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Kinetic and thermodynamic studies on methylene blue biosorption using corn-husk

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A low-cost waste biomass derived from corn plant (husk) was tested as alternative to other expensive treatment options, for the removal of Methylene Blue (*MB*), from aqueous solutions. The effects of different experimental parameters, such as biosorbent dosage, dye concentration, contact time, and temperature, on the adsorption process were investigated. Optimum value of discoloration was observed at pH 6.0 and 2 g L^{-1} biomass dosage. The amount of dye removed per adsorbent unit decreased with increasing adsorbent dosage, temperature, and increase with increasing the contact time, and concentration. Experimental data were modeled using first-order, pseudo-second-order, Elovich, and intraparticle diffusion kinetics models. The adsorption kinetics of *MB* could be described by the pseudo-second order reaction model. The experimental data were fitted to: Langmuir, Freundlich, Temkin, Redlich-Peterson, Toth, and Sips isotherm models and the best fitting was obtained with Sips model. Thermodynamic parameters ($\Delta H°$, $\Delta S°$ and $\Delta G°$) obtained revealed that *MB* adsorption is a spontaneous, exothermic and physical process. The obtained results indicated that corn husk as low-cost biomaterial is an attractive candidate for the removal of basic dye MB from aqueous solutions.

Keywords: Biosorption, Basic dye, Agro-waste, Isotherm, Kinetics, Thermodynamics

Introduction

Contamination of water, air, and soil with pollutants is a consequence of development of industry, so necessary for the satisfaction of modern human needs. Because of that, one of the most serious problems that the scientists are facing in the past two decades is the development of methods for decreasing of environmental pollution levels [1]. Synthetic dyes represent one of the most important groups of organic pollutants with estimated annual production of 7×10^8 kg/year and over 100,000 commercially available dyes [2, 3]. These compounds have a wide application in many fields of industries, such as: textile, paper, printing, rubber, plastics, leather, cosmetics, food and pharmaceutical industries.

Dyeing industry effluents present a high degree of coloration and the release into the environment without treatment may affect the ecosystem due to the toxicological impact and mutagenic character of dyes [4, 5], and by reduction of sunlight penetration and photosynthetic activity [3]. Also, dyes can be accumulating in sediment and soil, causing different problems to the ecological balance of the environment [6].

Synthetic dyes present a complex aromatic structure with high stability to aerobic digestion, light, temperature, detergent and microbial attack [1, 5], which makes them stable and resistant to biodegradation methods present in the environment, and to different chemical treatments [2, 7].

The conventional methods of dye removal involve the combination of physical and chemical processes such as adsorption, precipitation, sedimentation, ultrafiltration, oxidation processes, ozonation, coagulation/flocculation, ion exchange and reverse osmosis, and also biological degradation methods [2, 5, 8]. However, these methods often have the disadvantage of a high operating cost, formation of hazardous by-products or intensive energy requirements [1, 5, 8]. From these methods, adsorption has proved to be an effective alternative process, being an economic method that presents a simple operating design and highly efficiency for the removal of dyes from wastewater [2, 7].

For wastewater treatment, commercial activated carbon is currently the most widely used adsorbent due to its high adsorption capacity, surface area and degree of surface reactivity as well as a microporous structure. However, its use is limited by the operating cost and regeneration issues [1, 2, 9]. Therefore, non-conventional low-cost alternatives have been searched in the last years, easy available, renewable and environmentally friendly materials that can successfully replace the classical adsorbents. For this purpose, different agricultural biomasses were examined for the removal of different classes of dyes: bean [10], kohlrabi peel [11], capsicum seeds [12], olive pomace [13, 14], wheat waste [15,16], rice hull [17], sugar beet pulp [18], ginger [19], silk cotton hull [20], orange [1, 21] pineapple leaf [22], coconut bunch [9], cones [3,5], sawdust [4, 23, 24]; with or without chemically modifying [16, 17, 23]. These materials are abundant in nature, by-products or waste from different industries, which involve a very low acquisition cost. Utilization of different by-products for the wastewater treatment could be helpful not only economically, but also to the environment by solving the solid waste disposal problem [25].

The biggest problem when vegetable origin biosorbents are used is that they are only locally available and their transport over long distances would make the process economically unprofitable. Therefore, the aim of this study is to investigate the adsorbent properties of corn husk; corn is widely cultivated throughout the world, according to FAOSTAT organization (Food and Agriculture Organization of the United Nations), worldwide production was $844 \cdot 10^6$ tones in 2010, more than any other grain, adapting easily to different climate conditions, from which $9 \cdot 10^6$ tones represents the production on the Romanian territory.

Bioremoval of a pollutant using biosorbents is affected by several factors like the chemical nature of pollutant, specific surface properties of the biosorbent and environmental conditions [18].

Methylene blue (*MB*) was selected as a basic dye model in order to evaluate the adsorption capacity from aqueous solutions of corn husk, an agro-waste renewable and without economic value. *MB* does not belong to the class of the most dangerous pollutants, but acute exposure causes difficult breathing, increased heart rate, nausea, vomiting, diarrhea, shock, jaundice, quadriplegia, and tissue necrosis in humans [4, 13, 15]. Methylene blue can be used in different fields, including coloring paper, temporary hair colorant, dyeing cottons and wools [4]. The investigations were performed also using activated carbon, in order to compare the adsorption capacity of corn husk with those of activated carbon. The effects of contact time, adsorbent dose, initial dye concentration and temperature on *MB* adsorption were evaluated. The kinetics, thermodynamic parameters and the factors controlling the adsorption process were also calculated and discussed.

Materials and methods

Materials

Corn husk was obtained from a small farm near Timişoara, Romania. The waste material was abundantly washed with tap water in order to remove the dust and in the end with distilled water and dried in oven to 353 K until constant weight. The dried biomaterial was crushed using a domestic grinder and sieved. It were selected particles smaller than 630 µm. Powdered biosorbent was stored for further use without any other chemical or physical modification. Corn husk was characterized by means of FT-IR spectroscopy. FT-IR spectrum was recorded using a Shimadzu Prestige-21 spectrometer in the range 400-4000 cm^{-1}, using KBr pellets and resolution of 4 cm^{-1}.

