ISSN : 0974 - 7524 Volume 7 Issue 3

Physical CHEMISTRY
An Indian Journal

Trade Science Inc.

Full Paper

PCAIJ, 7(3), 2012 [110-116]

Kinetic and thermodynamic study of eosin Y dye biosorption by leaves of date palm (*Phoenix dactylifera L.*)

Adel Amini[1], Nader Bahramifar[1], Fereydoon Ashrafi[1], Hassan Ghasemenjad-Bosra*[2], Elahe Amini[1]

[1]Department of Chemistry, Payame Noor University (PNU), Sari University, Mazandaran, (IRAN)

[2]Department of Chemistry, Babol Branch, Islamic Azad University, Babol, (IRAN)

E-mail: h_ghasem2000@yahoo.it

Received: 1st February, 2012 ; Accepted: 27th February, 2012

ABSTRACT

Dyes and pigments to cater to the needs of not only the textile industries but also of other industries such as paper, rubber, plastics, paints, printing inks, art and craft, leather, food, drug and cosmetics. Eosin Y is as a model anionic dye that is used in wool and silk to give red colour with a yellow fluorescence. Generally dyes are stable to light, heat and oxidizing agents and are usually biologically non-degradable. The dye-bearing effluent, when discharged into water bodies, affects photosynthesis, aquatic life, and also humans. Many investigators have studied different techniques for removal of colored dye from wastewater. The leaves of date palms, *Phoenix dactylifera L.* were used as biosorption of phosphates from aqueous solution, dyes. Since adsorption of eosin Y is used by chitosan nanoparticles, activated carbon. The present study deal with the adsorption of eosin Y from aqueous solution using the Leaves of date palm of *Phoenix dactylifera L*. The concentration of dye was determined by a UV-visible spectrometer. In this study The effect of contact time, pH of solution, adsorbent dosage, initial eosin Y concentration and effect of temperature were investigated. The equilibrium and kinetics of the process were investigated as well. The eosin Y uptake increased with the increase of initial eosin Y concentration and decreased with increasing pH value. The Freundlich isotherm was found to be the most suitable for eosin Y adsorption on *Phoenix dactylifera* L date palm. A pseudo second-order kinetic model successfully explains the kinetic of reaction. The posetive values of ΔG, $\Delta H°$ and $\Delta S°$ indicate that the adsorption process is unspontaneous and endothermic in nature. For desorption of the dye from the adsorbent,It was observed that the desorption of the dye is favored at highly basic pH (desorption was 86.952 % at a pH of 13). Desorptions were obtained after 180 minute of operation. The results of present investigation show that the relatively low cost and high capabilities of the *Phoenix dactylifera* L date palm make them potentially attractive adsorbents for the removal of eosin Y from aqueous solution.

KEYWORDS

Eosin Y dye;
Adsorption;
Date palm;
Freundlich isotherm;
Biosorption;
Desorption.

INTRODUCTION

Various types of dyes are manufactured for printing and dyeing industries from coal tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene, xylene, etc. Dyes and pigments to cater to the needs of not only the textile industries but also of other industries such as paper, rubber, plastics, paints, printing inks, art and craft, leather, food, drug and cosmetics. Dyes are classified in three broad classes: (a) anionic: direct, acid and reactive dyes (b) cationic: all basic dyes and (c) non-ionic: dispersed dyes. Eosin Y is as a model anionic dye that is used in wool and silk to give red colour with a yellow fluorescence[1]. Generally dyes are stable to light, heat and oxidizing agents, and are usually biologically non-degradable[2]. The majority of these dyes are of synthetic origin and toxic in nature with suspected carcinogenic and genotoxic effects. The dye-bearing effluent, when discharged into water bodies, affects photosynthesis, aquatic life, and also humans[3]. The wastewaters from these industries are important source of water pollution. Many investigators have studied different techniques for removal of colored dye from wastewater, e.g. chemical coagulation/flocculation, different advanced oxidation processes, ozonations, cloud point extraction, nanofiltration, micellar enhanced, ultrafiltration, adsorption on to (i) agricultural solid waste (ii) calcined alunite (iii) various types of activated carbon and (iv) surfactant impregnated montmorillonite, etc[1]. So the wastewaters from the textile industries should be treated before their discharge into environment[2]. The leaves of date palms, *Phoenix dactylifera L.* were used as biosorption of phosphates from aqueous solution, dyes (methylene blue dye) and were evaluated as biomonitors of heavy metal contamination in the cities. Since adsorption of eosin Y is used by chitosan hydrobeads[3] chitosan nanoparticles[4] the solar photo-fenton processes[5] activated carbon[1].

