

MUHAMMAD IMRAN DIN
KIRAN IJAZ
KHALIDA NASEEM

Institute of Chemistry, University of
Punjab, Lahore-54590, Pakistan

SCIENTIFIC PAPER

UDC 633.61:66.081.3:544.4

BIOSORPTION POTENTIALS OF ACID MODIFIED *Saccharum bengalense* FOR REMOVAL OF METHYL VIOLET FROM AQUEOUS SOLUTIONS

Article Highlights

- Removal of methyl violet dye from aqueous solution by acid modified *Saccharum bengalense*
- Adsorption reaction follows pseudo second order kinetics
- Langmuir adsorption isotherm is best followed by adsorption data
- Adsorption of dye molecules on the surface of adsorbent is in single layer

Abstract

In the present work, Saccharum bengalense (SB) was treated with sulfuric acid to enhance its efficiency. Methyl violet (MV), a cationic dye, was removed from aqueous medium using acid modified S. bengalense (A-SB). Different parameters like adsorbent dosage, stirring speed, temperature, contact time and effect of initial concentration of dye on rate of adsorption of dye from aqueous medium was studied. Experimental data obtained from adsorption of MV was analyzed by applying pseudo first order, pseudo second order and intra-particle diffusion models and it was found that the data best follows the pseudo-second order kinetics. Thermodynamic parameters indicate that adsorption reaction was spontaneous, feasible and endothermic in nature. Different adsorption isotherm models, like Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin, were used to study the mechanism of adsorption process and experimental data was well fitted by the Langmuir adsorption isotherm.

Keywords: biosorption, Saccharum bengalense, kinetics, thermodynamics, dye.

During the last few years, industrial development has left deleterious effects on the environment. Dyes are used in many industries, especially in textile industry, Textile industries use different dyes for dyeing their products. Thus, as a result of poor dye fixation on fiber, 50% of dye is removed in water, which causes production of colored wastes, which are also contaminated with other organic pollutants [1]. Water contaminated with dyes affects people as this water is used for different purposes like drinking, washing and bathing [2]. Even low concentrations of dye, like 1.0

mg/L, can impart visible color to water, which makes it unfit for human use [3]. Dyes have the ability to absorb the specific wavelength of light so they interfere with sunlight to reach the water bodies, which causes harmful effects on the aquatic life. Dyes are highly carcinogenic, mutagenic and damage liver, kidneys, brain, central nervous system and reproductive system of human beings [4-6]. Due to high visibility and toxicity of dyes, their removal from contaminated water bodies has become very important [7].

Different techniques like chemical oxidation, membrane separation, coagulation, aerobic and anaerobic microbial degradation can be used for treatment of dye polluted wastewater but these methods have not attained much importance due to certain restrictions [8]. Among all these methods used for the treatment of wastewater, adsorption is preferred due to its high quality and the cheapness [9]. Wastewater

Correspondence: M.I. Din, Institute of Chemistry, University of Punjab, Lahore-54590, Pakistan.

E-mail: imrandin2007@gmail.com
Paper received: 17 December, 2015

Paper revised: 9 August, 2016

Paper accepted: 13 November, 2016

<https://doi.org/10.2298/CICEQ151217054D>

treated by using activated carbon in the adsorption process has become a very important aspect of recent research [10]. Therefore, effluent-containing wastewater is treated with activated carbon before its disposal in environment [11]. However, this method is not economically feasible due to requirements of the activated carbon regeneration and the decrease in its efficiency after recycling [12]. Presently, adsorption has become an economically suitable and realistic method for the removal of different pollutants like COD [13,14], gasses [15], heavy metals [16,17], phenol [18,19] and dyes [20-23] from aqueous media using the agricultural by-products as adsorbents. Literature studies showed that different researchers have used different methods for the activation of the adsorbent to enhance its adsorption capacity. Activation may be physical, such as carbonization, or chemical, by using chemical activating agents.

Xu *et al.* synthesized biochar from different crop residues and used it as an adsorbent for adsorption of methyl violet from aqueous medium [24]. They also showed that biochar have high ability to remove MV from aqueous medium. Tian *et al.* prepared nano-sized Fe₂O₃ modified baker yeast biomass and used it as efficient adsorbent for removal of MV from aqueous medium [25]. They also observed that adsorbent has capability to be removed from mixture magnetically due to presence of spherical nano-Fe₂O₃ on the surface of biomass. Ofomaja and his coworkers reported *Mansonia* wood sawdust as biosorbent for removal of MV from aqueous medium [26]. Effects of temperature and pH on the biosorption process were studied. They concluded from their experiment that biosorption process was strongly depending upon the pH of the medium and percentage removal efficiency of biosorbent was significantly high at pH > 7.

In our work, activated carbon was prepared from SB by chemical activation method and was used as adsorbent for removal of MV dye from aqueous medium. The novelty of our work is the use of acid modified *Saccharum bengalense* as biosorbent for removal of MV from aqueous medium, because researchers have not employed it as adsorbent for dye removal. Different parameters that affect the rate of adsorption of dye were also studied. The values of adsorbent dose, contact time temperature and stirring speed at which maximum adsorption rate was observed were used for further studies. Different models, such as pseudo-first order, pseudo-second order and intra-particle diffusion models were used to study the kinetics of adsorption of methyl violet on SB. Thermodynamic studies were done to estimate the nature and feasibility of the adsorption process. The mech-

anism of the adsorption process was studied using Langmuir, Freundlich, D-R and Temkin adsorption isotherms.

MATERIALS AND METHODS

Chemicals

Methyl violet (MV), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄) and hydrochloric acid (HCl) were of analytical grade and obtained from Sigma Aldrich. All chemicals were used as received without any further treatment.

