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Valorization of food wastes as sorbent for dye retention from aqueous medium

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ABSTRACT

In this paper, batch removal of Brilliant Red HE-3B (BRed) and Methylene Blue (MB) dyes onto apple seeds powder was studied in order to evaluate the sorptive properties of this food waste. The experimental data equilibrium was analyzed using the Langmuir, Freundlich, and Dubinin–Radushkevich adsorption models. Results of the study reveal that the Langmuir model best describes the dyes sorption processes. The monolayer sorption capacity was established to be 66.225 mg/g BRed and, respectively, 26.316 mg/g MB at 25°C. The values of the mean free energy obtained from the Dubinin–Radushkevich model indicated a porous structure of the sorbents and suggest that physical sorption is the main sorption type involved in the studied processes. The values of the thermodynamic parameters (ΔG, ΔH, and ΔS) showed that sorption of tested dyes was feasible, spontaneous, and endothermic under examined conditions. The Fourier transforms infrared spectroscopy has been used to investigate the interaction between apple seeds powder and dyes. Environmental scanning electron microscopy technique was used to analyze the surface morphology of the sorbent before and after dyes sorption.

Keywords: Aqueous medium; Apple seeds; Brilliant Red HE-3B reactive dye; Methylene Blue cationic dye; Sorption equilibrium; Thermodynamic studies

1. Introduction

Apple—*Malus domestica* (*Rosaceae* family) is the most widely used fruit on earth. Apple can be consumed either fresh or as juice, sauce, cider, jam, marmalade, or chips (dehydrated fruit slices), ensuring the normal growth, development, and overall well-being of human body. Apple fruit is a real cocktail of antioxidants, phytonutrients, flavonoids (quercetin, epicatechin, and procyanidin B2) and polyphenols, vitamin-C and beta-carotene, B-complex vitamins (riboflavin, thiamin, and pyridoxine/vitamin B-6), as well as minerals (potassium, phosphorus, and calcium). Therefore, consumption of these fruits not

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only provides natural elements to a harmonious development of organism, but also prevents the absorption of dietary LDL or bad cholesterol in intestines. At the same time, it protects human body from harmful effects of free radicals and increases its resistance against various infectious agents. Moreover, vitamins found in apples act as co-factors for enzymes in metabolism, as well as in different synthetic functions inside the body, while the presence of potassium helps in controlling heart rate and blood pressure [1,2]. These compounds are distributed in different ratios in all parts of the fruit: pulp, bark, seeds, and skin. Taking into account these considerations, it appears that the industrial exploitation of all these components is necessary.

After industrial processing of apple fruits results large amounts of secondary products which if improperly used can turn into waste, hence valuable biologically active substances may be lost [3–8]. In this context, scientists focus on the development of advanced processing technologies for recovering and converting the apple components into useful products for human or animal consumption. A possibility to capitalize the byproducts resulted from food industry may consist in extraction of their active components that can be further used in cosmetics, pharmacy, and nutrition [3,5,6,9–11].

At the same time, the possibility to integrate the resulted waste from different manufacturing stages into different biodegradation processes (anaerobic digestion or/and aerobic processes) as compost or worm compost in order to obtain biofuel or amendment to improve soil fertility can be considered [5,7,12–15].

Due to their lignocellulosic compositions, the agro-industrial wastes generated in different technological phases were tested as materials with adsorptive properties toward some chemical pollutants (metal ions, organic compounds) found in industrial effluents and domestic sewage [13–18].

Sorptive removal of dyes from aqueous media is now a recognized method due to its numerous advantages: (a) increased processing sensibility and selectivity; (b) reduced matrix effects; (c) possibility of simultaneous pre-concentration; (d) possibility to be assessed properly, and (e) possibility to use a vast category of materials as sorbents for wastewater treatment, such as materials with ion exchange properties, activated charcoal, natural or synthetic zeolite, and lignocellulosic materials which are found in nature or result as secondary products from industrial or agricultural transformation, active or inactive biomass which is specially produced, or result from industrial fermentation technology (food and pharmaceutical industry) [19–21]. Natural lignocellulosic materials represent a category of sorbents with broad applications, [22–25] due to their characteristics, as they: (a) are non-pollutant (do not lead to toxic residues) and easy accessible materials; (b) have low price; (c) can be processed continuously; (d) are highly hydrophilic, a fact that determines the rapid kinetics of the sorption process; (e) exhibit tolerance on biological molecules and possibility of functionalization; (f) can be utilized in different shapes (particles of different sizes, fibers, filters, and textures), and also in the case when use of common sorbents is ineffective; and (g) possess high porosity and good mechanical resistance. These materials, used in native or modified forms [13–28,30] can be applied in batch and fixed bed column techniques [22–29] in order to study a mono or binary dyes aqueous system [13–29,31].