The present study deal with the adsorption of eosin Y from aqueous solution using the Leaves of date palm of *Phoenix dactylifera L.* The *Phoenix dactylifera L.* date palm is one of the most cultivated palms around the world. It has a good tolerance to cold and dry-hot climates. After annually trimming operations, enormous quantities of date palm leaves wastes are thrown away, exception smaller scales for artisan products. Date palm leaves could offer an appreciable economic and environmental potential, which should be in a position to effectively contribute to their use as reinforcement in hot dry climates. In this study, the effects of various parameters such as, contact time, pH of solution, adsorbent dosage, initial eosin Y concentration and effect of temperature were examined.

MATERIALS AND METHODS

Preparation of the materials

The dye used in this study is eosin Y, which is anionic in nature (The structure of the dye is shown in Figure 1)[1].

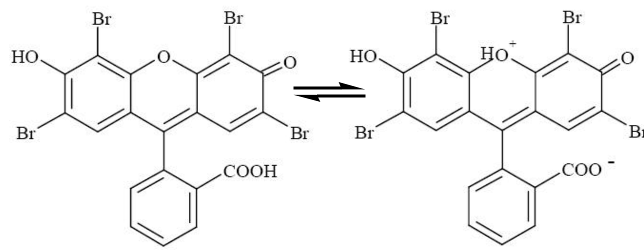

Figure 1 : Structure of eosin Y

Eosin Y was obtained from Merck. The dye solutions were prepared by dissolving accurately weighed amounts of dye in distilled water at concentrations of 50, 100, 150, 200, 250 and 300 (mg/l). 1.0, 0.1, 0.05 and 0.02 N hydrochloric acid and sodium hydroxide solutions were used to adjust the pH of the dye solution (Jenway pHmeter, model: 3510). The natural powder used in this research are from the leaves of *Phoenix dactylifera L. Phoenix dactylifera L.* date palm turn obtained from boshehr province (southern of Iran). In this study, we chose unwashed and dry leaves then cut and powdered them. Powder of *Phoenix dactylifera* L *L.* date palm was washed with distilled water and the solution was placed in a constant temperature bath and stirred with the help of a stirrer at 700 rpm (Jenway hotplate and stirrer, model: 1203). Then dried at 100 ^{0}C for 24 hour (Ehret oven, model: BK3064)[6].

Adsorption kinetic measurements

Eosin Y adsorption kinetics study was carried out with different initial concentrations of eosin Y and a fixed concentration of the adsorbents at room temprature (± 0.1^{0}C) (bath: Julabo, model: F12). Before the start of each kinetic experiment, 1000 mg of the sample was

Full Paper

loaded in a 1 Litre. Six levels of initial eosin Y concentrations 50, 100, 150, 200, 250 and 300 ppm were used. The pH of the solution was maintained at a defined value by manually adding HCl and/or NaOH solutions. The Erlenmeyer flask was capped and stirred magnetically at 700 rpm for 180 minutes to ensure approximate equilibrium. Five ml of solution was sampled for intervals between 0 and 180 minute of adsorption. At the end of the adsorption period, the solution was centrifuged with 5000 rpm for 5 minute. The concentration of dye was determined by a UV-visible spectrometer (GBC, Australia model: Cintra 20) at a wavelength (λ_{max}) of 517 nm[1].

