Biosorption of azo dye onto date seeds: Thermodynamic, kinetics and equilibrium studies

Amina Rezgui[a], Eric Guibal[b] and Taoufik Boubaker[a*]

[a]*Laboratoire C.H.P.N.R, Faculté des Sciences, Université de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisie*
[b]*Ecole des mines d'Alès, Centre des Matériaux des Mines d'Alès, C2MA/MPA/BCI, 6, Avenue de Clavières, F-30319 Alès cedex, France*

(Received: 25 June 2016, accepted: 19 September 2016)

Abstract: The aim of this paper is to study the date seeds potential for azo dye biosorption of from aqueous solution. As shown in SEM analysis, treated date seeds were found to be effective in methyl orange dye removal. Thermodynamic parameters depicted the exothermic nature of biosorption and the process was feasible and spontaneous at all temperatures (293-313 K). Kinetic results showed that the pseudo-second-order kinetic model was well fitted to the experimental data and indicated that the biosorption was classified as chemical process. The Langmuir and Dubinin–Radushkevich (D–R) isotherm models were applied to the equilibrium data. Adsorption data were well described by the Langmuir and the maximum uptake of methyl orange onto date seeds was found to be 47.61 mg g^{-1}. The mean free energy for azo dye from the D-R isotherms confirms that the methyl orange was chemisorbed onto treated date seeds.

Keywords: Date seeds, biosorption, SEM analysis, isotherms, kinetic, chemisorption.

INTRODUCTION

We recently conducted a study on heavy metals biosorption; we managed to use the raw date seeds, a low cost biomass to uptake Hg(II) and Zn(II) from aqueous media. Comparing with others lignocellulosic residues [1-3], interesting results were obtained; with a low biomass dose 4g L^{-1} maximum biosorption capacities were found to be 38.5 and 52.6 mg g^{-1} for mercury and zinc, respectively [4]. The originality of this work is manifested by the valorization of a very abundant lignocellulosic waste in Tunisia to solve one of the environmental issues that every country is facing "wastewater treatment".

On the basis of these results and in order to broaden the range of pollutants removed by this material, the aim of this work is to study the biosorption of Methyl Orange from aqueous solution using date seeds under the same conditions. It is worth noting that the choice of this dye is not an arbitrary. Methyl orange is a commonly used monoazo anionic dye in laboratory assays, textiles and other commercial products, azo dyes are toxic, mutagenic and carcinogenic [5-7]. In this paper, we report on the results of a kinetic investigation of the biosorption process. The kinetic data are used to determine the interaction mechanism between azo dye and the date seeds surface. The found results were confirmed by biosorption isotherms, approach of Langmuir and Dubinin-Radushkevich have been employed and discussed.

EXPERIMENTAL SECTION

1. Sorbent and materials

Date seeds selected for the present work were collected from date palm grown in Tozeur oasis (south west of Tunisia). The samples were collected and washed with distilled water to remove the particles adhering to the surface of the material before being dried in an oven at 70 °C for 3 h (to constant weight). The dried biomass was chopped, sieved and the particles with an average of 250 µm.

* Corresponding author, e-mail address : boubaker_taoufik@yahoo.fr; Tel. +216 73 500 275; Fax: +216 73 500 278

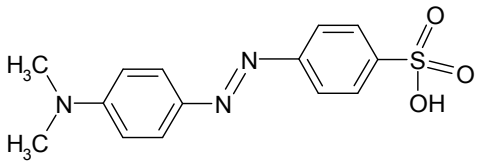

Figure 1. Molecular structure of Methyl Orange

Methyl Orange, purchased from RAL (Paris, France). The stock solution (1000 mg L^{-1}) was prepared by dissolving appropriate amount of the azo dye in one L of demineralized water (Milli-Q). The desirable experimental concentrations of solutions were obtained by using the Microlab 600 Series Diluter. The chemical structure of methyl orange is shown in Figure 1.

