



Removal of Orange 16 reactive dye from aqueous solutions by waste sunflower seed shells

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Abstract: In this work, the use of an agro-industrial waste, *i.e.*, sunflower seed shells, was investigated as a sorbent for the removal of Orange 16 reactive dye from aqueous environments. Batch experiments were performed as a function of pH, sorbent dose, dye concentration, temperature and contact time. The percent dye removal increased with increasing sorbent dose and temperature of the aqueous solution, and decreased with increasing dye concentration; the required contact time was five hours. The Freundlich, Langmuir, Dubinin–Radushkevich and Tempkin adsorption isotherms were used to describe the equilibrium sorption data and to determine the corresponding isotherm constants. The thermodynamic parameters, ΔG , ΔH and ΔS , were also determined. These parameters indicated that the sorption of reactive dye onto sunflower seed shells was a spontaneous, endothermic and entropy-driven process. The kinetic data were evaluated by pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models. The results of the kinetic study indicated that the sorption of Orange 16 reactive dye onto sunflower seed shells is a complex process and both chemical surface sorption and intra-particle diffusion contribute to the rate-limiting step. Therefore, the sunflower seed shell showed itself to be a promising cheap sorbent for the decolourization of aqueous coloured solutions or effluents.

Keywords: sorption; sunflower seed shell; reactive dye; Orange 16; equilibrium study.

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INTRODUCTION

The present environment protection policy imposes, among other requirements, not only the ensuring of water quality and protection of all water resources (together with the treatment technologies of industrial or municipal wastewater), but also the integrated management of wastes in the larger context of the depletion of raw materials as priority directions for the recognized organisms or organisations, both on the international and European level. In this context, an attempt was made to combine these two priorities: wastewater treatment and waste valorisation by solving the water depollution problem (water decolourization) using an industrial waste as an adsorptive material.

In the industrial sector, a high water consumer and wastewater producer is the textile industry, mainly textile chemical finishing processing. These industrial wastewaters have a very complex and heterogeneous composition, containing both inorganic and organic compounds in different amounts. For their treatment before discharge into the sewage system or for recycling in technological processes, many different methods, such as adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, coagulation–flocculation, extraction and gas stripping, *etc.* have been implemented.^{1–6} Many of these procedures are often complicated and time consuming, generate mud or other toxic wastes and may be ineffective or expensive for dilute dye systems.

From these procedures, adsorption is highlighted because of its numerous advantages, such as easiness of achievement and reduced implementation costs.⁵ However, the most important advantage in dye removal is the possibility to employ a large variety of adsorptive materials that can be selected based on the known structure of the textile dye. These materials can be synthetic (ion exchange polyamides, polyacrylonitrile fibres, celluloses, ion exchanger resins) and/or natural (peat, seashell, algae, lignite, wood, *etc.*).^{1,5,7–11} The high costs of adsorbent preparation re-directed research to the testing of low cost materials, included in the category of “non-conventional” or “low cost” materials, such as: *i*) industrial/agricultural/domestic waste or industrial/agricultural by-products (ash, sludge, sawdust, textile fibbers, mud, bark, seed, husk, straw, *etc.*) and *ii*) natural materials.^{5,11–15} The important advantages are: ease of preparation, potentially simple and economic “end-of-pipe” solution to the challenges set by new legislation covering effluent discharges, especially textile effluents.

Thus, the sorption of reactive dyes (*i.e.*, a reduction of the textile dye content in final textile effluents to a maximum of 200 mg dye L⁻¹) by agricultural by-products and wastes has been intensively studied and some of the obtained data are summarized in Table I. These sorptive materials can be used in their natural form or can be transformed into charcoal. The sorption capacity depends on the dye concentration in solution, temperature, and sorbent composition.

The results of these studies suggest that sorption onto agricultural by-products and wastes are progressing towards a perspective method.

TABLE I. Application of agricultural wastes as biosorbent for removal of different dyes

Type of agricultural waste	Retained dyes	Sorption capacity, $q / \text{mg g}^{-1}$	Ref.
Almond shell	Rhodamine 6G	32.6 (20 °C)	16
Sunflower seed hull (<i>Helianthus annuus</i> L.)	Methyl violet	92.59 (30 °C)	17
Sunflower seed shell	Reactive black 5	0.873	18
Palm shell powder	Methylene blue	121.5 (25 °C)	19
	Rhodamine 6G	105.0 (25 °C)	
Dehydrated peanut hull	Methylene blue	(92.0–108.0) (25 °C)	20
Untreated olive pomace	Reactive red 198	52.21 (20 °C)	21
Sawdust, two size fractions:	Brilliant red HE-3B	11.61 (20 °C)	22
SD-1 (particle size 1–2 mm)	Methylene blue	7.215 / 14.025 (20 °C)	
SD-2 (powder <0.1 mm)	Rhodamine B	7.309 / 10.764 (20 °C)	
	Crystal violet	12.594 / 20.877 (20 °C)	

Therefore, this paper presents the results of a study concerning the utilization of sunflower seed shells (agricultural waste) as a low-cost sorbent for the decolourization of different textile effluents which contain high molecular weight synthetic textile dyes (*i.e.*, to a maximum of 50–200 mg dye L⁻¹ in the final textile effluents). Moreover, the operational parameters of the sorption process were established. In addition, equilibrium, kinetic and thermodynamic studies were performed in order to establish all favourable conditions for the uptake of reactive dyes with large molecules.

EXPERIMENTAL

Materials and reagents

Sunflower seed shell was procured from the local oil industry. The seed shells were air-dried at room temperature for two days. Afterwards, they were grounded and sieved to obtain a particle size of 0.8 mm and stored in a plastic bottle for further use. No other chemical or physical treatments were used. The constituents of the sunflower shells were cellulose ($\approx 20\%$), lignin ($\approx 23\%$), pentosan ($\approx 12\%$), hexosane ($\approx 23\%$), polyuronic acids ($\approx 6\%$), furfural ($\approx 9\%$) and SR (solid residues) obtained from a total hydrolysis ($\approx 56\%$).