Desorption experiments

To evaluate eosin Y desorption from the samples, the residual solids retained on the filter paper were collected in 150 ml Erlenmeyer flask after filtration of the suspension from an adsorption test. The flask was covered with magnetic stirring at 700 rpm for 3 hour while pH was maintained at the same value as in the adsorption experiment. The suspension solution was centrifuged and analyzed for desorbed eosin Y in a similar way described previously. The quantity of desorbed eosin Y was determined by the amount of eosin Y in solution after the desorption experiment. The desorbability is expressed according to the capacity of desorption q_d (mg/g) and the capacityof the adsorption q_a (mg/g) of adsorbate, as follows:

$$\text{Desorbability}(\%) = \left(\frac{q_d}{q_a}\right) \times 100 \qquad (1)$$

Eosin uptake

The eosin Y uptake was calculated following the concentration difference method. The initial concentration C_i (mg/L) and left over eosin Y concentration at different time intervals, C_e (mg/g), were determined and the eosin Y uptake q_e (mg eosin Y adsorbed / g adsorbent) was calculatedfrom mass balance equation as follows:

$$q_e = \left(\frac{C_i - C_e}{M} \times V\right) \qquad (2)$$

Where *V* is the volume of the solution in litre and M is the mass of sorbent in gram. The extent of sorption in percentage is found from the relation:

$$\text{Sorption}(\%) = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \qquad (3)$$

All statistical analysis was done using Microsoft Excel 2003 version office XP[6].

RESULTS AND DISCUSSION

Effect of contact time

The results show that adsorption process is clearly time dependent. From this study, it is observed that most of the eosin Y specie uptake occurs within a time of 180 minute at 70% of the totally biosorbed for an initial eosin Y concentration of 100 (mg/l). For periods greater than 90 minute, the uptake is further increased but with a much slower rate. Equilibrium began establishing itself after approximately a contact period of 180 minute. Also, the outcome is generally in line with previous similar studies, such as the adsorption of eosin Y onto some natural and low cost adsorbent attains equilibrium at about 3 hour. Further increase in retention time does not seem to have any impact on the equilibrium concentration. Hence all the adsorption experi ments were carried in 180 minute.

Effect of pH on eosin Y adsorption

The pH of the aqueous solution is an important variable that influences the bisorption of ions at the solid-liquid interfaces. The pH value of the eosin Y solution plays an important role in the whole biosorption process and particularly on the biosorption capacity. With a similar procedure, the effect of pH on eosin Y specie adsorption onto *Phoenix dactylifera* L. date palm was examined in a series of experiments that used the same initial eosin Y concentration (100 mg/l) while maintaining pH at different values between1.0 and 8.0. To achieve the maximum adsorption capacity of the adsorbent for eosin Y ions it was found pH = 4.0. The results show that the uptake of eosin Y specie adsorption onto *Phoenix dactylifera* L. date palm tends to decrease with the increase of pH. This can be attributed to the fact that a higher pH value leads the surface to carry more negative charges and thus would more significantly repulse the negatively charged species in solution. Therefore, at higher pH value, the decrease of eosin Y adsorption capacity resulted from an increased repulsion between the more negatively charged eosin Y anions and negatively charged OH^- anions charged surface adsorbent sites. So with increasing acidity of the solution, the surface becomes more positively charged: consequently, higher removal is expected at low pH values.

Effect of adsorbent dosage

To achieve the maximum adsorption capacity of the adsorbent for eosin Y ions, the dose of *Phoenix dactylifera* L date palm materials was varied from 2.0 to 20.0 (g/l) and it was found that a dose of 8 (g/l) was sufficient for the maximum uptake of eosin Y ions under the reported experimental conditions. It is also seen that a further increase in adsorbent dose (greater than 8.0 (g/l)) affects the uptake of eosin Y adsorption greatly: the eosin Y uptake adsorption decreases. This result is related to the effect that for significant doses of *Phoenix dactylifera* L date palm, the leaves were rolled up the ones on the others and consequently there is not a good contact with the eosin Y ions dissolved in the followed solution.

Effect of initial eosin Y concentration

Experiments were undertaken to study the effect of varying initial concentration 50 - 300 (mg/l) on eosin Y specie removal onto *Phoenix dactylifera* L date palm. The experiment were carried out at 25 ^{0}C, an adsorbent dose at 8 (g/l), an agitation speed at 700 rpm and pH at 4 for a contact period of 180 minute. It was found that a dose of 100 (mg/l) was sufficient. The experiment indicates that all curves have the same shape. The eosin Y uptake decreased with increasing initial eosin Y concentration. This may be due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the adsorbate ion remains unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodated increase. Corresponding cumulative removal (mg/g) is lower at higher initial concentrations. This is attributable to decrease in contact between adsorbent and adsorbate at higher concentrations.

