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Sorption of reactive dyes from aqueous media using the lavender waste as biosorbent

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ABSTRACT

The sorption potential of lavender wastes for the removal of dye (i.e., reactive Orange 16 dye) from aqueous media has been studied. The wastes, which resulted from the process of obtaining lavender oil by steam distillation, were used for the dye sorption from aqueous solution in a batch system. It was studied the influence of some operational parameters (i.e., pH, temperature, contact time, biosorbent dose, dye concentration) on the sorption process efficiency. The experimental data were modeled using Freundlich, Langmuir (I and II) and Dubinin–Radushkevich adsorption isotherm models and the results underline that the equilibrium data were best fitted by Langmuir I isotherm with a biosorption capacity of about 26.38 mg/g at 20°C. Also, there were studied the thermodynamic and kinetic aspects of the sorption process using kinetic models following: pseudo I (Lagergren), pseudo II (model Ho), intraparticle diffusion model (Weber–Morris), film diffusion model (McKay) and Elovich model. The processed results concluded that the reactive dye sorption process onto lavender wastes was a physical–chemical process with good results at an ambient temperature around 20°C, for which the pseudo-second-order kinetic model is predominant, and the diffusion mechanism is a combination between film diffusion and intraparticle diffusion. Therefore, it is underlined the idea that lavender waste can be a promising adsorptive material for the sorption of reactive dyes from aqueous media.

Keywords: Aqueous medium; Lavender waste; Reactive dye removal; Sorption

1. Introduction

Sustainable production is one of the increasing challenges of the 21st century, responsible for the 'circular economy' concept implementation and new trends' development in many industrial, agriculture and commercial sectors. The importance of industrial and agricultural sustainability, achieved through the development of economically sound processes that minimize negative environmental impacts and reduce final waste production whilst improve the safety and economic viability, is continuously underlined and promoted. Industrial and agricultural waste utilization is an emerging field with great potential to drive sustainable production with diversified applications in wastewater treatment, polymer synthesis, extraction of useful compounds/chemicals and renewable energy. Thus, the use of agro-industrial wastes as (bio)adsorbent for wastewater treatment is of increasing interest and very attractive.

Special attention is accorded to adsorption/sorption/biosorption, generally defined as 'the accumulation of substances at an interface, outside or inside of the solid (bio) adsorbent matrix' which is mainly liquid–solid (bio-solid) interference/mass transfer in the case of water treatment and a recommendable treatment step for depollution of wastewaters in terms of the convenient relationship between the total cost involved and the treatment process efficiency.

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Commonly, dissolved substances tend to either accumulate at interfaces, and/or to disperse away from interfaces depending on their relative strength of attraction for themselves, or for the solvent [1–3]. As a result of accumulation at interfaces, it is lowering the surface tension of the solvent (water as universal solvent), permitting the wetting of the solid adsorbent surface, and concentration of the dissolved substance (sorbate) (e.g., different types of dyes) in closed proximity of the sorbent surface. The rate of adsorption will be proportional to the adsorbate concentration and usually described by the specific equilibrium isotherms, kinetic models, and thermodynamic issues.

The retaining of polluting species on the solid surface may occur by physisorption, chemisorption, biosorption, or combination of all these types. The difference lies in adsorbent origin as well process mechanism (active or passive) together with the nature of bonding between the pollutant and adsorbent (physical adsorption by van der Waals, hydrogen, hydrophobic or steric forces; chemisorption or biosorption by ion exchange, complexation, precipitation or mass transfer across the cell membrane, or solid surface of sorbent/inter- and/or intraparticle diffusion) [4].

If the flow rate is low, a simple manual batch process of sorption is most economic. For continuous industrial treatment (high flow rate), the sorption requires specific installations or reactors with various configurations (e.g., stirred reactors or basins, up-flow or down-flow packed bed reactors, fluidized bed reactors, rotating contactors, trickle filters, or air-lift reactors). Most of these installations are used in industrial effluent treatment applications for colored polluting species such as dyes [1,4]. In this context, certain agro-industrial wastes [5–8] maybe efficiently valorize as (bio)adsorbent in the treatment step of a few dye-containing wastewaters thus being solved two important concerns: (i) colored wastewater treatment for reducing its organic load and fulfillment of legal norms for discharge or reuse, and (ii) the valorization of certain agro-industrial wastes (possible after other useful compounds separation).

The aim of this paper is to investigate the sorptive properties of the lavender wastes, resulted after the process of steam distillation of the whole lavender plant for the extraction of volatile oils. To achieve this goal, it was necessary the physical–chemical characterization of the powder of lavender wastes, the study of some operational parameters influence on the sorption process efficiency for the reactive Orange 16 dye, and the analysis of all experimental data using different equilibrium isotherm and kinetic models in order to estimate the quantitative characteristic parameters, thermal effect, kinetic behavior and also to propose the mechanism of (bio)adsorption.

2. Materials and methods

2.1. Materials

2.1.1. (Bio)adsorbent

The material used as (bio)adsorbent is represented by lavender waste resulted from the process of obtaining lavender oil by steam distillation. The green plant introduced in the distillation installation comes from a lavender plantation of the region of Moldova. The vegetal material remaining after distillation was subjected to free drying in the atmosphere, then crushed, ground (mortared) and purified by extraction with 96% ethyl alcohol.