Methyl violet as adsorbate

Methyl violet (MV) was used as an adsorbate. It covers three compounds: MV-2B, MV-6B, and MV-10B, which differ in the number of methyl groups attached to amine. The change in color of dye depends upon the number of methyl groups present in it. In inks and paints, it is used as violet color, while in textile industry it is used as purple color dye. Methyl violet 6B is intermediate between 2B (less dark) and 10B (more dark) in color. Dipropylene, water and diethylene glycol are important solvent for this dye. We used methyl violet-6B (MV) as adsorbate and water as solvent for our work. 1 g of dye was dissolved in 1000 mL of deionized water to prepare stock solution of 1 g/1000 mL concentration. For experimental purposes, the concentration of dye was changed from 16 to 32 ppm and the optimum concentration of dye was found.

Acidic *S. Bengalense* as biosorbent

SB obtained from the bank of the river Ravi in Lahore, Pakistan, was washed with water to remove dust and unwanted particles. Then, the washed SB was dried under shade. After drying, the outer layer of samples was removed to obtain the inside pulp. A standard knife mill was used to mill the SB pulp and passed through 60-mesh screen. Milled SB was stored in air tight bottle for further use in experimental work. The weighed amount of SB was taken in a beaker and then H₂SO₄ (17 M) was added in it. The SB was dipped in acid for two hours. After that, it was washed with water and filtered. After filtration, the residue at the filter paper was dried in oven at 70 °C. After drying, the sample was ground with mortar so that all particles were of the same size and shape. These particles were placed in an airtight container for further use and labeled as A-SB.

Characterization of biosorbent

FTIR spectroscopy was used to analyze the SB and acid modified SB. FTIR analysis was done to find

the difference between vibrational frequencies of functional groups of SB and A-SB in range of 4000–400 cm^{-1} . For this purpose, samples were degassed for 2 h at 300 °C. The disc method was employed to analyze the samples by using a Tensor 27, Burker (Germany) FTIR spectrophotometer.

Biosorption experiments

Effect of adsorbent dose on the rate of adsorption of dye from aqueous solution was studied by varying the dose of adsorbent from 0.1 to 0.5 g in the adsorbent-adsorbate solution. The initial concentration of dye was kept constant while pH of solution was adjusted as 10. Solutions containing different adsorbent dose were stirred until equilibrium was established.

Effect of contact time on the rate of adsorption of dye was also studied by varying the shaking time from 10 to 70 min while the concentration of adsorbate-adsorbent was 0.2 g/50 mL at pH 10. After specific time interval, the solution was pipettes out from flasks, filtered and absorbance was measured using a 721 visible spectrophotometer (Shanghai Hansom Technology and Sales Limited, China)

Effect of temperature on the rate of adsorption of dye by biosorbent was studied by varying it in range of 10 to 60 °C while the concentration of adsorbent-adsorbate was 0.2 g/50 mL at pH 10 and contact time 50 min. Temperature was maintained during adsorption process until equilibrium was established and sample was pipette out for absorbance measurement. Rate of adsorption of dye was also studied by varying stirring speed from 100 to 175 rpm while all other parameters were kept constant. Stirring speed of 125 rpm at which maximum adsorption occur was found.

Effect of concentration of dye on the rate of adsorption process was also studied by changing its concentration from 16 to 32 ppm while all other factors were kept constant. Adsorbate-adsorbent solutions were stirred at optimum speed of 125 rpm to attain equilibrium and absorbance of relative solutions was found. Percentage removal efficiency was calculated for all parameters studied. It is the adsorption cap-

acity of adsorbent or amount of solute adsorbed on the adsorbent and can be represented as follows:

$$\text{Percentage removal } (R) = 100 \frac{C_o - C_e}{C_o} \quad (1)$$

where C_o (mg/L) and C_e (mg/L) are the concentration of solute in solution at start of adsorption process and at equilibrium, respectively, and q_e (mg/g) represents the biosorption capacity of SB at equilibrium and indicates the solute concentration adsorbed at the surface of adsorbent:

$$q_e = V \frac{C_o - C_e}{m} \quad (2)$$

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was used to study the structural hierarchies of SB and A-SB. Band positions for different functional groups present within SB and A-SB are given in Table 1. FTIR data indicates that SB and A-SB samples have common functional groups like amine and alcoholic groups. Secondary and tertiary alcoholic groups are present in SB while only tertiary alcoholic groups are present in A-SB samples. Both spectra also show that aromatic character is present in both samples. SB also has carbonyl groups. Literature survey shows that mostly FTIR spectra of SB have similar peaks which indicates the presence of different groups like hydroxyl group of alcohols, carbonyl group of aldehydes, ketones, ester and carboxylic acid and aromatic group [27,28].

Optimization of biosorption parameters

Effect of adsorbent dose

Percentage removal efficiency (R) of biosorbent increases with increase of biosorbent dose due to increase of availability of binding site as reported earlier [29]. It was observed that %R of biosorbent was increased with increase of adsorbent dose up to a certain limit. After that, further increase of adsorbent dose caused the overlapping of binding sites and adsorption capacity was decreased. Effect of adsorbent

Table 1. FT-IR analysis of SB and A-SB

Bond	Functional group	ν Range, cm^{-1}	SB, cm^{-1}	A-SB, cm^{-1}
v(C-N) s	Aliphatic amines	1020-1220	1035	1035
v(C-O) s	Secondary alcohols	1100	1104	-
v(C-O) s	Tertiary alcohols	1150-1200	1162	1167
v(C-O) s	Carbonyl group (acid)	1210-1320	1245	-
v(C-C) s	Aromatics	1400-1500	1508	-
v(C-H) s	Aromatics	860-900	900	874

dose on rate of adsorption was studied by varying adsorbent concentration from 0.1 to 0.5 g while all other factors were kept constant. Figure 1a shows the relation between adsorbent dose and its R . R of A-SB was increased with the increase of biosorbent dose and maximum R was attained at 0.2 g. At optimum dose (0.2 g/mL), R was 98.5%. Further increase of adsorbent dose decreased the value of R . Results

show that at high adsorbent concentration overlapping of binding sites occurs which decreases the value of R [29]. The results were in agreement with the previous work reported in literature [27,30].