Activated carbon was purchased from UTCHIM-ROMANIA. Like the corn husk, it was crushed and sieved; particles smaller than 630 µm were selected.

Methylene blue (basic dye, chemical formula: $C_{16}H_{18}ClN_3S$; molecular weight 319.86 g mol^{-1}) was supplied by CHEMICAL - ROMANIA and it was not purified prior to use. The chemical structure of *MB* is presented in Fig. 1.

Figure 1

Stock dye solution (1000 mg L^{-1}) was prepared by dissolving in distilled water; desired concentrations were prepared by dilution of the stock solution.

Batch biosorption experiments

Biosorption studies were performed in Erlenmeyer flask containing 50 mL of dye solution, and stirring at 200 rpm. In order to determine the optimum biosorption conditions, the experiments were conducted using different biosorbent mass, in the range of 1.0 to 3.0 g L^{-1}, and different dye concentrations in the range 20 to 100 mg L^{-1}. The effect of temperature on the biosorption process was studied at three different temperatures: 298, 313 and 333 K. Studies were carried out using an UVmini-1240 SHIMADZU spectrophotometer by monitoring the absorbance changes at maximum absorbance wavelength (665nm).

The assessment of biosorption capacity was done by calculating the adsorption capacity (1), and the removal percentage (2) of the *MB* dye:

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad (1)$$

$$\eta = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (2)$$

where: q_t is the amount of dye adsorbed per unit of bisorbent (mg g^{-1}); η the percentage of dye removal (%); C_0 initial concentration of dye solution (mg L^{-1}); C_t dye concentration at different periods of time (mg L^{-1}); C_e dye concentration at equilibrium (mg L^{-1}); V volume of solution (L); W mass of biosorbent (g).

Results and discussion

Biosorbent characterization

The chemical composition of the corn husk is: 82.7% carbohydrates and 6.6% lignin [26] which determines the existence of numerous hydroxyl groups and aromatic rings. The FT-IR spectrum of corn husk is presented in Fig. 2.

Figure 2

The broadband at 3200-3500 cm^{-1} is attributed to O-H stretching vibration in phenolic and aliphatic structures [27, 28]. The band at 2916.37 cm^{-1} is assigned to C-H stretching vibration in aromatic methoxyl groups and in methyl and methylene groups of side chains [28]. The band at 1732.08 cm^{-1} indicates the presence of C=O stretching of carbonyl group. The bands at 1633.71 cm^{-1}, 1517.97 cm^{-1} and 1429.25 cm^{-1} are characteristic for the aromatic skeleton vibrations. The band at 1373.32 cm^{-1} can be assigned to aliphatic C-H bending vibrations and phenolic OH [27]. The band at 1249.87 cm^{-1} can be assigned to C-O-C antisymetric stretching vibration and the band at 1055.99 cm^{-1} can be attributed to C-O-C symmetric vibration plus C-OH in primary alcohols [27, 29, 30]. The band at 1161.15 cm^{-1} and 1105.25 cm^{-1} can be assigned to C-OH stretching vibrations in phenol and respectively in secondary alcohols [27, 30].

This result is in accordance with the composition of lignocellulosic materials. The FTIR spectrum indicates that the corn husk presents different functional groups which may be potential biosorption sites for *MB* dye.

Effect of biosorbent mass

Biosorbent mass is an important factor, influencing the adsorption capacity for a given initial concentration of the dye solution. The effect of biosorbent mass in the adsorption of *MB* was followed using an initial dye concentration of 20 mg L^{-1} and varying the corn husk mass in the range 1÷3 g L^{-1}. Fig. 3 shows the variation in time of the amount of the dye adsorbed for three different biosorbent quantities (1, 2 and 3 g L^{-1}).

Figure 3

The results (Table 1) indicate that the quantity of dye adsorbed per unit of dry biosorbent decreased, and the uptake of the dye increase from 90.3% to 93.6% with increasing the biosorbent mass.

Table 1

By increasing the biosorbent dosage the number of active sites available for adsorption increased, facilitating the adsorption of dyes, which explain the increase of removal percentage. The decrease of adsorption capacity by increasing the biosorbent dosage (higher weight of biosorbent per dye ratio) is maybe due to the unsaturation of biosorbent sites, during the adsorption process. Similar results have been reported by other authors [15, 31, 32, 35] The further studies were carried out using 2 g L^{-1} biosorbent mass.

Effect of initial dye concentration and contact time

The evolution of the amount of the uptake dye as function of the contact time for different initial dye concentrations is presented in Fig 4.

Figure 4

The obtained data presented in Table 1show the increase of the amount of *MB* adsorbed at equilibrium, and the decrease of the percentage of dye removal with increasing the initial dye concentration [33, 34, 36]. It can be also noted the increase of equilibrium time with increasing the initial dye concentration [37], due to the fact that adsorption can occur both at the surface and in the pores of the biosorbent, and the diffusion to the internal adsorption sites requires a longer time.

It is evident that the increase of the amount of *MB* adsorbed is fast in the first hour of the process, and becomes much slower near the equilibrium. This can be explained by the large number of vacant sites available at the initial stage which gradually are occupied in time as a result of sorption process. These results indicating that the dye removal is concentration dependent.

Corn husk presents a good adsorption capacity of 41.55 mg g^{-1}, indicating that it could be considered a promising material for the removal of *MB* dye from aqueous solution.

Effect of temperature

The influence of temperature on the adsorption process was investigated at 298, 313, and 333 K, using a *MB* solution with 20 mg L^{-1} initial concentration, and pH 6. The results are presented in Fig. 5.

Figure 5

Watching the process in time, it can be observed that the necessary time for reaching equilibrium decreases from 80 minutes to 45 minutes with the increase of temperature, most of the dye being adsorbed in the first hour of the process. The adsorption capacity and the percentage of *MB* removal decreases with the increase of temperature suggesting that biosorption of *MB* is an exothermic process (Table 1). Similar results have been obtained for MB removal by other researchers [38-40, 62]. These results are economically advantageous because the *MB* removal can be conducted at environmental temperature (25°C) without additional costs for power generation.

