Chemical Engineering Journal 165 (2010) 457–464

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Equilibrium, thermodynamic and kinetic studies on adsorption of commercial dye by activated carbon derived from olive-waste cakes

R. Baccar[a,b,*], P. Blánquez[b], J. Bouzid[a], M. Feki[c], M. Sarrà[b]

[a] Laboratoire Eau Energie Environnement, Ecole Nationale d'Ingénieurs de Sfax, BP 1173-3038 Sfax, Tunisia
[b] Departament d'Enginyeria Química, Escola d'Enginyeria, Universitat Autònoma de Barcelona, Bellaterra 08193, Spain
[c] Unité de Recherche de Chimie Industrielle et Matériaux, Ecole Nationale d'Ingénieurs de Sfax, BP 1173-3038 Sfax, Tunisia

ARTICLE INFO

Article history:
Received 15 June 2010
Received in revised form
23 September 2010
Accepted 24 September 2010

Keywords:
Low cost adsorbent
Metal complex dye
Textile wastewater

ABSTRACT

Adsorption of Lanaset Grey G, an industrial metal complex dye, on activated carbon derived from Tunisian olive-waste cakes was explored. The equilibrium adsorption data, obtained at 25 °C, were analyzed by Langmuir Freundlich and Temkin models. The results indicate that the Langmuir model provides the best correlation of the experimental data. The adsorption capacity of the sorbent for Lanaset Grey G was found to be 108.7 mg g^{-1} which is better than the capacity of a commercial activated carbon. The kinetic studies, conducted at three temperatures (10, 25 and 37 °C), indicated that the adsorption process followed the pseudo-first-order kinetic model and increase of temperature enhanced both rate and efficiency of the dye uptake. The application of the intra-particle diffusion model revealed that the adsorption mechanism of this dye is rather a complex process and the intra-particle diffusion is involved in the overall rate of the adsorption process but it is not the only rate-controlling step. The calculated thermodynamics parameters showed the spontaneous and the endothermic nature of the adsorption process. The activation energy found to be 32.1 kJ mol^{-1}, could indicate a physical adsorption process. The presence of other components, commonly used in the textile industrial bath, did not affect the uptake extent of the target dye by the activated carbon. Olive-waste cakes activated carbon was shown to be a promising adsorbent for the efficient removal of metal complex dyes.

1. Introduction

Wastewater generated by textile industries is rated as the most polluting among all industrial sectors considering both volumes discharged and effluent composition. These effluents can damage the environment, if they are discharged directly into the surface waters or into wastewater treatment plant, as they contain dyes with complex and variable chemical structures. The metal complex dye group is one of the most important and widely used dye groups in the textile industry due to their excellent light fastness on substrates [1]. In commercial terms, the more important metal complex dyes are chromium, cobalt and copper complexes with azo ligands. Without adequate treatment, textile dyes can remain in the environment for an extended period of time [2]. Therefore, their removal from waste effluents becomes environmentally important. Many treatment processes have been applied for the removal of dyes from wastewater such as coagulation, flocculation, ozonation, membrane filtration, Fentons reagent, ion exchange and biological treatment [3–5]. These methods, however, display one or more limitations, such as low efficiency, high cost, generation of secondary pollution and narrow appliance range. Overcoming these limitations, chemists have been devoted to search for effective, economic and easy methods [6]. Adsorption process has gained favor recently as it is one of the most effective methods. Besides, adsorption onto activated carbonic (AC) is proven to be very effective in treating textile effluents [7,8]. However, its widespread use is restricted due to the high cost of conventional and commercial carbons. Therefore, in recent years, many researchers have tried to produce activated carbons using renewable and cheaper precursors which were mainly industrial and agricultural by-products (lignocellulosics) including peach stones [9], date stones [10,11], waste apple pulp in cider production [12], rice husks [13], pistachio-nut shells [14] and coir pitch [8]. The use of these materials as precursors for the preparation of activated carbon produces not only a useful and a low cost adsorbent for the purification of contaminated environments, but also contributes to minimizing the solid wastes. Olive-waste cakes are an agro-food waste predominantly produced in the Mediterranean countries and especially in Tunisia as it is the fourth largest olive oil producer in the world [15].

---

* Corresponding author at: Departament d'Enginyeria Química, Escola d'Enginyeria, Universitat Autònoma de Barcelona, Bellaterra 08193, Spain.
Tel.: +34 93 581 4798; fax: +34 93 581 2013.
E-mail address: Rim.baccar@uab.es (R. Baccar).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.09.033

The main objective of this study is to evaluate the adsorption potential of an activated carbon prepared from Tunisian olive-waste cakes for metal complex dyes, particularly Lanaset Grey G. It is to be noted that only a limited number of studies dealing with the removal of metal complex dyes have been found in the literature [1,16–18].

The adsorbent used in this work was prepared in the laboratory scale, from olive-waste cakes, via chemical activation using phosphoric acid as a dehydrating agent. Optimization of some process parameters and characterization of the optimal activated carbon were first investigated. Thereafter, the adsorption of the Lanaset Grey G was undertaken. The adsorption isotherms, kinetic and thermodynamic aspects of the retention process were explored. Finally, the effect of the additives, commonly used by the industry to dye the textile, on the uptake of the Lanaset Grey G by the adsorbent, was studied.

Concerning the target dye, Lanaset Grey G, it is a commercial mixture of several metal complex dyes used in the textile industry "Artextil S.A" located in Sabadell, Barcelona. The chemical formula of this water-soluble dye is unavailable. However, this material is known to contain cobalt II (0.79 wt%) and chromium III (2.5 wt%) as organo-metal complexes.

2. Materials and methods

2.1. Preparation of activated carbon

Exhausted olive-waste cakes, obtained from an oil factory "Agrozitex" located in Sfax, Tunisia, was used as raw material for the production of activated carbons via chemical activation. For this purpose, phosphoric acid (analytical grade) was retained as a dehydrating agent. Each preparation test was conducted as follows: 40 g of the crushed (Ø < 1.5 mm) and dried precursor was mixed with H_3PO_4 solutions having different concentrations (30–85% H_3PO_4 in weight). The impregnation ratio, defined by the weight ratio of impregnant (H_3PO_4) to precursor, was 1, 1.25, 1.5, 1.75, 1.85 and 2. The impregnation was carried out in a stirred pyrex reactor equipped with a reflux condenser. Stirring was used to ensure the access of the acid to the interior of the olive-waste cake particles. The temperature and the duration of the reaction were 104 °C and 2 h, respectively. Agitation and heating were ensured by a heating magnetic stirrer with connected temperature regulator probe made of Teflon. The pyrolysis of the impregnated material was conducted in a cylindrical stainless steel reactor, inserted into a tubular regulated furnace under continuous nitrogen flow (0.5 L min^{-1}). Pyrolysis temperature ranged from 350 to 650 °C, while pyrolysis time was maintained at 2 h. After cooling down to room temperature, under the same flow of nitrogen, the obtained activated carbon was thoroughly washed with hot distilled water until neutral pH. The sample was then dried at 105 °C overnight, ground (until a granulometry ranging between 100 and 160 μm) and finally kept in hermetic bottle for subsequent uses.