The main objective of this paper is to investigate the sorptive behavior of the apple seeds for the removal of anionic reactive dye Brilliant Red HE-3B (BRed) and cationic dye Methylene Blue (MB) from aqueous medium. The sorption equilibrium and thermodynamic were studied using different theoretical models in order to understand the process mechanism. The Fourier transforms infrared spectroscopy (FTIR) has been used to characterize the sorbent before and after loading the dyes in order to obtain additional information about possible ways to bind the dyes by the sorbent. Also the environmental scanning electron microscopy (ESEM) technique offers the possibility to examine the structure's morphology of the native sorbent and the material resulted after dyes loading.

2. Materials and methods

2.1. Materials

The experiments were carried out using apple seeds as sorbent, which is a waste from food industry. This material has been processed by drying at 90°C for 24 h, grinded and sieved to get final particles size of 1–2 mm. Main components in the structure of apple seeds are amygdalin (B17 vitamin), linoleic acid, oleic acid, and palmitic acid [32], which varies in different percentages depending on the apple species. The apple seeds have been previously processed for extraction of bioactive compounds by classical method of liquid–solid extraction using two solvents (n-hexan and methanol) accepted by pharmaceutical, cosmetics and food industries. The FTIR, UV–vis and fluorescence spectra analysis of extracts showed the complex composition of apple seeds. There have been observed various lipid fractions (represented by polycyclic unsaturated fatty acids, phospholipids, glycolipid, etc.), and a number of other organic components (phytosterols, tocopherols, carotenoids, etc.) [32]. All of these compounds alongside with lignocellulosic compounds from the sheath seeds contribute to sorptive properties (due to the characteristic functional groups) of the materials and increasing their ability to retain dye molecules by sorption.

The main characteristics of the selected commercial dyes are presented in Table 1.

2.2. Sorption methodology

The sorption experiments were performed in batch conditions, where samples of 0.05–0.1 g of apple seeds powder were contacted with 25 mL of aqueous dyes solutions of known initial concentration in Erlenmeyer flasks with capacity of 150 mL, placed in an oven at desired temperature. The initial pH solution was adjusted to the required value by using HCl 1 N or NaOH 1 N solutions using a Radelkis OP-271 pH/Ion analyzer. After a contact time of 24 h, the dyes concentrations in supernatant were spectrophotometrically determined with an UV-vis Digital Spectrophotometer, S 104D /WPA. The sorption capacity of the sorbent was evaluated by means of the amount of dye sorbed, Eq. (1):

$$q = \frac{C_0 - C}{G} \cdot V \text{ (mg of dye/g of sorbent)} \quad (1)$$

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

2.3. Error analysis

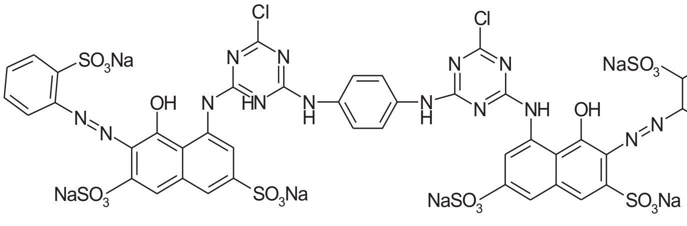
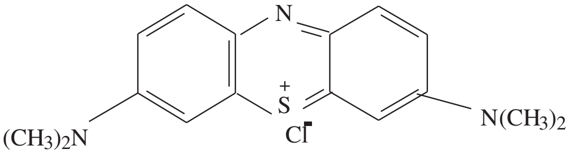
Transformation of non-linear isotherm equations to their linear forms is usually used to determine the quantitative parameters. This leads inevitably to some errors, which require analysis in order to evaluate the fit of equations to the experimental results. Although linear regression coefficient/coefficient of determination (R^2) is the most widely used error function in many studies, there are other complex error analysis methods in literature: sum of squares of the errors, standard deviation of relative errors, sum of absolute errors, average relative error, a hybrid error function, Marquardt's percent standard deviation, Spearman's correlation coefficient, and non-linear Chi-squared (χ^2) test which may be used to establish the proper equation [33–35]. Chi-square test (χ^2) and the residual root mean square error (RMSE) have been chosen for this study. The standard equations are written in the forms of Eqs. (2) and (3):

