Eng. & Tech. Journal, Vol.30, No.15, 2012

Adsorption of Direct Yellow 4 Dye on the Silica Prepared From Locally Available Sodium Silicate

Dr. Manal Obeid Hamza
Science for Women College, University of Baghdad/ Baghdad
Email: Manal_2005a@yahoo.com
Sameer Hakeem Kareem
Science for Women College, University of Baghdad/ Baghdad

Received on: 12/10/2011 & Accepted on: 1/3/2012

ABSTRACT

In this study the ability of removing direct yellow 4 dye (DY4) from aqueous solutions using silica as adsorbent was examined. The silica was prepared from locally available sodium silicate. The effect of various experimental parameters contact time, amount of silica used, pH, ionic strength and temperature were investigated in a batch adsorption technique. The obtained experimental data shows that, the adsorption of direct yellow 4 dye was increased directly with increasing concentration, amount of silica, added sodium chloride and temperature in optimum pH (7) and equilibrium time of 45 min. The kinetic data were analyzed through pseudo first-order, pseudo second-order and intraparticle diffusion models. The pseudo second-order model best represented adsorption kinetics. Additionally, this study used the Langmuir, Freundlich and Temkin isotherms to describe equilibrium adsorption and calculating thermodynamic values. The equilibrium adsorption of direct yellow 4 on silica is best fitted in the Langmuir isotherm (R^2=0.981).

Keywords*:* Dyes, Adsorption, Direct yellow 4, Wastewater, Silica.

امتزاز صبغة Direct Yellow 4 (DY4) على سطح السيليكا المحضرة من سيليكات الصوديوم المحلية

الخلاصة

تم في هذه الدراسة اختبار إمكانية إزالة صبغة direct yellow 4 (DY4) من المحاليل المائية باستخدام السيليكا التي تم تحضيرها من سيليكات الصوديوم المتوفرة محليا. تم تعيين تاثير مختلف المقاييس العملية مثل زمن الاتزان و الوزن الامثل للسيليكا و الدالة الحمضية و القوة الأيونية ودرجة الحرارة باستخدام تقنية الامتزاز بالوجبة. وقد اظهرت النتائج العملية المحصل عليها ان سعة الامتزاز تزداد بازدياد تركيز الصبغة ووزن السيليكا وعند إضافة الملح وارتفاع درجة الحرارة عند التركيز الهيدروجيني المتعادل وزمن اتزان 45 دقيقة. تم دراسة حركية الامتزاز من خلال ثلاث انماط حركية:

https://doi.org/10.30684/etj.30.15.5
2412-0758/University of Technology-Iraq, Baghdad, Iraq

الرتبة الاولى الكاذبة و الرتبة الثانية الكاذبة ونمط الانتشار البيني الدقائق. فضلا عن ذلك تم استخدام ايزوثرمات لنكماير و فرندلش و تيمكن لوصف اتزان الامتزاز و حساب القيم الثرموديناميكية وكان ايزوثيرم لنكماير اكثرها ملائمة لوصف امتزاز الصبغة على سطح السيليكا (R^2 =0.981).

INTRODUCTION

Many industries, including textile companies, dye manufacturers, food processing companies, paper and pulp mills, and electroplating factories, release wastewater containing dyes and thereby contaminate water resources. Also, the use of direct dyes has continuously increased in the textile industry and finishing processes since the development of synthetic fibers. Discharging dyes into the hydrosphere typically results in environmental damage as dyes give water undesirable color and reduce sunlight via absorption and decomposition [1]. In addition many dyes are toxic to aquatic communities; some of them can cause allergic dermatitis, skin irrigation, cancer and mutation in man [2].

Approximately 12% of synthetic textile dyes used each year is lost during manufacture and processing operation and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial waters [3]. Most dyestuffs are designed to be resistant to environmental conditions like light, effects of pH and microbial attack. Hence, their presence in wastewater is unwarranted, and it is desirable to remove coloring material from effluents, before their discharge in the environment, not only for aesthetic reasons [4, 5].

The removal of dye molecules from wastewaters is a matter of great interest in the field of water pollution. Several physical, chemical and biological methods such as coagulation /flocculation treatment, biodegradation process, oxidation methods, membrane filtration and adsorption have been reported and attempted for the removal of dyes from the wastewater. Among these numerous techniques of dye removal, it is now recognized that adsorption using solid adsorbents is an effective and useful process [6].

Review of literature indicates that the adsorption behavior of dyes with different adsorbents like activated carbons, clays, ion exchanger resins, Zeolites, nanoporous silica, soil, metal hydroxides, biogas residual slurry, have been thoroughly investigated [1-3, 7-10].

In this study the possibility of using silica prepared from locally available sodium silicate was evaluated for removal the direct yellow 4 dye (DY4) in batch method. The Langmuir, Frendlich and Temkin isotherms were utilized to fit equilibrium data. Adsorption rates were determined using pseudo first-order, pseudo second-order and intraparticle diffusion models. The study also included an investigation of change in thermodynamic parameters, $\Delta G°$, $\Delta H°$ and $\Delta S°$ during adsorption.

