Asian Journal of Chemistry; Vol. 27, No. 11 (2015), 4029-4033

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19063

Biosorprption of Anionic Dye Bezaktiv Yellow HE-4G on Mixture of Olive Stone and Date Pits in Packed Bed Column

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Received: 20 January 2015; *Accepted*: 11 March 2015; *Published online*: 16 July 2015; AJC-17395

In this paper, the adsorption of anionic dye Bezaktiv Yellow HE-4G onto mixture biosorbent, olive stones and date pits was investigated in packed bed column. The effect of operational parameter such as initial dye concentration, flow rate and height bed was evaluated. Thomas model was used to describe the adsorption data. Adjunction date pits to the mixture increase the per cent of dye adsorbent it is about 19 to 43.23 % when the date pits was added to the mixture between 12 to 15 %. The results indicated that the mixture of date pits and olive stone could be used as an adsorbent for textile waste water treatment without high cost.

Keywords: Adsorption, Olive stone, Date pits, Dye, Packed bed column.

INTRODUCTION

Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegradate[1]. Wastewaters from dyeing and finishing operations in the textile industry are generally high in both colour and organic content[2]. These coloured compounds are not only aesthetically displeasing but they also inhibit sunlight from penetring into the stream and reduce the photosynthetic reaction. Some dyes are also toxic and carcinogenic[3].

Wastewater containing dyes are normally treated by physical or chemical treatment process like flocculation, membrane filtration, electrikinetic coagulation, ion exchange, irradiation, precipitation and ozonation. However, these technologies are generally ineffective in colour removal, expensive and less adaptable to a wide range of dye waste water[4,5]. All these process are costly and cannot be used by many industries to treat the wide range of dye wastewater[6]. At present, there is a growing interest in using low-cost and non-conventional alternative materials instead of traditional adsorbents[2]. Biosorption is the cost effective technique for the dye removal[7].

Among agro-industrial wastes, olive stone is one of the most abundant in the Mediterranean basin[8]. The olive stone has some application such as combustible, natural fertilizer or additive in animal nutrition[9]. Date pits constitute roughly 10 % of the date palm. In Algeria, which is the largest date pits producer in the world, more than million ton of date pits are estimated to be generated annually. Date pits as a waste stream is a problem to the date industry, therefore its recycling or reuse are useful[9]. Although the obtained activated carbon by olive stone waste and date pits waste has been reported to be a suitable sorbent material[9].

The purpose of this study is to find an application for the reuse of a mixture of the date pits waste and olive stone waste in their native form. In practice, continuous flow operations in the packed bed column are more useful in large-scale waste water treatment. A packed bed is a large volume of waste water can be continuously treated using a defined quantity of sorbent in the column[10]. Moreover, few reports are available with treatment of textile wastewater containing synthetic dyes in packed bed column using different bio sorbent.

Therefore, in the present study, the treatment of textile waste water using a mixture of date pits and olive stone was investigated in a packed bed column. This research paper illustrates the use of different mixture of date pits waste and olive stone waste in their native form for the removal of reactive textile dye (Bezaktiv Yellow HE-4G).

EXPERIMENTAL

Dye solution: Dye used in this study is Bezaktiv yellow HE-4G obtained from firm Bezema Suisse. It is a monochlorotriazoique, the maximum adsorption wavelength of this dye is 360 nm.

The dye stock solution was prepared by dissolving accurately 1 g amounts of dye into 1000 mL of distilled water and the experimental solutions were obtained by diluting the stock solution to the required concentrations.

Adsorbents

Preparation of sorbent: Date pits were obtained from southern of Algeria and olive stones from northern of Algeria were used as starting material. The olive stones first washed with water to remove the adhering dirt and then it were input in hexane for 24 h to eliminate residual oil and then were washed with distilled water and were dried at 105 °C. Date pits were washed and dried at 105 °C.

