

Removal of Methyl Green Dye from Aqueous Solutions Using Activated Carbon Derived from Cryogenic Crushed Waste Tires

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ABSTRACT: Activated carbon obtained from cryogenic crushing of used tire prepared and characterized previously was used as an adsorbent for the removal of cationic dye “methyl green dye MG” from an aqueous solution. Batch adsorption studies were carried out as a function of varying parameters of the system such as initial solution pH, adsorbent dosage, initial dye concentration, and temperature. The experimental data were fitted using Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models. The Langmuir isotherm model fitted well the obtained experimental data. The maximum adsorption capacity of methyl green dye at pH 7 was found to be 71.43 mg/g. The results of the kinetics study indicated that the experimental data are fitted to the Pseudo-first order model. The thermodynamic properties of ΔG , ΔH , and ΔS were estimated for the adsorption processes and indicated that the latter was exothermic, spontaneous, and favorable. The developed activated carbon might be used in a favorable manner for removing methyl green from an aqueous solution.

KEYWORDS: Activated carbon; Cryogenic grinding; Environment; Isotherms; Used tire.

INTRODUCTION

The extensive use of dyes and pigments for coloring products manufactured in many industries such as textiles, paper, cosmetics, food, printing, pharmaceutical, leather, and rubber causes serious pollution problems to human health and the environment [1]. Dyes are highly toxic and can be a source of several sicknesses such as cancer, mutation, allergic dermatitis, skin irritation, etc. [2-4]. Besides, dyes are known to be stable to photo-degradation,

bio-degradation, and oxidizing agents [5]. Their complex aromatic molecular structure makes them resistant and difficult to treat [6-8]. Furthermore, global government legislation has grown more stringent. Thus it becomes necessary to develop methods for the removal of dyes from the wastewater.

Various treatment processes including, membrane filtration [9], microbial degradations [10], electrochemical [11],

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coagulation and flocculation [12], chemical oxidation [13], Solar photo-Fenton degradation [14], Arc-discharge method [15], and adsorption [16] were used for removing dye from effluents. Among numerous separation techniques attempted for dye removal, the adsorption using activated carbon has proven its effectiveness in treating effluents. However, its use is limited due to the expensive costs of commercial carbons. The particular advantage offered by this versatile adsorbent is its ability to remove hazardous materials from water, air, and many chemical and natural products [17,18]. This is due to its high surface area, extensive porosity, chemical stability, and the presence of many different types of surface functional groups on its surface. A challenge in the field of adsorbents research is to produce efficient adsorbents with specific properties including highly developed porosity and internal surface area from low-cost, readily available, and renewable starting materials.

Over recent years, research has focused on the production of activated carbons from natural and synthetic waste materials. A variety of starting materials have been used as a precursor for the activated carbon preparation, including waste tire [19-22], polymers [23] Cassava peel [24], nutshells [25], etc. It has been demonstrated in several previous works that wastes can serve as economical and effective adsorbents for the removal of pollutants from effluents. On the other hand, the reuse of these waste materials contributes to reducing waste disposal costs, land clearing, and environmental protection. They, also, add value to these solid wastes and provide a cheaper alternative to commercial adsorbents produced from non-renewable sources.

In this study, activated carbon prepared from cryogrinded waste tires by the H_3PO_4 -chemical activation method is used as an inexpensive adsorbent for removing dye pollutants from water. The effect of some operating parameters, such as pH of the solution, initial concentration of methyl green, contact time, temperature, and the adsorbent dose was studied in a batch system. Kinetics and isotherm studies were investigated to evaluate the adsorption capacity of cryogrinded waste tire-activated carbon. For this purpose, pseudo-first-order kinetic, pseudo-second-order kinetic, and intraparticle diffusion models were attempted. Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherms were used to fit the equilibrium data.

EXPERIMENTAL SECTION

Modification and activation of used tire

Modification of used tires has been investigated by our group recently and was reported in detail in another publication [26]. Herein, we only provide brief information on the modification methods and the optimal conditions used.

Activated carbon used in the present study was synthesized from cryogrinded waste tires. Prior to the experiments, the waste tire was cut mechanically to obtain 2-3 cm piece size. Then, this material was ground cryogenically, using liquid nitrogen as a refrigerant. The obtained powder was sieved and the particles ranging between 0.5mm and 2mm were retained for activated carbon preparation. Activated carbon was prepared by the chemical activation method using phosphoric acid (H_3PO_4) (20%) as a dehydrating agent. The resulting chemical-loaded sample was then heated in a muffle furnace, to the carbonization temperature of 650°C under nitrogen flow at a heating rate of 15 °C/min and held at that temperature for 2 h. After cooling the carbonized product was washed with hot and cold distilled water until neutral pH then dried at 105 °C, and stored in a desiccator for subsequent use.

