

AGRICULTURAL WASTE CORN COB AS A SORBENT FOR
REMOVING REACTIVE DYE ORANGE 16: EQUILIBRIUM AND
KINETIC STUDY

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Received March 5, 2010

The potential of corn cob, a natural low-cost lignocellulosic material, was investigated for the removal of reactive dye Orange 16 from an aqueous solution. Sorption isotherms were determined at 3 temperatures (5, 18 and 45 °C), in solutions with initial dye concentrations in the 37.05-370.5 mg L⁻¹ range. The equilibrium data were analyzed using Langmuir, Freundlich, Dubinin-Radushkevich and Tempkin isotherm models. The sorption equilibrium process was described well by the Langmuir isotherm model. According to the Langmuir isotherm, the maximum sorption capacity was estimated as 25.25 mg g⁻¹ (18 °C). The values of the mean free energy determined with the Dubinin-Radushkevich equation (9.713 kJ mol⁻¹ at 18 °C, as well as the thermodynamic parameters suggest that the mechanism of reactive dye sorption onto corn cob is a combination of electrostatic interactions and physical sorption. The kinetic data were studied in terms of pseudo-first and pseudo-second order kinetic models.

Keywords: corn cob, reactive dye Orange 16, sorption, equilibrium, kinetics, thermodynamic, aqueous medium

INTRODUCTION

Dye application processes produce wastewaters possessing unacceptable environmental risks. Many synthetic dyes are known as organic pollutants, with toxic effects for many life forms. Azo dyes are more toxic, due to their degradation products inducing toxic, carcinogenic or mutagenic effects. Also, the presence of dyes, even in low amounts, in water bodies has a negative aesthetic impact and obstructs light penetration and photosynthesis, which affects aquatic life.

Various techniques can be applied for the removal of different classes of dyes from industrial effluents, prior to their discharge into the environment, such as chemical precipitation, ion exchange, adsorption on activated carbon, coagulation-flocculation, advanced oxidation/reduction, along with the biological ones.¹⁻⁴ Many of these techniques,

even if very effective, can be expensive, due to their initial and operational high costs, generating sludge, requiring additional treatment and causing disposal problems.

Recently, sorption has become a subject of considerable interest, due to the advantages it provides, such as the possible utilization of different materials as adsorbents, cheap technological steps, easy maintenance, no special operational skills and local availability. Among the materials used as sorbents for dye removal, mention should be made of activated carbon, ion exchangers, polyamides, polyurethane foams, inorganic materials and, more recently, natural lignocellulosic materials, such as chitin and chitosan.⁵⁻¹⁰ The high cost of activated charcoal – the most commonly used sorbent – has redirected the researches towards cheaper and more available

materials with sorption properties as viable and agreed alternatives. Within this context, two types of “non-conventional” or “low-cost” materials: (i) industrial/agricultural/domestic wastes or industrial/agricultural by-products (ash, sludge, sawdust, textile fibers, mud, bark, straw, etc.), and (ii) natural materials (peat, seashell, algae, lignite, wood, etc.) were studied as possible sorbents for dye removal.^{2,11-17}

The main characteristic of the wastes from agricultural activities or agro-industrial processing is their large availability. Also, their use as sorbents involves minor treatments and low cost.^{18,19} Agricultural wastes are mainly of lignocellulosic nature (containing 35-55% cellulose, 25-35% hemicelluloses, 20-30% lignin, plus other structural components).²⁰ Due to their constituting polymers, porous structure and very high free-surface volume, lignocellulosic (plant-derived) resources, such as wood and agricultural wastes, show sorption characteristics for a wide range of solutes.

Corn cob, an agricultural waste product obtained from maize or corn, has become more and more important, and new uses,

such as the production of activated carbon,²¹ manufacture of biofuels²⁰ or as adsorbent for removing some pollutants,²⁰⁻²³ are developed each year.

The aim of this paper was to evaluate the potential of corn cob to remove the Orange 16 reactive dye from aqueous media as a function of initial dye concentration, temperature and contact time. Equilibrium sorption and kinetic data were analyzed through different models, to understand the possible sorption mechanism of the dye molecules on corn cob. To confirm the sorption mechanism, the FT-IR spectra were drawn and analyzed.

EXPERIMENTAL

Materials

The corn residues (corn cob) supplied by a local farmer (Romania) were air-dried, ground into small pieces, sieved (fractions with size < 800 μm being used) and stored at room temperature.

