

Removal of Textile Dyes (Maxilon Blue, and Methyl Orange) by Date Stones Activated Carbon

Mohammed Bassim Alqaragully

Department of Chemistry
College of Sciences for Women
Babylon University-Hilla/ Iraq
mohammed7basim@yahoo.com

Abstract: *In this study, activated carbon was developed from Date stones (DSAC). The experiments were carried out to explore textile dyes (maxilon blue (GRL), and Methyl Orange (MO)) uptake by DSAC. The surface structure of date stones and date stones activated by HNO₃ were analyzed by FT-IR, and scanning electronic microscopy (SEM).*

The influence of various experimental factors such as initial dye concentration, adsorbent dosage, temperature and pH of dye solution were investigated. The increase in initial pH in the ranges of 2-10 decrease the yields removal of methyl orange dye (MO) while increases of maxilon blue dye GRL on DSAC. The adsorption equilibrium was represented with Langmuir, Freundlich, and Tempkin isotherm models. The Temkin equation was found to have the correlation coefficient value in very good agreement of MO, while Freundlich equation was found to give a good coereletion of GRL dye. Adsorption process was spontaneous and exothermic in nature of MO dye, while endothermic in nature of GRL dye.

Keywords: *Activated carbon; Adsorption; Isotherm; Kinetics; Thermodynamics*

1. INTRODUCTION

Water pollution is one of the most undesirable environmental problems in the world and it requires solutions. Textile industries produce a lot of wastewater, which contains a number of contaminants, including acidic or caustic dissolved solids, toxic compounds, and any different dyes, Many of the organic dyes are hazardous and may affect aquatic life causing various diseases and disorders.[1]

Synthetic dyes are extensively used in various branches of the textile industry, paper printing, color photography, pharmaceutical, leather, cosmetics, plastic, and other industries. The discharges of industrial wastewater containing dyes cause a real environmental problems because of its high toxicity and possible accumulation in the environment[2, 3]. Synthetic dyes are a group of most dangerous pollutants in water. [4-6] The presence of even very low concentrations of dyes in water reduces light penetration through the water surface, precluding photosynthesis of the aqueous flora.[7]

Many of these dyes are carcinogenic, mutagenic, and teratogenic and also toxic to human beings, fish species, and microorganisms. Hence, their removal from aquatic wastewater becomes environmentally important.[8] A great variety of synthetic dyes are produced on a daily basis in dyestuff, textile, leather, paper and food industries[9]. Some natural biomaterials including agricultural products and other by-products with low costs have been explored as new sources in recent years. Thus, dye removal by agricultural by-products and other low cost sorbents has also been intensively investigated. Materials deriving from agricultural by-products can be useful to convert unwanted, surplus agricultural waste, of which billions of kilograms are produced annually, into a useful adsorbent, a value-added advantage[1]. Many specific examples are found where disposal of agricultural by-products has become a major, costly waste disposal problem[10].

Currently, there are several treatment technologies used in the removal of dyes from waste effluents such as electrochemical treatment, coagulation, precipitation, solvent extraction, membrane filtration and advanced oxidation process[10]. Activated carbon, a widely used adsorbent in industrial processes, is composed of a microporous, homogenous structure with high

surface area and shows radiation stability[11]. Its wide application is limited due to its high cost and difficulty to regenerate[12]. Thus, research on the production of activated carbon from a renewable, low-cost indigenous agricultural waste has gained attention worldwide because of its low cost and highly abundant characteristics[13, 14]. Some of the agricultural wastes that have been studied as a possible source of activated carbon are wood[15], bagasse[16], coir pith[17], orange peel[18], coffee husk[19], pine cone[20], Date tree[21], sunflower seed hull[22], pine-fruit stones[23], hazelnut husks[24], rice hulls[25], oil palm stones[12], and Date husk[26].

This present article presents new data and the process of removal a real textile dyes has been optimized for various reaction parameters. Equilibrium of the removal of adsorption of textile dyes (GRL, and MO) onto date stones activated carbon (DSAC) have been carried out in the present work. Thermodynamic studies have also been performed to understand the processes of removal of the selected dye on DSAC.

2. EXPERIMENTAL

2.1. Materials and Methods

The Maxilon Blue (GRL), and Methyl Orange (MO) dyes were provided by Al-Hilla of textile industries/Iraq. The respective chemical structures are shown in (Fig. 1). All the dyes were chemical products of analytical grade and were used without further purification.

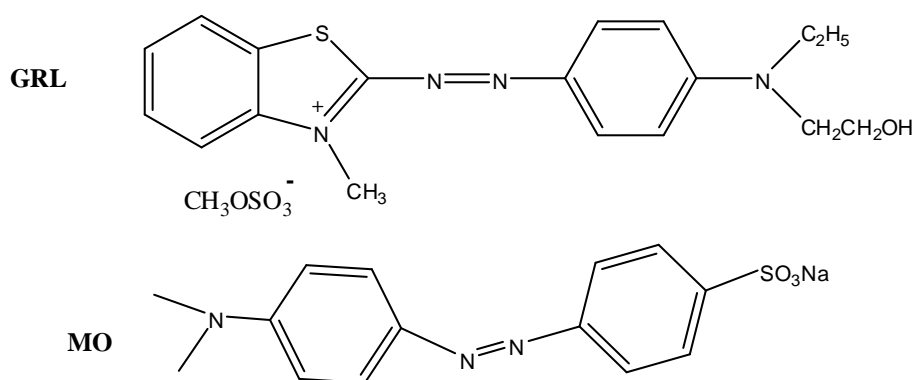


Fig. 1. Chemical structures of maxilon blue (GRL), and Methyl Orange (MO) dyes

A stock solution of 1000 mg/L was prepared by dissolving (1 gm) as an appropriate quantity of textile dye (GRL, or MO) in (1 L) double distilled water. Working solutions of desired concentrations were prepared by successive dilution.

