5 mg/L
	qe exp (mg/ g)	0.571	1.266
Pseudo –second order equation(11)	k_2 (g/mg.min)	0.671	0.195
	qe cal (mg/g)	0.588	1.329
	h (mg/g.min)	0.232	0.344
	R^2	0.9999	0.9984
Intraparticle diffusion model equation(14)	k_i (mg/g.min$^{0.5}$)	0.0111	0.0345
	C (mg/g)	0.4755	0.9736
	R^2	0.9138	0.8117

Conclusions

The eggshells could be used as a natural material, and low cost for the removal of DB dye from water and waste water effluent from textile factory. The optimum conditions are: amount of eggshell 0.835 g, initial dye concentration 10 mg/L, time 24 min, *p*H 4.2.

Langmuir and Freundlich model described the best fit with the data; the correlation coefficient $R^2 > 0.98$ .The process of adsorption of DB dye on eggshell fitted a Pseudo –second order kinetic model, which means that the adsorption is controlled by chemosorption. The more effected variables on adsorption of DB dye are pH and initial dye concentration, when *p*H acidic and less concentration gives better removal of dye.

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