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Valorization of food wastes (orange seeds) as adsorbent for dye retention from aqueous medium

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ABSTRACT

In order to understand the adsorption process mechanism and to evaluate the adsorptive properties of the citrus powder, the equilibrium, thermodynamic, and kinetic of the adsorption of the anionic reactive dye Orange 16 on the powder of orange seeds were studied using different theoretical models. The equilibrium adsorption data analyzed by Freundlich, Langmuir, and Dubinin–Radushkevich isotherm models revealed that Langmuir model best describes the dye sorption processes. The monolayer adsorption capacity of 1,111.11 mg/g reached at 25˚C and the values of the mean free energy (E) obtained from the Dubinin–Radushkevich model (5.45–6.48 kJ/mol) indicated a porous structure of the adsorbents and suggest that the physical adsorption is the main adsorption type involved in this studied processes. The values of the thermodynamic parameters (ΔG, ΔH, and ΔS) showed that the adsorption of tested dyes was feasible, spontaneous, and endothermic under examined conditions. The FTIR spectroscopy was used to characterize the adsorbent before and after loading the dyes in order to obtain additional information about possible ways to bind the dyes by the adsorbent. The obtained results showed that orange seeds, a waste material from food industry could be considered an efficient adsorbent for the removal of some textile dyes (especially with relatively low molecular weight) from aqueous media.

Keywords: Aqueous medium; Adsorption equilibrium; Orange seeds; Orange 16 dye; Thermodynamic parameters; Kinetic studies

1. Introduction

Orange—*Citrus sinensis* (Rutaceae family), a plant with origin disputed between India and China, is prevalent today on a fairly large area, being cultivated both in the natural land and in protected areas (greenhouses, apartments). Orange fruits can have different sizes, colors or shapes, both in terms of bark and pulp. They represent a complex mixture of organic substances and mineral assets, distributed among pulp,

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peel, and even seeds. The pulp of the fruit is rich in hesperidin, pectin, citric acid, ascorbic acid, betadine, fructose, along with a complex of vitamins (C, B1, B2, and B6), and a number of minerals (Fe, Ca, Mg, Ph, K, Na, and Zn). The skin is rich in essential oils that can be extracted by cold pressing, with a yield of 1.5–2.5%. The composition is directly influenced by the variety and maturity of the fruit at harvest, cultivation geographic area (soil, climate conditions). Hence, the consumption of these fruits (either pulp or peel) not only provides the elements of a harmonious development of the organism, but also prevents or treats different medical disorders, such as digestive disorders, avitaminoses, and nervous system disorders. Also, volatile compounds are of great use in food, cosmetics, or pharmaceuticals being used either as flavorings or for their antimicrobial effect. In this context, it is obvious that the valorization of every part of the fruit is important for the extraction of the organic compounds which are of medical interest or as additives in food, cosmetic, and pharmaceutical industry.

The industrial processing of orange fruits results in different amounts of byproducts, such as peel, pulp, skins, and seeds. In recent years, they developed and implemented a number of practical methods of recovery of such waste in order to obtain products with high commercial value. These methods are based on the metabolism of microbial or enzymatic processes and lead to the formation of enzymes, bioethanol, organic acids, heteropolysaccharides, aromatic, bacterial protein, prebiotic oligosaccharides, or biologically active compounds. Citrus residues are a good source of cellulose, pectin fiber, cold pressed oils, essences, D-limonene, ethanol, oil seeds, pectin, and flavonoids (hesperidin, narirutine, naringinine, and eriocitrin).

Also, various essential oils may be extracted and in the end the resulted new wastes can be integrated into different biodegradation processes (anaerobic digestion or/and aerobic processes) in order to obtain biofuel or amendment to improve soil fertility [1–5].

Considering their lignocellulosic compositions, the orange seeds could be tested as materials with adsorptive properties toward some chemical pollutants (metal ions, organic compounds) found in industrial effluents and domestic sewage.

Although it is fairly old, the adsorption remains one of the most used methods in the treatment of colored wastewaters because some of their main advantages: design simplicity without sophisticated equipment, inexpensiveness, specific physical–chemical interactions between dyes and the solid adsorbents, and low matrix effects [6–10]. Also, it offers the possibility of usage as adsorbents of a huge category of materials: ion-exchange resins or other materials with ion-exchange properties, activated charcoal, natural or synthetic zeolite, lignocellulosic materials from nature or as secondary products from industrial or agricultural activities, active or inactive biomass produced from food and pharmaceutical industry, and fermentation technology [6–8,11–13]. A significant category of solid adsorbents is the lignocellulosic materials characterized by the most important characteristics: the easy availability at a low price and the non-pollutant character which implies the formation of nontoxic residues, highly hydrophilicity, fact that determines a rapid kinetics of the sorption process, high porosity, and good mechanical resistance and can be utilized in different shapes (particles of different sizes, fibers, filters, textures) [11]. Particularly useful in practice is the fact that these materials, could be used in native or modified forms [6,7,11–24], applied in batch and/or fixed bed column techniques [6,11–26] facilitate the study of a mono or binary dyes aqueous system [6–25].

Agricultural wastes, part of this category of lignocellulosic material with adsorptive properties, represent a highly studied category of adsorbents for retaining different chemical species pollutants from aqueous medium [27–30]. Some examples of adsorbents based on agriculture and/or industrial food waste (in their natural form or after physic-chemical modified) investigated for the removal of dyes from aqueous solutions are listed in Table 1.

The main objective of this paper is to investigate the adsorptive performance of the orange seeds for the removal of reactive dye Orange 16 from aqueous medium. The adsorption equilibrium, thermodynamics, and kinetics were studied using different theoretical models in order to identify the process mechanism. The FTIR spectroscopy has been used to characterize the adsorbent before and after retaining the dye in order to obtain supplementary information about possible ways to bind the dye by the adsorbent.

2. Materials and methods

2.1. Materials

The experiments were carried out using orange seeds (from the various fruit varieties) as an adsorbent, which is a waste from the food industry. The material has been processed by drying it at the room temperature for a week, grounded, and sieved to get a final 2–4 mm particles size [3].