The dried olive stones and date pits were then crushed, milled and sieved into different particle sizes. Studies were focused on a size fraction of 0.4 to 0.8 mm, the olive stone waste with date pits waste are mixed at different percentage. In order to obtain homogenous sample of olive stone and date pits waste, we mix the olive stone with date pits at different percentage. The mixture of adsorbent was impregnated with H_3PO_4 (2 g of acid per gram of mixture) and was refluxed at 100 °C during 3 h. Next the mixture has been washed with distilled water until a neutral pH to eliminate the excess of H_3PO_4. The mixture of adsorbent was dried at 105 °C. In this study we used five samples and their compositions are given in Table-1.

TABLE-1
PERCENTAGE OF OLIVE STONE AND DATE PITS IN DIFFERENT MIXTURE

Sample number	Olive stone (%)	Date pits (%)
1	100	0
2	0	100
3	88	12
4	85	15
5	66	34

Experiments with packed bed column: The fixed bed column was made of glass tube 1.8 cm internal diameter and 30 cm in height. The concentration of studied dye solution in experiments 0.1, 0.25 and 0.5 g/L with fixed height of bed column at 5 cm and a fixed flow rate of 3.33 mL/min.

Desired flow rate were fixed using peristaltic pump (0.83, 3.33 and 5 mL/min) and the bed height was fixed at 5 cm and the concentration of dye solution was fixed at 0.5 g/L.

The effect of bed height on biosorption process in backed bed column was studied at three different bed heights 3, 5 and 7 cm and the flow rate was fixed at 0.83 mL/min and the dye solution was fixed at 0.5 g/L.

At the end of experiments biosorbent dye mixtures were centrifuged at 5000 rpm for 3 min and the supernatants were analyzed spectrophotometrically at 360 nm to determine the residual concentration of reactive dye.

Analysis of column data: The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of adsorption column. The breakthrough curves are plotted as final concentration (C_t)/initial concentration (C_0) *vs.* time.

The breakthrough time (t_b) is represented as the time at which the ratio of final concentration of effluent to the initial absorbance of effluent reaches 0.001 (C_f/C_i = 0.001). The exhaustion time (t_e) is represented as the time when the ratio of final concentration of effluent the initial concentration reaches 0.095 (C_f/C_i = 0.95).

RESULTS AND DISCUSSION

Effect of bed height on decolourization of textile wastewater in continuous bed column: The breakthrough time considerably shifted to higher times with the increase in bed height. Increasing the bed height from 3 to 7 cm led prolongation of both breakthrough time (30 to 180 min) and saturation time (420 to 600 min) for the mixture of biosorbent (100 % olive stone and 0 % date pits).

An increase in the height of the bed (mass of biosorbent) increase the contact time between the dye and biosorbent. It also increases the quantity of surface area of adsorbent which provides more binding sites for adsorption.

The breakthrough curves at the different bed heights were shown in Fig. 1 and the column parameters were evaluated and presented in Table-2.

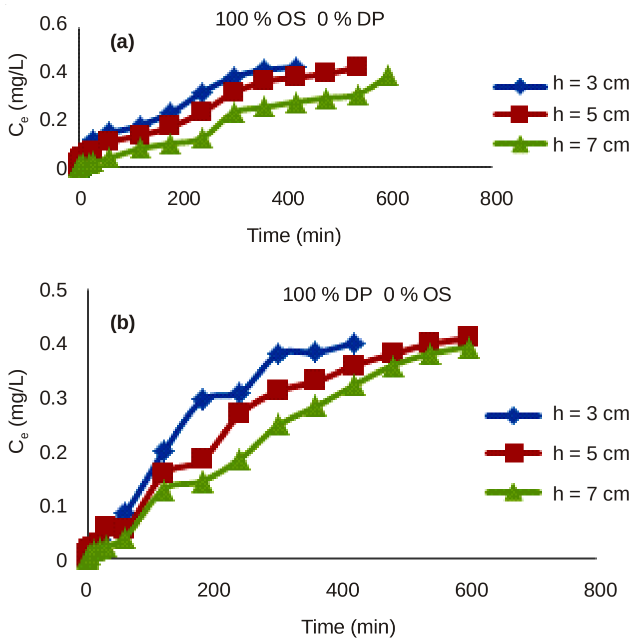

Fig. 1. Breakthrough curves for biosorption of BY HE-4G by 100 % olive stone (a) and 100 % date pits (b) packed in column at different bed heights. pH = 5.6, flow rate = 0.83 mL min^{-1}, C_0 = 0.5 g L^{-1}