Effect of temperature

Adsorption experiments were carried out for 100 (mg/l), eosin Y at four different temperature (5.0, 15.0, 25.0, 35.0, 45) ^{0}C using 8.0 g of *Phoenix dactylifera* L date palm per liter of the solution in order to observe the effect of temprature on the adsorption capacity. It was observed that with an increase in temperature, adsorption capacity increased. The thermodynamic parameters ΔG°, ΔS° and ΔH° for this adsorption process have been determined using the following equations:

$$\Delta G° = \Delta H° - T\,\Delta S° \quad (4)$$

$$\log K_C = \log\left(\frac{q_e}{C_e}\right) = \left(\frac{\Delta S°}{2.303R}\right) + \left(\frac{-\Delta H°}{2.303RT}\right) \quad (5)$$

Where q_e is the maximum amount of dye adsorbed per unit mass of the *Phoenix dactylifera* L date palm (mg/g). C_e is equilibrium concentration (mg/L) and *T* is temperature in Kelvin. It may be noted that the experimental data considered here for the calculation of the thermodynamic parameters (Δ*G*°, Δ*S*° and Δ*H*°) are in the linear range of the equilibrium adsorption isotherm. Therefore, Eq. 5 can be used with the experimental data to evaluate entropy of adsorption Δ*S*° and enthalpy of adsorption Δ*H*° from a plot of $\log(q_e/C_e)$ versus 1/*T*. The value of gibbs free energy (Δ*G*°) is then calculated from Eq. 4. The values of Δ*H*°, Δ*S*° and Δ*G*° are shown in TABLE 1 for the initial dye concentration of 100 (mg/l)[1].

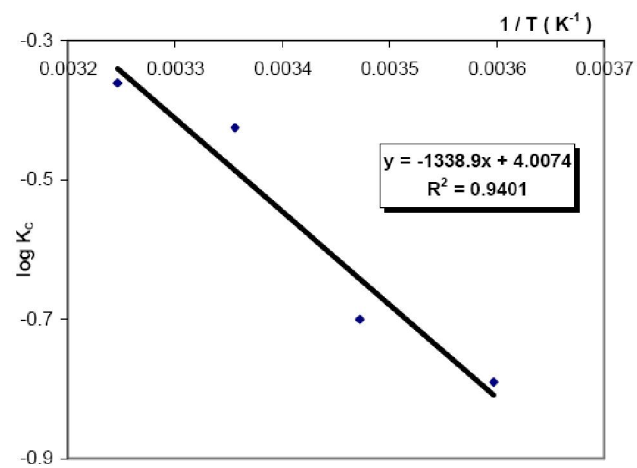

Figure 2 : Van't Hoff plot for the biosorption of eosinY on *Phoenix dactylifera* L date palm.

The posetive values of Δ*G*° and Δ*H*° indicate that the adsorption process is unspontaneous and endothermic in nature. The posetive value of Δ*S*° suggests increased randomness during adsorption.

Adsorption isotherms

Two well known models, namely the Langmuir and

TABLE 1 : Thermodynamic parameters for the adsorption of eosin dye in the *Phoenix dactylifera* L date palm

Dye concentration (mg/l)	ΔH^0 (kJ mol^{-1})	ΔS^0 (Jmol^{-1} K^{-1})	ΔG^0 (kJmol^{-1}) at temperature			
			278 K	288 K	298 K	308 K
100	25.636	76.73	4.205	3.858	2.426	2.126

Freundlich models, are used to analyze the experimental data.

Langmuir isotherm

The Langmuir adsorption isotherm is applicable in many adsorption processes. The basic assumption is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and no further adsorption thereafter. The Langmuir model is expressed as:

$$q_e = \left(\frac{QbC_e}{1+bC_e}\right) \quad (6)$$

A linear from of this expression is:

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{Qb} + \frac{C_e}{Q}\right) \quad (7)$$

Where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g), and C_e is the equilibrium concentration of the adsorbate (mg/l). The constants *Q* and *b* are Langmuir constants. Values of *Q* (mg/g)and *b* (l/g) are calculated from the intercept and slope of the plot of C_e/q_e versus C_e.

Freundlich isotherm

This model is indicative of the extent of heterogeneity of the surface of the adsorbent and is given by:

$$q_e = K_F C_e^{1/n} \quad (8)$$

Where K_F and *n* are Freundlich constant. Alinear form of the Freundlich expression is as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (9)$$

The constants K_F and *n* signify the adsorption capacity and intensity of adsorption, respectively. Values of K_F and *n* are calculated from the intercept and slope of the plot of log q_e versus log C_e [1].