The commercial textile reactive Orange 16 dye (C₂₂H₁₇O₁₁N₃S₃Na₂, MW = 617.54, $\lambda_{\text{max}} = 495 \text{ nm}$.) was used. Working solutions with concentration of 24.7–197.6 mg L⁻¹ were prepared by appropriate dilution with bidistilled water of a stock solution (500 mg L⁻¹).

Equilibrium studies

Sorption experiments were performed under batch conditions by suspending weighed samples of sorbent (usually 0.3 g) in 25 mL of aqueous dye solution of known initial concentration in flasks placed in a thermostated bath at the desired temperature. The initial solution pH was adjusted by adding 1 M HCl solution, and measured with a pH/EC/TDS Hanna Instruments pH-ion meter. After a determined time (usually 24 h), the phases were separated and the amount of dye in the supernatant was determined by measurement of the absorbance

at 495 nm, the λ_{\max} of the dye, using an UV-Vis digital spectrophotometer, model Jasco V-550, and calculation from a dye calibration curve.

The sorption capacity of the sorbent was evaluated from the amount of sorbed dye, q (mg of per g of sorbent):

$$q = 10^3(c_0 - c)V/G \quad (1)$$

and from the percent dye removal, $R\%$:

$$R\% = 100(c_0 - c) / c_0 \quad (2)$$

where c_0 and c are the initial and the equilibrium concentration of dye in aqueous solution (mg L^{-1}), respectively, G is the amount of sorbent (g), and V is the volume of the solution (mL).

Equilibrium modelling (sorption isotherms)

The relationship between the amount of sorbed dye and its equilibrium concentration was described by four sorption isotherm equations, *i.e.*, the Freundlich, Langmuir, Dubinin–Radushkevich and Temkin equations.^{23,24} The best-fit equilibrium model was established based on the linear regression correlation coefficients, R^2 .

The Freundlich isotherm, one of the most used empirical equations, assumes surface heterogeneity and exponential distribution of the active sites of the sorbent:²⁴

$$q = K_F c^{1/n} \quad (3)$$

where K_F and n are constants related to the adsorption capacity and sorption intensity (efficiency), respectively.

The Freundlich constants, K_F and n , were evaluated from the slope and intercept of corresponding plots of the graphical representation of the linearized equation.

In the Langmuir isotherm model, adsorption is based on the assumption that maximum adsorption corresponds to a monolayer of solute molecules on the sorbent surface, containing a finite number of energetically equivalent sites.²³ The Langmuir Equation can be used in the following form:

$$q = \frac{K_L c q_0}{1 + K_L c} \quad (4)$$

where q_0 is the maximum amount of solute sorbed (mg g^{-1}) and K_L is the constant related to the binding energy of solute (L mg^{-1}).

The numerical values of Langmuir constants were evaluated from the graphical presentation of $1/q$ vs. $1/c$.

In order to appreciate the nature of the sorption process, physical or chemical, the isotherm data were analyzed by the Dubinin–Radushkevich (DR) model,²⁴ expressed by the following equation:

$$\ln q = \ln q_0 - B\varepsilon^2 \quad (5)$$

where q_0 is the maximum sorption capacity, B is the activity coefficient related to the mean sorption energy and ε is the Polanyi potential, given by:

$$\varepsilon = RT \ln \left(1 + \frac{1}{c} \right) \quad (6)$$

The sorption energy can be determined using the following equation:

$$E = \frac{1}{\sqrt{2B}} \quad (7)$$

The Tempkin equation has the following form:²³

$$q = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln c \quad (8)$$

where b_T is the heat of sorption (kJ mol^{-1}), K_T is the intensity of sorption (L g^{-1}), R is the universal gas constant and T is the absolute temperature.

Kinetic studies

The effect of contact time on the sorption of reactive dye onto sunflower seed shells was determined by the "limited bath" technique. A sample of 0.3 g sorbent was added under stirring to 25 mL of dye solution at pH 1.0 and with an initial concentration of 49.4 mg L^{-1} . The temperature of solutions was maintained at 20°C . After different contact times (30–400 min), volumes of supernatant were removed for absorbance measurement and calculation of the dye content. The extent of sorption was expressed by the fractional attainment of equilibrium:

$$F = \frac{q_t}{q} \quad (9)$$

where q_t and q (mg g^{-1}) are the amount of dye sorbed at time t and at equilibrium (24 h), respectively.

Kinetic modelling

In order to analyze the sorption of Orange 16 reactive dye onto sunflower seed shells and to understand the dynamics of the sorption process in terms of the rate order, pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models were applied to the experimental data.^{16,17,25,26}

The pseudo first-order model (Lagergren, 1898) is usually expressed as:

$$\log (q - q_t) = -\frac{k_1}{2.303} t + \log q \quad (10)$$

where q and q_t are the amounts of sorbed dye (mg g^{-1}) at equilibrium (24 h) and respectively any time t (min), and k_1 is the Lagergren rate constant of the first-order sorption (min^{-1}).

The pseudo-second order model (Ho model, 1999) assumes that the sorption follows a second order mechanism and the rate-limiting step may be chemical sorption involving valence forces or covalent forces between sorbent and adsorbate.²⁷ The rate of a pseudo-second order reaction is expressed by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{1}{q} t \quad (11)$$

where k_2 is the rate constant of second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$) and $q^2 k_2 = h$ can be regarded as the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) as t approaches zero.