2.2. Characterization

2.2.1. Characterization of the prepared adsorbents

To optimize the preparation method, the effect of the main process parameters (acid concentration, impregnation ratio, temperature of pyrolysis step) on the performances of the prepared activated carbons was studied. These performances were expressed in terms of iodine and methylene blue numbers. The choice of these molecules is justified by their properties. Thus, the methylene blue is the most recognized probe molecule for assessing the ability of the sorbent to remove large molecules via its macroporosity (pore diameter greater than 1.5 nm) and this also serves as model compound for adsorption of organic contaminants from aqueous solutions [19]. On the contrary, the iodine number gives an indication on microporosity (pores less than 1 nm in diameter) and consequently on the specific surface area of the sorbent material.

2.2.2. Characterization of the adsorbent prepared under optimal conditions

Specific surface area of the activated carbon prepared under optimal conditions, which will be used later for the adsorption of the metal complex dye, was evaluated through N_2 adsorption at 77 K, using an Autosorb1-Quantachrome instrument. The BET (Brunauer–Emmet and Teller) model was applied to fit nitrogen adsorption isotherm and evaluate the surface area (S_{BET}) of the sorbent [20]. Crystalline phases eventually present in the adsorbent material were analyzed by powder X-ray diffraction (XRD analyzer Philips X Pert).

2.3. Adsorption studies

2.3.1. Chemicals

Lanaset Grey G, a dark blue powder composed of a mixture of metal complex dyes, was purchased from Ciba (Specialty Chemicals, Barcelona Ref. 080173.5). The additives used industrially with the dye Lanaset Grey G (Esterol 126, citric acid, Amplex DG and Antifoam) were supplied by the industry "Artextil S.A" located in Sabadell, Barcelona. All other chemicals used were of analytical grade. Solutions were prepared by dissolving the corresponding reagents in bidistilled water.

The activated carbon, prepared under the optimal conditions, was retained for all the following adsorption experiments.

2.3.2. Effect of pH on adsorption of Lanaset Grey G

The effect of pH on the dye uptake by the adsorbent was investigated at 25 °C using synthetic solutions containing 150 mg L^{-1} Lanaset Grey G. Adsorption tests were carried out by adding 0.50 g of activated carbon to a series of 500 mL Erlenmeyer flasks filled with 300 mL of the above solution at different pH values. The initial pH of the solutions was adjusted between 2 and 11 by adding either HCl (1 M) or NaOH (1 M). Solution pHs were measured by a high precision pH-meter (Metrohom, model 632), equipped with a combined glass electrode (Metrohm). Preliminary calibration was systematically carried out using suitable buffer solutions. To make sure that the equilibrium was reached, each suspension was magnetically stirred for 3 days at 250 rpm. Then, each dye solution was separated from the sorbent by centrifugation at 13,000 rpm for 5 min. The residual concentration of the Lanaset grey G (C_e) was measured at 590 nm using an UV/Visible spectrophotometer (UNICAM 8625).

For a given pH, the amount of dye adsorbed at equilibrium q_e (mg g^{-1}) was calculated from Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m_{AC}} \tag{1}$$

where C_0 and C_e (mg L^{-1}) are the liquid phase concentrations of dye at initial and equilibrium, respectively, V the volume of the solution (L) and m_{AC} is the mass of activated carbon used in the experiment (g).

2.3.3. Sorption isotherm and kinetic studies

Equilibrium and kinetics of the dye adsorption were studied here at 25 °C.

For the determination of equilibrium isotherm, adsorption tests were carried out by adding various amounts of adsorbent (0.10, 0.175, 0.30, 0.50 and 0.60 g) to a series of 500 mL Erlenmeyer flasks filled with 300 mL solution containing 150 mg L^{-1} of Lanaset Grey G. The solution was maintained at its natural pH 6. The flasks were shaken at 250 rpm with a magnetic stirrer and kept for 3 days to reach adsorption equilibrium. At the end of each experiment, the separation of the dye solution from the sorbent and the measurement of the residual concentration (C_e) of the Lanaset Grey G were conducted by the same method mentioned above.

The amount of dye adsorbed at equilibrium q_e ($mg\,g^{-1}$) was calculated by Eq. (1).

The procedure of kinetic tests was basically identical to those of equilibrium. Nevertheless, for each suspension, the liquid samples taken for dye analysis were realized at preset time intervals. The amount of dye adsorbed at time t, q_t ($mg\,g^{-1}$), was calculated by Eq. (1) by substituting C_e by C_t. The latter represents the liquid phase concentration of dye at any time t.

2.3.4. *Effect of temperature*

The effect of the temperature on the dye sorption process was investigated by time-based analyses, when the adsorption systems were analyzed until residual dye concentration in the solution became constant (equilibrium state). The kinetic adsorption runs were performed at three different temperatures, i.e. 15, 25 and 37 °C, using the same stock solution containing 150 $mg\,L^{-1}$ Lanaset Grey G at its natural pH 6. The agitation of the mixture was realized by a magnetic stirrer at 250 rpm. For each temperature, the quantities: C_t, q_t, C_e and q_e were determined as described above.

The rate and equilibrium data, obtained at the three temperatures considered, were used to evaluate the activation energy (E_a) and the thermodynamic parameters (ΔG°, ΔH° and ΔS°) of the dye adsorption process.

2.3.5. *Effect of the additives used in the textile bath on the adsorption*

In textile industry, the bath used to dye textiles contained apart from the dye Lanaset Grey G (150 $mg\,L^{-1}$), other components (additives), i.e. Esterol 126 (0.5 $g\,L^{-1}$); citric acid (1.5 $g\,L^{-1}$); Amplex DG (1 $g\,L^{-1}$) and Antifoam. The additive Esterol 126 is an equalizer, the citric acid is used to adjust the pH and the Amplex DG is used to avoid the reduction.

