

REVIEW ARTICLE

BATCH EQUILIBRIUM ADSORPTION OF METHYL ORANGE FROM AQUEOUS SOLUTION USING ANIMAL ACTIVATED CARBON FROM GUDALI BONES

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ABSTRACT

This paper presents the efficiency of animal activated carbon in the removal of methyl orange (MO) from aqueous solutions by adsorption. Batch experiments were conducted to study the effect of reaction parameters on the adsorption of the dye such as: contact time, initial concentrations of MB solution, adsorbent dosage, solution pH, and temperature. The surface properties were measured by some techniques including: Fourier transform infrared spectrometry and point of zero charge. Adsorption capacity for MO is 7.045 mg.g⁻¹ at 298 K under the optimum condition of pH of 3, adsorbent dosage of 10 g.L⁻¹, particle size of 0.2-0.05 mm, and contact time of 10 min. The kinetic data obtained from different experiments were analyzed using three kinetic models namely intra-particulate diffusion, pseudo-first-order and pseudo-second-order kinetics models. Among the kinetics models studied, the pseudo-second-order model was the best applicable model to describe the adsorption of MO onto activated carbon. Freundlich and Langmuir models were used to analyze the obtained experimental data. In comparison, both models were understood to be a better fit for the experimental data, these two models show the best fit with R² values of 0.999. The values of Gibbs free energy of adsorption $\Delta G^\circ < 0$; these negative values indicated the spontaneity of the adsorption process of MO onto activated carbon. The values of (ΔH°) and (ΔS°) were found to be 57.924 kJ.mol⁻¹ and 198.538 J mol⁻¹.K⁻¹, respectively. The thermodynamic parameters indicated that the adsorption of MO onto activated carbon was spontaneous and exothermic.

Key words: Activated carbon, Adsorption isotherms, Kinetic, Methyl orange, Thermodynamic parameters.

INTRODUCTION

Accumulation of dyes in wastewater from industries such as textiles, paper, cosmetics, rubber, and plastics has been regarded as a significant source of water pollution. Reactive dyes, an anionic dye, are most commonly used due to their provision of bright colors, excellent color fastness, and easy application (Annodurai *et al.*, 2008; Leechart *et al.*, 2009 and Domga *et al.*, 2015). However, many reactive dyes are toxic to organisms and may cause direct harm to aquatic life. Dyes are common constituents of effluents discharged by various industries, such as paper, textile, plastic, food and textile (Chung *et al.*, 1981 and Moghaddam *et al.*, 2010). The presence of small amounts of dye in water is highly visible and undesirable. Dyeing wastewater discharged into aqueous streams may make them unacceptable for public consumption (Gao *et al.*, 2007). Moreover, the discharging of untreated industrial effluents containing dyes decreases the penetration of sunlight into the water (Holzheu and Hoffmann, 2002; Ho *et al.*, 2009; Qiu *et al.*, 2010) and the photosynthetic activity is

affected significantly (Qiu *et al.*, 2010; Muqing *et al.*, 2015 and Domga *et al.*, 2015). Due to carcinogenic, mutagenic, toxic and allergenic nature of dyes, their occurrence in the aquatic system is highly dangerous (Eofomaja *et al.*, 2006; Mittal *et al.*, 2007; Jain *et al.*, 2008; Chen *et al.*, 2010; Weng *et al.*, 2013 and Muqing *et al.*, 2015). Thus, it is desirable to remove dyes from industrial effluents. A majority of the used dyes are azoreactive dyes which are bright in color due to the presence of one or several azo ($-\text{N}=\text{N}-$) groups associated with substituted aromatic structures (Bhatnagar *et al.*, 2005; Vinoth *et al.*, 2010). As the dyes are structurally complex, are of synthetic origin, and have high water solubility, their removal from effluent by the use of conventional physico-chemical and biological processes is difficult (Domga *et al.*, 2015 and Salleh *et al.*, 2011). Several researches have been performed to develop effective treatment technologies for wastewaters containing dyes, such as electrocoagulation, membrane filtration, electrochemical destruction, ion exchange, irradiation, advanced oxidation, ozonation, precipitation and adsorption involving the use of activated carbon (Laszlo *et al.*, 1996; Gemea *et al.*, 2003; López-Grimau *et al.*, 2006; Vinoth *et al.*, 2010; Muqing *et al.*, 2015; Domga *et al.*, 2015). The

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adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. This process is becoming an attractive and promising technology because of its simplicity, ease of operation and handling, sludge free operation and regeneration capacity (Eofomaja *et al.*, 2006; Muqing *et al.*, 2015 and Jain *et al.*, 2008). Activated carbon is the most popular adsorbent, which has been used with great success. However, activated carbon is expensive and its regeneration and reuse make it more costly. Consequently, many researchers have studied the feasibility of using low cost substances for the removal of various dyes and pollutants from wastewaters (Lakshmi *et al.*, 2009; Othman *et al.*, 2006; Prado *et al.*, 2004; Srivastava *et al.*, 2007 Muqing *et al.*, 2015 and Domga *et al.*, 2015). In this work, the animal activated carbon derived from the carbonization of *Gudali Zebu* cattle bones were used for the removal of methyl orange.