2. Batch biosorption experiments

The biosorption of methyl orange from aqueous solutions was carried out using a batch equilibrium method. For uptake kinetics the contact times were varied in the range 10-600 min. For the study of thermodynamic parameters, the effect of temperature was studied between 20 and 40 °C. All biosorption experiments were executed at pH 4.0, an optimum biomass dosage was selected as 4 g L^{-1} and with initial dye concentration C_o= 25 mg L^{-1}. It's important to note that the pH was not adjusted during the sorption step but was monitored at equilibrium. The isotherms studies were performed for different metal concentrations (in the range 5-600 mg L^{-1}).

Typically, a given volume V containing the appropriate dye concentration at fixed pH was shaken with the desired dose of activated sludge (m) at a rotation speed of 150 rpm (using a reciprocal shaker IKA HS 501, IKA Labortechnik, Germany), in a thermostatic chamber, with controlled temperature. Collected samples were filtrated (1.4 µm-pore size membrane filter) before being acidified with a 100 µL-volume of concentrated nitric acid and analyzed by UV-Vis spectrophotometer (Shimadzu UV-160) at 456 nm to determine the dye concentration. The biosorption efficiency and the equilibrium adsorbate (or biosorption capacity at equilibrium, q_e (mg g^{-1}), were calculated using Eqs. (1) and (2), respectively.

$$Biosorption\ \ (\%) = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

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

In these equations, C_i and C_e are the initial and equilibrium concentration of azo dye in mg L^{-1}.

RESULTS AND DISCUSSION

1. Characterization of treated date seeds

The textural properties of treated date seeds surface were observed with SEM analyses, before and after the biosorption of methyl Orange loading.

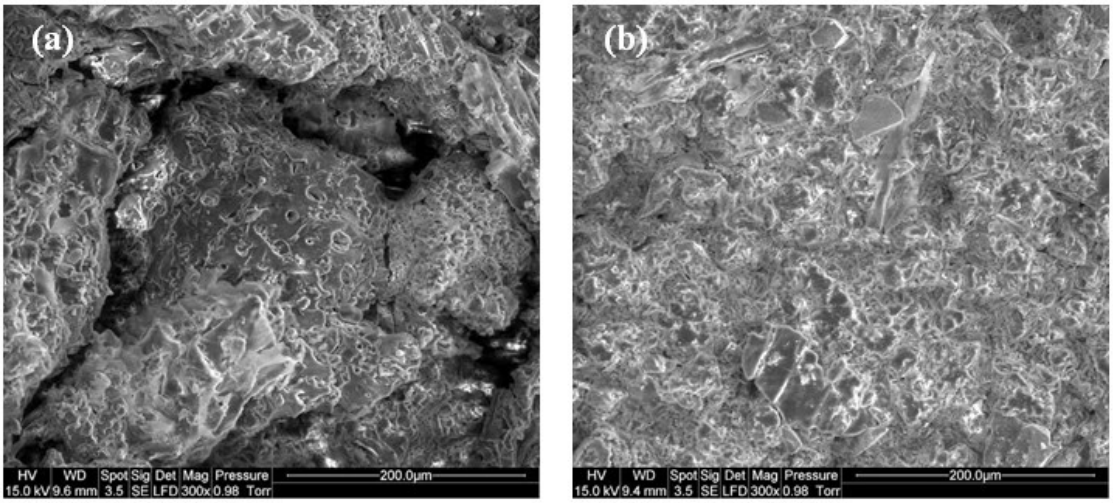

Figure 2. SEM photographs of treated date seeds before (a) and after (b) methyl orange biosorption.

The SEM image (Figure 2a) shows irregular and porous structure of the activated date seeds; the presence of pores suggests that there is a good possibility for the anionic dye to be trapped and adsorbed onto the surface of biosorbant (Figure 2b). The SEM analysis highlights azo dye biosorption phenomenon by chemically treated date seeds [8].