Reactive textile dye Orange 16 (Fig. 1, MW = 617.54, λ_{max} = 495 nm) was used as a commercial salt. Synthetic working solutions were prepared by appropriate dilution with bidistilled water of the stock solution (500 mg L⁻¹):

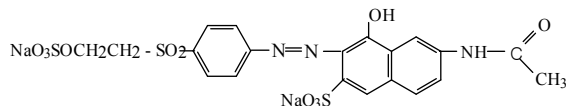


Figure 1: Structure of Orange 16 reactive dye

Equilibrium studies

Dye sorption on corn cob was studied in a batch system. A known volume of dye solution (25 mL) of varying initial concentrations (37.05-370.5 mg L⁻¹) was contacted with a fixed dose of sorbent (0.3 g) in 100 mL conical flasks, at constant temperature (thermostatic bath). The initial pH solution was adjusted to the required value (pH = 1), by adding 1N HCl solution, then measured with a Radelkis OP-271 pH/Ion analyzer. After reaching equilibrium (after 24 h), the sorbent was removed by filtration and the dye concentration in the filtrate was determined spectrophotometrically (UV-VIS Digital Spectrophotometer, model S 104D /WPA). The amount of dye sorbed by the corn cob, *q* (mg of dye/g of corn cob) was calculated with Equation (1):

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

where *C*₀ and *C* are the initial and equilibrium (residual) concentrations of dye in solution (mg

L⁻¹), *G* is the amount of sorbent (g) and *V* is the volume of the solution (L).

FTIR spectra of corn cob and corn cob with retained dye were recorded on solid samples in KBr pellets, by means of a FT-IR BioRad spectrometer FTS2000, with 4 cm⁻¹ resolution for 32 scans.

Kinetic studies

The effect of contact time on the sorption of reactive dye onto corn cob was determined by the “limited bath” technique. Samples of 0.3 g corn cob were added under stirring to a 25 mL solution of dye with pH = 1 and initial concentration of 49.4 mg/L. The temperature of the solutions was maintained at 25 °C. After different contact times (15-325 min), volumes of supernatant were taken for spectrophotometric measurements of the dye content. The extent of sorption was expressed by fractional attainment of equilibrium – Equation (2):

$$F = q_t/q \quad (2)$$

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

RESULTS AND DISCUSSION

Sorption equilibrium

In a previous work of ours,²⁴ batch sorption experiments were performed to establish the effect of the solution pH on the sorption of reactive dye Orange 16 onto corn cob. The results showed that sorption was strongly dependent on pH, the anionic dye being retained on the corn cob only from acidic solutions (maximum removal was attained at $\text{pH} = 1$), when the functional groups (phenolic hydroxyl and other hydroxyl groups) from the lignocellulosics are protonated and the sorbent surface is positively charged; the pH_{PZC} (zero point charge) of corn cob is of 6.5. Therefore, in the present study, equilibrium sorption experiments were carried out in solutions of initial $\text{pH} = 1$. The sorption isotherms of reactive dye Orange 16 on corn cob at 3 temperatures (5, 18 and 45 °C) are presented in Figure 2.

Over the studied dye concentration range (37.05-370.5 mg L^{-1}), the obtained isotherms were concave to the concentration axis, indicating an affinity for corn cob and a saturation trend at higher dye concentrations.

Monitoring the isotherms reveals a decrease in the value of adsorption, and a rise in temperature, indicating that the process of dye adsorption on adsorbents (alumina, Ulva and Sargassum) was exothermic in nature.

The relationship between the amount of dye sorbed and its equilibrium concentration was described by the 4 adsorption isotherm equations – the Freundlich, Langmuir, Dubinin-Radushkevich (DR) and Tempkin – the best-fit equilibrium model being established on the basis of the linear regression correlation coefficients, R^2 . The linear forms of the equations for the tested isotherm models are presented in Table 1.

The constant isotherms related to each adsorption model, calculated from the intercepts and slopes of the corresponding linear plots (Fig. 3), together with their correlation coefficients (R^2), are presented in Table 2.