2.2. Preparation of Activated Carbon (DSAC)

The Date stones was a collected from the food manufacturing industries in a local market of Al-Hilla/Iraq was the precursor used in the present study. The collected sample was crushed very well, then washed exhaustively with deionized water to remove adhering dirt particles from the surface, then dried by oven (70 °C) for 24 h. 50 g dried sample was put in a container and 100 ml concentrated HNO_3 was added as impregnating reagent, then kept for 24 h. After the acid was leached out the sample was washed with distilled water till neutral pH. For complete formation as cabanas material, it was performed by loading 25 g of the dried precursor into a muffle furnace for 2 h at 400 °C. The activated product was then washed with deionized water until the pH of the washing solution reached 6–7, then dried at 80 °C, for 24 h, crushed and sieved for experimental work.

2.3. Characterization of DSAC

Chemical functional groups were examined by FT-IR using KBr pellet method at room temperature. The spectra were retrieved in the wave number range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} by an infrared spectrometer type (FTIR-2000, PerkinElmer). The morphological features of the samples were studied by electron micrographs using SEM provided by the Department of materials, Tahrn University/ Iran. The powder samples were placed on carbon tapes, and then coated with a thin layer of gold -palladium in an argon atmosphere using

2.4. Adsorption equilibrium studies

DSAC samples were sieved to obtain average particle size 75 μm . 50 mg of DSAC was added to 100 ml solution of textile dyes (GRL or MO) in water placed in 250 ml capped conical flask. The initial concentration of dyes (C_0) was 10 ppm. The sample was kept in a shaker at room temperature (30 ± 1 °C) throughout the experiment, at pH 6. All experiments were performed at 120 rpm. The change of dye concentration with time was followed by withdrawing 2 ml samples at a predetermined time. The supernatant was centrifuged for two times, to confirm there is no fine particle in the a liquote. The concentration of GRL, and MO were determined at $\lambda = 599$ nm, and at $\lambda = 463$ nm respectively by using UV/VIS spectrophotometer, which was previously calibrated. The amount adsorbed was estimated by the difference between the initial concentration in aqueous solution and that found in the supernatant. The amount of dye-adsorbed $q_e(\text{mg g}^{-1})$ was determined by:

$$q_e = \frac{(C_0 - C_e) * V}{w} \quad (1)$$

The removal of percentage was determined by:

$$E\% = \frac{(C_0 - C_e)}{C_0} * 100 \quad (2)$$

where C_0 and C_e are the initial and final dye concentrations at equilibrium in the aqueous phase (mg dm^{-3}), respectively, V is the volume of dye solution (L) and W is the mass of adsorbent DSAC (gm).

2.5. Effect of Different Parameters on Adsorption Process

2.5.1. Effect of solution pH

The effect of solution pH was studied by agitating 50 mg of DSAC and 100 mL of (MO or GRL) dye concentration (10) mg/L using water-bath shaker at 30 °C.

The experiment was conducted at different pH from 2 to 10. Agitation was provided for 60 min contact time at a constant agitation speed of 120 rpm. The pH was adjusted by adding a few drops of diluted 0.5 N NaOH or 0.5 N HCl and measured by using a pH meter.

2.5.2. Effect of mass dosage

The effect of mass dosage was studied by agitating of different masses (0.01, 0.05, 0.1, 0.15, and 0.2) g , particle size 75 μm of DSAC and 100 mL of (MO or GRL) dye concentration (10 mg.L-1) using shaker water-bath at 30 °C. The experiment was conducted at pH 6. Agitation was provided for 60 min contact time at a constant agitation speed of 120 rpm.

2.5.3. Effect of solution temperature

The effect of solution temperature was studied by agitating of varients solution temperatures (10, 30, and 50 oC) , mass dosage 50 mg of DSAC and 100 mL of (MO or GRL) dye concentration (10 mg.L-1) using water-bath shaker at 30 °C. The experiment was conducted at pH 6. Agitation was provided for 60 min contact time at a constant agitation speed of 120 rpm.

3. RESULTS AND DISCUSSION

3.1. Surface Characterizations

In order to detect the functionality present in DSAC prior to and after (GRL, and MO) dyes adsorbed, Fourier transform infrared spectrometer, the range 4000–400 cm^{-1} .

Adsorption in the infrared (IR) region takes place due to the rotational and vibrational movement of the molecular groups and chemical bond of a molecule.

