

TWO-PARAMETER ISOTHERMS OF METHYL ORANGE SORPTION BY PINECONE DERIVED ACTIVATED CARBON

M. R. Samarghandi, M. Hadi*, S. Moayedi, F. Barjasteh Askari

Department of Environmental Health Engineering, School of Public Health, Center for Health Research, Hamadan University of Medical Sciences, Hamadan, Iran

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ABSTRACT

The adsorption of a mono azo dye methyl-orange (MeO) onto granular pinecone derived activated carbon (GPAC), from aqueous solutions, was studied in a batch system. Seven two-parameter isotherm models Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Halsey, Jovanovic and Hurkins-Jura were used to fit the experimental data. The results revealed that the adsorption isotherm models fitted the data in the order of Jovanovic ($X^2=1.374$) > Langmuir > Dubinin-Radushkevich > Temkin > Freundlich > Halsey > Hurkins-Jura isotherms. Adsorption isotherms modeling showed that the interaction of dye with activated carbon surface is localized monolayer adsorption. A comparison of kinetic models was evaluated for the pseudo-second order, Elovich and Lagergren kinetic models. Lagergren first order model was found to agree well with the experimental data ($X^2=9.231$). In order to determine the best-fit isotherm and kinetic models, two error analysis methods of Residual Mean Square Error and Chi-square statistic (X^2) were used to evaluate the data.

Key words: Adsorption isotherms, Methyl orange, Kinetic models, Activated carbon

INTRODUCTION

In general, there are four main methods of reducing color in textile effluent streams: physical methods such as membrane technology (Gholami *et al.*, 2001), chemical methods such as coagulation (Nabi Bidhendi *et al.*, 2007), photochemical oxidation (Rezaee *et al.*, 2008) processes, biological methods such as anaerobic/aerobic sequential process (Naimabadi *et al.*, 2009) and physico-chemical processes. Among the physico-chemical processes, adsorption technology is considered to be one the most effective and proven technology having potential application in both water and wastewater treatment (Venkat Mohan *et al.*, 2000).

Adsorption equilibria information is the most important piece of information in understanding

an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for the understanding of how much those components can be accommodated by a solid adsorbent (Duong, 1998).

Modeling of sorption isotherm data is important for predicting and comparing adsorption performance.

A few two-parameter isotherm models are available for modeling adsorption data. Freundlich (Freundlich, 1906) and Langmuir (Langmuir, 1918) models are the most commonly used two-parameter isotherms. Further, other two-parameter models such as Temkin (Temkin and Pyzhev, 1940), Dubinin (Dubinin and Radushkevich, 1947), Jovanovic (Jovanovic,

*Corresponding author: hadi_mfr@yahoo.com

Tel: +98 9189061738

1969), Halsey (Halsey, 1948) and Hurkins-Jura (Harkins and Jura, 1944) are also used in the literature (Shokoohi *et al.*, 2009).

Activated carbon is the most commonly used sorbent of dye removal by adsorption (Nassar and El-Geundi, 1991). Although commercial activated carbon is a preferred sorbent for color removal, its widespread use is restricted due to high cost. As such, alternative non-conventional sorbents have been investigated. It is well-known that natural materials, waste materials from industry and agriculture and biosorbents can be obtained and employed as inexpensive sorbents (Grégorio, 2006).

Many investigations have studied the feasibility of using inexpensive alternative materials like wood (Ho and McKay, 1998), tree fern (Ho *et al.*, 2005), sugarcane dust (Ho *et al.*, 2005), orange peel (Arami *et al.*, 2005), ewage sludge- based activated carbon (Sreedhar Reddy and Kotaiah, 2006) , perfil (Maximova and Koumanova, 2008), and, as carboneous precursors for the dye removal.

