

PLANT WASTES FOR REMOVAL OF TOXIC MALACHITE GREEN DYE

AL-AHMARY, K.¹ – ALMHYAWI, S.¹ – AL-TURKUSTANI, A.¹ – EL-GENDY, A.^{1,2} – OMAR, H.^{3,4*}

¹*Department of Chemistry, Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia*

²*Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, Egypt*

³*Department of Biological Science, Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia*

⁴*Department of Botany, Faculty of Science, Tanta University, Tanta, Egypt*

**Corresponding author*

e-mail: hananomar1@yahoo.com; phone: +96-656-567-9599

(Received 27th Jun 2018; accepted 28th Sep 2018)

Abstract. The wastes of *Myoporum laetum* and *Livistona chinensis* leaves were utilized for removal of malachite green dye (MG) from solution. The highest removal for dye was observed with *M. laetum* biomass at pH: 6, temperature: 35 °C, biomass dose: 0.3 g L⁻¹ and contact time: 120 min. The different concentrations of MG (5-35%) were highly removed by *M. laetum* (99.28% to 79.31%, respectively) as compared with *L. chinensis* (95.48-69.67%, respectively) at the optimum conditions. The sorption data were represented by Langmuir, Freundlich and Temkin isotherms. Adsorption was established well with isotherms of Langmuir and Freundlich. The study of thermodynamic suggested that the adsorption reaction was endothermic and the sorption of dye onto the biomass proceed in the forward direction and greatly promising process. The removal of dye was characterized by FT-IR analyses and the results confirmed that the groups responsible for the process of dye binding were hydroxyl or amino, and carboxylate or amide. The *M. laetum* cell wall showed a great porosity which permits the passage of dye molecules. The *M. laetum* biomass was more efficient than that of *L. chinensis*. The efficiency of the plant waste for a decolorizing solution containing dye, their abundance in nature and less processing requirements may lead to the emergence of low-cost adsorbents.

Keywords: *dye, plant leaves, equilibrium isotherm, thermodynamic, IR, SEM*

Introduction

Dyes are used in many industries and their extensive use causes pollution. Dyes are more difficult to degrade because they have a complex aromatic structure which makes them more stable (Seshadri et al., 1994). Dyes are toxic, mutagenic and difficult to be analyzed (Hammud, 2011). Thus, when the dye is discharged into waters it can affect the ecological system and human health. Dyes are dangerous to the aquatic living organisms (Vijayaraghavan and Yun, 2008). It causes problems to aquatic groups due to decreasing of light penetration and photosynthesis. The total amount of dyes generated in the world was found to be over 10,000 tons per year (Forgacs et al., 2004).

Malachite green is a dark green and belongs to triphenylmethane family. It is a water-soluble dye and can enter the cells due to their high lipid solubility (Albert, 1979). Malachite green dye is greatly used as a fungicide, bactericide, and antiprotozoal and for staining of cell and tissue samples (Hecht and Endemann, 1998). Malachite green play an important role as a food additive and in the process of paper coloring, silk, cotton, wool, leather, anthelmintic, and detergent (Srivastava et al., 2004). Its oral consumption is carcinogenic so that it is applied externally on ulcers

and wounds (Clifton-Hadley and Alderman, 1987). Therefore, the presence of malachite green dye in animal milk, fishes, and other foodstuff is very dangerous to the human being (Srivastava et al., 1995). The products formed from degradation of malachite green are not safe and have a carcinogenic effect (Srivastava et al., 2004). Previous studies confirmed that malachite green induced hurts to bones, skin, eyes, liver, kidney, heart, and spleen in animals (Sundarrajan et al., 2000).

In many parts of the world, the dye is still being used. Accordingly, it is important to find methods to eliminate dye from ponds or wastewater. It is important to eliminate dye from the water before its discharging to stream by using an effective treatment technique. The industrial separation method used for the purification of wastewater is the adsorption technique. As compared with other methods, adsorption is the first in terms of cost, ease of design, flexibility, the simplicity of procedure and insensitivity to toxic pollutants (Laxmi and Ahmaruzzaman, 2010). Lately, the use of biomass for removal of dye has been seriously studied as another economical, and feasible technique. The biological treatment is a superior technique for the adsorption due to their ability to remove dyes in a highly concentrated form. Recently, attention has been concentrated on algae (Deokar and Sabale, 2014), bacteria, fungi (Gupta et al., 2015) and plants (Kadirvelu et al., 2003). Adsorption of wastewater dyes by plant material or biomass is an eco-friendly and emerging process for removal of dyes in industrial effluents. The biomass is easy to be removed and can be stored for a long time without decomposition.

It is useful to understand and predict the mobility of toxic substances in the environment. Langmuir model is a common sorption isotherm and depends on reaction hypotheses (Langmuir, 1918). All the sites of adsorption are assumed to be identical, keep one molecule of the compound, energetically, and independent on the quantity of adsorbed. The model of Freundlich is empirical and based on the relation between the quantity of adsorbed and the concentration of remained solute (Freundlich, 1909).

The trees of *Myoporum laetum* and *Livistona chinensis* are found abundantly along streets of Jeddah city in Saudi Arabia. These trees are pruned annually making a huge accumulation and create great environmental problems. Therefore, economic utilization of these trees will be beneficial. The plant leaves can be dried and used as available biomaterials for the elimination of dye from solutions. The present study aimed to evaluate the efficiency of *Myoporum laetum* and *Livistona chinensis* leaves for removal of malachite green from solution. The effect of pH, contact time, dye concentrations, and temperature were determined to optimize the sorption conditions. The data of equilibrium biosorption was explained by Langmuir, Freundlich, and Temkin adsorption isotherm equations. The thermodynamic study, infrared spectroscopy, and scanning electron microscopy were investigated.

Materials and methods

Dye solution

Malachite green ($C_{52}H_{54}N_4O_{12}$) with a purity of 90% and molecular weight of 927.02 was attained from Merck, Germany. One gram of malachite green was dissolved in one liter of deionized water (1 g L^{-1}) to prepare the stock solution. Different concentrations ($5, 10, 15, 20, 25, 30$ and 35 mg L^{-1}) were prepared from the stock dye solution.

Preparation of biomass

The waste of *Myoporum laetum* and *Livistona chinensis* leaves were gathered from the streets of Jeddah, during the trimming season of trees in Saudi Arabia. The plant leaves were washed with water and then air dried at the Chemistry Lab., Faculty of Science, King Abdulaziz University. The dry constant was milled and sieved by using a standard sieve of 1.0 mm. The biomass was treated with 0.2% CaCl₂, dried at 45 °C and then kept until use.

Removal of dye

The bioremoval study was performed for 5 mg L⁻¹ dye solution using 0.5 g L⁻¹ biomass of leaves in Erlenmeyer flasks. The dye solution and biomass were agitated at 150 rpm for 1 h to detect the optimum factors of temperature, pH, contact time, and weight of biomass for removal of dye. The absorbance of the removed dye was measured by UV-1800 spectrophotometer at 616 nm. The dye removal percentage was represented by *Equation 1*.

$$\text{Removal of dye (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (\text{Eq.1})$$

where C_i represents the initial dye concentration and C_e is the concentration of dye at equilibrium.