Effect of contact time

Efficiency of adsorbent also depends upon the time duration of adsorbent-adsorbate contact. When

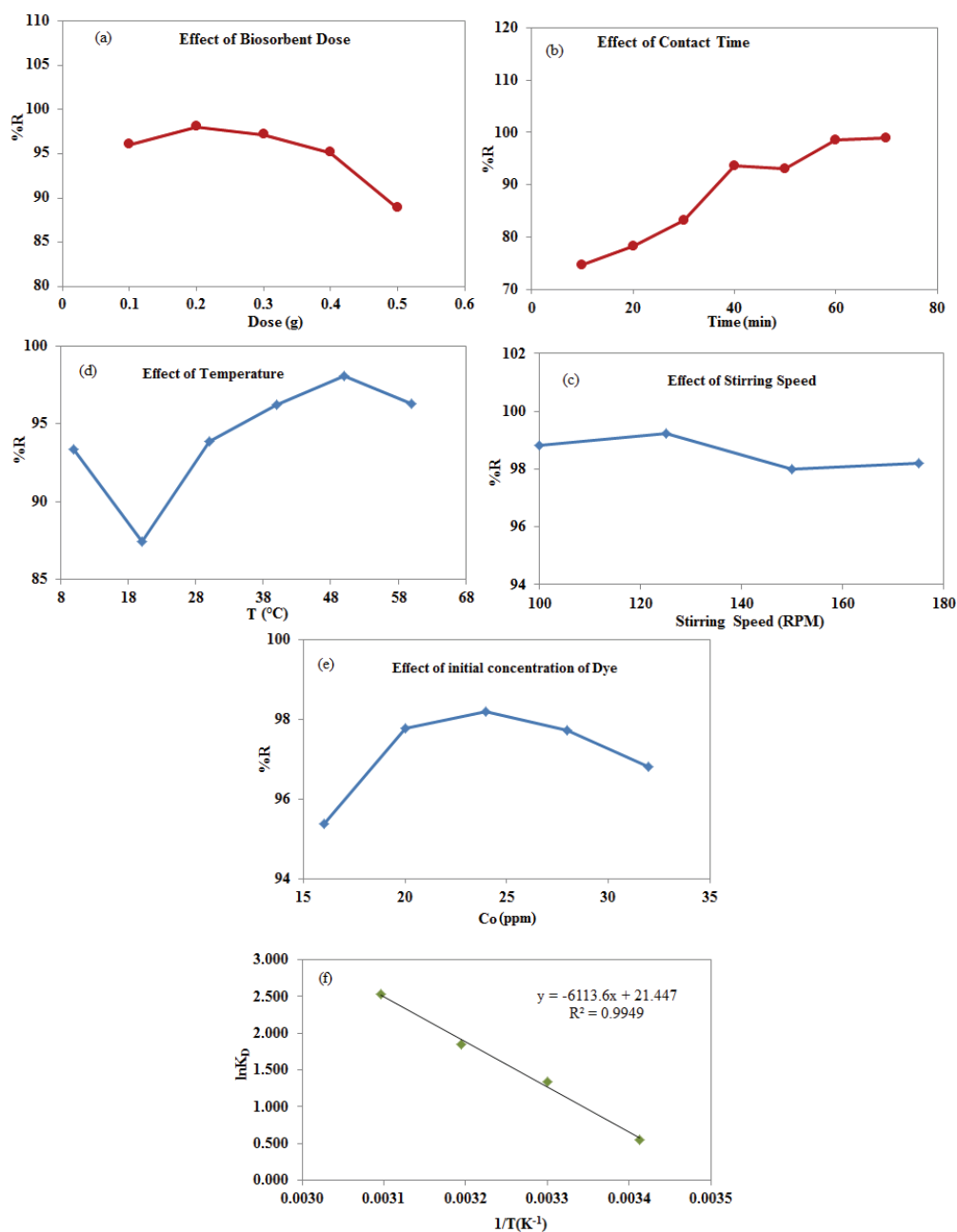


Figure 1. a) Effect of biosorbent dose (A-SB) for adsorption of MV at pH 10, $T = 323$ K, contact time = 50 min, stirring speed = 125 rpm; b) effect of contact time on biosorption of MV on A-SB at pH 10, $T = 323$ K and dose = 0.2 g/50 mL; c) effect of stirring speed on biosorption of MV on A-SB at $T = 313$ K, pH 10, dose = 0.2 g/50 mL, contact time = 50 min; d) effect of temperature on biosorption of MV on A-SB, pH 10, biosorbent dose = 0.2 g/50 mL, contact time = 50 min; e) effect of initial concentration of dye on adsorption of MV on A-SB, pH 10, biosorbent dose = 0.2 g/50 mL, contact time = 50 min, f) determination of thermodynamic parameters at pH 10, biosorbent dose = 0.2 g/50 mL, contact time = 50 min.

shorter time is required to attain equilibrium then efficiency of adsorbent to remove dyes from wastewater is high. At the start of contact time, rate of biosorption is high which becomes slower at the time near to the establishment of equilibrium. Different rate of adsorption during whole process is due to availability of active sites which are high at the start of reaction. Near equilibrium, molecules face inter repulsive forces as well as less binding sites are available so rate of adsorption becomes slow down [28]. The effect of contact time on R is leveled, continuous and single [31,32] as shown in Figure 1b. The R increases with increase of contact time but after some time it becomes constant. This stage is called equilibrium, at which all the binding sites of the adsorbent are occupied by the dye molecules and no further vacant sites are present for further adsorption of dye molecules [33,34]. The contact time of 50 min at which saturation occurs was used for further experimental work.

Effect of stirring speed

Literature survey shows that stirring speed has no significant effect on the value of R of adsorption during adsorption process. Effect of stirring speed was studied by varying its value from 100 to 175 rpm and all other parameters like biosorbent dose, contact time, temperature, pH and dye concentration were kept constant, as shown in Figure 1c. The value of R of A-SB increases slightly with the increase of stirring speed up to 125 rpm, but becomes constant with further increase in its value. Optimum stirring speed of 125 rpm, at which value of R was maximum, was used for further work.