Comparison between the adsorption capacity of corn husk and activated carbon

The efficiency of the corn husk as adsorbent for the removal of *MB* was compared with those of activated carbon. Fig. 6 shows comparatively, the amount of *MB* removed as a function of contact time using corn husk, and respectively activated carbon as adsorbents.

Figure 6

It can be noticed that the amount of *MB* removed by corn husk (9.34 mg g^{-1}) is comparable to those removed by activated carbon (9.83 mg g^{-1}). The very close removal capacity for the two adsorbents and the notable economic advantages of using corn husk, recommend it as a viable alternative for the *MB* removal.

Biosorption kinetics

Kinetic studies provide information regarding the kinetic parameters and the mechanism of MB biosorption onto corn husk. The biosorption kinetics of MB was investigated using four kinetic models, namely pseudo-first-order (3), pseudo-second-order (4), Elovich equation (5), and intraparticle diffusion models (6) [41-43].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{5}$$

$$q_t = k_i t^{0.5} + l \tag{6}$$

where, q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg g^{-1}); q_t is the amount of solute adsorbed at any time (mg g^{-1}); k is the adsorption rate constant, α is the initial sorption rate (mg g^{-1} min^{-1}), β is the desorption constant (g mg^{-1}), and l is the effect of boundary layer thickness.

The initial biosorption rate, h (mg g^{-1} min^{-1}), can be defined as:

$$h = k_2 q_e^2 \tag{7}$$

The correlation coefficients were used to determine the best fitting kinetic model. The comparison of the experimental adsorption capacity values (obtained at different temperatures) with the computed results estimated from equations 3 ÷ 6, are presented in Table 2.

Table 2

The correlation coefficient close to unity, low standard deviation, and experimental values for q_e similar to the calculated ones (Table 2) indicate that *MB* biosorption process is described by the pseudo-second-order model (Figure 7).

Figure 7

Similar results were reported for *MB* adsorption on meranti sawdust [4], olive pomace and charcoal [13], scolymus hispanicus [35], and banana stalk waste [44]. As the temperature increases, the k_2 constant increases indicating that the necessary time for reaching the equilibrium decreases with increasing temperature, and that the adsorption of *MB* on corn husk is an exothermic process.

In order to explain the diffusion mechanism the intraparticle diffusion model was used. The dye adsorption process involves several steps: dye diffusion through solution to the outer surface of the adsorbent (film diffusion), dye adsorption on the outer surface of the adsorbent, dye diffusion from the surface into the adsorbent interior (intraparticle diffusion) and, dye adsorption onto the active centres in the interior surface of the adsorbent.

From the plot of q_t versus $t^{0.5}$ the values of intraparticle diffusion rate constant (k_i) and the effect of boundary layer thickness (l) were calculated (Table 2). As can be seen from Fig 8, the plots are not linear over the whole time range which means that the intraparticle diffusion is not the rate determining step of the biosorption mechanism of *MB* onto corn husk. The boundary layer diffusion was also significant [16]. Maximum is the intercept length (l), adsorption is more boundary layer controlled.

Figure 8

The second-order rate constants listed in Table 2 were used to calculate the activation energy for MB biosorption on corn husk, using Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E}{RT} \tag{8}$$

where: E is the activation energy (J mol^{-1}), k_2 is the rate constant of biosorption (g mg^{-1} min^{-1}), A is the pre-exponential factor (g mg^{-1} min^{-1}), R is the general gas constant (J mol^{-1} K^{-1}) and T is the temperature (K).

The activation energy was calculated from the slope of linear fitted function of ln(k_2) versus 1/T and was found to be 32.02 KJ mol^{-1}, which indicates that the *MB* biosorption is a physical process. This value is of the same order of magnitude with the value in the literature [15, 23, 34, 45].

Biosorption isotherms

The study of the equilibrium biosorption isotherms is the most appropriate way in designing and assessing the performance of the biosorption process. Biosorption data, obtained at equilibrium, plotted as q_e, function of C_e, were fitted to five different sorption isotherm models: Langmuir, Freundlich, Temkin, Redlich-Peterson, Toth and Sips [46, 47]. Two two-parameter and three three-parameter equilibrium isotherm models were used to fit the experimental data as follows:

Langmuir isotherm model represented by the equation (9) is based on the assumptions [5, 48]: finite number of identical sites, homogeneously distributed over the adsorbent surface; monolayer coverage of adsorbate over the adsorbent surface; no interaction between the adsorbent molecules and the heat of adsorption is independent of the coverage of adsorbent surface.

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{9}$$

where q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}); C_e is the equilibrium dye concentration in the solution (mg L^{-1}); q_m is the maximum biosorption capacity of the biosorbent (mg g^{-1}); and K_L is the Langmuir constant (L mg^{-1}) and is related to the free energy of biosorption.

The essential characteristic of Langmuir isotherm can be expressed using a dimensionless constant, the separation factor R_L [5, 49]:

$$R_L = \frac{1}{1+(1+K_L C_0)} \tag{10}$$

where C_0 is the initial concentration of the dye (mg L^{-1}). The value of this coefficient indicates whether the isotherm is or not favourable: for $0< R_L <1$ the model is favourable; for $R_L >1$ the model is unfavorable and for value $R_L = 0$ the model is irreversible.

The *Freundlich empirical isotherm* is applicable to the adsorption on heterogeneous surfaces with interaction between adsorbed molecules. In this case, the heat of adsorption exponentially decreases with the coverage of adsorbent surface [5]. The Freundlich isotherm is expressed as [48]:

$$q_e = K_F C_e^{1/n} \tag{11}$$

where K_F is the Freundlich constant (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}), indicating the adsorption capacity of the adsorbent and $1/n$ (dimensionless) is a constants related to the intensity of adsorption.

The *Temkin isotherm* assumes the linear decrease of the heat of adsorption with the coverage of the adsorbent surface due to some adsorbate-adsorbent interaction [6, 48]. The Temkin isotherm is expressed as [35, 49]:

$$q_e = \frac{RT}{b}\ln\left(K_T C_e\right) \tag{12}$$

where: K_T is the Temkin isotherm equilibrium binding constant (L g^{-1}), b is the Temkin isotherm constant B = RT/b is a constant related to the heat of adsorption (J mol^{-1}).