TABLE-2
COLUMN DATA PARAMETERS OBTAINED AT DIFFERENT BED HEIGHTS

Samples	Bed height (cm)	t_e (min)	t_s (min)	m_0 (mg)	m (mg)	m_{ads} (mg)
100 % OS 0 % DP	3	20	420	150.20	174.3	24.10
	5	60	540	192.70	224.1	31.40
	7	180	600	196.70	249.0	52.30
100 % DP 0 % OS	3	60	420	140.13	174.3	52.30
	5	120	600	204.18	249.0	34.13
	7	120	600	204.18	249.0	44.82
88 % OS 12 % DP	3	60	480	170.51	199.2	28.69
	5	120	540	188.24	224.1	35.90
	7	120	540	164.90	224.1	59.20
85 % OS 15 % DP	3	60	420	139.78	174.3	34.52
	5	120	540	178.38	224.1	45.72
	7	120	540	167.62	224.1	56.48
66 % OS 34 % DP	3	60	420	139.70	174.3	34.60
	5	120	540	186.00	224.1	38.10
	7	120	540	162.69	224.1	61.41

OS = Olive stone; DP = Date pits

The results obtained in Table-2 shown that an increase of 12 % of date pits in the mixture have an increase of 19 % of the amount of dye adsorbed, it was obtained to de 24.1 mg and 28.69 mg when the percent of olive stone and date pits in the mixture was (100 % olive stone and 0 % date pits) and (88 % olive stone and 12 % date pits) respectively (when H = 3 cm), which is equivalent of 19 % increase in the amount of dye adsorbed. The maximum amount of dye adsorbed was 34.52 mg for the sample 4 (85 % olive stone, 15 % date pits) with an increase an increase in adsorption about 43.23 %, against 15 % of date pits in the mixture we have practically no amelioration in adsorption.

Effect of flow rate: Flow rate proved to be important characteristic affecting the performance of biosobent in the continuous mode. The breakthrough curves of BY HE-4G by mixture of biosorbent at different flow rate and at fixed bed height of 5 cm are shown in Fig. 2 and the column parameters are presented in Table-3.

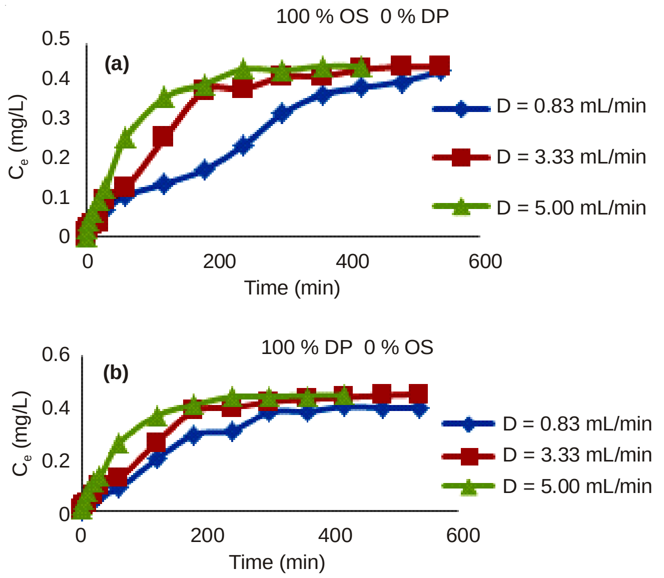

Fig. 2. Breakthrough curves for biosorption of BY HE-4G by 100 % OP (a) and 100 % date pits (b) packed at column at different flow rate. pH: 5.6, C_0 : 500 mg L^{-1}, bed height: 3 cm