EXPERIMENTAL

Chemical Materials

1-Sodium silicate (SiO_2 32%, Na_2O 14%) was obtained from Al-Ramady glass factory, Ministry of Industry and Minerals as silica source.
2-Hydrochloric acid (HCl 5%).

3-Direct yellow-4 dye was obtained from Al-Hilla Textile factory.

The specifications of direct yellow 4 dye are tabulated in table 1 and fig. 1.

Table (1).structure and characteristics of DY4

Name	Formula	Molecular weight	λ_{max} absorption
DY4	$C_{26}H_{18}N_4Na_2O_8S_2$	624.55 gm/mol	403 nm

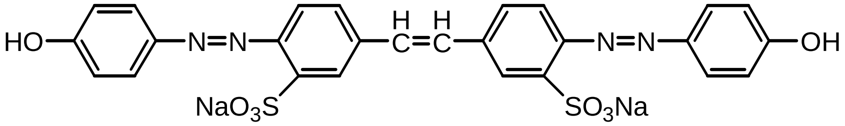

Figure (1): Chemical Structure of Direct Yellow 4

Preparation of Silica

Silica used in this study was prepared by adding (4.5 ml) of sodium silicate (16%) drop wise to (15 ml) of the hydrochloric acid (HCl 5%) while it stirred at 700 rpm and 30 °C. After 2 hours the colloidal mixture was filtered and the precipitate washed with a large amount of distilled water until the value of pH of washing water reaches 7. The resultant white crystal precipitate dried at 100 °C for 3 hours [11].

Method of Adsorption

All experiments of batch adsorption were carried out in a closed 100 ml conical flasks. The flask, which contained 0.2 g of prepared silica and 50 ml of dye solution (50 ppm), was placed in a temperature controlled water bath and shaken with speed 200 rpm for 45 min at 25°C and neutral pH. At the end of the equilibrium period, suspensions were centrifuged for 10 min and the concentration of dye in solutions before and after adsorption were measured with a quartz cell using UV-VIS Shimadzu T60 V spectrophotometer, at wavelength 403 nm. The amount of dye adsorption at equilibrium q_e (mg/g) was calculated, using the following equation:

$$q_e = \frac{(C_\circ - C_e)V}{W} \qquad \cdots (1)$$

Where C_0 is the initial dye concentration and C_e is the concentration at equilibrium. V is the volume of solution and W is the mass of the adsorbent (g). The percentage of dye removed from solution was calculated using the following equation:

$$\text{Removal percentage} = \frac{(C_2 - C_e)}{C_2} \times 100 \qquad .....(2)$$

RESULTS & DISCUSSION

Effect of Contact Time

Adsorption equilibrium studies were conducted with an adsorbent quantity of (0.2 gm) with 50 ml of dye (50 ppm). The experimental results of adsorption of direct yellow 4 on silica at different times by keeping other parameter constant are illustrated in fig.2. It shows that the adsorption process exhibited an immediate rapid adsorption and reached equilibrium within a short period of 45 min.

Effect of Adsorbent Amount

The effect of silica amount on the amount of dye adsorbed was investigated by contacting 50 ml of dye solution with initial dye concentration of 50 ppm at 25 °C for 45 min at a constant condition and different amount of silica (0.1-0.5 gm). After equilibrium, the samples were centrifuged and then concentration in the supernatant dye solution was analyzed. The plot of removal percentage versus adsorbent amount (gm) is shown in Figure (3). As seen, the adsorption percentage reached the maximum when the silica amount increased to 0.2 gm. The increase in percentage of dye removed with an increasing of adsorbent amount can be attributed to an increase in the adsorbent surface, which increased the availability of adsorption sites resulting from increase amount of the adsorbent. Therefore, the optimum silica amount that can be used in removal of DY4 is (0.2 gm) per 50 ml, and all experiments were carried on by using (0.2 gm) of adsorbent.

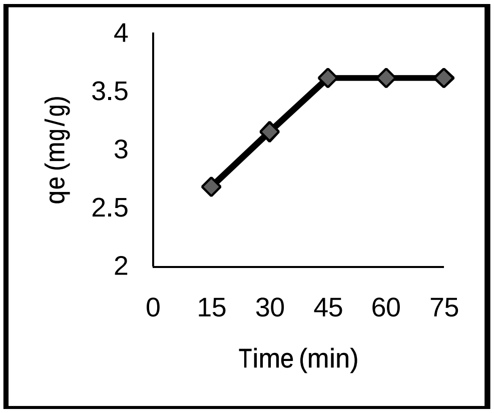

Figure (2): Effect of contact time on adsorption of DY4 on silica (C_o=50 ppm at pH 7, and 25°C)

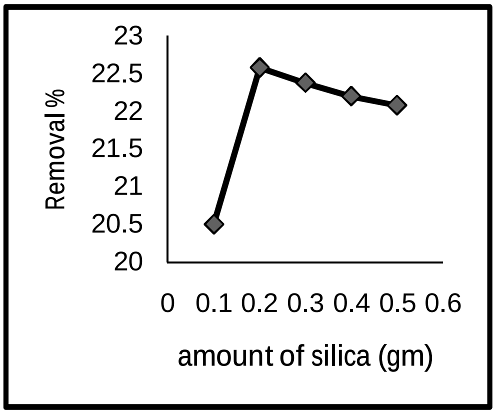

Figure (3): Effect of amount on adsorption of DY4 on silica (C_o=50 ppm at pH 7, 25°C, and 45 min)

