Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.789404

52 (2014) 1422–1433
February

Taylor & Francis
Taylor & Francis Group

Synthesis of activated carbon based on apricot stones for wastewater treatment

Karima Belaroui*, AbdelKrim Seghier, Mohamed Hadjel

Laboratoire des Sciences Technologie et Génie des Procédés LSTGP, Université des Sciences et de la Technologie Med-BOUDIAF d'Oran USTOMB, B.P.1505–EL M'nouer, Oran, Algérie
Tél./Fax: +213 41500056; email: kbelaroui@yahoo.fr

Received 11 December 2012; Accepted 20 March 2013

ABSTRACT

In this study, a methodology for the preparation of three activated carbons from agricultural waste is adapted in the laboratory. The raw material is ground manually in a mortar. The dried product is then sieved into different size classes. Three types of activation were applied to this agricultural waste. The first activation is physical, and uses two atmosphere types: steam and nitrogen Physical Treatment of Apricot Stones (PTAS), the second is chemical and uses concentrated sulfuric acid (Chemical Treatment of Apricot Stones (CTAS) and the third is a mixed activation which is both physical and chemical Mixed Treatment of Apricot Stones (MTAS). The materials obtained were characterized by sanning electron microscopy, Brunauer, Emmett and Teller and the iodine number. Next, the adsorption capacity of these activated carbons for the safranine dye was studied using sorption parameters such as kinetics, the isotherm, the pH and the temperature. The calculated $Q_{\max}$ values indicate that the PTAS, CTAS and MTAS samples show a better adsorption capacity for the safranine dye (243.90-274.27-294.11 mg/g); the results found during this study show that the sorption is increased with increased temperatures and concentrations, and that the pH does not show any influence. Finally, the results obtained were compared to those of other adsorbent materials that are described in the literature.

Keywords: Activated carbon; Adsorption; Kinetics; Wastewater treatment; Safranine dye

1. Introduction

The acceleration of the industrial activities born of the industrial revolution of the nineteenth century has created a new source of concern: the protection of the environment. Nowadays, industry occupies a large part of our daily lives. It offers clear advantages in the development of economy. However, it is one of the principal causes of many environmental problems.

The necessity of making businesses sustainable and competition between producers of the same products have led to a search for more reliable environmental management systems through the introduction of parameters to ensure compliance with the ISO 14000 standards.

One of such industries, the textile industry, generates water full of organic pollutants such as coloring agents which are resistant to conventional water treatments. The dyes are discharged with industrial waste which has a harmful effect on ecosystems.

---

*Corresponding author.

The elimination of dyes composed of organic molecules which carry aromatic nuclei using physico-chemical and biological treatments constitutes a major problem [1,2].

The chemical industry of the twenty-first century looks for an alternative to these conventional treatments by using an efficient physical process which is adsorption, even when the water contains only small amounts of toxic dyes [3,4]. This prompted us to use adsorption by our chosen activated carbon in the elimination of toxic dyes. Activated carbon is a natural adsorbent with significant advantages.

(1) It costs less than commercial activated carbons [5,6].
(2) It is very efficient.

Agricultural waste attracts the attention of green chemists due to its low cost. As mentioned in the literature, activation treatments have been applied to many types of agricultural waste to improve their specific surfaces, including date stones [7], grain sorghum [8], oil palm shell activated carbon [9] and olive stones [10].

In this study, apricot stones were chosen for the preparation of the three types of activated carbon using the following activation processes:

(1) Physical activation using two atmosphere types: 50% in volume of steam and 50% in volume of nitrogen is used.
(2) Chemical activation using concentrated sulfuric acid.
(3) Mixed activation which is both physical and chemical.

The materials obtained were characterized by SEM (model: TM330A, Jeol), BET and the iodine number. The carbon samples obtained were used to remove a safranine dye from an aqueous solution, and also to calculate adsorption capacity by referring to sorption parameters such as kinetics, isotherm, pH and temperature.

2. Experimental

2.1. Materials

Apricot stones obtained from the "JUCOR" fruit preserving plant located in the region of Relizane (Algeria) were used as the raw material for the production of activated carbons.

This raw material was washed many times with distilled water, and then put in a preheated furnace (model: Wise THERM) at a temperature of 100˚C for 48 h in order to reduce the moisture content. Next, it was ground manually in a mortar and sieved in a vibration sieve (model: RETSH 5657 HAAN) so as to obtain particles with a diameter between 1.25 and 2.5 mm. These particles then underwent different types of activation: chemical, physical and mixed, to obtain activated carbon with a large surface area and a high degree of microporosity.

The first type of activation was physical; 40 g of these apricot stone particles was put directly into a pressurized furnace (a cylindrical stainless steel reactor with two inflows (model: Carbolite S30 2AU)). Two atmosphere types were used: steam and nitrogen. The inert gas flow rate was 0.5 l/min. The activation was carried out at 600˚C for 1 h 30 min. Finally, the obtained product was rinsed with distilled water, and then dried at room temperature. This treated carbon will be termed physical treatment of apricot stones (PTAS).

The second type of activation was chemical; 40 g of these apricot stone particles was mixed with 200 ml of sulfuric acid (40% wt) [11] at a temperature of 170˚C for 2 h. The content was filtered and dried at 105˚C for 24 h, then put in an oven at 600˚C for 3 h and washed with HCl (0.1 M). Finally, it was neutralized with an aqueous solution of 0.1 M of NaOH [10], rinsed with distilled water in order to obtain a neutral pH and dried at 105˚C for 24 h. This treated carbon will be termed chemical treatment of apricot stones (CTAS).

The third type of activation was mixed; it was both physical and chemical: 40 g of these apricot stone particles was mixed with 200 ml of sulfuric acid (40% wt) [11] and put in a reactor equipped with a condenser and a reflux at 104˚C for 2 h. The content was filtered and dried at 105˚C for 24 h, then placed in a furnace (a cylindrical stainless steel reactor) fed with steam at 600˚C for 1 h 30 and washed with HCl (0.1 M). Finally, the obtained product was neutralized using a solution of 0.1 M of NaOH [10], rinsed with distilled water and dried at 105˚C for 24 h. This activated carbon will be termed mixed treatment of apricot stones (MTAS).

The dye used is safranine with the chemical structure $C_{20}H_{19}ClN_4$ (molar mass equal to 350.80 g/mol). Safranine is powdery, red-brown and odourless. This dye is widely used in the textile, nuclear and biological industries.