The *Redlich-Peterson isotherm* is an empirical with three parameters equation. This isotherm is valid over a wide range of concentations and combines elements from Langmuir and Freundlich isotherms. The Redlich-Peterson isotherm is expresed as [50, 51]:

$$q_e = \frac{K_{RP} C_e}{1+\alpha_{RP} C_e^{\beta}} \tag{13}$$

where: K_R is the Redlich-Peterson constant (L g^{-1}), α_R is also a constant ((L g^{-1})$^{\beta}$) and β is an exponent varying between 0 and 1.

Toth isotherm is derived from Langmuir equation with the purpose of reducing errors arising from experimental data. This model presumes a quasi-Gaussian distribution of energy. This is a three parameters isotherm, fits multilayer adsorption processes and is expressed by the equation [35, 51]:

$$q_e = \frac{q_m C_e}{\left(K_T + C_e^t\right)^{1/t}} \tag{14}$$

where: q_m the Toth maximum adsorption capacity (mg g^{-1}), K_T the Toth equilibrium constant , and t is the Toth isotherm constants.

The *Sips isotherm* is a three-parameter empirical equation, a combination of the Langmuir and Freundlich models. This equation is based on the Freundlich equation assumption, where the amount of adsorbed dye increases with the increase of initial concentration, but Sips equation presumes that the adsorption capacity has a finite limit when the concentration is sufficiently high. This model is represented as [35, 51]:

$$q_e = \frac{q_m K_S C_e^{1/n}}{1+K_S C_e^{1/n}} \tag{15}$$

where: K_S is the Sips constant ((L mg^{-1})^n) and n is the Sips model exponent. For $n = 1$, equation (17) reduces to Langmuir isotherm (eq. 9). Alternatively, for low equilibrium concentration, close to 0, the Sips isotherm reduces to the Freundlich isotherm (eq. 11).

Analysis of adsorption isotherms

The experimental equilibrium data for *MB* biosorption onto corn husk were fitted to the six isotherms models by plotting q_e versus c_e.

The analysis of the experimental data and determination of isotherms parameters were performed using the non-linear regression analysis from ORIGIN 6.1 software package. The main statistical criteria were the squared multiple regression coefficient (R^2), and the chi-square analysis (χ^2) (16).

$$\chi^2 = \sum \frac{\left(q_e - q_{e,m}\right)^2}{q_{e,m}} \qquad (16)$$

where: q_e is the equilibrium capacity (mg g^{-1}) obtained from experimental data, and $q_{e,\mathrm{m}}$ is the equilibrium capacity obtained by calculating from the model (mg g^{-1}).

The data obtained for the fitted models are presented in Table 3, and the comparison between experimental data and the best fitted sorption isotherm curves is presented in Fig. 9.

Table 3

Figure 9

Comparing the correlation coefficients of the analyzed isotherms, it follows that the Sips model yields a better fit for the experimental equilibrium data than the other isotherms. These results suggest that the adsorption process of the *MB* dye is following a combined Frendlich and Langmuir model: diffused adsorption at low dye concentration, and a monomolecular adsorption with a saturation value - at high dye concentrations. Similar results were reported for the adsorption of *MB* on yellow passion fruit waste [50, 52].

The maximum adsorption capacity of the corn husk determined from the Sips sorption isotherm curves was 50.69 mg g^{-1}, and the values are higher or comparable with the data reported before (Table 4). This data indicates that corn husk can be considered a promising material for the removal of *MB* dye from aqueous solution.

Table 4

In order to establish if the biosorption process is favorable or not, the R_L factor was determined from the Langmuir isotherm model. The obtained values for R_L parameter were in the range of 0.025–0.173 (Table 3), quite close to zero, indicating that the *MB* biosorption process on corn husk is favorable, and it is a relatively irreversible reaction [9, 44, 49, 53].

Biosorption thermodynamics

The thermodynamic parameters of biosorption process, including free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated using the following equations:

$$\Delta G^0 = -RT \ln K \qquad (17)$$

$$K = \frac{q_e}{C_e} \qquad (18)$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (19)$$

where K is the equilibrium constant, R is the universal gas constant (J mol^{-1} K^{-1}), T is temperature (K), q_e is the amount of *MB* biosorbed on the corn husk per liter of the solution at equilibrium (mg L^{-1}), C_e is the equilibrium concentration of the *MB* in the solution (mg L^{-1}).

The enthalpy $\Delta H°$ and entropy $\Delta S°$ of biosorption process were estimated from the slope and intercept of the plot of ln$K$ versus $1/T$ (figure not show).

The negative values of $\Delta G°$ (Table 5), calculated using K, indicate that the biosorption of *MB* onto corn husk is thermodynamically possible and it is a spontaneous process.

Table 5

The negative value of $\Delta H°$ confirms the exothermic nature of biosorption process. The value of $\Delta H°$ for the present study is less than 20 kJ/mol (Table 5), indicating that *MB* biosorption on corn husk is likely a physical process, which is in agreement with the results obtained from activation energy [34, 59, 60]

The positive value of $\Delta S°$ reflects the increased randomness at the solid-solution interface during the biosorption of MB on corn husk [49, 61].

Conclusions

The present study demonstrated that corn husk, a low-cost agro-waste biomass, can be successfully used as adsorbent for the removal of *MB* dye from aqueous solutions. The amount of dye removed increase with increasing the contact time, and initial dye concentration, and the percentage of dye removal increase with increasing the adsorbent dosage. The rate of adsorption was found to comply with pseudo-second-order kinetics with a correlation higher than 0.99. Equilibrium data fitted with the Sips isotherm equation, gave a maximum adsorption capacity of 50.69 mg g^{-1}. The obtained results at different temperatures indicate that *MB* adsorption onto corn husk is an exothermic and spontaneous process. The very close removal capacity for the corn husk compared with activated carbon and the notable economic advantages of using corn husk, recommend it as a viable alternative for the *MB* removal. The sorption process can be conducted at ambient temperatures with best results.

Taking into consideration the presented results, it can be concluded that corn husk can be an alternative adsorbent reported to other more expensive adsorbents used for coloured wastewater treatment.