Effect of pH

An important and effective factor for dye adsorption has been referred as pH is discussed in most related studies published in the literature [12–14]. To find a proper pH for the effective adsorption of dyes by the silica sorbent, experiments were performed at a pH range of (4-10). pH of the solutions was adjusted by adding 0.01M HCl and 0.01M NaOH for the sorbent at 50 ppm initial dye concentration. As shown in fig. (4), the maximum adsorption capacity was reached at pH (7) with (3.995 mg/g). The inhibition of the dye sorption on silica at acidic and basic pH ranges may be attributed to the increase of hydroxyl and hydrogen ions leading to formation of aqua complexes thereby retarding the dye adsorption [15].

Effect of Ionic Strength

Since large amounts of salts are generally utilized in the dyeing process, the effects of ionic strength on adsorption must be evaluated. The effect of ionic strength on the removal of DY4 by silica was studied by adding 5 ml of NaCl (0.001-0.1 M). Experimental results fig. (5) indicate that increasing solution ionic strength increased the adsorption of direct dye on silica. The significant increase in dye removal after an addition the salt NaCl can be attributed to an increase in dye dimerization in solutions [16].

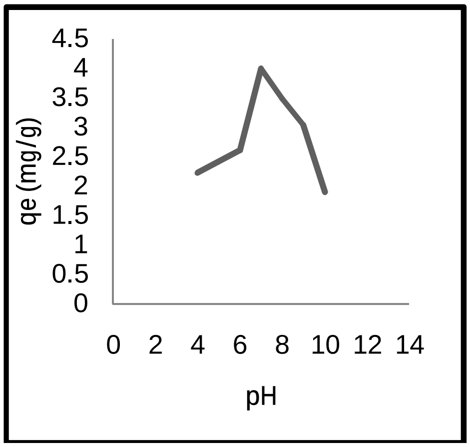

Figure (4): Effect of pH on DY4 adsorption on silica (C_o=50 ppm at 25°C, and 45 min)

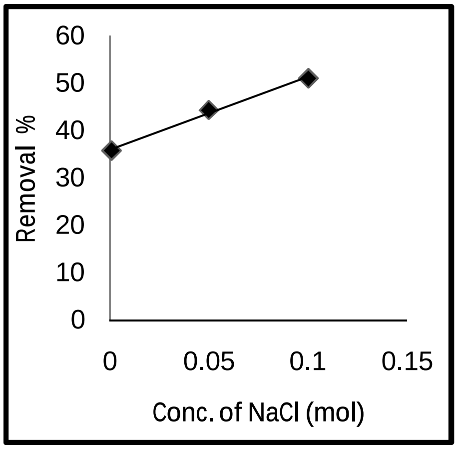

Figure (5): The effect of salt on removal DY4 By silica (C_o=50 ppm at pH 7, 25°C, and 45 min)

Adsorption Isotherms

The adsorption isotherm is the most important information, which indicates how adsorbate molecules are distributed between the liquid phase and solid phase when the adsorption process reaches equilibrium [11]. The adsorption process was performed at initial concentrations (10-50 ppm) and different temperatures (25-55°C). The results are listed in table (6).

Table (6) Equilibrium parameters for the adsorption of DY4 on silica at different temperatures

25 °C			35 °C			45 °C			55 °C		
C_o ppm	C_e mg/L	q_e mg/g	C_o ppm	C_e mg/L	q_e mg/g	C_o ppm	C_e mg/L	q_e mg/g	C_o ppm	C_e mg/L	q_e mg/g
10	8.59	0.352	10	8.48	0.380	10	7.68	0.580	10	6.85	0.787
15	12.68	0.580	15	12.41	0.647	15	11.44	0.890	15	11.31	0.922
20	16.12	0.837	20	15.65	0.970	20	15.41	1.147	20	15.39	1.152
30	25.85	1.037	30	25.2	1.152	30	24.79	1.302	30	24.26	1.387
40	34.1	1.475	40	33.51	1.622	40	33.15	1.712	40	32.78	1.805
50	41.78	2.055	50	41.51	2.122	50	41.16	2.209	50	39.79	2.552

Three most common isotherm equations namely, Langmuir, Freundlich and Temkin were tested in this work to describe equilibrium adsorption.

