Biosorption of methyl violet 2B by chemically treated Okoume sawdust: Kinetic, Isotherm and Thermodynamic studies

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Abstract

The ability of chemically treated Okoume sawdust (OST) to biosorb a hazardous triphenylmethane dye, methyl violet 2B (MV2B), from aqueous solutions has been studied in batch mode. Batch experiments were performed to examine the effect of operating parameters such as the effect of the initial basic dye concentration (5-30 mg/L), temperature (20-40°C), initial solution pH (2–9), biosorbent particle size (0.18–1.5 mm), contact time (0-120 min) on the removal of MV2B. Lagergren Pseudo-first-order, Blanchard pseudo-second-order, Elovich and Weber-Morris models were tested to fit the experimental data. The obtained results indicate that the biosorption process of MV2B onto OST obeyed a pseudo-second-order kinetics model (0.999≤ r ≤1). Equilibrium biosorption data at different temperatures were analyzed using Langmuir, Freundlich and Harkins-Jura isotherm models. Equilibrium data could be well described by the Langmuir model showing maximum monolayer biosorption capacity (q_m) of 102.04 mg/g at 20°C. Thermodynamic parameters such as $\Delta G°$, $\Delta S°$ and $\Delta H°$ were calculated, and the results suggest that the biosorption was a spontaneous physical and endothermic process.

Keywords: biosorption, chemically treated Okoume sawdust, batch study, methyl violet 2B dye, modeling

I. Introduction

Dyes are important pollutants causing environmental and health problems to human beings and to aquatic animals due to the large degree of presence of organic compounds. Therefore, it is necessary to treat the dye effluents according to a well-established pollution control and management. In fact a number of methodologies with varying degrees of success have been developed to manage water pollution, in order to protect the environment and offer people a better quality of life. In this approach, several scientific studies have considered various treating processes such as, membrane filtration, solvent extraction, carbon adsorption, reverse osmosis, precipitation as hydroxides or carbonates, capture on synthetic ion exchangers [1,2] and several biological routes. However, these methods are expensive mainly in developing countries and may generate a huge amount of waste causing disposal problems. For that reason it is necessary to develop a performing process able to efficiently and economically remove pollutants like dyes and heavy metals from aqueous solutions.

Recently, the biosorption process is receiving increasing attention and is becoming an attractive and promising technology [3]. The study of biosorption is of great importance from an environmental point of view, as it can be considered as an alternative technique for removing toxic pollutants from aqueous effluents. Methyl violet 2B is a basic dye, known to have harmful effects on living organisms even during short exposure times. Therefore the aim of the present investigations was to assess the efficiency of the removal of this dye from aqueous solutions using chemically treated Okoume sawdust (OST), an industrial waste greatly available and cheap, encouraging its use as a biosorbent for the removal of methyl violet dye (MV2B) from aqueous media

in a batch process. The effects of various operating parameters such as the initial dye concentrations, the contacting time, the initial solution pH, the particle size and the temperature on the MV2B removal, were investigated. The biosorption kinetics data were analyzed and tested with Lagergren Pseudo-first-order and Blanchard pseudo-second-order models. Equilibrium biosorption data at different temperatures were analysed using Langmuir, Freundlich, Elovich and Harkins-Jura isotherm models. Also, Thermodynamic parameters such as $\Delta G°$, $\Delta S°$ and $\Delta H°$ were calculated.

II. Materials and methods

II.1. Biosorbate and biosorbent

A priori the OST was washed with distilled water several times to remove any dirt particles and water soluble materials. The washed materials were then completely dried in an oven at 50°C. OST was mixed with a concentrated solution of sulfuric acid (H_2SO_4) during 24 h and then kept it in the oven at a temperature of 105°C until reaching a neutral pH. Finally, the obtained material was dried in an air circulating oven at 50°C for 48 h and stored in a desiccator ready for use.

The biosorbate was the methyl violet 2B (MV2B, a triphenyl methane cationic dye [C.I. number 42535; Basic Violet 1, chemical formula: $C_{24}H_{28}N_3Cl$, FW: 393.94 g/mol, λmax: 584 nm (measured)] and was obtained from Sigma chemical. The solution pH was adjusted using 0.1N HCl or NaOH aqueous solutions.