TABLE-3
COLUMN DATA OBTAINED FOR DIFFERENT FLOW RATE

Samples	Flow rate (mL min^{-1})	t_e (min)	t_s (min)	m_0 (mg)	m (mg)	m_{ads} (mg)
100 % OS 0 % DP	0.83	60	540	224.10	192.27	31.83
	3.33	60	480	633.61	796.00	162.39
	5.00	30	420	928.20	1050	121.80
100 % DP 0 % OS	0.83	120	540	178.83	224.1	45.27
	3.33	60	540	807.70	895.5	87.75
	5.00	30	420	940.80	1050	109.20
88 % OS 12 % DP	0.83	120	540	188.24	224.1	35.86
	3.33	120	480	700.48	796.0	95.52
	5.00	30	420	940.80	1050	109.2
85 % OS 15 % DP	0.83	120	540	178.38	224.1	45.72
	3.33	60	480	662.27	796.0	133.73
	5.00	20	420	919.80	1050	130.20
66 % OS 34 % DP	0.83	120	540	186.00	224.1	38.10
	3.33	120	480	665.45	796.0	130.55
	5.00	30	420	919.80	1050	130.20

OS = Olive stone; DP = Date pits

The increase in flow rate reduced the breakthrough time. The saturation time of the biosorbent bed was accomplished most rapidly at a highest flow rate of 3 mL min^{-1}.

An earlier breakthrough and exhaustion time were observed at higher flow rate, due to insufficient solute residence time[11] and when the residence of the solute in the column is not long enough for adsorption equilibrium to be reached at that flow rate, the dye solution leaves the column before equilibrium occurs[12].

The results obtained in Table-3 showed that an increase of 12 % of date pits in the mixture have an increase of 12.64 % of the amount of dye adsorbed, it was obtained to de 31.83 mg and 35.86 mg when the percent of olive stone and date pits in the mixture was (100 % olive stone and 0 % date pits) and (88 % olive stone and 12 % date pits) respectively (when flow rate = 0.83 mL min^{-1}). The maximum amount of dye adsorbed was 43.54 mg for the sample 4 (85 % olive stone, 15 % date pits) with an increase in adsorption about 43.54 %, against 15 % of date pits in the mixture we have practically less amelioration in adsorption.

Effect of the concentration of waste water: The effect of the initial dye concentration on the column adsorption parameters was studied and was investigated in Fig. 3 and Table-4.

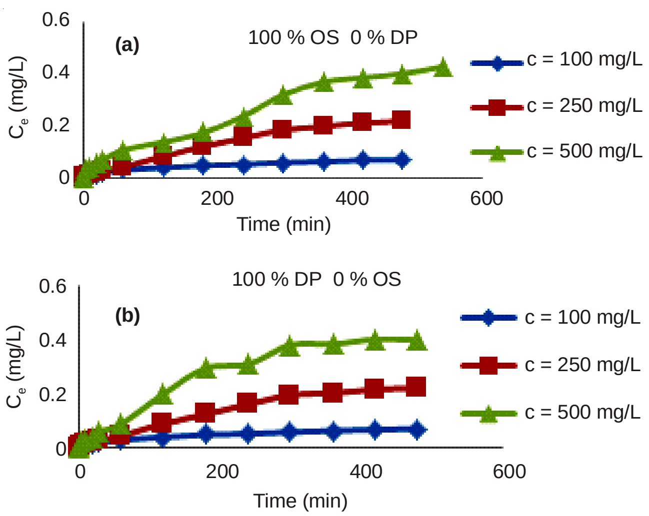

Fig. 3. Breakthrough curves for biosorption of BY HE-4G by 100 % olive stone (a) and 100 % date pits (b) packed in column at different concentration. pH: 5.6, bed height: 3 cm, flow rate: 0.83 mL min^{-1}

The concentration of dye solution was changing from 100 mg L^{-1} to 500 mg L^{-1} and 3.33 mL min^{-1} flow rate and 3 cm bed height. One the concentration of BY HE-4G in solution decrease gave delayed breakthrough curves and the treated volume was also higher, since the lower concentration gradient caused slower transport due to decreased diffusion coefficient[13]. One increasing of dye concentration (500 mg L^{-1}) the bed column satured quickly leading to earlier breakthrough and exhaustion time. The results shows that the highest uptake is obtained at the highest dye concentration; for the different dye concentration (100, 250 and 500 mg L^{-1}) the maximum bed capacities were respectively (12, 13.25 and 39.39 mg g^{-1}) for the sample of biosorbent (100 % olive stone 0 % date pits).