2.2. Method

2.2.1. Iodine number

The iodine number is defined in terms of the milligrams of iodine (I_2) adsorbed by 1 g of activated carbon when the iodine equilibrium concentration is 0.01 M [12]. In the present work, the three-point method was adopted. This avoids the use of the correction factor usually employed in the less accurate single-point method [13]. The procedure for iodine number determination was as follows: three dry samples of activated carbon were weighed out into three 250 ml conical flasks (sample weight ranged between 300 and 600 mg). 10 ml of 5% (in weight) hydrochloric acid solution was added to each flask and then mixed until the carbon became wet. The mixtures were then boiled for 30 s and finally cooled. 100 ml of 0.05 M standard iodine solution was added to each flask. The contents were shaken vigorously for 30 s and then filtered immediately. A 50 ml aliquot of each filtrate was titrated using a standardized 0.1 M sodium thiosulfate solution. For each sample, the obtained residual iodine concentration should be between 0.004 and 0.02 M. The plot of the amount of iodine adsorbed per gram of sorbent vs. residual iodine concentration gives a straight line which allows the iodine number to be determined graphically (ordinate corresponding to a residual concentration of 0.01 M).

2.2.2. Adsorption kinetics

A 100 mg of each material was put into a series of bottles containing 25 ml of a colored solution of 100, 200 and 300 mg/l. The suspensions were shaken for between 0 and 360 min at a speed of 560 rpm. Then, the samples were filtered and the filtrates were analyzed using a UV–visible spectrophotometer (PERKIN-ELMER LAMPDA 20) at 516 nm.

2.2.2.1. Pseudo-first-order equation. A pseudo first order equation can be expressed in linear form as:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t \quad [14,15] \tag{1}$$

where q_e and q_t are the amount of dye adsorbed (mg/g) onto the adsorbents at equilibrium and at time t, respectively, and K_1 is the rate constant of adsorption (min^{-1}). Values of K_1 were calculated from the plots of $\log(q_e - q_t)$ vs. t for different concentrations of the dye.

2.2.2.2. Pseudo-second-order equation. The pseudo second order adsorption kinetic rate equation is expressed as:

$$t/q_t = 1/K_2.q_e^2 + (1/q_e)t \quad [16,17] \tag{2}$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g). The second order rate constants were used to calculate the initial sorption rate. Values of K_2 and q_e were calculated from the intercept and the slope of the linear plots of t/q_t vs. t.

2.2.3. Effect of pH on the safranine dye removal

A mass of 100 mg of prepared activated carbon was put into a series of bottles containing 25 ml of a colored solution with a concentration of 100 mg/l and the pH was adjusted within the range of 4–9.

The mixtures obtained were stirred for 2 h and then filtered. The filtrates were analyzed using a UV–visible spectrophotometer as mentioned above.

2.2.4. Sorption isotherms

A 25 ml of a colored solution with concentrations varying from 0 to 1,500 mg/l was put into a series of bottles to which a mass of 100 mg of each material was added. All were shaken for a contact time previously determined during the kinetic study. The suspensions were filtered, and then analyzed using a UV–visible spectrophotometer at room temperature. Once the isotherms and mathematical models have been created, the capacities and constants of the models will be determined in order to compare them with previous studies.

2.2.5. Effect of temperature

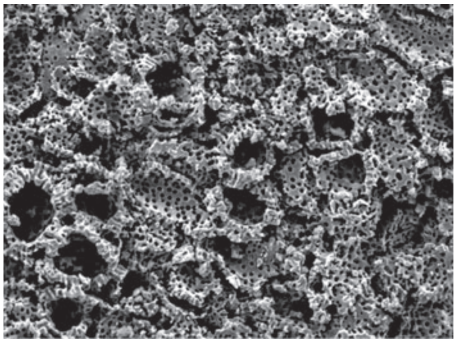
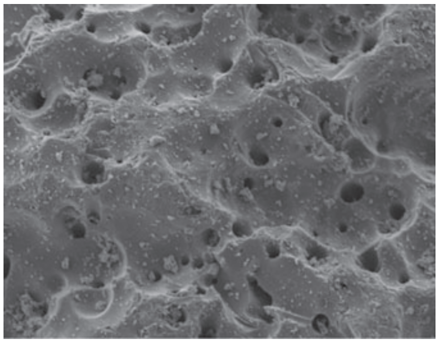
The influence of temperature on the removal process was studied at three different values (room temperature, 45°C and 55°C).

3. Results and discussions

3.1. Characterization of the treated apricot stones

The SEM images (Fig. 1) show the treated material (PTAS, CTAS and MTAS) to have a very porous morphology with pores of different sizes and shapes. The images also reveal that the external surface is full of cavities which suggests that the material has a high specific surface area. The surface of the raw material, however, is very smooth without any pores.

This type of porous morphology has already been observed on an olive cake treated with sulfuric acid [18] and a cornelian cherry treated with sulfuric acid at 200°C [20].

PTAS	CTAS
ACCEL_VOLT 5 MAG 1000 PIXEL_SIZE 0.0001 MICRON_MARKER 10 μm SPOT_SIZE 50	ACCEL_VOLT 5 MAG 1000 PIXEL_SIZE 0.0001 MICRON_MARKER 10 μm SPOT_SIZE 50
	

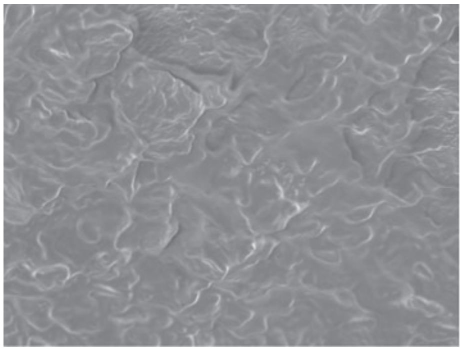
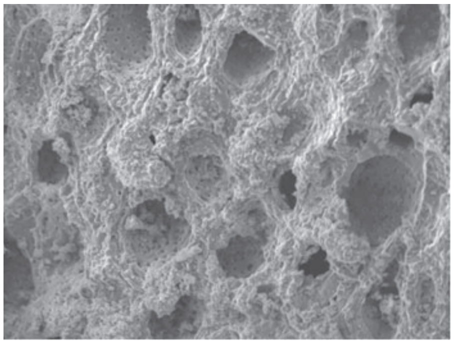
Raw apricot stones	MTAS
ACCEL_VOLT 5 MAG 1000 PIXEL_SIZE 0.0001 MICRON_MARKER 10 μm SPOT_SIZE 50	ACCEL_VOLT 5 MAG 1000 PIXEL_SIZE 0.0001 MICRON_MARKER 10 μm SPOT_SIZE 50
	

Fig. 1. SEM images of the apricot stones.