II.2. Procedures

The initial concentration of MV2B solution was 30 mg/L for all experiments, except for those carried out to examine the effect of initial dye concentration. For dye removal kinetic experiments, the batch method was used because of its simplicity. About 0.1 g of OST was contacted with 60 mL of dye solution in a sealed flask and

agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature. At predetermined intervals of time, sample filtrate of the mixture was withdrawn and analysed by a UV–Vis spectrophotometer for the concentration of dye. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature and stirring was provided at 250 rpm to ensure that equilibrium was reached. The analyses of the filtrate samples solutions were determined by measuring the absorbance at the maximum wavelength of 584 nm using a UV-visible spectrophotometer.

The amount of biosorption at any time, q_t (mg/g) was calculated by:

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

where C_0 and C_t (mg/L) are the liquid phase concentrations of dye at initial and any time t, respectively, V (L) is the volume of the solution and W (g) is the mass of the used biosorbent.

Biosorption equilibrium experiments were carried out for MV2B by adding a fixed amount of OST into a number of flasks containing definite volumes of the solution at different initial concentrations without varying the pH. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature (20-40°C) and agitated to ensure equilibrium to determine the maximum amount biosorbed at a constant stirring speed of 250 rpm followed by the filtration and analysis of the reaction mixtures.

The amount of biosorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_e (mg/L) is the liquid phase concentrations of dye at equilibrium time.

III. Results and discussion

III.1 Effect of operating conditions

III.1.1 Effect of initial MV2B concentration and contact time

The effects of the contacting time and the dye initial concentration on the biosorption uptake using OST at 20°C are shown in Figure 1 where it can be seen that the biosorption of MV2B increased with an increase in the initial dye concentration, confirming strong chemical interactions between MV2B and OST. This was due to increasing concentration gradients which acted as an increasing driving force to overcome all mass transfer resistances between the aqueous solution and solid phase. Figure 1 reveals that the biosorption of dye contacting time required to reach the equilibrium, at initial concentrations from 5 to 30 mg/L, was from 30 to 105 min respectively, and it was observed that the removal of dye biosorbed after equilibrium was from 2.22 at 13.94 mg/g, respectively.
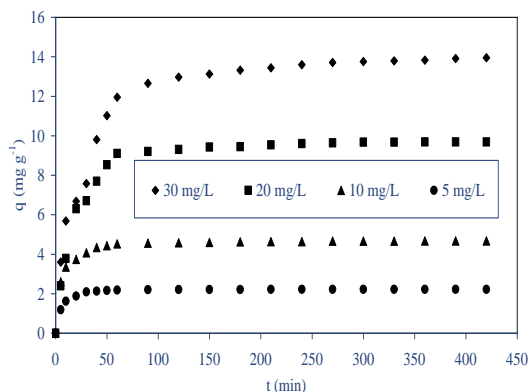

Figure 1. Effect of concentration and contact time on the biosorption of MV2B on OST

III.1.2 Effect of initial solution pH

The pH is considered as an essential parameter in the sorption process due to the fact that it affects the surface charge of the sorbent, the mechanism of the ionization degree of functional groups of the sorbate and the sorption process. Figure 2 shows the effect of initial pH on the biosorption of MV2B. It was observed that biosorption of MV2B was pH-dependent. In fact MV2B is a cationic dye which exists in aqueous solution in the form of positively charged ions, hence its degree of biosorption is primarily influenced by the surface charge on the biosorbent. The lower biosorption of MV2B at acidic pH was due to the presence of excess H^+ ions that compete with the dye cation for biosorption sites. As the pH of the system increases, the number of available positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favour the biosorption of dye cation due to electrostatic attraction. From figure 2 it was observed that the removal of dye biosorbed after equilibrium varied from 7.58 to 14.97 mg g^{-1}, respectively as pH increased from 2 to 9. Similar trend was observed for adsorption of Orange-G and Methyl Violet by bagass fly [4], methylene blue onto Posidonia oceanica (L.) fibres [5], yellow passion fruit peel [6] and methyl violet onto sunflower seed hull [7].
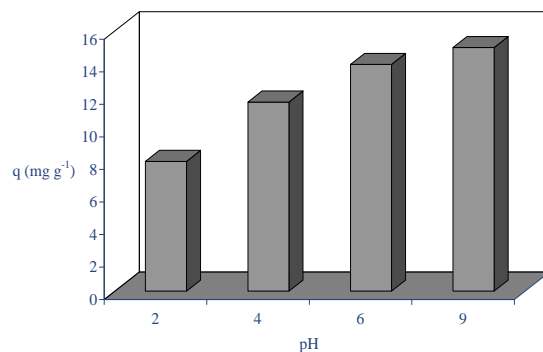