The intra-particle diffusion model (Webber and Morris, 1963) assumes that sorption is a multi-step process involving transport of adsorbate from the aqueous solution to the sorption sites of the sorbent (surface sorption) and the diffusion into pores (intra-particle diffusion). The validity of model is confirmed by linear plots of the Weber and Morris Equation:²⁸

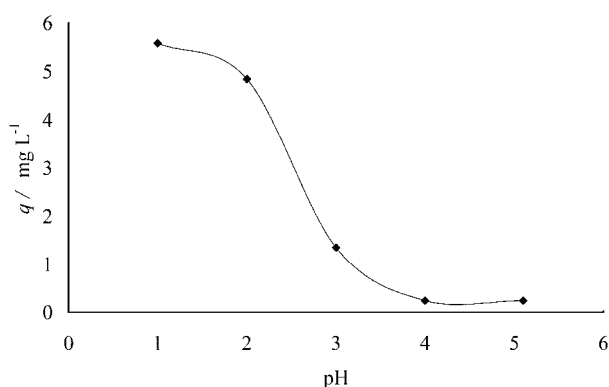
$$q = k_p t^{0.5} \quad (12)$$

where k_p is the rate constant for intra-particle diffusion ($\text{mg g}^{-1} \text{min}^{-0.5}$).

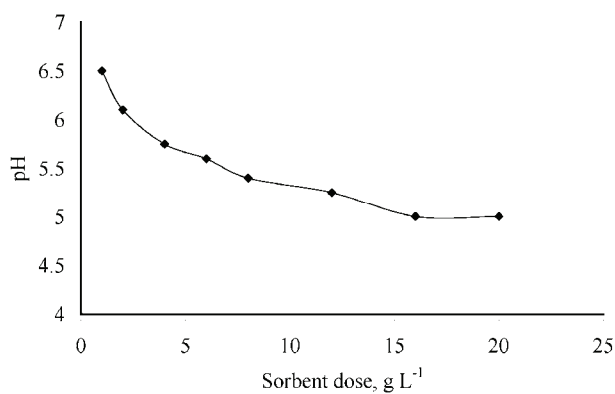
RESULTS AND DISCUSSION

Effect of pH on dye sorption

The effect of pH on the sorption of Orange 16 reactive dye was studied from solutions with different initial dye concentrations and a sunflower seed shells dose of 12 g L^{-1} . The results presented in Fig. 1a show that the removal efficiency was maximal in acidic media ($\text{pH} > 1$) and decreased sharply with increasing solution pH.



(a)



(b)

Fig. 1. a) Effect of pH on the sorption of the reactive dye onto sunflower seed shells. Conditions: $12 \text{ g sorbent L}^{-1}$, 24 h , $t = 25 \text{ }^\circ\text{C}$; b) The value of pH_{PZC} (pH of zero charge) for sunflower seed shells.

This behaviour may be correlated with the variation of the sunflower seed shell surface charge in dependence of the solution pH. The pH_{PZC} (pH of zero charge) of sunflower seed shells was determined by the method described by Nouri and Haghseresht²⁹ (Fig. 1b); the limiting pH 5 was considered as the pH_{PZC} value, when the sorbent surface was neutral. At values of $\text{pH} < \text{pH}_{\text{PZC}}$, the sorbent surface is positively charged and susceptible to electrostatic interactions with the polar portions of the Orange 16 reactive dye molecules (dissociated

sulphonic groups). At $\text{pH} > \text{pH}_{\text{PZC}}$, the sorbent surface was negatively charged and was not available to bind the anionic dye.

Effect of sorbent dose on dye sorption

The effect of sorbent dose on the removal of the reactive dye ($R\%$) and the sorption capacity (q) of sunflower seed shells were examined from solutions containing $86.45 \text{ mg dye L}^{-1}$ and $\text{pH } 1.0$ (Fig. 2).

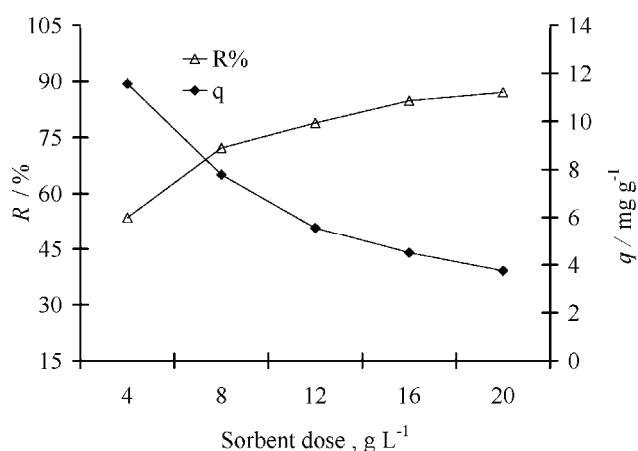


Fig. 2. Effect of sunflower seed shells dose on the sorption of the reactive dye. Conditions: $86.45 \text{ mg dye L}^{-1}$, $\text{pH } 1.0$, 24 h , $t = 25 \text{ }^\circ\text{C}$.

It can be seen that the increasing of the sunflower seed shells dose from 2 to 20 g L^{-1} increased the percentage of dye removal from 53.53 to 87.07% , due to the increasing number of available sorption sites. Simultaneously, the amount of reactive dye retained per unit weight of sorbent decreased from 11.57 to 3.75 mg g^{-1} , indicating a moderate sorptive capacity of the sunflower seed shells.

Effect of initial dye concentration and temperature on dye sorption

The effect of initial reactive dye concentration vs. the sorption capacity of sunflower seed shells was investigated from solutions of $\text{pH } 1.0$, for a sorbent dose of 12 g L^{-1} and the results are presented in Fig. 3. As can be seen, the amount of dye retained increased with the increasing initial dye concentration.