Adsorption data of eosin Y on the *Phoenix dactylifera* L date palm are calculated. The coefficients of these two-isotherm models for the Langmuir isotherm is (R^2= 0.8368) (Figure 2) and for Freundlich isotherm, is (R^2= 0.9283) (Figure 3). The data provide information on the maximum amount of *Phoenix dactylifera* L date palm required to adsorb a particular mass of eosin under specified system condition. Correlation coefficients are also calculated by fitting the experimental adsorption equilibrium data for the eosin Y- *Phoenix dactylifera* L date palm system, using both the Langmuir and freundlich adsorption isotherms. It was found that the adsorption isotherm for the eosin Y *Phoenix dactylifera* L date palm system is explained better by the Freundlich isotherm.

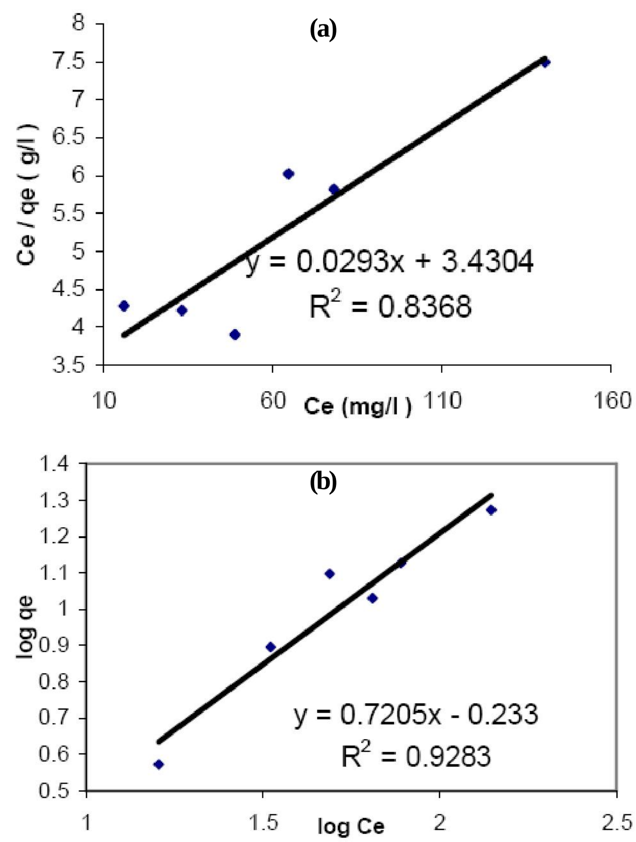

Figure 3 : Langmuir (a) and Freundlich (b) biosorption isotherm for eosin on *Phoenix dactylifera* L date palm.

TABLE 2 : Langmuir and Freundlich constants for the biosorption eosin on *Phoenix dactylifera* L date palm.

Constant in Langmuir model				Constant in Freundlich model		
T (^{O}K)	*Q* (mg/g)	*b* (l/g)	R_L (using in C_O=100mg/l)	T (^{O}K)	K_F (l/mg)	*n*
298	34.13	0.0085	0.539	298	0.5848	1.3879

Adsorption kinetics

The kinetics of the adsorption of eosin Y on *Phoenix dactylifera* L date palm have been described by first and pseudo second-order models. The Lagergren's equation for first-order kinetics is given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (10)$$

Where q_e and q_t are the amount of eosin Y adsorbed (mg/g) at equilibrium and at any time *t*, k_1 is the rate constant (min^{-1}). The plot of log (q_e-q_t) versus *t* gives a straight line for the first-order adsorption kinetics. The value of the first-order rate constant k_1 is obtained from the slope of the straight line.

The expression for the pseudo second-order rate equation is given as:

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_e^2} + \frac{t}{q_e}\right) \quad (11)$$

In Eq. 11, k_2 (g/mg min) is the rate constant for the pseudo second-order adsorption kinetics. The slope of the plot(t/q_t) vs. *t* gives the value of q_e and from the intercept k_2 can be calculated. The values of the rate constants are shown (Figure 4) that it is clear from the nature of fit and the correlation coefficients tabulated that the adsorption of eosin Y on *Phoenix dactylifera* L date palm is better represented by pseudo second-order kinetics[1].