Figure 2. Effect of initial solution pH on the removal of MV on OST

III.1.3 Effect of temperature

The effect of temperature on the sorption of MV2B by OST at equilibrium was investigated at three different temperatures of 20, 30 and 40°C at an initial dye concentration of 30mg/L, a natural pH of 6.0 and a biosorbent dose of 0.1g/60mL (Figure 3). It was observed that the biosorption uptake slightly increased with an increasing temperature where for an increase from 20 to 40°C, the biosorption capacity increased from 13.93 to 14.60 mg/g, respectively. This phenomenon indicates that the biosorption process was endothermic in nature.
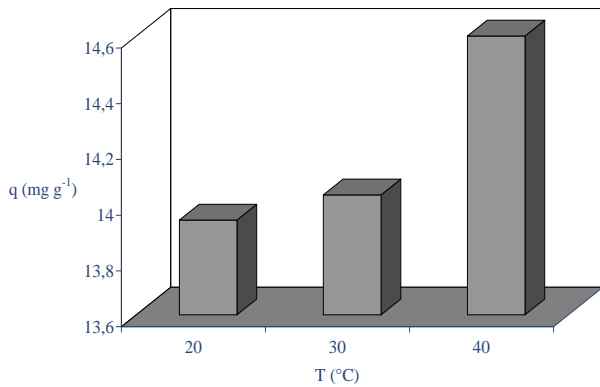
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Figure 3. Effect of temperature on the biosorption
of MV2B on OST

III.1.4. Effect of biosorbent particle size

Figure 4 shows the biosorption equilibrium of this
dye at three different particle sizes where it is
observed that the removal is enhanced as the
particle size decreases. The amount of MV2B
biosorption at equilibrium decreases with an
increase in particle size of OST. This is due to the
smaller particles which have a greater surface area
and to the access to the particle pores which is
facilitated when their size is small. It is moreover
believed that the breaking up of large particles to
form smaller ones opens some tiny sealed channels,
which might then become available for biosorption.
Therefore the biosorption by smaller particles is
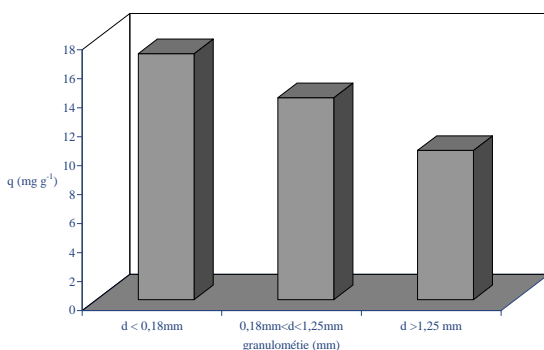higher than that by larger ones.

Figure. 4. Effect of particle size on the biosorption
of MV2B on OST

III.2 Biosorption kinetics studies

In order to investigate the mechanism of sorption
and potential rate-controlling steps such as mass
transport and chemical reaction processes, kinetic
models have been used to test experimental data.
These kinetic models included the Lagergren
pseudo-first order, the pseudo second-order, the
Elovich and intraparticle diffusion models.

III.2.1. Lagergren Pseudo-first-order model

Lagergren equation was used to investigate the
suitability of pseudo-first-order kinetic model and
obtain rate constants .This equation can be written
as [8]:

$$\ln \frac{q_e - q}{q_e} = -K_1 t \qquad (3)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of
dye sorbed at equilibrium and at any time t,
respectively, and k_1 (min^{-1}) is the rate constant for
Lagergren-first-order sorption. The straight line
plots of ln ($q_e - q_t$) against t of (Eq. 3) were made at
different initial dye concentrations. The k_1 values,
the correlation coefficients r, the predicted and
experimental q_e values are given in Table1 which
shows that the correlation coefficient values for
MV2B biosorption on OST changed in the range of
0.928 and 0.984. Also, the experimental $q_{e,exp}$
values were not in agreement with the calculated
$q_{e,cal}$ results, obtained from the linear plots. These
results have shown that the experimental data do
not agree with the pseudo-first-order kinetic model.