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Table 1. Influence of different parameters for the adsorption for the *MB* on corn husk

	Initial dye concentration (mg L^{-1})					Mass of biosorbent (g L^{-1})			Temperature (K)		
	20	30	50	70	100	1	2	3	298	313	333
q_e mg/g)	9.34	13.86	22.44	30.14	41.55	18.06	9.34	6.24	9.34	9.26	8.85
η (%)	93.40	92.39	89.74	86.12	83.10	90.30	93.40	93.60	93.40	92.55	88.54
t_e (min)	34	42	53	65	85	60	34	26	34	28	16

Table 2. Kinetic parameters for biosorption of *MB* onto corn husk.

Kinetic model	Kinetic parameters	Temperature		
		298	313	333
	$q_{e,exp}$ (mg·g^{-1})	9.34	9.26	8.85
First-order kinetic model	$q_{e,calc}$ (mg g^{-1})	12.17	3.01	0.31
	$k_1 \cdot 10^2$ (min^{-1})	11.98	9.73	7.36
	R^2	0.9853	0.9367	0.6525
	SD	0.1909	0.3302	0.5516
Pseudo-second-order kinetic model	$q_{e,calc}$ (mg g^{-1})	9.48	9.19	8.78
	$k_2 \cdot 10^2$ (g mg^{-1}min^{-1})	3.93	6.87	15.24
	h (mg g^{-1}min^{-1})	3.53	5.79	11.75
	R^2	0.9998	0.9999	0.9999
	SD	0.0175	0.0240	0.0405
Elovich model	α	180.61	18.23 e3	30.38 e11
	β	1.03	1.61	3.67
	R^2	0.9320	0.9016	0.8824
	SD	0.2967	0.2322	0.1121
Intrapart diffusion	k_i	0.88	0.67	0.30
	c	4.43	5.66	7.20
	R^2	0.9651	0.9826	0.9873
	SD	0.2656	0.1421	0.0544

Table 3. The isotherm parameters for the biosorption of *MB* on corn husk.

Isotherm Parameters	*Langmuir*	*Freundlich*	*Temkin*	*Redlich-Peterson*	*Toth*	*Sips*
K	0.19	14.58	3.11	8.24	1.12	0.16
q_m	47.95	-	-	-	78.05	50.69
R_L	0.025 ÷ 0.173	-	-	-	-	-
n	-	3.76	-	-	-	1.19
b	-	-	294.14	-	-	-
α_R	-	-	-	0.16	-	-
β	-	-	-	1.01	-	-
t	-	-	-	-	0.35	-
R^2	0.9944	0.9565	0.9815	0.9929	0.9841	0.9956
χ^2	1.75	13.85	4.22	2.57	5.79	1.58

Table 4. Comparison of adsorption capacity of various biosorbents for MB dye.

Adsorbent	Adsorption capacity (mg g^{-1})	References
Neef leaf	8.76 – 19.61	[54]
Palm-Trees Waste	8.4	[30]
Data stones	8.8	[30]
Fly ash	13.42	[55]
Yellow passion fruit	14	[28]
Wheat shells	16.56 – 21.50	[14]
Oak sawdust	29.94	[56]
Cherry sawdust	39.84	[56]
Indian rosewood sawdust	11.8 – 51.4	[57]
Rice husk	40.58	[58]
Corn husk	18.06 – 41.55	this work
Coconut bunch	30.42 – 65.55	[9]

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Table 5. Thermodynamic parameters for the biosorption of MB on corn husk.

T (K)	K	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
298	14.1515	-6.5651	-4.3792	15.9408
313	12.5135	-6.5755		
333	7.6957	-5.6497		

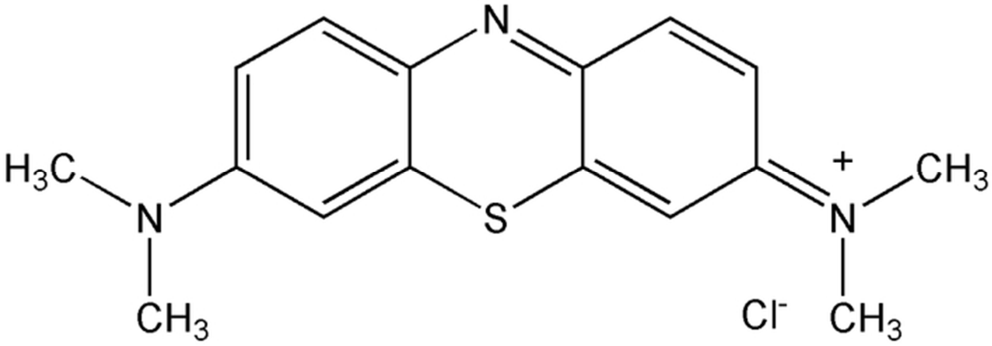

Fig. 1 Molecular structure of the MB dye
60x21mm (300 x 300 DPI)