2.1.2. Adsorbate

The Orange 16 (O16), a reactive dye (MW = 617.54 g/mol, λ_{max} = 495 nm) with chemical structure shown in Fig. 1, was selected as the chemical pollutant model of aqueous system for this study. Stock solution (with a concentration of 716 mg dye/L) was prepared from a commercial salty form of the dye (salt of analytical reagent grade) and distilled water; the working solutions were obtained from the stock solution by appropriate dilution with distilled water.

2.2. (Bio)adsorption methodology

The (bio)adsorption equilibrium studies were done using 50 mL-Erlenmeyer flasks in which were contacted amounts of 0.06 g (2.4 g/L) of lavender waste powder with 25 mL of dye solutions with different initial known concentrations (14.32–229.2 mg/L) and different pH values adjusted with the help 1 N HCl solution, at a constant selected temperature (5°C, 20°C, 50°C, in a thermostatic oven). The phase contact time was selected differently for the equilibrium study and for the kinetic study. After reaching the equilibrium times, the dye concentration in the solution was spectrophotometrically determined using a JK-VS-721N VIS spectrophotometer, at a maximum dye wavelength of 560 nm.

The (bio)adsorption capacity of the waste vegetal material was estimated using the amount of adsorbed dye (q, mg of dye/g of lavender waste) calculated as follows:

$$q = \frac{C_0 - C}{G} \cdot V \tag{1}$$

where C_0 and C are the initial and the equilibrium (residual) concentration of dye in solution (mg/L), G is the amount of lavender waste powder (g) and V is the volume of initial dye solution (L).

The equilibrium data were analyzed using three of the most known adsorption equilibrium models (Freundlich, Langmuir and Dubinin–Radushkevich) from the scientific literature. Their characteristics are presented in Table 1 [9].

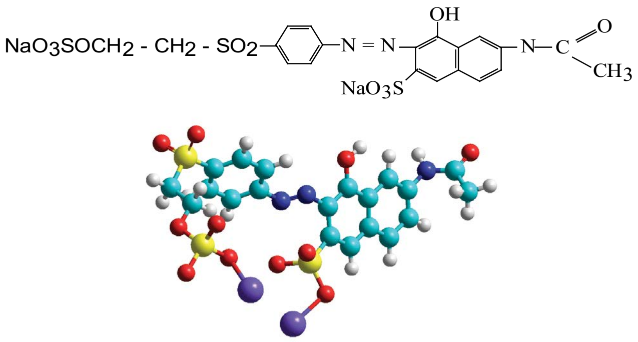
2.3. Thermodynamic of the adsorption process

The thermodynamic parameters were determined using Langmuir equilibrium constant and Eqs. (2) and (3) [10]:

$$\Delta G = -RT \ln K_L \tag{2}$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3}$$

where ΔG° is the free energy (kJ/mol), ΔH° is the process enthalpy (kJ/mol) and ΔS° is the adsorption entropy changes (kJ/mol K), R is the universal gas constant (8.314 J/mol K), T is the absolute temperature of the solution (K) and K_L is the value of Langmuir constant (L/mol).



Orange 16 C.I. 18097; Reactive anionic dye; λ_{max} = 495 nm; Concentration of the stock solution = 716 mg dye /L

Fig. 1. Reactive Orange 16 dye (C.I. 18097).

Table 1
Selected adsorption isotherm models

Adsorption isotherm model with their nonlinear and linear equation	Characteristics parameters
Freundlich – considers the heterogeneity of the surface and the exponential distribution of the active sites of the sorbent $q = K_F \cdot C^{1/n};\ \log q = \log K_F + \frac{1}{n}\log C$	K_F and $1/n$ – constants related to the adsorption capacity and intensity (efficiency), respectively; favorable adsorption corresponds to a value of $1 < n < 10$
Langmuir – considers the maximum sorption corresponding to a monolayer of molecules on the surface of the adsorbent, containing a finite number of equivalent energy sites $q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}$ $L_1 : \frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \cdot q_0} \cdot \frac{1}{C};\ L_2 : \frac{C}{q} = \frac{1}{q_0 \cdot K_L} + \frac{C}{q_0}$	q_0 is the maximum amount of adsorbed solute (mg/g) and K_L is the constant related to the binding energy of adsorbate (L/mg)
Dubinin–Radushkevich – allows the appreciation of the nature of the adsorption process, which can be physical or chemical, depending on the value of the adsorption energy, E: if $E < 8$ kJ/mol, it is characteristic of the physical sorption mechanism, and E values between 8 and 16 kJ/mol indicate an ion-exchange mechanism $q = q_0 \exp\left(-B \cdot \varepsilon^2\right);\ \ln q = \ln q_0 - B\varepsilon^2$ $\varepsilon = RT \ln\left(1 + \frac{1}{C}\right);\ E = \frac{1}{\sqrt{2B}}$	q_D is the maximum adsorption capacity (mg/g); B is the activity coefficient related to mean adsorption energy; ε is the Polanyi potential and E is the mean free energy of adsorption (kJ/mol)

2.4. Kinetic study

The extent of adsorption was expressed by the fractional attainment of equilibrium, F:

$$F = \frac{q_t}{q} \tag{4}$$

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

3. Results and discussion

3.1. Preliminary preparation of lavender waste and their physical–chemical characterization

The material (plant with stem, leaves and flowers) dried in a fresh air atmosphere was chopped and then crushed using a mechanic mill. The resulting powder was stored in a closed container. It was subsequently subjected to the purification of traces of extractable organic compounds by extraction with 96% ethyl alcohol. It was worked in a Soxhlet extraction installation respecting the solid: liquid ratio of 1:10 and a reflux time of 2 h. The spent solid was dried freely in the air for 2 d at room temperature of around 20°C, after which it was stored for further characterization and (bio)adsorption studies development. For the dry material were determined:

- the humidity using a KERN thermobalance;
- the ash content by calcination in the oven at T = 500°C for 5 h;
- the holocellulose content by treating the lavender waste sample with glacial acetic acid and sodium chlorite and

keeping the mixture in a water bath at T = 70°C for 2–3 h until the lavender turns white.