III.2.2. Pseudo-second-order model

Pseudo-second-order kinetic model can be
expressed as follows [8]:

$$\frac{t}{q} = \frac{1}{k_2 q^2_e} + \frac{1}{q_e} t \qquad (4)$$

where k_2 (min g mg^{-1}) is the rate constant for the
pseudo-second-order adsorption kinetics and h =
$k_2 q_e^2$, where h is the initial adsorption rate
(min mg g^{-1}). The pseudo-second-order rate
constant (k_2) and the equilibrium adsorption
capacity (q_e) can be determined experimentally

from the slope and intercept of the plot of t/q_t versus t. The pseudo-second-order rate constants k_2, the calculated $q_{e,cal}$ values and the corresponding linear regression correlation coefficients values r are given in Table 1 which shows that the correlation coefficient values for MV2B biosorption on OST varied in the range of 0.999 and 1. Also, the experimental $q_{e,exp}$ values were in agreement with the calculated $q_{e,cal}$ results obtained from the linear plots. These results showed that the experimental data do agree with the pseudo-second-order kinetic model.

III.2.3. Elovich equation

The Elovich equation is given as follows [9]:

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

where q_t is the adsorption capacity at time t (mg g^{-1}), α is the initial adsorption rate (mg g^{-1}min^{-1}) and β is the desorption constant (g mg^{-1}) during any one experiment.

Thus, the constants can be obtained from the slope and intercept of a straight line plot of q_t versus ln t. As seen in Table 1, the correlation coefficients for the Elovich equation varied in the range of 0.959 and 0.976. This result showed that the experimental data did not fit with the Elovich equation.

Table 1 Parameters of the kinetic models for the biosorption of MV2B onto OST

Kinetics models	Initial concentration C_0 of MV2B (mg L^{-1})			
	5	10	20	30
pseudo-first-order				
$q_{e,exp}$ (mg g^{-1})	**2.17**	**4.67**	**9.69**	**13.94**
$q_{e,cal}$ (mg g^{-1})	0.42	1.23	4.05	6.63
k_1(min^{-1})	0.027	0.017	0.014	0.012
r	0.928	0.965	0.984	0.980
Pseudo-second-order				
$q_{e,cal}$ (mg g^{-1})	2.32	4.71	10.01	14.55
k_2(gmg^{-1}min^{-1})	0.187	0.054	0.09	0.04
h(mg g^{-1}min^{-1})	0.933	1.215	0.885	0.824
r	1.000	1.000	0.999	0.999
Elovich				
α (mg g^{-1} min^{-1})	1.29	3.97	8.63	10.32
β (g mg^{-1})	0.128	0.752	0.630	0.503
r	0.959	0.973	0.968	0.976

III.2.4. intraparticle diffusion model

Weber and Morris plot [8] was used to investigate intraparticle diffusion mechanism. Intraparticle diffusion model is characterized by the relationship between specific sorption and the square root of time, according to the following equation:

$$q_t = k_i t^{1/2} + C \tag{6}$$

where q_t is the amount sorbed at any time (mg g^{-1}), k_i is intraparticular diffusion rate constant

(mg g^{-1} min$^{-1/2}$), $t^{1/2}$ is the square root of time (min$^{1/2}$) and C is the intercept, which represents the resistance to mass transfer in the external liquid film. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the limiting step. However, the linear plots (Figure. 5) at each concentration did not pass through the origin. This indicates that the intraparticle diffusion was not only rate controlling step.
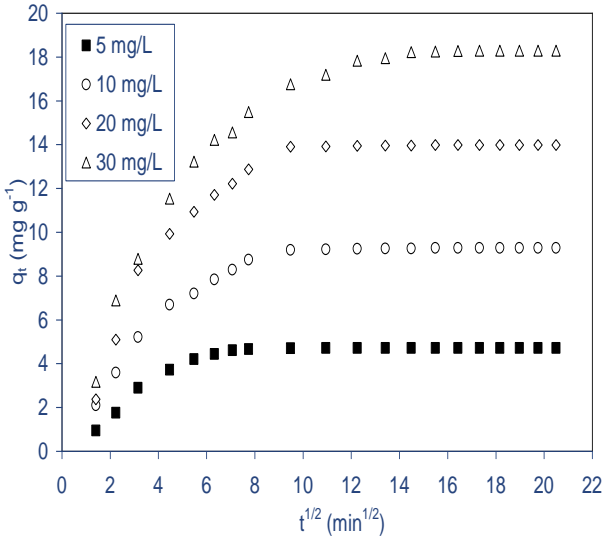
a