Solution pH, temperature, and contact time

Dye solutions with different pH (2, 4, 6, 8, and 10), temperature (25, 35, 45 and 55 °C), and contact time (ranged from 0.0 to 180 min) were prepared. The optimum conditions of pH, temperature, and contact time for the uptake of dye were estimated by the dry biomass.

Weight of biomass

To obtain the ideal weight of biomass for removal of malachite green from solution, different weights of dry biomass (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g L⁻¹) were prepared. At the optimal conditions of pH, temperature, and contact time, the removal of dye from solution was estimated.

Dye concentration

At the optimal condition of pH, temperature, contact time, and biomass, different concentrations of dye (5, 10, 15, 20, 25, 30, and 35 mg L⁻¹) were used to evaluate the efficiency of dry plant leaves for removal of dye from solution.

Adsorption isotherms

The different adsorption isotherms were evaluated at the optimal conditions of pH, temperature, contact time, biomass and dye concentration. The monolayer adsorption was represented by the model of Langmuir isotherm. The Langmuir model (Langmuir, 1918) was stated in *Equation 2*.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m} \left(\frac{1}{C_e} \right) \quad (\text{Eq.2})$$

where q_e is the amount dye absorbed onto the biomass (mg g^{-1}), q_m is the Langmuir constant that clarifies the highest capacity (mg g^{-1}), and b is the constant of Langmuir and represent the affinity of binding site (L mg^{-1}), C_e is the concentration of dye in the solution at equilibrium (mg L^{-1}), $1/bq_m$ is the intercept, and $1/q_m$ is the slope.

The affinity of biomass (adsorbent) to dye (adsorbate) was obtained from the factor of dimensionless separation (R_L). The R_L was discussed by Malik (2004) in *Equation 3*.

$$R_L = \frac{1}{1+bC_i} \quad (\text{Eq.3})$$

The shape of isotherm was found to be favorable ($0 < R_L < 1$), linear ($R_L = 1$), irreversible ($R_L = 0$), or unfavorable ($R_L > 1$),

The unfavorable sorption on dissimilar surfaces and multilayer sorption was described in the Freundlich model (Freundlich, 1906). The Freundlich model was represented in *Equation 4*.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{Eq.4})$$

where q_e is the dye adsorbed onto the biomass (mg g^{-1}) at equilibrium, K_F Freundlich isotherm constant (mg g^{-1}), n is the sorption intensity constant, and C_e represents the concentration of dye at equilibrium (mg L^{-1}).

The interactions of indirect adsorbent-adsorbate and the behavior of the adsorption systems on the heterogeneous surfaces was represented by the model of Temkin isotherm (Temkin and Pyzhev, 1940). The model of Temkin was found in *Equation 5*.

$$q_e = \frac{R_T}{b_T} \ln A_T + \frac{R_T}{b_T} \ln C_e \quad (\text{Eq.5})$$

where R is the gas constant, T is the absolute temperature, b_T is the Temkin isotherm constant (J mol^{-1}), A_T is the Temkin equilibrium constant (L g^{-1}), R_T/b_T is a constant related to the heat of adsorption (J mol^{-1}), and C_e is the concentration of dye (mg L^{-1}) at equilibrium. A_T and b_T were determined from the slope and intercept obtained by plotting q_e versus $\ln C_e$.

Thermodynamic study

The values of thermodynamic were assessed by studying the temperature changes with an equilibrium constant. The following equation illustrates the free energy of the sorption reaction (*Eq. 6*):

$$\Delta G^\circ = -R_T \ln K_c \quad (\text{Eq.6})$$

where ΔG° represents the variation in free energy (kJ mol^{-1}), R declares the gas constant ($8.314 \text{ kJ mol}^{-1}$), T indicates the absolute temperature, and K_c is the equilibrium constant.

The thermodynamic values were estimated by the change of temperature with the equilibrium constant as found in *Equation 7*.

$$\ln K_c = - \frac{\Delta H^\circ}{R_T} + \frac{\Delta S^\circ}{R} \quad (\text{Eq.7})$$

where ΔH° represents the enthalpy, and ΔS° is the entropy of the equilibrium process.

Infrared spectroscopy (IR)

The functional groups on the surface of the biomass were characterized by infrared spectrophotometer (Tensor 27, Netherlands).

Scanning electron microscopy (SEM)

Scanning electron microscopy (JEOL, JSM-5200 LV) was used to study the surface of the biomass before and after the treatment with dye.

Results

Influence of pH

As shown in *Figure 1*, the removal of malachite green (5 mg L^{-1}) onto 0.5 g L^{-1} biomass of *Myoporum laetum* and *Livistona chinensis* was increased with increasing the pH values. The removal of dye increased gradually from pH 2 (94.46%) up to pH 6 (99.01%) and then remained constant up to pH 10 by using the biomass of *M. laetum*. However, the removal of dye increased slowly at pH ranged from 4 to 8 (89.73% to 90.62%, respectively) and then highly increased at pH 10 (96.78%) by using *L. chinensis* biomass.

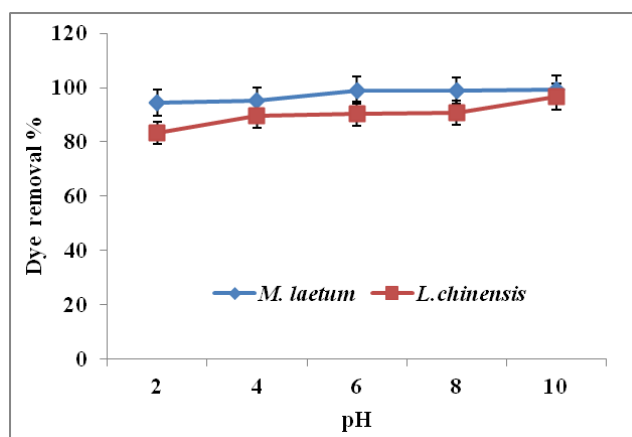


Figure 1. The effect of different pH values on the removal of malachite green (5 mg L^{-1}) by using the biomass of *M. laetum* and *L. chinensis* leaves. The data are the mean of three values \pm SD

Influence of temperature

Figure 2 represents the removal percentage of MG onto the plant biomass (0.5 g L^{-1}) at different temperatures (25, 35, 45, and 55 °C) after 1 h. The results showed that the

removal of MG increased with increasing temperature up to 35 °C for both biomasses of *M. laetum* (97.67%) and *L. chinensis* (92.32%). With increasing the temperature up to 55 °C, the removal of dye still constant with the biomass of *M. laetum* (97.67%) and decreased with *L. chinensis* biomass (89.46%). It can be noticed that the removal efficiency of MG onto the biomass of *M. laetum* was higher than *M. laetum*. The temperature of 35 °C was chosen as the optimum temperature for the uptake of MG from solution.