Pine is a suitable tree for decorative planting in parks and is used usually as a decorative plant in national parks. Thus ground pine-cone may be abundantly available and, it would be worthwhile to develop a low-cost adsorbent from this waste material which may also be regarded as a sustainable resource. However, the abundant supply of ground pine-cone as a waste from national parks makes production of activated carbon from this material more financially viable, since using grain or coal as raw materials for activated carbon will require manufacturers extra amount of money for procurement.

The present research was aimed to test various two-parameter isotherm models to describe the sorption data generated from methyl orange dye sorption by granular pine-cone derived activated carbon. Pearson's chi-square statistic was used to evaluate the goodness-of-fit of the isotherm. Residual Mean Square Error (RMSE) was also used as a measure of the differences between values predicted by a model and the values actually observed from the experimental data being modeled. The isotherm and kinetic models parameters were determined using the trial-and-error non-linear method by MATLAB Software.

MATERIALS AND METHODS

Facilities

Weighing of materials was preformed by using an analytical balance with precision of $\pm 0.0001\text{g}$ (model Sartorius ED124S). Drying of materials was carried out in an electric oven (model PARS TEB). Carbonization was carried out in a muffle furnace (model Exiton). The pH of solutions was measured using a digital pH-meter (model Sartorius Professional Meter PP-50). The dye solutions were stirred using an inductive stirring system (Oxitor IS 12) within a WTW- TS 606/2-i incubator. The samples were centrifuged using a 301 Sigma Centrifuge. The dye concentration in the samples was measured spectrometrically, using a UV-1700 Pharmaspec Shimadzo spectrophotometer.

Raw materials

Dried pine cone was used as the raw material to produce the adsorbent (GPAC). The pine cones were collected from the Mardom Park in front of Hamadan University of Medical Sciences of Iran. The ground pine-cone is advantageous over other carboneous materials because of its high density, high purity.

Amono-azo dye methylorange (p-dimethylamino-azobenzenesulfonic acid), (MeO) supplied by Merckco., having molecular formula of $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$ and molecular weight of 327.33, was used as adsorbate in this study. Methyl orange was chosen as a simple model of a series of common azo dyes largely used in the industry. Its structure, reported in Fig. 1, is characterized by sulphonic group, which is responsible for the high solubility of these dyes in water. When dissolved in distilled water, the UV-visible Spectrum of MeO showed two absorption maxima. The first band was observed at 270 nm and the second band, more intense, at 465. This former was used to monitor the adsorption of MeO. All other reagents, (NaOH or H_2SO_4) used throughout this work were of analytical grade.

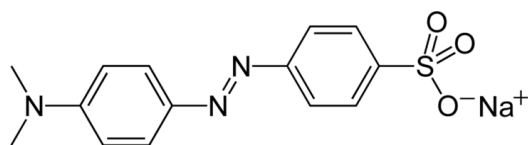


Fig. 1: Structural formula of methyl orange

Adsorbent preparation

granular activated carbon (GAC) was derived from the ground pine cone. The local GAC was produced by exposing the raw pine-cones to a thermal-chemical process. First of all the pine-cones were crushed and washed with hot water and then dried at 100° C in an oven overnight. A 50 g crushed sample was mixed with a pre-determined volume of phosphoric acid with concentration of 95% in the mass ratio of 1:10. This mixture was transferred to a stainless steel tube (50 mm diameter and 250 mm long). This tube was inserted to a muffle furnace, which was programmed to gradually reach up to 900° C within 3 hours, maintainence of this temperature for 1 hour, and then gradually cooling down to the room temperature.

The end product was repeatedly washed using hot distilled water until the washings showed pH>6.9; the washed sample was then again dried at 120°C in an oven overnight. The final sample was finally ground in a household-type blender and passed through a series of sieve (20, 30, 40, 50 U.S standard mesh sizes). A mixture of the residuals on 30, 40 and 50 sieves were kept in an air-tight bottle and used as adsorbent in this study. The average adsorbent particle size was 0.5 mm.