Figure.5 Intraparticle diffusion plots for the biosorption of MV2B on OST

III.3 Equilibrium isotherm studies

Various isotherm models have been used to describe the equilibrium data nature of biosorption. For this purpose, the biosorption equilibrium data were modeled by Langmuir, Freundlich and Harkins-Jura [8, 10] equations. The linear forms of these four isotherm models were represented as follows:

Langmuir: $\dfrac{C_e}{q_e} = \dfrac{1}{b\,q_m} + \dfrac{1}{q_m} \times C_e$ (7)

Freundlich: $\ln q_e = \ln K_F + \dfrac{1}{n_F} \ln C_e$ (8)

Harkins-Jura $\dfrac{1}{q^2_e} = \dfrac{B_{H\text{-}J}}{A_{H\text{-}J}} - \dfrac{1}{A} \log C_e$ (9)

where q_m is maximum biosorption capacity (mg/g), b is Langmuir constant (L/mg), K_F ($mg^{1-\frac{1}{n}}\,L^{\frac{1}{n}}/g$) is Freundlich biosorbent capacity, $1/n_F$ is heterogeneity factor (if $n_F > 1$, the biosorption is a favorable physical process), $A_{H\text{-}J}$ and $B_{H\text{-}J}$ were Harkins-Jura constants.
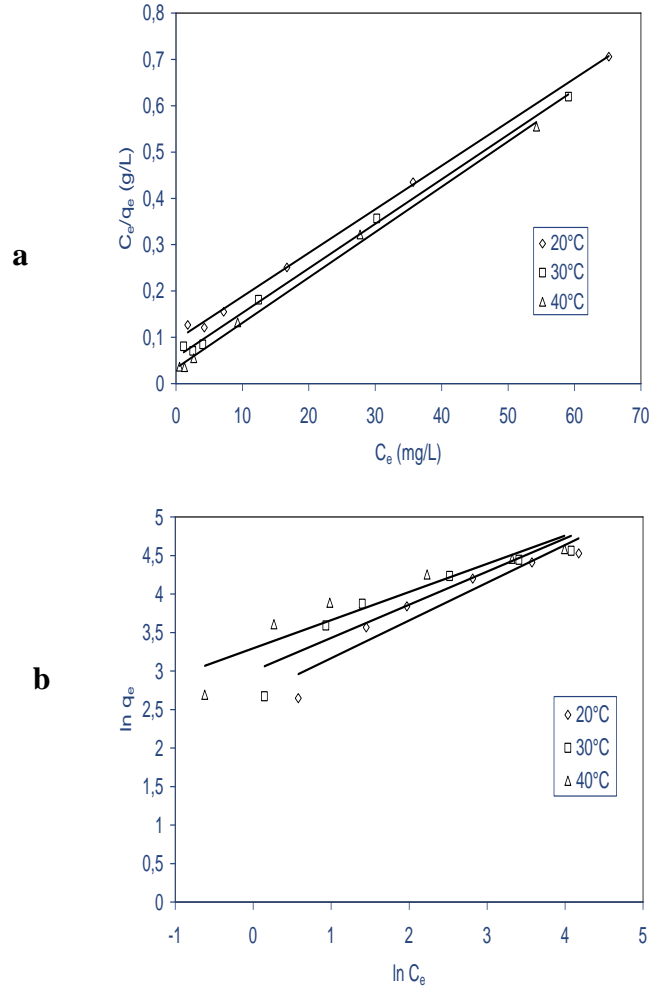
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Figure. 6 Linear plots of isotherm models for the biosorption of MV2B on OST: (a) Langmuir and (b) Freundlich
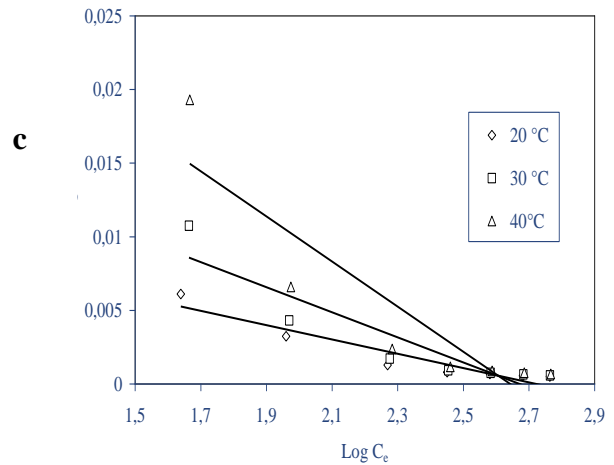
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Figure. 7 Linear plots of isotherm model for the biosorption of MV2B on OST: (c) Harkins-Jura