2. Biosorption thermodynamics

The thermodynamic parameters were evaluated: the Gibbs free energy change (ΔG°, kJ mol^{-1}), the standard enthalpy change (ΔH°, kJ mol^{-1}) and the standard entropy change (ΔS°, kJ mol^{-1}) can be calculated by using Van't Hoff equation [9] (Eq. (3)), in which R is the gas constant.

$$Ln\frac{q_e}{C_e} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \times \frac{1}{T} \qquad (3)$$

The effect of temperature on the biosorption of methyl orange onto treated date seeds is illustrated in Figure 3. As can be seen, good linear relationship ($R^2 = 0.994$) is obtained when Ln (q_e/C_e) values were plotted versus the inverse of the temperature. The linear least-squares analysis leads to values for the ΔH° and ΔS°, which were used to determined the free energy according $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ relationship [10].

The thermodynamic parameters are summarized in Table I. The negative values of ΔG° in the range

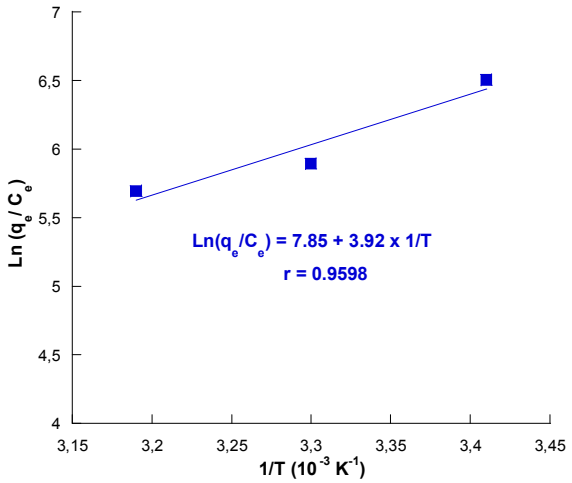

Figure 3. Determination of thermodynamic parameters for methyl orange biosorption.

Table I. Thermodynamic parameters for methyl orange biosorption.

ΔG° (kJ mol^{-1})	293 K	-13.29
	303 K	-13.04
	313 K	-11.93
ΔH° (kJ mol^{-1})	-32.57	
ΔS° (J mol^{-1} K^{-1})	-65.23	

of 20-40 °C show the feasibility and spontaneity of biosorption. The exothermic nature of methyl orange biosorption by treated date seeds was confirmed by the negative value of ΔH° (-32.57 kJ mol^{-1}). On the other hand, the negative ΔS° (-65.23 J mol^{-1} K^{-1}) values confirm a decrease in the randomness at the solid/solution interface during the biosorption process. Therefore, based on these data, the thermodynamic parameters showed that the biosorption process of azo dye was onto treated date seeds taken place via chemisorption [11].

3. Kinetic study

The kinetic behavior of methyl orange removal onto treated date seeds was studied to evaluate the rate of adsorbate uptake from aqueous solution, which controls the mechanism of dye adsorption. In order to investigate the mechanism of biosorption process, the kinetics models were fitted to the experimental data for the determination of potential rate-controlling steps of the methyl orange biosorption kinetics. It is found that the biosorption kinetics on the biomass may be well described by the pseudo second-order kinetic model [12]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where q_t and q_e (mg g^{-1}) are the amounts of the dye biosorbed at a given time t and equilibrium, respectively and k_2 (g mg^{-1} min^{-1}) is the rate constant of biosorption. The straight lines of the t/q_e versus t plots (Figure 4) suggest the applicability of this kinetic model in a temperature range of 20 to 40 °C.

As shown in Table II, the calculated values of the biosorption capacity at equilibrium ($q_{e,calc}$) and the experimental values ($q_{e,exp}$) are in the same

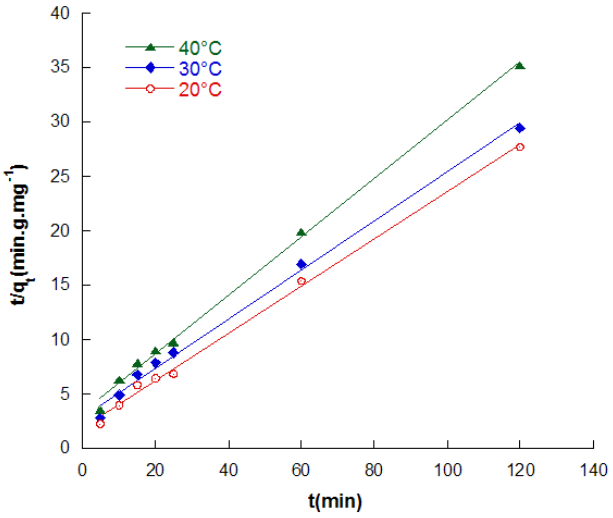

Figure 4. Pseudo-second-order kinetic plots for methyl orange biosorption onto date seeds (C_o = 25 mg L^{-1}, biomass dosage (BD) = 4 gL^{-1} and pH = 4.0).

