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Adsorption kinetics and thermodynamics of azo-dye Orange II onto highly porous titania aerogel

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ABSTRACT

We report herein a kinetic and thermodynamic study of the adsorption of azo-dye Orange II from aqueous solutions onto titania aerogels. Aerogels structure was confirmed by FTIR and N_2 adsorption revealed their specific surface area (500 m^2/g), pore volume (2.86 cm^3/g) and pore size (mean 13.9 nm). Adsorption tests were conducted in batch reactors under various conditions where the effect of pH, temperature, contact time, dye concentration, and adsorbent dose were studied. Experiments performed at pH 2 show the optimal adsorption due to the best surface charge interactions. The temperature shows a weak influence with a decrease in the adsorption uptake as the temperature increases. Adsorption kinetics is shown to be very fast and follows a pseudo second-order indicating the coexistence of chemisorption and physisorption with the intra-particle diffusion being the rate controlling step. The experimental data fit perfectly with Sips isotherms and reveal the ability of titania aerogel to adsorb 420 mg of Orange II per gram of adsorbent at the optimal conditions. The thermodynamic study reveals the activation energy (42.1 kJ mol^{-1}) and the changes in Gibbs free energy (1.2 kJ mol^{-1}), enthalpy (−16.4 kJ mol^{-1}), and entropy (−58 J mol^{-1} K^{-1}). The entire regeneration of the titania aerogel adsorption sites at pH 11 and 30 °C shows a total recovery of the dye and the efficient reusability and the economic interest of these adsorbing materials for environmental purposes.

1. Introduction

Dyes containing azo-aromatic groups are highly dispersible pollutants. They contribute to water toxicity and represent an increasing danger for the environment and human beings. These effluents discharged from various industries (e.g. textile, paper, leather, food, etc.) are known to be toxic [1], carcinogenic [2], mutagenic [3], teratogenic [4], and their release in the environment is a considerable source of non-aesthetic pollution since the existence of low concentrations of dyes is clearly visible. Thus, the removal of these colored compounds from wastewater is an important target from the environmental point of view. However, this process faces a major problem represented in the high stability of these azo-dyes in aqueous media and their resistance to light and oxidation agents [5]. Conventional treatment methods for the removal of dyes in wastewater include physical, chemical and biological processes such as adsorption [6], coagulation [7], oxidation [8], reduction [9], filtration [10], and biological treatment [11]. The physical adsorption process at solid-liquid interface is known to be a powerful method for decreasing the concentration of soluble dyes in effluents and has the advantage of being efficient and economic. A large number of adsorbing materials for soluble dyes have been studied such as activated carbon [12], alumina [13], clay [14], silica xerogel [15], titania [16], titania–silica mesoporous materials [17], waste materials [18–20] and many other materials. In this study we investigate for the first time the adsorption kinetics and thermodynamics of dyes from aqueous solutions onto highly porous titania aerogels. Well-known Orange II azo-dye whose molecular structure is shown in Fig. 1 was used as a model molecule for this purpose. This dye has been chosen as it is inexpensive and widely used in textile, pulp and paper industries. Table 1 regroups the results obtained in some recent research works where the adsorption of Orange II onto various adsorbents has been studied [21–28].

Aerogels obtained through the low-temperature sol–gel process [29] and dried under supercritical conditions [30] are exceptionally porous solids showing high specific surface areas (up to 1000 m^2/g), an extraordinarily large surface-to-volume ratio ($\sim 2 \times 10^9$ m^{-1}) and low densities (0.003–0.35 g cm^{-3}) [31–33]. These materials deserve particular interest due to their surface properties as well as the chemical reactivity of their surface groups.

The adsorption kinetics and thermodynamics were studied under various conditions and the adsorption equilibria were investigated to find out which isotherm model shows the best fitting to the experimental data. The effects of the adsorbate concentrations,

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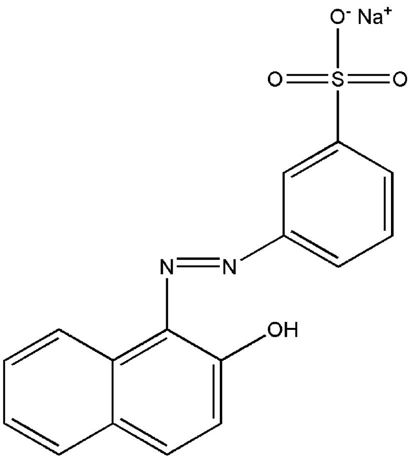

Fig. 1. Chemical structure of Orange II.

temperature, pH and adsorbent quantity were studied in order to determine the optimal adsorption conditions.

2. Experimental

2.1. Materials

The chemicals were used in this study as received and without further purification. Titanium isopropoxide ($Ti(OC_3H_7)_4$, TIP) was purchased from Sigma–Aldrich. Orange II ($C_{16}H_{11}N_2OSO_3Na$, C.I. 15510, C.I. Acid Orange 7, M.W. 350.32, certified pure) was provided from Acros Organics. Isopropanol and nitric acid (65%) were from Lab-Scan and Panreac, respectively. Double deionized water was prepared in our laboratory.

2.2. Synthesis of titania aerogels

Titania aerogels were prepared after the supercritical drying of wet alcogels synthesized through a one-pot sol–gel process. Titanium isopropoxide was mixed for 1 min in a polypropylene vial with isopropanol to which is added a nitric acid solution (65%). After stirring for another minute, deionized water is added and stirred together for 30 s before the stirring was stopped. The gelation of the sol was observed in the next few minutes and obtained gels were kept for aging for one day. The mixing steps as well as the gelation were performed at room temperature. The drying of the wet alcogels under supercritical carbon dioxide ($T_c = 31.1\,^{\circ}C$; $P_c = 73.7$ bar) led to the final titania aerogels. This terminal step was preceded by a 24 h-solvent exchange step, where the residual water and isopropanol in the alcogel were exchanged by acetone presenting a higher miscibility with liquid carbon dioxide. The final molar ratio TIP:Isopropanol:H_2O:HNO_3 for the synthesized titania aerogels was 1:20:4:8 $\times 10^{-2}$.

2.3. Titania aerogels characterization

The textural properties were determined by using the nitrogen sorption technique. The nitrogen adsorption–desorption isotherms were measured using a Nova 2200e high-speed surface area and pore size analyzer (Quantachrome Instruments). Prior to the measurement, titania aerogels were degassed for 5 h at 70 °C. The specific surface area was calculated according to the BET theory [34] while the pore size and pore volume were calculated by the BJH method [35] based on the desorption branch of the isotherm. The structural characterization of the titania aerogels was carried out using a Thermo Nicolet 4700 Fourier Transform Infrared Spectrometer equipped with a Class 1 Laser. The experiment was done in the range between 4000 and 400 cm^{-1} using the transmission KBr pellet technique where 1% in weight aerogel powder-containing potassium bromide pellets were used.