The FT-IR spectra were obtained to evaluate qualitatively the chemical structures of DSAC. (Fig. not shown) shows the FT-IR spectrum of DSAC, which indicated various surface functional

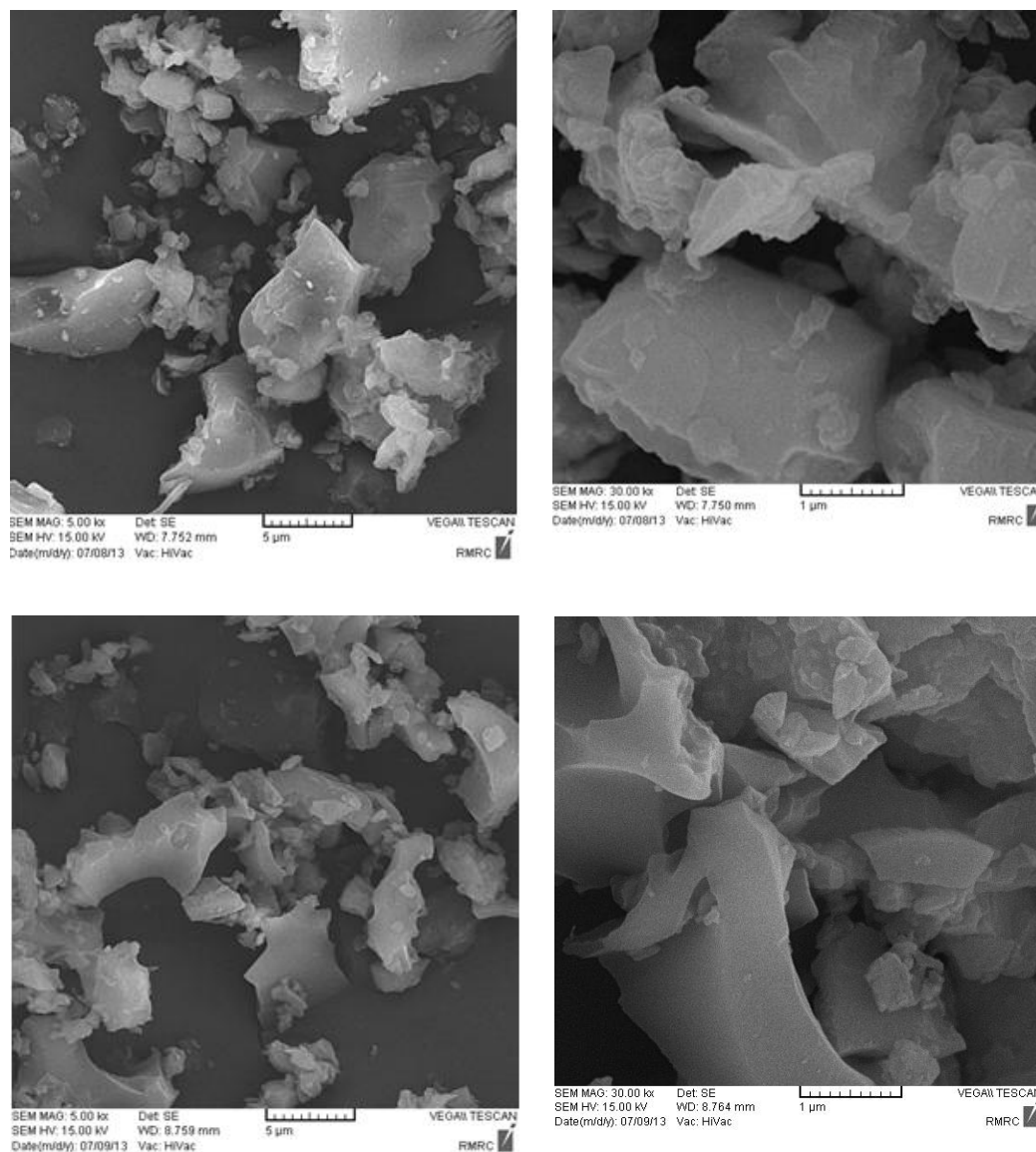


Fig. 2: SEM image of a) DSAC derived from Date stones surface, b) DSAC derived from activated Date stones surface by HNO₃.

groups. The broadband at around 3500 cm⁻¹ is typically attributed to hydroxyl groups. The region of the spectrum of 2220 cm⁻¹ is attributed to

groups. The broadband at around 3500 cm⁻¹ is typically attributed to hydroxyl groups. The region of the spectrum of 2220 cm⁻¹ is attributed to alkyne group (C ≡ C)The region of the spectrum of 1612 cm⁻¹ is attributed to axial deformation of carbonyl groups (C=O)[27]. The presence of hydroxyl groups, carbonyl group, ethers and aromatic compounds is an evidence of the lignocellulosic structure of Date stones as also observed in other materials such as Tunisian olive-waste cakes[28] , Brazilian Date stones[27], and jackfruit peel waste[29], result shows there is no real shift in our absorption peaks but the intensity become higher after absorption, this is indicated as a physical adsorption.

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. SEM of adsorbent material were taken before and after treated on Date stones surfaces (Fig.2). The SEM pictures of adsorbed samples show very distinguished dark spots which can be taken as a sign for effective acid treatment.

groups. The broadband at around 3500 cm^{-1} is typically attributed to hydroxyl groups. The region of the spectrum of 2220 cm^{-1} is attributed to alkyne group ($\text{C} \equiv \text{C}$) The region of the spectrum of 1612 cm^{-1} is attributed to axial deformation of carbonyl groups ($\text{C}=\text{O}$)[27]. The presence of hydroxyl groups, carbonyl group, ethers and aromatic compounds is an evidence of the lignocellulosic structure of Date stones as also observed in other materials such as Tunisian olive-waste cakes[28], Brazilian Date stones[27], and jackfruit peel waste[29], result shows there is no real shift in our absorption peaks but the intensity become higher after absorption, this is indicated as a physical adsorption Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. SEM of adsorbent material were taken before and after treated on Date stones surfaces (Fig.2). The SEM pictures of adsorbed samples show very distinguished dark spots which can be taken as a sign for effective acid treatment.