The seeds are lignocellulosic materials contain about 36% oil and 14% protein. The main components of the structure of the orange seeds are: crude

Table 1
Brief review of applications of agriculture and/or industrial food waste as adsorbents in removal of dyes

Sorbent	Dye	Refs.
Succharum bengalense	Congo Red	[12]
Apple seeds	Brilliant Red HE-3B; Methylene Blue	[15]
Rice husk modified	Methylene Blue	[16]
Swede rape straw (*Brassica napus* L.) natural and modified with tartaric acid	Methylene Blue	[18]
Poplar leaf	Methylene Blue	[19]
Mango seed	Anthraquinone and azo acid dyes	[20]
Rice husk modified with nitric acid and with peroxide	Malachite Green	[21]
Almond pistachio shell, walnut shell, tea waste and orange peel	Violet B	[22]
Okra waste	Basic Blue	[23]
Sugarcane baggase	Malachite Green	[24]
Lotus leaf	Methylene Blue	[26]
Wine processing waste sludge	Methylene Blue	[31]
Almond shell (*Prunus dulcis*)	Rhodamine 6G	[32]
Rice husk	Safranine	[33]
Papaya seeds	Methylene Blue	[34]
Sesame waste	Reactice Red 141	[35]
Sunflower seed shells	Orange 16; Methylene Blue	[36,37]
Corn cob	Methylene Blue	[37]

protein (3.06%); crude fat (54.2%), fibre (5.5%), carbohydrates (34.74%), and different minerals: 36.56 mg Ca/100 mg seeds powder, 719.79 mg Mg/100 mg powder, 145.11 mg K/100 mg powder, 39.7 mg P/100 mg powder, 15.71 mg Zn/100 mg powder, and a lower amount of Mn, Na, Cu, and Fe [38,39]. The orange seed's powder can be used as a material with sorptive properties, either in their natural form or after removal of various biologically active substances (such as various fatty acids or amino acids).

The dye used experimentally is Orange 16, a reactive anionic dye (C.I. 18097; MW = 735.6 g/mol and $\lambda_{max} = 560$ nm) with the chemical structure presented in Fig. 1. It was used as aqueous solution having a concentration of =715 mg dye/L.

2.2. Equilibrium adsorption experiments

Experimental studies were carried out in batch conditions by contacting into conical flasks of 150 mL of an established amount of the adsorbent with 25 mL aqueous Orange 16 dye solution of a known concentration. The concentration of the aqueous dye stock solution was 715 mg/L. The working solutions with concentrations between 42.9 and 429 mg/L were obtained by appropriate dilutions. The flasks were placed in a thermostatic bath (Poleko SLW 53) at three constant temperatures: 5, 20, and 40°C. The initial pH of the aqueous dye solutions was adjusted to the required value using 1 N HCl solutions. After a contact time of 24 h, 2 mL of aqueous supernatant was spectrophotometrically analyzed to determine the dye concentration.

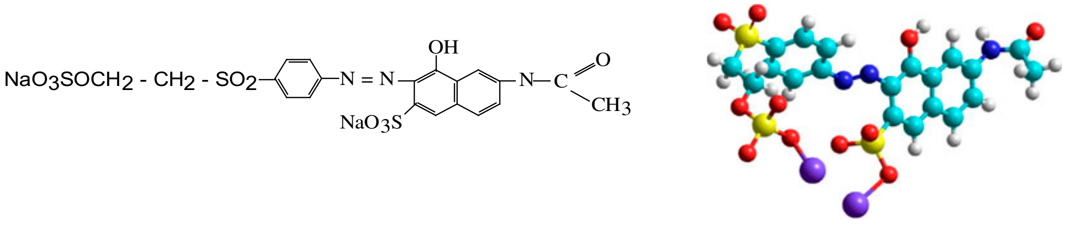

Fig. 1. Structure of reactive dye Orange 16.

The data resulting from the adsorption experiments were used to evaluate the seeds adsorption capacity, q (mg of dye/g of orange seeds):

$$q = \frac{C_0 - C}{G} V \quad (1)$$

where C_0 and C are the initial and the residual dye concentrations (mg/L), G is the adsorbent mass (g), and V is the solution volume (L).

2.3. Kinetic adsorption experiments

The influence of contact time on the adsorption of dye by orange seeds powder was studied in batch experiments, mixing 0.05 g of adsorbent and 25 mL of RO solution (42.9 and 57.2 mg/L, pH 3) at temperature of 25℃ for time intervals ranging from 5 min to 24 h. Finally, the adsorbent was separated by filtration and the dye content in the aqueous phase was determined spectrophotometrically. The extent of adsorption was expressed by the fractional attainment of equilibrium, F:

$$F = \frac{q_t}{q} \quad (2)$$

where q_t and q (mg/g) are the dye adsorbed at time t and at equilibrium (24 h).

2.4. Analytical methods

The residual concentrations of reactive Orange 16 dye in filtrate samples were spectrophotometrically determined by measuring the absorbance at the maximum dye wavelength of 495 nm with a JK-VS-721N vis spectrophotometer and interpolating using a calibration curve (working concentration range in the Lambert–Beer region is 5.72–42.9 mg/L).

Infrared spectroscopic measurements of the orange seeds powder were recorded on a FTIR BioRad spectrometer FTS2000 with 4 cm^{-1} resolution for 32 scans, using KBr pellets.

3. Results and discussions

3.1. Characterization of adsorbent before and after dye adsorption

The FTIR spectrum of orange seeds (Fig. 2) indicated numerous peaks associated with different functional groups, whose intensity depended on the origin, the isolation, and processing methods. A comparative study between spectra of the orange seed before and after loading with the Orange 16 reactive dye, in accordance with literature data, has led to the following observations:

(1) Many peaks allocated to different functional groups were observed, some of which are able to interact with molecular dye species (a band at range of 3,300–3,400 cm^{-1} O–H stretch in alcohols, phenols, 1,745 cm^{-1} C=O stretch in non-conjugated ketones and carboxyl groups, 1,648 cm^{-1} stretching vibration of C=O in conjugated ketones, 1,370–1,384 cm^{-1} O–H bending, 2,300–2,900 cm^{-1} from C–H).

(2) The intensity and position of peaks assigned to characteristic functional groups from orange seed were either minimized or slightly shifted after sorption of the reactive dye. These changes may be a consequence of the electrostatic interactions between positively charged functional groups of the sorbent (oxygen is easily protonated in acidic conditions) and the anionic dye.