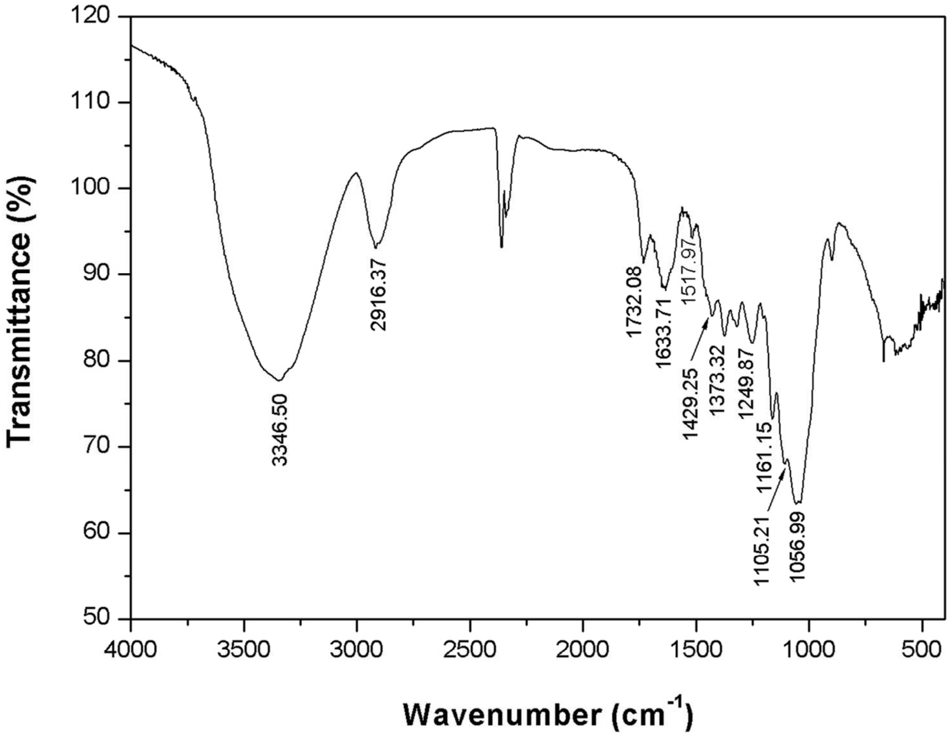

Fig. 2 The FT-IR spectrum of corn husk
128x96mm (300 x 300 DPI)

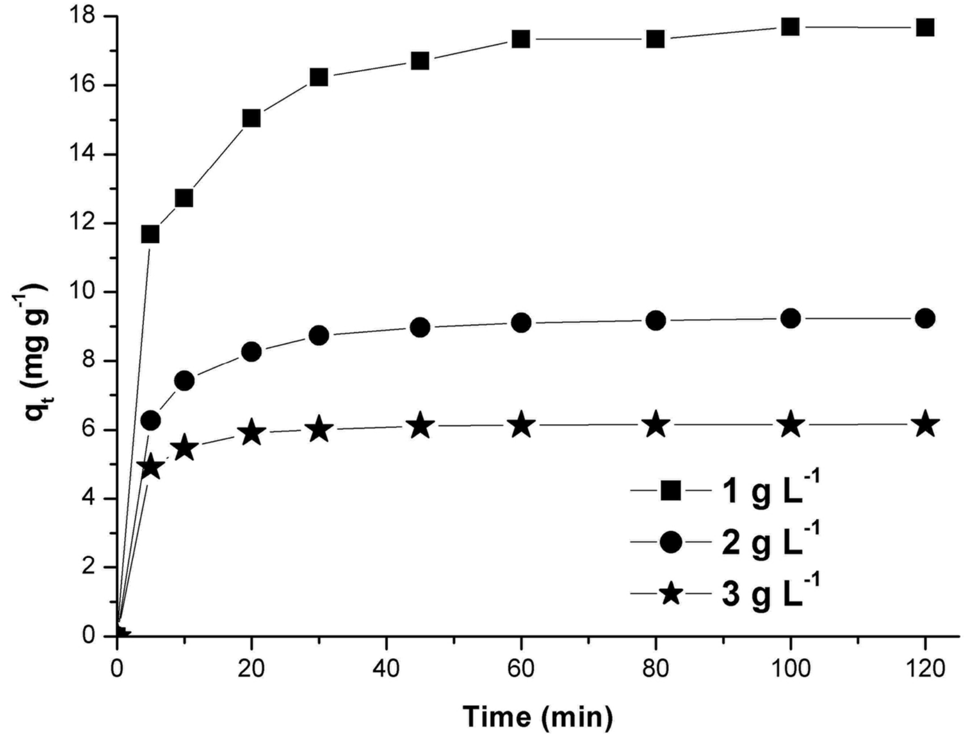

Fig. 3 The influence of the biosorbent mass (20 mg L-1, 298 K, pH 6) on the MB dye removal
132x103mm (300 x 300 DPI)

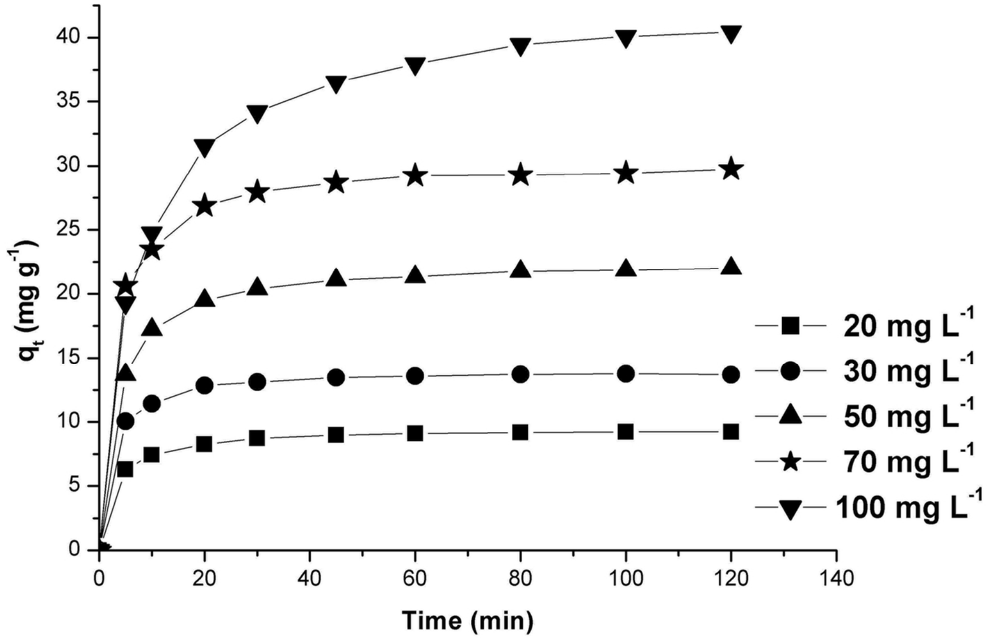

Fig. 4 Influence of the initial concentration and contact time (2g L-1, 298 K, pH 6) onto the MB dye removal
113x74mm (300 x 300 DPI)