- the lignin content using Klason–Komarov method;
- the cellulose content by treating the lavender waste sample with a mixture of HNO_3: $CH_3–CH_2–OH$ (v/v, volume ratio 1:5) and distilled water. The mixture was kept on a water bath for 2 h at T = 50°C, then filtered and left to dry in the oven for 4 h.

The results obtained are listed in Table 2.

3.2. Effect of the main physical–chemical operating parameters on dye (bio)adsorption

The study of some physical–chemical operating parameters' influences on the (bio)adsorption process efficiency for Orange 16 dye onto lavender waste was done to establish the operating conditions in which a higher (bio)adsorption capacity is obtained. The main influences followed were those of pH, the biosorbent concentration, temperature, phases contact time and the initial dye concentration in the aqueous solution (Table 3).

The analysis of experimental data provided by Fig. 2 leads to the following conclusions:

- (Bio)adsorption is dependent on the pH value of the aqueous solution because it influences both the charge of the (bio)adsorbent surface, by ionizing the functional groups and the ionic form in which the dye is found in the solution (transformation of sulfonate groups into sodium salt). Thus, a maximum adsorption capacity is observed at the pH value in a strongly acidic media (1.1). The increase of pH leads to the decrease of (bio) adsorption capacity up to the pH value of 4 after which it remains constant in the basic environment for the dye (bio)adsorption, at a value of 7–8.

Table 2
Physical–chemical characterization of lavender waste

Humidity of raw material, %M	9.41
Humidity after extraction, %M	11.812
Ash, %	11.76
Holocellulose, %	59.62
Lignin, %	34.05
Cellulose, %	25.53

Table 3
Physical–chemical operating parameters influencing Orange 16 dye (bio)adsorption onto lavender waste

Parameters	Studied limits of variation
pH	1–10
T, °C	5°C, 20°C, 50°C
t	10 min–24 h
Sorbent dose, g/L	2.4–50.4
Initial dye concentration in solution, mg/L	14.32–229.2

The obtained results were systematized in Fig. 2a–d.

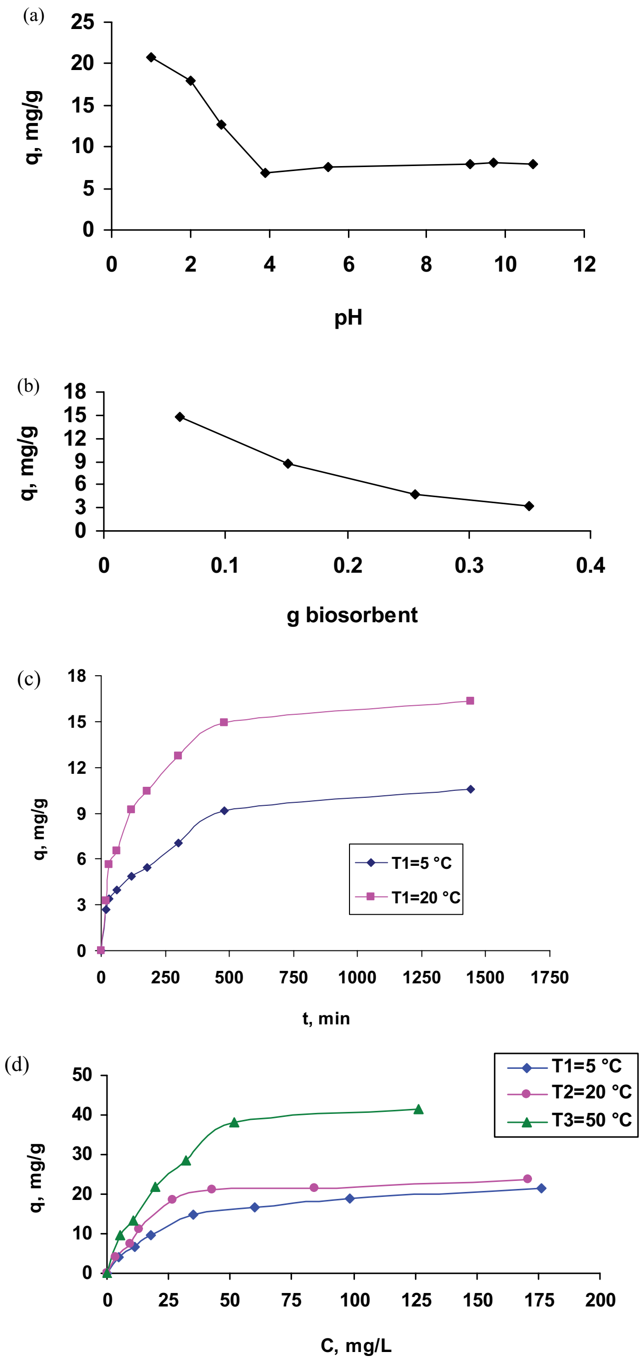


Fig. 2. Operating factors influencing the reactive Orange 16 dye adsorption onto lavender powder: the influence of (a) pH, (b) adsorbent dose, (c) contact time between phases, and (d) temperature and initial concentration of dye solution.

