

*Dedicated to Professor Dumitru Oancea
on the occasion on his 75th anniversary*

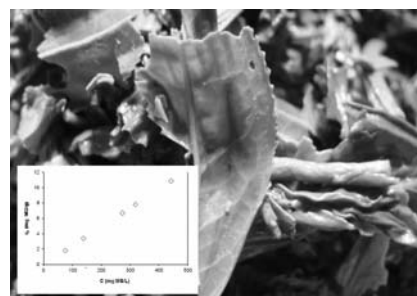
A GREEN APPROACH: MALACHITE GREEN ADSORPTION ONTO WASTE GREEN TEA BIOMASS. ISOTHERM AND KINETIC STUDIES

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Dye (malachite green, MG) removal from aqueous solution using a green approach, adsorption onto waste green tea biomass, was considered in this work. Influence of the initial concentration over the MG uptake was considered in order to collect the experimental data necessary for equilibrium and kinetic modelling. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm equations were used to model the obtained experimental data. The best fit was obtained for Dubinin-Radushkevich model ($R^2=0.994$) indicating a chemisorption process (16.01 kJ/mol). The maximum monolayer coverage from Langmuir isotherm model was determined to be 14.08 mg/g. The considered kinetic models (pseudo-first pseudo-second-order, Elovich, intra-particle film diffusion) showed that experimental data best fitted on the pseudo-second-order model. The obtained results showed that the considered green and low cost biomass is an efficient material for dye removal from wastewaters.



INTRODUCTION

The impact of organic pollutants release into the environment is increasing as a result of population explosion and rapid urbanization, industrial and technological development, waste generation from domestic and industrial sources. These have released many toxic and hazardous waters to humans and other living organisms.¹ A number of clean-up technologies have been developed over the years to remove organic dyes from the industrial wastewaters, among them are adsorption, coagulation, filtration, ion-exchange, electrolysis, advanced oxidation processes, etc.²⁻⁹

Adsorption is a well-known separation process and an effective method for water decontamination applications. Recently low cost agricultural by-products have been used as adsorbent materials. Between these, rice husk, wheat bran, coconut bunch waste, orange peel, banana peel, garlic peel, papaya seed, pineapple stem waste, sunflower stalks, silk cotton hull, maize cob, have been extensively researched and evaluated for dyes removal.¹⁰⁻¹⁷

Depending on the ionic charge of the chromophore group, dyes are generally classified as anionic, cationic and non-ionic. Cationic dyes are more toxic than anionic dyes.² The dye effluents can cause several health problems,

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damage the aesthetic quality of water and reduce light penetration and photosynthesis, and some of them are toxic or mutagenic, carcinogenic and allergenic.³ Malachite green (MG) is a basic triphenylmethane dye, used in acrylic, textile, paper, rubber, food industries and distilleries. It is toxic to humans and can cause liver tumour formation.^{2,3}

Waste green tea could be an efficient alternative for dyes removal from wastewater. Green tea *Camellia sinensis* is native to South-East Asia, the main producer being China.¹⁵ Canned or bottled tea drinks as well as instant tea drinks are produced on industrial scale and the producers encounter a problem in disposal of the waste tea leaves. Therefore, the valorisation of such waste as adsorbent could be a solution.^{18,19}

In this paper, adsorption of malachite green dye (MG) onto green tea waste (WGT) was considered. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models were used to analyse the experimental data. Also the adsorption kinetics models (pseudo-first pseudo-second-order, Elovich, intra-particle film diffusion) were used to evaluate the experimental data.

RESULTS AND DISCUSSION

The effect of initial MG concentration over the adsorption process

Experiments were conducted using 100 mL MG aqueous solutions with concentrations in the 75-445 mg MG/L range in batch conditions, under magnetic stirring at 300 rpm, at room temperature ($T = 22 \pm 2^\circ\text{C}$) and 4 g of WGT.