$$\chi^2 = \sum_{i=1}^{N} \frac{(q_{e,\exp} - q_{e,\text{calc}})^2}{q_{e,\text{calc}}} \quad (2)$$

$$\text{RMSE} = \sqrt{\frac{1}{N-2} \sum_{i=1}^{N} \frac{(q_{e,\exp} - q_{e,\text{calc}})^2}{q_{e,\text{calc}}}} \quad (3)$$

where $q_{e,\exp}$ and $q_{e,\text{calc}}$ represent the experimental and calculated values of sorption capacity (mg/g), and N is the number of experimental data.

Table 1
Characteristics of the selected dyes

Structure of the dyes	Characteristics
	Brilliant Red HE-3B; (Reactive Red 120); C.I. 25,810; Anionic, bifunctional reactive dye; MW = 1,463 g/mol; λ_{max} = 530 nm; and Concentration of the stock solution—500 mg/L
	Methylene Blue (Basic Blue 9); C.I. 52,015 Cationic, phenothiazine dye; MW =319.85 g/mol; λ_{max} = 660 nm; and Concentration of the stock solution—320 mg/L

Abbreviations: BRed—Brilliant Red HE-3B; MB—Methylene Blue.

2.4. Analytical methods for physicochemical characterization

2.4.1. Fourier transforms infrared spectroscopy

The FTIR spectra for the lignocellulosic material, the studied dyes, and the dyes attached to the sorbent were obtained using a Bruker Vertex 70 instrument. All the spectra were the results of 256 co-added scans at a resolution of 4 cm^{-1} in KBr pills, in the working range 400–4,000 cm^{-1}.

2.4.2. Environmental scanning electron microscopy

The structural characterization of the lignocellulosic sorbent powder, before and after dyes attaching, was performed by ESEM. The ESEM studies were performed on Quanta 200 instrument. Samples were fixed by means of colloidal silver on copper supports. The samples were covered with a thin layer of gold, by sputtering (EMITECH K 550x). The coated surface was examined by environmental scanning 200, operating at 5 kV with secondary electrons in high vacuum mode.

3. Results and discussion

3.1. Characterization of sorbent before and after dyes sorption

3.1.1. FTIR analysis

The FTIR spectrum of apple seeds (Fig. 1) evidenced numerous peaks allocated to different functional groups, some which are able to interact with molecular dye species (species as 3,456 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, 1,384 cm^{-1} O–H bending).

The interaction between the starting material (apple seeds—LC) and both dyes can be observed by the spectral changes in the FTIR spectra of LC + BRed (Fig. 1(a)) and LC + MB (Fig. 1(b)). The first pronounced observation can be seen in the FTIR region of OH adsorption: a strong and wide signal of OH groups was observed for LC sample, whereas this was much narrower and less intense for both LC + BRed and LC + MB samples. This suggests a strong interaction of OH groups present in the sorbent structure with both analyzed dyes. Also the shift of the peak from 3,436 to 3,423 cm^{-1} confirms this hypothesis. Moreover, a new peak adsorption at 1,710 cm^{-1} has also been present in the LC + MB spectrum, which originate from the MB structure.