(3) A distinct observation can be seen in the FTIR region of OH sorption: a strong and wide signal of OH groups was observed for seeds sample, whereas this was much narrower and less intense for seed + Orange samples. This indicates the possibility of strong interactions of OH groups present in the adsorbent structure with analyzed dye. Also, the changing of the peak from 3,396.64 to 3,425.57 cm^{-1} confirms this hypothesis.

(4) The intensity and position of peaks assigned to characteristic functional groups from orange seeds were either minimized (3,008.95–2,926.01 cm^{-1}; 1,544.98–1,539.9 cm^{-1}; 1,377.17–1,375.24 cm^{-1}) or slightly shifted (1,163.07–1,166.93 cm^{-1}; 721.38–723.3 cm^{-1}) after adsorption of the reactive dye. These changes can be associated to electrostatic interactions between positively charged functional groups of the adsorbent (oxygen is easily protonated in acidic conditions) and the anionic dye.

(5) Moreover, a new adsorption peak at 673.16 cm^{-1} has been present in the spectrum of the (seeds + Orange 16), which originated from the Orange 16 dye structure due to benzene ring.

(6) The FTIR spectra suggest that the adsorption mechanism could be a combination of electrostatic interaction and physical retention.

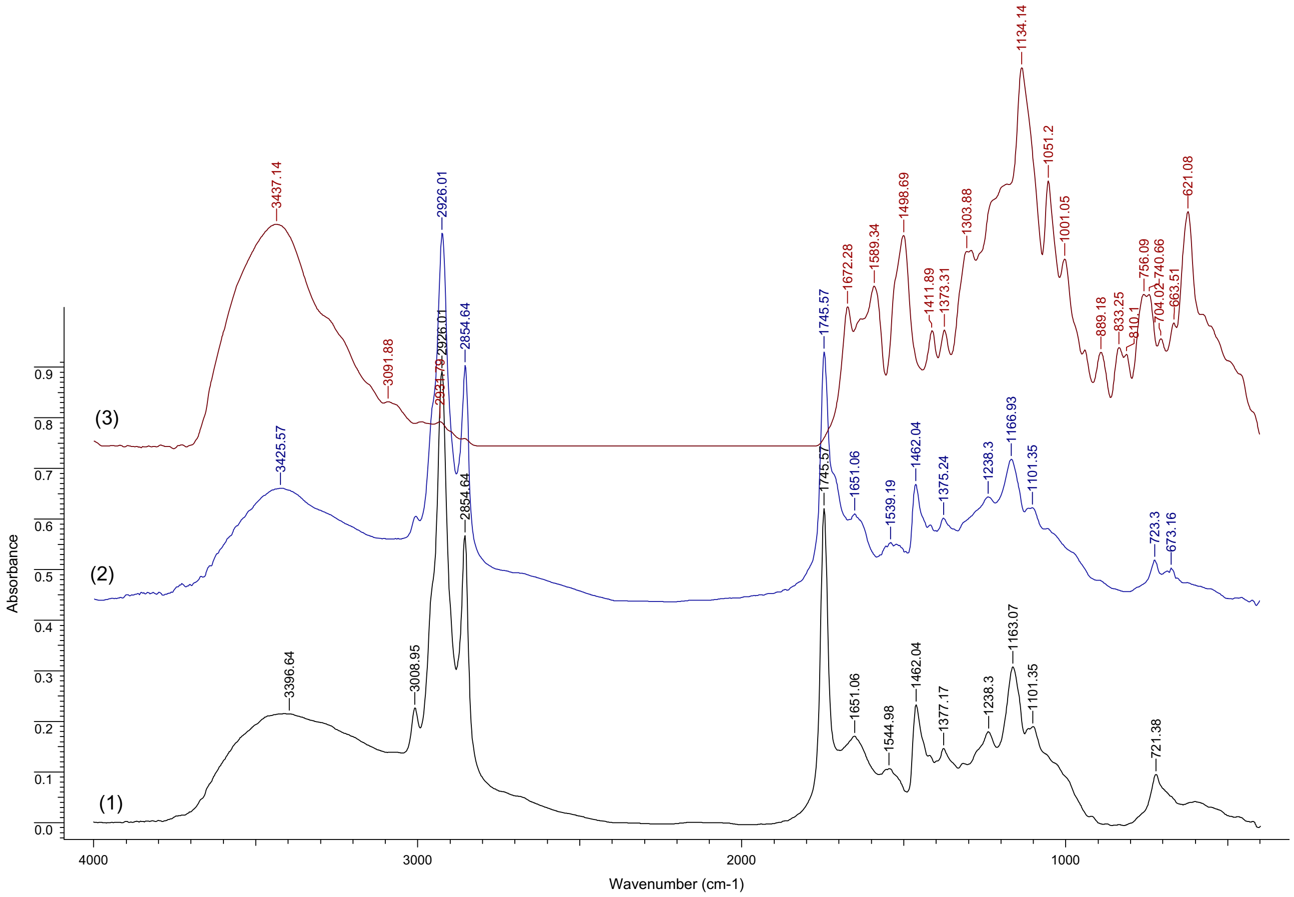

Fig. 2. FT-IR spectra of orange seed (1), orange seed with Orange 16 dye (2) and Orange 16 dye (3) samples.

3.2. Adsorption equilibrium

Previous experimental studies allowed the assessment of conditions needed for preparing an adsorbent based on orange seeds, with an enhanced adsorption capacity for the investigated dye [3].

The aim of the adsorption equilibrium study is to determine the quantitative characteristic parameters and to gain some information about the mechanism. These aspects can be achieved by processing the experimental data using different adsorption models. The equilibrium data were analyzed using three of the most known adsorption equilibrium models (Freundlich, Langmuir and Dubinin–Radushkevich—Fig. 3 and Table 2) [19,37].

The characteristic parameters related to each adsorption model were calculated from the intercepts and slopes of the corresponding linear plots (figures not shown). These, together with the values of the correlation coefficients (R^2), which have been used to assess which model describe better the adsorption process of reactive Orange 16 (RO) dye onto orange seeds, are presented in Table 2.