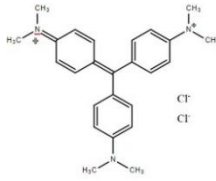
The activated carbon has particle sizes ranging between 100 and 160 μm . The surface area (S_{BET}), the total pore volume, and the average pore diameter of the prepared adsorbent, determined from the BET (Brunauer–Emmett, and Teller) methods, are 356 m^2/g , 0.49 cm^3/g , and 4.2 nm, respectively. The pH at the point of zero charges (pHpzc) is 5, which indicates that the majority of the functional groups at the adsorbent surface are acidic.

Adsorbate and chemicals

In order to evaluate the adsorption capacity of activated carbon obtained by cryogenic grinding used tires, Methyl green ($C_{26}H_{33}Cl_2N_3$) of technical grade, C.I. 42585 dye, obtained from Merck, was used without any additional purification. The physical and chemical properties of the dye are given in Table 1.

The solution was prepared by dissolving the required amount of dye in distilled water. The maximum absorption wavelength of the dye ($\lambda_{max}=633$ nm) was obtained by scanning an aqueous solution of the dye over the visible range. All other chemicals used in this study were of analytical grade.

Table 1: Chemical and physical properties of dye C.I. 42585 dye.

Usual name	C.I. 42585 dye
Molecular formula	$C_{26}H_{33}Cl_2N_3$
Molecular Structure	
IUPAC name	4-[[4-(dimethylamino) phenyl][4-(dimethylimino)- 2, 5-cyclohexadien-1-ylidene]methyl]-N-ethyl-N,N-dimethylbenzenaminium dichloride (methyl green);
Molecular Weight	458,47 g mol ⁻¹
Absorption Maxima (λ_{max})	633 nm
Nature dyes	C.I. 42585 dye is a triphenylmethane group of rosanilines. It derives from the hexamethylpararosaniline. It consists of three benzene rings with seven methyl groups linked by a carbon. It colors the silk.

Adsorption studies

To determine the equilibrium isotherm, adsorption tests at approximately $25^{\circ}\text{C} \pm 2$ were performed by adding a constant amount of adsorbent (0.25g) to a series of 100 mL Erlenmeyer flasks containing 50 mL of dye solution at a different initial concentration (10, 25, 50, 75, 100, 150, and 200 mg). The solutions were maintained at pH of 7 using HCl (1M) and NaOH (1 M) and a speed of 200 rpm were used in stirring the flasks for 3 h, to ensure that adsorption equilibrium was reached. After decantation and centrifugation, the residual concentration of Methyl green in the solution was measured at 633 nm using UV-visible spectrophotometer (Model SPECOR 200). A high-precision electronic balance (Kern ALS 220-4) with an accuracy of 0,00001 g was used for weighting the activated carbon and dye centrifugation was done by Hettich Zentrifugen universal 320. The amount of Methyl green dye at equilibrium q_e (mg/g) and percentage of elimination were calculated using the Equations (1) and (2), respectively:

$$q_e = \frac{(C_0 - C_e)}{m_{AC}} \quad (1)$$

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \quad (2)$$

Where:

C_0 : the initial dye concentrations in liquid phase (mg/L)

C_e : the equilibrium dye concentration in the liquid phase (mg/L),

V : the volume of the solution (L).

m_{AC} : the mass of the adsorbent used in the experiment (g).

RESULTS AND DISCUSSION

Effect of contact time

For the kinetic tests, 50 mL of dye solution of known concentration (100mg/L), pH =7, and amount of the adsorbent (0.25 g) were taken in a 100 mL Erlenmeyer flask. This mixture was agitated using a magnetic stirrer at a constant speed of 200 rpm. Liquid samples were collected at preset time intervals, filtrated, and analyzed for remaining dye concentration.

The quantity of dye-adsorbed q_t (mg/g) at time t was estimated using Eq. (1) by replacing C_e with C_t .

The effect of contact time for the removal of methyl green by the activated carbon is shown in Fig. 1.

The removal of dye increased with contact time. The methyl green was rapidly adsorbed before the first 60 min (approximately 40 mn), and then the adsorption proceeded at a slower rate before reaching equilibrium in about 1 hour. In the beginning, the methyl green ions were adsorbed by the external surface of the adsorbent and the adsorption was rapid. After saturation of the external surface, the methyl green ions entered the pores where they were absorbed by the internal surface of the particle [3, 27].