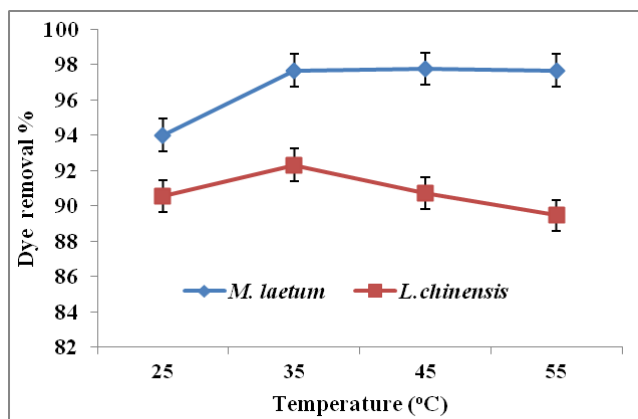


Figure 2. The effect of different temperatures on the removal of malachite green (5 mg L^{-1}) by using the biomass of *M. laetum* and *L. chinensis* leaves. The data are the mean of three values \pm SD

Influence of contact time

The removal of dye (5 mg L^{-1}) at a different time (0.0-180 min) by tested biomass (0.5 g L^{-1}) was explained in Figure 3. As shown in the results, the uptake of dye increased with increasing the contact time up to a certain extent. After this point, the removal percentage of MG is not affected. The removal of dye quickly increased through the first 10 min (57%) and then slowly increased until equilibrium at 120 and 160 min for *M. laetum* and *L. chinensis*, respectively. The maximum removal percentages were 96% and 88% by *M. laetum* and *L. chinensis*, respectively.

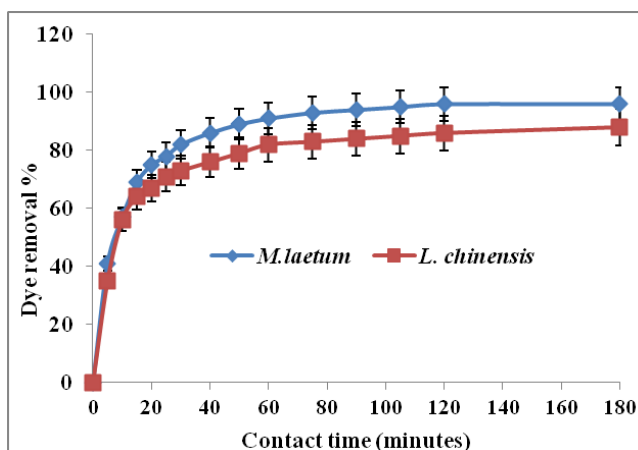


Figure 3. The effect of contact time on the removal of malachite green (5 mg L^{-1}) by using the biomass of *M. laetum* and *L. chinensis* leaves. The data are the mean of three values \pm SD

Influence of weight of biomass

The removal of MG from solution by 0.1-0.7 g biomass was illustrated in *Figure 4*. The results revealed that the removal of dye was greatly increased with increasing dose of biomass up to 0.3 g of *M. laetum* (99.11%) and 0.4 g of *L. chinensis* (95.98%) and then remained constant. As clear from the results, the biomass of *M. laetum* was more efficient than *L. chinensis* for the uptake of MG.

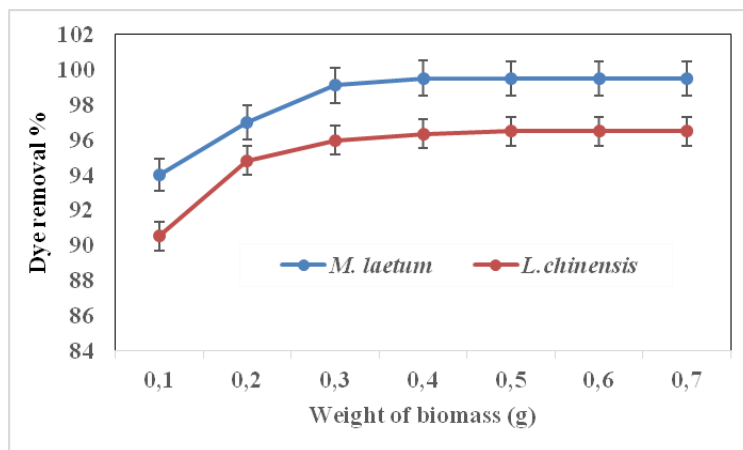


Figure 4. The effect of different weights of *M. laetum* and *L. chinensis* biomasses on the removal of malachite green (5 mg L^{-1}). The data are the mean of three values \pm SD

Influence of dye concentration

The influence of $5\text{-}35 \text{ mg L}^{-1}$ dye on the uptake of MG was investigated for both biomasses at the optimum conditions (*Fig. 5*). As shown from the above results the most favorable conditions for the removal of MG by using *M. laetum* were observed at pH: 6, temperature: $35 \text{ }^\circ\text{C}$, 0.3 g L^{-1} biomass dose and 120 min contact time. However, pH: 10, temperature: $35 \text{ }^\circ\text{C}$, 0.4 g L^{-1} biomass dose and 160 min contact time were the optimum condition for the removal of MG by using *L. chinensis*. The results presented that the percentage of MG uptake decreased with increasing the dye concentration from 5 to 35 mg L^{-1} . The maximum uptake of dye (99.28% and 95.48%) was attained at 5 mg L^{-1} by the biomass of *M. laetum* and *L. chinensis*, respectively. However, the biomass of *M. laetum* and *L. chinensis* showed the minimum removal percentage (79.31% and 69.67%, respectively) at 35 mg L^{-1} MG concentration.

Adsorption isotherms

It is important to design the most adsorption system for removal of MG dye. Thus, the equilibrium experimental data for adsorbed MG onto *M. laetum* and *L. chinensis* biomasses were studied using different isotherms of Langmuir and Freundlich and Temkin (*Table 1*). According to Langmuir isotherm, the values of intercept ($1/bq_m$) and slop ($1/q_m$) were attained from the plot of $1/q_e$ against $1/C_e$ for adsorption of MG onto the biomasses of *M. laetum* and *L. chinensis* (*Fig. 6a, b*). The results in *Table 1* revealed that the maximum capability (q_m) was found to be 50.065 and 42.212 mg g^{-1} for the biomass of *M. laetum* and *L. chinensis*, respectively. It can be noticed that the greatest capacity of adsorption of MG dye was recorded with *M. laetum*. Regarding to the

results of Langmuir isotherm, the highest binding site affinity (b) for MG was observed with *M. laetum* biomass (0.242 L mg^{-1}). The R_L values for both *M. laetum* and *L. chinensis* were found to be 0.176 and 0.106, respectively suggesting that the process of dye sorption is favorable (Table 1).