In order to investigate the effect of these additives on the uptake of the Lanaset Grey G by the adsorbent, a solution having the same composition of the industrial bath described above was prepared. The equilibrium isotherm, relating to the adsorption of Lanaset Grey G from this mixture, was established at 25 °C following the same procedure used for the individual dye (only Lanaset Grey G). Thus, adsorption tests were carried out by adding various amounts of adsorbent (0.10, 0.20, 0.30, 0.45, 0.60 and 1.00 g) to a series of 500 mL Erlenmeyer flasks filled with 300 mL of the prepared mixture. The separation of the solution from the sorbent and the measurement of the residual concentration of Lanaset Grey G were conducted by the same methods described above for the individual dye.

3. Results and discussion

3.1. *Preparation of activated carbons: effect of processing parameters*

Within the scope of our researches, an attempt has been made to optimize the process parameters which lead to an activated carbon with good characteristics. 3D response surfaces were plotted to represent our results. This representation showed the relative effects of any two variables when the remaining variables were kept constant.

As illustration, Fig. 1 shows the effect of the main process parameters (phosphoric acid concentration, impregnation ratio and temperature of pyrolysis step) and their mutual interactions on the performances of the prepared sorbents expressed in terms of iodine and methylene blue numbers.

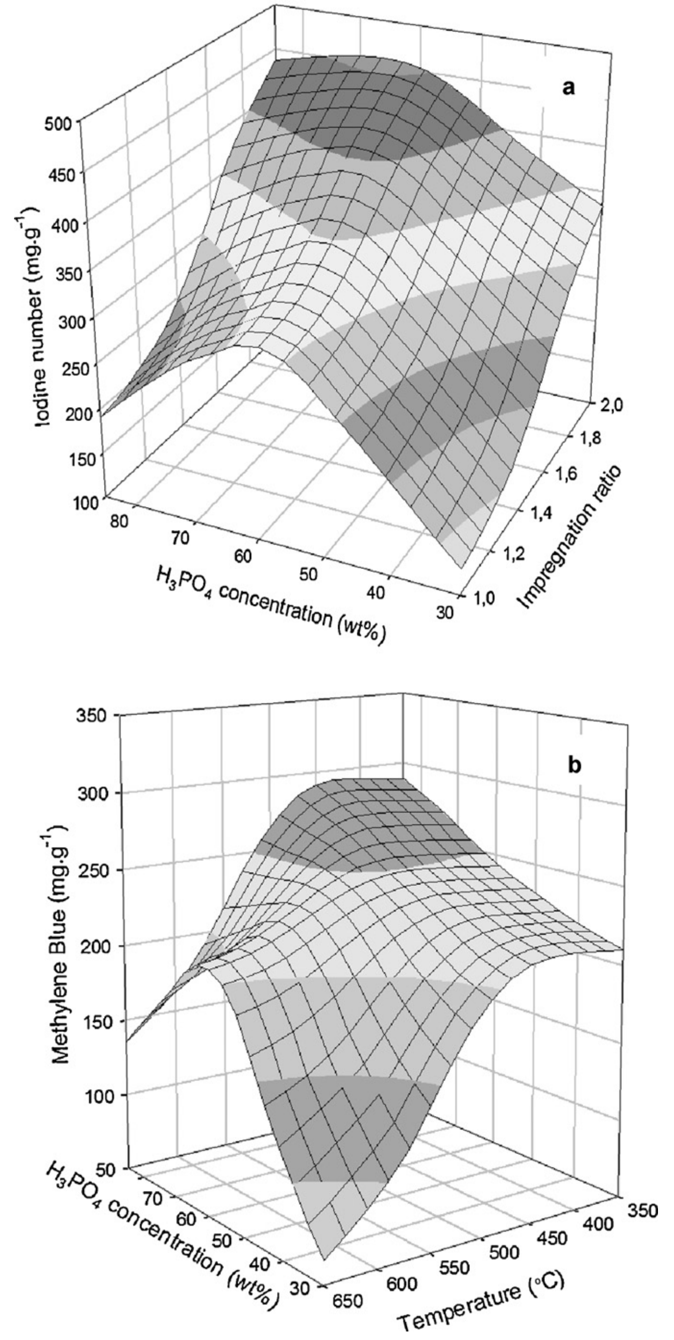

Fig. 1. (a) Effect of acid concentration and impregnation ratio on iodine number. (b) Effect of acid concentration and temperature on methylene blue number.

Acid concentration and impregnation ratio are important factors that govern the development of porosity of the prepared carbon [9]. The effect of these two parameters on the iodine number of the adsorbent is shown in Fig. 1a. As it can be discerned, the iodine number increases rapidly with an increase of acid concentration from 35% to 60% H_3PO_4 and until an impregnation ratio of 1.75. Beyond this impregnation ratio, the iodine number decreases while it increases slightly with acid concentration higher than 60% H_3PO_4. Taking into account this slight increase of the iodine number occurring in the acid concentration range 60–85% H_3PO_4 and the handling difficulties of the most concentrated commercial phosphoric acid (85% H_3PO_4 in weight) owing especially to its high viscosity, a concentration of 60% H_3PO_4 and an impregnation ratio of 1.75 seems to be the most suitable values for the development of the best iodine number and, consequently, to the best development of microporous structure.

The effect of temperature and acid concentration on methylene blue number is illustrated in Fig. 1b. As it can be seen, the quantity of methylene blue adsorbed increases with an increase of the temperature from 350 to 450 °C and an acid concentration from 30% to 85% H_3PO_4. Thus, keeping the pyrolysis temperature around its optimal value (i.e. 450 °C), leads to a better development of the sorbent macroporosity. Several investigators have established that in the case of H_3PO_4 activation of other agricultural materials (woods, coconut shell, date pits, grain sorghum), temperatures neighbouring 450 °C were also suitable to obtain optimal properties of the activated carbons [9,10,21,22].

The above results show that the most efficient activated carbon is that obtained under the followings optimal conditions: an acid concentration equal to 60% in weight, an impregnation ratio of 1.75 and a pyrolysis temperature of 450 °C. It is to note that results obtained when studying individually the effect of each parameter (acid concentration, impregnation ratio and pyrolysis temperature) on the whole considered properties, namely iodine and methylene blue numbers (results not shown), lead to the same optimal conditions [23].