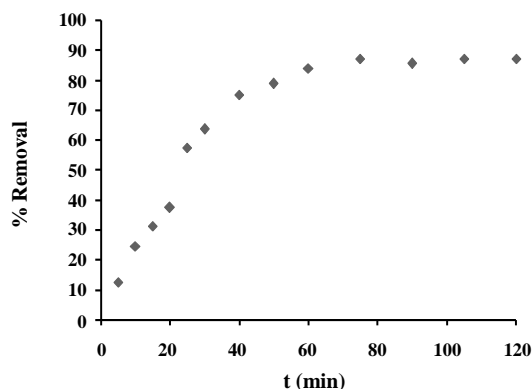


Fig. 1: Effect of contact time on the removal percentage of methyl green by the adsorbent ($T=25^{\circ}\text{C}$, $V = 50 \text{ mL}$; $\text{pH } 7$; $C_0 = 100 \text{ mg/L}$, stirring rate = 200 rpm; $m_{\text{AC}}=0.25\text{g}$).

This adsorption of methyl green by several adsorbents occurs with a relatively long contact time [28, 29]. Meanwhile, the contact time needed to reach the adsorption equilibrium of methyl green dye on activated carbon obtained from the used tire is approximately one hour. Similar results have been reported in the literature [3, 27, 30].

Effect of activated carbon dosage

Adsorbent dosage is an important parameter that can determine the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of the activated carbon dosage on dye removal was carried out by mixing 50 mL of methyl green solution with an initial dye concentration of 100 mg/L at ambient temperature ($25^{\circ}\text{C}\pm 2$) for 3 hours and pH of 7. Different quantities of activated carbon (0.05–0.3 g/50 mL of solution corresponding to 1–6 g per liter) for methyl green adsorption were investigated. Once the equilibrium was reached the samples were centrifuged and the solution was analyzed. The effect of activated carbon dosage on methyl green removal is illustrated in Fig. 2.

The results show that the percentage removal of methyl green increased with the activated carbon dosage up to a certain bound before reaching a constant value.

The maximum uptake (>96%) of methyl green was attained at an activated carbon dosage of 0.25 g per 50 mL of solution, corresponding to 5 g/L.

The increase in adsorption of methyl green onto the used tire-activated carbon is basically due to the existence of more active sites on the surface with increasing adsorbent dosage [31, 32].

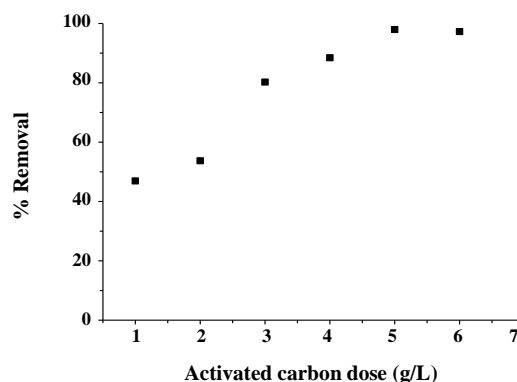


Fig. 2: Effect of activated carbon dosage on the percentage removal of methyl green ($T=25^{\circ}\text{C}$, $V = 50\text{mL}$, $\text{pH } 7$ $C_0 = 100 \text{ mg/L}$, stirring rate = 200 rpm; $t=3\text{h}$).

Effect of initial methyl green concentration

The effect of initial methyl green concentration on percentage removal of dye as well as the capacity of adsorption were studied. For this purpose, 0.25 g of adsorbent was added to 50 mL of dye solution, at different dye concentrations of 10, 25, 50, 75, 100, 150, and 200 mg/L. These experiments were carried out at pH 7. The equilibrium adsorption capacity increased with an increase in the initial dye concentration as shown in Fig. 3.a.

The effect of initial concentration on percentage removal of methyl green is shown in Fig.3.b. Dye removal strongly depends on concentration. The ratio of initial moles number of methyl green dye to the available adsorption sites is high for low concentrations, as opposed to high concentrations this ratio becomes lower. As concentration increases the number of active sites decreases and subsequently the percentage removal of dye decreases [33, 34].

Effect of pH

The effect of pH on the removal of dye by activated carbon was carried out with solutions containing 100 mg/L of the methyl green dye at a temperature of $25^{\circ}\text{C}\pm 2$. Adsorption tests were conducted by mixing 0.1 g of the adsorbent with a series of 50 mL of dye solution in a set of Erlenmeyer flasks. Each solution was taken at an indicated pH. The initial pH of the solution was adjusted to between 2 and 11. This was possible by adding either NaOH (1 M) or HCl (1 M). The pH of the solution was measured using a pH meter (model Hanna instruments pH 211).