Langmuir isotherm

The Langmuir isotherm is represented by the following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m\,K_L} + \left(\frac{1}{q_m}\right) C_e \qquad \cdots (3)$$

Where q_e is the amount of dye adsorbed per gram of silica (mg/g); C_e is the equilibrium concentration of dye in a solution (mg/L); K_L is the Langmuir constant (L/mg), which is related to the affinity of binding sites; and q_m is the theoretical

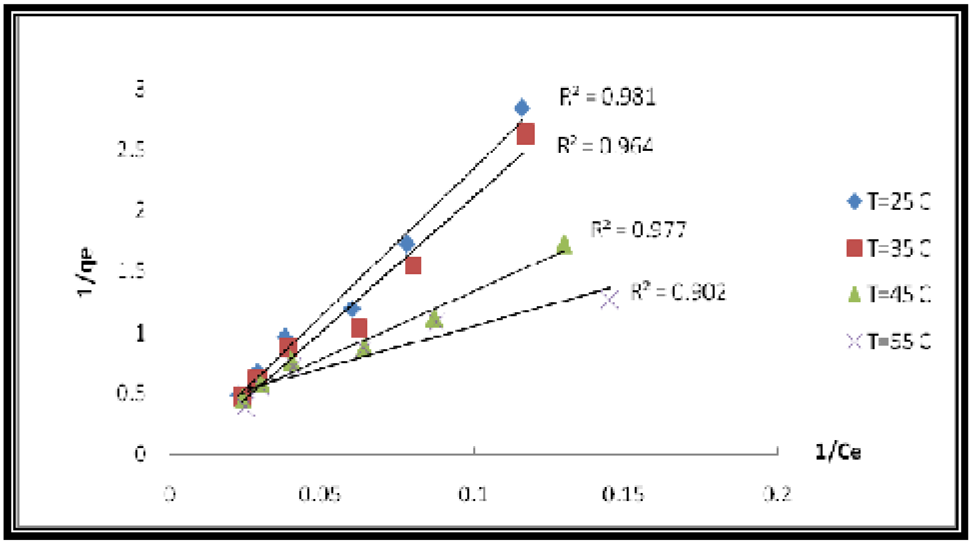

Figure (6): The linear plot of Langmuir isotherm of DY4 at different temperatures

saturation capacity of the monolayer (mg/g). Plots of $1/q_e$ versus $1/C_e$ give a straight line with the slope of $1/q_m.K_L$ and intercept $1/q_m$.

Freundlich isotherm

The linear form of Freundlich isotherm is expressed as:

$$\log q_e = log K_F + {}^{1}\!/_{n} \log C \qquad \cdots (4)$$

Where K_F and n are Freundlich constants, which represent adsorption capacity and adsorption strength, respectively. Both K_F and $1/n$ can be obtained from the intercept and slope of the linear plot of log (q_e) versus log (C_e).

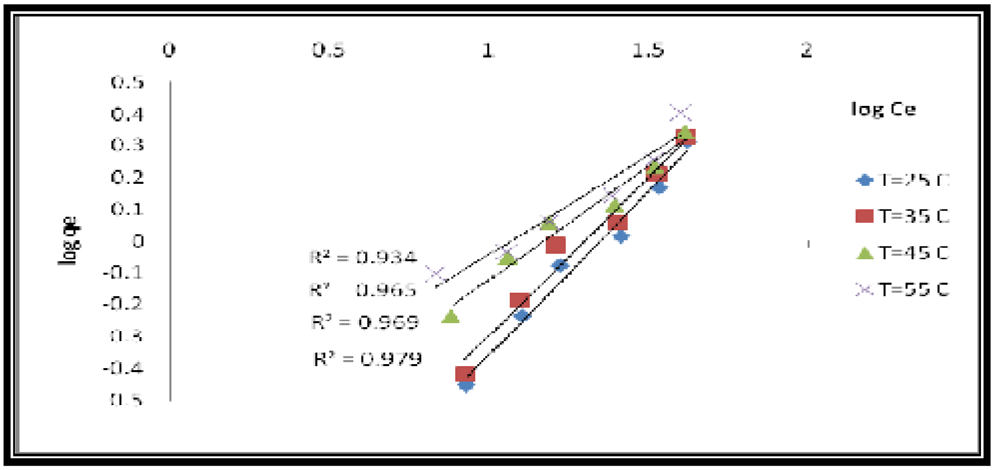

Figure (7): The linear plot of Frendlich isotherm of DY4 at different temperatures.

Temkin isotherm

The Temkin isotherm describes the behavior of adsorption systems on a heterogeneous surface, and is represented as follows [17]:

$$q_e = B_1 \ln K_t + B_1 \ln(C_e) \qquad \cdots (5)$$

Where B_1 is a constant related to adsorption heat, and K_t is the equilibrium binding constant (L/mol) corresponding to maximum binding energy. A plot of q_e versus ln (C_e) is used to determine isotherm constants fig. (8). Table (7) lists the three isotherms constants which are calculated from the slope and intercept of the linear plots at different temperatures.