MATERIAL AND METHODS

Preparation of Activated Carbon

The zebu cattle bones are degreased Gudali collected and thoroughly washed with distilled water and dried in an oven at 110°C for 24h, 200g zebu cattle Gudali bone were dried milled and sieved (0.2-5mm) for 18 h and impregnated with a solution of phosphoric acid H₃PO₄ 85%. Impregnated was washed with hot distilled water until neutral pH and dried at 110°C for 24h. Sample was then pyrolyzed for 2 h at 500°C which was conducted in the muffle furnace Heraeus, MR model 260E with a heating rate of 5°C.min⁻¹.

Point of zero charge

The point of zero charge (pH_{PZC}) of the MPW was determined by the solid addition methods [27]. To a series of 100 mL Erlenmeyer flasks, 45 mL of KNO₃ solution of known strength was transferred. The initial pH (pH_i) values of the solutions were roughly adjusted from 2 to 12 by adding either 0.1 N HNO₃ or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO₃ solution of the same strength. The pH_i values of the solutions were then accurately noted, and 0.1 g of activated carbon animal was added to each flask, which were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid (pH_f) were noted. The difference between the initial and final pH values (ΔpH) was plotted against the pH_i.

Spectroscopic study

Fourier Transform Infrared (FTIR) spectrophotometer was used in this study to identify the characteristic functional groups in the active carbon. 5 mg of the active carbon sample was mixed with dry potassium bromide (KBr). The mixture was thoroughly mixed and pressed at pressure of 4500 psi to form a KBr thin disc. Then the disc was measured to check the IR spectrum by using Perkin Elmer 2000 infrared spectrometer. The sample was scanned from 4000-400 cm⁻¹ for 16 times to increase the signal to noise ratio.

Preparation of Methyl orange solutions

Methyl Orange, 4-dimethylaminoazobenzene-4'-sulfonic acid (MO), its molecular formula is C₁₄H₁₄N₃NaO₃S (Fig. 1), a bright orange crystalline powder with a molecular weight of 327.34 and melting point around 300°C, was purchased from LABCHEM and used without further purification. The molecular structure of MO a water soluble dye is shown in Figure 1. MO is dark red in aqueous solution below pH 3 and the color brightens to orange as pH increases. A stock solution of MO (100 mg/L) was prepared by dissolving 0.100 g of the dye in 1 L of distilled water and filtered via Whatman filter paper (No. 1). The prepared stock solution was then wrapped with aluminum foil and stored in a dark to prevent exposure to direct light.

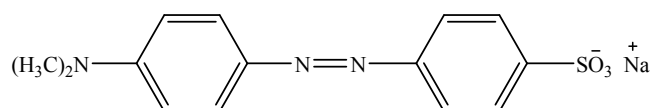


Fig. 1. Chemical structure of methyl orange

Determination of MO Concentration

UV-visible spectrum of MO absorption was obtained by a spectral scan from 300 to 1100 nm, of a 10ppm solution (Figure 2). This spectrum shows that the peak of absorption of is 465 nm. The concentrations of MO solution are obtained by measuring the absorbance at 465 nm by a spectrophotometer "Pharo 100".

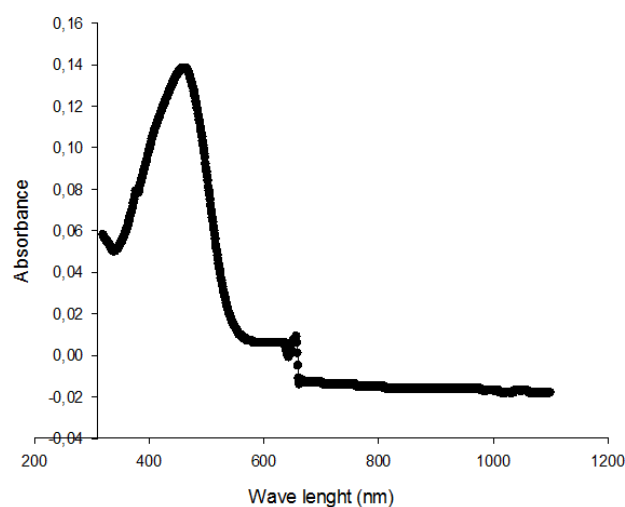


Fig. 2. Absorption spectrum of methyl orange

Batch adsorption experiments

Adsorption capacity of activated carbon animal was determined by contacting 1g (100 g L⁻¹) with 300 mL metal solutions of known concentration (10–60 mg L⁻¹) in 500 ml Erlenmeyer flasks, shaken on an orbital shaker at 120 rpm for 60 min at room temperature (25 ± 2 °C), followed by centrifugation at 5000 rpm for 5 min to separate activated carbon animal from the MO solution. Residual MO concentration in the supernatant MO solutions was determined by UV-visible spectrophotometry analysis. Rate of MO