3.2. Characteristics of the activated carbon prepared under the optimal conditions

It was found that the BET surface area, total pore volume and average pore diameter of the activated carbon were 793 $m^2\,g^{-1}$, 0.49 $cm^3\,g^{-1}$ and 4.2 nm, respectively. The XRD pattern of the sorbent did not show any peak. This indicates the amorphous nature of the carbon prepared from olive-waste cakes.

3.3. Effect of pH on dye adsorption

In this part, the pH of the dye solution was varied in the range 2–11.

Before presenting the pH dependence of the dye uptake by the sorbent, an important fact deserves to be pointed out. When adjusting at alkaline values the pH of the metal complex dye solutions used in this part, no precipitation of metal hydroxides ($Co(OH)_2$ and $Cr(OH)_3$) was observed. This means that the metallic species (Co^{2+} and Cr^{3+}), taking part of the chemical composition of the industrial dye, are strongly bounded to the organic groups (ligands) of the dye molecules. In other words, the organo-metal complex dye molecules do not dissociate since the addition of OH^- ions does not yield a precipitate of metal hydroxide. In fact, the more stable the complex, the smaller is the tendency of the complex to dissociate into its constituents. Thus, the free metal ion concentration is very small, so small in fact that the solubility product of metal hydroxide is not reached.

Concerning the effect of pH on the extent of dye adsorption, our experimental results (Fig. 2) showed no significant variation of the amount of solute adsorbed in the pH range explored. According to the findings of several investigations dealing with adsorption of dyes of different chemical structures, the effect of pH on the solute uptake by activated carbons can be high, moderate or slightly significant [8,13,24,25]. Adsorption is affected by the pH change of the solution since this parameter affects the degree of ionization of the dye and the surface properties of the sorbents. As a general rule, low pH values result in lowering the number of negatively charged sites of the activated carbon, increasing the number of positively charged sites thus enhancing the adsorption of anionic dyes. With the increase in pH values, the hydroxyl ion concentration increases and on the surface of the carbon the number of negatively charged sites increases so that the extent of adsorption of cationic dyes is increased [24,25]. For the dye used in this work, the results related to the pH effect are apparently surprising. However, a plausible explanation of this behavior may be the presence of both negatively and positively charged functional groupments in the dye molecules. In dependently of the origin of this insignificant effect of the pH, we estimate that this finding is quite meaningful in adsorption process application since it makes not indispensable any pH adjustment of the effluent before treatment.

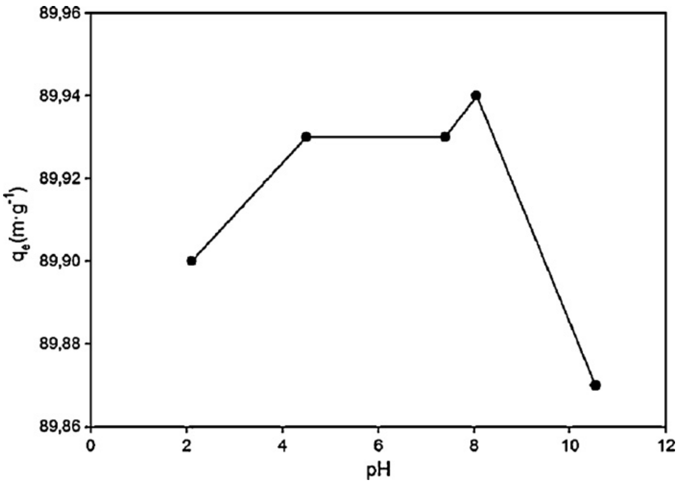

Fig. 2. Effect of pH on adsorption of Lanaset Grey G (C_0 = 150 mg L^{-1}; T = 25 °C).

3.4. Effect of contact time on dye adsorption

Fig. 3 shows the residual dye concentration versus contact time. As illustration we presented only the curves relative to 0.10, 0.30 and 0.60 g of adsorbent. The results indicate that the contact time needed to reach adsorption equilibrium of Lanaset Grey G on activated carbon is about 50 h for all the sorbent loadings considered. Thus, the chosen contact time of 3 days, used in our experiments, is enough sufficient to reach equilibrium state.

At the beginning, the dye is adsorbed by the exterior surface of the activated carbon, the adsorption rate is fast (Fig. 3). When the exterior adsorption surface reaches saturation, the dye enters into the pores of the adsorbent and is adsorbed by the interior surface of the particles. This phenomenon takes relatively long contact time. Chen et al. [26], for example, used 5 days as contact time for the

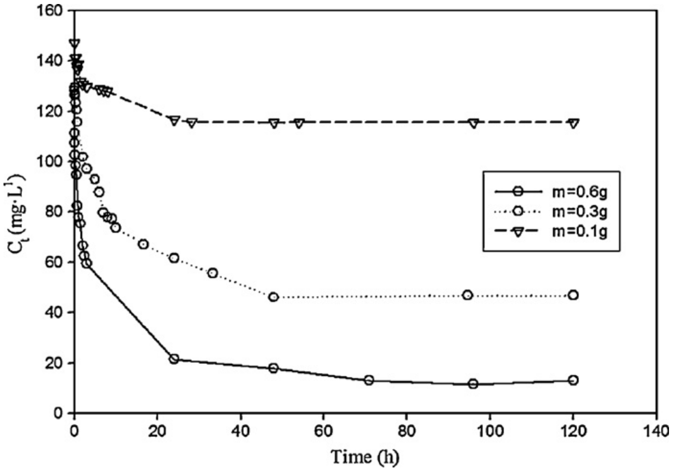

Fig. 3. Effect of contact time on Lanaset Grey G adsorption for different amounts of adsorbent (C_0 = 150 mg L^{-1}; T = 25 °C).

adsorption isotherm of dyestuffs on pitch. To make sure that full equilibrium was attained, Hameed et al. [27] used 48 h as a contact time for the adsorption of acid green 25 dye.

It is to be noted that the time-based results described above agree with the general theory of dye adsorption process: initially the dye molecules have to first encounter the boundary layer effect and then diffuse from the boundary layer film onto adsorbent surface and then finally they have to diffuse into the porous structure of the adsorbent [28]. Accordingly, the residual concentration of Lanaset Grey G decreases with time and, at some point in time, it reaches a constant value beyond which no more dye is further removed from the solution. At this point, the amount of the dye desorbing from the activated carbon is in a state of dynamic equilibrium with the amount of the dye being adsorbed on the carbon.