Thus the high driving force due to the high dye ion concentration resulted in better column performance[14].

TABLE-4
COLUMN DATA PARAMETERS OBTAINED AT DIFFERENT WASTEWATER CONCENTRATION

Samples	Conc. (mg L^{-1})	t_e (min)	t_s (min)	m_0 (mg)	m (mg)	m_{ads} (mg)
100 % OS 0 % DP	100	120	480	27.84	39.84	12.00
	250	60	420	73.90	87.15	13.25
	500	30	420	134.9	174.3	39.39
100 % DP 0 % OS	100	120	480	28.32	39.84	11.52
	250	60	420	77.00	87.15	10.15
	500	30	420	139.0	174.3	35.30
88 % OS 12 % DP	100	60	480	28.32	39.84	11.52
	250	60	420	76.34	87.15	10.81
	500	60	420	128.98	174.3	45.32
85 % OS 15 % DP	100	60	480	28.32	39.84	11.52
	250	60	420	76.34	87.15	10.81
	500	60	420	128.98	174.3	45.32
66 % OS 34 % DP	100	60	480	29.88	39.84	9.96
	250	60	420	74.94	87.15	12.21
	500	60	480	151.0	199.2	48.20

OS = Olive stone; DP = Date pits

The results given in Table-4 showed that an increase of 12 % of date pits in the mixture have an increase of 15 % of the amount of dye adsorbed, it was obtained to dye 39.39 mg and 45.32 mg when the percent of olive stone and date pits in the mixture was (100 % olive stone and 0 % date pits) and (88 % olive stone and 12 % date pits) respectively (when C_0 = 0.5 g L^{-1}). The maximum amount of dye adsorbed was 48.2 mg for the sample 5 (66 % olive stone, 34 % date pits) with an increase in adsorption about 22.36 %.

Modified Thomas model: Thomas model is one of the most general and widely used sorption models for describing column breakthrough data. This model assumes Langmuir kinetics of sorption-desorption and no axial dispersion and is derived with the assumption that the sorption is the rate driving force and obeys second-order reversible reaction kinetics[15].

The breakthrough curves obtained at different concentration, bed height and flow rate can be described using a modified form of Thomas model which can be represented as[16]:

$$C_I/C_t = 1 + \exp(K_{th}/F\ (Q_0M - C_I.V_{eff})) \quad (1)$$

The linearized modified Thomas model is given below:

$$\ln(C_i/C_t - 1) = K_{th}.Q_0.M/F - k_{th}.C_i.t \quad (2)$$

where C_i and C_t are the inlet and outlet dye concentration (mg L^{-1}), K_{Th} is the modified Thomas model rate constant (L mg^{-1} h^{-1}), Q_0 the maximum decolourization (mg g^{-1}) and M the biosorbent weight (g).

Thomas model gave a good fit of the experimental data, all the flow rate examined, with correlation coefficient greater than 0.7095 (Table-5) which would indicate that the external and internal diffusions were not the rate limiting step. The increase in the flow rate has an increase in the amount of the maximum adsorbed Q_0. The rate constant (K_{Th}) decreased with increasing initial dye concentration (Table-6), which indicates that the mass transport resistance increases.As can be seen in Table-5, as the the flow rate increased the value of K_{Th} and Q_0 increased. Thereafter, the value of Q_0 and K_{Th} decreased with increasing bed height as shown in Table-7.