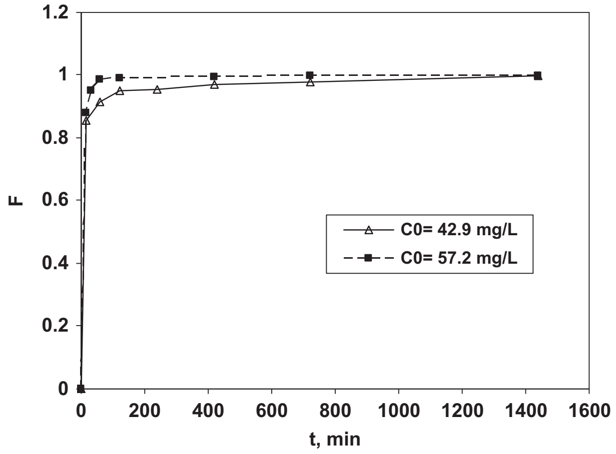

Fig. 3. Effect of contact time in the Orange 16 reactive dye adsorption onto orange seeds (adsorbent dose 2 g/L; pH 3; temperature 25℃).

The *Freundlich isotherm*, one of the most used empirical equations, takes into consideration the

Table 2
Characteristic isotherm parameters for adsorption of RO dye onto orange seeds powder

	Temperature (K)		
Isotherm	278	298	313
Freundlich			
$q = K_F \cdot C^{1/n}$; linearized form: $\log q = \log K_F + \frac{1}{n}\log C$			
K_F—adsorption capacity, $(\mathrm{mg/g})(\mathrm{L/mg})^{1/n}$; n—measure of adsorption intensity or surface heterogeneity			
K_F $(\mathrm{mg/g})(\mathrm{L/mg})^{1/n}$	19.783	22.06	19.985
n	0.853	1.076	1.18
R^2	0.9398	0.9635	0.9929
Langmuir			
$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}$; linearized form: $\frac{1}{q} = \frac{1}{q_0 \cdot K_L \cdot C} + \frac{1}{q_0}$			
q_0—saturation capacity, mg/g; K_L—binding (adsorption) energy, L/mg			
q_0 (mg/g)	1,250	1,111.11	344.827
K_L (L/mg)	0.02228	0.02055	0.613
R^2	0.981	0.9507	0.9959
Dubinin–Radushkevich			
$\ln q = \ln q_D - \beta_D \cdot \varepsilon^2$; $\varepsilon = R \cdot T \cdot \ln\left(1 + \frac{1}{C}\right)$; $E = \frac{1}{\sqrt{-2 \cdot \beta_D}}$			
q_D—the maximum amount adsorbed, mg/g; β_D—activity coefficient related to mean adsorption energy, $\mathrm{mol^2/kJ^2}$; ε—Polany potential; E—mean free energy of adsorption, kJ/mol			
q_0 (mg/g)	1,005.64	777.923	520.026
β $(\mathrm{mol^2/kJ^2})$	0.0168	0.0148	0.0119
E (kJ/mol)	5.455	5.812	6.482
R^2	0.9956	0.9818	0.981

Table 3
The apparent thermodynamic parameters of the adsorption of Orange 16 reactive dye on orange seeds powder

T (K)	K_L (L/mg)	K_L (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
278	0.02228	13.758	−6.06	+70.398	270.23
293	0.02055	12.69	−6.19		
313	0.613	378.5275	−15.45		

heterogeneity of the adsorbent surface and assumes that the adsorption process could be explained by an exponential distribution of active sites of the adsorbent [19,37]. The R^2 values higher than 0.9 indicate that the Freundlich model described the adsorption of the reactive dye onto orange seeds powder, and also the values of the Freundlich constant n (the measure of adsorption intensity) are greater than unit, suggesting a favorable adsorption process. Taking into account the evolution of the R^2 values, it can be said that adsorption takes place more favorable at the room temperature.

Table 4
Equations and the parameters of the applied kinetic models [33,42,43,45]

Kinetic model	Kinetic model parameters	Observations
Pseudo-first-order (Lagergren model) $\frac{dq_t}{dt} = k_1(q - q_t)$	k_1: rate constant of pseudo-first-order model, (1/min)	The pseudo-first-order model is well fitted for modeling of kinetic data if the plot $\log(q - q_t)$ vs. t gives straight lines which pass through the origin of axes, and the $q_{e,exp}$ values agree with the calculated $q_{e,exp}$
linearized form: $\log(q - q_t) = \log q - \frac{k_1}{2.303} t$	q_t and q (mg/g): the amounts of dye adsorbed at time t and at equilibrium (24 h), respectively	
Pseudo-second-order (Ho model) $\frac{dq_t}{dt} = k_2(q - q_t)^2$	k_2: rate constant of pseudo-second-order model, g/mg min	The sorption kinetic follows a pseudo-second-order kinetic model, and the adsorption processes could be controlled by chemical adsorption or chemisorption involving valence forces through sharing or exchange of electrons between the two phases involved, if it can observed a linearity of plots of t/q_t vs. t, and the values of q calculated are much closer to the experimental value
linearized form: $\frac{t}{q} = \frac{1}{k_2 q^2} + \frac{1}{q} t$	$k_2 q^2 = h$: initial adsorption rate, mg/g min	
Elovich model $q_t = \frac{\ln(\alpha \cdot \beta)}{\beta} + \frac{1}{\beta} \ln t$	α: constant about the initial adsorption rate (mg/g min) β: constant refers to the extent of surface coverage, and activation energy for chemisorption (g/mg)	Is applied in the adsorption system in which the adsorbent surface is heterogeneous (the case of the studied powder of orange seeds). The studied processes can be described as a chemical adsorption if the representation q vs. $\ln t$ must be linear and intersect the origin of the axes
Intraparticle diffusion model (Webber–Morris model)	k_d: rate constant for intraparticle diffusion, mg/g min$^{1/2}$	Diffusion-controlled kinetics; pore diffusion is the rate-limiting step if the plot q_t vs. $t^{1/2}$ is linear and passes through origin
$q = k_d t^{1/2} + c$	c: intercept to the y axis	
Film diffusion model, proposed by McKay $\ln(1 - F) = k_f t$	k_f: the rate constant for film diffusion, min^{-1} F: the fractional attainment	The film diffusion is involved in the adsorption process if the plot $\ln(1 - F)$ vs. t is linear, and it is the rate-limiting step if the line passes through origin