Figures 6 and 7 shows the plotted models including the fitted models at 20-40°C and the result parameters isotherm studies were summarized in Table 2.

Relying upon on the obtained correlation coefficient values (*r*), it was clear that Langmuir model provided a good fit (*r* ≥ 0.999) for the

experimental equilibrium biosorption data. The maximum biosorption capacity (q_m) of Langmuir was varying from 102.04 to 106 mg/g, respectively, from 20 to 40°C. As n_F > 1, indicating that biosorption of this dye on OST is a favorable physical process.

Table 2. Parameters of isotherm models for the removal of MV2B onto OST

Model	Parameters	T (°C)		
		20	30	40
Langmuir	q_m *(mg g^{-1})*	102.04	104.04	106.38
	b (L mg^{-1})	0.104	0.169	0.286
	r	0.999	0.999	0.999
Freundlich	K_F (mg$^{1-\frac{1}{n}}$ L$^{\frac{1}{n}}$ g^{-1})	14.48	20.04	26.90
	n_F	2.04	2.32	2.73
	r	0.952	0.932	0.932
Harkins-Jura	A_{H-J}	163.93	238.65	298.55
	B_{H-J}	0.245	0.132	0.187
	r	0.851	0.911	0.939

III.4 Thermodynamic parameters

The thermodynamic parameters that must be considered to determine the process as changes in enthalpy *(ΔH°)*, entropy *(ΔS°)* and free energy *(ΔG°)* are calculated using the following equations [11]:

$$\Delta G^o = -R_g T \ln b \qquad (10)$$

In which T (K) is the absolute temperature, Rg (kJ mol^{-1} K^{-1}) is the gas constant and b (L mol^{-1}) is the Langmuir equilibrium constant.

$\Delta G°$ (kJ mol^{-1}) is the function of change in enthalpy of sorption, $\Delta H°$ (kJ mol^{-1}) as well as change in standard entropy, $\Delta S°$ (J mol^{-1} K^{-1}):

$$\Delta G° = \Delta H° - T\Delta S° \qquad (11)$$

The thermodynamic parameters are collected in Table 3. The negative values of *ΔG°* demonstrate

the feasibility of the process and the spontaneous nature for the biosorption. The lower and negative value of *ΔS°* indicates that may imply that no remarkable change in entropy occurred during the biosorption of MV2B. The positive value of enthalpy change indicated the endothermic nature of the biosorption interaction. Similar thermodynamic results were found in the biosorption of malachite green by treated rice hush [8] and Brilliant Green by modified Bambusa Tulda [12].

Table 3. Thermodynamic parameters

T (°C)	*ΔH°* (kJ/mol)	*-ΔG°* (kJ/mol)	*ΔS°* (J/mol K)
20		5.74	
30	1.87	6.01	26.0
40		6.26	

IV. Conclusions

The results obtained in this study demonstrated the potential use of OST for the biosorption of MV2B dye from aqueous solutions. The biosorption kinetics is well described by the pseudo-second order model. However, for the biosorption mechanism, the intraparticle diffusion was not the only rate-limiting step. The maximum monolayer biosorption capacity was of 102, 04 mg/g at 20°C. The negative value of change in free energy ($\Delta G°$) and change enthalpy ($\Delta H°$) indicated the spontaneous nature for the biosorption and the endothermic nature of the biosorption interaction, respectively of this dye onto the OST.

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