3.2. Effect of Different Parameters of Adsorption Processes

3.2.1 Effect of pH

The pH of an initial dye solution exerts profound influence on the adsorptive uptake of adsorbate molecules, presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule[30], the changes in the structural and color stabilities as well as the degree of ionization for such adsorbate is also dependent on the pH of the solution [31]. The effect of pH on the adsorption of maxilon blue GRL and Methyl Orange MO dyes onto Date surface was studied at a pH range of (2, 4, 6, and 10) in the presence of different initial dye concentrations ($2\text{-}16\text{ mg.L}^{-1}$), results are shown in (Fig. 3).

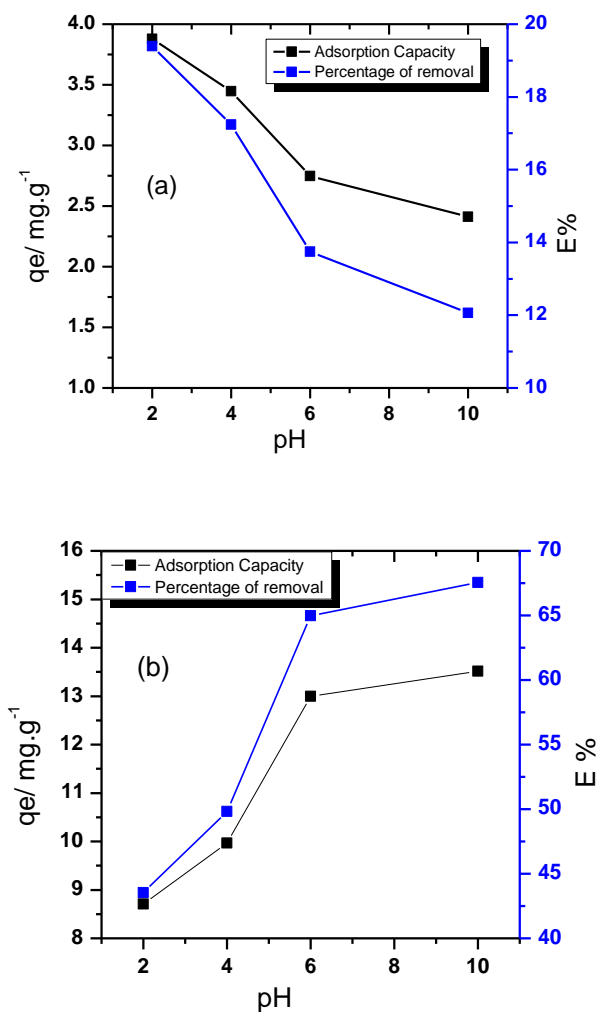


Fig. 3: Effect of solution pH on adsorption a) MO, and b) GRL: experimental conditions: Temp. 293 K, DSAC dosage 50 mg.L^{-1} , dye conc. 10 ppm , and particle size $75\text{ }\mu\text{m}$.

As shown in (Fig. 3), the dye uptake was found to decrease with an increase in pH solution of MO, while in verse versa occurs with GRL dye solution. At lower pH, the surface charge may be positively charged which enhance the adsorption process[18]. Lower adsorption of MO and GRL, at alkaline pH is provable due to the presence of excess of OH⁻ ions competing with the dye anions for the adsorption sites. At the acidic pH, the number of positively charged sites increase, which favors the adsorption of the anions due to electrostatic attraction. Moreover, the decrease in the adsorption of MO, and GRL with an increase of pH value is also due to the competition between anionic dye and excess OH⁻ ions in the solution, which may be due to the fact that the high concentration and high mobility OH⁻ ions are preferentially adsorbed compared to dye anions[18]. While increase in adsorption capacity of GRL dye with increased of pH of solution caused by attractive forces of dye and adsorbent surface.

3.2.2 Effect of Adsorbent Dose

The effect of the amount of the adsorbents was necessary in order to observe the minimum possible amount, which shows the maximum adsorption stoichiometric. The amounts of the adsorbent were varied from 0.005 to 0.200 g/100 ml of Date stones. The results are shown in (Fig. 4).