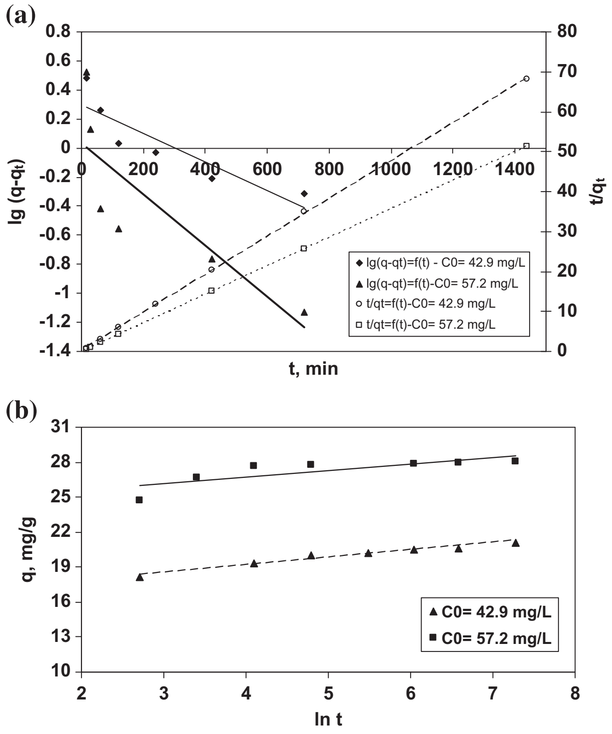

Fig. 4. The applicability of the pseudo-first-order and pseudo-second-order kinetic models (a) and Elovich model (b) in the RO reactive dye adsorption onto orange seeds (at two different concentrations, adsorbent dose 2 g/L; pH 3; temperature 25℃).

The *Langmuir isotherm* is based on the assumption that the maximum adsorption corresponds to a monolayer of solute molecules on the adsorbent surface, containing a finite number of energetically equivalent sites [19,37]. The values of Langmuir constants are summarized in Table 2. The calculated statistical parameters from Table 2 show that the isotherms data of Orange 16 reactive dye adsorption onto orange seeds powder can be better described by the Langmuir model, suggesting the formation of monolayer coverage of adsorbate at the external surface of the adsorbent. It is observed that the q_0 values decreases with the increasing temperature, suggesting that the adsorption process may be endothermic. At the same time, a decrease in the saturation capacity (monolayer coverage), q_0, which reflects a better accessibility of adsorption sites at lower temperature is observed. The value of adsorption capacity at temperature of 20℃ was found to be 1,111.11 mg dye/g of seeds powder, a value comparable with other adsorption capacities reported in literature for different agriculture waste used as low-cost adsorbents for the removal of dyes from aqueous medium (Table 1).

Table 5
Kinetic parameters for the Orange 16 reactive dye adsorption onto orange seeds powder

Kinetic model	Initial dye concentration (mg/L)	
q_{exp} (mg/g)	42.9	57.2
Pseudo-first-order kinetic		
k_1 (1/min)	0.0023	0.0032
q_e (mg/g)	1.964	0.669
R^2	0.7943	0.7738
Pseudo-second-order kinetic		
k_2 (g/mg min)	0.0055	0.0215
q_e (mg/g)	21.142	28.09
R^2	0.9999	1
Elovich model		
α (mg/g min)	1.9×10^{11}	2.62×10^{41}
β (g/mg)	1.589	3.683
R^2	0.9559	0.6769
Intra-particle diffusion		
k_{d1} (mg/g min$^{0.5}$)	0.2763	0.7396
C_1	17.07	22.177
R^2	0.9938	0.9167
k_{d2} (mg/g min$^{0.5}$)	0.0395	0.0122
C_2	19.613	27.645
R^2	0.986	0.9548

Dubinin–Radushkevich (DR) isotherm was used in order to appreciate the nature of the adsorption process—physical or chemical [19,37]. Specialized literature specifies that the values of mean free energy, E, less than 8 kJ/mol characterize a physical adsorption mechanism and values between 8 and 16 kJ/mol indicates an ion-exchange mechanism [40]. Evaluating the values of the adsorption energy obtained by D–R equation (Table 2), it may be observed that at a temperature of 25℃ (E = 5.812 kJ/mol) the adsorption of the dye occurs via a physical mechanism by van der Waals, hydrogen, dipole-dipole interactions and electrostatic attraction, respectively, between the positively charged surface of the adsorbent and the anionic dye. Increasing temperature also induces a slight increase in the free adsorption energy up to 6.482 kJ/mol at 45℃, due to the intensification of the dye diffusion.

3.3. Thermodynamic parameters

Supplementary information about the nature of adsorption process could be obtained by the analysis of thermodynamic parameters. It is well known that there are two main types of adsorption characterized by different values of thermodynamic parameters [41]:

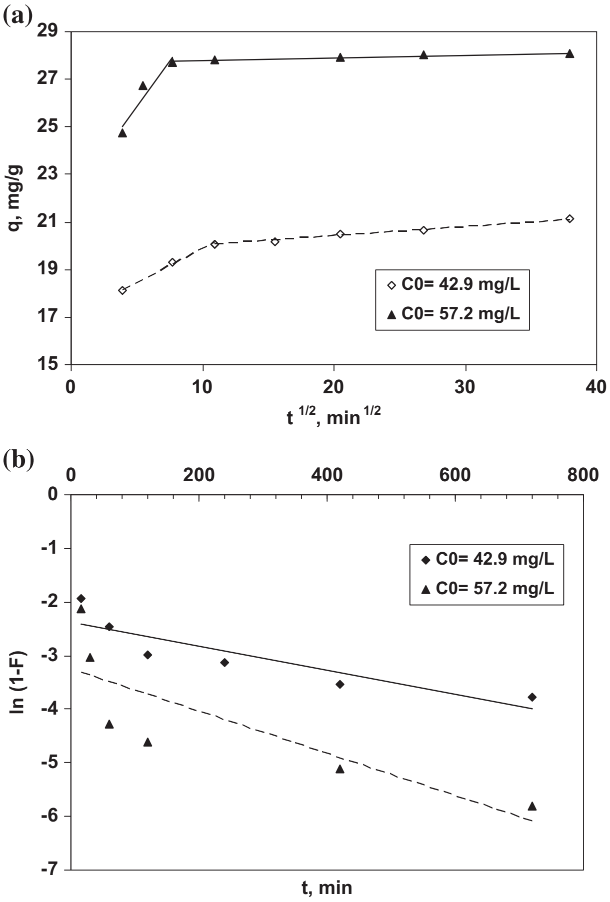

Fig. 5. The applicability of intraparticle diffusion kinetic model (a) and film diffusion model (b) in the RO dye adsorption onto orange seeds (at two different concentrations, adsorbent dose 2 g/L; pH 3; temperature 25˚C).