2.4. Adsorption studies

Several adsorption experiments were carried out in different experimental conditions. All experiments were performed in glass vials placed in a controlled-temperature shaking water bath operating at 200 rpm. In typical adsorption experiments, 30 mg of titania aerogel were added to 15 mL of 50 mg/L dye solution at 30, 40, and 50 °C. Aliquots were carefully withdrawn from the solution at predetermined time intervals over 24 h and the solution absorbance was measured in the UV–visible range at the maximum absorption ($\lambda = 483$ nm) using a JASCO V-570 UV/VIS/NIR spectrophotometer. Centrifugations performed on several samples showed that the aliquots were particle free and therefore there is no need to carry out centrifugations for taken aliquots. The amount of adsorbed dye on titania aerogels was calculated according to the following equation:

$$q_e = \frac{C_i - C_e}{m} V \qquad (1)$$

where q_e is the amount of dye adsorbed (mg/g), C_i and C_e are the initial and equilibrium liquid-phase concentrations of dye (mg/L), respectively, V is the volume of solution (L) and m is the amount of adsorbent (g).

The effect of pH was studied after the adjustment of the dye solutions pH between 1 and 12 using dilute HCl and NaOH solutions; A Corning Pinnacle 542 pH conductivity meter with a combined pH

Table 1
Comparison of the maximum monolayer adsorption capacities of Orange II onto various adsorbents.

Adsorbents	Maximum monolayer adsorption capacities (mg/g)	References
Chitosan bead	1940 (30 °C)	[21]
Commercial activated carbon fibers—generated from pitch	1260 (30 °C)	[22]
Commercial activated carbon fibers—made with polyacrylonitrile	230 (30 °C)	[22]
Sludge adsorbent	350 (30 °C)	[22]
Activated carbon	404 (25 °C)	[23]
$CuFe_2O_4$/activated carbon composite	392 (25 °C)	[23]
Activated carbon cloths	90 (30 °C)	[24]
Chitosan	116 (20 °C); 113 (60 °C)	[25]
Spent brewery grains	28.54 (20 °C); 30.47 (30 °C)	[26]
Unmodified zeolite	0.63 (25 °C)	[27]
Surfactant-modified zeolite	3.62 (35 °C)	[27]
Bottom ash	13.24 (50 °C); 12.68 (40 °C); 12.50 (30 °C)	[28]
De-oiled soya	9.58 (50 °C); 9.18 (40 °C); 8.87 (30 °C)	[28]

electrode was used for this purpose. The initial dye concentration was studied between 10 and 1500 mg/L and the dosage of titania aerogel was studied in the 10–150 mg range.

3. Results and discussion

3.1. FTIR characterization

The FTIR spectrum of the titania aerogel (Fig. 2) shows a broad band at 3447 cm^{-1} that corresponds to the overlapping of the O—H stretching bands of hydrogen-bonded water molecules (HO—H···H) and TiO···H stretching of surface titanol hydrogen-bonded to molecular water (TiO—H···H_2O) [29]. The sharp bands appearing at 1635 and 1384 cm^{-1} are easily attributed to the adsorbed water molecules deformation vibrations [36] and to the C–H symmetric deformation of –CH_2 groups [37], respectively. This latter vibration reveals the existence in the titania network of some unhydrolysed Ti–O–CH_3 surface groups [37]. The weak shoulder at around 1060 cm^{-1} is attributed to the stretching vibration of the TiO–C bond and the broad band appearing at 520 cm^{-1} with a shoulder at around 780 cm^{-1} corresponds to the Ti–O–Ti stretching vibrations [38].

3.2. Surface area and pore size distribution

The nitrogen adsorption–desorption isotherms (not shown) reveal a type IV isotherm according to the IUPAC classification of sorption isotherms [39]. This isotherm is typical for mesoporous materials and the hysteresis loop, which is a characteristic feature of these isotherms, is associated with the occurrence of pore condensation [40]. The specific surface area of the titania aerogels calculated according to the BET theory was found to be 500 m^2/g. These materials show also a very high pore volume (2.86 cm^3/g). The pore size distribution calculated according to the BJH method showed that the pore diameters are in the mesoporous range with an average pore diameter equal to 13.9 nm.

3.3. Effect of pH on adsorption

The pH is a noteworthy parameter in this study as it has a major effect on the protonation and deprotonation of the adsorbent and adsorbate functional groups. The electrostatic attraction or repulsion between the adsorbent and adsorbate depend on the surface charges of both entities.

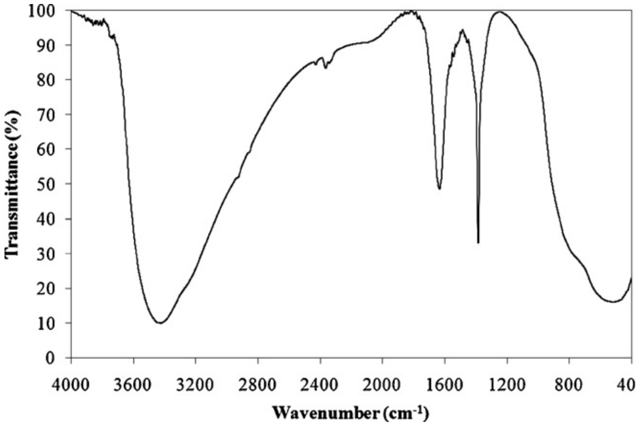

Fig. 2. FTIR spectrum of the titania aerogel.

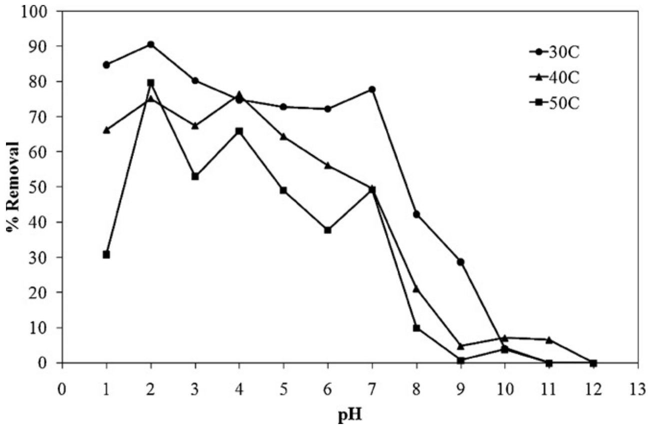

Fig. 3. Effect of pH on adsorption of Orange II on titania aerogels. Initial dye concentration = 50 mg/L; contact time = 24 h; mass of adsorbent = 30 mg; solution volume = 15 mL.