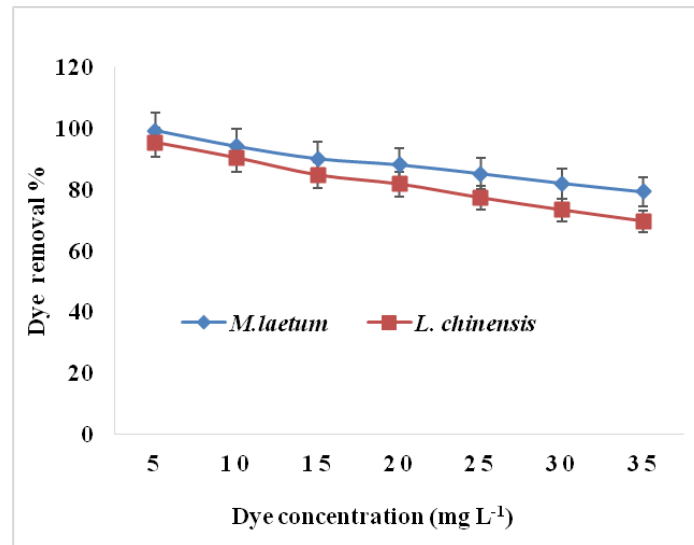


Figure 5. Removal of different concentrations of malachite green by using the biomass of *M. laetum* and *L. chinensis* leaves under the optimal conditions. The data are the mean of three values \pm SD

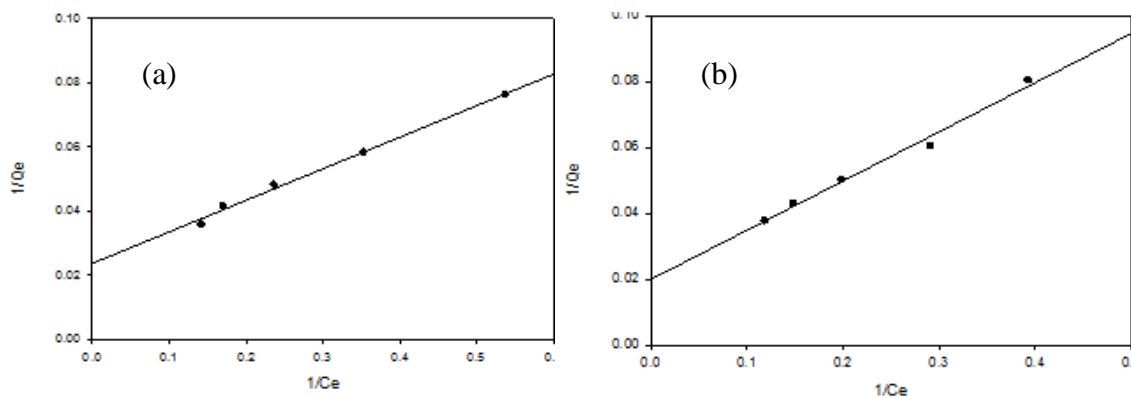


Figure 6. The linear plots of Langmuir isotherm for adsorption of malachite green onto the biomass of *M. laetum* (a) and *L. chinensis* leaves (b)

With regard to Freundlich isotherm, the results showed that the plotting of $\ln q_e$ versus $\ln C_e$ give a straight line with a slope of $1/n$ and intercept of $\ln K_F$ for adsorption of MG onto the tested biomasses (Fig. 7a, b). The values of n were found to be 1.839 and 1.655 for *M. laetum* and *L. chinensis*, respectively (Table 1). As a general, MG is favorably adsorbed onto the tested biomass where $n > 1$. The adsorption capacity (K_F) for *M. laetum* (9.497 mg g^{-1}) was higher than that of *L. chinensis* (7.419 mg g^{-1}). Therefore, *M. laetum* biomass obtained the greatest binding affinity and adsorption capacity for MG as compared with the biomass of *L. chinensis*.

Table 1. Parameters of Langmuir, Freundlich and Temkin isotherms for adsorption of malachite green onto the biomass of *M. laetum* and *L. chinensis* leaves

Isotherm		<i>M. laetum</i>	<i>L. chinensis</i>
Langmuir	q_m (mg g ⁻¹)	50.065	42.212
	b (L mg ⁻¹)	0.242	0.134
	R_L	0.176	0.106
	R^2	0.97	0.97
Freundlich	K_F (mg g ⁻¹)	9.497	7.419
	n	1.839	1.655
	R^2	0.97	0.99
Temkin	A_T (L mg ⁻¹)	1.791	1.590
	b_T	233.34	246.33
	R^2	0.86	0.94

q_m : Langmuir constant, b : affinity of binding site, R_L : dimensionless separation factor, R^2 : linear correlation coefficient, K_F : Freundlich isotherm constant, n : sorption intensity constant, A_T : Temkin isotherm equilibrium binding constant, b_T : Temkin isotherm constant

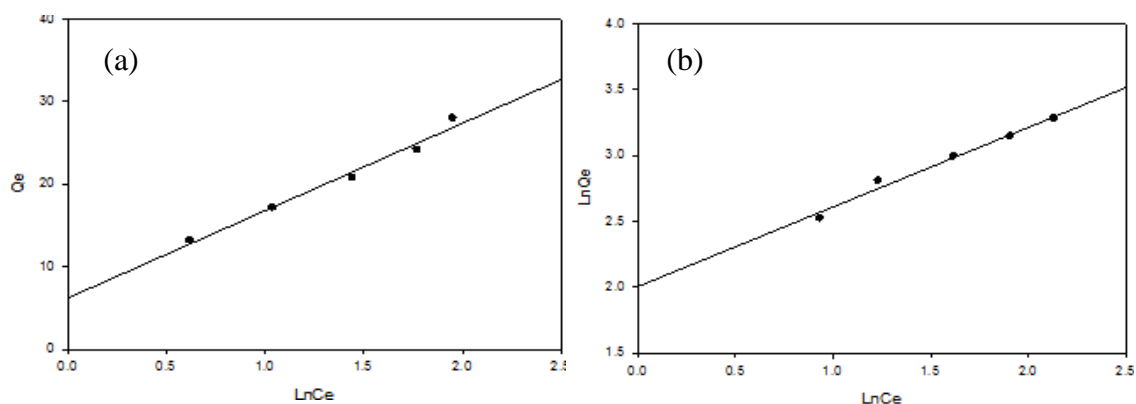


Figure 7. The linear plots of Freundlich isotherm for adsorption of malachite green onto the biomass of *M. laetum* (a) and *L. chinensis* leaves (b)

According to the Temkin isotherm, the constant of A_T and b_T for sorption of MG by *M. laetum* and *L. chinensis* dry leaves were attained from the slop of q_e against $\ln C_e$ (Fig. 8a, b). The results demonstrated that A_T was 1.791 and 1.590 L mg⁻¹ for *M. laetum* and *L. chinensis* biomass, respectively (Table 1). The b_T values were 233.34 and 246.33 for *M. laetum* and *L. chinensis* biomasses, respectively.

The results showed that the Langmuir isotherm for *M. laetum* biomass was linear within the entire studied concentration of dye with a linear correlation coefficient ($R^2 = 0.97$), suggesting that the data fit quite well with Langmuir model. The Langmuir isotherm confirms the monolayer sorption of MG by *M. laetum* biomass and heterogenous active sites distribution on the adsorbent. Depending on the great values of the correlation coefficient ($R^2 = 0.97$), the Freundlich model was also established to be a favorable model for explanation of the adsorption performance of MG by *M. laetum* biomass. Based on these results, it can be noticed that the adsorption of dye was well fitted by both Langmuir and Freundlich models for the biomass of *M. laetum*. It

can be concluded that both homogenous and heterogenous adsorption takes place throughout the process.