Adsorbent properties

The specific surface area of local GAC was obtained by determination of optimal concentration of methylene blue dye adsorbed onto GAC sorbent at constant temperature of 20°C. Adsorption test of methylene blue on prepared activated carbon was examined using a batch process by mixing 0.3 g of adsorbent in stoppered conical flasks with 100 mL of methylene blue solutions of concentration ranging from 100 to 1000 mg/L at a pH of 7.5±0.2. For all the concentration ranges studied (100–1000 mg/L), the mixture was magnetically stirred at a constant speed for three days which is more than sufficient time to reach equilibrium. Absorbance measurements were performed on methylene blue solutions at 660 nm to determine the equilibrium concentration. The calculated surface area was 734 m²/g.

The capacity of adsorbent for adsorption of dye can be evaluated through Iodine adsorption

from aqueous solutions using test conditions referred to as Iodine number determination. This indicates their relative activation level and the surface area available for micropores. Usually adsorbents with a high Iodine number have a high surface area and are suitable for adsorbing small compounds (Noszko *et al.*, 1984). The Iodine number was measured according to the standard procedure (ASTM D4607-94, 1999) by using the 0.1N standardized Iodine solution. Sample volumes of 100 mL of the Iodine solution were treated with 0.6, 0.9, and 1.2 g of the different samples. After equilibrium, the remaining Iodine in the supernatants was titrated with 0.1 N sodium thiosulfate solutions. The Iodine number was reported as the amount of iodine adsorbed per gram of adsorbent at a residual iodine concentration of 0.02 N. The calculated Iodine number value was 483.54 mg/g.

The apparent density was calculated by filling a calibrated cylinder with a given activated carbon weight and tapping the cylinder until a minimum volume was recorded. This density was referred as tapping or bulk density of adsorbent. For the real density a pycnometer method was used, which consisted of filling a pycnometer with the activated carbon, then adding a solvent (methanol) to fill the void, and at each step the weight was determined. The apparent and real density values were equal to 0.50 and 1.70 g/cm³ respectively.

The pore volume and the porosity were determined by using a volumetric method which consisted in filling a calibrated cylinder with a V_1 volume of activated carbon (mass m_1) and solvent (methanol) until volume V_2 (total mass m_2) was reached. Knowing the density of the solvent, total porosity volume (1.40 cm³/g) and the porosity (70 %) of the adsorbent were easily calculated.

The BET nitrogen surface area was determined to be 869 m²/g. This parameter was determined by Research Institute of Petroleum Industry (RIPI) in Tehran.

Dye concentration measurement and equilibrium experiment

An accurately weighed quantity of dye was dissolved in distilled water to prepare a stock solution (500 mg/L). Experimental solutions of the desired concentrations were obtained by

successive dilutions. The calibration curve for MeO was linear from 0.5 to 30 mg/L ($R^2=0.999$). The adsorption experiments were carried out in a batch process. Adsorption processes were studied in 250 mL Erlenmeyer flasks within an incubator container. The synthetic dye solutions were prepared by dissolving dye in distilled water to produce a solution of 150 mg/L. To determine the equilibrium time of MeO adsorption onto GPAC, an accurate amount of GPAC of (0.05 g) was added to an erlenmeyer flask with 100 cm³ volume containing 100 mL of dye solution (100 mg/L). The content of flask was mixed using a magnetic stirrer and 1 mL samples were taken at regular interval times.

The equilibrium times for MeO was determined to be 370 min. Accurately weighed amounts of GPAC sorbent of 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08 and 0.09 g were added to each flask with 250 mL dye solution (150 mg/L) at pH 7.5±0.2. The content of all erlenmeyer flasks were mixed for 370 min at 20.3° C using, magnetic stirrers at constant speed. 5 mL sample was taken after equilibrium was reached and centrifuged at 3800 rpm for 5 min. Then, dye concentration in the sample was measured spectrometrically. The amount of dye adsorbed onto the sorbent (q_e , mg/g), was calculated from Eq. (1) as follows:

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

Where C_e (mg/L) is the equilibrium concentration of dye in the solution, C_0 (mg/L) is initial dye concentration, m (g) is the amount of sorbent mass, q_e (mg/l) is the amount of adsorbed dye per unit mass of adsorbent, and V is the solution volume (L).