The effect of the dye solution initial pH on the adsorption was studied in the pH range 1–12. The initial Orange II concentration was 50 mg/L, the pH was adjusted using dilute HCl and NaOH solutions and the temperatures studied were 30, 40, and 50 °C. pH measurements showed stable values along the various experiments. It is worth to note that the UV–vis absorption spectra of this dye at different pH were identical. Measurements done after 24 h showed the maximum adsorption to be at pH 2 for the three temperatures with a significant decrease of the adsorption capacity of the titania aerogels as pH increased (Fig. 3). Since the point of zero charge of titanium oxide is 6.0 [41], the adsorbent exhibits a positive zeta potential at pH values lower than 6.0 due to the formation of positive Ti–OH_2^+ surface groups that increased as pH decreases. In the other side, Orange II molecules have two pK_a values (10.6 and 1) and thus three different forms of the azo-dye could exist in the aqueous solution depending on the pH of the medium, noted H_2L (doubly protonated, dominant for pH lower than 1), HL^- (mono protonated, dominant in the pH range between 1 and 10.6), and L^{2-} (non-protonated, dominant for pH values greater than 10.6), where L^{2-} is the Orange II molecule in the following form $C_{16}H_{11}N_2OSO_3^{2-}$ [16]. Consequently, H_2L and HL^- coexist with dominancy for HL^- for pH values between 1 and 2 while only HL^- is practically present in the solution for pH values between 2 and 9.6. HL^- and L^{2-} coexist in the pH range between 9.6 and 11.6 with HL^- dominant between 9.6 and 10.6, and L^{2-} dominant between 10.6 and 11.6. For pH greater than 11.6, only L^{2-} is practically present. In the experiments performed at pH between 2 and 6, the increase in positively charged titania sites as pH decreases led to the increase of the electrostatic attraction between the surface positive charges and the negatively charged dye molecules (HL^-) and therefore to the increase of the adsorption capacity of the adsorbent. It is clear that a significant competition took place at low pH between the anionic dye molecules and the hydroxyl ions (OH^-) present at low concentration in order to counterbalance the positive charge of the adsorbent sites (Ti–OH_2^+). As H_2L and HL^- coexist when the pH is between 1 and 2, this results in a partial adsorption of the dye (only HL^-) onto the titania surface. This explains the decrease of the adsorption capacity at pH 1 compared to what is obtained at pH 2. On the other hand, the titania aerogel surface becomes negatively charged at pH greater than 6.0 and the negatively charged surface groups (TiO^-) increase as pH increases. Accordingly, an electrostatic repulsion between the negatively charged dye and the surface groups took place and led to a significant decrease of the adsorption capacity of titania aerogels.

3.4. Effect of contact time

The effect of contact time between Orange II and 30 mg of titania aerogel was studied for solutions where the concentration of the dye was 50 mg/L. The experiments were performed at 30, 40,

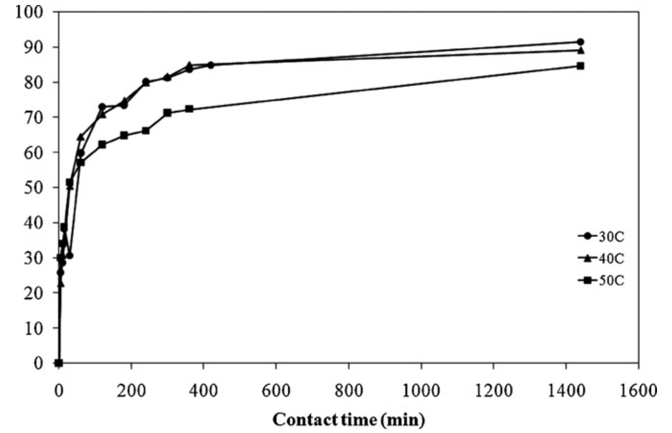

Fig. 4. Variation of adsorbed amount of Orange II with time. Initial dye concentration = 50 mg/L; mass of adsorbent = 30 mg; solution volume = 15 mL; pH 2.

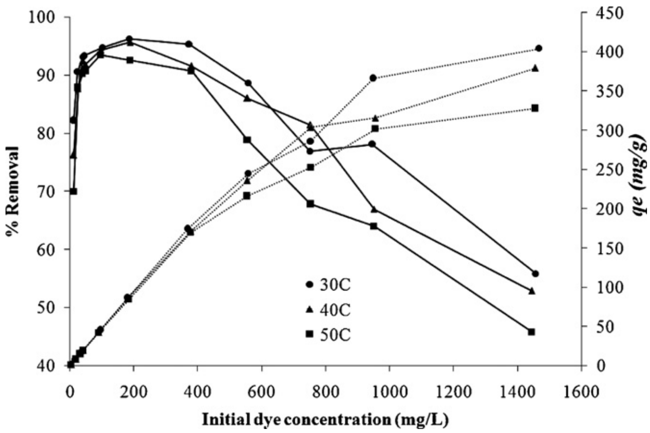

Fig. 5. Effect of initial dye concentration on adsorption of Orange II. Initial dye concentration = 50–1500 mg/L; contact time = 24 h; mass of adsorbent = 30 mg; solution volume = 15 mL; pH 2.

and 50 °C and the pH was adjusted to 2. We observed the adsorption of a large quantity of dye onto the aerogels after a very short contact time (Fig. 4) where the uptake of approximately 50% of the molecules was noticed within the first 30 min of the experiments. A weak dependence on the temperature was observed for the experiments carried out at 30 and 40 °C where both samples showed approximately the same adsorbed quantities at specific contact times. However, the experiment done at 50 °C showed smaller adsorbed quantities. The difference in the adsorption ability of the titania aerogel and its dependence on the temperature could be due to the decrease of the adsorption equilibrium constant while increasing the temperature. Further experiments were performed with 24 h contact time to guarantee the maximum adsorption and a complete equilibrium condition.

3.5. *Effect of dye concentration*

Although dye–dye hydrophobic interactions and self-association or aggregation of dye molecules are known, Orange II shows a very high solubility in aqueous solutions (116 g/L at 30 °C) and an aggregation mean number equal to 1 for dye concentrations lower than 0.01 M [42]. Accordingly, the dye molecules are considered to be none aggregated in all performed experiments even with those carried out with high concentration as they did not overcome the critical aggregation concentration. The maximum uptake of titania aerogel after 24 h has been studied as a function of the initial dye concentrations between 10 mg/L and 1500 mg/L. The pH of the solutions was adjusted to 2 and the experiments were performed at 30, 40, and 50 °C. The percent removals were found to have maxima for the solutions where the dye concentrations were around 200 mg/L (Fig. 5). The adsorption percentage exceeded 95% at these conditions although it was noticed that, for all studied conditions, the amount of titania aerogel used (30 mg) was able to adsorb more than 50% of the dye molecules existing in the aqueous solutions. By comparing the adsorbed quantities of dye after 24 h (q_e) for the experiments performed with different initial concentrations, we noticed the linearity of the uptake capacity of the aerogel for dye concentrations smaller than 400 mg/L. This means that the dye concentration has no effect on the adsorption mechanism when the dye concentration is lower than 400 mg/L. The measured uptake capacity of the aerogel is approximately 175 mg/g for a 400 mg/L solution regardless the adsorption temperature. For greater concentrations, this uptake capacity increases to 331, 382 and 407 mg/g when the dye concentration was 1500 mg/L for the experiments performed at 50, 40, and 30 °C, respectively.