adsorption by activated carbon animal was determined by analyzing residual MO ions in the supernatant after contact periods of 10, 20, 30, 40, 50 and 60 min. The solid phase mass was varied between 0.2 and 0.6 g adsorbent. For determining the effect of pH on MO adsorption by activated carbon animal, initial pH of the MO solution was adjusted to the desired value (3–11) using 0.1 M HCl or 0.1 M NaOH. Final pH of the adsorbate–adsorbent adsorption mixture was measured at adsorption equilibrium. MO-free and activated carbon animal-free blanks were used as the controls. All the experiments were performed in triplicate. Adsorption capacities were obtained using a mass balance equation [3]:

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

Where q_e is the equilibrium adsorption capacity per gram dry weight of the adsorbent (mg/g), C_0 is the initial concentration of MO in the solution (mg/L), C_e is the final or equilibrium concentration of MO in the solution (mg/L), V is the volume of the solution (L), and m is the dry weight of the adsorbent (g).

Adsorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Analysis of equilibrium adsorption data by fitting different linear isotherm models is an important step to find the suitable model that can be used for design purposes (Haghsersht *et al.*, 1998). The studies of adsorption isotherms are carried out on two well-known isotherms, the Langmuir and the Freundlich adsorption isotherm models. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. While, the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage (Weng *et al.*, 2013). The applicability of the isotherm equation is compared by judging the correlation coefficients R^2 .

RESULTS AND DISCUSSION

Infrared Spectroscopy of Adsorbent

Figure 3 shows at 3224cm^{-1} a band that corresponds to the –OH stretching vibration of alcohols. There is also a band between 2019 – 1943cm^{-1} indicating the presence of the triple bond of the alkyne moiety, the band at 1454 – 1416cm^{-1} indicates the presence of the C=C (aromatics) and a bending vibration in the plane of alcohols (–OH). The peak at 1210 marks the presence of the phenol group and that located between 1187 to 1155cm^{-1} indicates deformation of –OH and –COOH, vibration deformation –C O C group of ether and the presence of the phosphonate group (P=O) from the activation of the material by H_3PO_4 . The peak at 1023cm^{-1} indicates the presence of alkene group (–CH=CH₂), the peak at 872cm^{-1} indicated the presence of the –C N bond of the amide, the 724cm^{-1} indicates the presence of vibration out of

the plane of the –N H group of the amine deformation. The peaks at 494 – 599cm^{-1} are the stretching vibrations of halogens. The spectrum therefore suggested the presence of groups such as phenol, amide, amine, alkene, alkyne, alkane, carboxylic acid and ether.

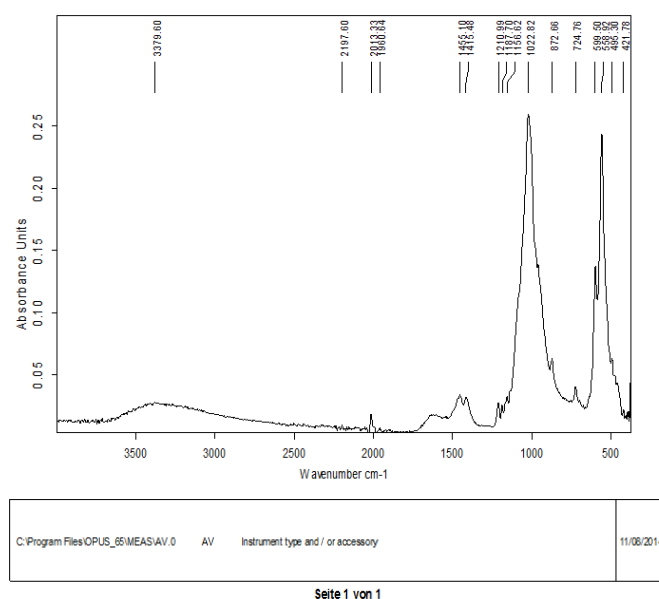
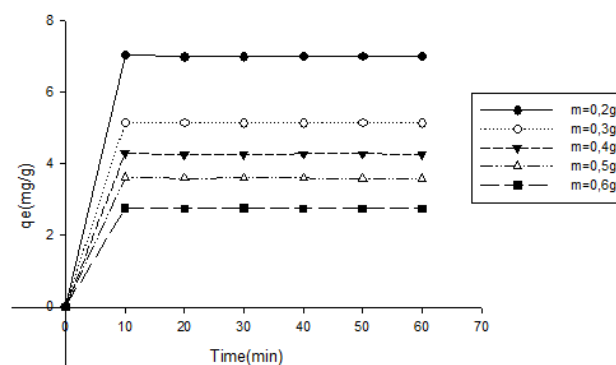


