

Malt Bagasse Waste as Biosorbent for Malachite Green: An Ecofriendly Approach for Dye Removal from Aqueous Solution

H. C. O. Reis, A. S. Cossolin, B. A. P. Santos, K. C. Castro, G. M. Pereira, V. C. Silva, P. T. Sousa Jr, E. L. Dall'Oglio, L. G. Vasconcelos, E. B. Morais

Abstract—In this study, malt bagasse, a low-cost waste biomass, was tested as a biosorbent to remove the cationic dye Malachite green (MG) from aqueous solution. Batch biosorption experiments were investigated as functions of different experimental parameters such as initial pH, salt (NaCl) concentration, contact time, temperature and initial dye concentration. Higher removal rates of MG were obtained at pH 8 and 10. The equilibrium and kinetic studies suggest that the biosorption follows Langmuir isotherm and the pseudo-second-order model. The maximum monolayer adsorption capacity was estimated at 117.65 mg/g (at 45 °C). According to Dubinin–Radushkevich (D-R) isotherm model, biosorption of MG onto malt bagasse occurs physically. The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy indicated that the MG biosorption onto malt bagasse is spontaneous and endothermic. The results of the ionic strength effect indicated that the biosorption process under study had a strong tolerance under high salt concentrations. It can be concluded that malt bagasse waste has potential for application as biosorbent for removal of MG from aqueous solution.

Keywords—Color removal, kinetic and isotherm studies, thermodynamic parameters, FTIR.

I. INTRODUCTION

THE removal of pollutants from wastewater is a matter of great interest to control the environmental pollution. Among the numerous industrial activities, textile is one of the main contributors for surface water bodies' degradation once their wastewater contains different classes of dyes, heavy metals, surfactants, extreme pH and high values of salts, total solids, BOD and COD [1], [2]. The discharge of textile wastewater into the receiving stream is not only aesthetically unpleasant but can also lead to the depletion of dissolved oxygen and reduction of light penetration and photosynthetic activity [3], [4]. Furthermore, many textile dyes and their

metabolites are potentially toxic, mutagenic and carcinogenic to living systems [5], [6].

Treatment of textile wastewaters is very difficult due to the complex and stable aromatic structure of synthetic dyes. Nevertheless, physical, chemical and electrical methods, such as coagulation, ultrafiltration, advanced oxidation processes, irradiation, electrolysis and ozonation are available for the treatment of dye-containing wastewater [7]–[11]. However, the long operation time, high sludge production, intensive energy requirements, and formation of toxic by-products in some cases can make these technologies impractical and expensive to operate [12].

Adsorption is an efficient and economic process to remove pollutants from wastewater [13]. In the past decade, several studies have focused on adsorption of dyes from aqueous solution and wastewater using biomasses as adsorbent, such as orange bagasse [14], rice husk [15], yeast slurry from brewery [16], lignocellulosic industrial waste [17], walnut shell [18] and macroalgae [19]. Biomasses have gained particular attention because of easy availability, low cost and effectiveness. Generally, these materials are plentiful in nature, or are by-products or waste from industrial processes, having low or no economic value [20]. Malt bagasse is a by-product generated in large amounts in beer industry, which makes it an interesting target for the examination of its dye biosorption potential. In the literature, biosorption studies on textile dyes using malt bagasse show unsatisfactory results, mainly because there is a high number of dyes commercially available, more than 100,000 [21], and a high chemical diversity of these compounds.

In this study, the cationic triphenylmethane dye, MG, was used as a model compound. MG is widely used for coloring purpose of cotton, wool, silk polyacrylonitrile, nylon, paper and leather [22]. Furthermore, it is used as antifungal, antibacterial and anti-parasitical therapeutic agent in aquaculture and animal husbandry [23]. However, MG is environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals [24]. According to reports on animal study, MG was found to exhibit mutagenic, carcinogenic, genotoxic and teratogenic properties [25]–[27]. Although the use of this dye has been banned in several countries, it is still being used due to its ready availability, low cost and effectiveness.

The main purpose of this study was to evaluate the ability of malt bagasse waste to remove MG from aqueous solution under different experimental conditions, including initial pH,

Eduardo B. Morais is with the Department of Sanitary and Environmental Engineering, Federal University of Mato Grosso, Cuiabá, MT, 78060-900, Brazil (corresponding author, phone: +55 65 36158722; e-mail: beraldo_morais@yahoo.com.br)

Hélen C. O. Reis, Aline S. Cossolin, Bruna A. P. Santos, Ketinny. C. Castro are with the Department of Sanitary and Environmental Engineering, Federal University of Mato Grosso, Cuiabá, MT, 78060-900, Brazil (e-mail: helenreis08@gmail.com, aline.cossolin@gmail.com, bruna.santos_assis@hotmail.com, ketinnycamargo@gmail.com).

Gabriele M. Pereira, Virginia C. Silva, Paulo T. Sousa Jr, Evandro L. Dall'Oglio, Leonardo G. Vasconcelos are with Department of Chemistry, Federal University of Mato Grosso, Cuiabá, MT, 78060-900, Brazil. (e-mail: gabriele_menezes@gmail.com, pauloteixeiradesousa@gmail.com, vcsilvia@gmail.com, dallochio.evandro@gmail.com, vasconceloslg@gmail.com).

contact time, temperature, salt (NaCl) concentration and dye concentration. Furthermore, analyses on kinetic, isotherm and thermodynamic of dye removal were also performed as well as the characterization of malt bagasse was evaluated by Fourier transform infrared spectroscopy (FTIR).

II. MATERIALS AND METHODS

A. Dye Solution

The cationic dye MG (empirical formula $C_{23}H_{25}ClN_2$; molecular weight = 364.90) was purchased from VETEC – Sigma-Aldrich, Brazil, and its chemical structure is shown in Fig. 1. Stock solutions of MG were prepared by dissolving the powdered dyestuff in distilled water (1.0 g/L) and the other concentrations were obtained by diluting this stock dye solution. The pH of the solution was adjusted to the desired value by adding 0.1 M HCl or 0.1 M NaOH. The maximum absorbance ($\lambda_{max} = 617$) of MG was determined by a UV-Visible spectrophotometer (Hach DR6000).

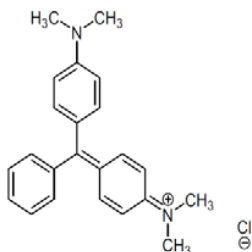


Fig. 1 Chemical structure of MG dye

B. Preparation of Biosorbent

Malt bagasse waste was obtained from an artisanal brewery in Brazil. It was washed several times with distilled water for removing dirt and soluble impurities, and then dried at 80 °C to constant weight. Next, malt bagasse was crushed and sieved, using an ASTM Standard sieve, to select the particle sizes between 500 and 250 μ m and then stored in desiccators for further use.