3.6. *Effect of adsorbent dose*

The effect of the aerogel quantity used for adsorption was tested. The adsorbent masses were between 10 and 150 mg per experiment. 15 mL of 50 mg/L dye solutions were used, the pH was adjusted to 2, and the studied temperatures were 30, 40 and 50 °C. The UV–visible spectroscopic measurements showed that a minimum of 94% of the initial dye amount was adsorbed onto the titania aerogel in all experimental conditions. The plot of the relative adsorbed amount of dye q_e (in mg of dye per g of adsorbent) versus the quantity of adsorbent (Fig. 6) shows a decrease in q_e as the quantity of adsorbent increases, with no effect of temperature. The plot of $1/q_e$ versus the adsorbent quantity shows a linear plot revealing the availability of the adsorption sites when large adsorbent quantities are used as well as in the experiments where very small quantities were tested. Therefore, 10 mg of titania aerogel are able to remove more than 94% of Orange II molecules existing in 15 mL of a 50 mg/L dye solution.

3.7. *Adsorption isotherms*

The adsorption isotherm experimental data collected at different dye concentrations and various temperatures were fitted with three common adsorption models: Langmuir [43], Freundlich [44], and Sips (also known by Langmuir–Freundlich) [45] isotherm mod-

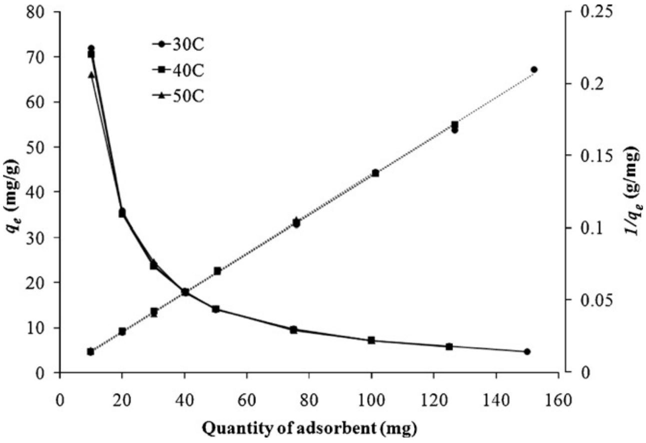

Fig. 6. Influence of titania aerogel loadings on amount of Orange II adsorbed after 24 h. Initial dye concentration = 50 mg/L; contact time = 24 h; solution volume = 15 mL; pH 2.

Table 2
Langmuir, Freundlich, and Sips isotherms coefficients for adsorption of Orange II onto titania aerogels.

T (°C)	Langmuir isotherm			Freundlich isotherm			Sips isotherm			
	$q_{\max}$	K_L	R^2	n	K_F	R^2	n	$q_{\max}$	K_S	R^2
30	402.82	0.0301	0.9721	2.7218	42.74	0.9048	1.0886	420.43	0.0346	0.9728
40	387.10	0.0235	0.9877	2.7012	38.03	0.9077	1.0084	388.47	0.0240	0.9877
50	332.29	0.0221	0.9827	2.6738	30.95	0.9197	1.0466	339.54	0.0243	0.9829

els. The Langmuir equation is given as

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

where $q_{\max}$ is the monolayer capacity of the adsorbent (mg/g) and K_L is the Langmuir equilibrium constant (L/g).

The Freundlich equation is given as

$$q_e = K_F C_e^{1/n} \tag{3}$$

where n is the heterogeneity factor and K_F is the Freundlich constant (L/g). n and K_F are generally temperature dependent. The parameter n could be considered as the parameter characterizing the system heterogeneity which could be related to the solid, to the adsorbate or to a combination of both. n is usually greater than unity and the larger is its value, the adsorption isotherm becomes more nonlinear and the system becomes more heterogeneous [46].

The Sips equation is given as

$$q_e = \frac{C_e^{1/n}}{(1/q_{\max}K_s) + (C_e^{1/n}/q_{\max})} \tag{4}$$

where K_s is the Sips equilibrium constant (L/g). Sips isotherm is proposed as an extension of the Freundlich equation, but it has a finite limit when the pressure is sufficiently high [46].

The graphically calculated $q_{\max}$, K_L, and R^2 (Langmuir isotherm), n, K_F, and R^2 (Freundlich isotherm), n, $q_{\max}$, K_S, and R^2 (Sips isotherm) are regrouped in Table 2. The Freundlich model reveals a thermodynamically favorable adsorption of Orange II onto the aerogel surface as the Freundlich constants n are greater than 2 [47]. The comparison of the three adsorption models (Fig. 7) shows the Sips isotherm to be the best with a high similarity with the Langmuir isotherm. The Sips constants n range between 1.01 and 1.09, extremely close to 1 for which the Sips model is reduced to the Langmuir one. Theoretically calculated $q_{\max}$ that are the maximum monolayer capacities of the adsorbent are 420, 388, and 340 mg/g for the experiments performed at 30, 40, and 50 °C, respectively. The comparison of the adsorption capacity of titania aerogel to previous studies (regrouped in Table 1) shows that the titania aerogel used in this work has a large adsorption capacity and ranges within the best and most efficient adsorbents of Orange II. The experimentally adsorbed amounts of Orange II for dye solutions at 1500 mg/L (407, 382, and 331 mg/g for 30, 40, and 50 °C respectively; Section 3.5) correspond to 97% or more of the monolayer capacity of the titania aerogels. The calculation based on the monolayer capacities of the adsorbent at 30 °C (420 mg/g) and the calculated specific surface area of the titania aerogel (500 m^2/g) reveals that the average surface available for the adsorption of one molecule of Orange II is 69 Å^2.

3.8. Adsorption kinetics

The adsorption kinetics was studied at 30–50 °C range. The adsorption rate was monitored by studying the contact time up to 24 h and compared to theoretical models. Pseudo first-order and pseudo second-order kinetic models were tested in this study where the experimental data obtained for various contact time were used.

The pseudo first-order equation is

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where q_e is the adsorption capacity of the titania aerorgel at equilibrium (mg/g), q_t is the amount of dye adsorbed at time t (mg/g) and k_1 is the pseudo first-order rate constant (min^{-1}).