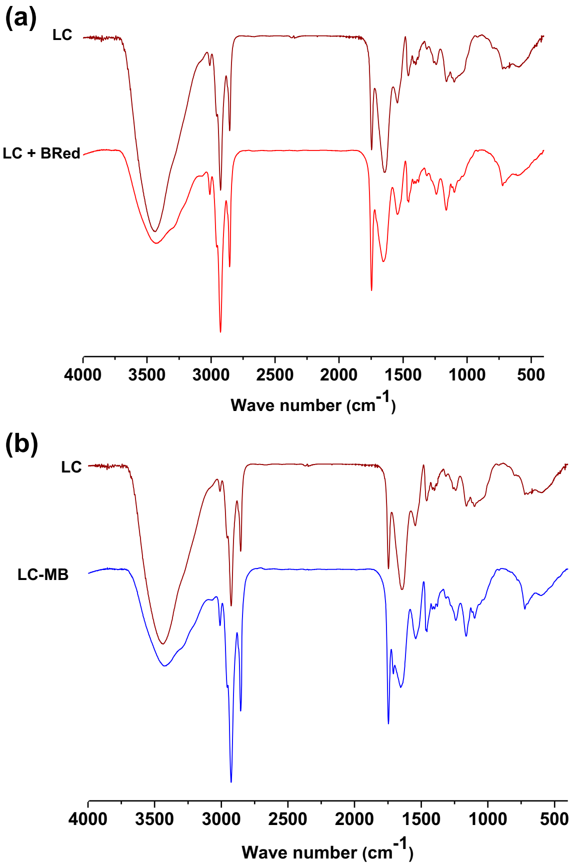


Fig. 1. The FTIR spectra of apple seeds (LC) before and after BRed adsorption (a) and MB adsorption (b).

3.1.2. Surface morphology analysis

In order to evaluate the impact of the dyes on the apple seeds (LC) morphology, as well as the structural changes which may occur during the adsorption process, ESEM technique has been used (Fig. 2).

The ESEM images of the samples at 150 times magnification were acquired aiming at assessing the influence of the dyes on the apple seeds surface morphology. The photographs reveal that the absorption of the dyes on apple seeds has no impact on the morphology and integrity of surface. The sorption processes therefore neither reduces the size of the particle, nor destroy the surface appearance of the apple seeds.

The bottom pictures performed at 5,000 times magnification showed that the dyes particles are present on both surface and pores of the apple seeds.

3.2. Sorption equilibrium

Previous experimental studies allowed assessment of conditions needed for preparing a sorbent based on apple seeds, with an enhanced sorption capacity for

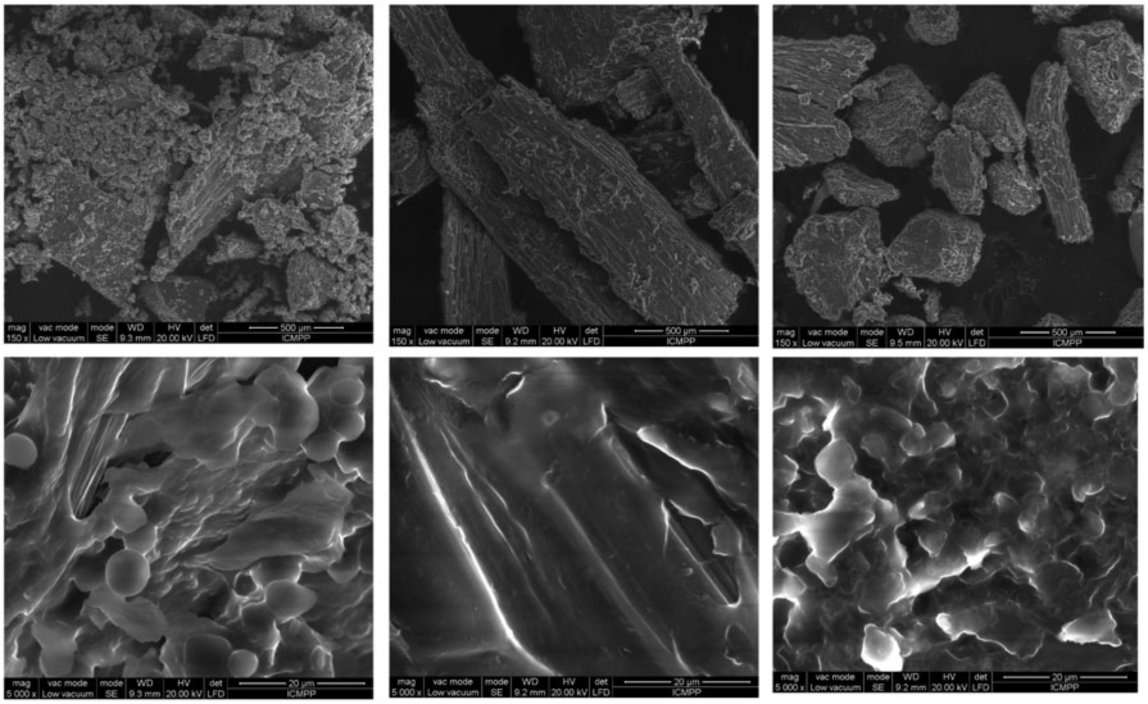


Fig. 2. ESEM microphotographs of the LC (left), LC + BRed (middle), LC + MB (right) at two different magnifications: 150 times (top) and 5,000 times (bottom).

investigated dyes. The maximum sorption capacities were achieved at pH of initial dye solution equal to 3 and 6, respectively.