Effect of temperature

Effect of temperature on the adsorption process indicates whether reaction is endothermic or exothermic. When adsorption capacity of adsorbate increases with increase of temperature it is called endothermic process. Increase in temperature may increase the movement of dye molecules or increase the number of active sites as a result R of adsorbent increases [35]. While in case of endothermic adsorption process, rate of adsorption decreases with increase of temperature because of decrease in attractive forces between the molecules of dye and active sites of adsorbate [36,37]. Figure 1d shows that when the temperature of the medium was increased from 10 to 60 °C, the value of R was increased up to 50 °C but further increase of temperature decreased the R of the adsorbent.

Effect of dye concentration

R of adsorbent for dye from aqueous solution also depends upon the initial dye concentration. R of

adsorbent for different concentration of dye decreases with increase of dye concentration due to saturation of binding sites of adsorbent as reported earlier [38]. When the concentration of dye is low, some binding sites are unoccupied and value of R increases. But with the increase of initial concentration of dye, availability of active site decreases because number of active sites remain fixed due to constant concentration of the adsorbent [39]. Dye concentration was varied between 16 to 32 ppm while all other parameters were kept constant to study its effect as shown in Figure 1e. It can be seen from Figure 1e that R increases with increase of dye concentration up to a specific value after which R decreases with increase of dye concentration. Results are compatible with previous reported work [40]. At high dye concentration, competition increases between its molecules for binding sites as a result R decreases [41].

Thermodynamic study

Different thermodynamic parameters for the biosorption of MV on the surface of A-SB were also studied by making use of following equations [42,43]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

$$\Delta G^\circ = -RT \ln K_D \quad (4)$$

$$K_D = \frac{C_{AS}}{C_e} \quad (5)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where ΔG° and ΔH° are Gibbs free energy and enthalpy change respectively, T is temperature, ΔS° is the entropy change, while K_D is the distribution coefficient. C_{AS} and C_e are the total amount of adsorbate adsorbed and its amount at equilibrium, respectively.

The value of ΔH° , ΔG° and ΔS° was calculated by plotting a graph between $1/T$ and $\log K_D$ using Eq. (6), as shown in Figure 1f. The value of ΔH° was calculated from slope while the value of ΔS° was calculated from intercept of the graph. Different thermodynamic parameters like ΔH° , ΔG° and ΔS° calculated for biosorption of MV from the aqueous medium using A-SB are given in Table 2. The value of ΔG° was calculated at temperature 313 K using Eq. (3) because maximum amount of MV was adsorbed on SB at this temperature. The value of ΔG° shows the nature along with feasibility of biosorption process. The negative value of ΔG° in adsorption of MV shows that the reaction is spontaneous and energetically feasible [44]. The value of ΔH° can be posi-

Table 2. Thermodynamic parameters for biosorption of MV on A-SB

Thermodynamic parameter	Parameters value	Conclusion
$\Delta G^\circ / \text{J mol}^{-1}$ at 313 K	-6817.49	Negative sign indicates spontaneous and feasible nature
$\Delta H^\circ / \text{J mol}^{-1}$	50825	Endothermic process
$\Delta S^\circ / \text{J mol}^{-1} \text{K}$	178.25	Increase in randomness at the surface of solid-solution

tive or negative depending upon the nature of biosorption process. Here, positive value ΔH° for biosorption process shows that the reaction is endothermic in nature of reaction [45,46]. The value of ΔS° shows the change in randomness of atoms which are being adsorbed on the surface of adsorbent [47]. Its value can also be positive or negative. Positive value of entropy change for adsorption of MV by SB shows that adsorption rate increases with increase of randomness of reactant atoms [48].

Adsorption isotherms

Adsorption isotherms show the adsorption capacity of adsorbent and adsorption mechanism of how dye molecules interact with its active sites. Different isotherms - Temkin, Freundlich, Langmuir and D-R - were employed to analyze the data. These isotherms also explain whether the adsorption of MV molecules on the surface of SB was monolayer or multilayer. For this purpose, data was obtained by carrying the adsorption process at optimum conditions of temperature, pH, stirring speed, concentration of dye and contact time.

Langmuir adsorption isotherm

The Langmuir adsorption isotherm was presented by Irving Langmuir in 1916 to explain the mechanism of adsorption of gas molecules over the surface of activated carbon [49,50]. This isotherm also shows that adsorbate molecules do not interfere with each other during adsorption process and they are restricted to form a monolayer [50]. This isotherm also explains that once the dye molecule is adsorbed at one site then further adsorption does not occur at that site [55].

Graph was plotted between C_e/q_e and C_e as shown in Figure 2a. C_e (mg/L) and q_e mg/g represents the concentration of dye in solution and concentration of dye on adsorbent at equilibrium, respectively.

The value of q_m was found from the slope while the value of K_L was calculated from intercept of the graph shown in Figure 2a. Langmuir parameters for adsorption of MV on the surface of A-SB surface are given in Table 3. The value of correlation coefficient R^2 is 0.981 which is approximately equal to unity and