Experimental results showed that the quantity of adsorbed MG increased with the increase of the MG concentration, from 1.81 to 10.85 mg/g for 75 and 445 mg MG/L, respectively (Fig. 1). As the initial concentration increased, adsorption equilibrium was reached slower, after about 240 minutes, by comparison with only 80 minutes for small concentrations (75-140 mg MG/L).

Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and solid phases, based on a set of assumptions that are related to the

heterogeneity/homogeneity of the solid surface, the type of coverage and the possibility of interaction between the adsorbate species.²⁰ In this study, equilibrium data were analysed using the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms models, which are the most used isotherms in adsorption studies, which allow data analysis using linear regression analysis.

Langmuir adsorption isotherm

The Langmuir isotherm model assumes a monolayer coverage and also that the adsorbent surface contains a finite number of identical sites of uniform energy (homogeneous surface), one molecule adsorbs on each adsorption site and there are no interactions between adsorbate molecules on adjacent sites. The Langmuir isotherm equation has a hyperbolic form:^{21,22}

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

where q_e is the solid-phase adsorbate concentration at equilibrium (mg/g), q_{\max} is the maximum adsorption capacity corresponding to the monolayer adsorption capacity (mg/g), C_e is the concentration of MG solution at equilibrium (mg/L), Table 1, K_L (L/mg) is related to the strength of adsorbent-adsorbate affinity.

The linear form of the Langmuir isotherm can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (2)$$

The important features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , dimensionless constant referred to as separation factor or equilibrium parameter.²³

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (3)$$

where, C_0 is the highest initial concentration (mg/L), and R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$.²³

The maximum monolayer coverage capacity (q_{\max}) from Langmuir isotherm model was determined to be 14.08 mg/g, K_L is 0.0068 L/mg, while R_L is 0.513 indicating that the adsorption equilibrium was favourable. The R^2 value is 0.947, Table 2.

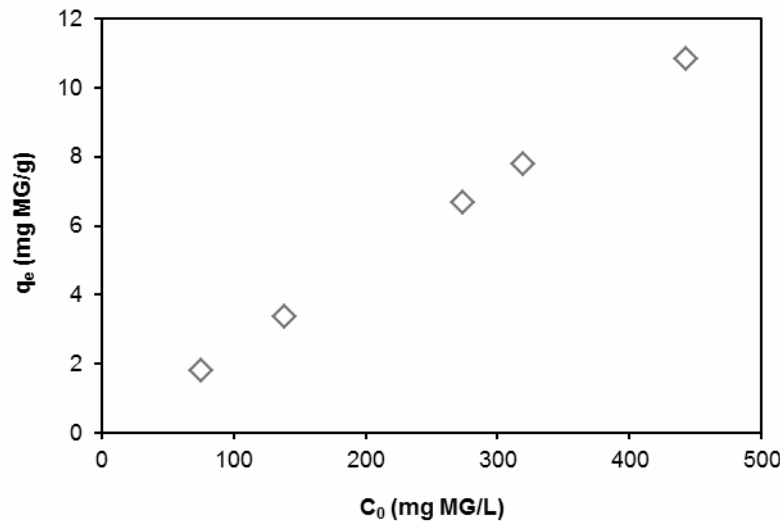


Fig. 1 – Influence of initial dye concentration over the amount of adsorbed MG (100 mL solution, 4 g WGT, 300 rpm, 22±2°C).