C. Biosorption Assays

Biosorption assays were conducted with 250 mL Erlenmeyer flasks containing 100 mL aqueous solution of MG. Flasks were agitated on a rotary shaker at 150 rpm. In order to predict the effect of some physicochemical variables on the removal of MG by malt bagasse, variables such as pH (2, 4, 6, 8 and 10), salt (NaCl) concentration (1.0, 2.5, 5.0, 7.5 and 10 g/L), contact time (0-120 min), temperature (25, 35 and 45 °C) and initial dye concentration (50, 100, 150, 200 and 300 mg/L) were evaluated. After equilibrium to be reached at each experiment, the malt bagasse was removed from the suspension by filtration (membrane filter ϕ 0.45 μ m) and the residual dye in the solution was measured quantitatively by UV-Vis spectrophotometer (Hach DR6000) at $\lambda_{max} = 617$ nm. The biosorption experiments were executed in triplicates. To calculate the dye removal efficiency, R (%), and dye biosorption capacity (q_e , mg/g) of malt bagasse waste at the equilibrium (1) and (2) were used, respectively:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_e) \cdot V}{B} \quad (2)$$

where C_i and C_e are the initial and the equilibrium dye concentrations (mg/L) and B is the biosorbent concentration in solution (g/L).

D. FTIR Analysis

FTIR analyses were used to determine the functional groups on the malt bagasse and their responsibility for MG adsorption. FTIR was performed on a Shimadzu IRAffinity-1 spectrophotometer (Model: IRAffinity-1; Catalogue Number: 206-73500-38; Serial Number: A21374902249S1; Brand: Shimadzu Corporation spectrophotometer). After adsorption of MG until adsorption equilibrium, the residual dye solution was filtered (membrane filter ϕ 0.45 μ m) and the residual biosorbent dried at 80 °C for 48 h after washing with ultra-pure water three times. The samples (1 mg biosorbent) were mixed with spectroscopically pure KBr (100 mg), and pellets were fixed in a sample holder. The qualitative analyses were carried out using the following parameters: Measured Mode (% Transmittance), Apodization (Happ Genzel), Number of Scans (200), Resolution (16), Range (400-4700 cm^{-1}), Gain (1). The acquisitions of spectra were made using IRSolution software (Version 1.50). The background obtained from KBr disks was automatically subtracted from the sample disks spectra.

III. RESULTS AND DISCUSSION

A. Effect of pH

The effect of initial pH on the removal of MG by malt bagasse waste at a dye concentration of 50 mg/L, 1.0 g/L biosorbent, 25 °C and contact time of 120 min is illustrated in Fig. 2. pH significantly influenced the MG biosorption of malt bagasse, probably because this parameter affects the ionizing functional groups of cells walls [28], [29]. The biosorption of the dye was maximum at pH 8 and 10 (85.7 and 86.9%, respectively). The higher uptakes that were obtained at basic conditions may be explained in terms of electrostatic interactions between MG and biosorbent [30]. At lower values of pH, the different functional groups on the surface of biosorbent are protonated and thereby limit the approach of positively charged dye cations [31]. As the pH becomes higher, the net electronegativity of the biosorbent increases due to deprotonation of different functional groups and then the electrostatic interactions between the negatively charged biosorbent and the positively charged MG dye cations lead to dye removal from the solution. The increase in dye biosorption at higher pH may also be related to the reduction of H^+ ions, which compete with dye cations at lower pH for the same sites on the biosorbent surface [31]. Similar results were reported by Tsai et al. [32] using beer brewery waste to remove the cationic dye methylene blue. Whereas pH of textile wastewater is commonly alkaline [33], the pH 10 was used in subsequent studies.

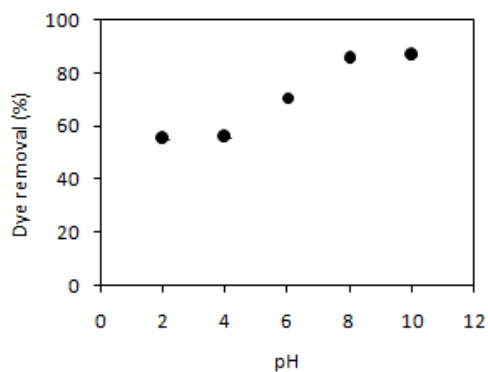


Fig. 2 Effect of pH on biosorption of MG by malt bagasse waste (biosorbent dosage = 1.0 g/L, [MG] = 50 mg/L, contact time = 120 min, temperature = 25 °C)

B. Effect of Contact Time

An ideal biosorbent should quickly adsorb the pollutant from liquid phase and establish the equilibrium. So, the effect of contact time as a function of temperature was studied at a dye concentration of 50 mg/L, 1.0 g/L biosorbent and pH 10. As shown in Fig. 3, for the given temperatures, a rapid biosorption of MG occurred within the first 10 min and was gradually slowed down until the equilibrium, which was achieved at 60 min. The fast biosorption during the first initial 10 min could be explained by the large number of free active binding sites on the adsorbent surface at the beginning of the experiments. Also, it can be seen that removal of MG increased from 86.9 to 97.7% when the temperature was increased from 25 to 45 °C. An increase in MG removal capacity of the biosorbent with temperature indicates the biosorption of MG on malt bagasse is kinetically controlled by an endothermic process.

C. Effect of Salt Concentration (NaCl)

In general, textile wastewater contains high amounts of salts (up to 10 g/L NaCl or Na₂SO₄) [34]. In this study, the effect of salt concentration (NaCl) on the biosorption of MG by malt bagasse waste was evaluated at a dye concentration of 50 mg/L, pH 10, 45 °C, 1.0 g/L biosorbent. When salt concentration was increased from 0.0 to 10.0 g/L it was found that the effect of NaCl on the dye removal was practically negligible (Fig. 4). This indicates that an elevated ionic strength with NaCl does not electrostatically interfere with the binding of MG to the active sites of biosorbent significantly, and therefore, from a practical point of view, the malt bagasse can be used for removal of MG from salt-containing wastewaters [30].

D. Effect of Initial Concentration of Dye

The effect of initial concentration of MG on removal capacity of the malt bagasse waste was investigated using solutions of dye ranging from 50 to 300 mg/L, pH 10, and 45 °C. Fig. 5 indicated that the removal of dye decreased with increasing initial dye concentration. This effect can be explained by a fixed number of adsorption sites for a given biosorbent dosage, which become saturated at a certain dye

concentration. However, the biosorption capacity increased 65 mg/g when the initial dye concentration was raised from 50 to 300 mg/L. The initial dye concentration results in an increased adsorption capacity because it provides a driving force to overcome all mass transfer resistances of dyes between the aqueous and solid phase [35].