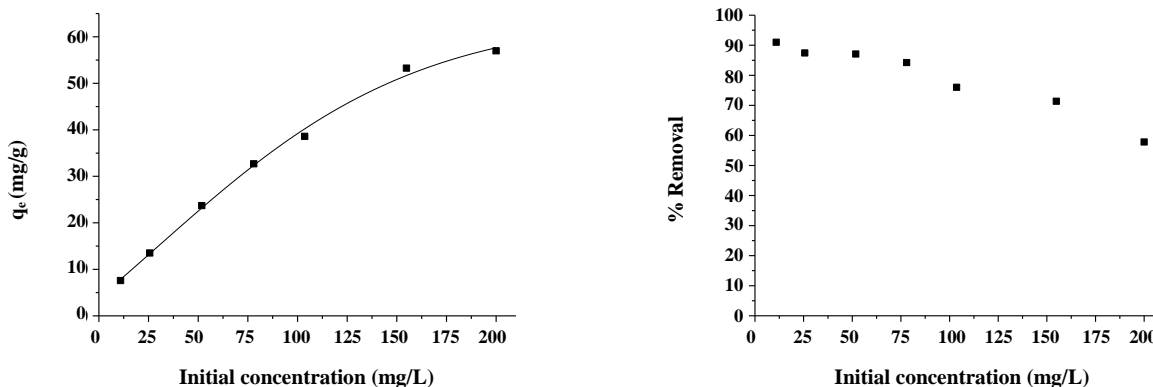


Fig. 3: Effect of initial concentration (a)-on methyl green adsorption capacity by activated carbon. (b)-on percentage removal of methyl green by activated carbon. ($T=25^{\circ}\text{C}$, $V = 50 \text{ mL}$; $\text{pH } 7$; stirring rate = 200 rpm; $m_{\text{AC}}=0.25\text{g}$).

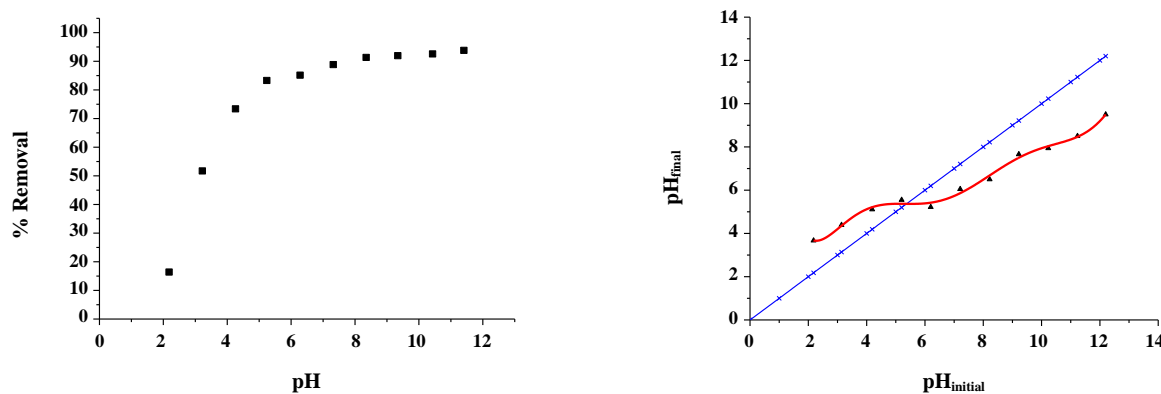


Fig. 4: Effect of pH (a)- on percentage removal of methyl green ($T=25^{\circ}\text{C}$, $V = 50 \text{ mL}$; $C_0 = 100 \text{ mg/L}$, stirring rate = 200 rpm; $m_{\text{AC}}=0.25\text{g}$), (b)- Variation of final pH against initial pH.

The suspension was stirred using magnet stir for 3 h at 200 rpm. The obtained solution was centrifuged and analyzed to determine the final concentration of the methyl green.

The effect of pH on the adsorption of methyl green dye by using tire-activated carbon is shown in Fig. 4a.

The results show that the adsorption of dye onto the adsorbent was significantly affected by solution pH. It was found that the amount of dye adsorbed increases from 18.2 to 92.76% with increasing pH from 2 to 11.

Note that the pH affected the behavior of C.I. 42585, mainly in basic medium ($\text{pH} = 11$ to 12), which was observed visually, a loss of color of the solution, thus turning transparent. Therefore, the study is limited to a pH range between $2 < \text{pH} < 11$. Similar results were found by S.Ponchami *et al* [35].

The point of zero charges (pH_{PZC}) of the developed activated carbon was measured to determine the total

surface charge. A dose of 0.25 g of the activated carbon was added to 50 mL of 0.01M NaCl solution in different flasks. The pH of each solution was adjusted to pH values of 2, 4, 6, 8, 10, and 12 by adding a few drops of HCl (0.1 mol/L) or NaOH (0.1 mol/L) solutions. Then, the mixtures were agitated for 24 h at a temperature of $25 \pm 2^{\circ}\text{C}$ and the final pH was measured. The value of the point at which the curve pH_{final} versus $\text{pH}_{\text{initial}}$ crosses the line $\text{pH}_{\text{initial}}$ equals to pH_{final} was taken as the pH_{PZC} (Fig. 4.b.). At a solution pH lower than pH_{PZC} , the total surface charge is positive, whereas at a solution pH higher than pH_{PZC} the total surface charge is negative.