The pseudo second-order equation is

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{6}$$

where k_2 is the pseudo second-order rate constant (mg^{-1} g min^{-1}). The results show that the pseudo second-order kinetic model fits perfectly the experimental data with linear regression coefficients greater than 0.9976 (Fig. 8). Experimentally calculated k_2 values at 30, 40 and 50 °C are 9.66×10^{-4}, 1.43×10^{-3} and

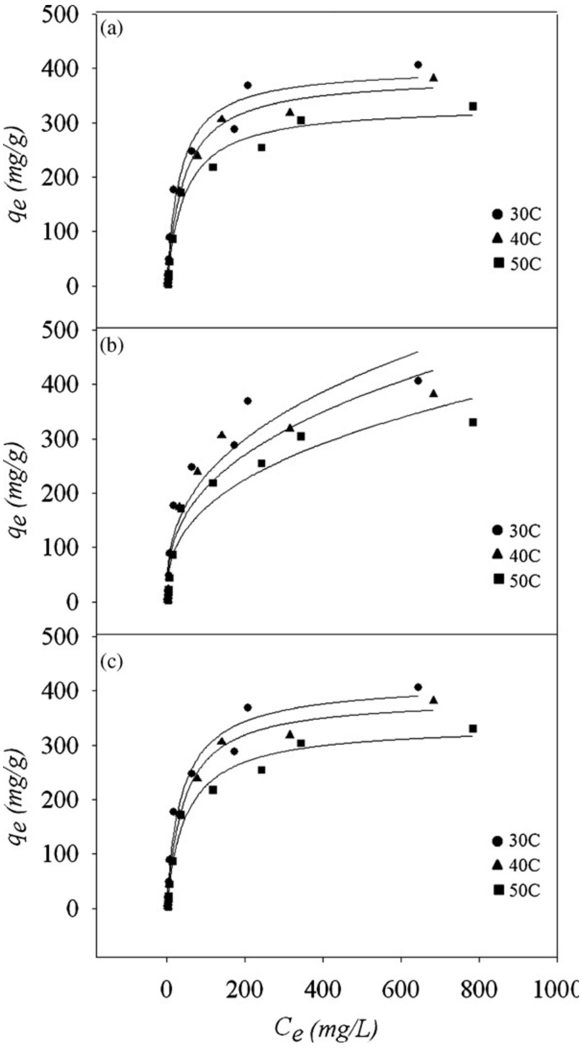

Fig. 7. Langmuir (a), Freundlich (b), and Sips (c) isotherm plots for adsorption of Orange II on titania aerogels. Initial dye concentration = 50–1500 mg/L; contact time = 24 h; mass of adsorbent = 30 mg; solution volume = 15 mL; pH 2.

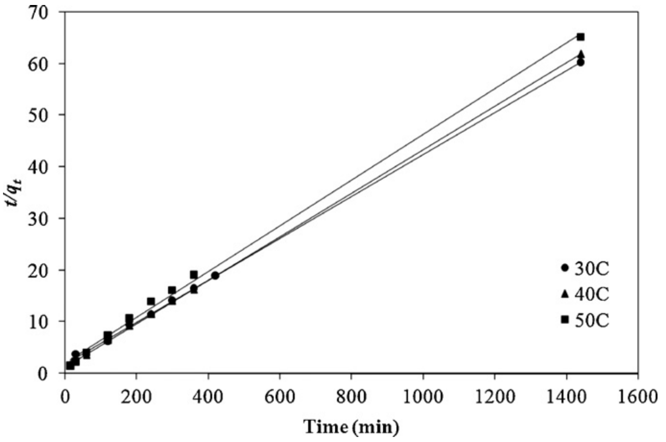

Fig. 8. Pseudo second-order kinetic plots for adsorption of Orange II on titania aerogels. Initial dye concentration = 50 mg/L; mass of adsorbent = 30 mg; solution volume = 15 mL; pH 2.

$2.73\times10^{-3}\,\mathrm{mg^{-1}\,g\,min^{-1}}$, respectively. A pseudo second-order suggests that this adsorption depends on the adsorbate as well as the adsorbent and involves chemisorption process in addition to physisorption. The chemisorption might be the rate limiting step where valency forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate [48].

3.9. Adsorption thermodynamics

The activation energy (E_a) for the adsorption of Orange II onto the surface of the aerogel was calculated from the rate constants (k_2) obtained for reactions performed at 30, 40 and 50 °C where 50 mg/L dye solutions were used. Arrhenius equation was used for this purpose:

$$k = Ae^{-E_a/RT} \tag{7}$$

where A is the Arrhenius frequency factor, R is the ideal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$) and T is the adsorption temperature in Kelvin. The activation energy calculated from the slope of the linear plot of $\ln k$ versus the inverse of the temperature (not shown) was found to be $42.1\,\mathrm{kJ\,mol^{-1}}$. This value existing at the interface between the physisorption (5–$40\,\mathrm{kJ\,mol^{-1}}$) and the chemisorption (40–$800\,\mathrm{kJ\,mol^{-1}}$) ranges [49], revealed both physisorption and chemisorption to take place. This is in an excellent agreement with what was found in the adsorption kinetics (Section 3.8) where we found that the adsorption involves chemisorption in addition to physisorption.

The change in Gibbs free energy ΔG° of the adsorption was calculated according to the following equation:

$$\Delta G^\circ = -RT\,\ln K_C \tag{8}$$

where K_C is the equilibrium constant. K_C is the ratio of the concentration of the dye on adsorbent at equilibrium (q_e) to the remaining concentration of the dye in solution at equilibrium (C_e). We considered the equilibrium to be reached after 24 h.

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

We noted a slight decrease of K_C with the increase of the temperature, suggesting that the adsorption is thermodynamically stable [50].

In the other hand, ΔG° is determined from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{10}$$

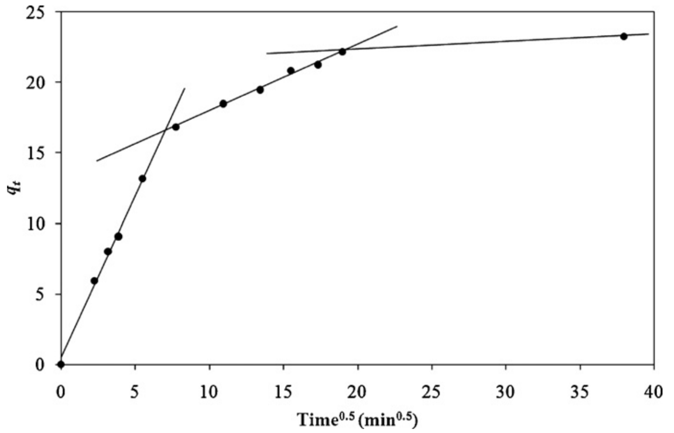

Fig. 9. Intra-particle diffusion plots. Initial dye concentration = 50 mg/L; mass of adsorbent = 30 mg; solution volume = 15 mL; pH 2; T = 40 °C.