Furthermore, the high surface area (Table 1) of the treated material is also confirmed by the values for iodine number obtained for the samples (800, 824, and 890 mg/g for PTAS, CTAS and MTAS respectively). Iodine number is often considered as a measure of adsorbency for activated carbon [10].

Table 1
BET parameters

Samples	SSA (m^2/g)
MTAS	481.0
PTAS	587.4
CTAS	629.3

SSA-Specific Surface Area.

3.2. *Effect of contact time and initial dye concentration*

The adsorbent dosage is an important parameter because this parameter determines the capacity of the adsorbent for a given dye concentration and also determines the sorbent–sorbate equilibrium of the system. Fig. 2 shows that the removal of safranine depends on the initial concentration of the adsorbate and the adsorbent dosage.

The effect of contact time on the adsorption of safranine dye onto the three activated carbons is also presented in Fig. 2. The adsorbate concentrations of the solutions were measured over time.

Three different stages can be distinguished: the first stage represents the instantaneous adsorption of the dye within 35 min, the second shows an equilibrium developing between 35 and 100 min, and the third stage indicates the establishment of an

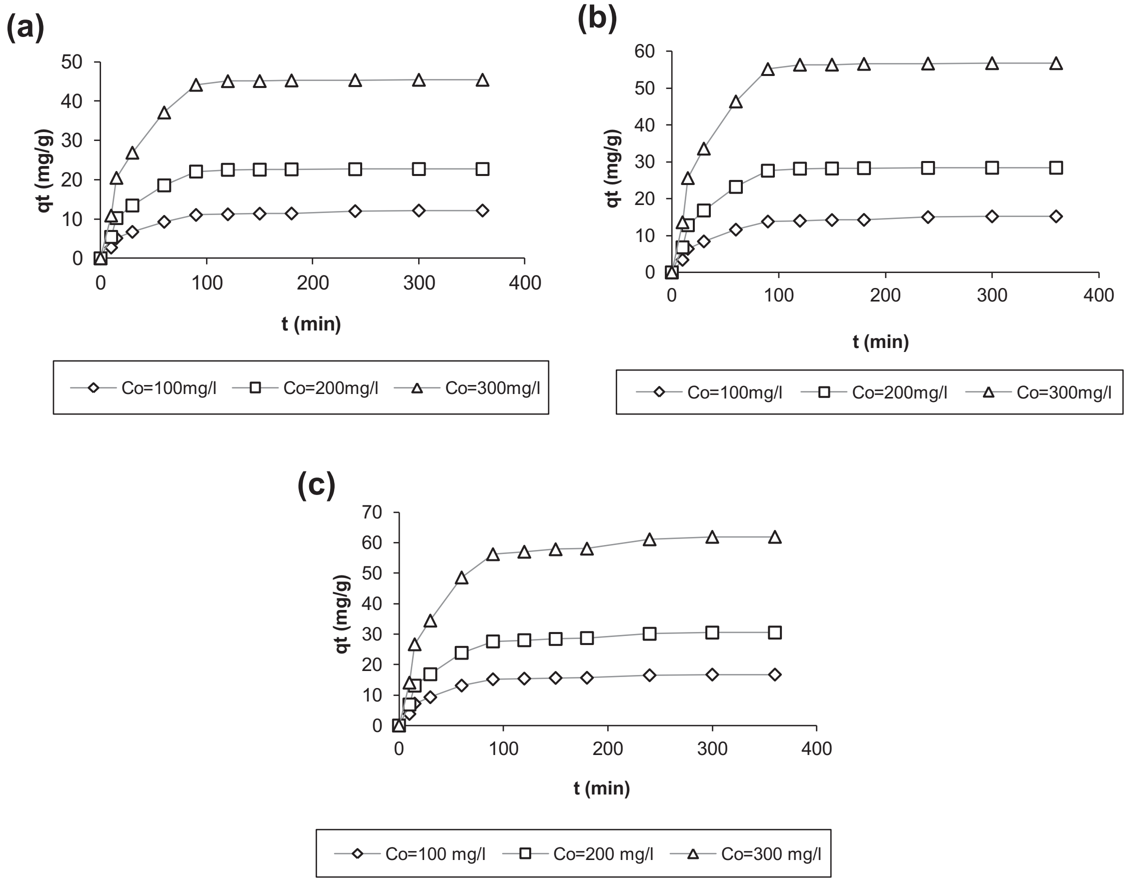


Fig. 2. Kinetic study of (a) PTAS, (b) CTAS, (c) MTAS.

equilibrium after 100 min. The same kinetic behavior has been reported by many authors [17–21].

These graphs also show that the adsorption rate increases with increased initial concentration. It is notable that the amount of dye adsorbed increases from 12.16 to 45.44 mg/g for the PTAS sample, from 15.2 to 56.8 mg/g for the CTAS sample and from 16.72 to 61.92 for the MTAS sample. It is obvious that the removal of the dye was dependent on the concentration of the dye since the increase in the initial dye concentration increased the amount of the dye adsorbed.

3.3. Pseudo-first order and pseudo-second order

The curves formed by the plots in Fig. 3 show that the safranine dye does not follow first order adsorption kinetics. However, the straight linear plots of Fig. 4 show that the adsorption does follow second order adsorption kinetics.

Therefore, using the characteristic equation of pseudo second order, the values of K_2 calculated from the lines plotted in Fig. 4 are presented in Table 2. The straight lines present good coefficients of correlation, R^2.

3.4. Effect of pH

The graphs presented in Fig. 5 clearly show that variation in pH does not affect the adsorption rate. Thus, whatever the initial pH is, the adsorbed amount per gram of adsorbent remains the same. The same kinetic behavior has been reported by many authors [10].