The experimental data were processed using different sorption isotherms models in order to determine the characteristic quantitative parameters and to gain some information about the involved mechanism. The sorption isotherm is defined as the amount of sorbate retained by the unit of adsorbent (q, mg/g) as a function of the sorbate concentration, at equilibrium, in liquid phase (C, mg/L). The sorption isotherms of studied sorption systems are presented in Fig. 3.

The equilibrium data were analyzed using three of the most known sorption equilibrium models from literature (Freundlich, Langmuir and Dubinin–Radushkevich) [21,36] and are presented in Table 2.

The isotherms shapes show that they are of the type L (Fig. 3), concordant to Giles classification [37], suggesting a monolayer coverage of the dyes on sorbent surface.

The characteristic parameters related to each sorption model were calculated from the intercepts and slopes of the corresponding linear plots (figures not shown). These, together with their uncertainties (standard deviation) as well as with the values of the correlation coefficients (R^2), the residual RMSEs, and Chi-square test (χ^2), which have been used to assess which model describe better the sorption process of BRed and MB dyes onto apple seeds, are presented in Table 3.

Analyzing the data from Table 3, one may see that the values of the correlation coefficients (R^2), residual RMSE, and Chi-square (χ^2) test indicate that the sorption of the two studied dyes onto apple seeds powder can be described in different manners: by Langmuir model in the case of BRed dye and by Freundlich model in the case of cationic dye MB. This confirms the strong dependence between development of process and both sorbent and dye structures. Thus, the higher affinity of sorbent for red dye, could be explained by presence of more functional groups in the lignocellulosic structure of sorbent, which are capable to better retain the anionic molecules, compared with the cationic species.

The values of the Freundlich constant n are greater than unit, suggesting a favorable sorption process. Also, it was observed that an increase of temperature has determined an increase of the saturation capacity (monolayer coverage), q_o (from Langmuir model), which indicates a better accessibility of sorption sites. The value of sorption capacity at 25°C has been found to be 66.25 mg/g for BRed dye and 26.3158 mg/g for MB dye, respectively, values that are comparable with

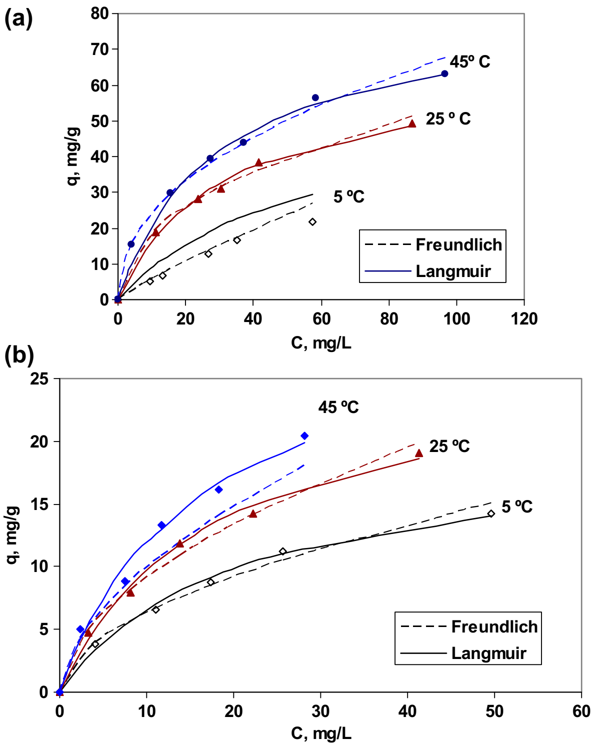


Fig. 3. Sorption isotherms of BRed HE-3B (a) and MB (b) dyes onto apple seeds powder with the results fitted to the Freundlich and Langmuir equations; ◆▲☐ experimental points. Operating conditions: (a) pH 3; (b) pH 6; 4 g/L sorbent dose; and temperature: 5, 25, and 45˚C.

those reported in literature for lignocellulosic sorbents (Table 4).