3.5. *Adsorption isotherm*

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state.

Three isotherm models, relating to adsorption equilibrium, have been tested in the present research, namely Langmuir, Freundlich and Temkin isotherm models.

Langmuir model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of surface. The Langmuir isotherm is described by Eq. (2):

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_{max} and K_L are Langmuir constants related to adsorption capacity (maximum amount adsorbed per gram of adsorbent (mg g^{-1})) and energy of sorption (L mg^{-1}), respectively. Values of q_{max} and K_L can be calculated from the slope and intercept of the linear plot of C_e/q_e against C_e.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L, defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where C_0 is the initial dye concentration. The value of R_L indicates the type of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 1$).

The empirical Freundlich model, which is known to be satisfactory for low concentrations and based on sorption on a heterogeneous surface, is expressed by Eq. (4):

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. These parameters can be calculated from the intercept and the slope of the linear plot $\log q_e$ versus $\log C_e$.

Temkin model considers the effects of indirect adsorbate/adsorbate interactions on adsorption isotherm. It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate/adsorbate interactions.

The Temkin isotherm can be expressed by Eq. (5):

$$q_e = \frac{RT}{b} \ln(A C_e) \quad (5)$$

where constant $B = RT/b = (RT/\Delta E) q_{max}$, R the universal gas constant (8.314 J mol^{-1} K^{-1}), T the temperature (K), $\Delta E = (-\Delta H)$ the variation of adsorption energy (J mol^{-1}), A the Temkin equilibrium constant (L mg^{-1}) corresponding to the maximum binding energy and q_{max} is the adsorption (maximum) capacity [29,30]. If the adsorption obeys Temkin equation, A and B can be obtained from the slope and intercept of the plot q_e against $\ln C_e$.

Table 1
Langmuir, Freundlich and Temkin isotherm model parameters and correlation coefficients for adsorption of Lanaset Grey G at 25 °C.

Isotherms	Parameters
Langmuir	q_{max} = 108.7 mg g^{-1} R_L = 0.031 R^2 = 0.998
Freundlich	K_F = 48.6 mg g^{-1} (L mg^{-1})$^{1/n}$ n = 5.847 R^2 = 0.859
Temkin	A = 15.8 L mg^{-1} B = 14.4 R^2 = 0.854

Table 1 presents the parameters corresponding to the Langmuir, Freundlich and Temkin isotherms established at 25 °C. A comparison of R^2 values for the three models indicates that the Langmuir equation provides the best correlation of the experimental data. The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogenous distribution of active sites on the activated carbon surface. Similar observations were reported for the adsorption of metal complex dyes on pine sawdust [1]. The adsorption capacity (q_{max}) determined from Langmuir model was 108.7 mg g^{-1}. The value of R_L in the present investigation was found to be 0.031, confirming the favorable adsorption of the Lanaset Grey G.

For the sake of comparison, values of some adsorbent capacities – towards Lanaset Grey G and other dyes – available in the literature are shown in Table 2. As it can be seen, the capacity of the carbon used in this work (108.7 mg g^{-1}) compare well and sometimes more favorable than those of other sorbents prepared from agricultural wastes or of the commercial activated carbon CAL.

3.6. *Adsorption kinetics*

3.6.1. *Pseudo-first and pseudo-second order equations*

The modeling of adsorption kinetics was investigated by two common models, namely, the Lagergren pseudo-first order and pseudo-second order models. The linear forms of these two models are expressed by Eqs. (6) and (7), respectively:

$$\log(q_e - q_t) = \log q_e - K_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where the terms q_e and q_t have the same meaning previously mentioned and are expressed in mg g^{-1}, K_1 and K_2 are the pseudo first-order and the pseudo second order model rate constants, expressed in min^{-1} and g mg^{-1} min^{-1}, respectively.

The calculated q_e, K_1, K_2 and the corresponding linear regression coefficient R^2 values are presented in Table 3. The applicability of the kinetic model is compared by judging the correlation coefficients R^2 and the agreement between the calculated and the experimental q_e values. In a view of these both considerations, we may conclude that the pseudo first-order mechanism is predominant. Note that this result is in agreement with those reported in several papers dealing with adsorption of organic solutes on activated carbons [25,36–38].

3.6.2. *Intra-particle diffusion*

Intra-particle diffusion model based on the theory proposed by Weber and Morris [39] was tested to identify the diffusion mechanism. According to this theory, adsorbate uptake q_t varies almost

Table 2
Comparison of the adsorption capacity of the (AC) prepared from olive-waste cakes and other adsorbents for different dyes.

Adsorbent	Adsorbate	Adsorbent capacity $q_{\max}$ (mg g^{-1})	References
AC from olive-waste cakes	Lanaset Grey G	108.7	This work
AC from rice husk	Acid blue	50.0	[31]
AC from orange peel	Direct blue-86	37.3	[32]
Pine sawdust	Metal complex blue	82.0	[33]
Pine sawdust	Metal complex yellow	105.0	[33]
Wood	Acid blue 25	17.5	[26]
Hazelnut shell	Acid blue 25	60.2	[34]
Commercial AC F400 (Chemviron)	Lanaset Grey G	454.5	[35]
Commercial AC CAL (Chemviron)	Lanaset Grey G	56.8	[35]

Table 3
Parameters of the first and second order kinetic models.

Adsorbent amounts (g)	$q_{e,\exp}$ (mg g^{-1})	First order kinetic model			Second order kinetic model		
		K_1 (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	$K_2 \times 10^5$ (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2
$m = 0.10$	113.6	0.0019	106.4	0.997	8	71.2	0.961
$m = 0.30$	103.2	0.0009	105.2	0.995	6	60.8	0.869
$m = 0.50$	80.2	0.0019	80.0	0.998	2	41.5	0.968
$m = 0.60$	68.5	0.0014	68.9	0.991	25.5	39.6	0.942

proportionally with the square root of the contact time, $t^{1/2}$ rather than t:

$$q_t = k_{\mathrm{id}} t^{1/2} + C \qquad (8)$$

where C is the intercept and k_{id} (mg g^{-1} h$^{-1/2}$) is the intra-particle diffusion rate constant. If intra-particle diffusion occurs, then q_t versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting step is only due to the intra-particle diffusion. Otherwise, some other mechanisms along with intra-particle diffusion as involved. In most cases, this plot gives general features of three stages: initial curved portion, followed by an intermediate linear portion and a plateau. The initial sharper, is due to the instantaneous adsorption or external surface adsorption (external mass transfer). The intermediate linear part is due to intra-particle diffusion and the plateau to the equilibrium stage where intra-particle diffusion starts to slow down due to extremely low solute concentrations in the solution [40].