To appreciate which model describes better the sorption process of reactive dye Orange 16 sorption onto corn cob, the values of the regression correlation coefficients R^2

were compared (Table 2). It may be observed that Langmuir isotherm models give a good fit to the sorption experimental data, at all studied temperatures. The K_L values, which reflect the binding energy between dye molecules and corn cob, decrease with a further increase in temperature, suggesting that the sorption of Orange dye on the corn cob is an exothermic process and that the mechanism was mainly physical adsorption, enhanced by a chemical effect.¹⁶

The saturation capacity (monolayer coverage), q_o , has a similar behaviour, probably due to a decreased surface activity. The value of sorption capacity at 18 °C was found to be of 25.25 mg dye g^{-1} corn cob, comparable with those reported in literature for some other wood waste materials used, like sorbents.²⁰⁻²³

For the Freundlich model, the graphical representation of a linearised equation gives a straight line with value n between 1 and 10, showing a favourable adsorption of Orange 16 dye by corn cob.

The Tempkin isotherm takes into account the sorbate species–sorbent interactions, assuming that the decrease in the sorption heat is linear rather than logarithmic, as implied in the Freundlich equation.^{28,29} The values of the correlation coefficients for the Tempkin isotherm model range between 0.9804 and 0.996 at all studied temperatures, confirming the better fit of equilibrium data, in comparison with the Freundlich isotherm model.

The sorption capacity in the DR equation, which may represent the total specific meso- and macro-pore volume of the sorbent, was of 169.006 mg g^{-1} (18 °C), much higher than the q_o value obtained using the Langmuir isotherm model, and indicating the porous structure of corn cob. The magnitude of the mean energy of sorption, E , is useful for estimating the mechanism of sorption: physical (1-8 kJ mol^{-1}), ion exchange (9-16 kJ mol^{-1}) or chemical (>16 kJ mol^{-1}).²⁸ The lower values (9.534/9.713/9.36 kJ mol^{-1}) of the mean free sorption energy determined with equation DR (Table 2) revealed that the adsorption of the anionic dye on corn cob involves electrostatic interactions, as well as physical adsorption, due to the van der Waals forces.

Thermodynamic parameters

To evaluate the effect of temperature on Orange 16 dye sorption upon corn cob, and

to understand the nature of sorption, the apparent thermodynamic parameters were determined,²⁵ (Table 3) using the values of the binding Langmuir constant, K_L ($L \text{ mol}^{-1}$), and Eqs. (3)-(4):

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

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

where ΔG is apparent free energy, ΔH apparent is enthalpy and ΔS apparent is entropy changes of sorption, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K).

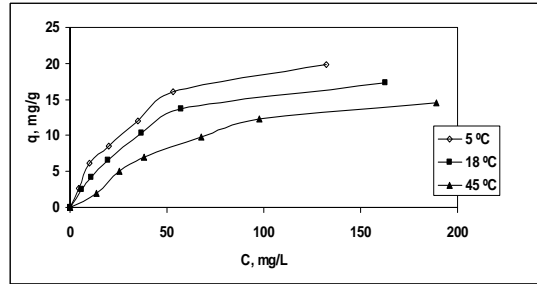


Figure 2: Sorption isotherms of reactive dye Orange 16 onto corn cob

Table 1
Mathematical forms and parameters of tested isotherm models

Sorption isotherm model	Linear form of equation	Isotherm parameters, significance	Ref.
Freundlich	$\lg q = \lg K_F + 1/n \lg C$	K_F – adsorption capacity n – adsorption intensity	25
Langmuir	$\frac{1}{q} = \frac{1}{q_0 \cdot K_L \cdot C} + \frac{1}{q_0}$	q_0 – saturation capacity K_L – binding (sorption) energy	25
Tempkin	$q = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C$	b_T – heat of sorption K_T – intensity of sorption (maximum binding energy)	26
Dubinin-Radushkevich	$\ln q = \ln q_0 - \beta_D \varepsilon^2$ $\varepsilon = RT \ln(1 + \frac{1}{C})$ $E = \frac{1}{\sqrt{-2\beta_D}}$	q_0 – the maximum amount sorbed β_D – sorption energy ε – Polanyi potential E – mean free energy of sorption	27