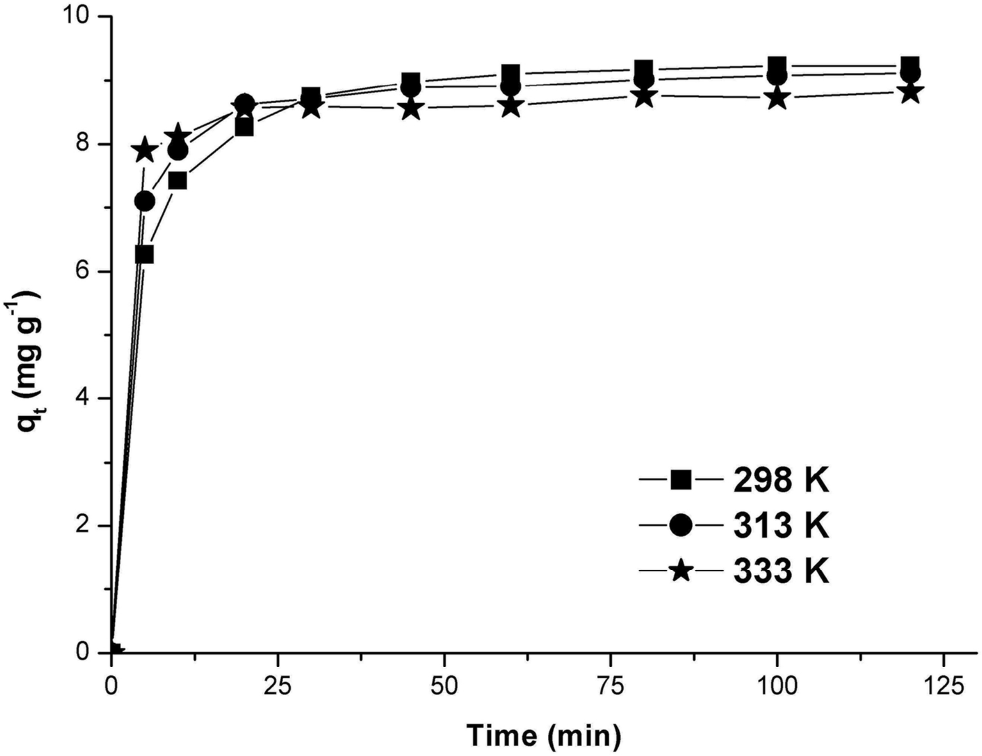

Fig. 5 The influence of the temperature (20 mg L-1, 2 g L-1, pH 6) onto the MB dye removal
132x102mm (300 x 300 DPI)

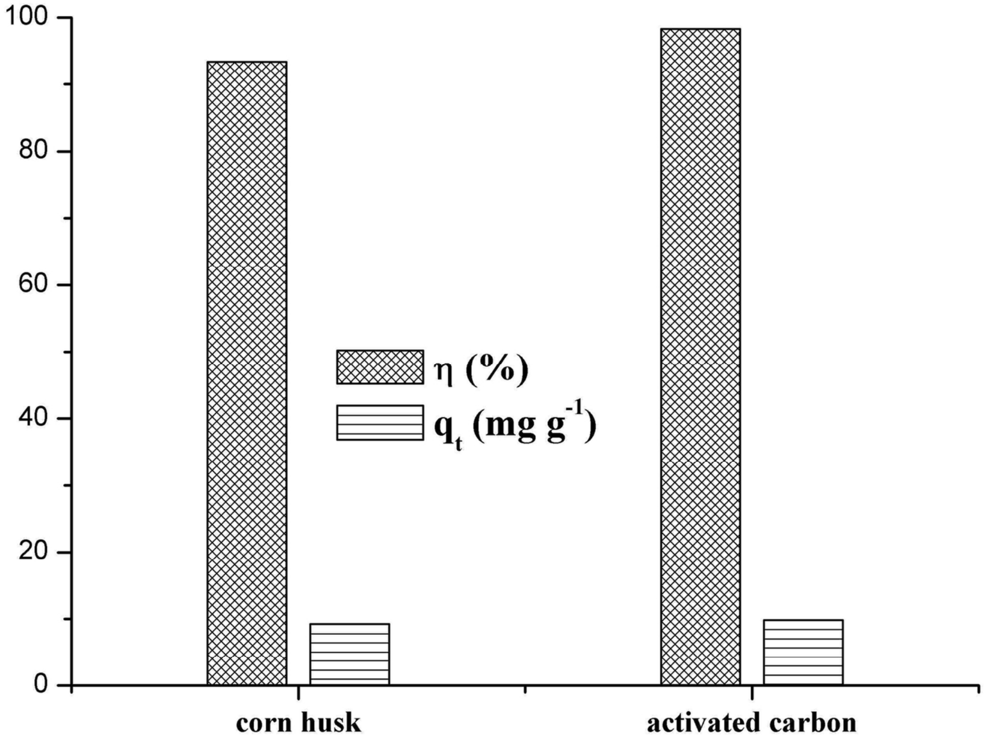

Fig. 6 The amount of MB removed using corn husk, respectively activated carbon as adsorbents (C0 20 mg L-1, 298 K, pH 6, biosorbent mass 2 g L-1)
133x104mm (300 x 300 DPI)