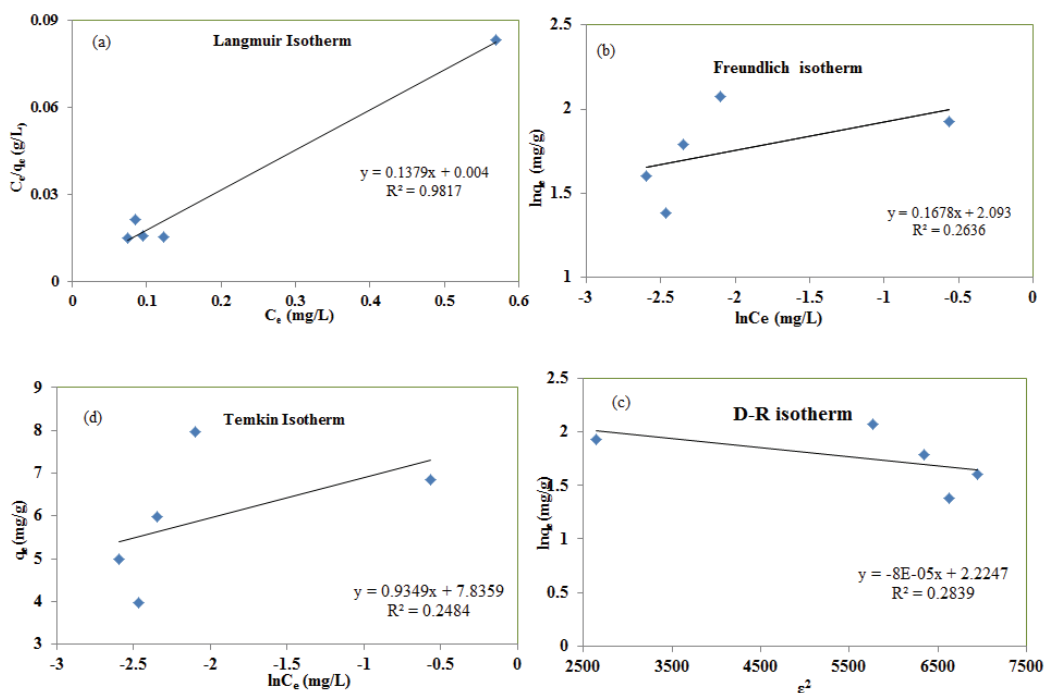


Figure 2. a) Langmuir, b) Freundlich, c) D-R and d) Temkin isotherm at pH 10, biosorbent dose 0.2 g/50 mL, contact time = 50 min, $T = 313 \text{ K}$ and stirring speed = 125 rpm.

indicates that Langmuir isotherm best explain the adsorption process of MV on the surface of A-SB. The calculated value of q_m is 7.299 mg/g. The validity of Langmuir isotherm indicates that monolayer adsorption of dye molecules occurs on the surface of SB while no interaction exists between adsorbed dye molecules. Ozdemir *et al.* found the adsorption capacity of Sepiolite for methyl violet as 2.55 mg/g at 50 °C temperatures by employing the Langmuir adsorption isotherm [34]. A comparison of q_m values for methyl violet to be adsorbed by different adsorbent using the Langmuir adsorption isotherm is given in Table 4.

Table 3. Parameters of different adsorption isotherms

Adsorption Isotherm	Parameters of adsorption isotherms		
Langmuir	$K_L / L\ m^{-1}$	$q_m / mg\ g^{-1}$	R^2
	34.25	7.299	0.981
Freundlich	K_F	n	R^2
	8.109	6.25	0.263
D-R	β	$q_m / mg\ g^{-1}$	R^2
	8×10^{-5}	9.24	0.283
Temkin	$K_T / g\ L^{-1}$	β	R^2
	4396	0.934	0.248

Table 4. A comparison for methyl violet (MV) capacity of different biosorbents

Adsorbent	MV capacity $q_m / mg\ g^{-1}$	Reference
Sepiolite	2.550	[34]
Sepiolite	2.330	[33]
Banana peel	12.20	[51]
Orange peel	11.50	[51]
Duckweed	332.5	[52]
<i>Artocarpus odoratissimus</i> skin	184.6	[53]
Water lettuce	267.6	[54]
Acid modified <i>S. bengalense</i>	7.299	Our study

Freundlich adsorption isotherm

Kuster and Freundlich presented a model in 1894 to explain the non-ideal and reversible adsorption process. They explain in their work that adsorption takes place on the heterogeneous surface in the form of multilayers [55]. The Freundlich adsorption isotherm is represented as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (7)$$

In this equation, K_f is the dimensionless constant which represents the adsorption capacity while n represents the intensity of adsorption. q_e and C_e are

the equilibrium concentrations of adsorbate at adsorbent and in solution, respectively. Figure 2b shows the plot between $\ln q_e$ and $\ln C_e$ from which value of correlation coefficient was calculated which is not compatible with literature. It means experimental data cannot be explained by Freundlich adsorption isotherm and multilayer adsorption of MV dye molecules does not occur at the surface of A-SB. The values of correlation coefficient (R^2) for Langmuir and Freundlich isotherms indicate that adsorption of MV on the surface of A-SB follows the former isotherm as compares to the latter one.

Dubinina Radushkevich (D-R) isotherm

D-R model is represented by equation as follows [56]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

where q_m (mg/g) and β ($\text{mol}^2\ \text{K}/\text{J}^2$) are theoretical saturation capacity and D-R constant, respectively, and ε in term of C_e is given as follows [42]:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9)$$

D-R model explains the nature of surface of adsorbent like heterogeneity or homogeneity [57]. A graph was plotted between $\ln q_e$ and ε^2 as shown in Figure 2c. The values of D-R parameter calculated from graph shown in Figure 2c are given in Table 3. Value of E_s (kJ/mol) can be calculated from [58]:

$$E_s = \frac{1}{\sqrt{\beta}} \quad (10)$$

Two factors are usually involved to decide whether data follows the D-R isotherm or not. The first one is the value of R^2 and the second is the comparative analysis of calculated and actual value of q_m for the adsorption process. Here, the value of R^2 is not close to unity and the value of q_m is not comparable to experimental value. Thus, the results show that adsorption of MV on the surface of SB does not follow the D-R model.

Temkin adsorption isotherm

This isotherm model shows that the value of heat of adsorption decreases linearly for the molecules that are present in the same layer during adsorbent-adsorbate interaction [59]. The equation for Temkin adsorption isotherm is as follows:

$$q_e = \beta \ln K_t + \beta \ln C_e \quad (11)$$

In this equation, K_t (1/g) and β are equilibrium binding constant and adsorption heat respectively.

Graph for Temkin adsorption isotherm is shown in Figure 2d and data is given in Table 3. The R^2 value shows that adsorption process does not follow Temkin adsorption isotherm.