- Fig. 2b shows a decrease in the (bio)adsorption capacity from 14.75 to 3.181 mg/g as the amount of sorbent increases from 0.06 to 0.5 g/25 mL of dye solution.
- Fig. 2c shows an increase in the (bio)adsorption capacity with the contact time, an increase that is faster in the first 500 min regardless of temperature, and which follows a slower increase in aqueous solution as phases' contact time attained equilibrium.

- From Fig. 2d it is evident the increase of the (bio)adsorption capacity with the increase of the initial dye concentration in the aqueous solution until the saturation value of the sorbent is reached.

3.3. Study of (bio)adsorption equilibrium

The (bio)adsorption isotherm is represented by the amount of dye retained by the unit of biosorbent (q, mg/g) as a function of the dye concentration at equilibrium in the liquid phase (C, mg/L). These isotherms could be described by a lot of isotherm models in order to evaluate the quantitative characteristic parameters and to acquire preliminary information about the involved mechanism.

The (bio)adsorption data with proposed isotherm models (characterized in Table 1) of reactive Orange 16 dye on the powder of lavender wastes are presented in Figs. 2d and 3.

The characteristic parameters for each adsorption model (Freundlich, Langmuir I or II and Dubinin–Radushkevich), calculated from the intercepts and slopes of the linear plots (Fig. 4) are summarized in Table 3. In order to appreciate which model describes better the (bio)adsorption process of reactive Orange 16 dye onto lavender wastes, the selection was performed based on the value of the correlation coefficients, R^2.

Analyzing the data presented in Table 4, the next conclusions may be issued:

- The values of Freundlich parameters, K_F and n increase with increasing the temperature, showing that the (bio)adsorption process is favorable at relatively high temperature;
- The values of the correlation coefficients higher than 0.98 show that the Langmuir model was more suitable to describe the (bio)adsorption process. Although the two Langmuir models have comparable results, taking into account the correlation coefficient R^2 model I is best suited than model II.
- The values obtained for the maximum (bio)adsorption capacity, from Langmuir I model (q_0, mg/g), increase with increasing the temperature, showing that the (bio)adsorption process can be endothermic, favored by relatively high temperature.

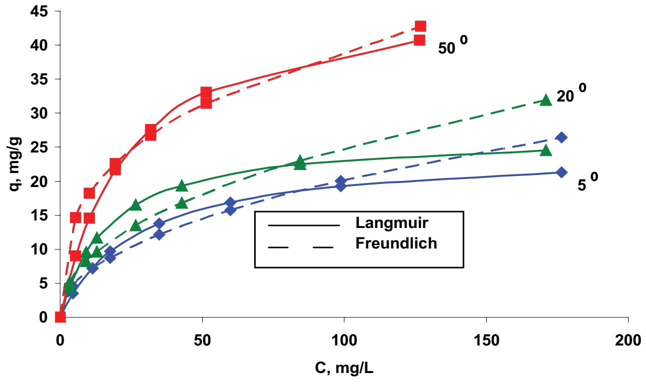


Fig. 3. Modelled isotherms of Orange 16 dye (bio)adsorption onto powder of lavender waste. Conditions: pH = 1.1; contact time = 24 h; bioadsorbent concentration = 2.4 g/L.

Table 4
Quantitative characteristic parameters for the anionic Orange 16 dye (bio)adsorption on powder of lavender waste