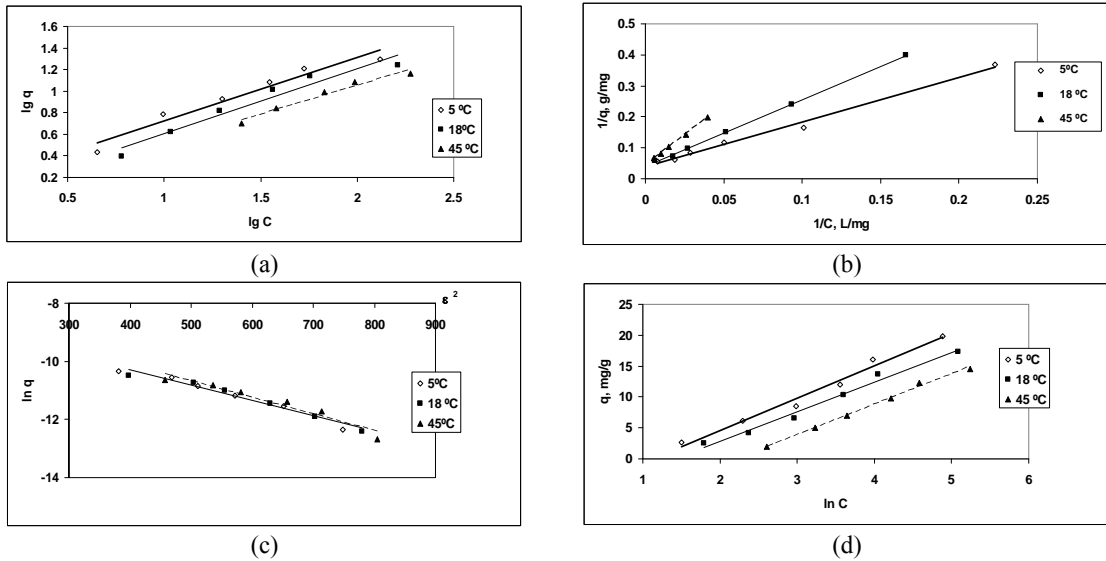


Figure 3: Freundlich (a), Langmuir (b), Dubinin-Radushkevich (c) and Tempkin (d) plots for sorption of reactive dye Orange 16 on corn cob at 3 temperatures

Table 2
Isotherm parameters for reactive dye Orange 16 sorption onto corn cob

Type of isotherm	T (K)		
	278	291	318
Freundlich			
K_F (mg/g)(L/mg) ^{1/n}	1.383	1.09	0.965
n	1.706	1.66	3.43
R ²	0.952	0.9485	0.9649
Langmuir			
q ₀ (mg/g)	26.11	25.25	21.98
K _L (L/mg)	0.0264	0.0183	0.0119
R ²	0.9915	0.9994	0.9984
Dubinin-Radushkevich (DR)			
q ₀ (mg/g)	186.76	169.006	242.314
β (mol ² /kJ)	0.0055	0.0053	0.0057
E (kJ/mol)	9.534	9.713	9.36
R ²	0.9696	0.9693	0.9305
Tempkin			
b _T (kJ/mol)	442.35	498.105	539.231
K _T (L/g)	0.327	0.246	0.1105
R ²	0.9804	0.9841	0.996

Table 3
Apparent thermodynamic constants of reactive dye Orange 16 sorption process onto corn cob

T (K)	K _L (L mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔH _s (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
278	16302.00	-22.343		
291	11300.25	-22.578	-14.324	28.853
318	7348.25	-23.535		

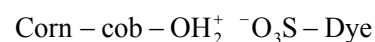
The negative values of the apparent free energy change (ΔG) indicate that reactive dye sorption on corn cob is spontaneous and thermodynamically feasible on the studied temperature range (278-318 K). The values of ΔG decrease with the increase in temperature, showing that the spontaneity of sorption is inversely proportional to temperature.³¹

The negative values of ΔH (-14.324 kJ mol⁻¹) suggest the exothermic nature of the sorption process of Orange 16 reactive dye onto corn cob.

The positive value of entropy change (ΔS) characterizes the increased randomness at the solid-solution interface during dye sorption and some structural changes in both sorbate and sorbent.³¹ The positive entropy reflects the release of high amounts of water molecules, due to the sorption of large hydrated anions onto corn cob sorbent, as well as the electrostatic interactions between the oppositely charged groups. It can be

suggested that the driving force of sorption is an entropy effect.