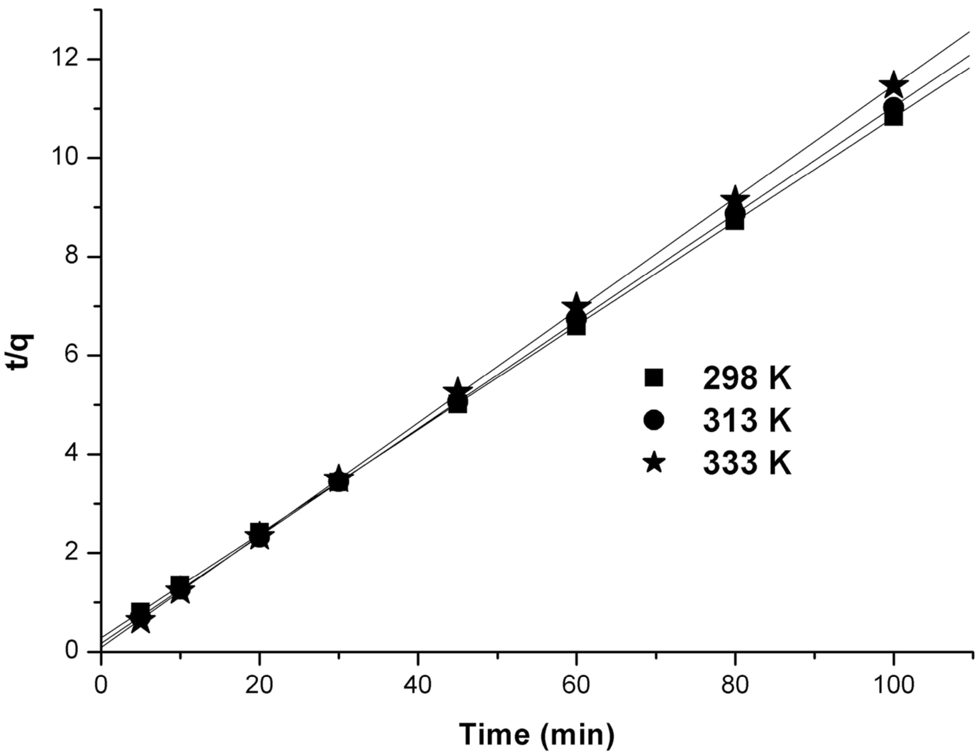

Figure 7. Pseudo-second order kinetic model fitting for the adsorption of MB dye on corn husk
140x112mm (300 x 300 DPI)

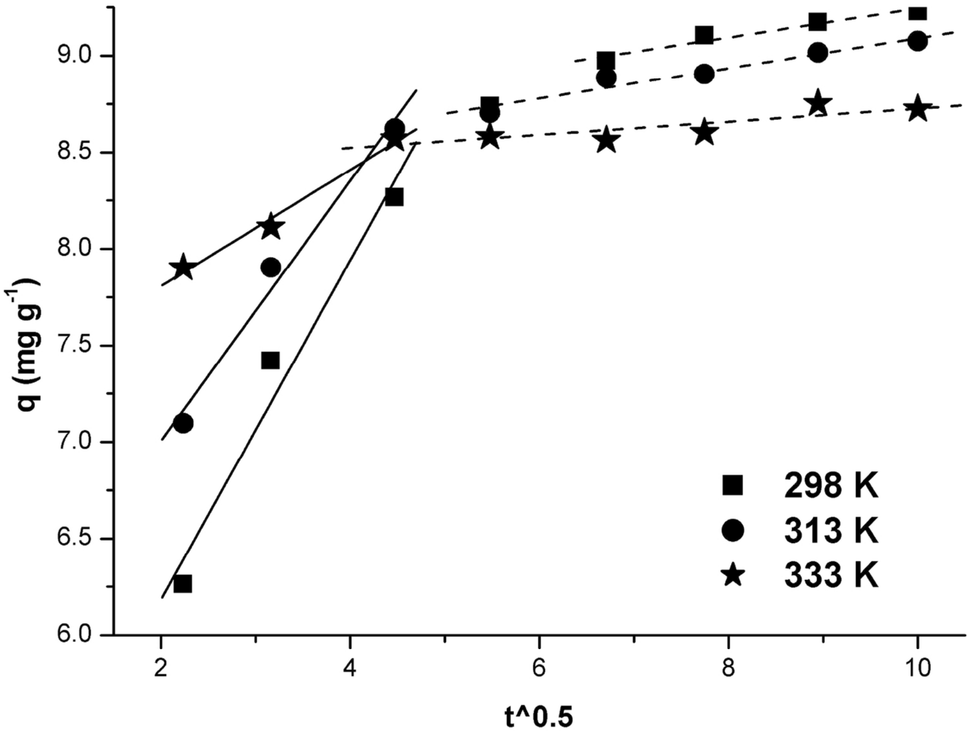

Figure 8 The intraparticle diffusion of MB by corn husk
132x100mm (300 x 300 DPI)

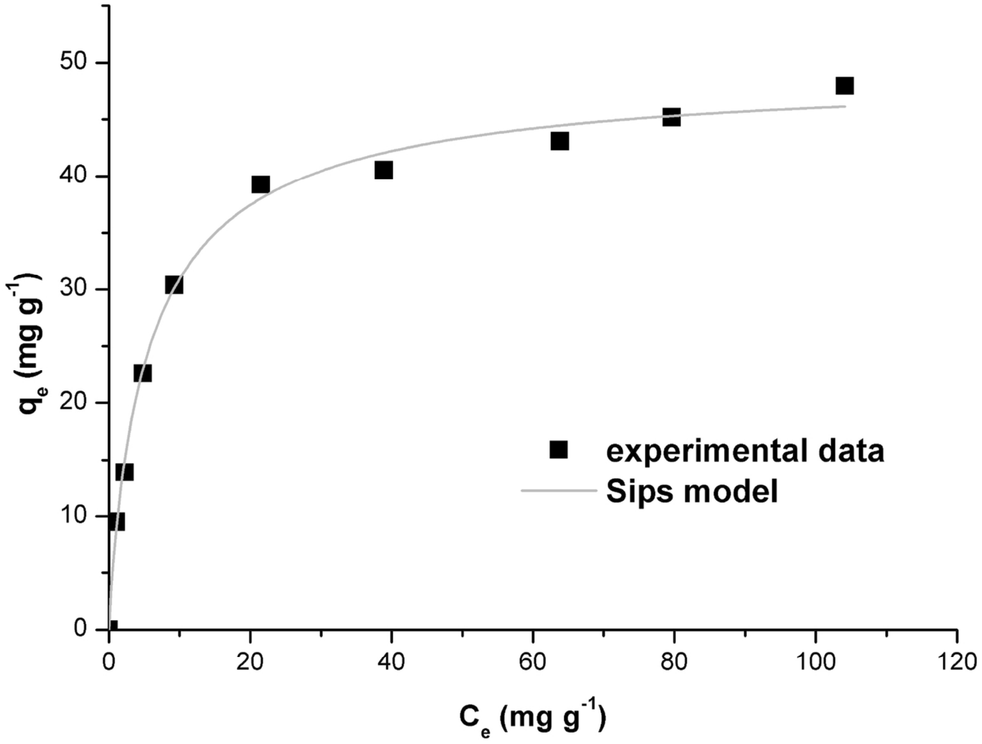

Figure 9. Correlations between experimental data and Sips adsorption isotherm for MB biosorption on corn husk
133x102mm (300 x 300 DPI)