where ΔH° is the change in the enthalpy of adsorption and ΔS° is the change in the entropy. The combination of Eqs. (9) and (10) leads to the van't Hoff equation written as follows:

$$\ln K_C = -\frac{\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R} \tag{11}$$

ΔH° and ΔS° were calculated from the slope and intercept of the linear plot of $\ln K_C$ versus $1/T$ (not shown). The results show that the enthalpy of adsorption ΔH° was $-16.4\,\mathrm{kJ\,mol^{-1}}$ and ΔS° was $-58\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Using the Eq. (10), the standard free energy change (ΔG°) was found to be $1.2\,\mathrm{kJ\,mol^{-1}}$ at 30 °C. This value indicates that the adsorption is not spontaneous at this temperature. However the negative values of ΔH° and ΔS° indicate that the adsorption will be spontaneous at lower temperatures [51]. The negative value of ΔH° reflects an exothermic adsorption and indicates that the adsorption is favored at low temperature. The negative entropy states that the Orange II molecules were orderly adsorbed on the surface of the titania aerogel.

3.10. Adsorption mechanism

The dye adsorption process from aqueous solution onto porous solids involves several steps: (i) transport in the solution; (ii) diffusion through the liquid film surrounding the solid particle, known by external diffusion or boundary layer diffusion; (iii) diffusion within the liquid included in the pore, known by internal diffusion or intra-particle diffusion; (iv) adsorption or desorption on the sur-

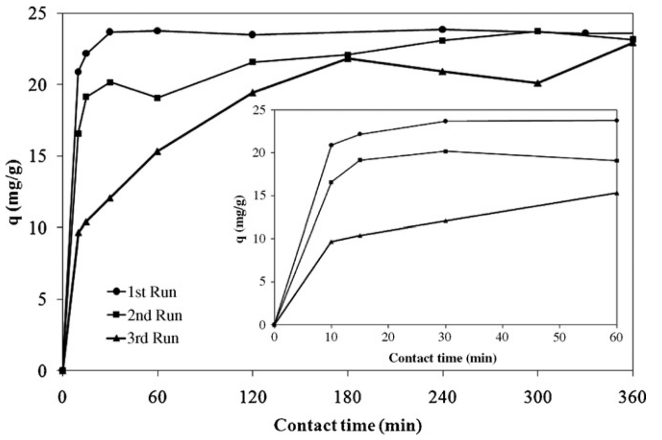

Fig. 10. Effect of consecutive experiments on the adsorption of Orange II onto titania aerogels (zoom in is done for the first hour). Initial dye concentration = 50 mg/L; mass of adsorbent = 30 mg; solution volume = 15 mL; pH 2.

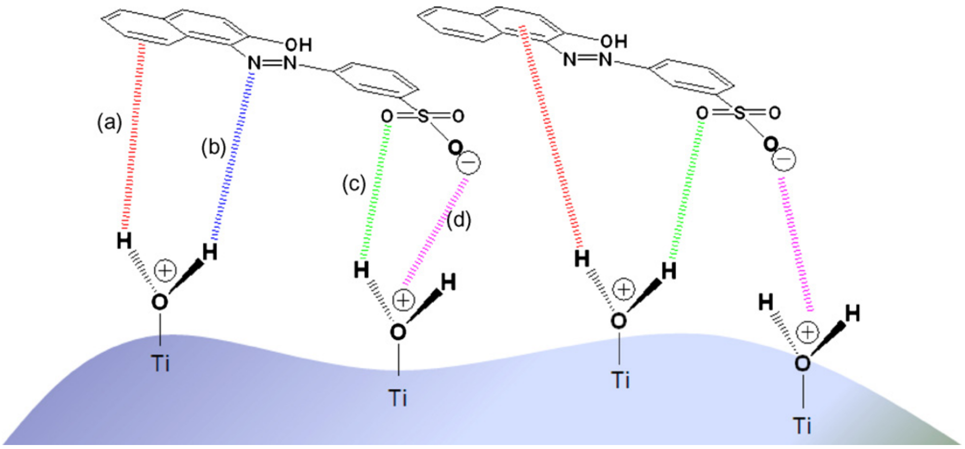

Fig. 11. Scheme of the Orange II adsorption on the titania aerogel surface; (a–c) Yoshida H-bonding between the titanol groups and the aromatic rings, nitrogen atoms, and oxygen atoms in the dye molecule, respectively. (d) The electrostatic interaction between the protonated surface groups and the anionic dye.

face of the interior sites [52]. The first step has no rate limitation effect as the experiments were performed at rapid shaking conditions. In addition, previous studies showed that the last step is a very fast process for the adsorption of organic molecules onto porous adsorbents [53]. Accordingly, we suspect the boundary layer diffusion or the intra-particle diffusion to be the rate controlling factors. Based on Fick's second law, Weber and Morriss [54] indicated that if the adsorption process is influenced by the intra-particle diffusion, the uptake of the dye q_t should vary linearly with the square root of time t. This dependence could be expressed as follows:

$$q_t = k_{\mathrm{ipd}} t^{0.5} + C \tag{12}$$

where k_{ipd} is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$) and C is the intercept.

The plot of the experimental data obtained at 40 °C (Fig. 9) showed that the plots are not linear over the whole time range; however, they exhibit a tri-linearity revealing the existence of three successive adsorption steps [50] (similar trends were obtained at 30 and 50 °C—not shown). The first stage being faster than the second is attributed to the external surface adsorption correlated to the boundary layer diffusion. Consequently, the second linear part attributed to the intra-particle diffusion states that this latter is highly involved in the rate control of this mechanism. The third linearity is attributed to the equilibrium stage. It is worth to note the fact that the second linear plots did not pass by the origin which indicates that the intra-particle diffusion is involved in the adsorption process but it is not the only rate controlling step. Other mechanisms such as complexation or ion-exchange could also control this adsorption [50].

3.11. *Recovery of dye and reusability of adsorbent*

The recovery of the dye from the titania aerogel was carried out at 30 °C. pH 11 was selected for this purpose where, according to the effect of the pH on surface charges and adsorption (Section 3.3), no attraction between the titania aerogel and the dye takes place and therefore the ability of the aerogel to adsorb Orange II molecules is negligible. Hence, the desorption is expected to be maximal. The dye recovery experiment showed a complete desorption of the dye (100% of what was adsorbed) after 30 min (not shown). The adsorbent was collected by filtration, washed several times with double deionized water, and left to dry at 40 °C for 24 h. The adsorption capacity of the regenerated titania aerogel (2nd and 3rd runs) was tested under similar conditions as in Section 3.4 and compared to the first use (1st run). 30 mg of the regenerated adsorbent were added to a 50 mg/L Orange II solution at pH 2. The experiment was performed at 30 °C. The comparison of the uptake capacity of the recycled adsorbent (Fig. 10) showed an excellent adsorption ability where, by comparing the 2nd and 3rd runs to the 1st, approximately 80% of the adsorption capacity of the adsorbent was maintained after 10 min contact time in the 2nd run and approximately 45% in the 3rd run, and therefore a decrease in the initial adsorption rates is observed when increasing the number of runs. However, approximately 100% of the initial dye amount was completely adsorbed on the titania aerogels after 6 h of solid–liquid contact for the three compared runs.