In addition, the magnitude of ΔH and ΔG gives a suggestion on the nature of sorption.³¹ Literature data³⁰⁻³⁴ show that physical sorption is characterized by values of ΔH no higher than 4.2 kJ mol⁻¹, and a ΔG value lower than 40 kJ mol⁻¹. According to the data from Table 3, sorption of Orange 16 dye on corn cob in acidic media is rather a physical adsorption, and not chemisorption. The forces involved in adsorption can range from weak van der Waals forces to electrostatic attractions between the ionized sulfonyl groups of the dye molecule and the positively charged surface of corn cob:



Infrared study of Orange 16 dye binding onto corn cob

More information on the mechanism of dye binding onto corn cob was obtained by

infrared analysis. The FTIR spectra of corn cob before and after sorption of reactive dye Orange 16 from aqueous solutions of pH = 1 are plotted in Figure 4.

The corn cob spectra present many overlapped bands, whose intensity depends on the origin and on the isolation method applied.

A comparison between the spectra of corn cob before and after loading with the Orange 16 dye, agreeing with literature data,³⁵ shows that:

- the occurrence of specific bands from 1710.86 and 1726.29 cm^{-1} suggests the formation of compounds of ionic association between lignin (an aromatic compound of the vegetable tissues) and reactive dye Orange 16;
- at an acidic pH value, due to the presence of the hydroxyl groups from the lateral chain, the lignin from corn cob can be converted into conjugated structures with deficit electron centre (δ^+) highlighted by the band at 704.02 cm^{-1} . Its disappearance from the corn cob-dye (line 2, Fig. 6) IR spectrum confirms the ionic bonds established between

corn cob and the sorbed dye (a charged organic molecule consisting of polar and non-polar regions).

The intensity and position of peaks assigned to the characteristic functional groups from corn cob were either minimized or slightly shifted after the sorption of the reactive dye; these changes can be attributed to the electrostatic interactions between the positively charged functional groups of the sorbent (oxygen being easily protonated under acidic conditions) and the anionic dye.

The FT-IR spectra suggest that the adsorption mechanism is a combination of electrostatic interaction and physical sorption.

Sorption kinetics study

The effect of contact time on the removal of Orange 16 reactive dye from a solution of pH = 1 and 49.4 mg L^{-1} initial concentration, by sorption onto corn cob, is showed in Figure 5. According to it, the time period required for maximum removal of the reactive dye was up to 350 min; however, the sorption half-time ($t_{1/2}$) was up to 25-30 min.

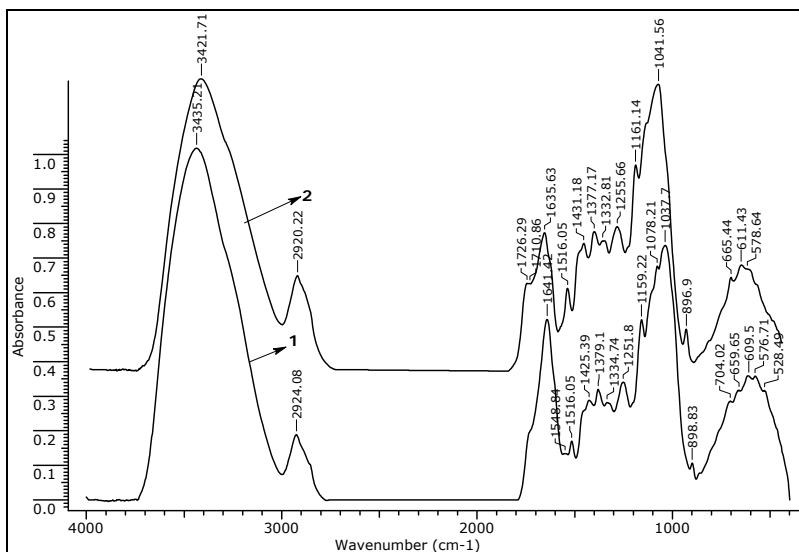


Figure 4: FT-IR spectra of corn cob (1) and orange corn cob (2) samples

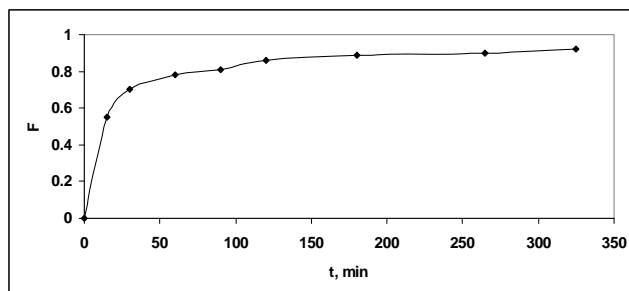


Figure 5: Fractional attainment of equilibrium (F) versus time for sorption of reactive dye Orange 16 on corn cob