By using Dubinin–Radushkevich (D–R) model, one can assess the physical or chemical nature of the sorption process. The sorption energy values obtained, in range of 6.041–8.165 kJ/mol for BRed dye and 5.488–6.623 kJ/mol in case of MB, suggest that sorption is probably a physical process that involves electrostatic attraction between the charged surface of the sorbent and the corresponding ionic forms of the dyes. Also, these values confirm a best retention of the red dye. In the case of BRed dye, it was observed that by increasing the temperature up to 45˚C, a chemisorption process may occur in a small extent.

In conclusion, the values of sorption energy calculated by using D–R equations (Table 2) and presented in Table 3 indicate that the physical–chemical process plays a major role in sorption of BRed and MB dyes onto apple seeds powder, and the type of sorption is influenced rather by physical forces than by chemical ones, depending on operational parameters of the process and also by the structure of dyes [38].

3.3. Thermodynamic parameters

In order to gain additional information about the nature of sorption process, the apparent thermodynamic parameters were calculated (Tables 5 and 6), using the values of equilibrium constant, *K*. The

Table 2
The characteristics of the selected isotherm models

	Sorption isotherm model		
Characteristics	Freundlich	Langmuir	Dubinin–Radushkevich
Assumption	The surface heterogeneity and exponential distribution of active sites of the sorbent	Maximum adsorption corresponds to a monolayer of solute molecules on the sorbent surface, containing a finite number of energetically equivalent sites	Suggests the nature of the sorption process—physical or chemical: $E > 8$ kJ/mol characterizes a physical sorption mechanism and values between 8 and 16 kJ/mol indicates an ion exchange mechanism
Non-linear/ Linear form of equation	$q = K_F \cdot C^{1/n}$ $\lg q = \lg\ K_F + 1/n\ \lg\ C$	$q = \frac{K_L \cdot C \cdot q_0}{1+K_L \cdot C}$ $\frac{C}{q} = \frac{1}{q_0\ \ K_L} + \frac{C}{q_0}$	$q =\ q_D \exp(-B\varepsilon^2)$ $\ln q = \ln(q_D - B\varepsilon^2)$ $\varepsilon = RT\ \ln\ (1 + \frac{1}{C}); E = \frac{1}{\sqrt{-2B}}$
Isotherms parameters, significance	K_F and $1/n$ are constants related to the biosorption capacity and biosorption intensity (efficiency), respectively; a favorable sorption correspond to a value of $1 < n < 10$	q_0 is the maximum amount of sorbed solute (mg/g) and K_L is the constant related to the binding energy of solute (L/mg)	q_D is the maximum sorption capacity (mg/g); B is the activity coefficient related to mean sorption energy; ε is the the Polanyi potential, and E—mean free energy of sorption (kJ/mol)

Table 3
Characteristic isotherm parameters for sorption of BRed dye and MB dye onto apple seeds powder

T, K	278		298		318	
Dye	BRed	MB	BRed	MB	BRed	MB
Freundlich isotherm						
K_F (mg/g) (L/mg)$^{1/n}$	0.7384 ± 0.25	1.7956 ± 0.15	6.2289 ± 0.68	2.25 ± 0.33	8.4052 ± 0.57	2.948 ± 0.24
n	1.1265 ± 0.11	1.836 ± 0.1	2.1197 ± 0.1	1.8196 ± 0.1	2.192 ± 0.1	1.711 ± 0.1
R^2	0.9737	0.9915	0.9872	0.9915	0.9926	0.9906
RMSE	2.451	0.5656	1.5492	0.63465	2.7418	0.594
χ^2	0.6902	0.101724	0.2357	0.1207	0.495	0.1237
Langmuir isotherm						
q_0 , mg g^{-1}	55.47 ± 5.7	19.78 ± 1.3	66.441 ± 3.5	26.3258 ± 1.97	82.176 ± 3.2	30.632 ± 4.2
K_L , L mg^{-1}	0.01952 ± 0.005	0.049695 ± 0.007	0.03203 ± 0.0168	0.05877 ± 0.01	0.03433 ± 0.004	0.0655 ± 0.01
R^2	0.9797	0.9878	0.9919	0.9838	0.9954	0.9479
RMSE	0.4206	0.3104	1.0508	0.499	1.306	1.853
χ^2	0.002275	0.04716	0.1336	0.9836	0.141	1.0341
Dubinin–Radushkevich (D–R)						
q_0, mg g^{-1}	64.416 ± 7.075	19.7 ± 1.1055	82.5532 ± 3.91	27.117 ± 1.63	103.88	31.735 ± 3.23
B, mol^2 kJ^{-2}	0.0137	0.0166	0.0101	0.0136	0.0075	0.0114
E, kJ mol^{-1}	6.032 ± 0.47	5.491 ± 0.155	7.022 ± 0.16	6.0634 ± 0.17	8.165	6.634 ± 0.44
R^2	0.9553	0.9906	0.9935	0.9906	0.967	0.9765
RMSE	0.4962	0.34901	0.97493	0.3949	4.9147	0.7182
χ^2	0.001794	0.0558	0.10856	0.0627	2.1815	0.1911