All experiments were conducted in triplicate, and the mean values have been reported.

Chi-square and the residual errors

To evaluate the fitness of kinetic and isotherm equations to the experimental data, the residual root mean square error (RMSE) was used to measure the kinetic and isotherm constants. RMSE can be defined as:

$$RMSE = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (q_{e,exp} - q_{e,calc})^2} \quad (2)$$

The chi-square statistic (Ho, 2004) is given as:

$$X^2 = \sum_{i=1}^N \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,calc}} \quad (3)$$

If data from the model are similar to the experimental data, X^2 will be a small number; if they are different, X^2 will be a large number.

The subscripts “exp” and ‘calc” show the experimental and calculated values and N is the number of observations in the experimental data. The small the RMSE value, the better the curve fitting (Tsai and Juang, 2000).

RESULTS

Adsorption isotherm models

In general, the adsorption isotherm describes how adsorbates interact with adsorbents and therefore it is critical in optimizing the use of adsorbents. Table 1 shows the parameters of the isotherm models for the adsorption of MeO onto GPAC. The value of standard error was reported for each parameter separately. The chi-square statistic and RMSE for each model are also presented in Table1.

The Langmuir(Langmuir, 1918) equation, is valid for monolayer sorption onto a surface with a finite number of identical sites, given by Eq. (4):

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

Where q_m (mg/g) is the maximum amount of adsorbed dye per unit mass of sorbent corresponding to complete coverage of the adsorptive sites, b (L/mg) is the Langmuir constant related to the energy of adsorption. Fig. 2 shows the experimental data and the non-linear form of the Langmuir model. The non-linear parameters of the Langmuir model, q_m and b are listed in Table1.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L (Hall *et al.*, 1966) which is defined by Eq. (5):

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

Table 1: Parameters of the isotherm models for the adsorption of MeO onto GPAC

Model	Parameter	Value	Standard error	X ²	P-value	RMSE
Langmuir	q _m	404.42	26.71	2.498	0.9271	9.068
	b	0.022	0.003			
Freundlich	k _f	35.41	7.297	5.581	0.5893	13.317
	n	2.224	0.252			
Dubinin-Radushkevich	B	0.237	0.017	2.755	0.9066	8.186
	Q _s	279.42	6.106			
Jovanovic	k _j	0.025	0.002	1.374	0.9863	6.723
	q _{max}	297.77	9.530			
Hurkins-Jura	B ₂	5.371	0.216	497.62	0.0000	95.920
	A	59154.73	11415.66			
Halsey	k _H	0.000	0.000	5.583	0.5891	13.317
	n	-2.224	0.241			
Temkin	b _T	24.292	1.939	2.760	0.9062	9.745
	K _T	0.162	0.027			

According to the value of R_L, the isotherm shape can be interpreted as Table 2. The dimensionless separation factor calculated for MeO was 0.0000165.

Table 2: Langmuir isotherm constant parameter, R_L

R _L value	Type of isotherm
R _L >1	Unfavorable
R _L =1	Linear
R _L =0	Irreversible
0< R _L <1	Favorable

The empirical Freundlich (Freundlich, 1906) equation based on sorption onto heterogeneous surface is given by Eq. (6):

$$q_e = k_f C_e^{1/n} \tag{6}$$

Where C_e (mg/L) is the equilibrium concentration and q_e (mg/g) is the amount adsorbed dye per unit mass of the adsorbent. The constant n is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface (Bansal and Goyal, 2005). k_f (mg^{1-1/n}L^{1/n}/g) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent. The Freundlich exponent, n, should have values lying in the range of 1 to 10 for classification as favorable adsorption (Freundlich, 1906). The non-linear form of this model is shown in Fig. 2

and its parameters are also showed in Table 1. Tempkin and Pyzhev (Tempkin and Pyzhev, 1940) studied the heat of adsorption and the adsorbent-adsorbate interaction on surfaces. The Temkin isotherm equation is given as below:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \tag{7}$$

Where, T (°K) is the absolute temperature, R is the universal gas constant (8.314 kJ/kmol.°K), K_T is the equilibrium binding constant (L/mg), and b_T is the variation of adsorption energy (kJ/mol). K_T and b_T values are recorded in Table 1. These parameters were calculated by non-linear regression fitting as shown in Fig. 2.