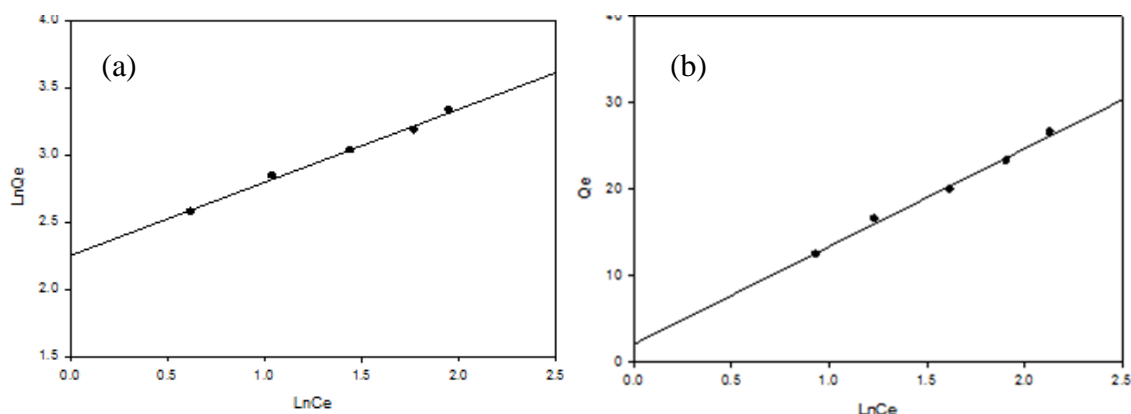


Figure 8. The linear plots of Temkin isotherm for adsorption of malachite green onto the biomass of *M. laetum* (a) and *L. chinensis* leaves (b)

As compared with other isotherms, the highest value of the correlation coefficient ($R^2 = 0.99$) was observed with the biomass of *L. chinensis*. This result clarified that the Freundlich model was the most favorable to describe the adsorption equation data for *L. chinensis* biomass.

According to Temkin isotherm, the correlation coefficients (R^2) of *M. laetum* and *L. chinensis* biomasses were ranged between 0.86 and 0.94, respectively (Table 1). This result elucidated that Temkin equation represents the poor fit as compared with the other isotherms for both biomasses.

Thermodynamic study

In the present study, the values of thermodynamic were given in Table 2. The ΔG° was determined as -6.3 kJ mol^{-1} and -4.8 kJ mol^{-1} for *M. laetum* and *L. chinensis*, respectively. The highest affinity for removal of MG by the biomass of *M. laetum* may be returned to the highest value of $-\Delta G^\circ$ as compared with *L. chinensis* biomass. The sorption process of MG by the tested biomass was spontaneous and highly favorable due to the negative values of ΔG° . The values of ΔH° and ΔS° were represented by 8.5 kJ mol^{-1} and 49 kJ mol^{-1} , respectively for *M. laetum* and 7.3 kJ mol^{-1} and 40 kJ mol^{-1} , respectively for *L. chinensis* (Table 2).

IR spectral analysis

The IR spectral analysis of raw biomass of *M. laetum* showed different functional groups at 3435 cm^{-1} due to $-\text{OH}$ and $-\text{NH}$ stretching, at 2923 cm^{-1} attributed to C-H stretching vibration, at 1627 cm^{-1} assigned to $-\text{COO}^-$ stretching or amide I and amide II and finally at 1035 cm^{-1} due to N-H bending vibration or C-OH stretching vibration of alcohol (Fig. 9a). However, the IR spectrum of *M. laetum* biomass after dye sorption (Fig. 9b) exhibited change in the position and intensity of adsorption bands at 3435 , 1627 and 1037 cm^{-1} due to hydroxyl or amino groups, and carboxylate or amide groups. These results showed the contribution of these groups in the biosorption of MG dye by *M. laetum* biomass.

Table 2. Parameters of thermodynamic and activation energy for adsorption of malachite green onto the biomass of *M. laetum* and *L. chinensis* leaves

Plant	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹)
<i>M. laetum</i>	-6.3	8.5	49
<i>L. chinensis</i>	-4.8	7.3	40

ΔG° : variation in free energy, ΔH° : enthalpy of equilibrium, ΔS° : entropy of equilibrium

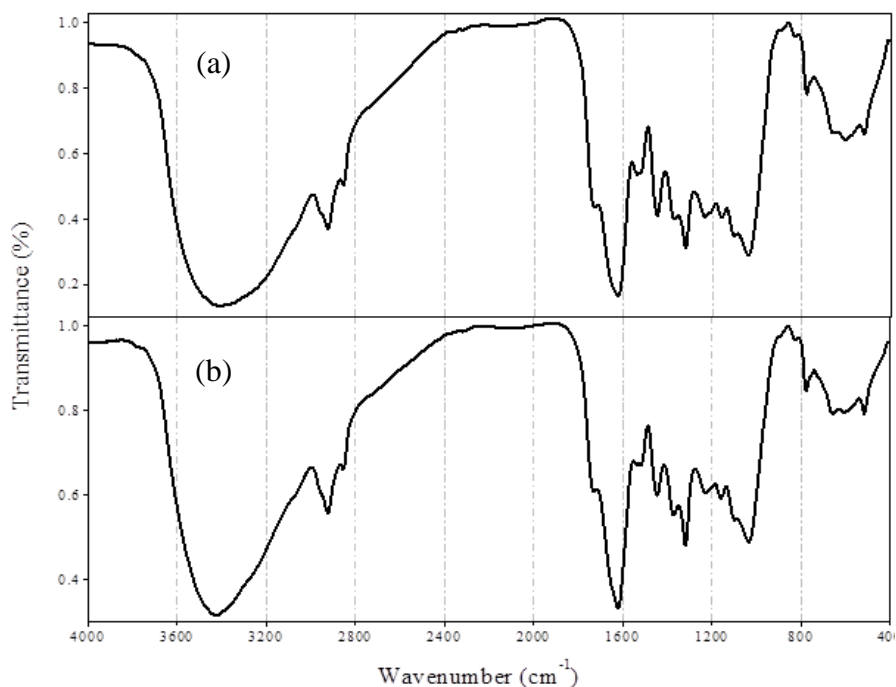


Figure 9. FTIR spectrum of *M. laetum* biomass before (a) and after (b) adsorption of malachite green

The IR spectrum of raw biomass of *L. chinensis* (Fig. 10a) exhibited a broad peak for adsorption at 3436 cm⁻¹ attributable to -OH and -NH stretching vibration, 2923 cm⁻¹ due to stretching vibration of C-H, 1631 cm⁻¹ caused by COO⁻ group or amide group and 1034 cm⁻¹ assigned to N-H bending or stretching vibration of C-OH. The adsorption bands after dye treatments revealed some changes in the position and intensity of the above absorption bands especially at 1631 cm⁻¹ due to carboxylate or amide groups which confirm the participation of these groups in dye biosorption by *L. chinensis* biomass (Fig. 10b).

Scanning electron microscopy micrographs (SEM)

Evaluation of the morphological changes on the surface of *M. laetum* biomass, which is the most efficient for sorption of MG dye adsorption, was performed by using scanning electron microscopy. Before the removal of MG by the biomass, the cells were rich with high porous structure exhibited hole-like (Fig. 11a). The surface of the biomass cells became rough and meanders after the removal of dye ions, due to precipitation of dye ions around the cell surface (Fig. 11b).