Table 1

Experimental data used to determine isotherm models parameters

C_0 (mg/L)	q_e (mg/g)	C_e (mg/L)
75	1.81	2.99
140	3.38	3.77
273	5.66	6.69
319	7.80	6.92
445	10.85	8.81

Table 2

Langmuir, Freundlich, Dubinin–Radushkevich and Temkin parameters models calculated using linear regression analysis for MG dye adsorption on WGT; $C_0 = 75\text{--}445$ mg/L, 300 rpm, room temperature

Langmuir			Freundlich		Dubinin–Radushkevich			Temkin			
K_L (L/mg)	q_{max} (mg/g)	R^2	n	K_F ($\text{mg}^{(1-1/n)}\text{L}^{1/n}/\text{g}$)	R^2	q_s (mg/g)	E (kJ/mol)	R^2	A_T (L/g)	B	R^2
0.0068	14.084	0.947	1.130	1.281	0.893	10.275	16.010	0.994	0.512	6.030	0.981

Freundlich isotherm

Freundlich isotherm is an empirical equation, which assumes that the adsorption process takes place on a heterogeneous surface.²⁴ These data often fit the empirical equation proposed by Freundlich, which has the following linear form:²⁴⁻²⁶

$$\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e \quad (4)$$

where, K_F is Freundlich isotherm constant ($\text{mg}^{(1-1/n)}\text{L}^{1/n}/\text{g}$), n is related to intensity of adsorption, C_e is the equilibrium concentration of adsorbate (mg/L), and q_e is the amount of MG per gram of the WGT at equilibrium (mg/g), Table 1.

K_F and n are parameters characteristic of the adsorbent-adsorbate system, which must be determined by data fitting using linear regression, which is generally used to determine the parameters of isotherm models.²⁷ Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate adsorption data where $1/n$ is a heterogeneity parameter, the smaller $1/n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between 1 and 10, this indicates a favourable adsorption process.^{28,29} From the data calculated for MG adsorption onto WGT,

$n = 1.130$ indicating that the adsorption process is favourable. The R^2 value is 0.893, Table 2.

Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is mostly applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface.^{30,31}

$$q_e = q_s \exp(-K_D \varepsilon^2) \quad (5)$$

$$\ln q_e = \ln q_s - K_D \varepsilon^2 \quad (6)$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), q_s is theoretical isotherm saturation capacity (mg/g), K_D is Dubinin–Radushkevich isotherm constant (mol^2/kJ^2), R is the gas constant (8.314 J/mol K), T is absolute temperature (K), C_e is adsorbate equilibrium concentration (mg/L).

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

Dubinin–Radushkevich isotherm is usually applied to distinguish between the physical and chemical adsorption. using the mean free energy value, E per molecule of adsorbate (<8 kJ/mol physical adsorption, 8-16 kJ/mol adsorption due to ion exchange, >16 kJ/mol chemical adsorption), which can be computed using the following relationship.^{20,32}

$$E = \frac{1}{\sqrt{2K_D}} \quad (8)$$

From the linear plot of Dubinin–Radushkevich model, Eq. (6), q_s was determined to be 30.04 mg/g and the mean free energy, $E = 16.01$ kJ/mol, indicating a chemical process ($R^2 = 0.994$), due to exchange of ions, Table 2.

Temkin isotherm

This isotherm contains a factor that explicitly takes into account the adsorbent–adsorbate interactions. Ignoring the extremely low and large value of concentrations, the model assumes that the heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The model is given by the following equation.³³⁻³⁵

$$q_e = B \ln A_T + B \ln C_e \quad (9)$$

$$B = \frac{RT}{b_T} \quad (10)$$

where A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant (J/mol), R is universal gas constant (8.314 J/mol K), T is absolute temperature (K), B is a constant related to heat of adsorption.

By plotting q_e against $\ln C_e$, the constants were determined from the slope and intercept, to be $A_T = 0.512$ L/g and $B = 6.03$, while R^2 value is 0.981, slightly lower than in case of Dubinin–Radushkevich, Table 2. Based on the linear regression correlation coefficient, R^2 , the obtained equilibrium data for MG-WGT system were better fitted on the Dubinin–Radushkevich model, Table 2.

Similar systems, malachite green on lemon peel²⁶, degreased coffee bean³², solar red and brittle blue on *Eucalyptus angophoroides* bark³⁶, brilliant green on NaOH treated sawdust³⁷ were investigated and presented in the literature. Our results are in good agreement with previously reported studies.