(1) *physical*, determined by weak forces and characterized by ΔH value not more higher than 4.2 kJ/mol and ΔG values lower than −16 kJ/mol;
(2) *chemical*, as a result of the action of forces much stronger than those implicated in physical process, and characterized by ΔH value higher than 21 kJ/mol and ΔG higher than 20 kJ/mol.

In order to understand the nature of Orange 16 dye adsorption on orange seeds powder adsorbent, the apparent thermodynamic parameters were calculated (Table 3), using the values of Langmuir constant, K_L (L/mol), the following equations [37] and linear dependence ln K vs. $1/T$ (not presented in the paper):

$$\Delta G = -RT \ln K_L \quad (3)$$

$$\ln K_L = -\Delta H/RT + \Delta S/R \quad (4)$$

where ΔG is free energy, kJ/mol; ΔH is enthalpy, kJ/mol, and ΔS is adsorption entropy changes, J/mol K; R is the universal gas constant (8.31 J/mol K), and T is the absolute temperature (K) of solution.

The negative values of apparent free energy change (ΔG) underline that the reactive dye adsorption on orange seeds powder is thermodynamically feasible and spontaneous at any temperature between 5 and 45˚C. These values suggest that the mechanism could be a combination between physical adsorption and ion-exchange. The positive value of apparent enthalpy change (ΔH) obtained from the slope of linear dependence ln K_L vs. $1/T$ highlights the possibility of an endothermic process of dye adsorption process. Also, the value is not so high, confirming that the mechanism of adsorption process is more physical than chemical, involving weak interactions between reactive dye molecules and the charged groups onto adsorbent surface. The positive value of entropy change (ΔS) characterizes the increased randomness at the solid–solution interface during the dye adsorption and some structural changes in the adsorbate and adsorbent. The positive entropy reflects the electrostatic interactions between opposite charge groups and corresponds to an increase in the degree of freedom of the adsorbed species.

3.4. Kinetic studies

3.4.1. Influence of contact time

Among the most important operational parameters of an adsorption process is the time of contact between the liquid and solid phases. It may be used to characterize, model, and optimize the adsorption process. The effect of the phases of the contact time on the Orange 16 reactive dye removal by powder orange seeds is presented in Fig. 3.

As seen in Fig. 3, the values of the fractional attainment of equilibrium rapidly increase with the time of contact, during the first 200 min, and after that the rate of dye adsorption (for both concentrations) became slower and the time period required for maximum removal of dyes was found to last up to 4 h. Also, the adsorption half-times ($t_{1/2}$) were determined until 15 min for both dye concentrations.

3.4.2. Kinetic modeling

The scientific literature considers that the dye adsorption process at the solid–liquid interface could be described by three major steps [27,42,43]:

1. The diffusion of the dye molecules from bulk solution to the adsorbent surface through the boundary layer (film diffusion).
2. The diffusion of dye molecules from the surface into the pores of the solid particle (pore diffusion or intraparticle diffusion).
3. The interaction of dye with the active sites on the surface of the adsorbent.

The adsorption kinetic is governed by the slowest of these processes. Also, it is very well known that in the adsorption processes, the most important is the diffusion in the liquid film surrounding the adsorbent particles (external diffusion) and the diffusion in adsorbent particle (internal diffusion).

In order to investigate the type of mechanism (particle diffusion/film diffusion or chemical reaction) involved in the adsorption of Orange 16 reactive dye onto the studied adsorbent and to establish the rate determining step of the process, the kinetic data were processed and interpreted using some of the most used kinetic models from the literature presented in Table 4 [42].

The kinetic parameters related to each model, calculated from the intercepts and slopes of the corresponding linear plots (Fig. 4), are presented in Table 5. The fitting of each model to the experimental data were estimated using the linear regression correlation coefficient, R^2 values.

The comparative study of the data presented in Table 5 and the graphic representations from Fig. 3 led to the following conclusions about the kinetics of adsorption process studied:

1. The plot $\ln(q - q_t)$ vs. t gives straight lines which did not pass through the origin of axes. Also, the $q_{e,\exp}$ values did not agree with the calculated $q_{e,\exp}$, all of these, suggesting that the pseudo-first-order model is not well fitted for modeling of the kinetic data.
2. The linearity of plots of t/q_t vs. t, the values of q calculated closer to the experimental value, and the highest values of the correlation coefficient, R^2, suggested that the adsorption kinetics on orange seeds powder follows a pseudo-second-order kinetic model, and the dye adsorption process could be controlled by chemical adsorption or chemisorption involving valence forces through sharing or exchange of electrons between the two phases involved.
3. The R^2 values greater than 0.95 for the studied adsorption system (low concentration) suggest that the data fit the Elovich equation well in this case. But, the linear representation q vs. $\ln t$ which do not intersect at the origin of the axes, confirmed that chemisorption cannot be the only step that controls the studied adsorption processes, and the diffusion processes remain the step that could control the adsorption dye onto orange seeds powder.

These first three findings lead to the conclusion that the adsorption rate is governed by either liquid-phase mass transport, or by intra-particle mass transport. So, in order to obtain information about the diffusion mechanism, the kinetic results were analyzed by the *intra-particle diffusion model* (by Webber-Morris) and *film diffusion model* (by McKay) [42,44].

The lines of graphical representation (Webber–Morris model) from Fig. 5(a) are linear, then *intra-particle diffusion* occurs, but none passing through the origins, which underline the assumption that both diffusion mechanisms (*intra-particle* and *film*) are involved in the adsorption processes, and may be the rate determining step. The multi-linearity of the plots, for each concentration, indicates that two or more steps influence the adsorption process [42,44]. The first part could be regularly associated with the film *diffusion* (external mass transfer) [45], while the second linear part recommends the *intra-particle diffusion* (into the porous structure of the adsorbent) [46]. The graphical representation of McKay model (Fig. 5(b)) confirms that *film diffusion* is not involved in the adsorption process because the plot $\ln(1 - F)$ vs. t isn't linear, and it is not the rate-limiting step because the line passes not through origin. This behavior is true for both concentrations of dye.