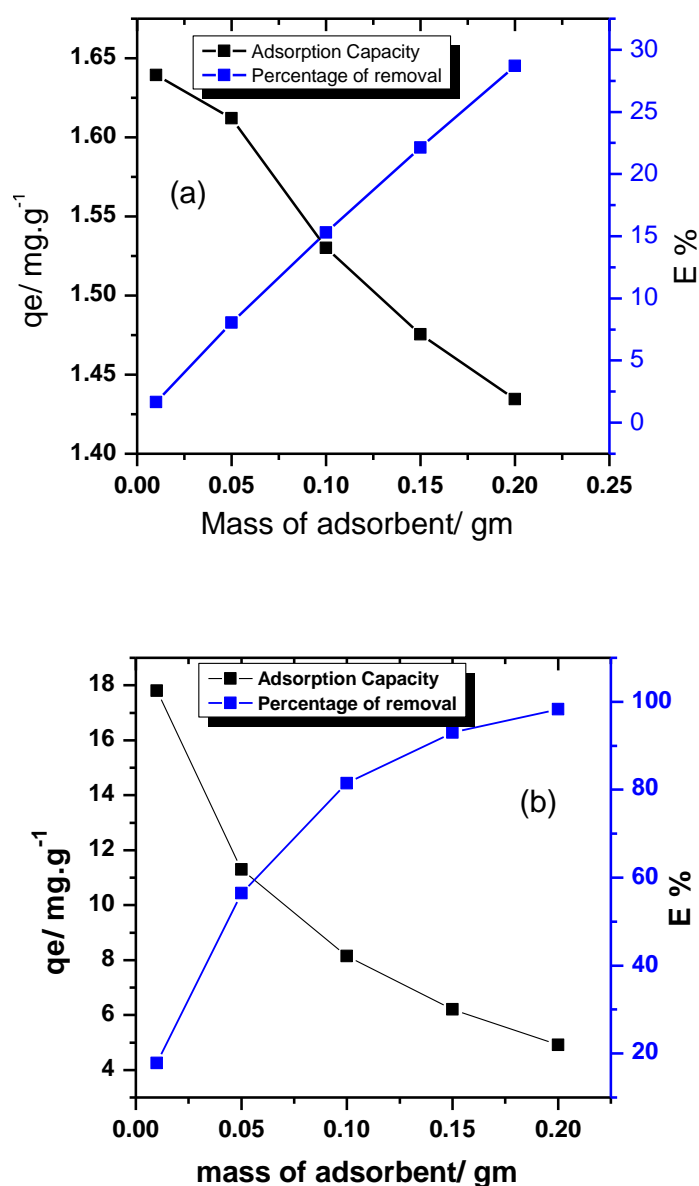


Fig. 4: Effect of mass adsorbent on adsorption a) MO, and b) GRL: experimental conditions: Temp. 303 K, pH 6, dye conc. 10 ppm, and particle size 75 μ m.

It is clear from (Fig. 4), an increase in the percentage of the dye removal with adsorbent mass was related to increases in the adsorbent surface areas, enhancing the number of adsorption sites available for adsorption as reported already in other cases. [32, 33] The increase in the removal of dyes with adsorbent dose due to the introduction of more binding sites for adsorption. The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose [34, 35].

3.2.3 Effect of temperature

To determine whether the ongoing adsorption process was endothermic or exothermic in nature. The adsorption isotherms were determined for various dye-adsorbent systems. The removal of maxilon blue GRL and Methyl Orange MO has been studied at a temperature of (288, 298, and 313 K).

Temperature has a pronounced effect on the adsorption process from the change in temperature will cause changes in the equilibrium capacity of the adsorbent for adsorption of particular adsorbate. The uptake of dye decrease with the increase in temperature, indicating the exothermic nature of the adsorption reaction, while increases temperature indicated the endothermic nature of adsorption reaction. It was explained that as the temperature increased, the physical bonding between the organic compounds (including dyes) and the active sites of the adsorbent weakened. Besides, a decrease in the degree of freedom of adsorbed species and a decrease in available adsorption active sites.[12]

3.2.4 Thermodynamic Study

The Thermodynamic Parameters, Including The Free Energy Changes (ΔG^0), Standard Enthalpy Changes (ΔH^0) And The Entropy Changes (ΔS^0) Associated With The Adsorption Process, Can Be Used To Deduce The Adsorption Mechanism. They Can Be Calculated By The Dependence Of Thermodynamic Equilibrium Constant (K_e) On Temperatures[36]:

$$\Delta G^0 = -RT \ln K_e \quad (3)$$

$$\ln K_0 = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (4)$$

The thermodynamic equilibrium constant (K_e) for the adsorption of (MO and GRL) on DSAC can be calculated, Eqn.[37]:

$$K_e = \frac{q_e}{c_e} \quad (5)$$

The calculated values of K_0 and the correlation coefficients are listed in Table 1.

According to Eqn. (5), the values of ΔG^0 were calculated and listed in Table 1. The values of ΔG^0 of (dye/DSAC adsorption systems) are all negative, which indicates the spontaneous adsorption processes. Moreover, the increase in the absolute value of ΔG^0 with increasing temperature indicates that higher temperatures facilitated the adsorption.

The value of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the van't Hoff plot (Eqn. (4)) of $\ln K_e$ against $1/T$, respectively, and the results are shown in Fig. (5) and listed in Table 1. The negative value of ΔH^0 indicates that the adsorption process is exothermic, while the positive value give an indication of endothermic processes.