The amount of sorbed dye per unit mass of sunflower seed shells increased from 1.65 to 13.24 mg L^{-1} when the initial dye concentration was increased from 24.7 to 197.6 mg L^{-1} at 278 K temperature. This is probably due to the enhancement of dye molecules migration into the internal macroporous and mesoporous structure of the sorbent at high initial dye concentrations in the aqueous solutions.

The dye sorption onto sunflower seed shells was also dependent on solution temperature. It can be clearly observed in Fig. 3 that the amount of Orange 16 reactive dye sorbed from solutions of $\text{pH } 1.0$ with different initial dye concen-

trations increased with increasing temperature; the effect being more pronounced at high concentrations.

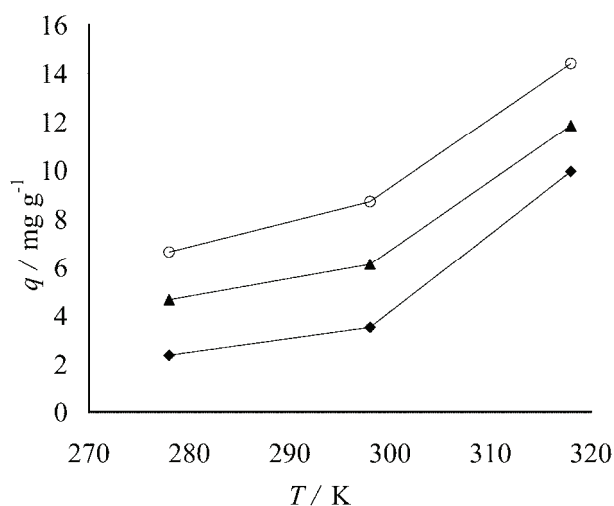


Fig. 3. Effect of the initial dye concentration on the sorption of the reactive dye. Conditions: pH 1.0, 12 g sorbent L⁻¹, 24 h; ○ – $c = 37.05 \text{ mg L}^{-1}$; ▲ – $c = 86.45 \text{ mg L}^{-1}$; ◆ – $c = 123.5 \text{ mg L}^{-1}$.

Effect of contact time on dye sorption

The effect of contact time of the phases on the sorption of Orange 16 reactive dye onto sunflower seed shells is presented in Fig. 4.

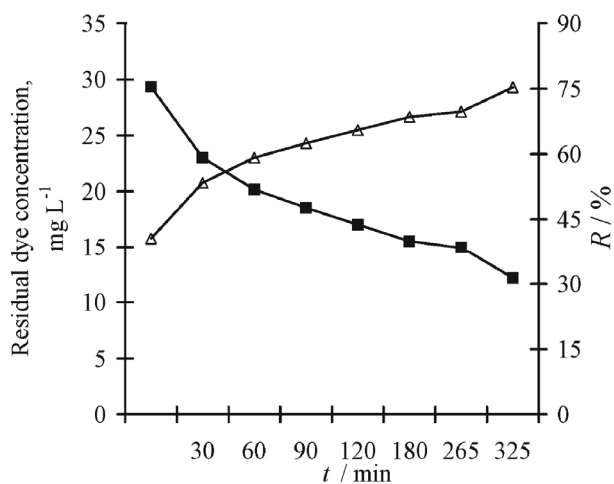


Fig. 4. Effect of the contact time on the removal of Orange 16 reactive dye by sunflower seed shells. Conditions: pH 1.0, 12 g sorbent L⁻¹, 25 °C; ■ – residual dye concentration; Δ – R.

The obtained data showed that the removal of reactive dye was faster in the initial stages of the contact period; the residual concentration of reactive dye in the solution rapidly decreased vs. time up to 300 minutes, and thereafter slowly decreases to the equilibrium value. This fact can be explained by the large num-

ber of vacant surface sites available for dye sorption during the initial stages of sorption. The increasing dye removal percent with increasing contact time (Fig. 4) suggests a more rapid dye removal from solutions with higher initial concentrations, because of the increased concentration gradient between the solution and the sorbent surface.

Sorption equilibrium

An analysis of the equilibrium data by fitting them to different isotherm models (Eq. (3)–(5) and (8)) is very important for an estimation of the practical sorption capacity and for optimization of the design of the sorption system. The isotherms of Orange 16 reactive dye sorption onto sunflower seed shells at three temperatures (5, 25 and 45 °C) are presented in Fig. 5.

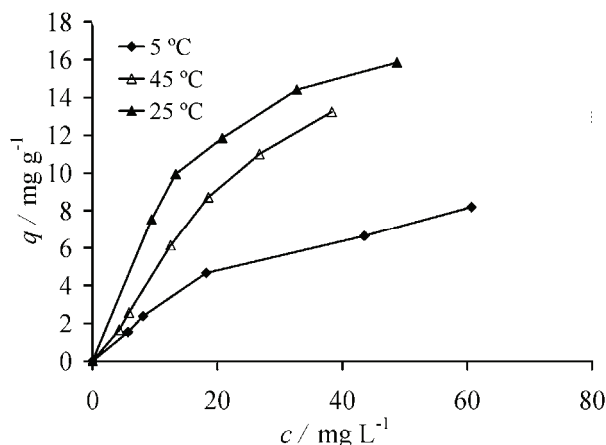


Fig. 5. The sorption isotherms of Orange 16 reactive dye onto sunflower seed shells at three temperatures. Condition: pH 1.0, 12 g sorbent L⁻¹.

In the studied dye concentration range (27.7–197.6 mg L⁻¹), the obtained isotherms were concave to the concentration axis, indicating an affinity for sunflower seed shells and a saturation trend at high dye concentrations. An increase in temperature increased the amount of sorbed dye.

The parameters related to each isotherm, calculated from the intercepts and slopes of the corresponding linear plots (Figs. 6a–6d) together with their correlation coefficients (R^2) are presented in Table II.

As can be seen from Table II, the value of Freundlich parameters, K_F and n , increase with increasing temperature, showing that the sorption of the reactive dye was more favourable at high temperatures. In all cases, the value of n was greater than unity, indicating a beneficial adsorption.