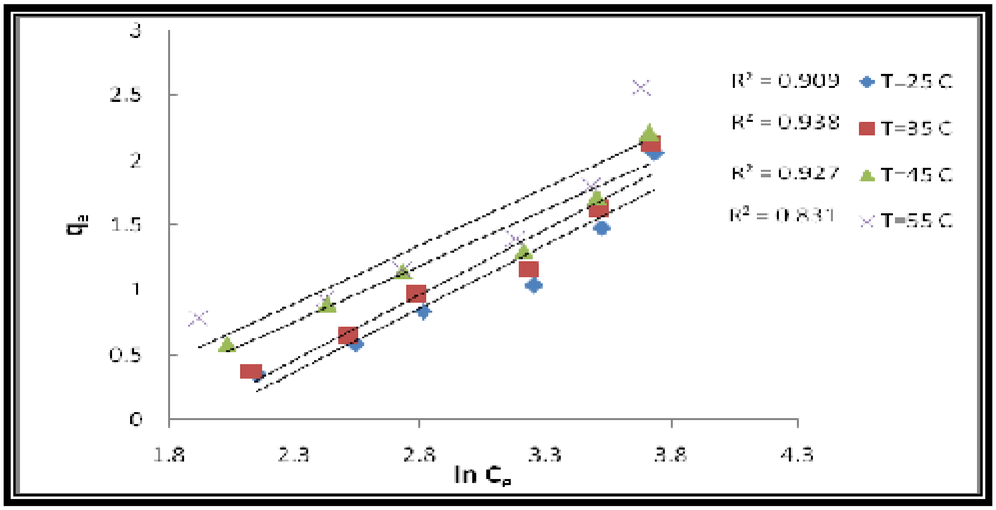

Figure (8): The linear plot of Temkin isotherm of DY4 at different temperatures.

Table (7) isotherm parameters for removal DY4 by silica.

Langmuir constants	**k_L (L/mg)**	**q_m *(mg/g)***	**R^2**		**S MAINTAB**
			Excel	**MAINTAB**	
25 °C	1.792	0.074	0.981	0.981	0.1320
35 °C	2.022	0.092	0.964	0.965	0.1674
45 °C	2.486	0.223	0.977	0.977	0.0772
55 °C	2.498	0.364	0.902	0.903	0.1143
Frendich constants	**log k_F**	**1/n**			
25 °C	-1.392	1.034	0.979	0.979	0.0443
35 °C	-1.305	1.003	0.969	0.970	0.0528
45 °C	-0.839	0.718	0.965	0.966	0.0425
55 °C	-0.670	0.627	0.934	0.935	0.0540
Temkin constants	**K_t**	**B_1**			
25 °C	-0.51	981	0.909	0.909	0.2101
35 °C	-0.54	1012	O.938	O.938	0.1776
45 °C	-0.70	866	0.927	0.928	0.1756
55 °C	-0.77	893	0.831	0.831	0.3014

As seen, these plots gave a different linearity's with a range of correlation coefficient (R^2) between 0.831 and 0.981. Based on R^2 the adsorption of DY4 is best fitted in the Langmuir isotherm. Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of sample surface, i.e., each dye molecule adsorbent adsorption has equal adsorption activation energy and demonstrates the formation of monolayer coverage of DY4 molecule on the outer surface of adsorbent. The values of (1/n) ranging between 0 and 1 are a measure of surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. It's clear from the Table (7) that two values of 1/n were greater than 1 confirming the non heterogeneous (homogeneous) of the surface of adsorbent.

Thermodynamic Analyses

Thermodynamic parameters provide the information of energetic changes associated with adsorption; therefore, these parameters should be accurately evaluated. The Langmuir isotherm was applied to calculate the thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0.

ΔG^0 of adsorption is calculated from equation 6 [1]:

$$\Delta G^\circ = -RTlnK_L \qquad \cdots (6)$$

ΔH^0 and ΔS^0 of adsorption are estimated from the slope and intercept of Vant Hoff equation (equation 7).

$$\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad \cdots (7)$$

The Vant Hoff plot for the adsorption of DY4 dye onto silica is given in fig. (9), while the thermodynamic parameters obtained are given in Table (8).

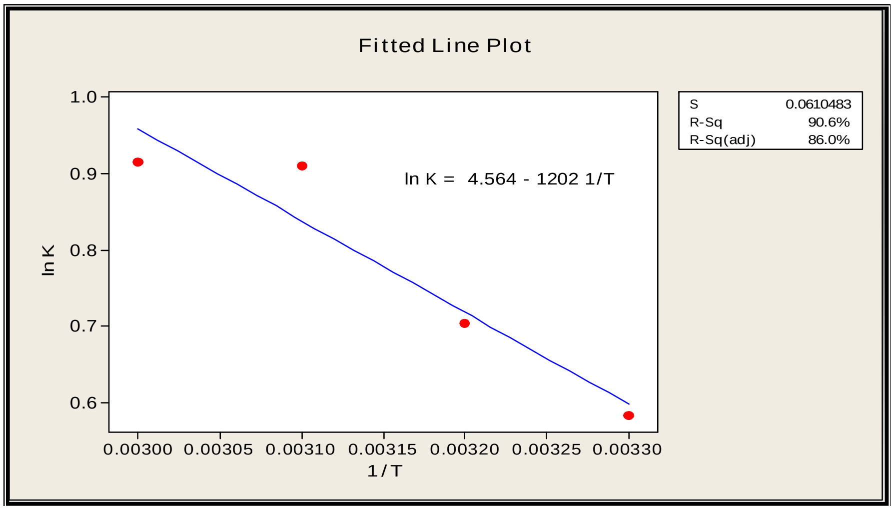

Figure (9): Vant Hoft plot of DY4 adsorption on silica

Table (8) the thermodynamic parameters of removal DY4 by silica

$\Delta H°$ $(KJ.mol^{-1})$	$\Delta S°$ $(J.mol^{-1}.K^{-1})$	$\Delta G°$ $(KJ.mol^{-1})$			
		298 °C	308 °C	318 °C	328 °C
9.993	37.945	-1.444	-1.802	-2.405	-2.495