Plot of the quantity of Lanaset Grey G adsorbed against square root of time is shown in Fig. 4. It can be observed that the plots are not linear over the whole time range and the graphs of this figure reflect a dual nature, with initial linear portion followed by a plateau. The fact that the first curved portion of the plots seems to be absent implies that the external surface adsorption (stage 1) is relatively very fast and the stage of intra-particle diffusion (stage 2) is rapidly attained and continued to 50 h. Finally, equilibrium adsorption (stage 3) starts after 50 h. The dye molecules are slowly transported via intra-particle diffusion into the particles and are finally retained in the pores. The linear portion of the curve does not pass the origin and the latter stage of Lanaset Grey adsorption does not follow Webber–Morris equation. It may be concluded that the adsorption mechanism of this dye is rather a complex process and the intra-particle diffusion was not the only rate-controlling step. The results obtained agreed with those found by Monser and Adhoum [41] for the adsorption of tartrazine onto activated carbon.

Table 4
Thermodynamic parameters for the adsorption of Lanaset Grey G onto activated carbon prepared from Tunisian olive-waste cakes at different temperatures.

ΔS° (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})		
		288 K	298 K	310 K
169.7	49.0	−0.14	−1.56	−3.60

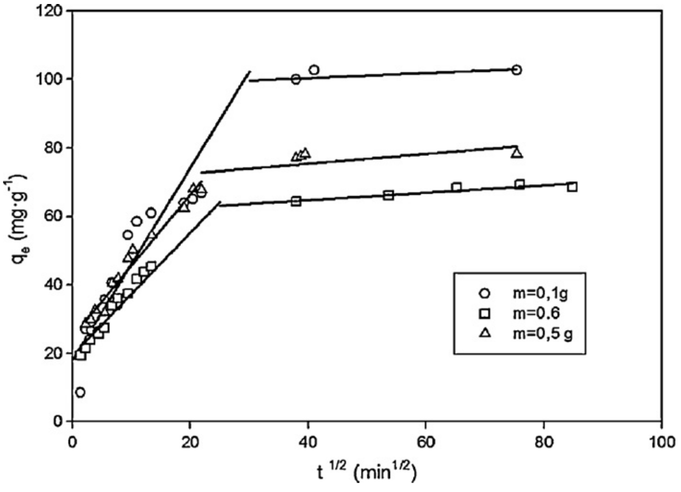

Fig. 4. Plots of Lanaset Grey G uptake against square root of contact time.

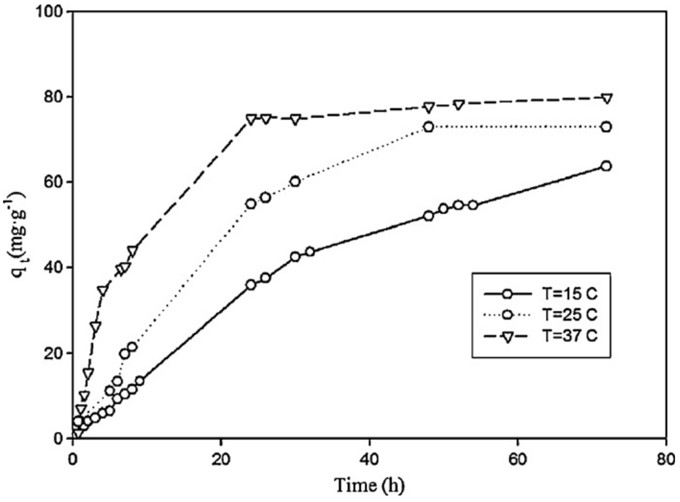

Fig. 5. Variation of dye uptake with contact time at different temperatures (15, 25 and 37 °C).

Table 5
Parameters of the first and second order kinetic models at various temperatures.

	$q_{e,exp}$ (mg g^{-1})	First order kinetic model			Second order Kinetic model		
		K_1 (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	$K_2 \times 10^6$ (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2
$T = 15\,^{\circ}$C	63.7	0.0006	67.5	0.998	1.2	151.5	0.771
$T = 25\,^{\circ}$C	72.9	0.0010	80.6	0.994	4.5	113.6	0.861
$T = 37\,^{\circ}$C	79.9	0.0013	66.4	0.956	12.0	101.0	0.852

3.7. Effect of temperature

Adsorption experiments were carried out for different contact times at three different temperatures 15, 25 and 37 °C. For each temperature considered, the values of C_e and q_e corresponding to the equilibrium state were also determined. The results related to the time dependence of q_t are shown in Fig. 5. It was found that the uptake of the dye by the sorbent adsorption capacity increases with the increasing temperature from 15 to 37 °C, indicating that the adsorption is an endothermic process [27,42].

The equilibrium constant K_D of the adsorption process, expressed in L g^{-1}, can be used to estimate the thermodynamic parameters due to its dependence on temperature. The changes in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption process were determined using Eqs. (9)–(11):

$$K_D = \frac{q_e}{C_e} \tag{9}$$

$$\Delta G^{\circ} = -RT \ln K_D \tag{10}$$

$$\ln K_D = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{11}$$

A Van't Hoff plot of $\ln K_D$ as a function of $1/T$ (figure not shown) yields to a straight line. The ΔH° and ΔS° parameters were calculated from the slope and intercept of the plot, respectively. The values of the thermodynamic parameters are listed in Table 4.

The positive value of ΔS° means an increase in the randomness at the solid/solution interface during the adsorption of the dye on the activated carbon [43]. Such positive value may be explained as follows: in the adsorption of the dye, the adsorbate species displace adsorbed solvent molecules to gain more translational entropy than was lost by the adsorbate, thus allowing randomness in the system. The ΔH° parameter was found to be 49.02 kJ mol^{-1}. The positive value of ΔH° further confirms the endothermic nature of the adsorption process [44]. The decrease in ΔG° values shows the feasibility of adsorption as the temperature increased. Similar results were reported by Li et al. [45] for the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fiber.

On considering the time-profiles of dye uptake presented in Fig. 5, the effect of temperature on the adsorption kinetics was also investigated by the Lagergren pseudo-first order and pseudo-second order models. The parameters related to each model were presented in Table 5.