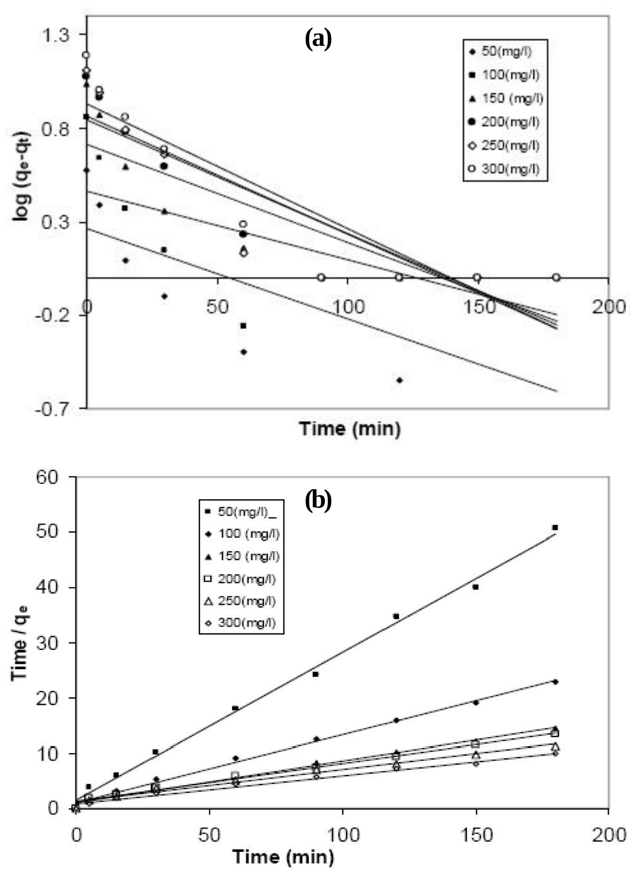

Figure 4 : Pseudo first-order (a) and Pseudo second-order (b) kinetic models data for biosorption of eosin on *Phoenix dactylifera* L date palm.

Desorption study

The test of eosin Y desorption were coducted with initial eosin Y concentration (100 mg/l) at pH 11. The eosin Y desorbability can be defined as the ratio of the desorbed eosin Y over the total adsorbed eosin Y by the adsorbent. Therefore, the desorbability of eosin Y can be used to indicate the amount of the desorbed eosin Y in percentage from eosin Y loaded onto *Phoenix dactylifera* L date palm material. The amount of the desorbed eosin Y is slightly increased with the increase of the adsorbed eosin Y. These results indicate that the eosin Y adsorption onto *Phoenix dactylifera* L date palm is not completely reversible and the bonding between the sample particles and adsorbed eosin is likely strong. It is relatively difficult for the adsorbed eosin Y to be desorbed from the samples.

Desorption kinetics

It is proposed that the desorption rate at any instant would be proportional to the driving force, i.e. The difference between the initial (at *t* =0) amount of the adsorbed dye and the day concentration in the solution, at any time *t*. The dye concentration in the solution in turn would be related to the amount of the dye still remaining adsorbed, through a mass balance this is mathematically represented by the following equation:

$$\left(\frac{dq}{dt}\right) = \alpha(q_0 - kq) \quad (12)$$

Where α and *k* are the constants ($k \neq 1$). q_0 and *q* are the amount of adsorbed dye present per gram of *Phoenix dactylifera* L date palm at time *t* =o and at any time *t = t*,respectively. Integrating Eq. 12 between *t* =0 and any time, the following expression of the percentage desorption is obtained[1].

$$D = 100 \times \left(\frac{k-1}{k}\right)[1 - e^{-kat}] \quad (13)$$

Where *D* is defined as $D = \left(1 - \frac{q}{q_0}\right) \times 100$ (14)

The values of k and α can be determined from the experimental data under various operating condition.

Effect of pH

The effect of pH on the percentage desorption of dye without adding any surfactants is studied. At higher pH, the dye molecules become anionic in nature and adsorption is restricted, as discussed in section 3.2. Thus, with the increase in pH, desorption increases. it can be seen that after 180 minute of operation, desorption of dye increases from about 49.37 % to 86.95% when pH increases from 11 to 13.