Table 4
Comparison of sorption capacity for some dyes onto various sorbents

Dyes	Sorbent	q_0, mg/g	Refs.
Safranine	Rice husk	19.36	[34]
Malachite green	Peel of *Cucumis sativa* fruit	36.23	[38]
Congo red	Cattail root	34.59	[39]
Rhodamine 6G	Almond shell (*Prunus dulcis*)	32.6	[40]
Methylene Blue	Poplar leaf	142.77	[29]
Methyl Violet	Sunflower seeds	92.59	[41]
Methylene Blue	Corncob	117.3	[42]
Methylene Blue	Swede rape straw	128.2	[30]
Lurazol Brown	Sawdust	16.37	[25]
Acid blue 8; Acid blue 324; Acid green 25; Acid green 27; Acid orange 7; Acid orange 8; Acid orange 10; Acid red 1	Husk of mango seed	9.2/ 12.8/ 8.6/ 12.3/ 17.3/ 15.2/ 8.3/ 11.2	[31]
Orange 16	Sunflower seed shell	21.74	[43]
Orange 16	Corn cob	25.25	[44]
Brilliant Red HE-3B; Methylene Blue; Crystal Violet; Rhodamine B; Orange 16	Sawdust	11.61/7.215/12.594/ 7.309/8.554	[45]

literature presents various methods to evaluate equilibrium constant [46]. Among these, the equilibrium constant K was chosen to be determined by plotting $\ln q_e/C_e$ against q_e at different temperatures, according to the Khan and Sing method [47]. The obtained values of K_d (Tables 5 and 6) corresponding to dyes sorption on apple seeds increased with increase in temperature. The different values of magnitude

Table 5
Thermodynamic parameters of the BRed anionic dye adsorption onto apple seeds powder

T, K	Equilibrium constant		ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0, J/mol K	R^2
278	K_d, L/g	1.422	−0.813	22.115	82.94	0.9741
298		3.1899	−2.871			
318		4.697	−4.09			
278	K_L, L/mol	28455.4	−7.74	10.676	124.67	0.7912
298		49909.8	−8.893			
318		50253.2	−9.053			

Table 6
Thermodynamic parameters of the MB cationic dye adsorption onto apple seeds powder

T, K	Equilibrium constant		ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0, J/mol K	R^2
278	K_d, L/g	1.2966	−0.6002	12.079	45.875	0.9687
298		2.034	−1.7588			
318		2.489	−2.4109			
278	K_L, L/mol	15915.2	−22.361	5.057	98.69	0.9922
298		18812.8	−24.38			
318		20928.0	−26.303			

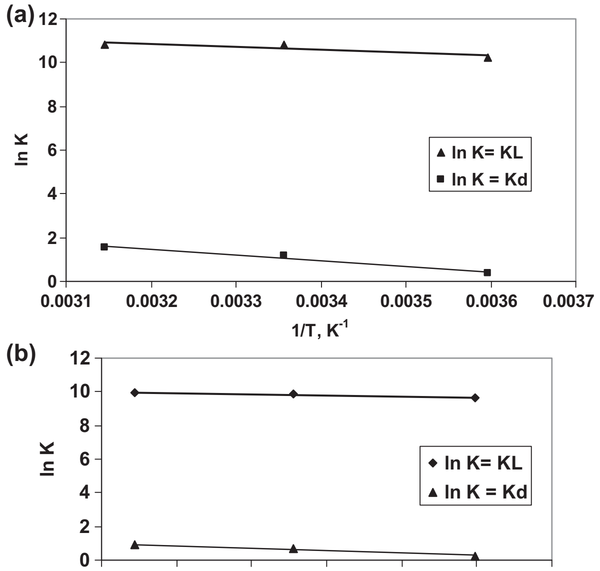


Fig. 4. Plots of ln *K* vs. *1/T* for the sorption of BRed (a) and MB (b) onto apple seeds powder using equilibrium constant, K_d and Langmuir constant, K_L. Operating conditions: (a) pH 3; (b) pH 6; 4 g sorbent/L sorbent dose; and temperature: 5, 25, and 45˚C.

suggest the existence of differences in composition and porosity of this waste used as sorbent. Also, the Langmuir constant K_L (expressed in L/mol) can be considered as equilibrium constant.