3.5. Adsorption isotherm

3.5.1. Effect of temperature

The adsorption isotherms (Fig. 6) show that the minimum amount of the safranine dye is adsorbed at 25°C. Hence, it can be said that temperature increase favors the removal of the dye, with adsorption capacities from 149 to 193 mg/g at 25 and 55°C respectively for the PTAS sample, from 166 to 214 mg/g at 25 and 55°C respectively for the CTAS sample and from 182

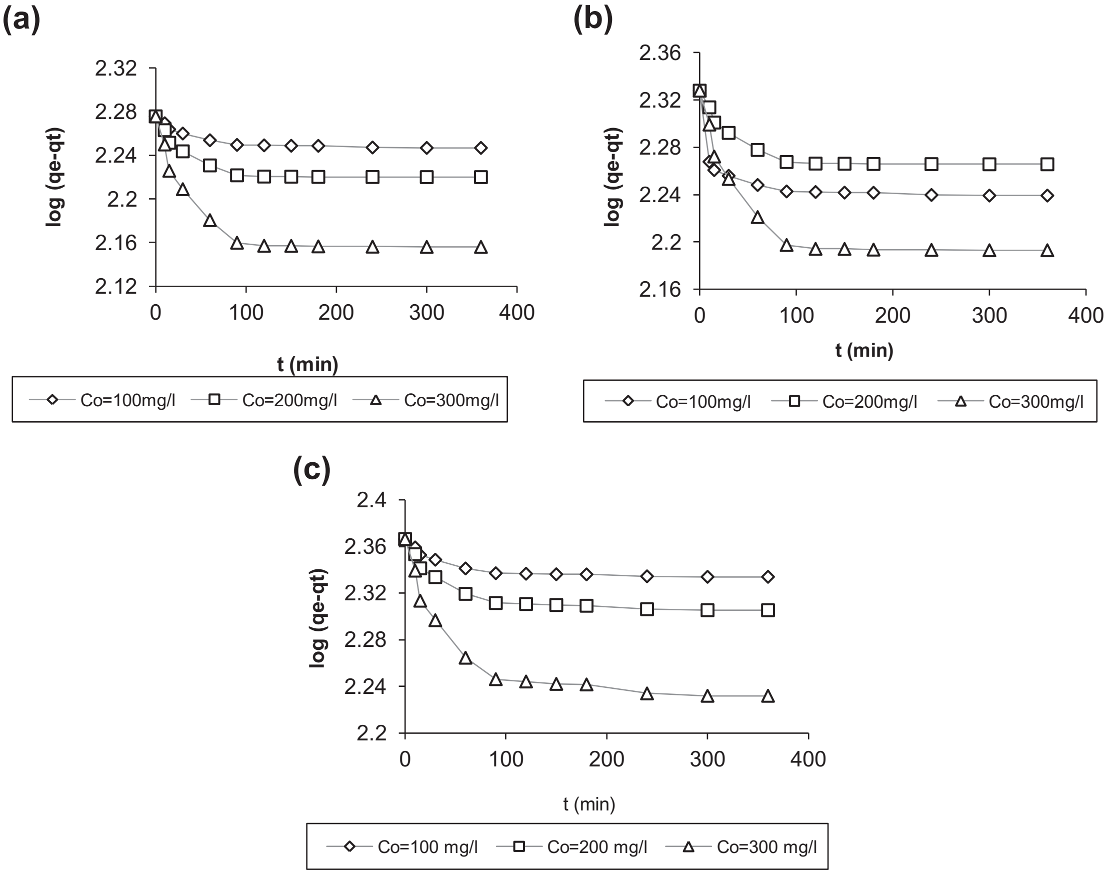


Fig. 3. Pseudo first order plots: (a) PTAS, (b) CTAS, (c) MTAS.

to 233 mg/g at 25 and 55˚C respectively for the MTAS sample.

3.5.2. Controlling adsorption model

The plot of the adsorbed amount per unit mass of the solid vs. the initial concentration of the adsorbate at a constant temperature represents the adsorption isotherm. Many mathematical models are proposed to present the adsorption isotherms among which Freundlich and Langmuir can be mentioned.

3.5.2.1. Freundlich model. The Freundlich model is represented by the equation:

$$Q = K \times C_{e}^{1/n} \quad [22] \tag{3}$$

where Q: the equilibrium sorption concentration of solute per gram of adsorbent (mg/g); C_e: the equilibrium aqueous concentration of the solute (mg/L).

K and n are Freundlich constants which correspond to the adsorption capacity and the intensity of adsorption.

These constants are determined experimentally by representing the Freundlich equation in logarithmic form:

$$\log Q = 1/n \log C_e + \log K \tag{4}$$

In the literature, adsorption is favorable when the values of 1/n are between 1 and 10 [23]. This same result has been obtained in the removal of the safranine using the PTAS, CTAS and MTAS samples. In this case, the values of $1/n$ are about 2 (Table 3). Therefore, using the Freundlich model (Fig. 7), the adsorption is shown to be favorable.

3.5.2.2. Langmuir model. The Langmuir model is given by the equation:

$$Q_e = (Q_{\max} \times b \times C_e)/(1 + b \times C_e) \quad [22–24] \tag{5}$$