The values of the correlation coefficients from Table II show that the experimental data were better fitted by the Langmuir model of monolayer coverage of the sorbent with reactive dye molecules. This is in accordance with the shape of the sorption isotherms, which correspond to type L2 (Langmuir type) in the Giles

classification.³⁰ The values of q_0 , which reflect the accessibility of sorption sites, and the Langmuir constant K_L , which reflect the binding energy between reactive dye molecules and sunflower seed shells, increase with increasing temperature, indicating that the sorption is an endothermic process.

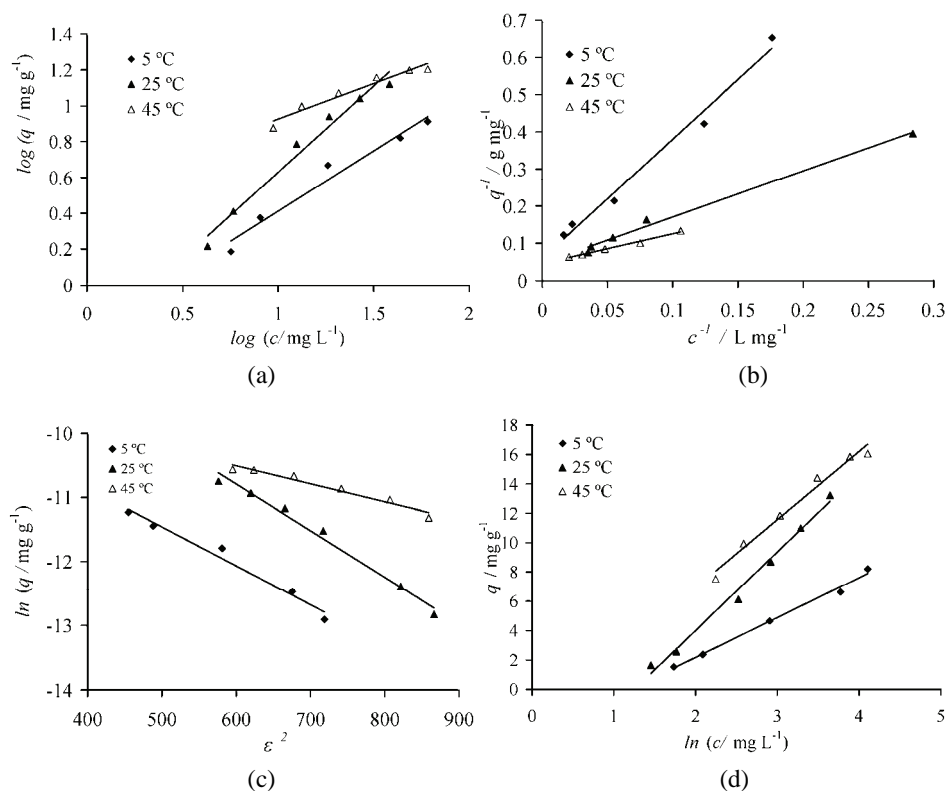


Fig. 6. Freundlich (a), Langmuir (b), DR (c) and Tempkin (d) plots for the sorption of Orange 16 reactive dye onto sunflower seed shells at three temperatures.

The sorption energy determined in the DR equation (Table II) revealed a possible ion exchange mechanism for the reactive dye sorption onto sunflower seed shells (the sorption energy was between 8 and 16 kJ mol^{-1}).²⁴ Mean free energy values lower than 8 kJ mol^{-1} characterize a physical sorption mechanism, while values between 8 and 16 kJ mol^{-1} indicate an ion exchange mechanism.²⁴

The values of the correlation coefficients for the Tempkin isotherm model were between 0.9804 and 0.99 at all studied temperatures, which confirms the better fit of equilibrium data as compared with the Freundlich isotherm model. The Tempkin isotherm takes into account some indirect sorbate–sorber interactions, and assumes that because of these interactions the heat of sorption is li-

near rather logarithmic, as implied in the Freundlich equation and decreases linearly with coverage.^{17,25,31}

TABLE II. Isotherm parameters for the sorption of reactive dye Orange 16 onto sunflower seed shells

Parameter	T / K		
	278	298	318
Freundlich			
$K_F / (\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$	0.545	0.4627	3.3799
n	1.486	1.0375	2.516
Linear regression equation	$y = 0.6739x - 0.2623$	$y = 0.9638x - 0.3347$	$y = 0.3974x + 0.5289$
R^2	0.9683	0.9773	0.9495
Langmuir			
$q_0 / \text{mg g}^{-1}$	17.036	21.74	22.12
$K_L / \text{L mg}^{-1}$	0.0182	0.0206	0.0579
Linear regression equation	$y = 3.2159x + 0.0587$	$y = 1.244x + 0.046$	$y = 0.7807x + 0.0469$
R^2	0.9852	0.9923	0.9884
Dubinin–Radushkevich (DR)			
$q_0 / \text{mg g}^{-1}$	13.661	1007.406	91.21
$B / \text{mol}^2 \text{kJ}^{-1}$	0.0061	0.0073	0.0028
$E / \text{kJ mol}^{-1}$	9.05	8.276	13.36
Linear regression equation	$y = -0.0061x - 8.4122$	$y = -0.0073x - 6.4183$	$y = -0.0028x - 8.8203$
R^2	0.9757	0.9848	0.9576
Tempkin			
$b_T / \text{kJ mol}^{-1}$	850.67	462.561	569.16
$K_T / \text{L g}^{-1}$	0.301	0.286	0.599
Linear regression equation	$y = 2.7157x - 3.2566$	$y = 5.3562x - 6.7025$	$y = 4.6452x - 2.3738$
R^2	0.9931	0.99	0.9804