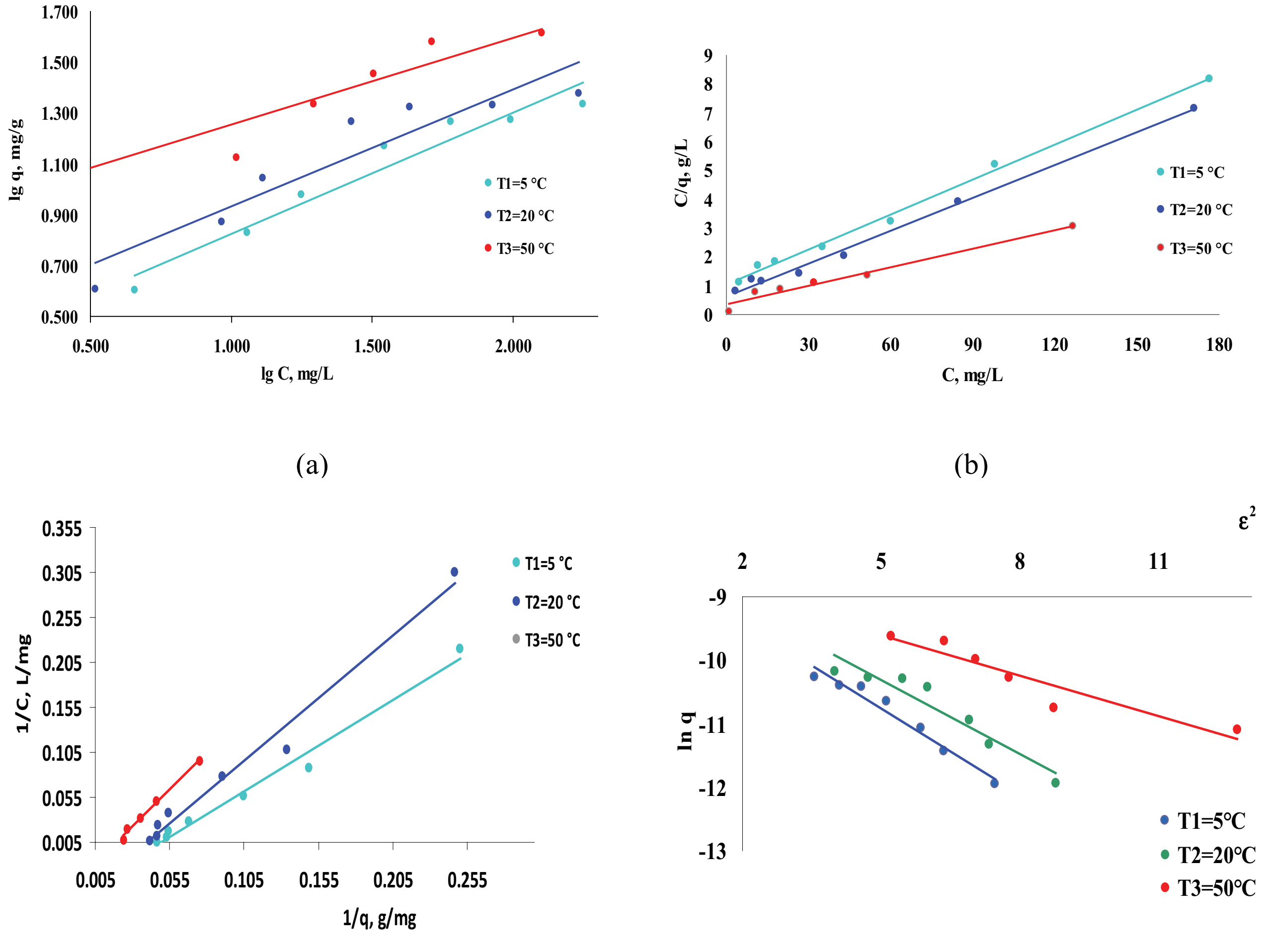
Isotherms	Temperatures		
	T_1 = 278 K	T_2 = 293 K	T_3 = 323 K
Freundlich			
K_F	2.23	2.95	8.17
n	2.09	2.16	2.92
R^2	0.942	0.88	0.9092
Langmuir I, $C = f(C/q)$			
K_L	0.03675	0.0592	0.0413
q	24.57	26.38	50.25
R^2	0.9965	0.9946	0.9907
Langmuir II, $1/q = f(1/C)$			
K_L	0.0481	0.0526	0.0426
q	21.645	26.954	48.54
R^2	0.9854	0.9828	0.9821
Dubinin–Radushkevich			
β	0.0045	0.0039	0.0021
q, mg/g	126.23	144.604	121.025
E, kJ/mol	10.541	11.323	15.430
R^2	0.9621	0.9125	0.8868

- The mean free adsorption energy, E, calculated by Dubinin–Radushkevich equation, was useful to estimate the nature of the adsorption process (physical or chemical) [11]. The obtained values in the range 10.5–15.4 kL/mol indicate a potential ion-exchange mechanism involved in Orange 16 dye (bio)adsorption onto lavender wastes.
- Also, the values of the (bio)adsorption capacity in the Dubinin–Radushkevich equation, q_0 (represents the total specific meso- and macropore volume of the biosorbent, mg/g), are much larger than q_0 value resulted using the Langmuir I isotherm model, for all three temperatures. This can be explained by taking into account the existence of the porous structure of the biosorbent.
- The value obtained for the (bio)adsorption capacity, according to the Langmuir I model is comparable with other adsorption capacities reported in the literature for different types of vegetal biomass for removal of dyes from aqueous medium (Table 5).

3.4. Study of (bio)adsorption thermodynamics

In order to establish the influence of temperature on the Orange 16 dye biosorption onto a powder of lavender waste, and to obtain other information about the nature of the sorption process, the thermodynamic parameters were calculated (Table 6) from the values of Langmuir constant, K_L (L/mol), and Eqs. (2) and (3) [16,17].

It is known that the interaction forces between biosorbent and adsorbate determine two types of adsorption



(a) (b)

(c) (d)

Fig. 4. Linearized form of Freundlich (a), Langmuir I (b), Langmuir II (c), and Dubinin–Radushkevich (d) plots for the anionic Orange 16 dye (bio)adsorption on the powder of lavender wastes. Conditions: pH = 1.1; contact time = 24 h; biosorbent dose = 2.4 g/L.

Table 5
Some applications of biomass as adsorbents in removal of dyes

Biosorbent	Dye	Biosorption capacity, mg/g	Ref.
Chia seeds (after oil extraction)	Reactive Yellow B2R	76.3359	[12]
Banana/cucumber/potato peels	Methylene blue	211.9/107.2/179.9	[13]
	Orange G	20.9/23.6/40.5	
Magnetic pectin–*Chlorella vulgaris*	Methylene blue	175.66	[14]
	Methyl orange	109.11	
	Toluidine blue O	227.05	
	Crystal violet	196.21	
	Safranin O	287.62	
	Malachite green	247.23	
Yeast slurry from brewery	Reactive Red 239	152.9	[15]
	Reactive Black B	162.7	
	Direct Blue 85	139.2	
Powder of lavender wastes	Orange 16	26.385	This study

characterized by different values of thermodynamic parameters [18]:

- physical, determined by weak forces and characterized by ΔH value no higher than 4.2 kJ/mol and ΔG values lower than –16 kJ/mol;
- chemical, because of the action of forces much stronger than those involved in physical process, and characterized by ΔH value higher than 21 kJ/mol and ΔG higher than 20 kJ/mol.