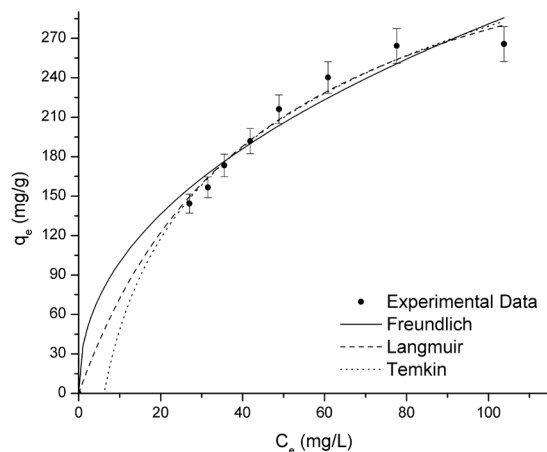


Fig 2: Langmuir, Freundlich and Temkin isotherms for the adsorption of MeO by GPAC

The Harkin-Jura (Harkins and Jura, 1944) adsorption isotherm can be expressed as :

$$q_e = \left(\frac{A}{B_2 + \log C_e} \right)^{1/2} \quad (8)$$

Where (A_H) and B_2 are isotherm parameter and constant. The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution.

The Halsey (Halsey, 1948) adsorption isotherm can be given as :

$$q_e = \text{Exp} \left(\frac{\ln k_H - \ln C_e}{n} \right) \quad (9)$$

Where k_H and n are the Halsey isotherm constant and exponent, respectively. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of the adsorbent. Fig. 3 shows the experimental data and the non-linear form of the Hurkins-Jura and Halsey models. The related non-linear parameters are listed in Table1.

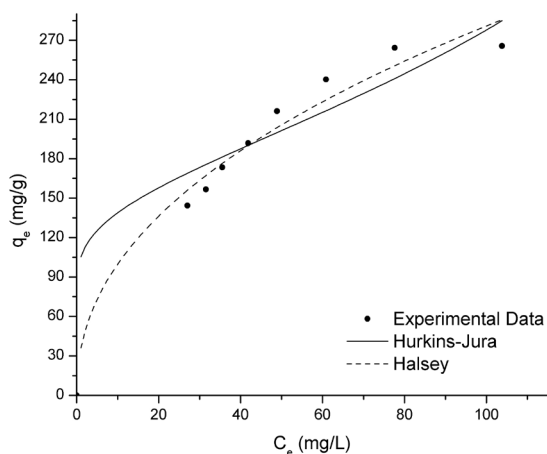


Fig 3: Hurkins-Jura and Halsey isotherms for the adsorption of MeO by GPAC

Dubinin-Radushkevich (Dubinin, 1960) isotherm is generally expressed as follows:

$$q_e = Q_s \text{Exp} \left(-B \varepsilon^2 \right) \quad (10)$$

Radushkevich (Radushkevich, 1949) and Dubinin (Dubinin, 1965) have reported that the characteristic sorption curve is related to the

porous structure of the sorbent. The constant, B_D , is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy can be computed using the following relationship (Hasany and Chaudhary, 1996):

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

The model of an adsorption surface considered by Jovanovic (Jovanovic, 1969) is essentially the same as that considered by Langmuir. The same kind of approximation leads to the result that monolayer adsorption of mobile hard discs is described by the Langmuir isotherm. Jovanovic model can be shown using the following relationship:

$$q_e = q_{\max} \left(1 - e^{(k_j C_e)} \right) \quad (12)$$

Fig. 4 shows the experimental data and the non-linear form of the Dubinin-Radushkevich and Jovanovic models. Their related parameters are listed in Table1.