4. Conclusion

In order to evaluate the adsorptive behavior of orange seeds powder toward Orange 16 reactive dye, the equilibrium, thermodynamic, and kinetic studies were carried out in batch systems. The results obtained led to the following conclusions:

1. The equilibrium adsorption data analyzed by Freundlich, Langmuir, and Dubinin–Radushkevich isotherm models revealed that Langmuir isotherms describe the correct equilibrium adsorption data. The monolayer adsorption

capacity of 1,111.11 mg/g reached at 25°C is in the range with previously reported data on the adsorption capacity of different low cost adsorbents. The values of the mean free energy (E) obtained from the Dubinin–Radushkevich model (5.45–6.48 kJ/mol) suggest that weak van der Waals forces (dipole-dipole interactions, hydrogen bonding) and electrostatic interactions contribute to the adsorption of the studied reactive dye by orange seeds powder.

(2) The values of thermodynamic parameters confirm the feasibility and the exothermic behavior of the adsorption process, and suggest that the adsorption is more a physical process indifferent of value of initial dye concentrations in aqueous system.

(3) Kinetic data at two initial dye concentrations were analyzed using different kinetic models (pseudo-first-order, pseudo-second-order, intraparticle diffusion model, and McKay model). The results showed that Orange 16 dye adsorption by orange seeds powder follows pseudo-second-order kinetics and both diffusion mechanisms (*intra-particle* and *film*) are involved in the adsorption process.

(4) Based on the results obtained from this study, it can be said that orange seeds powder can be considered a promising and eco-friendly adsorbent, with a low cost production for the removal of dyes, with not too high molecular weight, from an aqueous environment.

References

[1] C.S.K. Lin, L.A. Pfaltzgraff, L. Herrero-Davila, E.B. Mubofu, S. Abderrahim, J.H. Clark, A.A. Koutinas, N. Kopsahelis, K. Stamatelatou, F. Dickson, S. Thankappan, Z. Mohamed, R. Brocklesby, R. Luque, Food waste as a valuable resource for the production of chemicals, materials and fuels, Current situation and global perspective, Energy Environ. Sci. 6 (2013) 426–464.

[2] R. Liguori, A. Amore, V. Faraco, Waste valorization by biotechnological conversion into added value products, Appl. Microbiol. Biotechnol. 97 (2013) 6129–6147.

[3] D. Suteu, C. Zaharia, Study of reactive dye sorption from aqueous solutions onto citrus seed, Proceeding of the XIX-th International Conference “INVENTICA 2015”, Iasi, 2015, CD.

[4] E. Virmond, J.D. Rocha, R.F.P.M. Moreira, H.J. José, Valorization of agroindustrial solid residues and residues from biofuel production chains by thermochemical conversion: A review, citing Brazil as a case study, Braz. J. Chem. Eng. 30 (2013) 197–230.

[5] D. Suteu, A.C. Blaga, M. Badeanu, Preliminary study concerning the anaerobic digestion of food industrial wastes, Bull. Inst. Polit. Iasi 57 (2011) 79–85.

[6] C. Zaharia, D. Suteu, Textile organic dyes—Characteristics, polluting effects, and separation/elimination procedures from industrial effluents. A critical overview, in: T. Puzyn, A. Mostrag-Szlichtyng (Eds.), Organic Pollutants Ten Years After the Stockholm Convention—Environmental and Analytical Update, Intech, Rijeka, 2012, pp. 57–86.

[7] S.J. Allen, B. Koumanova, Decolourisation of water/wastewater using adsorption (review), J. Univ. Chem. Technol. Metall. 40 (2005) 175–192.

[8] M. Kharub, Use of various technologies, methods and adsorbents for removal of dye, J. Environ. Res. Dev. 6 (3A) (2012) 879–883.

[9] M.N. Rashed, Adsorption technique for the removal of organic pollutants from water and wastewater, in: M. Nageeb Rashed (Ed.), Organic Pollutants—Monitoring, Risk and Treatment, Intech, Rijeka, 2013, pp. 167–194.

[10] S.M. Kanawade, Treatment on dye industrial wastewater by using adsorption, Int. J. Chem. Mater. Sci. 2(3) (2014) 059–067.

[11] D. Suteu, C. Zaharia, T. Malutan, Biosorbents based on lignin used in biosorption processes from wastewater treatment, in: R.J. Paterson (Ed.), Lignin: Properties and Applications in Biotechnology and Bioenergy, Nova Science, New York, NY, 2011, pp. 279–305.

[12] M.I. Din, Z. Hussain, M.M. Athar, A. Madni, S. Ahmad, Biosorption of toxic Congo Red dye from aqueous solution by eco-friendly biosorbent *Succharum bengalense*, Desalin. Water Treat. 51 (2013) 5840–5847.

[13] D. Suteu, S. Coseri, D. Bilba, Macroporous polymeric ion exchangers as adsorbents for the removal of cationic dye basic blue 9 from aqueous solutions, J. Appl. Polym. Sci. 131(1) (2014), doi: 10.1002/app.3962.

[14] D. Suteu, C. Zaharia, T. Malutan, Equilibrium, kinetic, and thermodynamic studies of Basic Blue 9 dye sorption on agro-industrial lignocellulosic materials, Cent. Eur. J. Chem. 10 (2012) 913–926.

[15] D. Suteu, S. Coseri, M. Badeanu, C. Zaharia, Valorization of food wastes as sorbent for dye retention from aqueous medium, Desalin. Water Treat. 54(9) (2015) 2570–2580.

[16] M.C. Shih, Kinetics of the batch adsorption of methylene blue from aqueous solutions onto rice husk: Effect of acid-modified process and dye concentration, Desalin. Water Treat. 37 (2012) 200–214.

[17] S. Chowdhury, P. Das Saha, Scale-up of a dye adsorption process using chemically modified rice husk: Optimization using response surface methodology, Desalin. Water Treat. 37 (2012) 331–336.