Analyzing the data from Table 6, leads to the following ideas:

- The negative values of Gibbs free energy, $\Delta G°$ indicated that the anionic dye sorption on studied sorbent is a spontaneous process. According to the information from the literature ($\Delta G°$ between –20 and 0 kJ/mol indicates a potential mechanism of physical adsorption), the calculated values of $\Delta G°$ suggest a potential physical mechanism for the studied biosorption process.
- The negative value of biosorption enthalpy ($\Delta H°$) calculated from the slope of linear dependence $\ln K_L$ vs. $1/T$ suggests the exothermic nature of dye biosorption. But the value of $\Delta H°$ is insufficient for chemical sorption (which should be in the range of –40 to –800 kJ/mol [16]). Additional information in this area indicates that both physical and chemical interactions can be involved in the (bio)adsorption process on a solid surface, but the energy needed is different (therefore, for physical bondings as Van der Waals: 4–10 kJ/mol, hydrophobic bonding: 5 kJ/mol, coordination bonding: 40 kJ/mol, dipole–dipole bondings: 2–29 kJ/mol and, in the case of chemical bondings, the energy must be >60 kJ/mol [17]). Taking into account all these data and the obtained value for E energy (Table 2) in the Orange 16 dye sorption process onto biosorbent based on the powder of lavender waste it could be suggested that the mechanism of adsorption is a combination of physical than chemical binding forces.

3.5. Study of phases contact time influence on biosorption process

The study of phases contact time onto the (bio)adsorption capacity of reactive Orange 16 dye retained on lavender waste powder, allows to establish the minimal time required for the equilibrium attainment (Fig. 5), the time required to retain 50% of the amount of dye ($t^{1/2}$), but also to obtain some data necessary for the kinetic modeling of the (bio)adsorption process using series of kinetic models.

As can be seen from Fig. 5, in the case of the two temperatures at which the (bio)adsorption process was studied, the values of parameter F increase rapidly with the contact time, especially in the first 500 min, after which the (bio)adsorption rate decreases due to the occupation of most active centers on the surface of the sorbent, the biosorption process becoming slower. The minimal time required for optimal dye removal proved to be up to 500 min. Also, the half-life ($t^{1/2}$) decreases with increase of temperature from values around 180 min at 5°C to values around 110 min at 20°C. The obtained results confirmed the exothermic nature of the studied (bio)adsorption processes.

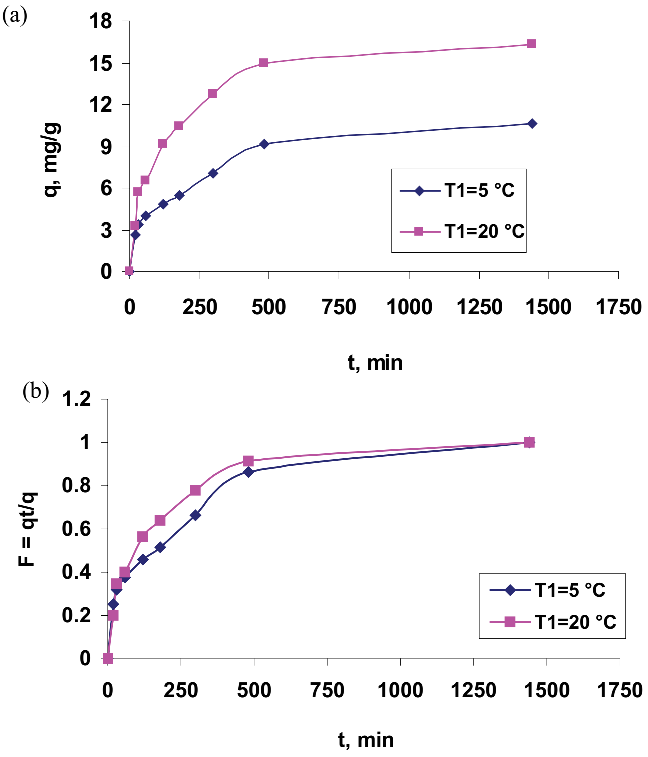


Fig. 5. Influence of phase contact time on retention of Orange 16 reactive dye onto lavender waste powder as biosorbent: (a) $q = f(t)$ and (b) $F = f(t)$. Conditions: C_0 = 85.92 mg/L; pH = 1.1; T = 20°C.

3.6. Kinetic modeling of the (bio)adsorption process

It is well known that in the (bio)adsorption process, the mechanism underlying its development/production may involve three distinct processes or a combination of them:

- diffusion of dye molecules through the wetted layer on the surface of the biosorbent (diffusion in the film);
- diffusion in the pores of the biosorbent (diffusion in pores or intraparticle diffusion);
- chemical reactions (ion exchange, complexation) that may occur between dye molecules and functional groups on the surface of the biosorbent.

The slowest rate of these processes determines the decisive stage of the (bio)adsorption process. The identification of the determining rate stage as well as of the mechanism involved in the achievement of the (bio)adsorption process is done by processing the experimental data using a series of kinetic models known and presented in the scientific literature (Table 7) [17–22]:

- kinetic model pseudo I (Lagergren)
- kinetic model pseudo II (model Ho)

- intraparticle diffusion model (Weber–Morris)
- film diffusion model (McKay)
- Elovich model

The kinetic parameters were calculated for each of all applied models considering the graphical representations of the basic equations, or their linearized forms (Fig. 5) and their values are systematized in Table 7. The assessment of the way in which the experimental data fit into a certain kinetic model was made by considering the value of the correlation coefficient, R^2.