CONCLUSIONS

Adsorption of eosin Y on *Phoenix dactylifera* L date palm was studied in this paper. The effect of various operating conditions, namely, pH, initial dye concentration and temperature were investigated for the operation. The equilibrium and kinetics of the process were investigated as well. Removal of eosin Y from aqueous solution onto *Phoenix dactylifera* L date palm was carried out at room temperature. Results indicate that pH, initial eosin Y concentration and adsorbent dosage impacted eosin Y species removal. The eosin Y uptake increased with the increase of initial eosin Y concentration and decreased with increasing pH value. It is also seen that a further increase in adsorbent dose (greater than 8 (g/l) affect the uptake of eosin Y biosorption greatly. The conditions of maximum biosorption of the eosin Y ions were optimized. In nature and in normal treatment, the treated waters are usually at pH from 1.0 to 8.0, so the adsorption capacity of eosin is about 8.77 (mg/g) at pH 4, for an adsorbent dosage of 8 (g/l), initial eosin concentration of 100 (mg/l), with Efficiency of biosorption (Ra = 71.37 %), under a constant temperature of 5 - 35^{0}C, and the equilibrium state was reached within 180 minute of exposure time. The Freundlich isotherm was found to be the most suitable for eosin Y adsorption on *Phoenix dactylifera* L date palm. A pseudo second-order kinetic model successfully explains the kinetic data. For desorption of the dye from the adsorbent, a number of pH values and different surfactants were used (pH = 11 – 13). It was observed that the desorption of the dye is favored at highly basic pH (desorption was 86.95% at a pH of 13). Desorptions were obtained after 180 minute of operation. The results of present investigation show that the relatively low cost and high capabilities of the *Phoenix dactylifera* L date palm make them potentially attractive adsorbents for the removal of eosin Y from aqueous solution.

REFERENCES

[1] M.K.Purkait, S.DasGupta, S.De; J.Envir.Manage, **76**, 135 **(2005)**.
[2] Y.Wang, Y.Mu, Q.B.Zhao, H.Q.Yu; Separation and Purification Technology, **50**, 1 **(2006)**.
[3] S.Chatterjee, S.Chatterjee, B.P.Chatterjee, A.R.Das; J.Coll.Inter.Sci., **288**, 30 **(2005)**.
[4] W.L.Du, Z.R.Xu, X.Y.Han, Y.L.Xu, Z.G.Miao; J.Hazard.Mater, **153**, 152 **(2008)**.
[5] H.Zheng, Y.Pan, X.Xiang; J.Hazard.Mater, **141**, 457-464 **(2007)**.
[6] Kh.Riahi, B.B.Thayer, A.B.Mammou, A.B.Ammar, M.H.Jaafoura; J.Hazard.Mater, **170**, 511-519 **(2009)**.
[7] T.Fernandez, U.K.Samersen, X.Joseph, N.V.Unnikrishnan; Journal of Materials Processing Technology, **30**.
[8] A.Bendahou, A.Dufresne, H.Kaddami, Y.Habibi; Carbohydrate Polymers, **68**, 601-608 **(2007)**.
[9] A.H.Bu-Olayan, B.V.Thomas; Journal of Arid Environments, **51**, 133-139 **(2002)**.
[10] Abdelaziz L.Al-Khlaifat, Omar A.Al-Khashman; Atmospheric Environment, **41**, 8891-8897 **(2007)**.
[11] Y.S.Ho, G.Mckay; Process Biochemistry, **34**, 451-465 **(1999)**.
[12] Y.S.Ho; Water Research, **40**, 119-125 **(2006)**.
[13] A.H.Bu-Olayan, B.V.Thomas; Journal of Arid Environments, **51**, 133-139 **(2002)**.
[14] Senol Sert, Ceren Kutahyali, Suleyman Inan, Zeynep Talip, Berkan Cetinkaya, Meral Eral; Hydrometallurgy, **90**, 13-18 **(2008)**.
[15] A.Y.Dursan; Biochemical Engineering Journal, **28**, 187-195 **(2006)**.
[16] A.Kapoor, T.Viraraghavan, D.R.Cullimore; Bioresource Technology, **70(1)**, 95-104 **(1999)**.