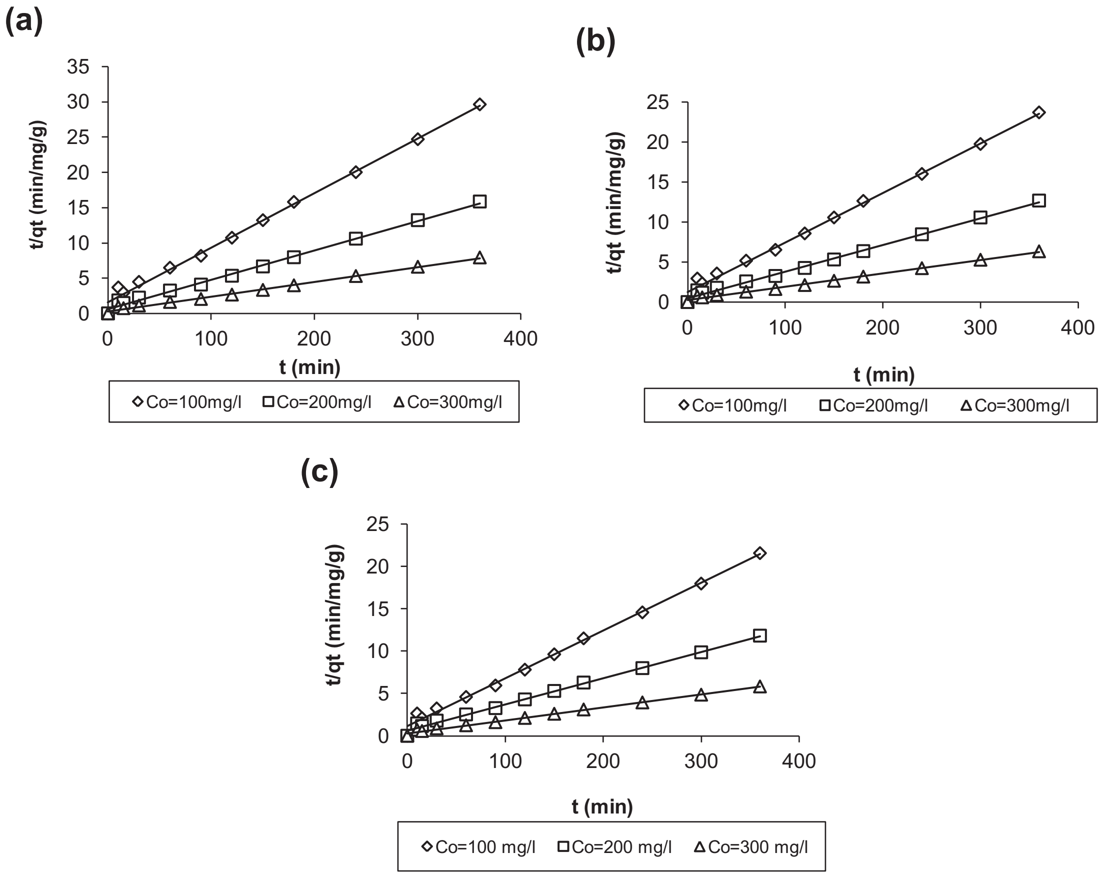


Fig. 4. Pseudo second order plots: (a) PTAS, (b) CTAS, (c) MTAS.

Table 2
Sorption rate parameters

Adsorbent	C_o(mg/l)	First-order parameters R^2	Second-order parameters K_2 (g/mg h)	R^2
PTAS	100	0.605	0.22065325	0.99
	200	0.539	0.15856222	0.99
	300	0.548	0.07972482	0.99
CTAS	100	0.350	0.17628618	0.99
	200	0.540	0.12684005	0.99
	300	0.550	0.06346871	0.99
MTAS	100	0.597	0.16622795	0.99
	200	0.607	0.09017567	0.99
	300	0.617	0.04487666	0.99

C_o-Initial dye concentration. K_2-Second order rate constant. R^2-Coefficient of correlation.

where Q_e: the amount of dye removed per gram of sorbent (mg/g); Q_{max}: the maximum sorption capacity (mg/g); C_e: the dye concentration in the equilibrium solution (mg/L); b: Langmuir constant.

The Langmuir model can be written in another way to enable us to determine the constants Q_{max} and b:

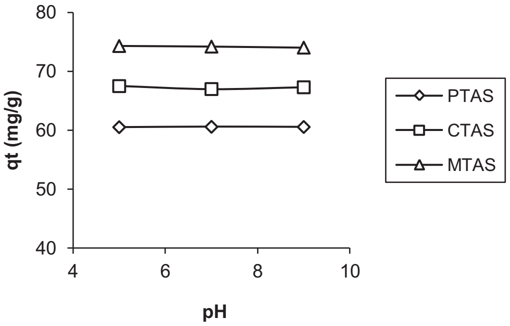


Fig. 5. Effect of pH.

$$1/Q_e = 1/Q_{max} + 1/(b \times Q_{max}) \times 1/C_e \quad (6)$$

The safranine dye adsorption for the three activated carbons prepared at different temperatures is well described using the Langmuir model.

The obtained straight lines (Fig. 8) give correlation coefficients of between 0.97 and 0.99. The maximum sorption capacity can be estimated for different samples from the representative graphs of the adsorption by referring to the characteristic equation of Langmuir. Table 4 shows that the adsorption capacity is proportional to the temperature in the three cases studied. It also shows that the PTAS, CTAS and MTAS samples have significant adsorption capacities of 243.90, 270.27 and 294.11 mg/g respectively at 55°C.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, that is given by Eq. (7):

$$R_L = 1/(1 + b \times C_0) \quad [26] \quad (7)$$

where C_0 is the highest initial concentration of adsorbate (mg/L), and b (L/mg) is the Langmuir constant. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). R_L values between 0 and 1 indicate favorable adsorption. The value of R_L in the present investigation was found to be between

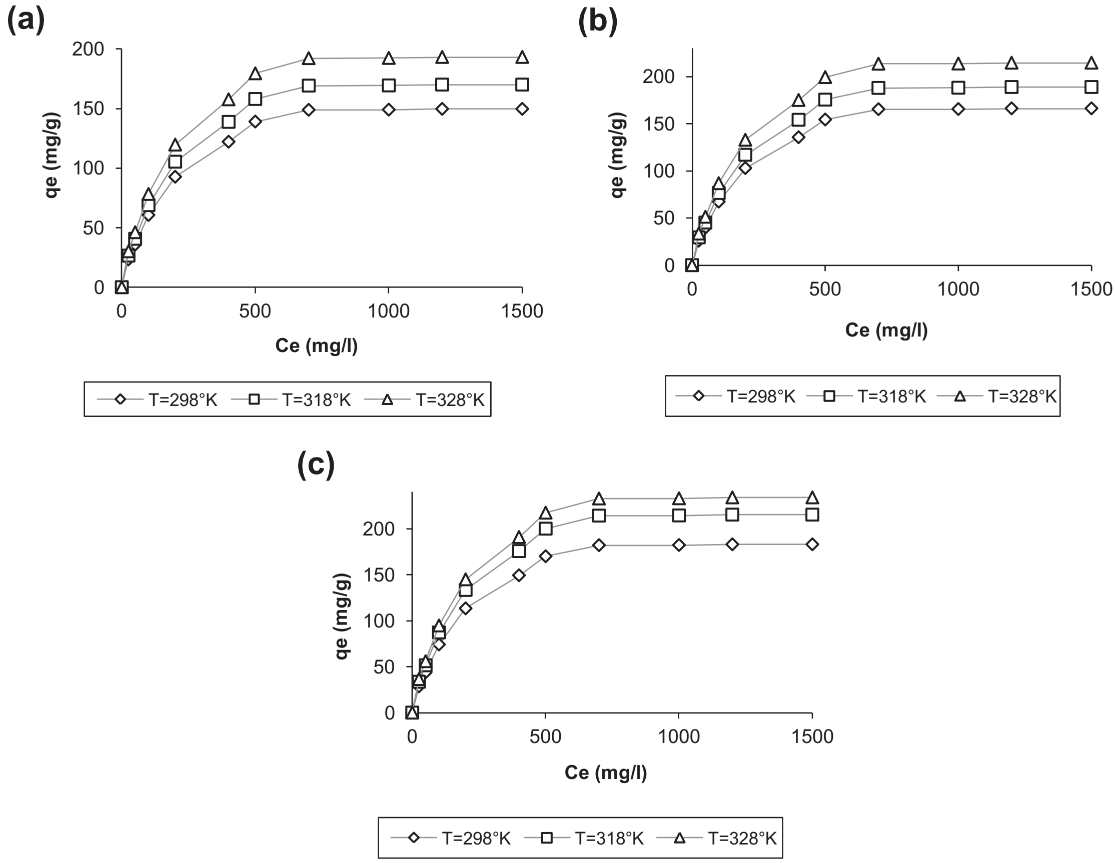


Fig. 6. Effect of temperature: (a) PTAS, (b) CTAS, (c) MTAS.