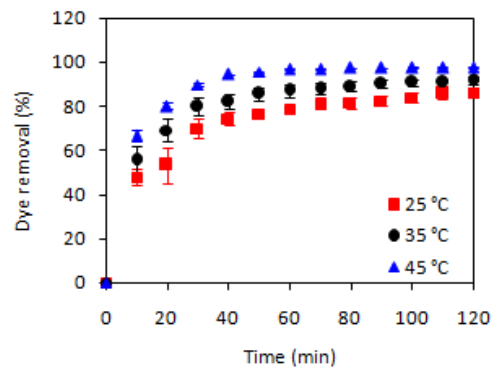


Fig. 3 Effect of contact time on the biosorption of MG by malt bagasse waste at different temperatures (pH = 10, biosorbent dosage = 1.0 g/L, [MG] = 50 mg/L)

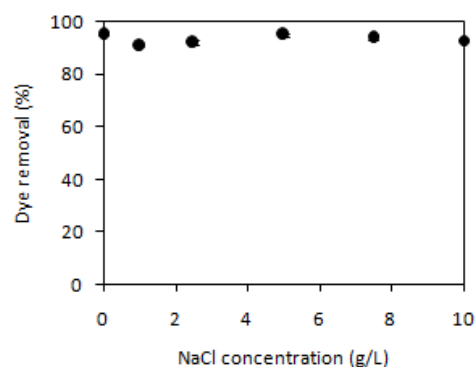


Fig. 4 Effect of salt concentration (NaCl) on biosorption of MG by malt bagasse waste (pH = 10, biosorbent dosage = 1.0 g/L, [MG] = 50 mg/L, contact time = 120 min, temperature = 45 °C)

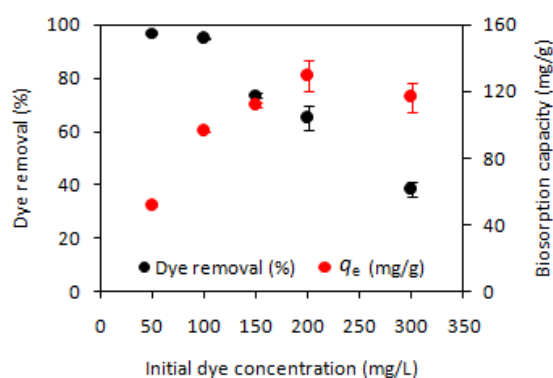


Fig. 5 Effect of initial dye concentration on the biosorption of MG by malt bagasse waste (pH = 10, biosorbent dosage = 1.0 g/L, contact time = 120 min, temperature = 45 °C)

E. Biosorption Kinetics

The adsorption is a time-dependent process. So, kinetic studies are useful for the design and evaluation of sorbents [36]. In this study, kinetic studies on MG removal were conducted with constant initial dye concentration (50 mg/L), 1.0 g/L biosorbent, at temperatures of 25, 35 and 45 °C. Mostly used kinetic models including pseudo-first order [37], pseudo-second order [38] and intraparticle diffusion [39] were applied to experimental data.

The linear forms of pseudo first-order and pseudo second-order models are expressed by (3) and (4):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of dye adsorbed by biosorbent at equilibrium and at time t , respectively. K_1 (1/min) and K_2 (g/mg min) are the pseudo-first order and pseudo-second order adsorption rate constants, respectively.

The pseudo-first order constants K_1 and q_e were calculated from the slope and intercept of the plot between $\ln(q_e - q_t)$ versus t (Fig. 6 (a)). The kinetic data in Table I demonstrated that although pseudo-first order model resulted in good fits for all temperatures ($0.941 < R^2 < 0.987$), the experimental q_e values (43.1, 45.7 and 48.8 mg/g at 25, 35 and 45 °C) did not agree with the calculated ones (28.25, 24.43 and 32.43 mg/g at 25, 35 and 45 °C). Therefore, this result suggests that this model was not appropriate for describing the adsorption kinetics of MG onto malt bagasse waste.

The pseudo-second order constants K_2 and q_e were calculated from the slope and intercept of the plot between t/q_t versus t (Fig. 6 (b)). The fitting of the kinetic data in the pseudo-second order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.999$) for all temperatures and the biosorption capacities (q_e) estimated were much closer to experimental q_e values (Table I). By increasing the temperature, the pseudo-second order rate constant values changed from 0.0018 to 0.0049 g/mg min. So, it can be inferred that the MG biosorption onto malt bagasse waste followed pseudo-second order kinetics. Similar results during studies of MG adsorption on other biomasses have been reported in the literature [35], [40].

The intraparticle diffusion model was used to identify the diffusion mechanisms and is represented by (5):

$$q_t = K_{id} t^{0.5} + C \quad (5)$$

where C is the intercept (mg/g) and K_{id} is the intraparticle diffusion rate constant (mg/g min^{0.5}). By plotting q_t versus $t^{0.5}$, the values of K_{id} and C were obtained. According to this model, if the plot crosses the origin ($C = 0$), the adsorption process is controlled only by intraparticle diffusion. Fig. 6 (c) showed similar overall features of multilinear plots with two steps. The first step is attributed to the external surface

adsorption or instantaneous diffusion stage, during which a large amount of MG is rapidly adsorbed by the external surface of the biosorbent [41]. This is considered the fast step, demonstrated by the highest K_{id} constant values (Table I). The second step is the gradual biosorption stage controlled by intraparticle diffusion. As the plots did not cross the origin ($C \neq 0$), they suggest that the intraparticle diffusion is not the only mechanism of biosorption operating and probably, the biosorption kinetics of MG onto malt bagasse waste was controlled by both surface and intraparticle diffusion processes.

TABLE I
KINETIC PARAMETERS ESTIMATED BY THE PSEUDO FIRST-ORDER, PSEUDO SECOND-ORDER AND INTRAPARTICLE DIFFUSION MODELS FOR THE MG BIOSORPTION ONTO MALT BAGASSE WASTE

Parameters	Temperature (°C)		
	25	35	45
$q_{experimental}$ (mg/g)	43.1	45.7	48.8
<i>Pseudo-first order</i>			
K_1 (1/min)	0.035	0.039	0.067
q_1 (mg/g)	28.25	24.43	32.43
R^2	0.941	0.987	0.986
<i>Pseudo-second order</i>			
K_2 (g/mg min)	0.0018	0.0028	51.02
q_2 (mg/g)	46.95	48.54	51.02
R^2	0.998	0.999	0.999
<i>Intraparticle diffusion</i>			
<i>Step 1</i>			
K_{id} (mg/g min ^{0.5})	4.058	3.866	3.859
C (mg/g)	13.67	19.70	25.18
R^2	0.931	0.949	0.950
<i>Step 2</i>			
K_{id} (mg/g min ^{0.5})	1.149	0.689	0.146
C (mg/g)	33.54	41.28	50.31
R^2	0.988	0.965	0.927

F. Biosorption Isotherms

Biosorption isotherms provide essential information in optimizing the use of adsorbents. In this study, the equilibrium experiments were performed with different initial dye concentrations (50-300 mg/L), using 1.0 g/L biosorbent at 45 °C. The Langmuir [42], Freundlich [43] and D-R [44] models are commonly used to describe adsorption isotherms and, therefore, were applied to describe the equilibrium biosorption data of MG onto malt bagasse waste.