Kinetics of methyl violet adsorption

Kinetics of adsorption of MV on the surface of SB was studied by employing different kinetic models as pseudo-first order, pseudo-second order and intra-particle diffusion model etc. Pseudo-first order was proposed by Lagergen in 1898. It is employed to observe the mechanism of adsorption of liquid or solid samples. It is represented by the following equation [60]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (12)$$

After integration, Eq. (12) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

In this equation, k_1 is pseudo-first order rate constant while q_t (mg/g) is adsorption capacity at any time t . Graph was plotted between $\ln(q_e - q_t)$ vs. time to study the pseudo-first order kinetics of the adsorption of MV on the surface of SB as shown in Figure 3a and data is given in Table 5. The value of R^2 is small as compared to experimental predicted value which indicates that the adsorption of MV on the surface of A-SB does not follow pseudo first order kin-

etics. Also, the value of q_e is not comparable with literature.

Table 5. Kinetic parameters for biosorption of MV on A-SB

Kinetic Model	Parameters of kinetic models			
Pseudo-first-order	k_1	$q_e / \text{mg g}^{-1}$	$q_c / \text{mg g}^{-1}$	R^2
	34.25	6.18	2.07	0.29
Pseudo-second order	k_2	$q_e / \text{mg g}^{-1}$	$q_c / \text{mg g}^{-1}$	R^2
	0.022	6.18	6.72	0.99
Intraparticle diffusion model	K_{id}	$q_e / \text{mg g}^{-1}$	C	R^2
	0.325	6.18	3.558	0.95
Elovich kinetic model	$\alpha / \text{mg g}^{-1} \text{min}^{-1}$	$q_e / \text{mg g}^{-1}$	$\beta / \text{mg g}^{-1}$	R^2
	20.73	6.18	0.864	0.923

Pseudo-second order kinetic model was proposed on the basis that chemisorption are followed by the process of sorption [60].

The equation of pseudo second order is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (14)$$

After integration, Eq. (14) becomes:

$$\frac{t}{q_t} = \frac{1}{k_1 q_e^2} + \frac{t}{q_e} \quad (15)$$

In this equation, k_2 (g/(mg min)) is pseudo-second order rate constant while q_t (mg/g) is the adsorption capacity of adsorbent at time t Figure 3b shows

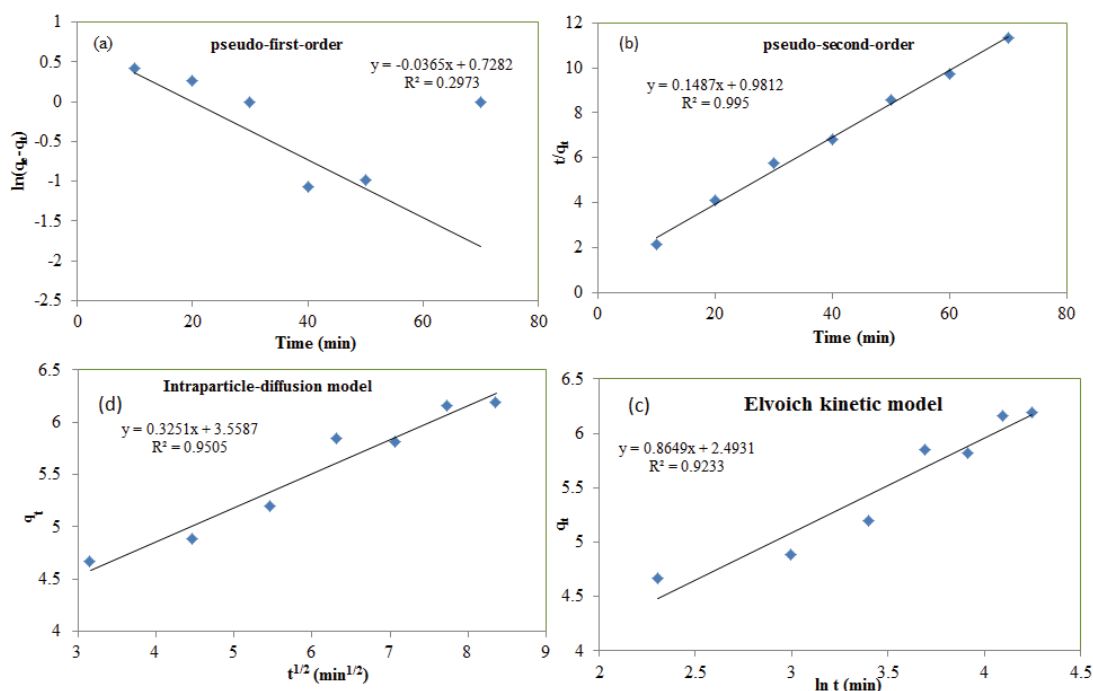


Figure 3. a) Pseudo-first-order, b) pseudo-second-order, c) Elovich and d) intra-particle diffusion kinetic model at pH 10, biosorbent dose = 0.2 g/50 mL, contact time = 50 min, $T = 323$ K, stirring speed = 125 rpm.

the graph between t/q_t and t to study pseudo-second order kinetics. Data for pseudo second order for the adsorption of MV on the surface of adsorbent is given in Table 5. Calculated value of R^2 for pseudo-second order is very close to unity as compared to other kinetic models. It shows that adsorption is best followed by pseudo second order kinetics. The calculated value of q_e is 6.72 mg/g while value of reported value of q_e is 6.18 mg/g which are approximately close to experimental ideal value. Hameed used sun flower seed hull as biosorbent for removal of MV dye from aqueous medium [61]. He reported that adsorption process best follow the pseudo-second order kinetic model as compared to pseudo-first order kinetic model because R^2 value exceeded 0.99 in case of former as compared to later one. He also showed that q_e value calculated from pseudo second order was more consistent to reported values. Similar results were found by other researchers for adsorption of methyl violet dye using different biosorbent [29,33,62,63].

Elovich kinetic model

This model is represented by:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (16)$$

where α ($\text{mol g}^{-1} \text{min}^{-1}$) is sorption rate at the initial stage, and β (g mol^{-1}) is the desorption constant. The Elovich equation is converted to a simple form by supposing that $\alpha\beta t \gg 1$ and integrating. After applying the conditions above, the simple form becomes:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \quad (17)$$

By plotting a graph between q_t and $\ln t$ a straight line is obtained with intercept $\beta \ln(\alpha\beta)$ and slope β which help to calculate the value of constants that are α and β . In order to check if the data fits this model or not, a graph was plotted between q_t and $\ln t$, which is shown in Figure 3c and calculated values are given in Table 5. Value of R^2 is very far from unity, which indicates that data is not well fitted with this model for adsorption process of MV over SB.