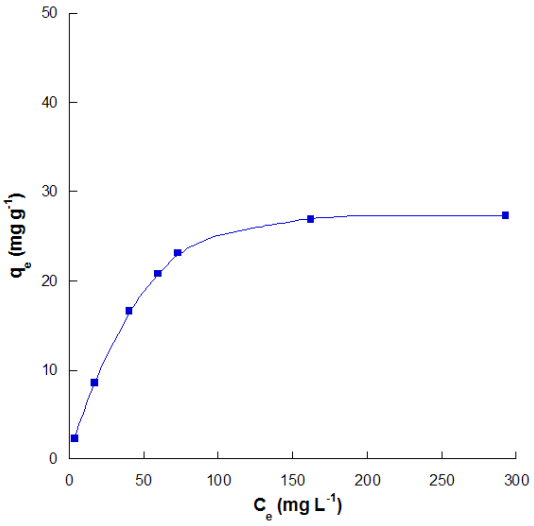

Figure 5. Methyl Orange biosorption isotherm onto treated date seeds at 20 °C with biomass dosage (BD) = 4 g L^{-1} and pH = 4.0.

order which confirms that the pseudo-second order model is the most appropriate for describing the kinetic profiles. This model is frequently associated to a mechanism involving chemical interaction between the sorbent and the solute [13].

4. Biosorption isotherms

The biosorption isotherms are characterized by definite parameters, whose values express the surface properties and affinity of biosorbent for azo dye; the isotherms are basically important to describe how dye interacts with adsorbents. Several isotherm equations have been developed and employed for such analysis. Important isotherms such as Langmuir and Dubunin-Radushkevich (D–R) isotherms were applied in this study. Figure 5 show the biosorption isotherm of Methyl Orange dye at 20 °C on the treated biomass.

Table II. The pseudo-second order parameters for methyl orange biosorption onto treated date seeds at different temperatures.

T (°C)	$q_{e,exp}$ (mg g^{-1})	$q_{e,calc}$ (mg g^{-1})
20	4.67	4.83
30	4.31	4.52
40	3.53	3.70

The Langmuir isotherm is based on the assumption that the biosorption process takes place at specific homogeneous sites within the biosorbent surface and that once a dye molecule occupies a site, no further biosorption can take place at that site, which concluded that the adsorption process is monolayer in nature [14]. This model can be written in linear form

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (5)$$

Where q_{max} is the monolayer biosorption capacity of the biosorbent (mg g^{-1}) and b is the Langmuir biosorption constant (L mg^{-1}). The values of q_{max} and Langmuir constant b were calculated from the linear plot of C_e/q_e versus C_e (Figure 6).

The well-linear straight confirm that the equilibrium data fitted is very well to the Langmuir model in the studied concentration range of methyl orange. This model is the very suitable to describe the biosorption process. The monolayer maximum biosorption capacity is calculated 44.05 mg g^{-1}. The Langmuir model was also reported to be the most adequate model in describing azo dyes biosorption from aqueous solution [15-17].