Study of thermodynamic parameters

To evaluate the effect of temperature on the Orange 16 reactive dye sorption onto sunflower seed shells and to understand the nature of the sorption, it is necessary to determine the apparent thermodynamic parameters using the values of binding Langmuir constant, K_L (L mol^{-1}), and the Gibbs and van't Hoff equations.^{16,32}

The negative values of apparent free energy change (ΔG in the range -27.7 to $-21.6 \text{ kJ mol}^{-1}$) indicate that sorption of the reactive dye onto sunflower seed shells is spontaneous and thermodynamically feasible in the studied temperature range (278–318 K). The values of ΔG decreased with increasing tempe-

ature, showing that the spontaneity of sorption process is inversely proportional to the temperature.²⁵

The positive value of the enthalpy change ($\Delta H = 21.0 \text{ kJ mol}^{-1}$) confirmed the endothermic nature of sorption process of Orange 16 reactive dye onto sunflower seed shells.

The positive value of entropy change ($\Delta S = 152.0 \text{ J mol}^{-1}\text{K}^{-1}$) suggests increased randomness at the solid–liquid interface during the sorption of reactive dye and some structural changes in the sorbate and the sorbent.¹⁶ It could be suggested that the driving force of sorption is an entropy effect.

Moreover, the magnitudes of ΔH and ΔG give information about the nature of the sorption process. The literature data indicate that physical sorption is determined by weak forces, and is characterized by ΔH value no higher than 4.2 kJ mol^{-1} and, respectively, ΔG values lower than -16 kJ mol^{-1} ; chemical sorption is determined by forces much stronger than those implicated in physical processes, and is characterized by ΔH values higher than 21 kJ mol^{-1} and ΔG values higher than 20 kJ mol^{-1} .^{16,32}

The obtained data show that the sorption of Orange 16 reactive dye onto sunflower seed shells occurred by weak physical interaction and ion exchange between the surface of the sorbent and the dye molecules, as a consequence of surface charge on the sorbent at pH values lower than pH_{PZC} . The forces involved in the sorption can range from weak van der Waals forces to electrostatic attractions between the ionized sulphonyl groups of the dye molecule and the positively charged surface of the sunflower shells (SSS):



Infrared study of Orange 16 reactive dye binding onto sunflower seed shells

In order to obtain more information about the mechanism of dye binding onto sunflower seed shells, an infrared analysis was performed. The FTIR spectra of the sunflower seed shells before and after sorption of Orange 16 reactive dye from aqueous solutions of pH 1.0 are presented in Fig. 7.

Sunflower seed shells spectra present many overlapped bands, whose intensity depend on the origin and isolation method.

A comparison between spectra of sunflower seed shells before and after loading with the Orange 16 reactive dye, in accord with literature data, indicates that:

- the appearance of a specific band at 2854.64 cm^{-1} (2924.09 cm^{-1} is specific for the Orange reactive dye) with a different peak height to the corresponding band in the spectrum of seed shells alone in case (1) and the association of seed shell – Orange reactive dye in case (2) suggest the formation of ionic associations between sunflower seed shells and Orange 16 reactive dye;

– at acidic pH values, due to the presence of hydroxyl groups from the lateral chain (*i.e.*, sunflower seed shell – OH + H⁺), the sunflower seed shells can be associated in conjugated structures with the reactive dye (–O₃S–Dye), highlighted by the band of 2854.64 cm⁻¹. The height increase of the specific band at 2854.64 cm⁻¹ in the IR spectrum, due to sunflower seed shell – dye association (line 2, Fig. 7), confirms the establishment of ionic bonds between the sunflower seed shells and sorbed dye (a charged organic molecule consisting of polar and non-polar regions);