The Langmuir isotherm model assumes that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. The Langmuir model is expressed in (6):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (6)$$

where q_e (mg/g) is the amount of dye adsorbed by the biosorbent at equilibrium, C_e (mg/L) is the dye concentration in the solution at equilibrium, q_{max} (mg/g) is the maximum monolayer adsorption capacity, and K_L (L/mg) is the Langmuir constant related to the affinity of the binding sites and adsorption energy. By plotting C_e/q_e versus C_e , K_L and q_{max}

were calculated. The Langmuir model has a high linear correlation coefficient ($R^2 = 0.997$, Fig. 7 (a) and Table II), indicating the formation of a monolayer of MG covering the malt bagasse. The maximum monolayer dye biosorption capacity (q_{\max}) of the biosorbent is 117.65 mg/g (Table II). The maximum adsorption capacities of MG onto various biosorbents reported in the literature are listed in Table III. The adsorption capacity of malt bagasse waste obtained for MG in this investigation is higher than those of many corresponding adsorbent materials.

The empirical Freundlich model is based on heterogeneous surface sorption and can be expressed as in (7):

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

where K_f ((mg/g) (mg/L) $^{-1/n}$) and n (dimensionless) are the Freundlich constants related to the biosorption capacity and biosorption intensity, respectively. The values of K_f and n were calculated by plotting $\ln q_e$ and $\ln C_e$ and were estimated at 58.557 and 6.13, respectively. As can be seen in Fig. 7 (b) and Table II, the Freundlich model does not fit the data of biosorption experiment as well as Langmuir model, as indicated by the values of the correlation coefficients ($R^2 = 0.750$).

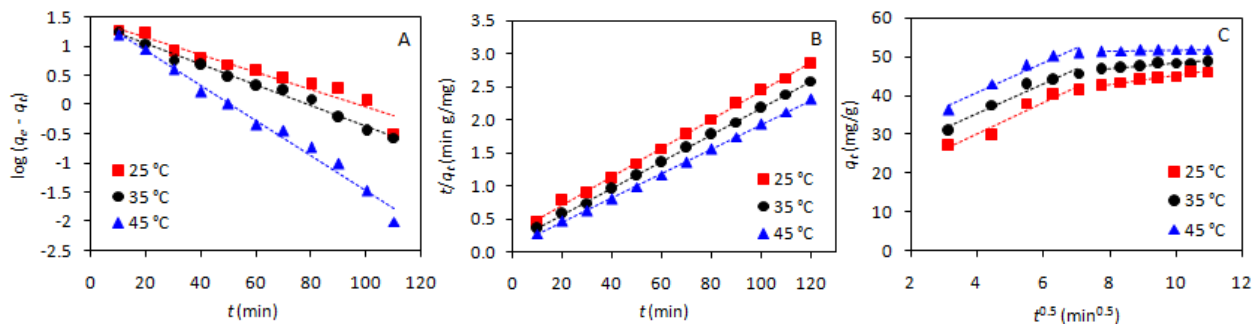


Fig. 6 Plots for pseudo-first order (a), pseudo-second order (b) and intraparticle diffusion (c) models for the biosorption of MG onto malt bagasse waste, at different temperatures

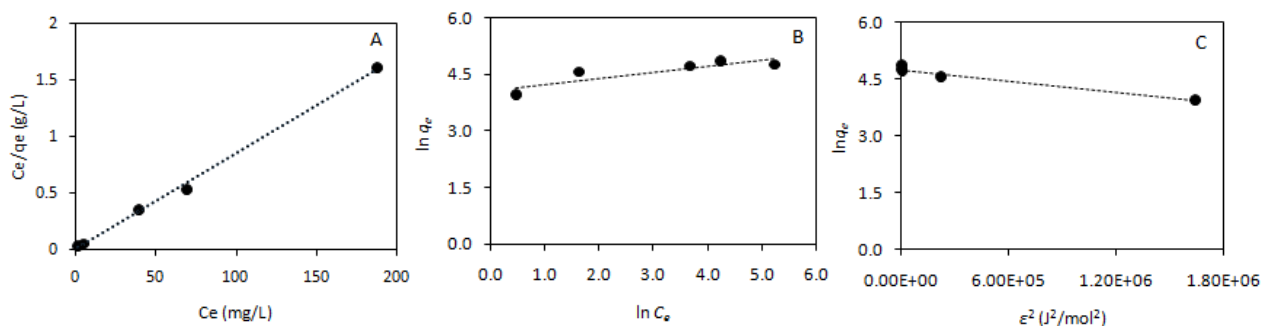


Fig. 7 Plots for Langmuir (a), Freundlich (b) and D-R isotherms (c) for the biosorption of MG onto malt bagasse waste

TABLE II
BIOSORPTION ISOTHERM CONSTANTS FOR THE BIOSORPTION OF MG ONTO MALT BAGASSE WASTE

Langmuir model			Freundlich model			D-R model		
q_{\max} (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)(mg/L) $^{-1/n}$	n	R^2	q_s (mg/g)	B (mol 2 /J 2)	E (kJ/mol)
117.65	3.864	0.997	58.557	6.13	0.750	116.32	5.0×10^{-7}	1.00

TABLE III
COMPARISON OF MG ADSORPTION CAPACITY FOR DIFFERENT BIOSORBENTS

Biosorbent	T (°C)	pH	q_{\max} (mg g $^{-1}$)	Reference
<i>Caulerpa racemosa</i> var. <i>cylindracea</i> (marine alga)	45	6.0	25.67	[45]
Sodium carbonate treated rice husk	50	7.0	27.03	[46]
Potato peel	25	4.0	32.39	[47]
Pine tree root decayed by brown-rot fungi	40	4.0	42.63	[4]
Forestry waste mixture	Room temperature	8.0	52.61	[48]
Leaf of pineapple (<i>Ananas comosus</i>)		9.0	54.64	[49]
Corn cob		8.0	80.64	[50]
Walnut shell	Room temperature	Ambient pH	90.80	[18]
Thermally activated <i>Pithophora</i> sp. (algae)		5.0	117.65	[51]
Malt bagasse	45	10	117.65	This study
Lignin sulfonate-based mesoporous materials	55	7.0	150.38	[52]
<i>Casuarina equisetifolia</i> needle	45	Ambient pH	154.30	[53]
Ginger waste	50	9.0	188.60	[54]

The D-R isotherm model was used to distinguish the nature of biosorption as physical or chemical. The linear form of the D-R isotherm equation is given by (8):

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

where q_e is the amount of dye adsorbed per unit mass of biosorbent, q_m is the theoretical adsorption capacity (mg/g), β is a constant related to biosorption energy and ε the Polanyi potential, which is calculated by (9):

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

where R (8.314 J/mol K) is the ideal gas constant and T (K) is the absolute temperature.