Lower adsorption capacity at lower pH (acidic medium), is mainly due on one hand to the competition between H^+ cations present in excess in the solution and cationic molecules dye for the same adsorption site onto the surface of the activated carbon. On the other hand,

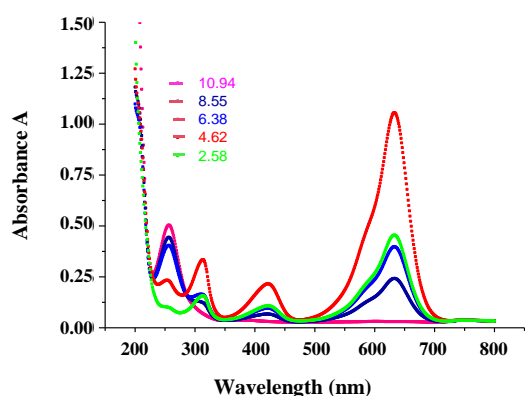


Fig. 5: Impact of pH on the absorption spectrum of the methyl green.

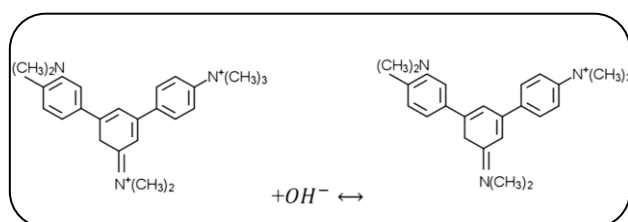


Fig. 6: Molecular structure of C.I. 42585 (Methyl Green) and the carbinol.

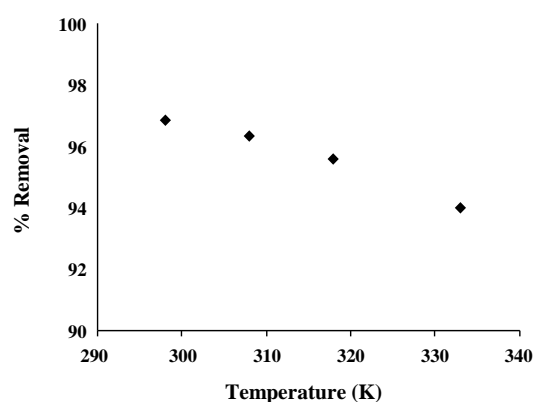


Fig. 7: Effect of temperature on methyl green dye removal ($V = 50 \text{ mL}$; $\text{pH} = 7$; $C_0 = 100 \text{ mg/L}$, stirring rate = 200 rpm; $m_{AC} = 0.25 \text{ g}$).

at pH below pH_{pzc} , the surface is positively charged resulting in the decrease of percentage removal due to repulsion electrostatic forces between dye protons and the positively charged surface. At higher pH, $\text{pH} > \text{pH}_{\text{pzc}}$, the surface of used tire-activated carbon is negatively charged, leading to an increase in percentage removal due to

attraction electrostatic forces between dye protons and negatively charged surface.

Therefore, the increase in pH had an influence on the group auxochrome, which is a saturated group linked to a chromophore that can change the wavelength and intensity of the absorption. Ex: OH, NH_2Cl , CH_3 ... Consequently, the pH had hypochromic effect (decrease of absorption intensity) on the methyl green (Fig.5).

Zollinger [36, 37] suggested that the effects could be explained by the relatively slow addition of OH^- to the Methyl green cation, forming a carbinol compound that should behave as a monovalent cation (Fig. 6), the reaction being:



Effect of temperature

The temperature effect on the methyl green adsorption process was carried at temperatures of 298, 308, 318, and 333K. For this purpose, 50 mL of dye solution at a concentration of 100 mg/L and pH 7 was mixed with 0.25 g of the adsorbent. The mixture was agitated for 3 h using a thermostatic water bath shaker. Then, the solution was centrifuged and analyzed to determine the residual concentration of methyl green dye.

As seen in Fig. 7, the adsorption ability of used tire activated carbon for methyl green dye decreased with increasing temperature indicating that the removal of methyl green dye onto used tire adsorbent is an exothermic process.

This can be explained by the weakening of the bonds between active sites of adsorbents and molecules of the green methyl dye at high temperatures.

Many authors have achieved similar results for the adsorption of dyes on various adsorbents [3, 38].

Modeling of adsorption isotherm

In order to optimize the design of the sorption process, the equilibrium adsorption isotherm was represented by plotting experimental results of methyl green adsorption onto used tire activated carbon using the four most commonly used models, namely, Langmuir, Freundlich, Temkin, and Dubinin-Raduschkevich.

The Langmuir isotherm model [39-43] assumes that the adsorption process takes place on a homogeneous surface with a finite number of identical sites.

The Langmuir equation is valid for monolayer adsorption and one of its linear forms is given in Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

Where

q_m is the maximum adsorption capacity (mg/g).