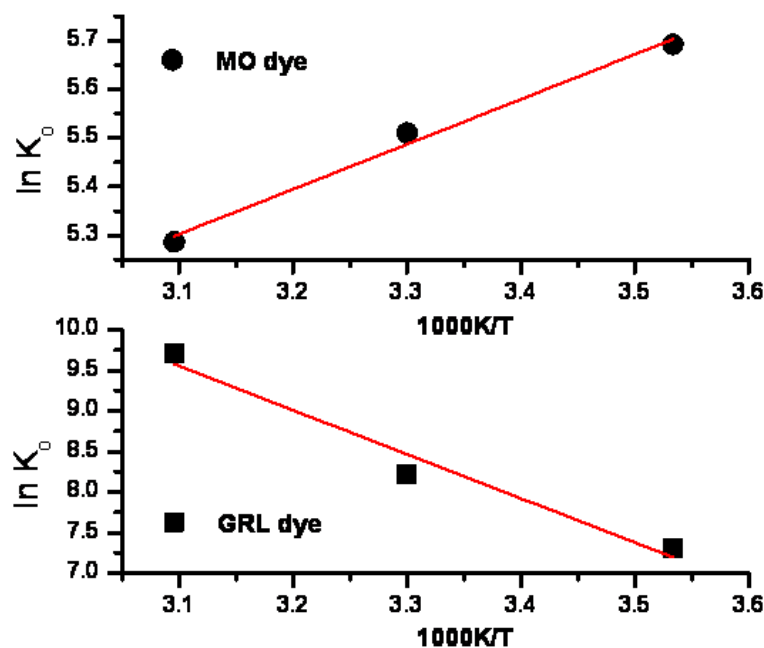


Fig. 5. Effect of temperature on adsorption a) MO, and b) GRL: experimental conditions: particle size 75 μm , DSAC dosage 50 mg.L^{-1} , dye conc. 10 ppm, and pH 6.

Table 1. Thermodynamic functions ΔG , ΔS and, ΔH of GRL and MO adsorbed on the DSAC.

DSAC adsorbent/ GRL adsorbate				
T/K	K_e	$\Delta G^\circ/\text{kJ.mol}^{-1}$	$\Delta H^\circ/\text{kJ.mol}^{-1}$	$\Delta S^\circ/\text{J.K}^{-1}.\text{mol}^{-1}$
283	1495.017	-17.1992	45.2043	219.03
303	3695.906	-20.6947		
323	16407.41	-26.0633		
DSAC adsorbent/ MO adsorbate				
T/K	K_e	$\Delta G^\circ/\text{kJ.mol}^{-1}$	$\Delta H^\circ/\text{kJ.mol}^{-1}$	$\Delta S^\circ/\text{J.K}^{-1}.\text{mol}^{-1}$
283	296.53	-13.3928	-7.6834	19.95927
303	247.191	-13.8809		
323	197.6048	-14.1959		

3.3. Models of Adsorption Isotherms

In order to analyze the characteristics of the adsorption isotherms, several models including Langmuir [38] Freundlich [39], and Tempkin[40] have been used to analyze the equilibrium adsorption data.

The non-linearized form of Langmuir isotherm model can be described as the following equation.

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

where K_L (L/mg) is the Langmuir adsorption constant related to the energy of adsorption, q_{max} and q_e (mg/g) are the maximum and equilibrium adsorption capacity, respectively.

The non-linearized form of Freundlich isotherm model is given as the following equation:

$$q_e = K_f C_e^{1/n} \tag{7}$$

while K_F (L/mg) is the Freundlich constant, and $1/n$ is the heterogeneity factor.

K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; if the value is above unity adsorption is a favorable physical process.[41]

The non-linearized form of Tempkin isotherm is represented by Eqn (8):

$$q_e = \frac{RT}{b} \log(K_T C_e) \tag{8}$$

Where b Tempkin constant related to the heat of adsorption(kJ/mol), R : Gas constant (8.314 J/mol.K), T : Temperature (K), and K_T : Emprical Tempkin constant related to the equilibrium binding constant related to the maximum binding energy (L/mg), (L/mol)

The Tempkin isotherm takes into account the effects of the interaction of the adsorbate and the adsorbing species. By ignoring the extremely low and large concentration values, the model assumes that the heat of adsorption (a function of temperature) of all of the molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbate-adsorbent interactions[42]. By comparing the three models, it seems that the model of Temkin is the most adapted for the fitting of adsorption isotherms, then Langmuir model more adapted than Fruendlich models. Results are shown in (Fig. 6), the calculated parameters of three models are illustrated in Table 2.

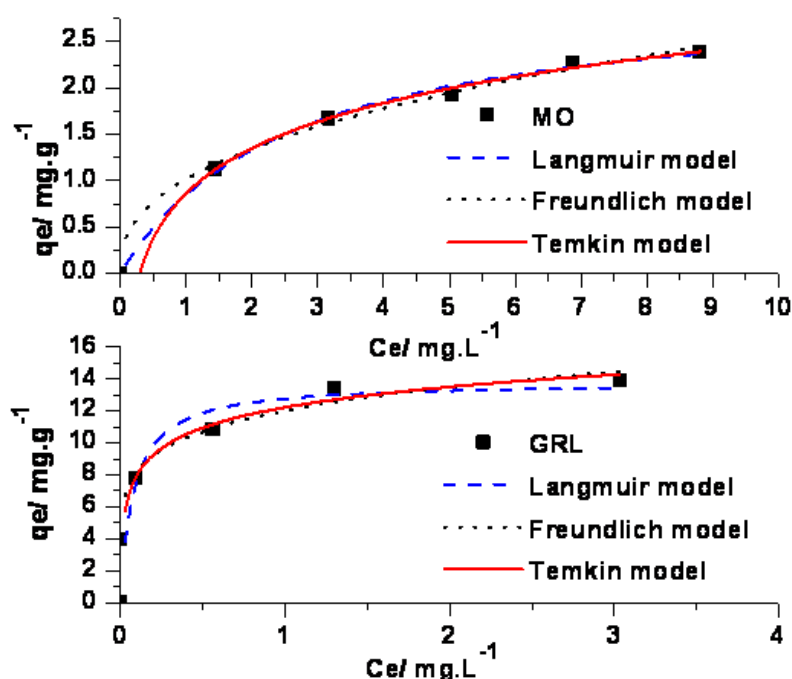


Fig. 6: Adsorption isotherm models fitted to experimental adsorption of a) MO, and b) GRL (pH 6, Temp. 303, particle size 75 μ m, mass dosage 0.05 gm/100 ml):

Table 2. Parameters for different parameters isotherms models for the adsorption of GRL, and MO dye onto DSAC at different temperatures.