As previously observed, the results fitted the first-order model for the three temperatures considered. The correlation coefficients of the first order model for 15 °C and 25 °C were higher than 0.99 except for 37 °C which is equal to 0.954. The data given in Table 5 also shows that the pseudo-first order rate constant K_1 increases with temperature indicating enhancement of the adsorption kinetics as the temperature increases. This enhancement reflects again the endothermic character of the adsorption process. The activation energy E_a for Lanaset Grey G adsorption was determined from the slope of the Arrhenius plot of $\ln K_1$ versus temperature ($1/T$) (figure not shown) and was found to be 32.1 kJ mol^{-1}. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5–40 kJ mol^{-1}, while higher activation energies (40–800 kJ mol^{-1}) suggest chemisorptions [27]. Consequently, the relatively low activation energy (32.1 kJ mol^{-1}) obtained for the adsorption of Lanaset Grey G on the activated carbon may involve a physical sorption.

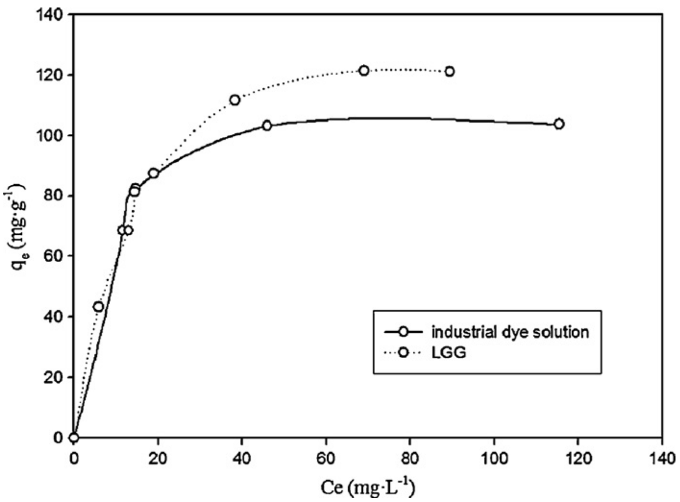

Fig. 6. Equilibrium adsorption isotherms of individual Lanaset Grey G and industrial dye solution onto activated carbon at 25 °C.

3.8. Adsorption of dye from industrial solution

The adsorption isotherms of the dye present in industrial solution and of the individual Lanaset Grey G are presented in Fig. 6. The results relating to the industrial solution were fitted to Langmuir and Freundlich isotherm models. A comparison of R^2 values for the two models indicates that the Langmuir equation ($R^2 = 0.997$) fits better the experimental data than the Freundlich equation ($R^2 = 0.897$). The same results were found previously for the individual dye (only Grey Lanaset G). When comparing the maximum adsorption capacity (q_{max}) of the activated carbon towards the dye in the industrial solution (133.9 mg g^{-1}) with that for the individual Lanaset Grey G (108.7 mg g^{-1}), we can conclude that the added components did not affect the uptake extent of the target solute by the activated carbon. This means that the dye competes well with the additives for the adsorption sites of the sorbent. The value of R_L was found to be $0 < 0.072 < 1$ indicating the favorable uptake of the dye from the industrial solution.

4. Conclusions

Based on the results obtained within the framework of this study, it appears that the activated carbon prepared from Tunisian olive-waste cakes constitutes a good adsorbent for removing a metal complex dye: Lanaset Grey G. The main conclusions that can be drawn from the current investigation are given below:

- The Langmuir model provides the best correlation of the experimental equilibrium data. The adsorption capacity of the activated carbon was determined as 108.7 mg g^{-1} which compares well those of other sorbents prepared from agricultural wastes and is more favorable than that of the commercial granular activated carbon “CAL” from Chemviron Carbon ($56.8\,\mathrm{mg\,g^{-1}}$).

- The adsorption system obeys the pseudo first-order kinetic model represented by the Lagergren equation. Moreover, the increase of the temperature enhances the kinetics of dye uptake.
- The adsorption mechanism of this dye is rather a complex process and the intra-particle diffusion was not the only rate-controlling step.
- The calculated thermodynamic parameters show the spontaneous and endothermic natures of the adsorption process.
- The low value of the activation energy shows that dye adsorption process by the activated carbon may involve a physical sorption.
- When comparing the adsorption capacity of the activated carbon towards the dye in the industrial solution ($133.9\,\mathrm{mg\,g^{-1}}$) with that of individual dye ($108.7\,\mathrm{mg\,g^{-1}}$), we can conclude that the added components do not affect the maximum uptake of the target solute by the sorbent.

Acknowledgements

This work was been supported by the Spanish Ministry of Foreign Affairs and Cooperation, AECID program (Project A/016195/08). The Department of Chemical Engineering of the Universitat Autònoma de Barcelona is the Unit of Biochemical Engineering of the Centre de Referència en Biotecnologia de la Generalitat de Catalunya. P. Blánquez and M. Sarrà are members of a Consolidated Research Group of Catalonia (2009SGR656). The authors are grateful to MATGAS (organization of Materials and Gases) for their technical assistance.

References

[1] M. Ozacar, A.I. Sengil, Adsorption of metal complex dyes from aqueous solution by pine sawdust, Bioresource Technol. 96 (2005) 791–795.

[2] T. Li, J.T. Guthrie, Colour removal from aqueous solutions of metal-complex azo dyes using bacterial cells of Shewanella strain J18 143, Bioresource Technol. 101 (2010) 4291–4295.

[3] P. Blánquez, M. Sarra, T. Vicent, Development of a continuous process to adapt the textile wastewater treatment by fungi to industrial conditions, Process Biochem. 43 (2008) 1–7.

[4] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresource Technol. 97 (2006) 1061–1085.

[5] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technol. 77 (2001) 247–255.

[6] H. Runping, L. Zoua, X. Zhaoc, Y. Xua, F. Xua, Y. Li, Y. Wanga, Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper(II) from solution in fixed bed column, Chem. Eng. J. 149 (2009) 123–131.

[7] A.R. Binupriya, M. Sathishkumar, K. Swaminathan, C.S. Ku, S.E. Yun, Comparative studies on removal of Congo red by native and modified mycelial pellets of *Trametes versicolor* in various reactor modes, Bioresource Technol. 99 (2008) 1080–1088.

[8] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigments 54 (2002) 47–58.

[9] M. Molina-Sabio, F. Rodríguez-Reinoso, F. Caturla, M.J. Sellés, Porosity in granular carbons activated with phosphoric acid, Carbon 33 (1995) 1105–1113.