Table 3
Freundlich model parameters

Samples	T (°C)	n	K_f	R^2
PTAS	25	2.01	5.51	0.95
	45	2.17	7.29	0.94
	55	2.40	11.34	0.90
CTAS	25	2.12	6.87	0.93
	45	2.15	8.00	0.90
	55	2.18	9.72	0.91
MTAS	25	2.08	7.26	0.93
	45	2.11	8.59	0.93
	55	2.14	9.90	0.93

K_f and n-Freundlich constants.

0.38 and 0.65 indicating that the adsorption is favorable.

3.6. Thermodynamic parameters

The amount of dye adsorbed at different temperatures has been examined to obtain thermodynamic parameters (ΔG°, ΔH°, ΔS°) for the adsorption systems using the following equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

K_d: the distribution coefficient (amounts of removed safranine per gram of adsorbent divided by its concentration in the liquid phase); (ΔH°): the variation of the standard enthalpy (J/mol); (ΔS°): the variation of the standard entropy (J/mol. °K); R: ideal gas constant (8.32 J/mol. °K); T: temperature (°K).

According to the thermodynamic parameters [28], the variation of the Gibbs free energy (ΔG°) is linked to the enthalpy variation (ΔH°) and the entropy variation (ΔS°) at a constant temperature by the following relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

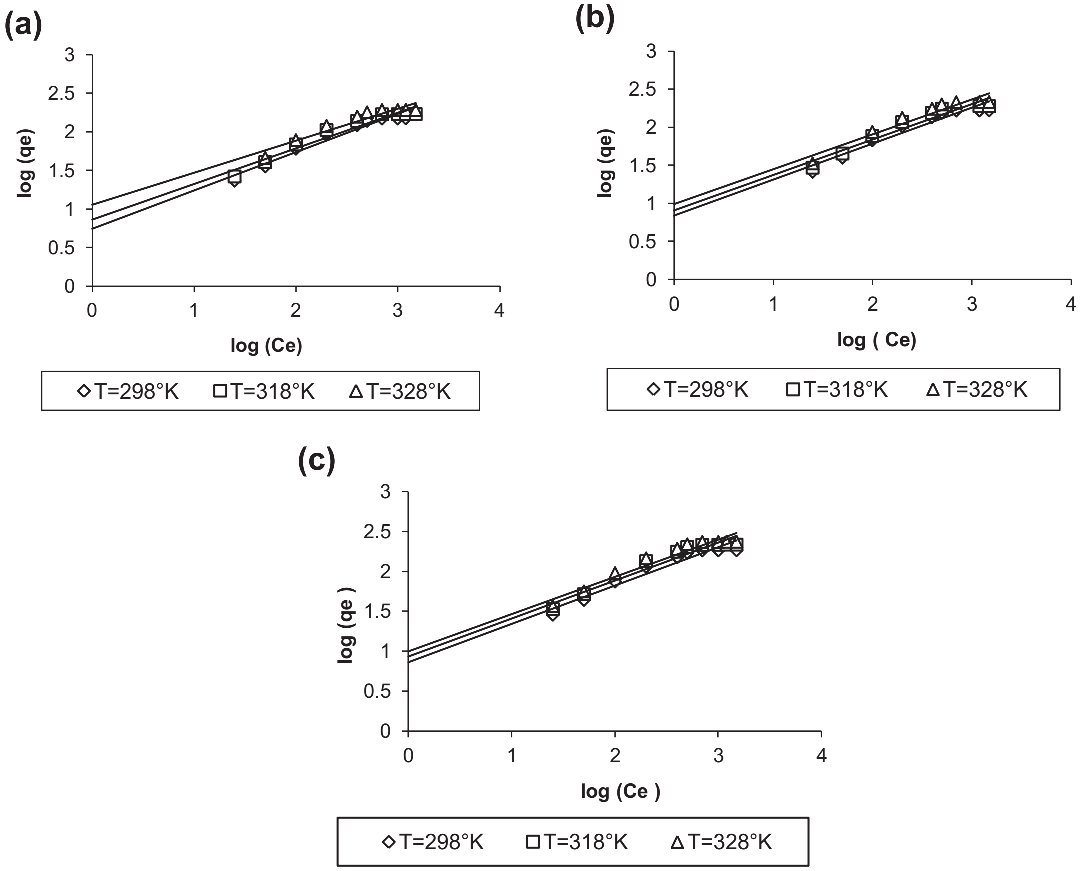


Fig. 7. Freundlich model: (a) PTAS, (b) CTAS, (c) MTAS.