As shown in table (8), the negative values of $\Delta G°$ at different temperatures indicate the spontaneous nature of the adsorption process. Positive $\Delta H°$ reveals endothermic adsorption, while the positive value of $\Delta S°$ suggests the increased randomness at the solid/liquid interface during the adsorption of the dye onto silica. A similar trend has been reported for the adsorption of Congo red onto coir pith carbon and fly ash [18].

Kinetics analysis

Adsorption kinetics, indicating the adsorption rate, is an important characteristic of adsorbents [3]. The pseudo first-order, pseudo-second order and intraparticle diffusion models were adopted to test the following experimental data:

Table (9) kinetic parameters of removal DY4 by silica.

Time (min)	C_t (mg/L)	q_t (mg/g)	q_e (mg/g)
15	43.90	1.524	
20	43.33	1.666	
25	43.15	1.711	2.055
30	42.83	1.791	
35	42.10	1.975	
40	42.05	1.987	
45	41.78	2.055	

The Pseudo-First Order Kinetic Model

This model has been widely used to predict dye adsorption kinetics. A linear form of pseudo-first order model described by ***lagergren*** [19]:

$$ln(q_e - q_t) = lnq_e - k_1 t \qquad \cdots (8)$$

Where q_e and q_t *are* the adsorption capacities (mg/g) at equilibrium and at time *t*, respectively, k_1 is the rate constant of pseudo-first order adsorption ($Lmin^{-1}$). The plot of log (q_e-q_t) versus *t* for the adsorption of DY4 onto silica was drawn in fig. (10), while the values of k_1 and q_e which calculated from the slope and intercept were listed in Table (10).

The R^2 values obtained was relatively small (0.894) indicating that the pseudo-first order model couldn’t be used to describe the adsorption behavior of DY4 onto silica.

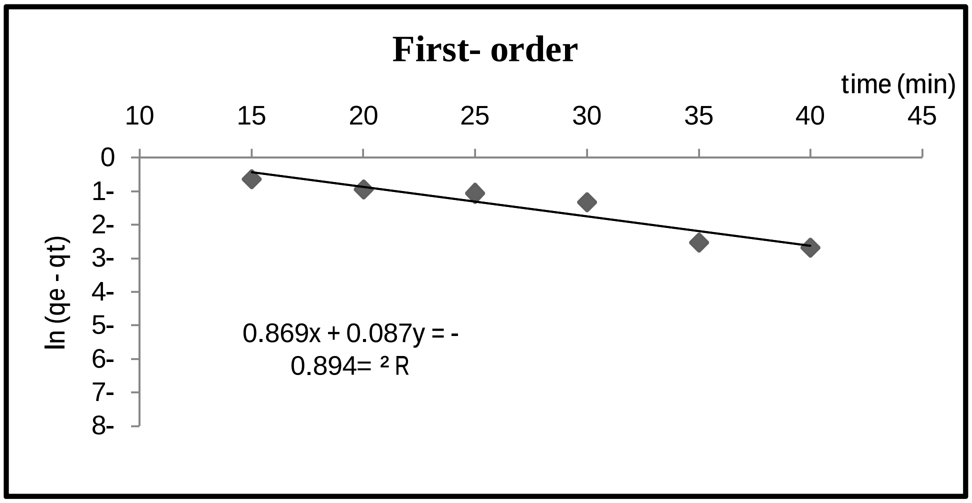

Figure (10) linear plot of pseudo first order from adsorption of DY4 on silica (C_o=50 ppm at pH 7, 25°C, and 45 min)

The Pseudo Second-Order Model

The pseudo second-order rate equation of ***Mckay and Ho*** can be represented in the following form [20]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad \cdots (9)$$

The rate constant of the pseudo second-order model constants k_2 (g/mg.min) can be determined experimentally from the slope and intercept of plot t/q_t versus t. The linear plot of t/q_t versus t is shown in fig. (11) and the value of k_2 is listed in Table (10).