Using equilibrium constant, Gibbs free energy variation was calculated by Eq. (4).

$$\Delta G^0 = -RT \ \ln K \tag{4}$$

Based on the Gibbs free energy change, the enthalpy change (ΔH^0) and entropy change (ΔS^0) have been calculated at constant temperature using the van't Hoff equation (Eq. (5)) [21,36].

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{5}$$

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

The values of thermodynamic parameters ΔH^0 and ΔS^0 estimated by plotting ln *K* vs. *1/T* (Fig. 4) are given in Tables 5 and 6. In order to evaluate the degree of fitness of the van't Hoff equation to the experimental data, it was used the linear regression coefficient R^2 (Tables 5 and 6).

Based on the data from Tables 5 and 6, the following observations result:

- A difference between the values of the thermodynamic parameters obtained by using Langmuir constant (K_L) and equilibrium constant (K_d) has been observed. This could be explained by the different order of magnitude of these two constants attributed to different behaviors of the studied systems in the sorption processes; in both cases the values of both enthalpy and entropy changes are positive, while those of free energy change are negative. These results highlight the much better retention of red dye.

- The negative value of Gibbs free energy (ΔG^0) increases with temperature increase, suggesting that the dyes sorption onto apple seeds powder used as sorbents is an endothermic process, thermodynamically feasible, and spontaneous in nature. In agreement with literature data, the value of this thermodynamic parameter does not confirm the precise type of sorption process. This is a physical–chemical process which at a moment of time can be more physical or chemical according to the physical conditions of operation and structure of the dye [40]. The magnitude of ΔG^0 values (Tables 5 and 6) confirms the fact that the physical adsorption, occurring through weaker van der Waals forces, hydrogen bonding, and electrostatic interactions between sorption sites and sorbed species, is an important mechanism in the studied sorption processes.
- The positive values of enthalpy change (ΔH^0) determined from the slope of $ln\ K$ vs. $1/T$ plot, highlight the endothermic nature of the sorption process that is in agreement with the increase of sorption capacity by increasing temperature (Table 3). Its low value, in the case of MB dye sorption, confirms a physical sorption process, and a relative low value in the red dye retention lead to conclusion that sorption process occurs through a combination of physical van der Waals interactions and electrostatic attractions in the case of the last [40].
- The positive value of entropy change (ΔS^0) is characteristic to the increased randomness at the solid–liquid interface during sorption of dye, indicating also some structural changes in both sorbate and sorbent. At the same time, the positive values, equally different for the two systems, evidenced the electrostatic interactions between opposite charge groups and may be a result of the increase in the degree of freedom of the adsorbed species.

4. Conclusions

The results obtained show that apple seeds, a waste material from food industry (freely, abundantly material that do not require additional pretreatment process) could be an efficient sorbent for removal of some textile dyes from different aqueous media. All experimental results show that retention is more effective for BRed reactive dye, fact explained by the structures of both sorbent and dyes. Thus, in the structure of lignocellulosic material much more ionizable functional groups are found which are able to retain the red dye molecules (dissociated sulfonic groups). This affects the entire behavior of the sorbent during the sorption process, in terms of the type of sorption, the model that best describes the process, the process energy, and thermodynamic behavior. The equilibrium sorption data for BRed is in good agreement with Langmuir isotherm, while those for MB dye better fit the Freundlich model. The sorption capacity was about 66.225 mg/g (BRed) and 26.316 mg/g (MB), respectively, at 25˚C. The values of thermodynamic parameters confirm the feasibility and the endothermic behavior of the bio sorption, confirming the complex nature (physical–chemical) of the process.

These conclusions represent a real starting point for future kinetic studies of these two sorption systems, studies that will determine the mechanism of the sorption processes and will establish the rate determining step.

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