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L, which is defined as

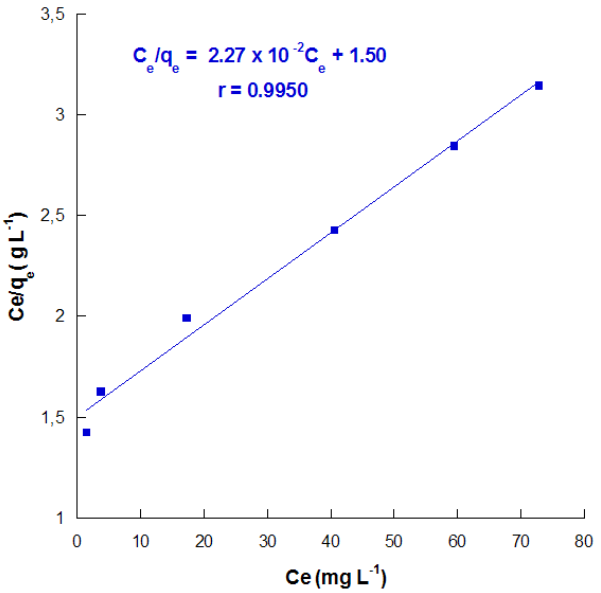

Figure 6. Langmuir isotherm plot for Methyl Orange biosorption isotherm onto treated date seeds.

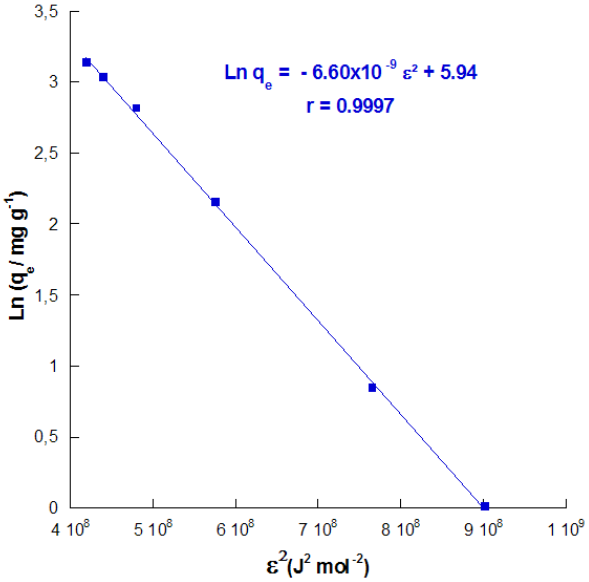

Figure 7. D-R isotherm plot for Methyl Orange biosorption isotherm onto treated date seeds.

$$R_L = \frac{1}{1+bC_0} \quad (6)$$

As described by Mckay et al. [18], the value of R_L indicates the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The dimensionless constants R_L was found to be 0.74 for methyl orange biosorption isotherm, so the dye biosorption can be considered to be favorable.

In order to determine the type of biosorption, the equilibrium data were also tested with the Dubinin-Radushkevich (D–R) model. The D–R isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. The linear presentation of the D–R isotherm equation [19] is expressed by

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (7)$$

where β is the activity coefficient related to adsorption mean free energy (mol^2 J^{-2}) and ε is the Polanyi potential [$\varepsilon = RT\ln(1+\frac{1}{C_e})$].

The D–R isotherm model well fitted the equilibrium data for dye biosorption (Figure 7). The expression of biosorption mean free energy (E, kJ mol^{-1}) is given by equation (8).

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

The E (kJ/mol) value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ mol^{-1}, the adsorption process takes place chemically and while E < 8 kJ mol^{-1}, the adsorption process proceeds physically [19]. The mean biosorption energy was calculated as 8.70 kJ mol^{-1} for methyl orange biosorption. These results indicated that the biosorption processes of this dye onto date seeds may be carried out via chemisorption involving valence forces through sharing or exchange of electrons between methyl orange and biomass. All the isotherm parameters are listed in Table III.

Table III. The Langmuir and D-R parameters for methyl orange biosorption isotherm onto treated date seeds.

Langmuir parameters			D-R parameters	
q_m (mg g^{-1})	b (L mg^{-1})	R_L	β (mol² J^{-2})	E (kJ mol^{-1})
44.05	1.38 × 10^{-2}	0.74	6.60 × 10^{-9}	8.70

The biosorption isotherms study confirms that the biosorption of methyl orange onto treated biomass was taken place by chemisorption, this results was previously confirmed (kinetic and thermodynamic studies). Similar results were been obtained for other azo dyes [20-21].