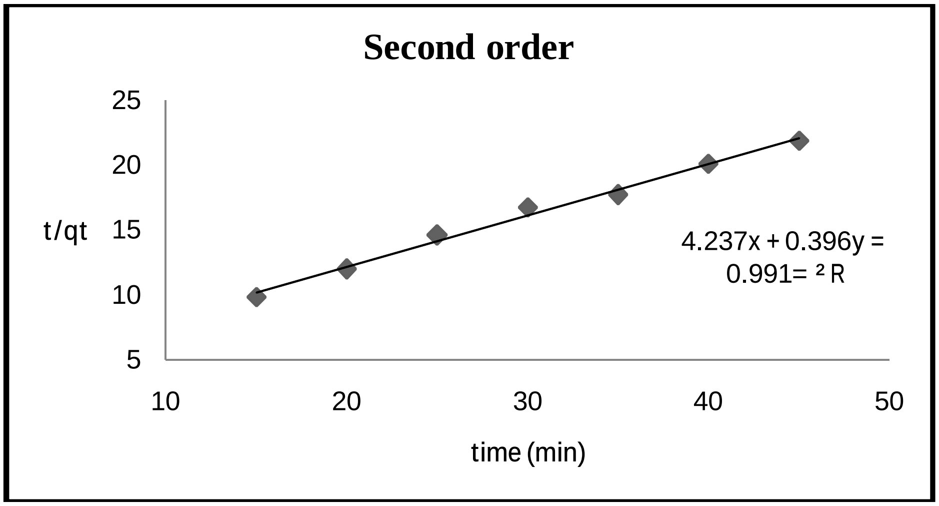

Figure (11) linear plot of pseudo second order from adsorption of DY4 on silica (C_o=50 ppm at pH 7, 25°C, and 45 min).

The obtained R^2 value was high (0.991) which indicates that the adsorption of DY4 perfectly complies with pseudo second order reaction. Similar kinetic results have also been reported for the adsorption of certain dyes onto Aspergillus niger [21] and onto Peat [22].

The Intraparticle Diffusion Model

The effect of intraparticle diffusion resistance on the adsorption can be determined by the following relationship [23]:

$$q = k_D\, t^{1/2} + C \qquad \cdots (10)$$

Where C is the intercept and k_D is the intraparticle diffusion rate constant ($mg/gmin^{0.5}$), which can be determined from the slope of the linear plot of q_t versus $t^{1/2}$.

Fig. (12) presents a linear fit of this model for adsorption of DY4, and the value of k_D were shown in Table (10).

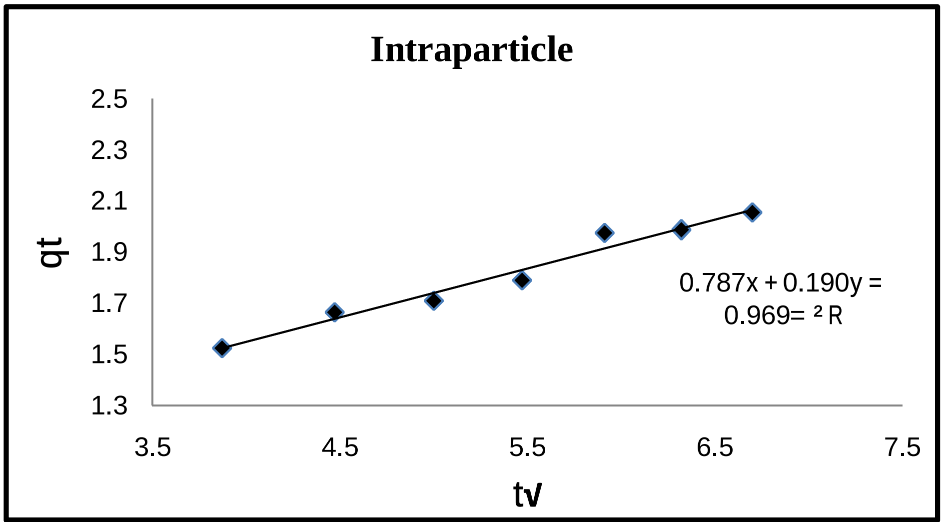

Figure (12) linear plot of intraparticle diffusion from adsorption of DY4 on silica (C_o=50 ppm at pH 7, 25°C, and 45 min).

The intraparticle diffusion plot do not pass through the origin ($C \neq 0$), these indicated the presence of intraparticle diffusion process, but this is not the only rate controlling step and other mechanisms such as surface reaction play an important role in the process [24]. Similar results were reported for the adsorption of dyes onto rice husk [25] and onto perlite [26].

Table (10): kinetic constants for the removal of DY4 by silica.

Pseudo-first order	**K_1 (L min^{-1})**	**R^2**
	0.087	0.894
Pseudo-second order	**K_2 (g/mg min)**	0.991
	0.037	
Intraparticale diffusion	**K_D (mg/g $min^{0.5}$)**	0.969
	0.190	

CONCLUSIONS

The main following conclusions can be formulated from the foregoing results:

1. The silica prepared from locally available sodium silicate was successfully removed direct yellow 4 dye from aqueous solutions.
2. The adsorption of direct yellow 4 dye was increased directly with increasing concentration, amount of silica and added sodium chloride.
3. The obtained data for the adsorption is best fitted in the Langmuir isotherm.
4. The thermodynamic parameters (ΔG°, ΔH° and ΔS°) indicate the spontaneous, endothermic, and randomness increase of the adsorption respectively.
5. The adsorption complies with pseudo second order reaction.

REFERENCES

[1]Chao-Yin Kuo, Chung-Hsin Wu and Jane-Yii Wu, *Adsorption of Direct Dyes from Aqueous Solutions by Carbon Nanotubes: Determination of Equilibrium, Kinetics and Thermodynamics Parameters*, Journal of Colloid and Interface Science 327, (2008), 308–315.