Adsorption kinetics

Several adsorption kinetic models, such as pseudo-first and pseudo-second-order, Elovich, intra-particle and film diffusion, were used to test the experimental data.

The pseudo-first and pseudo-second-order kinetic models

Pseudo-first and pseudo-second-order models can correlate the adsorbate up-take rate with the bulk concentration of the adsorbate. Usually linear regression is used to determine the best fitting kinetic rate equation (correlation coefficients, R^2).^{38,39}

Lagergren suggested a first-order equation for the adsorption of liquid/solid system based on solid capacity, which can be expressed in linear form as follows:³⁸

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (11)$$

where q_e and q_t are the amounts of adsorbate in the adsorbent (mg/g) at equilibrium and time t , respectively, t is time (min), k_1 is the rate constant of the first order adsorption (L/min).

The pseudo-second-order kinetic model is derived on the basis of the adsorption capacity of the solid phase.²² The linear form of the model is expressed as follows:^{39,40}

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

where q_e and q_t are the amounts adsorbed at equilibrium and time t , respectively (mg/g), t is time (min), k_2 is the rate constant of the second order adsorption (g/mg·min).

In order to determine the rate constant and equilibrium MG uptake, the straight line plots of $\ln(q_e - q_t)$ and t/q_t against t , were made using different initial MG concentrations. Correlation coefficients from 0.859 to 0.960 for pseudo-first-order and from 0.994 to 1.000 for pseudo-second-order model were obtained, Table 3 showing that MG adsorption on WGT can be classified as pseudo-second-order, fact confirmed by the literature results. Calculated values of q_e , Table 3, are very close to the experimental values, Table 1, confirming that MG adsorption on WGT follows the pseudo-second-order kinetic model.^{19,40}

Elovich kinetic model

The simplified Elovich equation^{41,42} is generally expressed as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (13)$$

where α is the initial adsorption rate (mg/g·min), and β is the desorption constant (g/mg).

Elovich plots of q_t versus $\ln(t)$ gives a linear relationship, with a slope of $(1/\beta)$ and intercept $(1/\beta)\ln(\alpha\beta)$. Calculated values of α , β and R^2 are presented in Table 3. The low values of the

correlation coefficients, between 0.895 and 0.917, suggest that this model is not suitable to describe the MG on WGT adsorption process.

Intra-particle and film diffusion model

In order to evaluate the contribution of diffusional processes during the MG adsorption onto WGT which is a porous material, intra-particle and film diffusion models were also considered.

The intra-particle diffusion model (Webber and Morris) can be written as follows.⁴³

$$q_t = k_{ip} \cdot t^{0.5} \quad (14)$$

where k_{ip} is the intra-particle diffusion rate constant (mg/g·min^{0.5}).

The film diffusion model (Boyd) is expressed as:⁴⁴

$$\ln(1 - F) = -k_{fd} \cdot t \quad (15)$$

where F is the fraction attainment at equilibrium ($F = q_t/q_e$), and k_{fd} is the liquid film diffusion rate constant (L/min).

If the obtained plots give straight lines passing through origin, internal or film diffusion is considered to be rate determining step.⁴⁵ Also from the slope of these plots, intra-particle and film diffusion rate constants can be determined, Table 4. Very small values of the intercept in the case of intra-particle diffusion model suggest that intra-particle diffusion could be a rate determining step towards the end of the adsorption process (molecules are diffusing through the pores towards the still available adsorption sites). Similar results were obtained in the case of MG adsorption on calcium alginate nanoparticles⁴⁶ or *Avena sativa* (oat) hull.⁴⁷

Table 3

Pseudo-first, pseudo-second-order and Elovich coefficients for MG adsorption on WGT;
C₀ = 75-445 mg/L, 300 rpm, room temperature