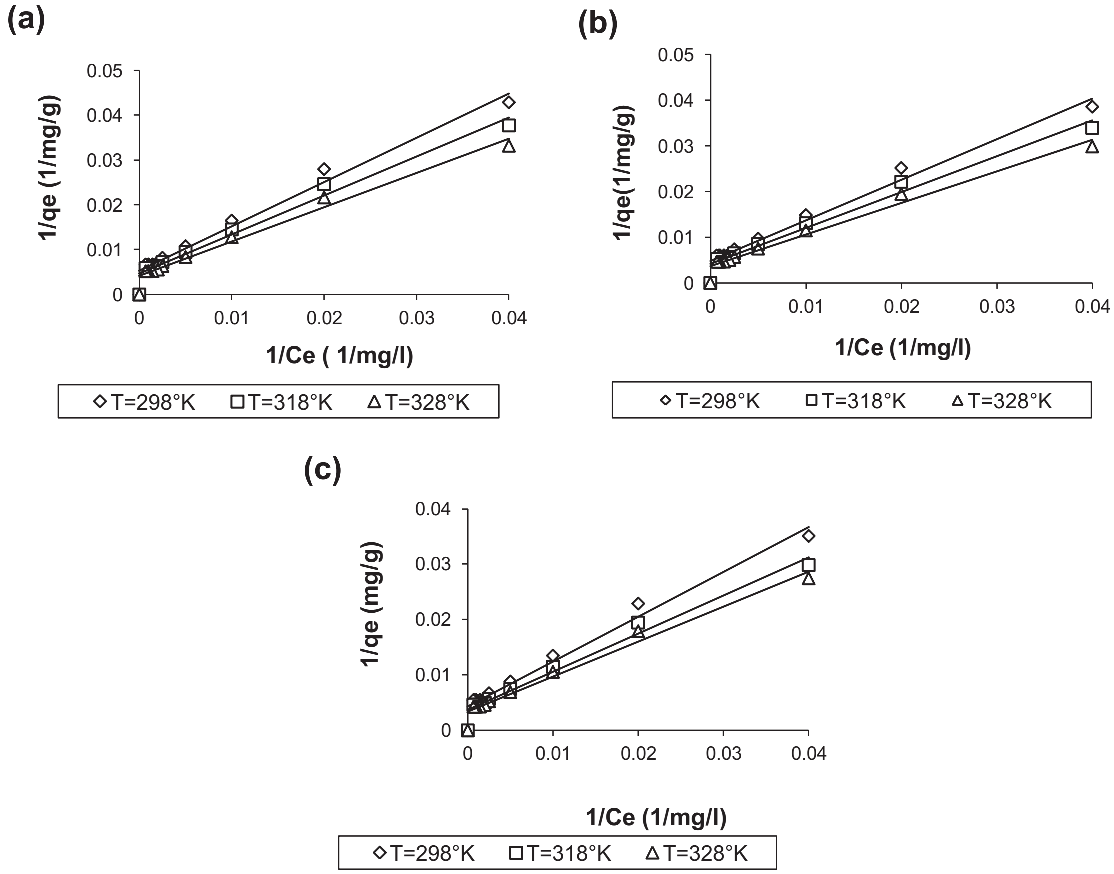


Fig. 8. Langmuir model: (a) PTAS, (b) CTAS, (c) MTAS.

Table 4
Langmuir model parameters

Adsorbent	T (°C)	$Q_{\max}$ (mg/g)	b	R^2
PTAS	25	188.67	0.0054	0.97
	45	217.39	0.0052	0.97
	55	243.90	0.0053	0.97
CTAS	25	212.76	0.0052	0.98
	45	238.09	0.0053	0.96
	55	270.27	0.0053	0.97
MTAS	25	232.55	0.0053	0.99
	45	270.27	0.0053	0.98
	55	294.11	0.0053	0.97

$Q_{\max}$-maximum sorption capacity.
b-Langmuir constant.

ΔH° and ΔS° were calculated from the slope and intercept of van't Hoff plots of $\ln K_d$ vs. $1/T$. The results given in Table 5 show that the values for ΔH° are negative, which indicates that the process of adsorption is exothermal.

The positive values for ΔS° show that there was a disorder at the solid-liquid interface during the dye adsorption. This entropy variation can be used to describe the randomness at the solid-solution interface during the removal process. The negative values for ΔG° indicate that the adsorption process is totally spontaneous. Furthermore, the values for ΔG° decrease as the temperature increases, thus showing the feasibility of the adsorption process at increased temperatures. The same results were communicated by Krobba et al. [19] and Kula et al. [20].

3.7. Comparison of the results with other studies

Table 6, which compares the adsorption capacities of the PTAS, CTAS and MTAS samples with materials used by other authors, shows the PTAS, CTAS and MTAS samples to have had better results.

The activated carbon samples prepared by physical activation seem to be the least adsorbent samples. The

Table 5
Thermodynamic parameters

Samples	T (°C)	ΔS° (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	ΔG°(kJ mol^{-1})
PTAS	25	41.56	−11.55	−23.94
	45			−24.77
	55			−25.18
CTAS	25	83.97	−24.01	−49.03
	45			−50.71
	55			−51.55
MTAS	25	228.09	−66.83	−134.80
	45			−139.36
	55			−141.64

ΔS° – variation of the standard entropy. ΔH° – variation of the standard enthalpy. ΔG° – variation of the Gibb's free energy.

Table 6
Comparison of maximum adsorption capacities of various dyes by some adsorbents

Adsorbent	Adsorbate	Q_{max} (mg/g)	References
Rice husk carbon	Safranine	294.1	[14]
Palm fruit bunch particles	Basic Yellow	327	[28]
Activated palm kernel shell carbon Basic	Blue 9	311	[29]
Peat-Kudzu	Astrazon Yellow 7GL	300-270	[30,31]
Activated carbon	Basic Violet 10-Basic Violet 3-Basic Red 9	254-244-127	[32]
Sepiolite	Astrazon Blue FGRL	209	[18]
ASAC	Astrazon Blue FGRL	202	[18]
Activated carbon	Maxilon Schwarz FBL-01	159	[33]
Fly ash	Astrazon Blue FGRL	152	[18]
Clay	Basic Red 9-Basic Violet 3-Basic Violet 4	345-70-51	[34]
PTAS	Safranine	243.9	This study
CTAS	Safranine	274.27	This study
MTAS	Safranine	294.11	This study

Q_{max}-maximum sorption capacity.

samples prepared using mixed activation show the highest adsorption capacities, and consequently this is the most efficient product. Mixed activation is more effective than both physical activation and chemical activation.

4. Conclusion

The present study focused on the adsorption of safranine dye from aqueous solution using agricultural waste products such as apricot stones prepared as activated carbon as a low cost adsorbent. Our work consisted of applying three types of activation to apricot stones to produce activated carbon for the treatment of wastewater containing colored pollutants from a textile industry through the physical process of "adsorption". In the experiments, we tested three types of activation; the first activation was physical (PTAS) and used two atmosphere types, the second activation was chemical (CTAS) using concentrated sulfuric acid and the last activation was a mixed activation (MTAS).

The external surfaces of the prepared activated carbon showed the presence of pores, in contrast to the raw apricot stones. The specific surface area of these adsorbents was found to be 587.4, 629.3 and 481.0 m^2/g for the PTAS, CTAS and MTAS samples respectively.