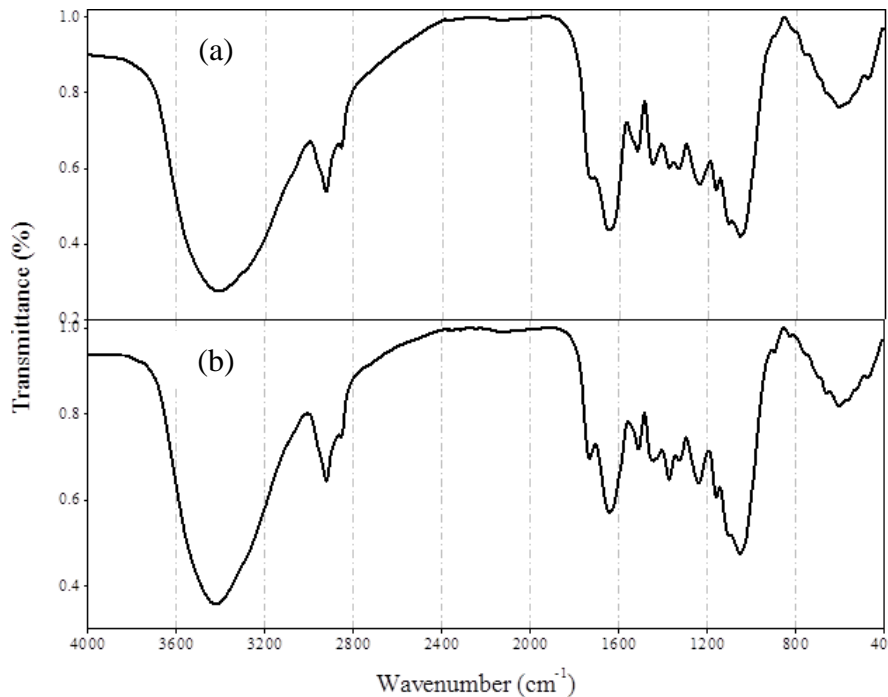


Figure 10. FTIR spectrum of *L. chinensis* biomass (a) before and (b) after adsorption of malachite green

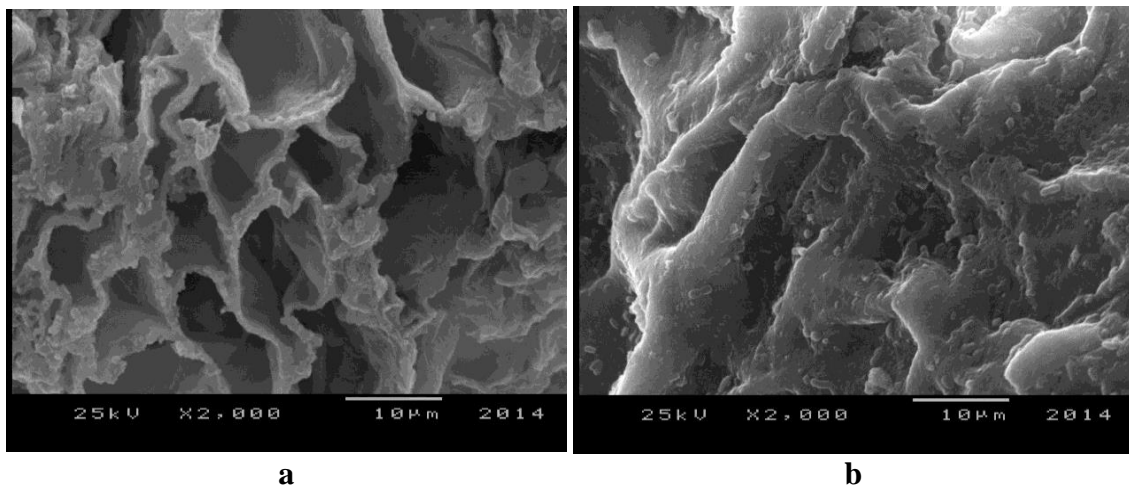


Figure 11. Scanning electron microscopy micrographs of *M. laetum* surface before (a) and after (b) adsorption of malachite green

Discussion

The waste materials of the dry leaves of the plant can be used for the removal process of dye. The removal process was found to be affected by the pH values of the dye solution. In agreement with the current result, Anbia and Ghaffari (2011) showed that the uptake of malachite green from solution using adsorbent was found to increase at high pH. They reported that the pH effects on the charge, functional groups, and ionization degree on the biomass active sites, in addition to the chemistry of dye solution. The MG is a cationic basic dye and contains a negatively charged chloride ion,

a positive charged organic ion, and a positive nitrogen ion. The color intensity and stability of MG structure were found to be affected by the pH value (Mall et al., 2006). They showed that the pH range 3-7 made the color of MG stable, and the reduction of color increased with increasing pH from 7 to 11 in the solution of MG.

The pH value of the solution effect on the functional groups on the active sites of the biomass and the degree of ionization of dye which effects on the process of uptake (Nandi et al., 2009). MG is protonated in the acidic medium and deprotonated at high values of pH. The low removal of MG at acidic pH may be related to the competition between the abundant hydrogen ions, adsorption sites on the biomass and the dye cations. In our study, the great adsorption of MG at pH 8-10 may be related to the changes in the structure of MG molecules as mentioned by Sun and Tomkinson (2001). Maurya et al. (2006) found that deprotonating of different functional groups of the biomass lead to an increase in the removal dye.

The results showed that the removal of MG by the tested biomass increased with increasing temperature. This result indicates that high temperature is favorable for the removal of MG from aqueous solution. The rate of diffusion of the dye molecules is a temperature dependent process. In accordance with the present result, Demierege et al. (2015) showed that the biosorption of dye by using mushroom stump wastes increased with increasing temperature from 20 °C to 50 °C due to the increase in surface activity and kinetic energy of dye molecules. Increase in temperature may increase the mobility of the large dye ion and consequently increase the adsorption process (Singla et al., 2016). A sufficient energy is required for a number of molecules to make an interaction with the active site at the surface (Doğan and Alkan, 2003). An increase in temperature causes fast diffusion of dye molecules across the internal pores of the adsorbent particles and the external boundary layer due to the less resistance of viscous forces in the aqueous solution (Banerjee and Chattopadhyaya, 2017). The increase in adsorption capacity may be due to the enlargement of the pore size of adsorbents at high temperature (Demirbas et al., 2008).

The present result indicated that removal of MG dye by using the tested biomasses showed an increase with increasing contact time through the first minutes and then slowly increased until equilibrium. The uptake of dye does not increase with more increase in contact time as a result of the accumulation of dye on the available sites of adsorption on biomass material (Eren, 2009; Singla et al., 2016). The biomass of *M. laetum* reached equilibrium earlier than and that of *L. chinensis*. This result suggests that there are a higher affinity and stronger electrostatic force of attraction between MG dye and the binding-sites and functional groups on the wall surface of *M. laetum* biomass as compared with that of *L. chinensis*. The uptake of dye returned to the great number of active and vacant sites on the adsorbent surface at equilibrium time (Vijayaraghavan et al., 2008). Ashish et al. (2017) showed that the removal of MG dye occurs at the high-speed rate by *Limonia acidissima* (98.87%) after 3.30 h of equilibrium time. Malik et al. (2007) suggested that a monolayer of dye is formed on the surface of the biomass, and the rate of the dye uptake is controlled by the rate of transported dye from the exterior to the interior site of the biomass. This result suggests that there are a higher affinity and stronger electrostatic force of attraction between MG dye and the binding-sites and functional groups on the wall surface of the biomass.