From the analysis of the two kinetic models: pseudo-first-order and pseudo-second-order (Fig. 6a and Table 6) it is observed that:

- The plot ln($q - q_t$) vs. t representing the pseudo-first-order kinetic model (Lagergren) gives a straight line, but it does not pass through the origin of axes. Also,

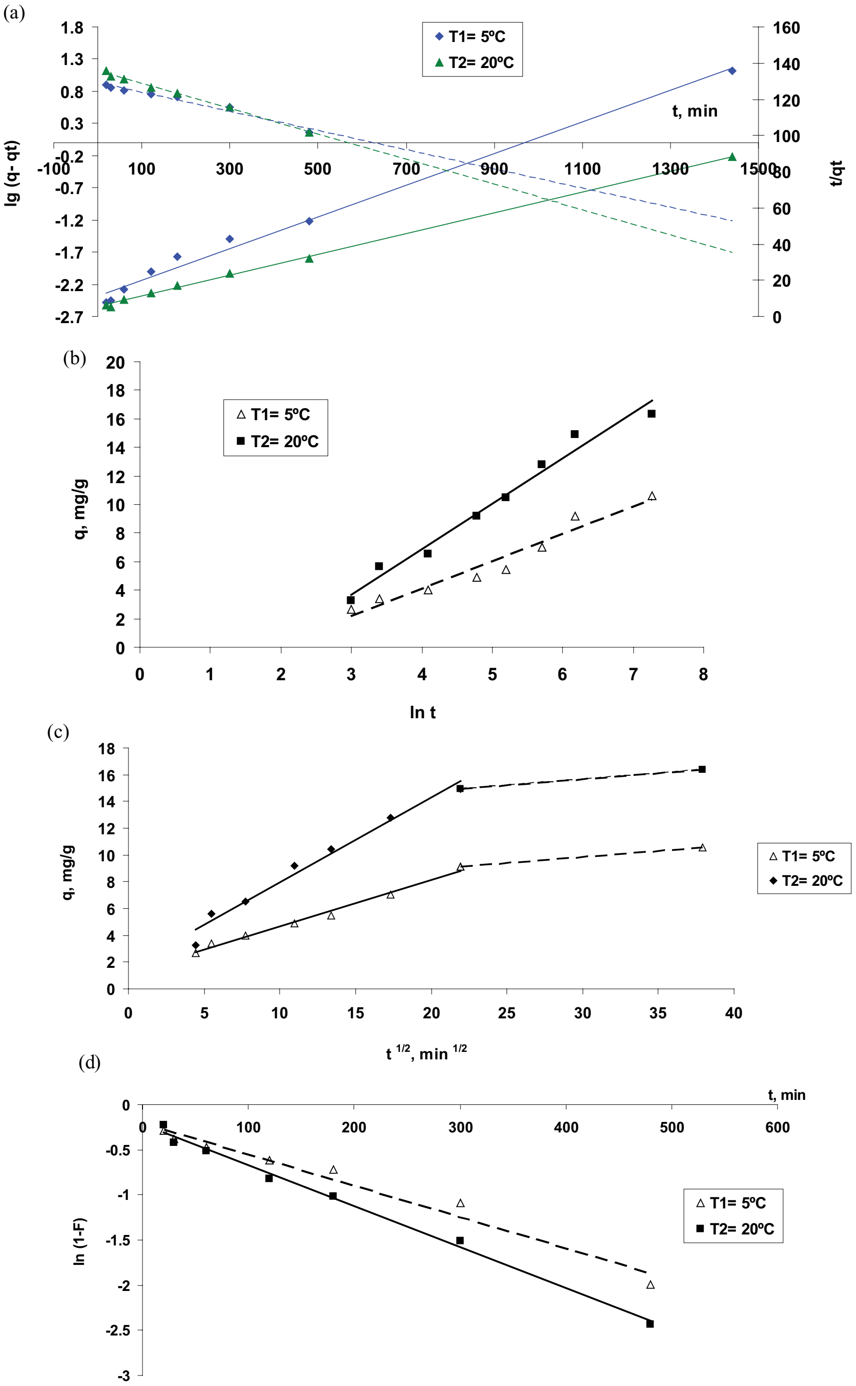


Fig. 6. Graphical representation of the kinetic models for Orange 16 dye (bio)adsorption onto lavender waste: (a) pseudo-first-order (Lagergren) and pseudo-second-order (Ho) models, (b) Elovich model, (c) Weber–Morris model, and (d) McKay model.

Table 6
Thermodynamic parameters of the Orange 16 dye sorption onto powder of lavender waste

Thermodynamic parameter	T_1 = 278 K	T_2 = 293 K	T_3 = 323 K
K_L, L/mol	23.467	36.435	35.817
ΔG, J/mol	–7,293.455	–8,758.709	–9,609.599
ΔH, J/mol		–6,199.999	
ΔS, J/mol K		49.512	

Table 7
The values of kinetic parameters of the (bio)adsorption process of reactive dye Orange 16 onto lavender wastes