C_e is the equilibrium concentration of dye at the equilibrium time (mg/L)

K_L is the Langmuir constant (L/mg).

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant R_L , which is defined as:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (5)$$

The nature of the adsorption process is either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

C_0 : the initial dye concentrations in the liquid phase

The empirical equation of the Freundlich isotherm assumes the heterogeneous adsorbent surface with a non-uniform heat distribution of heat of sorption [39].

The Linear form of this isotherm can be expressed as follows.

$$\ln q_e = \ln K_F \frac{1}{n} + \ln C_e \quad (6)$$

Where K_F (L/mg) represents the capacity of adsorption, and n represents the intensity of the adsorption.

The Temkin isotherm is based on the assumption that the heat of adsorption of all molecules in the layer would decrease linearly with surface coverage [39]. This model takes into account indirect interactions between adsorbate molecules and is represented as

$$q_e = \beta \ln(A C_e) \quad (7)$$

And its linearized form is

$$\ln q_e = \beta \ln A + \beta \ln C_e \quad (8)$$

Where

$\beta = RT/b$ and b (J/mol) is the Temkin constant related to the heat of adsorption;

A (L/g) is the Temkin isotherm constant;

$R = 8.314$ J/mol.K is the universal gas constant.

T (K) is the absolute temperature.

The Dubinin–Radushkevich [44] isotherm is derived from the adsorption of vapors in micropore solids on energetically non-homogeneous surfaces. It determines if the adsorption process is chemical or physical.

It is represented in the following form (9):

$$q_e = q_t \exp(-K \varepsilon^2) \quad (9)$$

And its linearized form is

$$\ln q_e = \ln q_t - K \varepsilon^2 \quad (10)$$

Where q_t is the theoretical saturation capacity (mg/g), K is the Dubinin–Radushkevich constant (kJ^2/mol^2), and ε is the Polanyi potential.

The constant ε can be calculated from Eq. (11):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (11)$$

The slope of the plot of $\ln q_e$ versus ε^2 gives K (mol^2/kJ^2) and the intercept yields the adsorption capacity, q_m (mg/g). The mean free energy of adsorption (E), is defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the sorbent, was calculated from the K value using the following relation (Eq. (12)) [45]:

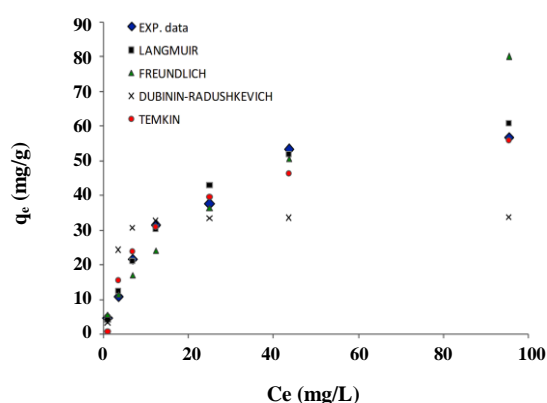
$$E = \frac{1}{\sqrt{2K}} \quad (12)$$

Fig. 8 shows the fit of the isotherm models previously defined to the experimental data for the adsorption of methyl green onto adsorbent issued from the cryogenic grinding of used tires. Parameters of the models employed in this study are summarized in Table 2. According to *Giles et al.* classification [46], the isotherms displayed an L curve pattern with a concavity toward the abscissa axis. This pattern indicates that the adsorption process occurs as monolayer adsorption on a homogeneous surface in a finite number of identical sites without interaction between solute molecules [47,48].

From Table 2, it was observed that the value of the correlation coefficient for the Langmuir isotherm equation ($R^2 = 0.992$) was higher than those of Freundlich, Dubinin–Radushkevich, and Temkin equations. These results

Table 2: Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich coefficients values for adsorption of methyl green at 25°C±2.

isotherm	Parameters		
Langmuir	KL	qm (mg/g)	R ²
	0.504	71.43	0.992
Freundlich	1/n	KF (Lmg ⁻¹)	R ²
	1.7	5.17	0.948
Temkin	kT (L/mg)	B	R ²
	1.03	12.16	0.953
Dubinin-Radushkevich	E(kJ)	qt (mg g ⁻¹)	R ²
	0.79	33.58	0.735