The values of q_m and β were determined from the slope and intercept of the linear plot of $\ln q_e$ versus ε^2 (Fig. 7 (c)). The mean free energy of biosorption (E , kJ/mol), represented by (10), was estimated using the constant β :

$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

When E value falls within the range from 8 to 16 kJ/mol, the biosorption process is controlled by a chemical mechanism, while for $E < 8$ kJ/mol, the biosorption process occurs through a physical mechanism. As can be seen from Table II, the calculated mean free biosorption energy (E) was 1.00 kJ/mol, which indicates that the biosorption process of MG onto malt bagasse waste was probably physically controlled.

G. Thermodynamic Studies

The thermodynamics parameters of MG biosorption onto malt bagasse waste, *i.e.*, Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated by (11) and (12):

$$\Delta G^\circ = -RT \ln K_D \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

The combination of above equations gives:

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T} \quad (13)$$

where K_D (q_e/C_e) is the distribution coefficient, T (K) is the absolute temperature and R is the universal gas constant (8.314 J/K mol). Values of ΔH° and ΔS° were determined from the slope and intercept equation of the plot between $\ln K_D$ as a function of $1/T$ (Fig. 8). The thermodynamic results are listed in Table IV. The negative values of ΔG° indicate that the MG biosorption onto malt bagasse is spontaneous and feasible at all the studied temperatures (25, 35 and 45 °C). The

change in the standard enthalpy (ΔH°) was positive (85.7 kJ/mol) suggesting that the biosorption is endothermic in nature. The ΔS° parameter was also found to be positive suggesting that the randomness at the biosorbent/solution interface increases during the biosorption of the dye.

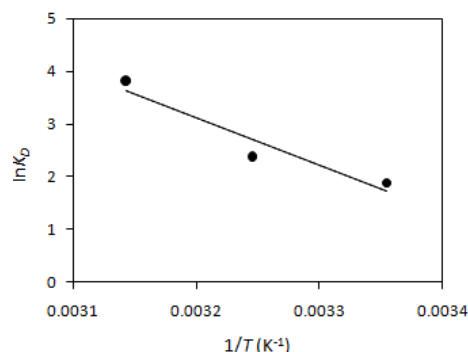


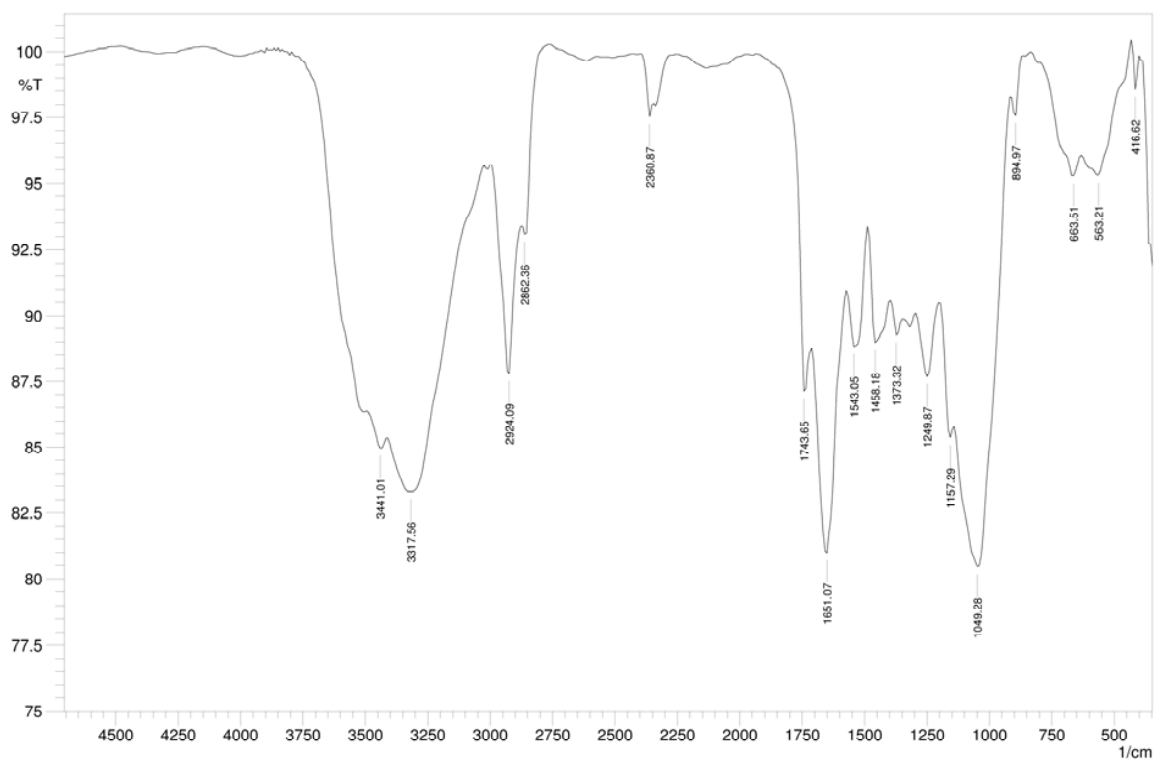
Fig. 8 Plot of $\ln K_D$ versus $1/T$ for estimation of thermodynamic parameters