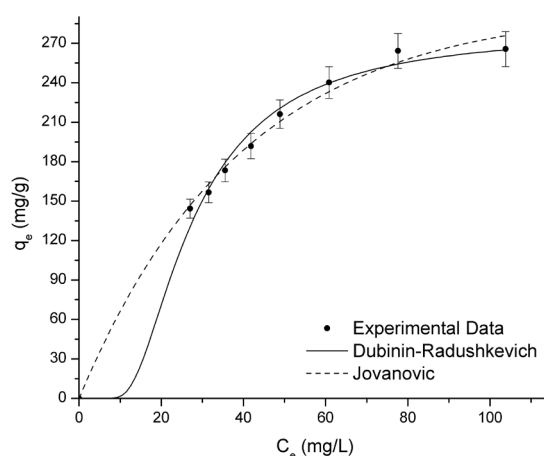


Fig 4: Dubinin-Radushkevich and Jovanovic isotherms for the adsorption of MeO by GPAC

Adsorption kinetic models

For evaluating the adsorption kinetics of MeO dye, pseudo-second order (Ho and McKay, 1999), first-order (Lagergren, 1898) and Elovich (Low, 1960) kinetic models were used. The conformity between experimental data and the model-predicted values was expressed by non linear

Chi-square statistic and the residual mean square error (RMSE).

The Lagergren first-order kinetic model is expressed as Eq. (13):

$$q_t = q_e - \exp(\ln q_e - k_1 t) \quad (13)$$

Where k_1 (g/mg min) is the rate constant of pseudo-first order model, t is time. q_e and q_t are the amounts of adsorbed dye at equilibrium time and at time t .

The pseudo-second order rate equation is expressed as Eq. (14):

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \quad (14)$$

Where k_2 is the rate constant of pseudo-second order model (g/mg.min).

The pseudo-second order kinetic model considers the rate-limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent (Ho and McKay, 1998).

The Elovich kinetic model is generally expressed as Eq. (15):

$$q_t = \frac{\ln \alpha \beta}{\beta} + \frac{1}{\beta} \ln t \quad (15)$$

Where α is the initial adsorption rate (mg/g.min), β is the desorption constant (g/mg) during any experiment. The non linear first-order Lagergren, pseudo-second order and Elovich kinetic models for the sorption of MeO on GPAC are presented in Fig. 5. The parameters of kinetic models and their corresponding Chi-square and RMSE values are also shown in Table 4.

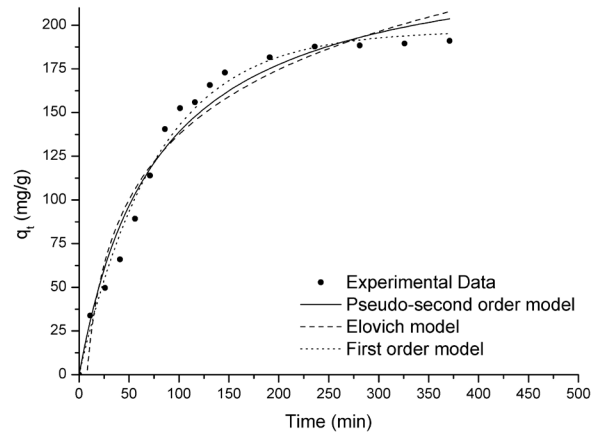


Fig 5: Kinetic experimental data and first- order, pseudo second-order and Elovich models (pH =7.5±0.2 and temperature =20±0.2°C)