[18] Y. Feng, H. Zhou, G. Liu, J. Qiao, J. Wang, H. Lu, L. Yang, Y. Wu, Methylene blue adsorption onto swede rape straw (*Brassica napus* L.) modified by tartaric acid: Equilibrium, kinetic and adsorption mechanisms, Bioresour. Technol. 125 (2012) 138–144.

[19] X. Han, X. Niu, X. Ma, Adsorption characteristics of methylene blue on poplar leaf in batch mode: Equilibrium, kinetics and thermodynamics, Korean J. Chem. Eng. 29 (2012) 494–502.

[20] M.M. Dávila-Jiménez, M.P. Elizalde-González, V. Hernández-Montoya, Performance of mango seed adsorbents in the adsorption of anthraquinone and azo acid dyes in single and binary aqueous solutions, Bioresour. Technol. 100 (2009) 6199–6206.

[21] B. Ramarajn, P. Manoj Kumar Reddy, C. Subrahmanyan, Low cost adsorbents from agriculture waste for removal of dyes, Environ. Prog. Sustainable Energy 33(1) (2013) 38–46.

[22] S. Hashemian, J. Sbayegan, A comparative study of cellulose agricultural waste (almond pistachio shell, walnut shell, tea waste and orange peel) fir adsorption of Violet B dye from aqueous solution, Orient. J. Chem. 30(4) (2014) 2091–2098.

[23] M.N. Almaghrabi, S. Matar, M.A. Hashem, Textile effluent treatment by agriculture solid waste, Sci. Res. J. 4 (2015) 55–65.

[24] N. Sharma, B. Kumar Naudi, Utilization of Sugarcane Baggase an agricultural waste to remove Malachite Green dye from aqueous solutions, J. Mater. Environ. Sci. 4(6) (2013) 1052–1065.

[25] E. Cheong Khoo, S.T. Ong, S.T. Ha, Removal of basic dyes from aqueous environment in single and binary systems by sugarcane bagasse in a fixed-bed column, Desalin. Water Treat. 37 (2012) 215–222.

[26] X. Han, W. Wang, X. Ma, Adsorption characteristics of methylene blue onto agricultural wastes lotus leaf in bath and column modes, Water Sci. Technol. 64(3) (2011) 654–660.

[27] D.K. Mahmoud, M.A.M. Salleh, W.A.W.A. Karim, Characterization and evaluation agricultural solid wastes as adsorbents: A review, J. Purity Util. React. Environ. 1 (2012) 451–459.

[28] K.S. Bharathi, S.I. Ramesh, Removal of dyes using agricultural waste as low-cost adsorbents: A review, Appl. Water Sci. 3(4) (2013) 773–790.

[29] F.S. Abbas, Dyes removal from wastewater using agriculture waste, Adv. Environ. Biol. 7(6) (2013) 1019–1026.

[30] A. Bhatnagar, M. Sillanpää, Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review, Chem. Eng. J. 157(2–3) (2010) 277–296.

[31] C.C. Liu, Y.S. Li, Y.M. Chen, H.H. Li, M.K. Wang, Removal of methylene blue from aqueous solution using wine-processing waste sludge, Water Sci. Technol. 65(12) (2012) 2191–2199.

[32] H.B. Senturk, D. Ozdes, C. Duran, Biosorption of Rhodamine 6G from aqueous solutions onto almond shell (*Prunus dulcis*) as a low cost biosorbent, Desalination 252 (2010) 81–87.

[33] S. Chowdhury, P. Soha, Adsorption kinetic modeling of Safranine onto rice husk biomatrix using pseudo-first and pseudo-second-order kinetic models. Comparison of linear and non-linear methods, CLEAN—Soil Air Water 39(3) (2011) 274–282.

[34] D.S. Paz, A. Baiotto, M. Schwaab, M.A. Mazutti, M.M. Bassaco, D.A. Bertuol, E.L. Foletto, L. Meili, Use of papaya seeds as a biosorbent of methylene blue from aqueous solution, Water Sci. Technol. 68(2) (2013) 441–447.

[35] H. Sohrabi, E. Ameri, Adsorption equilibrium, kinetics and thermodynamics assessment of the removal of the reactive red 141 dye using sesame waste, Desalin. Water Treat. (2015) 1–2, doi: 10.1080/19443994.

[36] D. Suteu, C. Zaharia, T. Malutan, Removal of orange 16 reactive dye from aqueous solutions by waste sunflower seed shells, J. Serb. Chem. Soc. 76(4) (2011) 607–624.

[37] D. Suteu, C. Zaharia, T. Malutan, Equilibrium, kinetic, and thermodynamic studies of Basic Blue 9 dye sorption on agro-industrial lignocellulosic materials, Cent. Eur. J. Chem. 10(6) (2012) 1913–1926.

[38] T.A. El-Adawy, E.H. Rahma, A.A. El-Bedawy, A.M. Gafar, Properties of some citrus seeds. Part 3. Evaluation as a new source of protein and oil, Nahrung/Food 43(6) (1999) 385–391.

[39] F. Samia El-Safy, R.H. Salen, M.E. Abd El-Ghany, Chemical and nutritional evaluation of different seed flours as novel sources of protein, World J. Dairy Food Sci. 7(1) (2012) 59–65.

[40] K.Y. Foo, B.H. Hameed, Insight into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (2010) 1–10.

[41] M.M. Dubinin, L.V. Radushkevich, Equation of theof the characteristic curve of activated charcoal, Proc. Acad. Sci. USSR Phys. Chem. Sect. 55 (1947) 331–333.

[42] G. Crini, P.M. Badot, Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature, Prog. Polym. Sci. 33 (2008) 399–447.

[43] D. Suteu, S. Coseri, L. Rusu, Kinetics studies on the adsorption behaviour of Basic Blue 9 dye on macroporous ion exchanger resins, Desalin. Water Treat. 57 (2016) 14665–14673, doi: 10.1080/19443994.2015.1063464.

[44] K.M. Doke, E.M. Khan, Adsorption thermodynamics to clean up wastewater; critical review, Rev. Environ. Sci. Biotechnol. 12(1) (2012) 25–44.

[45] G.M. Walker, L. Hansen, J.-A. Hanna, S.J. Allen, Kinetics of a reactive dye adsorption onto dolomitic sorbents, Water Res. 37(9) (2003) 2081–2089.

[46] V.C. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics, Colloids Surf. A 272 (2006) 89–104.