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

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

[12] F. Suarez-Garcia, A. Martiner-Alonso, J.D. Tascon, Pyrolysis of apple pulp: chemical activation with phosphoric acid, Anal. Appl. Pyrol. 63 (2002) 283–301.

[13] Y. Guo, J. Zhao, H. Zhang, S. Yang, J. Qi, Z. Wang, H. Xu, Use of rice husk-based porous carbon for adsorption of Rhodamine B from aqueous solutions, Dyes Pigments 66 (2005) 123–128.

[14] T. Yang, L.A. Chong, Textural and chemical proprieties of zinc chloride activated carbons prepared from pistachio-nut shells, Mater. Chem. Phys. 100 (2006) 438–444.

[15] F. Sellami, R. Jarboui, S. Achica, K. Medhioub, E. Ammar, Co-composting of oil exhausted olive-cake, poultry manure and industrial residues of agro-food activity for soil amendment, Bioresource Technol. 99 (2008) 1177–1188.

[16] G.S. Gupta, G. Prasad, V.N. Singh, Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal, Water Res. 24 (1990) 45–50.

[17] A. Stolz, Basic and applied aspects in the microbial degradation of azo dyes, Appl. Microbiol. Biotechnol. 56 (2001) 69–80.

[18] M.H. Vijaykumar, Y. Veeranagouda, K. Neelakanteshwar, T.B. Karegoudar, Decolorization of 1:2 metal complex dye Acid blue 193 by a newly isolated fungus, *Cladosporium cladosporioides*, World J. Microb. Biotechnol. 22 (2006) 157–162.

[19] A. Bacaoui, A. Yaacoubi, A. Dahbi, C. Bennouna, R. Phan Tan Luu, F.J. Maldonado-Hodar, J. Rivera-Utrilla, C. Moreno-Castilla, Optimization of conditions for the preparation of activated carbons from olive-waste cakes, Carbon 39 (2001) 425–432.

[20] T. Vernersson, P.R. Bonelli, E.G. Cerrela, A.L. Cukierman, Arundo donax cane as a precursor for activated carbons preparation by phosphoric acid activation, Bioresource Technol. 83 (2002) 95–104.

[21] Y. Diao, W.P. Walawender, L.T. Fan, Activated carbon prepared from phosphoric acid activation of grain sorghum, Bioresource Technol. (2002) 8145–8152.

[22] M. Jagtoyen, F. Derbyshire, Some considerations of the origins of porosity in carbons from chemically activated wood, Carbon 31 (1993) 1185–1192.

[23] R. Baccar, J. Bouzid, M. Feki, A. Montiel, Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions, J. Hazard. Mater. 162 (2009) 1522–1529.

[24] M.J. Iqbal, M.N. Ashiq, Adsorption of dyes from aqueous solutions on activated charcoal, J. Hazard. Mater. B139 (2007) 57–66.

[25] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal – a review, J. Environ. Manage. 90 (2009) 2313–2342.

[26] B.N. Chen, C.W. Hui, G. Mckay, Film-pore diffusion modeling and contact time optimization for the adsorption of dyestuffs on pitch, Chem. Eng. J. 84 (2001) 77–94.

[27] B.H. Hameed, A.A. Ahmad, N. Aziz, Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash, Chem. Eng. J. 133 (2007) 195–203.

[28] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 154 (2008) 337–346.

[29] S. Kundu, A.K. Gupta, Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization, Chem. Eng. J. 122 (2006) 93–106.

[30] O. Hamdaoui, E. Naffrechoux, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part II. Two-parameter models and equations allowing determination of thermodynamic parameters, J. Hazard. Mater. 147 (2007) 381–394.

[31] M.M. Mohamed, Acid dye removal: comparison of surfactant-modified mesoporous FSM-16 with activated carbon derived rice husk, J. Colloid Interf. Sci. 272 (2004) 28–34.

[32] A. El Nemr, O. Abdelwahab, A. El-Sikaily, A. Khaled, Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel, J. Hazard. Mater. 161 (2009) 102–110.

[33] M. Ozacar, I.A. Sengýl, Two-stage batch sorber design using second-order kinetic model for the sorption of metal complex dyes onto pine sawdust, Biochem. Eng. J. 21 (2004) 39–45.

[34] F. Ferrero, Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust, J. Hazard. Mater. 142 (2007) 144–152.

[35] P. Blánquez, M. Sarrà, Continuous adsorption process of GLG textile dye onto GAC: a balanced solution between the use of GAC and the treatment capacity, Chem. Eng. Comm., in press.

[36] J. Rajeev, V.K. Gupta, S. Sikarwar, Adsorption and desorption studies on hazardous dye Naphthol Yellow, J. Hazard. Mater. 182 (2010) 749–756.

[37] P. Galiatsatou, M. Metaxas, D. Arapoglou, V. Kasselouri-Rigopoulou, Treatment of olive millwastewater with activated carbons from agricultural by-products, Waste Manage. 22 (2002) 803–812.

[38] M. Belmouden, A. Assabane, Y. Ait Ichou, Removal of 2,4-dichloro phenoxy-acetic acid from aqueous solution by adsorption on activated carbon. A kinetic study, Ann. Chim. Sci. Mater. 26 (2) (2001) 79–85.

[39] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solutions, J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31–60.

[40] A.A.M. Daifullah, S.M. Yakout, S.A. Elreefy, Adsorption of fluoride in aqueous solutions using $KMnO_4$-modified activated carbon derived from steam pyrolysis of rice straw, J. Hazard. Mater. 147 (2007) 633–643.

[41] L. Monser, N. Adhoum, Tartrazine modified activated carbon for the removal of Pb(II), Cd(II) and Cr(III), J. Hazard. Mater. 16 (2009) 263–269.

[42] Y.S. Al-Degs, M.I. El-Barghouthi, A.H. El-Sheikh, G.M. Walker, Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon, Dyes Pigments 77 (2008) 16–23.

[43] A. Aziz, M.S. Ouali, E. El Hadj, L.C.H. 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.

[44] A.A. Ruhan, A. Sari, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass, Chem. Eng. J. 15 (2009) 255–261.

[45] K. Li, Z. Zheng, H. Xingfa, Z. Guohua, F. Jingwei, Z. Jibiao, Equilibrium, kinetic and thermodynamic studies on the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fiber, J. Hazard. Mater. 166 (2009) 213–220.