[2] Hariharasuthan, R. and A. Nageswara Rao, *Comparative Studies of Sorel's Cement on Selected Dyes*, Indian Journal of Science and Technology Vol. 4 No. 4 (2011) 410-4139.

[3] Weber, E.J. and V.C. Stickney, *Water Pollution by Synthetic Textiles Dyes*, Water Res. 27, (1993), 63.

[4] Albanis,T.A. D.G. Hela, T.M. Sakellarides and T.G. Danis, *Removal of Dyes from Aqueous Solutions by Adsorption on Mixtures of Fly Ash and Soil in Batch and Column Techniques*, Global Nest: the Int. J. Vol 2, No 3, (2004), 237-244.

[5] Pagga,U.M. and K. Taeger, *Development of a Method for Adsorption of Dyestuffs on Activated Sludge*, Water Resources, 28, (1994), 1051-1057.

[6] Davis,L. and C. Randal, *Development of Color Removal Potential in Organisms Treating Pulp and Paper Wastewaters,* J. WPCF, 50, (1978), 382-386.

[7] Arvanitoyannis,I. I. Eleftheriadis, and E. Tsatsaroni, *Influence of pH on Adsorption of Dye-Containing Effluents with Different Bentonites*, Chemosphere, 18, (1989), 1707-1711.

[8] Nyholm,N. B.N. Jacobsen, B.M. Pedersen, O. Poulsen, A. Damborg, and B. Schultz, *Removal of Organic Oicropollutants at ppb Levels in Laboratory Activated Sludge Under Various Operating Conditions*, Water Resources, 26, (1992), 339-353.

[9] Mavros, P. A.C. Daniilidou, N.K. Lazaridis and L. Stergiou, *Color Removal from Aqueous Solutions*, Part I, Flotation. Environ. Technol, 15, (1994), 601-616.

[10] Manoochehri, M. H. B. Sadeghi1, A. Khorsand, S. H. roohbakhsh, Z. sarikhani, *Equilibrium studies for the Adsorption of Acid Red 14 and Direct Yellow 86 Dyes from Aqueous Solution*, Journal of Applied Chemical Research, 16, (2011), 21-26.

[11] Huo,Q. D. Maargolese and G.D. Stucky, Surfactant Control of Phases in the Synthesis of Mesoporous Silica-Based Material, Chem. Mater. 8, (1996), 1147-1151.

[12] Alley.R. *Water Quality Control Handbook*, 8, McGraw Hill, 125, (2005).

[13]F. Woodard, *Industrial Waste Treatment Handbook*, Butterworth- Heinemann, (2001), 376.

[14] Benefield, L.D. J.F. Judkins, B.L. Weand. *Process Chemistry for Water and Wastewater Treatment*, Prentice-Hall, Inc, 191, (1982).

[15]]*Dye from Aqueous Phase onto Coal based Sorbent: Kinetic and Mechanistic Study*, J. Hazard Mter., B90, (2002), 189-204.

[16] AI-Degs, Y.S. M.I. EI-Barghouthi, A.H. EI-Sheikh, G.M. Walker, *Dyes Pigment*, 77, (2008), 16.

[17] Temkin,M.I. V. Pyzhev, Acta. Physiochim. URSS 12, (1940), 327-221.

[18] Accmiogllu,B. Adsorption of Congo red from aqueous solution onto calcium-rich fly ash, J. Colloid and Interface Science, 274, (2004), 371-379.

[19] Ho,Y.S. J.C.Y. Ng, G. Mckay, *Kinetics of Pollutant Sorption by Biosorbents*: Review, Sep. Purif. Methods, 29, (2009), 189-232.

[20] Mckay, G. and Y.S. Ho, *Pseudo-Second Order Model for Sorption Processes*, Process Biochem., 34, (1999), 451-465.

[21] Viraraghavan, Y. Fu. T. Adv. Environ. Res. 7, (2002), 239.

[22] Ho, Y.S. and G. Mckay, J. Eng. Chem., 70, (1998), 115.

[23] Weber, W.J. J.C. Morris, *Proceedings of the International Conference on Water Pollution Symosium*, Vol.2, Pergamon, Oxford, (1962), 231-266.

[24] Bulut, E. M. Ozacar and A.I. Sengil, *Equilibrium and Kinitic Data and Process Desighn for Adsorption of Congo red onto Bentanite*, J. Haz. Mat., (2008), 613-622.

[25] Vadivclan, V. and V.K. Kumar, Equilibrium, *Kinitic Mechanism and Process Design for the Sorption of Methylene Blue onto Rice Husk*, J. Colloid Interface Sci., 286 (1), (2005), 90-100.

[26] Vijayakumar,G. M. Dharmendirakumar, S. Renganathen, S. Sivanesan, G. Baskar and E.P. Kuppannagounder, *Removal of Congo Red from Aqueous Solution by Perlite*, Clean Soil, Air Water, 37 (4-5), (2009), 355-364.