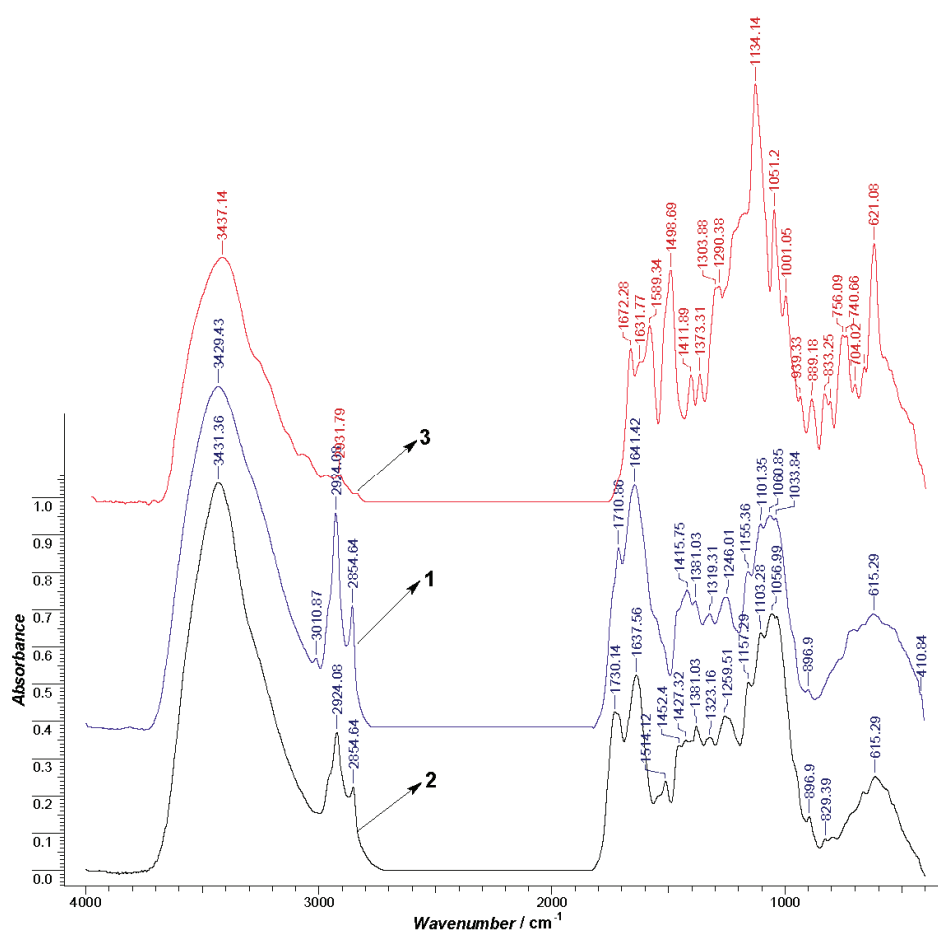


Fig. 7. FTIR Spectra of sunflower seed shells (1), Orange 16-sunflower seed shells (2) and Orange 16 dye (3) samples.

– the intensity and position of peaks assigned to characteristic functional groups from the sunflower seed shells were either minimized or slightly shifted after sorption of the reactive dye; these changes can be attributed to electrostatic

interactions between the positively charged functional groups of the sorbent (oxygen is easily protonated in acidic conditions) and the anionic dye;

– the FTIR spectra suggest that the adsorption mechanism could be considered as a combination of electrostatic interaction and physical sorption.

Kinetics study

It was seen from Fig. 8 that the kinetics of sorption of the tested dye onto sunflower seed shells is composed of two ranges: 1) an initial rapid range in which the sorption was fast on the external surface of the sorbent and the equilibrium was achieved rapidly (within 300 minutes) and 2) a slower second range during which the sorption process of Orange 16 reactive dye onto sunflower seed shells was completed.²⁵

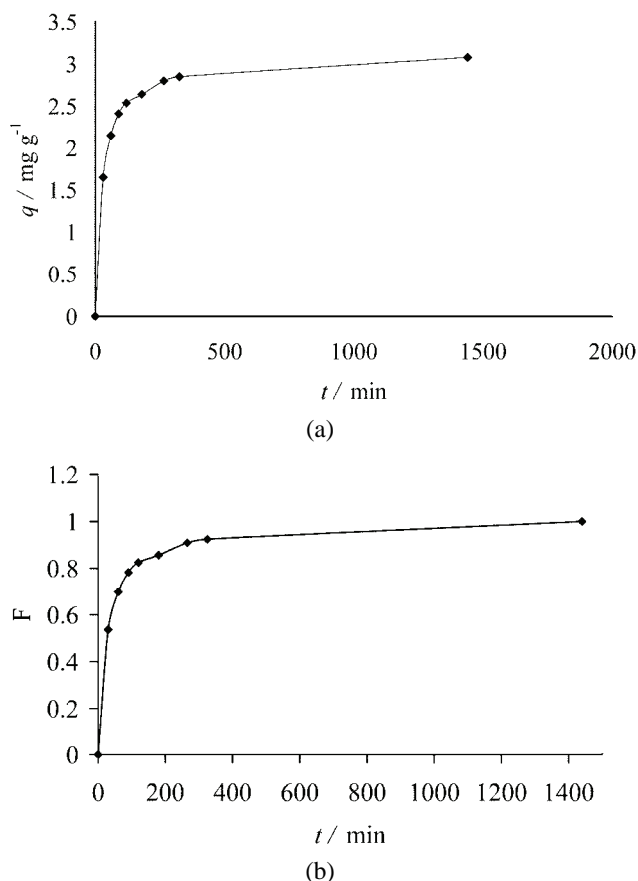


Fig. 8. Effect of contact time on the sorption capacity (a) of sunflower seed shells for Orange 16 fractional attainment of equilibrium (F) vs. time (b).
Conditions: pH 1.0, 12 g sorbent L⁻¹, 25 °C.

The constants of the pseudo first-order model (Lagergren, 1898) calculated from the linear plots of $\log (q_e - q)$ vs. t (Fig. 9) and the corresponding correlation coefficients are presented in Table III. The R^2 value of 0.861 suggested that the Lagergren model was not well fitted in the modelling of kinetic data; also, the estimated values of q_e were not in very good agreement with the experimental ones. The constants of the pseudo-second order model (Ho model, 1999) were determined from plots t/q vs. t (Fig. 9) and the corresponding values are presented in Table III.