Kinetic model	Temperature, K	
	278	293
Pseudo-first-order (Lagergren model)		
General equation $\frac{dq_t}{dt} = k_1\left(q - q_t\right)$ with their linearized form: $\log\left(q - q_t\right) = \log q - \frac{k_1}{2.303}t$		
k_1: rate constant of pseudo-first-order model, (min^{-1}); q_t and q (mg/g): the amounts of dye adsorbed at time t and at equilibrium (24 h), respectively		
k_1, min^{-1}	–0.003454	–0.004606
q_e, mg/g	8.602	13.119
R^2	0.9705	0.99936
Pseudo-second-order (Ho model)		
General equation $\frac{dq_t}{dt} = k_2\left(q - q_t\right)^2$ with their linearized form: $\frac{t}{q} = \frac{1}{k_2 q^2} + \frac{1}{q}t$		
k_2: rate constant of pseudo-second-order model, g/mg min; $k_2 q^2 = h$: initial biosorption rate, mg/g min		
k_2, g/mg min	6.8857×10^{-4}	6.044×10^{-4}
q_e, mg/g	11.402	17.422
R^2	0.9893	0.9985
Elovich model		
General equation $q_t = \frac{\ln(\alpha \cdot \beta)}{\beta} + \frac{1}{\beta}\ln t$		
α: constant about the initial biosorption rate (mg/g min); β: constant refers to the extent of surface coverage, and activation energy for chemisorption (g/mg)		
α, mg/g min	12.28	19.903
β, g/mg	0.524	0.3151
R^2	0.9486	0.9769
Intraparticle diffusion model (Weber–Morris model)		
General equation $q = k_d t^{1/2} + c$		
k_d: rate constant for intraparticle diffusion, mg/g min$^{1/2}$; c: intercept to the y-axis		
k_{d1}, mg/g min$^{0.5}$	0.6346	0.3485
C_1	1.5977	1.1755
R^2	0.9743	0.9858
k_{d2}, mg/g min$^{0.5}$	0.0897	0.09
C_2	12.955	7.1831
R^2	1	1
Film diffusion model, proposed by McKay		
General equation $\ln\left(1 - F\right) = K_F t$		
K_F: the rate constant for film diffusion, min^{-1}; F: the fractional attainment		
R^2	0.9707	0.9935

$q^*_{\text{calculated}}$ = 26.385 mg/g at 298 K (Table 4).

the experimental $q_{e,\exp}$ values are not in agreement with the calculated $q_{e,\text{calculated}}$ ones, and the k_1 constants have negative values. All of these findings suggest that the pseudo-first-order model is not well fitted for modeling the presented kinetic data.

- The linearity of plots of t/q_t vs. t, representing the pseudo-second-order kinetic model, the values of q calculated closer to the experimental ones, and the highest values of the correlation coefficient, R^2, suggested that the (bio)adsorption kinetics onto lavender waste follow a pseudo-second-order kinetic model, and the dye (bio)adsorption process can be controlled by chemical adsorption or chemisorption involving valence forces through sharing, or exchange of electrons and ions between the two phases involved.

In order to obtain more information about the mechanism of the (bio)adsorption process and about the rate that governed this process, it was applied the Elovich model (Fig. 6b). The R^2 values greater than 0.95 for the studied biosorption system (low concentration) suggest that the data fit well the Elovich equation. But the linear representation q vs. $\ln t$ does not intersect the origin of the axes, which confirms that chemisorption cannot be the only step that controls the studied biosorption process, and the diffusion processes remain the step that can control the dye adsorption onto the lavender waste powder.

All these data obtained so far lead to the conclusion that the biosorption rate is governed by either wetted phase mass transport, or by intraparticle mass transport. Thus, in order to obtain more detailed information about the diffusion mechanism, the kinetic results were analyzed by the intraparticle diffusion model (by Weber–Morris) and film diffusion model (by McKay) [19,23].

The lines of graphical representation (Weber–Morris model) from Fig. 6c are linear, then intra-particle diffusion occurs, but none passing through the origins, which suggests the hypothesis that both diffusion mechanisms (intra-particle and film) are involved in the sorption processes, and maybe the rate-determining step. The multilinearity of the plots indicates that two or more steps influence the biosorption process [19,23]. The first part could be often associated with the film diffusion (external mass transfer) [21], while the second linear part indicates the intra-particle diffusion (into the porous structure of the biosorbent) [24]. The graphical representation of the McKay model (Fig. 6d) suggests that film diffusion could be involved in the biosorption process because the plot $\ln(1-F)$ vs. t is linear, but it is not the rate-limiting step because the line passes not through the origin. This behavior is available for both temperatures.

Summarizing all performed results, it was underlined that the studied biosorption process proceeded through a predominant mechanism of diffusion: film diffusion complemented by intraparticle diffusion.

4. Conclusions

The results of this study show that the tested residual biomass represented by the lavender wastes could be considered as a potential biosorbent for the removal of Orange 16 reactive dye from aqueous solutions at pH 1.1 in the concentration of 2.4 g/L.

The equilibrium biosorption data were analyzed by Freundlich, Langmuir, and Dubinin–Radushkevich isotherm adsorption models, and are better described by Langmuir I isotherm model. The most important values obtained were the biosorption capacities of about 26.8 mg/g at 20°C and the free energy of sorption (E, kJ/mol) with the values in the range of 10.5–15.4 which revealed a physical mechanism for the reactive anionic dye biosorption onto lavender wastes. This observation was confirmed also, by the values of the thermodynamic parameters (ΔH, kJ/mol) and by the kinetic study. The values of thermodynamic parameters confirm also, the feasibility and the exothermic behavior of the biosorption process.

The results obtained in this paper indicate a new direction of recovery of lavender waste resulting from the extraction of volatile oils by steam distillation. The waste loaded with the dye could be introduced later in anaerobic or aerobic degradation processes in the production of soil amendment, or energy valorization.

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