Intra-particle diffusion model

The intra-particle diffusion model is represented by:

$$q_t = K_{id} \sqrt{t} + C \quad (18)$$

In this equation, K_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the inter-particle diffusion rate constant. A graph was plotted between q_t (mg/g) and $t^{1/2}$ to study the validity of model for adsorption of MV over the surface of SB adsorbent as shown in Figure 3d. Passing of straight line from origin of graph decides whether it is con-

trolling step or not. By using Figure 3d parameters of intra-particle diffusion model were calculated which are given in Table 5. The R^2 value for biosorption process was not close to unity, which means that it does not follow the intra-particle diffusion model.

CONCLUSION

The results showed that *Saccharum bengalense* (SB) is an effective biosorbent for the adsorption of methyl violet (MV) from aqueous solution. At 323 K temperature, 98% MV dye was removed using 0.2 g/25 mL of biosorbent while, pH and stirring speed were adjusted as 10 and 125 rpm, respectively. The results indicated that the time required to attain equilibrium was 50 min. Experimental data showed that adsorption process best followed the Langmuir adsorption isotherm. The dye molecules formed single layer over the binding sites of *S. bengalense* surface. Thermodynamic parameters showed that the adsorption process is endothermic, spontaneous and feasible, as the adsorption rate increases with increase of temperature of the medium.

Acknowledgment

This work was supported by University of the Punjab, Lahore, Pakistan, under a research project grant for the fiscal year 2015-2016.

REFERENCES

- [1] N. Mohan, N. Balasubramanian, C.A. Basha, J. Hazard. Mater. **147** (2007) 644-651
- [2] R. Malik, D. Ramteke, S. Wate, Waste Manage. **27** (2007) 1129-1138
- [3] K. Kadirvelu, C. Karthika, N. Vennilamani, S. Pattabhi, Chemosphere **60** (2005) 1009-1017
- [4] D. Shen, J. Fan, W. Zhou, B. Gao, Q. Yue, Q. Kang, J. Hazard. Mater. **172** (2009) 99-107
- [5] M. Sulak, E. Demirbas, M. Kobya, Bioresour. Technol. **98** (2007) 2590-2598
- [6] R. Qadeer, Colloids Surfaces.. A **293** (2007) 217-223
- [7] Y. Al-Degs, M. Khraisheh, S. Allen, M. Ahmad, G. Walker, Chem. Eng. J. **128** (2007) 163-167
- [8] M.K. Aroua, C.Y. Yin, F. Lim, W. Kan, W.M.A.W. Daud, J. Hazard. Mater. **166** (2009) 1526-1529
- [9] V.C. Srivastava, I.D. Mall, I.M. Mishra, Chem. Eng. J. **132** (2007) 267-278
- [10] M.H. El-Naas, S. Al-Zuhair, M.A. Alhaji, J. Hazard. Mater. **173** (2010) 750-757
- [11] A. Ahmad, B. Hameed, J. Hazard. Mater. **172** (2009) 1538-1543
- [12] M. Ahmad, W.W. Daud, M. Aroua, Colloids Surfaces, A **312** (2008) 131-135