Clearly, the breakthrough curves shown in Fig. 4 shows that it have a lead difference between the experimental and

TABLE-5
MODIFIED THOMAS MODEL PARAMETERS OBTAINED AT DIFFERENT FLOW RATE

Samples	Flow rate (mL/min)	K_{Th} (L mg^{-1} h^{-1}·10^{-5})	q_0 (mg/g)	R^2
100 % OS 0 % DP	0.83	2.60	809.0	0.8037
	3.33	2.24	4675.4	0.7543
	5.00	1.88	8707.3	0.7095
100 % DP 0 % OS	0.83	2.04	1253.6	0.7677
	3.33	2.28	4482.3	0.7584
	5.00	2.60	4583.5	0.7198
88 % OS 12 % DP	0.83	2.16	1573.1	0.7887
	3.33	2.32	5227.0	0.8209
	5.00	2.32	5256.7	0.7107
85 % OS 15 % DP	0.83	2.16	1573.1	0.7887
	3.33	2.32	5227.0	0.8209
	5.00	2.40	5081.5	0.7107
66 % OS 34 % DP	0.83	2.18	1558.0	0.8107
	3.33	2.26	5299.9	0.8243
	5.00	2.34	5230.0	0.7227

OS = Olive stone; DP = Date pits

TABLE-6
MODIFIED THOMAS MODEL PARAMETERS OBTAINED AT DIFFERENT DYE CONCENTRATION

Samples	Conc. (mg/L)	K_{Th} (L mg^{-1} h^{-1}·10^{-5})	q_0 (mg/g)	R^2
100 % OS 0 % DP	100	1.74	3461.9	0.7081
	250	2.56	3010.1	0.8426
	500	1.90	3427.5	0.8062
100 % DP 0 % OS	100	1.74	3384.32	0.7016
	250	2.56	2904.30	0.8410
	500	2.62	2804.80	0.7987
88 % OS 12 % DP	100	1.74	3401.4	0.7035
	250	2.82	2725.6	0.8276
	500	2.82	2725.6	0.8276
85 % OS 15 % DP	100	1.44	3366.78	0.7201
	250	2.12	3759.58	0.7977
	500	2.54	3051.70	0.8435
66 % OS 34 % DP	100	1.74	3332.0	0.6948
	250	2.60	2970.4	0.8404
	500	2.38	3516.8	0.8018

OS = Olive stone; DP = Date pits

TABLE-7
MODIFIED THOMAS MODEL PARAMETERS OBTAINED AT DIFFERENT BED HEIGHT

Samples	Height (cm)	K_{Th} (L mg^{-1} h^{-1}·10^{-5})	q_0 (mg/g)	R^2
100 % OS 0 % DP	3	2.34	4146.0	0.8042
	5	1.92	3414.6	0.8082
	7	1.94	3398.8	0.8120
100 % DP 0 % OS	3	3.02	4196.3	0.8121
	5	2.06	3747.3	0.7801
	7	2.12	3083.4	0.8207
88 % OS 12 % DP	3	2.4	5055.20	0.8138
	5	2.14	3705.70	0.8013
	7	2.08	3090.04	0.8009
85 % OS 15 % DP	3	2.62	4647.6	0.7983
	5	2.12	3759.5	0.7977
	7	2.14	4197.3	0.8310
66 % OS 34 % DP	3	2.62	5674.9	0.8075
	5	2.18	3750.4	0.8107
	7	2.12	3076.0	0.8110