The adsorption characteristics have been examined through the variations in the parameters of contact time, initial dye concentration, pH and temperature. The experimental data was analyzed using Langmuir and Freundlich isotherm models. The Langmuir model provided the best correlation with the experimental equilibrium data. However, adsorption was also shown to be favorable using the Freundlich model. The adsorption systems obeyed the pseudo second order kinetic model. The maximum adsorption capacity of the MTAS activated carbon samples was 294.11 mg/g at 55˚C, which is clearly higher than the capacities mentioned in the literature in which the authors use other materials that are more expensive such as clay. The establishment of the isotherms at different temperatures enabled us to deduce the thermodynamic parameters: the enthalpy, the entropy and the variation of the free energy. Our calculations showed that our materials demonstrated exothermic behavior. The results obtained by calculating the variation of the free energy ΔG° reveals that the adsorption, in this case, is a spontaneous phenomenon.

Having drawn these conclusions, we can say that our objective for this study has been achieved, but the task of broadening the horizons of the application of this type of product to other types of dyes and other types of pollution, particularly mineral pollution, still remains.

References

[1] G. McKay, Adsorption of dyestuffs from aqueous solutions with activated carbon, part l, equilibrium and batch contact time studies, J. Chem. Technol. Biotechnol. 32 (1982) 759–772.

[2] G. McKay, Waste colour removal from textile effluents, Am. Dyestuff Rep. 68 (1979) 29–34.

[3] P. Nigarn, L.M. Banat, D. Singh, R. Marchant, Microbial process for decolourisation of textile effluents containing azo, diazo and reactive dyes, Process Biochem. 31 (1996) 435.

[4] Y. Fu, T. Viraraghavan, Fungal decolorization of dye wastewaters: A review, Bioresour. Technol. 79 (2001) 251–262.

[5] V. Gomez, M.S. Larrechi, M.P. Callao, Kinetic and adsorption study of acid dye removal using activated carbon, Chemosphere 69 (2007) 1151–1158.

[6] S.K. Khare, K.K. Panday, R.M. Srivastava, V.N. Singh, Removal of Victoria Blue from aqueous solution by fly ash, J. Chem. Technol. Biotechnol. 38 (1987) 99–104.

[7] B.S. Girgis, A.N.A. El-Hendawy, Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid, Micropor. Mesopor. Mat. 52 (2002) 105–117.

[8] Y. Diao, W.P. Walawender, L.T. Fan, Activated carbons prepared from phosphoric acid activation of grain sorghum, Bioresour. Technol. 81 (2002) 45–52.

[9] M. Hasan, A.L. Ahmad, B.H. Hameed, Adsorption of reactive dye onto cross-linked chitosan/oil palm ash composite beads, Chem. Eng. J. 136 (2008) 164–172.

[10] A. Aziz, M.S. Ouali, E.H. Elandaloussi, L.C. De Menorval, M. Lindheimer, Chemically modified olive stone: A low-cost sorbent for heavy metals and basic dyes removal from aqueous solutions, J. Hazard. Mater. 163 (2009) 441–447.

[11] B.H. Hameed, A.A. Ahmed, N. Azziz, Isotherms, Kinetics and thermodynamics of acid dye adsorption on activated palm ash, Chem. Eng. J. 133 (2007) 195–203.

[12] N.M. Haimour, S. Emeish, Utilization of date stones for production of activated carbon using phosphoric acid, Waste Manage. 26 (2006) 51–60.

[13] ASTM, Standard Test Method for Determination of Iodine Number of Activated Carbon. ASTM Committee on Standards, ASTM D 4607–94, ASTM, Philadelphia, PA, 1999.

[14] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of acid yellow 36, Dyes Pigm. 56 (2003) 239–249.

[15] V.K. Gupta, C.K. Jain, A. Imran, M. Sharma, V.K. Saini, Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste, Water Research 37 (2003) 4038–4044.

[16] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[17] B. Karagozoglu, M. Tasdemir, E. Demirbas, M. Kobya, The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon: Kinetic and equilibrium studies, J. Hazard. Mater. 147 (2007) 297–306.

[18] G. Cimino, R.M. Cappello, C. Caristi, G. Toscano, Characterization of carbons from olive cake by sorption of wastewater pollutants, Chemosphere 61 (2005) 947–955.

[19] A. Krobba, D. Nibou, S. Amokrane, H. Mekatel, Adsorption of copper (II) onto molecular sieves NaY, Desal. Wat. Treat. 37 (2012) 31–37.

[20] I. Kula, M. Ugurlu, H. Karaoglu, A. Celik, Adsorption of Cd (II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl2 activation, Bioresource Technol. 99 (2008) 492–501.

[21] Z. Bouberka, S. Kacha, M. Kameche, S. Elmaleh, Z. Derriche, Sorption study of an acid dye from aqueous solution using modified clays, J. Hazard. Mater. 119 (2005) 117–124.

[22] B.H. Hameed, J.M. Salman, A.L. Ahmad, Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones, J. Hazard. Mater. 163 (2009) 121–126.

[23] W.T. Tsai, J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin, C.W. Yeh, Characterization and adsorption properties of eggshells and eggshell membrane, Bioresour. Technol. 97 (2006) 488–493.

[24] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc 40 (1918) 1361–1403.

[25] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, I & EC Fundam. 5 (1966) 212–223.

[26] A.S. Ozcam, A. Ozcam, Adsorption of acid dyes from aqueous solution onto acid-activated bentonite, J. Colloid Interf. Sc. 276 (2003) 39–46.

[27] M. Alkan, S. Celikcapa, O. Demirbas, M. Dogan, Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite, Dyes Pigm. 65 (2005) 251–259.

[28] M.M. Nassar, Y.H. Magdy, Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles, Chem. Eng. J. 66 (1997) 223–226.

[29] A. Jumasiah, T.G. Chuah, J. Gimbon, T.S.Y. Choong, I. Azni, Adsorption of basic dye onto palm kernel shell activated carbon: sorption equilibrium and kinetics studies, Desal. Wat. Treat. 186 (2005) 57–64.

[30] S.J. Allen, G. Mckay, K.Y.H. Khader, Multi-component sorption isotherms of basic dyes onto peat, Environ. Pollut. 52 (1988) 39–53.

[31] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Comparison of optimized isotherm models for basic dye adsorption by kudzu, Bioresour. Technol. 88 (2003) 143–152.

[32] K.V. Kumar, S. Sivanesan, Isotherm parameters for basic dyes onto activated carbon: comparison of linear and non-linear method, J. Hazard. Mat. 129 (2006) 147–150.

[33] V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, Adsorption of basic dyes on granular activated carbon and natural zeolite, Water Res. 35 (2001) 3357–3366.

[34] W.T. Tsai, Y.M. Chang, C.W. Lai, C.C. Lo, Adsorption of basic dyes in aqueous solution by clay adsorbent from regenerated bleaching earth, Appl. Clay Sci. 29 (2005) 149–154.