CONCLUSION

The present investigation showed that date seeds can effectively be used as a cheap abundant material for azo dye removal from aqueous solutions under different operating parameters. The calculated thermodynamic parameters showed that the dye biosorption onto treated biomass was feasible, spontaneous and exothermic under examined conditions. The pseudo-second-order kinetic model exhibited the best correlation for the experimental data. The Langmuir adsorption isotherm model was better used to represent the experimental data and the monolayer biosorption capacity was obtained 44.05 mg g^{-1} for methyl orange. The mean free energy values evaluated from the D–R model indicated that the biosorption of dye onto date seeds biomass was taken place by chemisorption. Therefore, for purely economic considerations, biosorption using date seeds is an effective, promissing and an eco-friendly alternative for dyes uptake from aqueous media.

REFERENCES

[1] S. N. M. Yusoff, A. Kamari, W. P. Putra, C. F. Ishak, A. Mohamed, N. Hashim, I. M. Isa, *J. Envir. Protect*., **2014**, 5, 289.

[2] Y. S. Ho, C. C. Wang, *J. Hazard. Mater*., **2008**, 156, 398.

[3] D. K. Mondal, N. B. Kumar, M. K. Purkait, *Environ. Chem. Eng*. **2013**, 1, 891.

[4] A. Rezgui, Y. Hannachi, E. Guibal, T. Boubaker, unpublished work.

[5] B. B. Hayes, S. Azadi, R. R. Sullivan, B. J. Meade, *J. Allergy Clin. Immunol.*, **2004**, 113(12), 72.

[6] Y. Badr, M.G.A. El-Wahed, M.A. Mahmoud, *J. Hazard. Mater*., **2008**, 154, 245.

[7] N. Puvaneswari, J. Muthukrishnan, P. Gunasekaran, *Indian J. Exp. Biol*., **2006**, 44, 618.

[8] M. Ahmaruzzaman, *Separ. Sci. Technol*., **2012**, 47, 2381.

[9] R. Jiang, Y. Q. Fu, H. Y. Zhu, J. Yao, L. Xiao, *J. Appl. Polym. Sci*., **2012**, 125, E540.

[10] Y. Ren, H. A. Abbood, F. He, H. Peng, K. Huang, *Chem. Eng. J*., **2013**, 226, 300.

[11] A. Roy, B. Adhikari, S. B. Majumder, *Ind. Eng. Chem. Res*., **2013**, 52, 6502.

[12] Y. S. Ho, G. McKay, *Process Biochem.* **1999**, 34, 451.

[13] R. F. Gomes, A. C. Neto de Azevedo, G.B. A. Pereira, E. C. Muniz, A. R. Fajardo, F. H. A. Rodrigues, *J. Colloid Interface Sci*., **2015**, 454, 200.

[14] I. Langmuir, *J. Am. Chem. Soc*., **1918**, 40, 1361.

[15] M. K. Sankar, K. M. Kumar, B. V. Ranganathan, *Int. J. Environ. Sci. Technol*., **2015**, 12, 2957.

[16] Y. Guo, J. Deng, J. Zhu, C. Zhou, C. Zhou, X. Zhou, R. Bai, *RSC Adv*., **2016**, 6, 39762.

[17] E. Daneshvar, M. Kousha, M. Jokar, N. Koutahzadeh, E. Guibal, Chem.Eng. J., **2012**, 204-206, 225.

[18] G. Mckay, H.S. Blair, J.R. Gardener, *J. Appl. Polym. Sci*., **1982**, 27, 3043.

[19] M. M. Dubinin, E. D. Zaverina, L. V. Radushkevich, *Zh. Fiz. Khim*., **1947**, 2, 1351.

[20] T. Vidhyadevi, A. Murugesan, S.S. Kalaivani, M.P. Premkumar, V. Vinoth kumar, L. Ravikumar, S. Sivanesan, *Desalin Water Treat*., **2014,** 52, 3477.

[21] A. Mittal, V. Thakur, V. Gajbe, *Environ Sci. Pollut Res*., **2013**, 20 (1), 260.