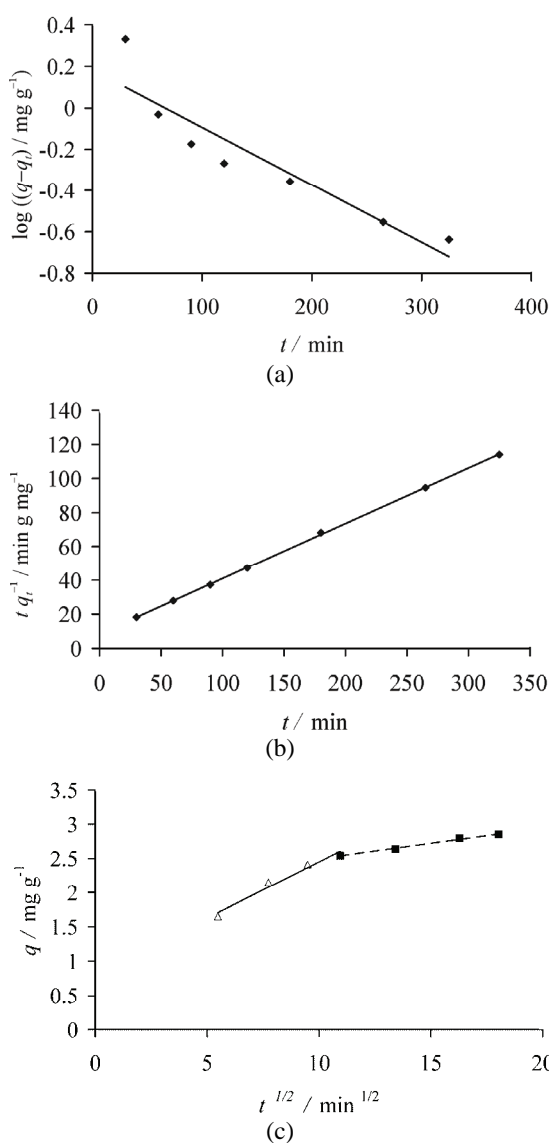


Fig. 9. Pseudo-first (a) and pseudo-second (b) order kinetics and intra-particle diffusion model (c) of Orange 16 reactive dye sorption onto sunflower seed shell: $T = 20\text{ }^{\circ}\text{C}$; $\text{pH} = 1.0$; $c_0 = 49.4\text{ mg L}^{-1}$; $12\text{ g sorbent L}^{-1}$.

TABLE III. The kinetic parameters of the sorption process of Orange 16 reactive dye onto sunflower seed shells

Kinetic model	Parameter	Value
Lagergren model – pseudo-first kinetic model	k_1 / min^{-1}	0.00645
	$q_0 / \text{mg g}^{-1}$	1.529
	R^2	0.861
Ho model – pseudo-second kinetic model	$k_2 / \text{g mg}^{-1} \cdot \text{min}^{-1}$	0.0105
	$h / \text{mg g}^{-1} \cdot \text{min}^{-1}$	0.1191
	$q_0 / \text{mg g}^{-1}$	3.07
	R^2	0.9998
Intra-particle diffusion model	$k_{p1} / \text{mg g}^{-1} \text{min}^{-0.5}$	0.1643
	R_1^2	0.9684
	$k_{p2} / \text{mg g}^{-1} \text{min}^{-0.5}$	0.0456
	R_2^2	0.9903

The extremely high value of the correlation coefficient (Table III) shows a good compliance of the data with the pseudo-second order kinetic model and suggests that chemical sorption instead of mass transfer may be the rate-limiting step for the sorption process. It can be seen in Fig. 9 that the regression does not pass through the origin, which suggests that intraparticle diffusion is not the only rate-limiting step.

It can be observed in Fig. 9c that, after saturation of the surface (within the first 120 min), the data fit a linear equation of the form q vs. $t^{0.5}$ ($R_2^2 > R_1^2$), indicating diffusion of sorbate species through the internal porous structure of the sunflower seed shell.

It can be concluded that the sorption of Orange 16 reactive dye onto sunflower seed shell is a complex process and both surface sorption and intraparticle diffusion contributes to the rate limiting steps.

CONCLUSIONS

Sunflower seed shell as a waste material can be considered an effective sorbent for the removal of Orange 16 reactive dye from aqueous solutions at pH 1.0.

The sorption of reactive dye onto sunflower seed shell is dependent on the initial solution pH, the dose of sunflower seed shell, the dye concentration and temperature. The best pH value was 1 for the sorption of the tested anionic dye. The sorption of dye increases with increasing of the sunflower seed shell dose, dye concentration and temperature.

The experimental data were analyzed using Freundlich, Langmuir, Dubinin–Radushkevich and Tempkin models. The Langmuir isotherm model characterized the equilibrium sorption data the best; the monolayer sorption capacities were 21.7 and 22.1 mg g^{-1} at 25 and 45 °C, respectively. The value of sorption energy determined by the DR model suggested a combined mechanism of phy-

sical sorption and electrostatic interactions between sorbent surface and the dye molecules.

The values of thermodynamic parameters suggest a feasible, spontaneous and endothermic sorption process between the surface of the sorbent and the dye molecules.

The kinetic of the reactive dye sorption onto sunflower seed shell was found to follow a pseudo-second-order rate equation. The Orange 16 reactive dye sorption onto sunflower seed shell is a complex process and both chemical surface sorption and intraparticle diffusion contribute to the rate-limiting step.

A comparison between the obtained values of the maximum sorption capacity of the sunflower seed shell for reactive dye removal with those reported in literature for other ligno–cellulose sorbents (Table I) confirms the conclusion that this material has a good sorption capacity and can be used for the treatment of coloured wastewaters or effluents containing moderate amount of dye.

ИЗВОД

УКЛАЊАЊЕ РЕАКТИВНЕ БОЈЕ ОРАНЖ 16 ИЗ ВОДЕНОГ РАСТВОРА ОТПАДНИМ ЉУСКАМА СУНЦОКРЕТА

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У овом раду испитана је употреба агроиндустријског отпада у виду љуски сунцокрета као сорбента за уклањање реактивне боје Оранж 16 из водених средина. Изведени су шаржни експерименти у функцији рН, дозе сорбента, концентрације боје, температуре и времена контакта. Процент уклоњене боје увећава се са растом дозе сорбента и температуре воденог раствора, а опада са порастом концентрације боје: потребно време контакта је пет часова. Коришћене су адсорпционе изотерме Freundlich, Langmuir, Dubinin–Radushkevich и Tempkin за описивање података о сорпционој равнотежи и за одређивање одговарајућих изотермских константи. Такође су одређени термодинамички параметри (ΔG , ΔH и ΔS), који су указали на то да је сорпција ове боје на љускама сунцокрета спонтан и ендотермички процес вођен ентропијом. Кинетички подаци су тестирани моделима псеудопрвог, псеудодругог реда и моделом интрачестичне дифузије. Резултати кинетичког проучавања указују на то да је сорпција Оранж 16 на љускама сунцокрета сложен процес, у којем ступњу ограничавања брзине доприносе и површинска хемисорпција и интрачестична дифузија. Стога, љуска сунцокрета може бити обећавајући јефтин сорбент за обезбојавање водених раствора или ефлуената.

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