As shown in the results, the removal of dye was greatly increased with increasing the weight of biomass up to certain limits and then remained constant. At first, the rate of dye removal has been found to be rapid and slowed down as the biomass dose increased

(Salleh et al., 2003; Omar et al., 2018). This can be explained depending on the fact that, at a lower weight of biomass the dye is more available and due to this, the removal of dye per unit weight of biomass is higher. In addition, the increase in the adsorbent dose leads to an increase in the adsorbed dye due to increases in the number of available adsorption sites and the surface area of adsorbent (Mane et al., 2007). As clear from the results, the biomass of *M. laetum* was more efficient than *L. chinensis* in the removal of dye. This may be returned to the availability of more binding sites on the surface of *M. laetum* biomass.

The removal of dye decreased gradually with increasing dye concentration at the optimum condition as shown in the present study. This result may be returned to the increase in the gradient pressure between solution and biomass which drive the dye molecules from the solution to the surface of the biomass (Rasool and Lee, 2015). The decrease in the removal capacity with increasing dye concentration may be due to the higher quantity of adsorbate than the adsorbent dose (Chen and Zhao, 2009). At high concentration of dye, the available sites of sorption became fewer as compared to the concentration of dye and so the uptake of dye is associated with the initial concentration of dye.

Equations of equilibrium isotherm were used to illustrate experimental absorption data. These equations parameters and the thermodynamic properties explain both the mechanism of sorption and adsorbent affinity. Graphically it is likely to elucidate the isotherm of equilibrium adsorption by plotting liquid phase concentration against solid phase concentration. It is necessary to determine the foremost acceptable correlation for the equilibrium curve, to enhance the design of an adsorption system to eliminate dyes from effluents. Consequently, the association of equilibrium data using theoretical and experimental equation is essential for the sorption interpretation and expectation of the adsorption range.

According to the Langmuir isotherm results, the *M. laetum* biomass recorded the greatest affinity of the binding site (b) to MG. In addition, the R_L low values elucidated that the removal of MG was favorable by the biomass. The low value of R_L means high adsorbent to adsorbate affinity (Jelinek et al., 2015). Depending on the high values of linear correlation coefficient (R^2), the models of Langmuir and Freundlich were found to be more favorable for explaining the sorption MG onto *M. laetum* and *L. chinensis* biomass. In addition, homogeneous and heterogeneous adsorption energy occurred throughout the removal of MG by the biomass. Hii et al. (2011) confirmed that the high values of the linear correlation coefficient ($R^2 > 0.95$) of each model of Langmuir and Freundlich are favorable for a description of the sorption of the dye by *Aristaeomorpha foliacea*. The confirmation of Langmuir and Freundlich isotherms to the sorption study showed that the tested biomass may exhibit monolayer adsorption and heterogeneous surface conditions (Kumari and Abraham, 2007). The results of Temkin isotherm proposed that the heat of molecule adsorption decreased linearly in the layer. Fil (2016) reported that the negative value of ΔG° for all temperatures proposed that the adsorption process was spontaneous. The ΔH° within the range of 0.5-20.9 kJ mol⁻¹ means that the removal of MG by tested biomass was physical biosorption (Ahmet and Mustafa, 2008). The positive ΔS° values represent the decrease in the degree of freedom on the adsorbent surface during MG sorption process.

The IR analysis explained that the interaction between the biomass and MG were ionic between MG and carboxylate group, and coordinate bond was found between MG and the lone pair of electrons on the -OH or -NH₂ groups. In addition, forces of van der

Waals between nonpolar groups of biomass and MG, and ion-dipole interaction between the negative dipole end of the carbonyl group and MG. According to the results of IR, the changes in the position of functional groups on the tested biomass after treatment with MG confirmed the contribution of these groups in the dye removal as suggested by Jayaraj et al. (2011). Zhai et al. (2014) explained that the plant cell walls consist of carbohydrate, protein, lignin, hemicellulose, cellulose microfibrils and aromatic compounds. These molecules on the surface of the cell have carboxyl, amino, phosphate, thiol, and sulfhydryl functional groups (Tüzün et al., 2005).

The surface of the tested biomass became rough and meanders after exposure to the ions of MG because of the precipitation of dye at the surface of the biomass cell. This result may be due to the linkage of dye ions with the functional groups of cell surface and replacement of the ions for some of the cations in the cell wall matrix. The differences in the morphology and the structure of the biomass cell wall lead to the presence of differences in the efficiency of dye removal. The increase of dye removal may be related to the pores on the surface of plant biomass which allow the free passage of dye molecules (Deokar, 2016). The irregular surface of biomass cells, make the sorption of solution ions possible on different parts of these materials.

Conclusions

The color removal of dye from wastewater is a matter of concern due to its toxicity. The easily available and low-cost biomass such as the waste of *M. laetum* and *L. chinensis* leaves were found to have the unlimited capacity for the removal of MG and thus decrease the toxic effect of dye in the solution. The efficiency of *M. laetum* biomass was higher than *L. chinensis* biomass for adsorption of MG. The present study confirmed that the plant biomaterial which is discarded as a waste can be used for the removal of dyes from wastewater and make the water cleaner for various uses. This is an economical and environmentally-friendly alternative to various other methods that use a large number of chemicals to treat wastewater.

REFERENCES

- [1] Ahmet, S., Mustafa, T. (2008): Biosorption of total chromium from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies. – Journal of Hazardous Materials 160: 349-355.
- [2] Albert, A. (1979): Selective Toxicology. Sixth ed. – Chapman and Hall, London.
- [3] Anbia, M., Ghaffari, A. (2011): Removal of malachite green from dye wastewater using mesoporous carbon adsorbent. – Journal of the Iranian Chemical Society 8: S67-S76.
- [4] Ashish, S., Sartape, A., Aniruddha, M., Mandhare, A., Vikas, V., Jadhav, B., Prakash, D., Raut, B., Mansing, A., Anuse, A., Sanjay, S., Kolekar, S. (2017): Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. – The Arabian Journal of Chemistry 10: 3229-3238.
- [5] Banerjee, S., Chattopadhyaya, M. (2017): Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. – The Arabian Journal of Chemistry 10: 1629-1638.
- [6] Chen, H., Zhao, J. (2009): Adsorption study for removal of Congo red anionic dye using organo-attapulgit. – Adsorption 15: 381-389.