4. Conclusions

An adsorption study of Orange II from aqueous solutions onto porous titania aerogel was performed where the effect of various parameters was tested and kinetic and thermodynamic models were suggested. The characterization of these sol–gel materials revealed the abundance of surface titanol groups available for adsorption. The adsorbents exhibit also a high porosity with a pore volume equal to 2.86 cm^3/g, a pore size distribution centered at 13.9 nm, and a surface area around 500 m^2/g. The adsorption study showed the titania aerogel as highly efficient adsorbent of Orange II. At pH smaller than the titania PZC (i.e. pH < 6.0), the adsorbent's surface is partially protonated, favoring the electrostatic interaction with the dye existing at this pH in its anionic form. In addition, Orange II molecules are attracted by the titania surface due to Yoshida hydrogen bonding between the titanol groups and the aromatic rings, the nitrogen atoms and the oxygen atoms. A schematic presentation of the adsorption process is given in Fig. 11. The optimum uptake capacity was found at pH 2. Fast adsorption of the dye was noticed within the first 30 min of the experiment where more than 12 mg of Orange II (50% of the initial dye amount) were adsorbed onto 1 g of titania aerogel. A weak influence of the temperature on the adsorption was observed with the experiments performed at 50 °C revealing the lowest adsorption. The modification of the adsorbent dose indicated that 10 mg or less of titania aerogel are able to remove more than 94% of the dye molecules existing in the solution. The uptake capacity of 30 mg of titania aerogel was the maximum for dye concentrations around 200 mg/L. The calculation based on this latter conclusion revealed that 7.5 mg (less than 10 mg) of titania aerogel is the optimal adsorbent dose for the purification of 15 mL of 50 mg/L Orange II aqueous solution. The adsorption experimental data fitted with theoretical models met the Sips adsorption isotherm model and showed that the titania aerogel is able to adsorb up to 420 mg of Orange II per gram of adsorbent. The experiments showed also that the adsorption follows a pseudo second-order kinetics model that indicates that the adsorption involves chemical reactions in addition to physisorption. We suggest an adsorption mechanism based on a fast diffusion of the dye within the solution to reach the surface of the adsorbent. In the boundary layer the diffusion is slower than the previous step to slow down to the minimum within the particle. Accordingly, we suspect the intra-particle diffusion to be the main factor in the rate control of this mechanism. The thermodynamic study revealed an exothermic and ordered adsorption process. The recovery of Orange II from the titania aerogel, carried out at pH 11 and 30 °C, was complete (100%) after 30 min and the regenerated aerogel was reused for adsorption three times and showed high adsorption efficiency. This study showed the titania aerogel to be highly efficient adsorbing material, economically attractive, easily regenerated and reusable several times.