The kinetic sorption data were processed to understand the dynamics of the sorption process in terms of the rate order, using two kinetic models, the pseudo-first order and the pseudo-second order kinetic model.²⁶

The pseudo first-order Lagergren model is usually expressed as:

$$\lg(q - q_t) = -\frac{k_1}{2.303} t + \lg q \quad (5)$$

where q and q_t are the amounts of sorbed dye (mg g^{-1}) at equilibrium (24 h) and at any time t (min), respectively, and k_1 is the Lagergren rate constant of the first-order sorption (min^{-1}). The constants of the model calculated from the linear plots of $\lg(q_e - q)$ vs. t (Fig. 6) and the corresponding correlation coefficients are presented in Table 5.

A R^2 value of 0.909 suggests that the Lagergren model is not better in modelling kinetic data; also, the estimated values of q_e do not agree very well with the experimental ones (3.126 mg g^{-1}).

The pseudo-second order model (Ho model) assumes that sorption follows a

second-order mechanism and that the rate limiting step may be chemical sorption, involving valence forces or covalent forces between sorbent and adsorbate.³⁶ The rate of pseudo-second order reaction is expressed by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{1}{q} \cdot t \quad (6)$$

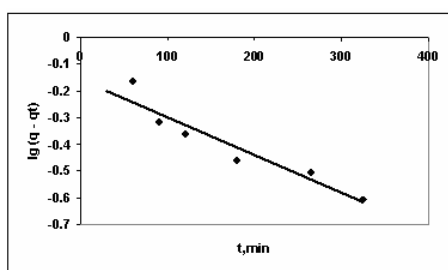
where k_2 is the rate constant of second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$) and $q^2 \cdot k_2 = h$ can be regarded as the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) as t approaches zero.

The constants of the model were determined from plots t/q vs. t (Fig. 6), the corresponding values being presented in Table 4.

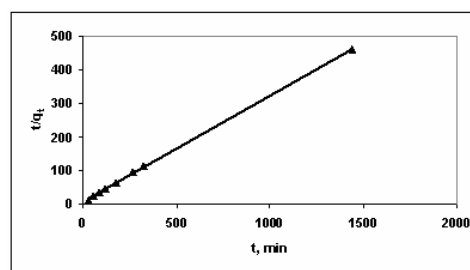
The extremely high correlation coefficient shows a good compliance with the pseudo-second order kinetic model, suggesting that chemical sorption, and not mass transfer, is the rate-limiting step for sorption.

Table 4
Kinetic parameters of reactive dye Orange 16 sorption on corn cob

Pseudo-first kinetic model			Pseudo-second kinetic model			
k_1 (min^{-1})	q_0 (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	h ($\text{mg g}^{-1} \text{min}^{-1}$)	q_0 (mg g^{-1})	R^2
0.00322	1.433	0.9095	0.0199	0.1538	2.78	0.9996



(a)



(b)

Figure 6: Applicability of pseudo-first (a) and pseudo-second (b) kinetic models to reactive dye Orange 16 sorption on corn cob; 49.4 mgL^{-1} , 25°C and $\text{pH} = 1$

CONCLUSIONS

The results of the study reveal that corn cob could be fruitfully used as a biosorbent for the removal of textile reactive dyes, such as Orange 16, from aqueous solutions of $\text{pH} = 1$.

The equilibrium sorption data were analyzed according to the Freundlich, Langmuir, Dubinin-Radushkevich and Tempkin isotherm models. The Langmuir isotherm represents best the equilibrium

sorption data; the monolayer sorption capacity of 25.25 mg g^{-1} was obtained at 18°C . The values of the apparent thermodynamic parameters confirm the feasibility of sorption and suggest an entropy-driven, exothermic sorption process. The sorption of reactive dye Orange 16 onto corn cob could be explained by the combined effects of the ion exchange interactions and physical adsorption, as confirmed by the values of the mean free sorption energy

calculated by the Dubinin-Raduskevich equation, of apparent thermodynamic parameters and of the FT-IR spectra.

The kinetic studies show a good agreement of the experimental data with the pseudo-second order model.

These results will be the starting point for further research, on other types of textile dyes, usually present in the industrial wastewater from textile chemical finishing processes.

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