TABLE IV
THERMODYNAMIC PARAMETERS ESTIMATED FOR MG BIOSORPTION ONTO MALT BAGASSE

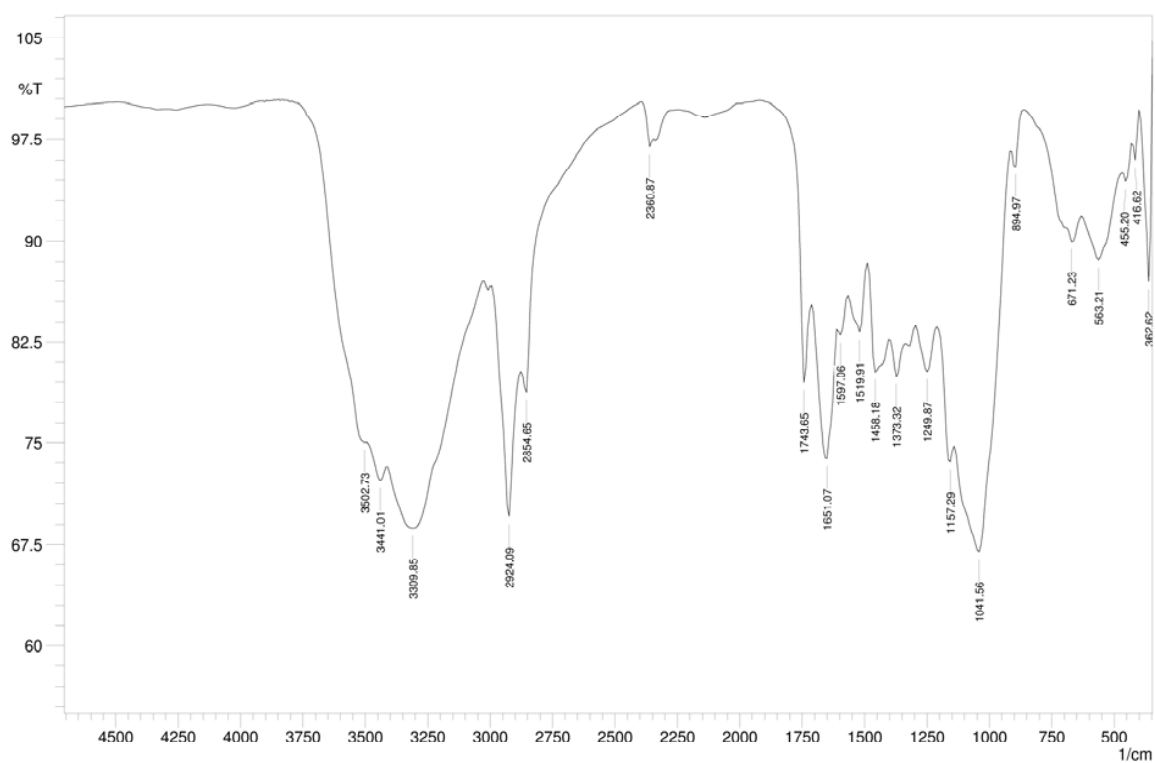
T (°C)	K_D	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
25	6.66	-4.699	85.7	0.297
35	10.77	-6.090		
45	44.89	-10.062		

H. FTIR Analysis

FTIR technique is an important tool to identify the functional groups in the surface of an adsorbent. As seen in the spectrum of malt bagasse (Fig. 9 (a)), a strong and broad band ranging 3200-3600 cm^{-1} is indicative of the presence of O-H and N-H groups. The peaks at 2924.09 and 2854.65 cm^{-1} are attributed to the C-H stretching vibration of methyl and methylene groups [55]. The band at 1743.65 cm^{-1} corresponds to C=O stretching vibration likely in esters [56] while protein-related bonds of amide I (C=O stretching) and amide II (combination of N-H bending and C-N stretching) are observed at 1651.07 and 1543.05 cm^{-1} , respectively [57]. The bands at 1458.18 and 1373.3 cm^{-1} are assigned to the bending vibrations of C-H [58] and C-N stretching vibrations are observed at 1249.87 cm^{-1} . The peak at 1049.28 cm^{-1} is attributed to C-O or C-N stretching vibrations of primary alcohols or amines [59]. The spectrum of MG-loaded malt bagasse suggests that various functional groups detected on the surface are involved in the adsorption (Fig. 9 (b)). The peaks observed around 3317.56 (O-H/N-H), 2862.36 (C-H), 1543.05 (N-H/C-N) and 1049.28 (C-O/C-N) were significantly changed. The shifts of these bands may indicate the possibility of malt bagasse interaction with MG dye molecules via these functional groups.



(a)



(b)

Fig. 9 FTIR spectra of malt bagasse before MG adsorption (a) and after MG adsorption (b)

IV. CONCLUSION

In this study, malt bagasse waste was evaluated as a possible biosorbent for removal of MG, a cationic dye, from aqueous solution. The biosorption process proved to be dependent on the pH of the solution, temperature, contact time, and initial concentration of dye. Maximum biosorption rates were obtained at pH 8 and 10. The kinetics of the biosorption process followed pseudo-second-order model. Experimental equilibrium data provided best fit with the Langmuir isotherm model and the maximum biosorption capacity was estimated at 117.65 mg/g (at 45 °C). According to D-R isotherm model, biosorption of MG onto malt bagasse occurs physically. Thermodynamic parameters, ΔG° and ΔH° , indicated that the MG biosorption onto malt bagasse is spontaneous and endothermic. In conclusion, malt bagasse may be an economic, effective and ecofriendly option for the removal of the cationic dye MG from aqueous media.

ACKNOWLEDGMENT

This study was financially supported by CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) under Grant 486168/2013-1