<i>Isotherm models</i>	<i>Parameters</i>	<i>MO</i>	<i>GRL</i>
Langmuir	q_m (mg.g ⁻¹)	3.07066±0.1411	13.80816±0.76485
	K_L (L.mg ⁻¹)	0.38281±0.051	12.42688±4.20335
	R^2	0.98379	0.87417
Freundlich	K_F	1.01962±0.05396	12.02202±0.37472
	1/n	0.40137±0.02953	0.1665±0.02813
	R^2	0.98324	0.93195
Tempkin	b/J.mole ⁻¹	3.42644±0.41184	15.4451±2.234
	K_T	0.70164±0.03055	1.85434±0.79242
	R^2	0.99758	0.86288

4. CONCLUSIONS

Date stones as an alternative adsorbent surface for removal of textile dyes (GRL, and MO) in this study. The shifting of peaks in FTIR spectrum confirmed the GRL and MO dyes adsorption onto DSAC. The SEM study also made support to it by observing difference in surface morphology of adsorbent before and after activated by HNO₃. Adsorption isotherms of these dyes on DSAC were studied and modeled using three isotherm models with more than two-parameter. The classification of the models according to the simulation of the adsorption isotherms is: Tempkin >Langmuir> Freundlich. Thermodynamic study demonstrates the spontaneous and exothermic nature of adsorption process due to negative values of both free energy change and enthalpy change.

REFERENCES

- [1] Vieira AP, Santana, S. A., Bezerra, C. B., Silva, H. S., Chaves, J. P., de-Melo, J. P., da-Silva F., Edson C., Airoidi, C., Kinetics and thermodynamics of textile dye adsorption from aqueous solutions using babassu coconut mesocarp, *Journal of Hazardous Materials*. 166 (2009) 1272-1278.
- [2] Hassan AF, Abdel-Mohsen AM, Fouda MMG, Comparative study of calcium alginate, activated carbon, and their composite beads on methylene blue adsorption, *Carbohydrate Polymers*. 102 (2014) 192-198.
- [3] Hajati S, Ghaedi M, Karimi F, Barazesh B, Sahraei R, D, A., Competitive adsorption of Direct Yellow 12 and Reactive Orange 12 on ZnS:Mn nanoparticles loaded on activated carbon as novel adsorbent, *J Ind Eng Chem*. 20 (2014) 564–571.
- [4] Forgacs E, Cserhati T, O, G. , Removal of synthetic dyes from wastewaters: a review, *Environ Int* 30 (2004) 953-971.
- [5] Robinson T, McMullan, G., Marchant, R., Nigam, P., Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresource Technology*. 77 (2001) 247-255.
- [6] Nakagawa K, Namba A, Mukai SR, Tamon H, Ariyadejwanich P, T, W., Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes, *Water Research*. 38 (2004) 1791-1798.
- [7] Hanafiah MM, Ngah WW, Zolkafly SH, Teong LC, M, Z. A., Acid Blue 25 adsorption on base treated Shorea dasyphylla sawdust: Kinetic, isotherm, thermodynamic and spectroscopic analysis, *Journal of Environmental Sciences*. 24 (2012) 261-268.