OS = Olive stone; DP = Date pits

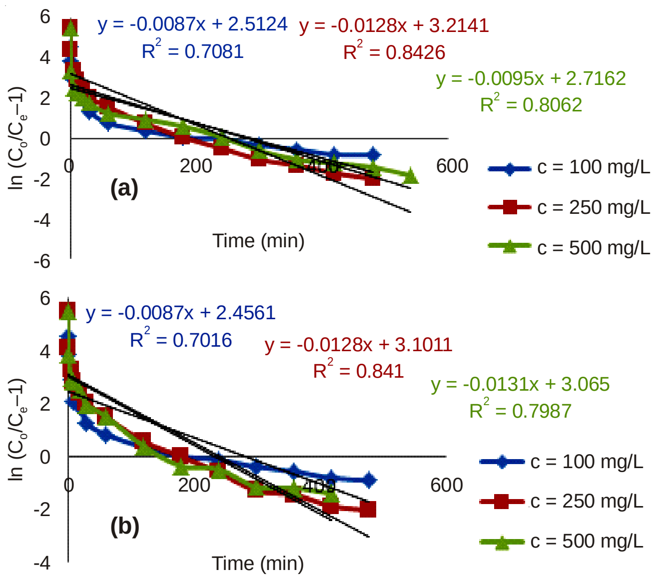

Fig. 4. Modified Thomas model for biosorption of BY HE-4G 100 % olive stone (a) and 100 % date pits (b) packed in column at different concentration. pH: 5.6, flow rate: 0.83 mL min^{-1}, bed height: 3 cm

predicted values calculated by Thomas model for the parameter examined. This confirms the possible applicability of this model in describing the experimental data.

The R^2 value greater than 0.70 for the majority of the parameters studied indicating good linearity. It can, therefore, be said that the Thomas model equations of linear regression analysis describes the breakthrough data under the studied conditions.

Conclusion

In this work we have studied the dependence of adsorption on mixture of adsobent (date pits and olive stone) and adsorbate characteristics by column study. The backed column studies showed that:

- The increase in bed height caused an increase in the amount of dye adsorbed and an extension of the breakthrough time and exhaustion time.
- The increase in concentration of dye wastewater caused a decrease in breakthrough and exhaustion time and the bed column were satured quickly.
- The increase in flow rate reduced the breakthrough time and exhaustion time.
- An amelioration in the amount of dye adsorbent by the mixture of date pits and olive stone when the mixture content 12 and 15 % of date pits (19 and 37.1 % respectively) and against 15 % (34 % of date pits) we have practically less amelioration.
- The column adsorption was inadequately describing by the linearized Thomas model.

REFERENCES

1. Z. Eren and F.N. Acar, *Desalination*, **194**, 1 (2006).
2. N. Barka, S. Qourzal, A. Assabbane, A. Nounah and Y. Ait-Ichou, *J. Saudi Chem. Soc.*, **15**, 263 (2010).
3. T. Robinson, B. Chandron and P. Nigam, *Water Res.*, **36**, 2824 (2002).
4. V.K. Gupta and Suhas, *J. Environ. Manage.*, **90**, 2313 (2009).
5. A. Srinivasan and T. Viraraghavan, *J. Environ. Manage.*, **91**, 1915 (2010).
6. A. Khaled, A. El Nemr, A. El-Sikaily and O. Abdelwahab, *Desalination*, **238**, 210 (2009).
7. Y. Safa and H.N. Bhatti, *Chem. Eng. J.*, **167**, 35 (2011).
8. F. Pagnanelli, C.C. Viggi and L. Toro, *Appl. Surf. Sci.*, **256**, 5492 (2010).
9. H. Aksas, M.Z. Boureghda, H. Babaci and K. Louhab, *Res. J. Chem. Environ.*, **16**, 174 (2012).
10. D. Charumathi and N. Das, *Desalination*, **285**, 22 (2012).
11. K. Vijayaraghavan, J. Jegan, K. Palanivelu and M. Velan, *Sep. Purif. Technol.*, **44**, 53 (2005).
12. S. Ghorai and K.K. Pant, *Sep. Purif. Technol.*, **42**, 265 (2005).
13. T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran and M. Velan, *J. Hazard. Mater.*, **125**, 121 (2005).
14. E. Malkoc, Y. Nuhoglu and M. Dundar, *J. Hazard. Mater.*, **138**, 142 (2006).
15. Z. Aksu and F. Gonen, *Process Biochem.*, **39**, 599 (2004).
16. K. Vijayaraghavan, M.W. Lee and Y.S. Yun, *Bioresour. Technol.*, **99**, 5778 (2008).