REFERENCES

- [1] K. Kumar, G. K. Singh, M. G. Dastidar, T. R. Sreekrishnan, Effect of mixed liquor volatile suspended solids (MLVSS) and hydraulic retention time (HRT) on the performance of activated sludge process during the biotreatment of real textile wastewater. *Water Resour. Ind.* 2014, 5: 1–8.
- [2] D. R. Manenti, P. A. Soares, A. N. Módenes, F. R. Espinoza-Quñones, R. A. R. Boaventura, R. Bergamasco, V. J. P. Vilar, Insights into solar photo-Fenton process using iron(III)-organic ligand complexes applied to real textile wastewater treatment. *Chem. Eng. J.* 2015, 266: 203–212.
- [3] L. C. Juang, C. K. Lee, C. C. Wang, S. H. Hung, M. D. Lyu, Adsorptive removal of Acid Red 1 from aqueous solution with surfactant modified titanate nanotubes. *Environ. Eng. Sci.* 2008, 25: 519–528.
- [4] H. Zhang, Y. Tang, X. Liu, Z. Ke, X. Su, D. Cai, X. Wang, Y. Liu, Q. Huang, Z. Yu, Improved adsorptive capacity of pine wood decayed by fungi *Poria cocos* for removal of Malachite green from aqueous solutions. *Desalination*, 2011, 274: 97–104.
- [5] R. Nilsson, R. Nordlinder, U. Wass, B. Meding, L. Belin, Asthma, rhinitis, and dermatitis in workers exposed to reactive dyes. *Br. J. Ind. Med.* 1993, 50: 65–70.
- [6] I. M. Banat, P. Nigam, D. Singh, R. Marchant, Microbial decolorization of textile-dye-containing effluents: a review. *Bioresour. Technol.* 1997, 58: 217–227.
- [7] J. M. Aquino, G. F. Pereira, R. C. Rocha-Filho, N. Bocchi, S. R. Biaggio, Combined Coagulation and Electrochemical Process to Treat and Detoxify a Real Textile Effluent. *Water. Air. Soil Pollut.* 2016, 227: 1–12.
- [8] S. He, W. Sun, J. Wang, L. Chen, Y. Zhang, J. Yu, Enhancement of biodegradability of real textile and dyeing wastewater by electron beam irradiation. *Radiat. Phys. Chem.* 2016, 124: 203–207.
- [9] E. Hu, S. Shang, X. Tao, S. Jiang, K. Chiu, Regeneration and reuse of highly polluting textile dyeing effluents through catalytic ozonation with carbon aerogel catalysts. *J. Clean. Prod.* 2016, 137: 1055–1065.
- [10] J. Lin, W. Ye, M. Baltaru, Y. Pan, N.J. Bernstein, P. Gao, S. Balta, M. Vlad, A. Volodin, A. Sotto, P. Luis, A.L. Zydney, B. Van Der Bruggen, Tight ultrafiltration membranes for enhanced separation of dyes and Na_2SO_4 during textile wastewater treatment. *J. Memb. Sci.* 2016, 514: 217–228.
- [11] Y. Han, H. Li, M. Liu, Y. Sang, C. Liang, J. Chen, Purification treatment of dyes wastewater with a novel micro-electrolysis reactor. *Sep. Purif. Technol.* 2016, 170: 241–247.
- [12] F. Deniz, R. Aysun, Dye biosorption onto pistachio by-product: A green environmental engineering approach. *J. Mol. Liq.* 2016, 219: 194–200.
- [13] D. Karadag, M. Turan, E. Akgul, S. Tok, A. Faki, Adsorption equilibrium and kinetics of Reactive Black 5 and Reactive Red 239 in aqueous solution onto surfactant-modified zeolite. *J. Chem. Eng. Data.* 2007, 52: 1615–1620.
- [14] L. D. Fiorentin, D. E. G. Trigueros, A. N. Módenes, F. R. Espinoza-Quñones, N. C. Pereira, S. T. D. Barros, O. A. A. Santos, Biosorption of reactive blue 5G dye onto drying orange bagasse in batch system: Kinetic and equilibrium modeling. *Chem. Eng. J.* 2010, 163: 68–77.
- [15] Y. Safa, H. Nawaz, Biosorption of Direct Red-31 and Direct Orange-26 dyes by rice husk: Application of factorial design analysis. *Chem. Eng. Res. Des.* 2011, 89: 2566–2574.
- [16] K. C. Castro, A. S. Cossolin, H. C. O Reis, E. B. Morais, Biosorption of anionic textile dyes from aqueous solution by yeast slurry from brewery. *Braz. Arch. Biol. Technol.* 2017, 60: 1–13.
- [17] S. T. Akar, D. Yilmazer, S. Celik, Y. Y. Balk, T. Akar, Effective biodecolorization potential of surface modified lignocellulosic industrial waste biomass. *Chem. Eng. J.* 2015, 259: 286–292.
- [18] M. K. Dahri, M. R. R. Kooh, L. B. L. Lim, Water remediation using low cost adsorbent walnut shell for removal of Malachite green: Equilibrium, kinetics, thermodynamic and regeneration studies. *J. Environ. Chem. Eng.* 2014, 2: 1434–1444.
- [19] E. Daneshvar, A. Vazirzadeh, A. Niazi, M. Sillanpää, A. Bhatnagar, A comparative study of methylene blue biosorption using different modified brown, red and green macroalgae – Effect of pretreatment. *Chem. Eng. J.* 2017, 307: 435–446.
- [20] Ö. Tunç, H. Tanaci, Z. Aksu, Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye. *J. Hazard. Mater.* 2009, 163: 187–198.
- [21] H. Fan, J. Yang, T. Gao, H. Yuan, Removal of a low-molecular basic dye (Azure Blue) from aqueous solutions by a native biomass of a newly isolated *Cladosporium* sp.: Kinetics, equilibrium and biosorption simulation. *J. Taiwan Inst. Chem. Eng.* 2012, 43: 386–392.
- [22] G. Crini, H. N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. *Sep. Purif. Technol.* 2007, 53: 97–110.
- [23] P. Geetha, M. S. Latha, M. Koshy, Biosorption of Malachite green dye from aqueous solution by calcium alginate nanoparticles: Equilibrium study. *J. Mol. Liq.* 2015, 212: 723–730.
- [24] S. Srivastava, R. Sinha, D. Roy, Toxicological effects of Malachite green. *Aquat. Toxicol.* 2004, 66: 319–329.
- [25] A. Panandiker, C. Fernandes, T. K. Rao, K. V. Rao, Morphological transformation of Syrian hamster embryo cells in primary culture by malachite green correlates well with the evidence for formation of reactive free radicals. *Cancer Lett.* 1993, 74: 31–36.
- [26] T. Zahn, T. Braunbeck, Cytotoxic effects of sublethal concentrations of malachite green in isolated hepatocytes from rainbow trout (*Oncorhynchus mykiss*). *Toxicol. In Vitro.* 1995, 9: 729–741.
- [27] S. J. Culp, P. W. Mellick, R. W. Trotter, K. J. Greenlees, R. L. Kodell, F. A. Beland, Carcinogenicity of Malachite green chloride and leucomalachite green in B6C3F1 mice and F344 rats. *Food Chem. Toxicol.* 2006, 44: 1204–1212.
- [28] T. Akar, I. Tosun, Z. Kaynak, E. Kavas, G. Incirkus, S.T. Akar, Assessment of the biosorption characteristics of a macro-fungus for the decolorization of Acid Red 44 (AR44) dye. *J. Hazard. Mater.* 2009, 171: 865–871.
- [29] A. R. Khataee, F. Vafaei, M. Jannatkah, Biosorption of three textile dyes from contaminated water by filamentous green algal *Spirogyra* sp.: Kinetic, isotherm and thermodynamic studies. *Int. Biodeterior. Biodegrad.* 2013, 83: 33–40.
- [30] S. W. Won, H. J. Kim, S. H. Choi, B. W. Chung, K. J. Kim, Y. S. Yun, Performance, kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste biomass of *Corynebacterium glutamicum* as a low-cost biosorbent. *Chem. Eng. J.* 2006, 121: 37–43.
- [31] P. Saha, S. Chowdhury, S. Gupta, I. Kumar, Insight into adsorption equilibrium, kinetics and thermodynamics of Malachite Green onto clayey soil of Indian origin. *Chem. Eng. J.* 2010, 165: 874–882.
- [32] W. T. Tsai, H. C. Hsu, T. Y. Su, K. Y. Lin, C. M. Lin, Removal of basic dye (methylene blue) from wastewaters utilizing beer brewery waste. *J. Hazard. Mater.* 2008, 154: 73–78.
- [33] P. Kaushik, A. Malik, Fungal dye decolorization: recent advances and future potential. *Environ. Int.* 2009, 35: 127–141.
- [34] M.S. Uddin, J. Zhou, Y. Qu, J. Guo, P. Wang, L.H. Zhao, Biodecolorization of azo dye acid red B under high salinity condition. *Bull. Environ. Contam. Toxicol.* 79 (2007) 440–4.
- [35] S. Chowdhury, R. Mishra, P. Saha, P. Kushwaha, Adsorption

- thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. *Desalination*. 2011, 265: 159–168.
- [36] S. Y. Kim, M. R. Jin, C. H. Chung, Y. S. Yun, K. Y. Jahng, K. Y. Yu, Biosorption of cationic basic dye and cadmium by the novel biosorbent *Bacillus catenulatus* JB-022 strain. *J. Biosci. Bioeng.* 2015, 119: 433–439.
- [37] S. Lagergren S, Zur theorie der sogenannten adsorption gelster stoffe. *K Sven Vetenskapsakad Handl.* 1898, 24: 1-39.
- [38] Y. S. Ho, G. McKay. Kinetic models for the sorption of dye from aqueous solution by wood. *Trans Chem Eng.* 1998, 76 (2): 183-191.
- [39] M. J. Weber, J. C. Morris. Kinetic of adsorption on carbon from solution. *J Sanit Eng. Div ASCE.* 1963, 89: 31-60.
- [40] A. Witek-Krowiak. Analysis of influence of process conditions on kinetics of malachite green biosorption onto beech sawdust. *Chem Eng J.* 2011, 171(3): 976–985.
- [41] F. Zhang, B. Ma, X. Jiang, Y. Ji, Dual function magnetic hydroxyapatite nanopowder for removal of malachite green and Congo red from aqueous solution. *Powder Technol.* 2016, 302: 207–214.
- [42] I. Langmuir. The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc.* 1918, 40(9): 1361-1403.
- [43] H. Freundlich. Over the adsorption in the solution. *J Phys Chem.* 1906, 57: 385-470.
- [44] M. M. Dubinin, L. V. Radushkevich. Equation of the characteristic curve of activated charcoal, *Proc Acad Sci. USSR.* 1947, 55: 331–333.
- [45] Z. Bekçi, Y. Seki, L. Cavas, Removal of Malachite green by using an invasive marine alga *Caulerpa racemosa* var. *cylindracea*. *J. Hazard. Mater.* 2009, 161: 1454–1460.
- [46] B. Kumar, U. Kumar, Adsorption of malachite green in aqueous solution onto sodium carbonate treated rice husk. *Korean J. Chem. Eng.* 2015, 32: 1655–1666.
- [47] E. K. Guechi, O. Hamdaoui, Sorption of Malachite green from aqueous solution by potato peel: Kinetics and equilibrium modeling using non-linear analysis method. *Arab. J. Chem.* 2011, 9: S416–S424.
- [48] F. Deniz, R.A. Kepekci, Bioremoval of Malachite green from water sample by forestry waste mixture as potential biosorbent. *Microchem. J.* 2017, 132: 172–178.
- [49] S. Chowdhury, S. Chakraborty, P. Saha, Biosorption of Basic Green 4 from aqueous solution by *Ananas comosus* (pineapple) leaf powder, *Colloids and Surfaces B: Biointerfaces.* 2011, 84: 520-527.
- [50] G. H. Sonawane, V. S. Shrivastava, Kinetics of decolourization of malachite green from aqueous medium by maize cob (*Zea mays*): An agricultural solid waste, *Desalination.* 2009, 247: 430–441.
- [51] K. V. Kumar, S. Sivanesan, V. Ramamurthi, Adsorption of Malachite green onto *Pithophora* sp., a fresh water algae: Equilibrium and kinetic modeling. *Process. Biochem.* 2005, 40: 2865–2872.
- [52] Y. Tang, Y. Zeng, T. Hu, Q. Zhou, Y. Peng, Preparation of lignin sulfonate-based mesoporous materials for adsorbing Malachite green from aqueous solution. *J. Environ. Chem. Eng.* 2016, 4: 2900–2910.
- [53] M. K. Dahri, M. R. R. Kooh, L. B. L. Lim, Application of *Casuarina equisetifolia* needle for the removal of methylene blue and malachite green dyes from aqueous solution. *Alexandria Eng. J.* 2015, 54: 1253–1263.
- [54] R. Ahmad, R. Kumar, Adsorption studies of hazardous Malachite green onto treated ginger waste. *J. Environ. Manage.* 2010, 91: 1032–1038.
- [55] K. B. Fontana, E. S. Chaves, J. D. S. Sanchez, E. R. L. R. Watanabe, J. M. T. A. Pietrobelli, G. G. Lenzi. Textile dye removal from aqueous solutions by malt bagasse: Isotherm, kinetic and thermodynamic studies. *Ecotoxicol Environ Saf.* 2016, 124: 329–336.
- [56] G. Markou, D. Mitrogiannis, K. Muylaert, A. Çelekli, H. Bozkurt. Biosorption and retention of orthophosphate onto Ca(OH)₂-pretreated biomass of *Phragmites* sp. *J Environ Sci.* 2015, 45: 49–59.
- [57] Q. Li, L. Chai, Z. Yang, Q. Wang. Kinetics and thermodynamics of Pb(II) adsorption onto modified spent grain from aqueous solutions. *Appl Surf Sci.* 2009, 255(7): 4298–4303.
- [58] T. Akar, I. Tosun, Z. Kaynak, E. Ozkara, O. Yeni, E. N. Sahin, S. T. Akar, An attractive agro-industrial by-product in environmental cleanup: Dye biosorption potential of untreated olive pomace. *J Hazard Mater.* 2009, 166: 1217–1225.
- [59] A. I. Ferraz, C. Amorim, T. Tavares, J. A. Teixeira. Chromium (III) biosorption onto spent grains residual from brewing industry: equilibrium, kinetics and column studies. *Int J Environ Sci Technol.* 2015, 12: 1591–1602.