- [8] Konicki W, Sibera D, Mijowska E, Lendzion-Bielun Z, N, U., Equilibrium and kinetic studies on acid dye Acid Red 88 adsorption by magnetic ZnFe₂O₄ spinel ferrite nanoparticles, *J Colloid Interf Sci.* 398 (2013) 152-160.
- [9] Sharma P, Kaur H, Sharma M, S, V., A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste, *Environmental Monitoring and Assessment.* 183 (2011) 151-195.
- [10] Crini G, Non-conventional low-cost adsorbents for dye removal: A review, *Bioresource Technology.* 97 (2006) 1061-1085.
- [11] Iqbal MJ, A, M. N., Adsorption of dyes from aqueous solutions on activated charcoal, *J Hazard Mater.* 139 (2007) 57-66.
- [12] Tan IW, Ahmad AL, H, B. H., Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, *Desalination.* 225 (2008) 13-28.
- [13] da Silva LG, Ruggiero R, Gontijo PM, et al., Adsorption of Brilliant Red 2BE dye from water solutions by a chemically modified sugarcane bagasse lignin, *Chemical Engineering Journal.* 168 (2011) 620-628.
- [14] Amin NK, Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics, *Journal of Hazardous Materials.* 165 (2009) 52-62.
- [15] Acharya J, Sahu JN, Sahoo BK, Mohanty CR, M, B. C., Removal of chromium(VI) from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride, *Chem Eng J.* 150 (2009) 25-39.
- [16] Tsai WT, Chang CY, Lin MC, Chien SF, Sun HF, H, M. F., Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl₂ activation, *Chemosphere.* 45 (2001) 51-58.
- [17] Namasiyayam C, K, D., Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, *Dyes and Pigments.* 54 (2002) 47-58.
- [18] Khaled A, El Nembr A, Ei-Sikaily A, A, A., Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon, *Desalination.* 238 (2009) 210-232.
- [19] Ahmad MA, R, N. K., Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon, *Chem Eng J.* 170 (2011) 154-161.
- [20] Gecgel U, K, H., Adsorption of Remazol Brilliant Blue R on activated carbon prepared from a pine cone, *Nat Prod Res.* 26 (2012) 659-664.
- [21] Senthilkumaar S, Kalaamani P, S, C.V., Liquid phase adsorption of Crystal violet onto activated carbons derived from male flowers of coconut tree, *J Hazard Mater.* 136 (2006) 800-808.
- [22] Thinakaran N, Baskaralingam P, Pulikesi M, Panneerselvam P, S, S., Removal of Acid Violet 17 from aqueous solutions by adsorption onto activated carbon prepared from sunflower seed hull, *J Hazard Mater.* 151 (2008) 316-322.
- [23] Royer B, Cardoso NF, Lima EC, et al., Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions: Kinetic and equilibrium study, *J Hazard Mater.* 164 (2009) 1213-1222.
- [24] Ozer C, Imamoglu, M., Turhan, Y., Boysan, F., Removal of methylene blue from aqueous solutions using phosphoric acid activated carbon produced from hazelnut husks, *Toxicological and Environmental Chemistry.* 94 (2013) 1283-1293.
- [25] Tekem M, Imamoglu M, B, N., Adsorption of some textile dyes on activated carbon prepared from rice hulls, *Fresenius Environ Bull.* 18 (2009) 709-714.
- [26] Foo KY, H, B. H., Coconut husk derived activated carbon via microwave induced activation: Effects of activation agents, preparation parameters and adsorption performance, *Chem Eng J.* 184 (2012) 57-65.
- [27] Cazetta AL, Vargas AM, Nogami EM, et al., NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption, *Chem Eng J.* 174 (2011) 117-125.
- [28] Baccar R, Bouzid J, Feki M, M, A., Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions, *J Hazard Mater.* 162 (2009) 1522-1529.

- [29] Prahas D, Kartika Y, Indraswati N, I, S., Activated carbon from jackfruit peel waste by H₃PO₄ chemical activation: Pore structure and surface chemistry characterization, *Chem Eng J.* 140 (2008) 32-42.
- [30] Rattanaphani S, Chairat M, Bremner JB, R, V., An adsorption and thermodynamic study of lac dyeing on cotton pretreated with chitosan, *Dyes and Pigments.* 72 (2007) 88-96.
- [31] Aeed A, Sharif M, I, M., Application potential of grapefruit peel as dye sorbent: Kinetics, equilibrium and mechanism of crystal violet adsorption, *J Hazard Mater.* 179 (2010) 564-572.
- [32] Xia C, Jing Y, Jia Y, Yue D, Ma J, Y, X., Adsorption properties of congo red from aqueous solution on modified hectorite: Kinetic and thermodynamic studies, *Desalination.* 265 (2011) 81-87.
- [33] Hu Z, Chen H, Ji F, Y, S., Removal of Congo Red from aqueous solution by cattail root, *Journal of Hazardous Materials.* 173 (2010) 292-297.
- [34] Yener J, Kopac T, Dogu G, D, T., Adsorption of Basic Yellow 28 from aqueous solutions with clinoptilolite and amberlite, *J Colloid Interf Sci.* 294 (2006) 255-264.
- [35] Malik R, Ramteke DS, W, S. R., Adsorption of malachite green on groundnut shell waste based powdered activated carbon, *Waste Manage.* 27 (2007) 1129-1138.
- [36] Li Q, Yue Q, Su Y, Gao B, S, H., Equilibrium, thermodynamics and process design to minimize adsorbent amount for the adsorption of acid dyes onto cationic polymer-loaded bentonite, *Chem Eng J.* 158 (2010) 489-497.
- [37] Gupta VK, Singh P, R, N., Adsorption behavior of Hg(II), Pb(II), and Cd(II) from aqueous solution on Duolite C-433: a synthetic resin, *J Colloid Interface Sci.* 275 (2004) 398-402.
- [38] Langmuir I, Adsorption of gases on plain surfaces of glass mica platinum, *J Am Chem Soc.* 40 (1918) 1361-1403.
- [39] Freundlich H, H, W., The Adsorption of cis- and trans-Azobenzene, *J Am Chem Soc.* 61 (1939) 2228-2230.
- [40] Tempkin MJ, P, V., Kinetics of ammonia synthesis on promoted iron catalysts, *Acta Physicochim URSS.* 12 (1940) 217-222.
- [41] Senthil Kumar P, Ramalingam, S., Senthamarai, C., Niranjanaa, M., Vijayalakshmi, P., Sivanesan, S., Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions, *Desalination.* 261 (2010) 52-60.
- [42] Aharoni C, U, M., Kinetics of activated chemisorption. Part 2. Theoretical models, *J Chem Soc, Faraday Trans.* 73 (1977) 456-464.