C ₀ (mg/L)	Pseudo-first order			Pseudo-second order			Elovich		
	k ₁ (1/min)	q _m (mg/g)	R ²	k ₂ ·10 ⁻² (g/mg·min)	q _{e calc} (mg/g)	R ²	α (mg/g·min)	β (g/mg)	R ²
75	0.023	0.627	0.859	18.72	1.832	0.994	0.343	3.122	0.895
140	0.025	1.346	0.860	9.13	3.424	0.999	1.207	1.665	0.898
273	0.027	3.106	0.920	2.56	6.86	0.999	2.366	0.844	0.899
319	0.030	4.909	0.960	2.40	7.88	0.991	3.81	0.687	0.900
445	0.033	7.844	0.906	2.36	11.03	1.000	4.87	0.494	0.917

Table 4

Intra-particle and film diffusion rate coefficients for MG adsorption on WGT;
 $C_0 = 75 - 445$ mg MG/L, 300 rpm, room temperature

C_0 (mg/L)	Intra-particle diffusion			Film diffusion		
	k_{ip} (mg/g·min ^{0.5})	Intercept	R ²	k_{fd} (1/min)	Intercept	R ²
75	0.533	0.001	0.989	0.023	1.06	0.859
140	1.866	0.004	0.999	0.025	0.921	0.908
273	3.673	0.014	0.997	0.027	0.867	0.920
319	4.293	0.041	0.998	0.030	0.463	0.960
445	6.011	0.087	0.999	0.033	0.323	0.906

EXPERIMENTAL

Materials

The adsorption process was realised using waste green tea (WGT), collected from a local coffee and tea house. The green tea residual leaves were repeatedly washed several times with distillate water until the filtered water was clear. The sample was then oven dried at 80°C for 48 h. Finally, the adsorbent sample was ground and sieved to obtain the particle size in the 200-400 µm range.

The dye stock solution (1000 mg/L) was obtained by dissolving the necessary quantity of solid substance, malachite green (MG), analytical purity reagent, in distilled water. Solutions with known concentration in 75-445 mg MG/L range were prepared from the stock solution.

Adsorption experiments

Adsorption process was conducted in batch conditions, in dynamic regime (300 rpm), through the contact of a certain amount of adsorbent (4 g) with a volume of 100 mL MG dye aqueous solution of various concentrations (75-445 mg mg/L). The adsorption process was conducted until equilibrium was reached (240 min established from preliminary experiments). Dye concentration in solution was determined using a Jenway 6305 UV-VIS spectrophotometer, at a wavelength of 618 nm, after a preliminary centrifugation (for 5 min at 10000 rpm) and appropriate dilution. Samples were collected at established time intervals.

All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

The MG amount adsorbed by WGT was calculated using the following equation:

$$q = \frac{(C_0 - C_t) \cdot V}{m \cdot 1000} \quad (16)$$

where C_0 is the initial MG concentration (mg/L), C_t is time t MG concentration (mg/L), V is the aqueous solution volume (mL), and m is the adsorbent quantity (g).

Experimental data were used to establish adsorption equilibrium and kinetic models which better describe the adsorption process.

CONCLUSIONS

The adsorption process of MG from aqueous solution using WGT has been investigated in batch

mode. The maximum experimental amount of MG adsorbed was calculated to be 10.85 mg/g for an initial concentration of 445 mg MG/L, while the maximum monolayer coverage capacity determined from Langmuir isotherm model was 14.08 mg/g. Between the four isotherm models considered, experimental data best fitted on the Dubinin–Radushkevich model. Also based on the results obtained from the isotherm models, the considered adsorption process was identified to take place as a chemical process. The adsorption experimental data follows pseudo-second-order reaction kinetics ($R^2 > 0.994$). Based on the obtained data it can be concluded that waste green tea biomass could be used as an effective adsorbent for malachite green removal from wastewaters.

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