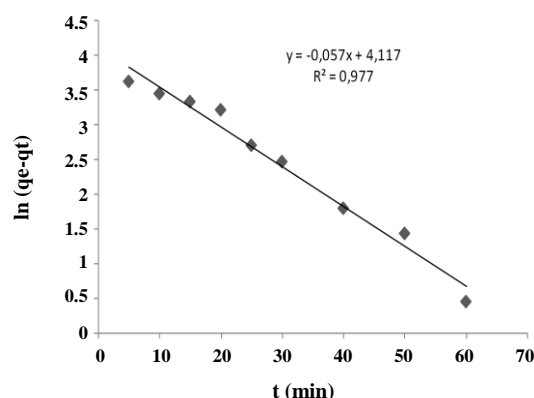
**Fig. 8: Fit of the adsorption isotherm: experimental data, Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich.**

indicate that the adsorption of methyl green on the prepared activated carbon follows the Langmuir isotherm and the corresponding parameters, maximum adsorption capacity (q_{max}) and K_L were found to be 71.43 mg/g and 0.504, respectively. The values of R_L estimated with the corresponding initial concentrations in the liquid phase C_0 are between 0 and 1, indicating that the adsorption process is favorable. The value of n derived from the Freundlich equation was greater than 1 confirming that the adsorption is favorable [49]. The free energy E , calculated from the Dubinin-Radushkevich isotherm model, was found to be 0.79 kJ/mol, indicating the adsorption process of methyl green dye onto used tire activated carbon is physical in nature [50].

Adsorption kinetics

Pseudo-first and pseudo-second-order equations

The data for the adsorption of methyl green on used tire-activated carbon were applied to two common models,

**Fig. 9: The pseudo-First-order kinetic model.**

specifically, the pseudo first and second-order kinetic models.

The applicability of the kinetic model is compared by judging the correlation coefficients, R^2 , and the agreement between the calculated ($q_{e,cal}$) and the experimental ($q_{e,exp}$) values.

Linear fitting of the plots of $\ln(q_e - q_t)$ against t and t/q_t against t was performed as shown in Fig.9 and Fig.10.

The obtained results obtained from the two kinetics models are illustrated in Table 3.

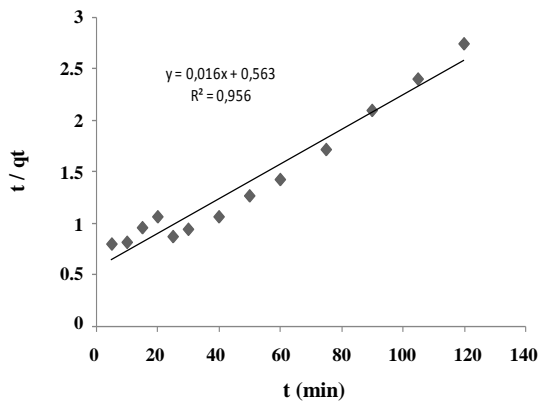
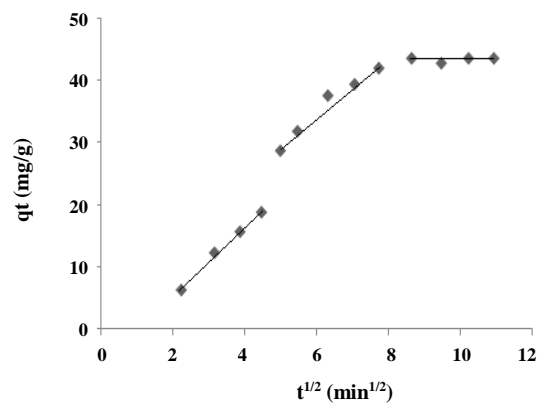
The correlation coefficient of the first order kinetic model (0.996) is greater than the second-order kinetic model (0.825) on one hand. On the other hand, $q_{e,cal}$ values, and $q_{e,exp}$ values are estimated for the pseudo-second-order are significantly different from each other. Meanwhile, these values are comparable to the pseudo-first-order kinetic model. In light of these considerations, we can conclude that the methyl green adsorption system is defined by the pseudo-first-order model. A similar kinetic result

Table 3: The results of the pseudo first and second order kinetic models.

	Pseudo-first order model		
	K_1 (min^{-1})	$q_{e,\text{cal}}$ (mg/g)	R^2
$q_{e,\text{exp}}$ (mg/g) 43.6	0.057	49	0.977
	Pseudo-second order model		
	K_2 (mg/gmin)	$q_{e,\text{cal}}$ (mg/g)	R^2
	0.00045	62.5	0.956

Table 4: The parameters obtained from the intraparticle diffusion model.

	Parameters	K_{id}	C	R^2
Intraparticle diffusion	Region 1	5.56	5.853	0.994
	Region 2	4.81	5.508	0.966

**Fig. 10: The pseudo-second-order kinetic model.****Fig. 11: Intraparticle diffusion model plot for the adsorption of methyl green on used tire activated carbon.**

has also been reported for the adsorption of methyl green onto graphene sheets [51].

Intra-particle diffusion model

According to this model, the plot of uptake should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate-controlling step [52].

The graph of q_t against $t^{1/2}$ reveals three regions (Fig. 11).

The first region was interpreted as the diffusion of methyl green molecules on the external surface of the activated carbon. The second region shows diffusion into pores (intraparticle diffusion) of the activated carbon

and finally, the third region (plateau) corresponds to the equilibrium stage in which the intraparticle diffusion starts to slow down. Constants calculated for both regions (first and second) are given in Table 4.