- [7] Clifton-Hadley, R. S., Alderman, D. J. (1987): The effects of malachite green on proliferative kidney disease. – *Journal of Fish Diseases* 10: 101-107.
- [8] Demierege, S., Toptas, A., Ayan, E., Yasa, I., Yanik, J. (2015): Removal of textile dyes from aqueous solutions by biosorption on mushroom stump wastes. – *Chemistry and Ecology* DOI: 10.1080/02757540.2014.976209.
- [9] Demirbas, E., Kobya, M., Sulak, M. T. (2008): Adsorption kinetics of a basic dye from aqueous solutions onto apricot stones activated carbon. – *Bioresource Technology* 99: 5368-5373.
- [10] Deokar, R. R. (2016): *Enteromorpha intestinalis*: low cost biosorbents for biosorption methylene blue. – *International Journal of Recent Scientific Research* 7: 9291-9297.
- [11] Deokar, R. R., Sabale, A. B. (2014). Biosorption of methylene blue from aqueous solution on to green seaweeds. – *International Journal of Recent Scientific Research* 5: 347-351.
- [12] Doğan, M., Alkan, M. (2003): Adsorption kinetics of methyl violet onto perlite. – *Chemosphere* 50: 517-528.
- [13] Eren, E. (2009): Investigation of a basic dye removal from aqueous solution onto chemically modified *Unye bentonite*. – *Journal of Hazardous Materials* 166: 88-93.
- [14] Fil, B. A. (2016): Isotherm, kinetic, and thermodynamic studies on the adsorption behavior of malachite green dye onto montmorillonite clay. – *Particulate Science and Technology* 34: 118-126.
- [15] Forgacs, E., Cserháti, T., Oros, G. (2004): Removal of synthetic dyes from wastewaters: a review. – *Environment International* 30: 953-971.
- [16] Freundlich, H. M. F. (1906): Over the adsorption in solution. – *The Journal of Physical Chemistry* 57: 358-371.
- [17] Gupta, V. K., Khamparia, S., Tyag, I., Jaspal, D., Malviya, A. (2015): Decolorization of mixture of dyes: A critical review. – *Global Journal of Environmental Science and Management* 1: 71-94.
- [18] Hammud, H. H. (2011): Biosorption studies of methylene blue by Mediterranean algae *Carolina* and its chemically modified forms. Linear and nonlinear models' prediction based on statistical error calculation. – *International Journal of Chemistry* 3: 147-163.
- [19] Hecht, T., Endemann, F. (1998): The impact of parasites, infections and disease on the development of aquaculture in sub-Saharan Africa. – *Journal of Applied Ichthyology* 14: 213-221.
- [20] Hii, S. L., Estrop, L. L., Wong, C. L. (2011): Adsorption of reactive blue 4 onto the chemically modified red seaweed *Amphiroa foliacea*: equilibrium, kinetics and modeling studies. – *International Journal of Physical Science* 6: 7171-7182.
- [21] Jayaraj, R., Mohan, M. C., Prasath, P. M., Khan, T. H. (2011): Malachite green dye removal using the seaweed *Enteromorpha*. – *European Journal of Chemistry* 8: 649-656.
- [22] Jelínek, L., Procházková, G., Quintelas, C., Beldíková, E., Brányik, T. (2015): *Chlorella vulgaris* biomass enriched by biosorption of polyphenols. – *Algal Research* 10: 1-7.
- [23] Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N., Pattabhi, S. (2003) Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. – *Bioresource Technology* 87: 129-132.
- [24] Kumari, K., Abraham, T. (2007): Biosorption of anionic textile dyes by nonviable biomass of fungi and yeast. – *Bioresource Technology* 98: 1704-1710.
- [25] Langmuir, I. (1918): The adsorption of gases on plane surfaces of glass, mica and platinum. – *Journal of the American Chemical Society* 40: 1361-1403.
- [26] Laxmi, G. S., Ahmaruzzaman, M. (2010): Adsorption technique for the removal of phenolic compounds from wastewater using low-cost natural adsorbents. – *Assam University Journal of Science and Technology: Physical Sciences and Technology* 5: 156-166.

- [27] Malik, P. K. (2004): Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. – *Journal of Hazardous Materials* 113: 81-88.
- [28] Malik, R., Ramteke, D. S., Wate, S. R. (2007): Adsorption of malachite green on groundnut shell waste based powdered activated carbon. – *Waste Management* 27: 1129-1138.
- [29] Mall, I. D., Srivastava, V. C., Kumar, G. V. A., Mishra, I. M. (2006): Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution. – *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 278: 175-187.
- [30] Mane, V. S., Mal, I. D., Srivastava, V. C. (2007): Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution. – *Dyes and Pigments* 73: 269-278.
- [31] Maurya, N. S., Mittal, A. K., Cornel, P., Rother, E. (2006): Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH. – *Bioresource Technology* 97: 512-521.
- [32] Nandi, B., Goswami, A., Purkait, M. (2009): Removal of cationic dyes from aqueous solutions by kaolin: kinetic and equilibrium studies. – *Applied Clay Science* 42: 583-590.
- [33] Omar, H., El-Gendy, A., Al-Ahmary, K. (2018): Bioremoval of toxic dye by using different marine macroalgae. – *Turkish Journal of Botany* 42: 15-27. DOI: 10.3906/bot-1703-4.
- [34] Rasool, K., Lee, D. S. (2015): Characteristics, kinetics and thermodynamics of Congo red biosorption by activated sulfidogenic sludge from an aqueous solution. – *International Journal of Environmental Science and Technology* 12: 571-580.
- [35] Salleh, M. A., Mahmoud, D. K., Karim, W. A., Idris, A. (2003): Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. – *Desalination* 280: 1-13.
- [36] Seshadri, S., Bishop, P. L., Agha, A. M. (1994): Anaerobic/aerobic treatment of selected Azo dyes in wastewater. – *Waste Management* 14: 127-137.
- [37] Singla, S., Kaushal, J., Mahajan, P. (2016): Removal of dyes from wastewater by plant waste: a review. – *International Journal of Advanced Research in Science, Engineering and Technology* 5: 228-239.
- [38] Srivastava, S. J., Singh, N. D., Srivastava, A. K., Sinha, R. (1995): Acute toxicity of malachite green and its effects on certain blood parameters of a catfish, *Heteropneustes fossilis*. – *Aquatic Toxicology* 31: 241-247.
- [39] Srivastava, S., Sinha, R., Roy, D. (2004): Toxicological effects of malachite green. – *Aquatic Toxicology* 66: 319-329.
- [40] Sun, R., Tomkinson, J. (2001): Fractional separation and physico-chemical analysis of lignins from the black liquor of oil palm trunk fiber pulping. – *Separation and Purification Technology* 24: 529-539.
- [41] Sundarajan, M., Frenandis, A. Z., Subrahmanyam, G., Prabhudesai, S., Krishnamurthy, S. C., Rao, K. V. (2000): Overexpression of G1/S cyclins and PCNA and their relationship to tyrosine phosphorylation and dephosphorylation during tumor promotion by metanil yellow and malachite green. – *Toxicology Letters* 116: 119-130.
- [42] Temkin, M. J., Pyzhev, V. (1940): Kinetics of ammonia synthesis on promoted iron catalysts. – *Acta Physicochimica U. S. S. R* 12: 217-222.
- [43] Tüzün, I., Bayramoğlu, G., Yalçın, E., Başaran, G., Çelik, G., Arıca, M. Y. (2005): Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto micro algae *Chlamydomonas reinhardtii*. – *Journal of Environmental Management* 77: 85-92.
- [44] Vijayaraghavan, K., Yun, Y. S. (2008): Biosorption of C. I. reactive black 5 from aqueous solution using acid-treated biomass of brown seaweed *Laminaria* sp. – *Dyes and Pigments* 76: 726-732.

- [45] Vijayaraghavan, K., Mao, J., Yun, Y. S. (2008): Biosorption of methylene blue from aqueous solution using free and polysulfone-immobilized *Corynebacterium glutamicum*: Batch and column studies. – *Bioresource Technology* 99: 2864-2871.
- [46] Zhai, S., Horikawa, Y., Imai, T., Sugiyama, J. (2014): Cell wall ultrastructure of palm leaf fibers. – *The International Association of Wood Anatomists* 35: 127-137.