Table 3: Parameters of the kinetic models for the adsorption of MeO onto GPAC

Model	Parameter	Value	Standard errors	X ²	P-Value	RMSE
Pseudo-Second order	k ₂	0.0001	0.0000	15.143	0.3684	10.995
	q _e	246.09	12.004			
First-order	q _e	196.84	4.2297	9.231	0.8159	7.401
	K ₁	0.0129	0.0008			
Elovich	α	6.9418	0.9112	33.292	0.0026	14.001
	β	0.0186	0.0013			

DISCUSSION

Adsorption isotherm models

The values of maximum adsorption capacity determined using Langmuir model was higher than the experimental adsorbed amount (≈250 mg/g) and corresponded to the adsorption isotherm plateau, which is unacceptable. The Langmuir capacity can also be used to compare the efficiency of pine cone-derived activated carbon tested as adsorbent for MeO dye sorption. Table 5 makes such a comparison and shows that GPAC is advantageous over carbons made

from other materials and other non carbonaceous adsorbents because of high sorption capacity based on Langmuir model. The value of b (L/mg) parameter of the Langmuir model is the constant representing the affinity of sorbate to sorbent. Higher b values mean more affinity of sorbate to sorbent. b parameter of the Langmuir model for the sorption of MeO onto GPAC in this study is 0.022 L/mg. Annadurai *et al.* (Annadurai *et al.*, 2002) reported 11.4 L/mg and 16.5 L/mg for b in the sorption of methyl orange dye by banana and orange peels, respectively. Comparison of

these values with b parameter of the Langmuir model in this study reveals that the affinity of

MeO to GPAC is lower than the affinity of MeO to banana and Orange peels.

Table 4: Dye sorption by sorbents: a selection of the Langmuir constant, q_m of various related substances from the literature

Dye	Adsorbent	q_m (mg/g)	References
Methyl orange	Banana peel	21	(Annadurai <i>et al.</i> , 2002)
Methyl orange	Orange peel	20.5	(Annadurai <i>et al.</i> , 2002)
Methyl orange	Calcined layered double hydroxides	200	(Ni <i>et al.</i> , 2007)
Methyl orange	Hypercrosslinked polymeric adsorbent	70.9	(Huang <i>et al.</i> , 2008)
Methyl orange	Diaminoethane sporopollenin biopolymer	4.7	(Kucukosmanoglu <i>et al.</i> , 2006)
Methyl orange	Pine cone derived activated carbon	404.4	This study

The obtained R_L value for the sorption of MeO onto GPAC is less than 1 (0.0000165) and greater than zero indicating favorable adsorption.

As shown in Fig. 2, the Freundlich isotherm did not show a satisfactory fit to the experimental data as indicated by Chi-square statistic and RMSE. However, the Langmuir isotherm showed a better fit to adsorption data than Freundlich isotherm. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the GPAC surface; since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous (Langmuir, 1918). It is apparent that value of Freundlich constant, n , indicates favorable adsorption, as it was equal to 2.224. The variation of adsorption energy in Temkin model, b_T , was positive (24.292 kJ/mol) for MeO compound, which indicates that the adsorption reaction is exothermic. The Temkin theoretical isotherm curve is compared with the corresponding experimental data in Fig. 2 and its obtained mean square error and chi-square statistic values are presented in Table 1. The experimental equilibrium curves are close to those predicted by the Temkin model. Consequently, the Temkin isotherm can describe the adsorption isotherms of MeO onto GPAC acceptably, but still, there is a need to be compared with other models.

As can be seen in Table 1, the values of Chi-square statistic and RMSE for Hurkins-Jura model were 497.62 and 95.92, respectively which are very high in comparison with other models. This reveals that Hurkins-Jura model could not describe the experimental isotherm data in the sorption of MeO onto GPAC. This result also shows that the sorption of MeO onto GPAC can not be explained by assumption of multilayer

adsorption phenomena.

The Halsey model also could not describe the sorption of MeO onto GPAC acceptably, because this model also assumes a multilayer behavior for the sorption of a sorbent onto adsorbent and its corresponding Chi-square and RMSE values in Table 1 concurred with this result.