- [13] M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, J. Hazard. Mater. **141** (2007) 77-85
- [14] M.K. Aroua, S. Leong, L. Teo, C.Y. Yin, W.M.A.W. Daud, Bioresour. Technol. **99** (2008) 5786-5792
- [15] N.H. Phan, S. Rio, C. Faur, L. Le Coq, P. Le Cloirec, T.H. Nguyen, Carbon **44** (2006) 2569-2577
- [16] N. El Hannafi, M. Boumakhla, T. Berrama, Z. Bendjama, Desalination **223** (2008) 264-268
- [17] C.-H. Weng, Y.-T. Lin, T.-W. Tzeng, J. Hazard. Mater. **170** (2009) 417-424
- [18] M. El-Halwany, Desalination **250** (2010) 208-213
- [19] M. Arulkumar, P. Sathishkumar, T. Palvannan, J. Hazard. Mater. **186** (2011) 827-834
- [20] V. Gupta, J. Environ. Manage. **90** (2009) 2313-2342
- [21] A. Demirbas, J. Hazard. Mater. **167** (2009) 1-9
- [22] D. Ghosh, K.G. Bhattacharyya, Appl. Clay. Sci. **20** (2002) 295-300
- [23] A.E. Ofomaja, Biochem. Eng. J. **40** (2008) 8-18
- [24] R.-K. Xu, S.-C. Xiao, J.-H. Yuan, A.-Z. Zhao, Bioresour. Technol. **102** (2011) 10293-10298
- [25] Y. Tian, C. Ji, M. Zhao, M. Xu, Y. Zhang, R. Wang, Chem. Eng. J. **165** (2010) 474-481
- [26] A.E. Ofomaja, Y.-S. Ho, Bioresour. Technol. **99** (2008) 5411-5417
- [27] M.I. Din, M.L. Mirza, Int. J. Bio. Macromol. **54** (2013) 99-108
- [28] M.I. Din, U. Farooq, M. Athar, M. Latif Mirza, Desalin. Water. Treat. **52** (2014) 5856-5868
- [29] I.D. Mall, V.C. Srivastava, N.K. Agarwal, Dyes. Pigm. **69** (2006) 210-223
- [30] M. Imran Din, M.L. Mirza, S. Ata, M. Athar, I.U. Mohsin, J. Chem. **2013** (2012)
- [31] T.C.R. Bertolini, J.C. Izidoro, C.P. Magdalena, D.A. Fungaro, J. Chem. **5** (2013) 179-191
- [32] M.I. Din, Z. Hussain, M.L. Mirza, M.M. Athar, A. Madni, S. Ahmad, Desalin. Water. Treat. **51** (2013) 5638-5648
- [33] M. Dogan, Y. Ozdemir, M. Alkan, Dyes. Pigm. **75** (2007) 701-713
- [34] Y. Ozdemir, M. Dogan, M. Alkan, Microporous. Mesoporous. Mater. **96** (2006) 419-427
- [35] F. Carrasco-Marin, M.A. Alvarez-Merino, C. Moreno-Castilla, Fuel **75** (1996) 966-970
- [36] M. Illan-Gomez, A. Garcia-Garcia, C. Salinas-Martinez de Lecea, A. Linares-Solano, Energy. Fuels. **10** (1996) 1108-1114
- [37] R. Ahmad, R. Kumar, Appl. Surf. Sci. **257** (2010) 1628-1633
- [38] F. Rozada, L. Calvo, A. Garcia, J. Martin-Villacorta, M. Otero, Bioresour. Technol. **87** (2003) 221-230
- [39] G. Calzaferri, D. Bruhwiler, S. Megelski, M. Pfenniger, M. Pauchard, B. Hennessy, H. Maas, A. Devaux, U. Graf, Solid. State. Sci. **2** (2000) 421-447
- [40] T. Robinson, B. Chandran, P. Nigam, Water. Res. **36** (2002) 2824-2830
- [41] Z. Eren, F.N. Acar, Desalination **194** (2006) 1-10
- [42] R.A. Anayurt, A. Sari, M. Tuzen, Chem. Eng. J. **151** (2009) 255-261
- [43] S. Suresh, V. Srivastava, I. Mishra, J. Chem. Eng. Data. **56** (2010) 811-818
- [44] S. Chowdhury, R. Mishra, P. Saha, P. Kushwaha, Desalination **265** (2011) 159-168
- [45] A.P. Vieira, S.A. Santana, C.W. Bezerra, H.A. Silva, J.A. Chaves, J.C. de Melo, E.C. da Silva Filho, C. Airoidi, J. Hazard. Mater. **166** (2009) 1272-1278
- [46] M. Horsfall Jnr, A.I. Spiff, Electron. J. Biotechnol. **8** (2005) 43-50
- [47] R. Prabakaran, S. Arivoli, Eur. J. Appl. Eng. Sci. **1** (2012) 134-142
- [48] O. Lawal, A. Sanni, I. Ajayi, O. Rabiun, J. Hazard. Mater. **177** (2010) 829-835
- [49] K. Foo, B. Hameed, Chem. Eng. J. **156** (2010) 2-10
- [50] T. Robinson, B. Chandran, P. Nigam, Water. Res. **36** (2002) 2824-2830
- [51] G. Annadurai, R.-S. Juang, D.-J. Lee, J. Hazard. Mater. **92** (2002) 263-274
- [52] L.B. Lim, N. Priyantha, C.M. Chan, D. Matassan, H.I. Chieng, M. Kooh, Arab. J. Sci. Eng. **39** (2014) 6757-6765
- [53] L.B. Lim, N. Priyantha, C. Hei Ing, M. Khairud Dahri, D. Tennakoon, T. Zehra, M. Suklueng, Desalin. Water. Treat. **53** (2015) 964-975
- [54] L.B. Lim, N. Priyantha, C.M. Chan, D. Matassan, H.I. Chieng, M.R.R. Kooh, Desalin. Water. Treat. **57** (2016) 8319-8329
- [55] H. Chen, J. Zhao, Adsorption **15** (2009) 381-389.
- [56] M.M. Montazer-Rahmati, P. Rabbani, A. Abdolali, A.R. Keshtkar, J. Hazard. Mater. **185** (2011) 401-407.
- [57] P. Mourao, P. Carrott, M.R. Carrott, Carbon **44** (2006) 2422-2429.
- [58] S.N. Milmile, J.V. Pande, S. Karmakar, A. Bansiwala, T. Chakrabarti, R.B. Biniwale, Desalination **276** (2011) 38-44
- [59] N. Ahalya, T. Ramachandra, R. Kanamadi, Res. J. Chem. Environ. **7** (2003) 71-79
- [60] E. Sabah, M. Turan, M. Celik, Water. Res. **36** (2002) 3957-3964
- [61] B. Hameed, J. Hazard. Mater. **154** (2008) 204-212
- [62] A.E. Ofomaja, Chem. Eng. J. **143** (2008) 85-95
- [63] S. Cengiz, L. Cavas, Mar. Biotechnol. **12** (2010) 728-736.

MUHAMMAD IMRAN DIN
KIRAN IJAZ
KHALIDA NASEEM

Institute of Chemistry, University of
Punjab, Lahore-54590, Pakistan

NAUČNI RAD

BIOSORPCIONI POTENCIJALI KISELINSKI MODIFIKOVANE *Saccharum bengalense* ZA UKLANJANJE METIL-VIOLETA IZ VODENIH RASTVORA

Šećerna trska Saccharum bengalense (SB) je tretirana sumpornom kiselinom radi povećanja njene sorpcione efikasnosti. Kationska boja, metil-violet (MV), je uklonjena iz vodenog rastvora pomoću kiselinski modifikovan trske (A-SB). Istraženi su različiti parametri, kao što su: doza adsorbenta, brzina mešanja, temperatura, vreme kontakta i početna koncentracija boje, na brzinu adsorpcije boje iz vodenog rastvora. Eksperimentalni podaci za adsorpciju MV analizirani su primenom modela pseudo-prvog reda, pseudo-drugog reda i unutra-čestične difuzije. Utvrđeno je da podaci najbolje prate kinetiku pseudo-drugog reda. Termodinamički parametri ukazuju na to da je reakcija adsorpcije spontana, izvodljiva i endotermna po prirodi. Za utvrđivanje mehanizma adsorpcionog procesa korišćeni su različiti izotermni modeli adsorpcije, kao što su: izoterme Lengmira, Frojndliha, Dubinin-Raduškeviča i Tjomkina, a eksperimentalni podaci se dobro slažu sa izotermom Lengmira.

Ključne reči: biosorpcija, Saccharum bengalense, kinetika, termodinamika, boja.