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References

[1] M.S. Tsuboy, J.P.F. Angeli, M.S. Mantovani, S. Knasmüller, G.A. Umbuzeiro, L.R. Ribeiro, Genotoxic, mutagenic and cytotoxic effects of the commercial dye CI Disperse Blue 291 in the human hepatic cell line HepG2, Toxicology in Vitro 21 (2007) 1650–1655.
[2] K. Golka, S. Kopps, Z.W. Myslak, Carcinogenicity of azo colorants: influence of solubility and bioavailability, Toxicology Letters 151 (2004) 203–210.
[3] K.T. Chung, Mutagenicity and carcinogenicity of aromatic amines metabolically produced from azo dyes, Journal of Environmental Science and Health, Part C 18 (2000) 51–71.
[4] A.R. Beaudoin, M.J. Pickering, Teratogenic activity of several synthetic compounds structurally related to trypan blue, The Anatomical Record 137 (1995) 297–305.
[5] S. Seshadri, P.L. Bishop, A.M. Agha, Anaerobic/aerobic treatment of selected azo dyes in wastewater, Waste Management 14 (1994) 127–137.
[6] K.C. Maheria, U.V. Chudasama, Sorptive removal of dyes using titanium phosphate, Industrial & Engineering Chemistry Research 46 (2007) 6852–6857.
[7] B. Shi, G. Li, D. Wang, C. Feng, H. Tang, Removal of direct dyes by coagulation: the performance of preformed polymeric aluminum species, Journal of Hazardous Materials 143 (2007) 567–574.
[8] F.L. Emmert Iii, J. Thomas, B. Hon, A.J. Gengenbach, Metalloporphyrin catalyzed oxidation of methyl yellow and related azo compounds, Inorganica Chimica Acta 361 (2008) 2243–2251.
[9] H.-Y. Shu, M.-C. Chang, H.-H. Yu, W.-H. Chen, Reduction of an azo dye Acid Black 24 solution using synthesized nanoscale zerovalent iron particles, Journal of Colloid and Interface Science 314 (2007) 89–97.
[10] G. Capar, U. Yetis, L. Yilmaz, Membrane based strategies for the pre-treatment of acid dye bath wastewaters, Journal of Hazardous Materials 135 (2006) 423–430.
[11] D. Georgiou, A. Aivasidis, Decoloration of textile wastewater by means of a fluidized-bed loop reactor and immobilized anaerobic bacteria, Journal of Hazardous Materials 135 (2006) 372–377.
[12] M. Valix, W.H. Cheung, G. McKay, Roles of the textural and surface chemical properties of activated carbon in the adsorption of acid blue dye, Langmuir 22 (2006) 4574–4582.
[13] C. Kannan, T. Sundaram, T. Palvannan, Environmentally stable adsorbent of tetrahedral silica and non-tetrahedral alumina for removal and recovery of malachite green dye from aqueous solution, Journal of Hazardous Materials 157 (2008) 137–145.
[14] P. Liu, L. Zhang, Adsorption of dyes from aqueous solutions or suspensions with clay nano-adsorbents, Separation and Purification Technology 58 (2007) 32–39.
[15] F.A. Pavan, S.L.P. Dias, E.C. Lima, E.V. Benvenutti, Removal of Congo red from aqueous solution by anilinepropylsilica xerogel, Dyes and Pigments 76 (2008) 64–69.
[16] K. Bourikas, M. Stylidi, D.I. Kondarides, X.E. Verykios, Adsorption of Acid Orange 7 on the surface of titanium dioxide, Langmuir 21 (2005) 9222–9230.
[17] P.V. Messina, P.C. Schulz, Adsorption of reactive dyes on titania–silica mesoporous materials, Journal of Colloid and Interface Science 299 (2006) 305–320.
[18] V.K. Gupta, A. Mittal, G. Vibha, J. Mittal, Adsorption of basic fuchsin using waste materials—bottom ash and deoiled soya—as adsorbents, Journal of Colloid and Interface Science 319 (2008) 30–39.
[19] V.K. Gupta, A. Imran, V.K. Saini, Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA13 from aqueous solutions using carbon slurry developed from a waste material, Journal of Colloid and Interface Science 315 (2007) 87–93.
[20] V.K. Gupta, A. Mittal, L. Kurup, J. Mittal, Adsorption of a hazardous dye, erythrosine, over hen feathers, Journal of Colloid and Interface Science 304 (2006) 52–57.
[21] M.-S. Chiou, P.-Y. Ho, H.-Y. Li, Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads, Dyes and Pigments 60 (2004) 69–84.
[22] C. Hsiu-Mei, C. Ting-Chien, P. San-De, H.-L. Chiang, Adsorption characteristics of Orange II and Chrysophenine on sludge adsorbent and activated carbon fibers, Journal of Hazardous Materials 161 (2009) 1384–1390.
[23] G. Zhang, J. Qu, H. Liu, A.T. Cooper, R. Wu, $CuFe_2O_4$/activated carbon composite: a novel magnetic adsorbent for the removal of acid orange II and catalytic regeneration, Chemosphere 68 (2007) 1058–1066.
[24] H. Métivier-Pignon, C. Faur-Brasquet, P. Le Cloirec, Adsorption of dyes onto activated carbon cloths: approach of adsorption mechanisms and coupling of ACC with ultrafiltration to treat coloured wastewaters, Separation and Purification Technology 31 (2003) 3–11.
[25] I. Uzun, F. Güzel, Rate studies on the adsorption of some dyestuffs and p-nitrophenol by chitosan and monocarboxymethylated(mcm)-chitosan from aqueous solution, Journal of Hazardous Materials 118 (2005) 141–154.
[26] J. Pedro Silva, S. Sousa, J. Rodrigues, H. Antunes, J.J. Porter, I. Gonçalves, S. Ferreira-Dias, Adsorption of acid orange 7 dye in aqueous solutions by spent brewery grains, Separation and Purification Technology 40 (2004) 309–315.
[27] X. Jin, M.-q. Jiang, X.-q. Shan, Z.-g. Pei, Z. Chen, Adsorption of methylene blue and orange II onto unmodified and surfactant-modified zeolite, Journal of Colloid and Interface Science (2008), doi:10.1016/j.jcis.2008.08.066.
[28] V.K. Gupta, A. Mittal, V. Gajbe, J. Mittal, Removal and recovery of the hazardous azo dye acid Orange 7 through Adsorption over waste materials: bottom ash and de-oiled soya, Industrial & Engineering Chemistry Research 45 (2006) 1446–1453.
[29] C.J. Brinker, G.W. Scherer, Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing, Academic Press, New York, 1990.
[30] S.S. Kistler, Coherent expanded aerogels and jellies, Nature 127 (1931) 741.
[31] H. El Rassy, P. Buisson, B. Bouali, A. Perrard, A.C. Pierre, Surface characterization of silica aerogels with different proportions of hydrophobic groups, dried by the CO_2 supercritical method, Langmuir 19 (2003) 358–363.
[32] Z. Novak, M. Habulin, V. Krmelj, Z. Knez, Silica aerogels as supports for lipase catalyzed esterifications at sub- and supercritical conditions, The Journal of Supercritical Fluids 27 (2003) 169–178.
[33] C.A.M. Mulder, J.G. Van Lierop, Preparation, densification and characterization of autocalve dried SiO_2 gels, in: J. Fricke (Ed.), Aerogels, Springer Verlag, 1986, p. 68.
[34] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, Journal of the American Chemical Society 60 (1938) 309–319.
[35] E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances. I: Computations from nitrogen isotherms, Journal of the American Chemical Society 73 (1951) 373–380.
[36] G. Socrates, Infrared and Raman Characteristic Group frequencies: Tables and Charts, third ed., John Wiley & Sons, 2001.
[37] H. Gunzler, H.-U. Gremlich, IR Spectroscopy: An Introduction, Wiley-VCH, 2002.
[38] J. Yu, S. Liu, H. Ju, Glucose sensor for flow injection analysis of serum glucose based on immobilization of glucose oxidase in titania sol–gel membrane, Biosensors and Bioelectronics 19 (2003) 401–409.
[39] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size, and Density, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2004.
[40] R.J. Hunter, Zeta Potential in Colloid Science, Academic Press, New York, 1981.
[41] G.A. Parks, The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems, Chemical Reviews 65 (1965) 177–198.
[42] S. Bracko, J. Span, Osmotic coefficients of C.I. Acid Orange 7 in aqueous solution and in the presence of simple electrolyte, Dyes and Pigments 35 (1997) 165–169.
[43] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, Journal of the American Chemical Society 40 (1918) 1361–1403.
[44] H. Freundlich, Of the adsorption of gases. Section II. Kinetics and energetics of gas adsorption. Introductory paper to section II, Transactions of the Faraday Society 28 (1932) 195–201.
[45] R. Sips, On the structure of a catalyst surface, The Journal of Chemical Physics 16 (1948) 490–495.
[46] D.D. Duong, Adsorption analysis: equilibria and kinetics, Imperial College Press, London, 1998.
[47] R.E. Treybal, Mass Transfer Operations, third ed., McGraw-Hill Companies, 1980.
[48] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochemistry 34 (1999) 451–465.
[49] H. Nollet, M. Roels, P. Lutgen, P. Van der Meeren, W. Verstraete, Removal of PCBs from wastewater using fly ash, Chemosphere 53 (2003) 655–665.
[50] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials, Chemical Engineering Journal (2008), doi:10.1016/j.cej.2008.09.009.
[51] W.L. Masterton, C.N. Hurley, Chemistry: Principles and Reactions, fifth ed., Brooks/Cole, 2003.
[52] Z. Aksu, A.I. Tatll, Ö. Tunç, A comparative adsorption/biosorption study of Acid Blue 161: effect of temperature on equilibrium and kinetic parameters, Chemical Engineering Journal 142 (2008) 23–39.
[53] M. Sarkar, P.K. Acharya, B. Bhattacharya, Modeling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters, Journal of Colloid and Interface Science 266 (2003) 28–32.
[54] W.J. Weber, J.C. Morriss, Kinetics of adsorption on carbon from solution, Journal of the Sanitary Engineering Division 89 (1963) 31–60.