As shown in Table 1, Dubinin-Radushkevich model provides better agreement with experimental data in comparison with Temkin, Freundlich, Halsey and Hurkis-Jura models. The values of X^2 for Dubinin-Radushkevich and Langmuir models are almost close together but comparison of their maximum monolayer capacity show that Dubinin-Radushkevich reveals a better agreement with experimental data. The value of Q_s was 279.42 mg/g which is more close to experimental capacity (≈ 250 mg/g) in comparison with corresponding Langmuir parameter (q_m) which is almost two times (404.4 mg/g) of the experimental capacity. Consequently, Dubinin-Radushkevich better explained the MeO sorption experimental data than Langmuir model.

The X^2 and RMSE values for Jovanovic model were 1.374 and 6.723 respectively (Table 1) which were lower than all other isotherm models. This result shows the sorption of MeO onto GPAC can be better explained by approximation of monolayer localized adsorption without lateral interaction. This Jovanovic model is essentially the same as that considered by Langmuir, except that allowance is made in the former for the surface binding vibrations of an adsorbed species. The Jovanovic equation represents another approximation for monolayer localized adsorption without lateral interactions. As the results show the Jovanovic and Langmuir models having the same assumptions, could explain the

sorption of MeO onto GPAC acceptably.

Adsorption kinetic models

As can be seen from Table 4, the values of Chi-square statistic and the P-value of the first-order model are 9.231 and 0.8159 which are lower and more than corresponding values for other models, respectively. This results show pseudo-first order equation of Lagergren could fit well over the range of contact times and describe well the rated of dye sorption onto GPAC. The obtained RMSE for Lagergren model was 7.401 and confirm the results.

As shown in Table 4, the values of Chi-square statistic and its P-value of Pseudo-second order model are 15.143 and 0.3684 respectively, which are more and lower than corresponding values for First-order model, respectively. Based on the results obtained from the analysis of the sorption data with Pseudo-Second Order kinetic model it can be suggested that the Pseudo-Second Order kinetic model after Pseudo-First Order equation of Lagergren could describe the sorption of MeO onto GPAC.

Chi-square statistic and RMSE for Elovich model are shown in Table 4. The Chi-square statistic value and corresponding P-value for Elovich model were obtained as 33.292 and 0.0026, respectively. Comparison of Chi-square statistic for Elovich and Lagergren first order models show that the later described the rate of dye sorption onto GPAC better than Elovich model. Based on the results obtained from the analysis of the sorption data with kinetic models, it can be suggested that the Lagergren model described the sorption of MeO onto GPAC better than other models.

The results of the present investigation showed that the produced activated carbon from pinecone has considerable potential for the removal of mono azo dye, methyl orange, from aqueous solution. The obtained results showed that the adsorption equilibrium data fitted well to Jovanovic and Langmuir models. The description of the sorption of MeO onto GPAC by the Jovanovic and Langmuir models is a pointer to homogeneity of the surface of the GPAC and monolayer adsorption nature of the MeO onto GPAC. This conclusion concurred with another investigations, the sorption of methyl orange dye

on kudzu, sweet potato, corn, rice, wheat, potato and snake gourd starches which was reported by Boki *et al.* (Boki *et al.*, 2006). They suggested that methyl orange was confined to a monolayer on surface hydroxyl groups of the starches.

The sorption process was described by Lagergren first order model. The Lagergren first order model showed satisfactory fits with the experimental data with low Chi-square values and is important in the sorption of MeO onto GPAC. These results imply that physic-sorption mechanism may play an important role for the adsorption of MeO dye onto GPAC. This conclusion agrees with those reported by Atmani *et al.* who reported for the adsorption of methyl orange dye on the raw and treated skin almonds (Atmani *et al.*, 2009). There is a need to conduct same studies to asses the abilities of pinecone derived activated carbon for removal of other dyes and investigations to study of kinetic models of dyes sorption, to facilitate comparisons with other non-activated and activated sorbents.

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