The K_{id1} values smaller than K_{id2} values set forth that the adsorption rate of intraparticle diffusion is established by the intraparticle diffusion step. A similar phenomenon has been observed in the adsorption of cationic dyes on various carbons [53;54]. However, since the curve does not pass through the origin, it was interpreted that the intraparticle diffusion model is not a rate-determining step and the adsorption rate is determined by both intraparticle diffusions as well as diffusion to the external surface step [55,56].

Thermodynamic study

Equilibrium data of methyl green adsorption onto cryogrinded used tire activated carbon at different temperatures were used to evaluate the feasibility and to estimate the thermodynamic parameters (ΔG , ΔH , and ΔS) of the adsorption process. The change in free energy (ΔG) of the reaction thermodynamics can be calculated by the following equation:

$$\Delta G = \Delta H - T \Delta S \quad (13)$$

The equilibrium constant, K_d , of the adsorption process (L/g) can be used to estimate the thermodynamic parameters. The changes in every parameter, the enthalpy (ΔH), and the entropy (ΔS) of this process were estimated by the following Equations (14)–(16):

$$K_d = \frac{q_e}{C_e} \quad (14)$$

$$\Delta G = -R T \ln K_d \quad (15)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{R T} \quad (16)$$

The results and the values of these thermodynamic parameters are illustrated in Table 5.

ΔH and ΔS were calculated from the slope and intercept of the Van't Hoff plots of $\ln K_d$ versus $1/T$ (Fig. 12).

The negative values of ΔG indicate the feasibility and spontaneous nature of methyl green adsorption onto used tire-activated carbon. The negative value of ΔH indicates the exothermic nature of methyl green adsorption. In addition, the value of ΔH is less than 40 kJ/mol, indicating the possibility of physical adsorption. The positive value of ΔS suggests that there was a good affinity of the adsorbent for the methyl green dye and there was an increase in the randomness at the solid/liquid interface.

CONCLUSIONS

In this study, a methyl green adsorption experiment on activated carbon prepared from cryogrinded tires was conducted by batch technique. The adsorption was found to be strongly dependent on pH and the maximum adsorption of Methyl green by activated carbon was reached at pH 7.

Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin equations were used to describe the adsorption of

Table 5: Thermodynamic parameters for the removal of methyl green onto activated carbon.

T (K)	ΔG (J/mol.K)	ΔH (kJ/mol)	ΔS (kJ/mol)
298	-22.41	-5.05	58.01
308	-22.93		
318	-23.50		
333	-24.36		

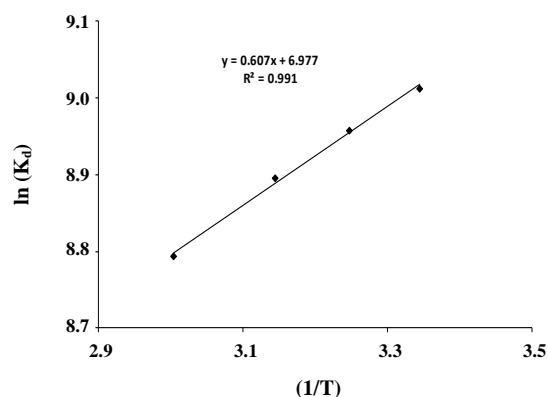


Fig. 12: Plots of $\ln(K_d)$ versus $1/T$ for methyl green adsorption on activated carbon.

Methyl green onto prepared activated carbon. The adsorption of Methyl green was best represented by the Langmuir model which indicated that the adsorption process occurs as monolayer adsorption on a homogeneous surface in a finite number of identical sites without interaction between solute molecules. The maximum adsorption capacity was found to be 71.43 mg/g by using a small amount (5g/L) of the adsorbent confirming the effectiveness of the activated carbon for the removal of methyl green from aqueous solution.

The mean free energy calculated by the Dubinin–Radushkevich equation (0.79 kJ/mol, physical in nature) indicated the possibility of regeneration and reuse of used tire-activated carbon.

Kinetic studies showed that the pseudo-first-order rate equation was able to provide a realistic description of the adsorption kinetic of Methyl green and thermodynamic parameters indicated that the process is exothermic ($\Delta H < 0$), spontaneous, and more favorable at low temperatures ($\Delta G < 0$). The positive value of entropy ΔS indicates that there was an increase in the randomness at the solid/liquid interface of the system. Besides, the value of enthalpy

change ($\Delta H < 40\text{Kj/mol}$), confirms the possibility of regeneration and reuse of used tire-activated carbon. On the basis of the results of this work, it can be concluded that waste tires can be effectively used as a substitute for the preparation of activated carbon and its use as an effective and promising adsorbent for the removal of methyl green from aqueous solution.

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