Fig. 3. FTIR spectrum of activated carbon animal



Effects of Adsorbent Mass

Effect of adsorbents dosage: The typical results in Fig. 4 show that for an increase in each adsorbent dosage, the adsorbent sites available upon the dye molecules also increase and consequently poor adsorption. This is due to electrostatic attraction forces between particles that constitute the surface of adsorbents, the decrease of molecular diffusion of the MO. Another consequence is the reduction of activated sites at the surface of the adsorbents and also the matter rate transfer of MO at the surface of the adsorbents, this means that the quantity of MO adsorbed per unit mass of adsorbent has its limit with the adsorbent dosage. Similar result has been obtained by Rajesh *et al.* 2010[30] during the removal of malachite green using Hydrilla Verticillate biomass, Gaston *et al.* (2014) during the removal of MO using kaolinite, metakaolinite and activated geopolymers and Domga *et al.* (2015) during the removal of methylene blue using activated carbon animal. It can be concluded that the optimum mass of activated carbon

animal for adsorption is 0.2g and this mass was used for the rest of the study.

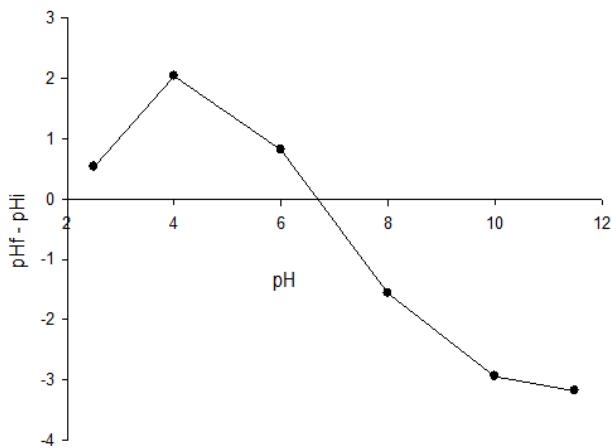


Fig. 5. pH_{zpc}

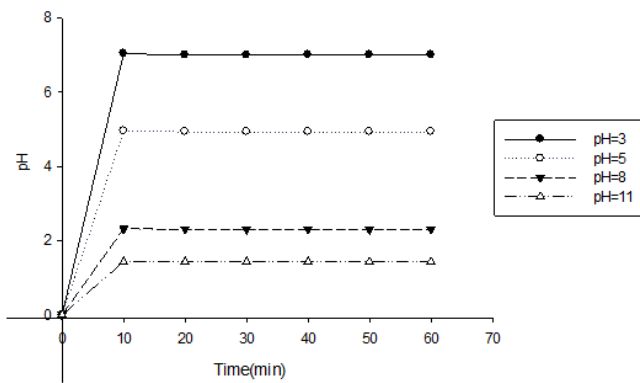


Fig. 6. Effect of pH

Effect of pH

pH has a very significant effect on the adsorption process since the pH of the solution influences the surface properties of the adsorbents as well as the degree of ionization and the speciation of the dye (Ho and McKay, 1999) Consequently, the effect of the pH of the solution on the adsorption of MO by activated carbon animal was studied in the pH range of 3-11. The adsorbed amount of activated carbon animal was found to increase with increasing solution pH (Figure 7).

This is due to the pH_{zpc} of activated carbon and anionic nature of MO. The adsorbent pH pzc is 6.84, which means that the surface of activated carbon particles has a negative charge at pH above 6.84. If the solution pH is higher than pH_{pzc}, higher density of negative ions will occupy the adsorption sites and consequently decrease the dye adsorption. This is confirmed by the low MO adsorption at pH 11. On the other hand when the solution pH is lower than 6.84, the positive charge on adsorbent surface enhance the sorption of MO. It can be concluded that the optimum pH for MO adsorption is 3.0 and this pH was used for the rest of the study. Similar result was obtained by Ozcan and Ozcan, (2004), Lim *et al.* (2010) during the removal of acid dyes onto acid activated bentonite and Gaston *et al.* (2014) during the removal of MO using kaolinite, metakaolinite and activated geopolymer.

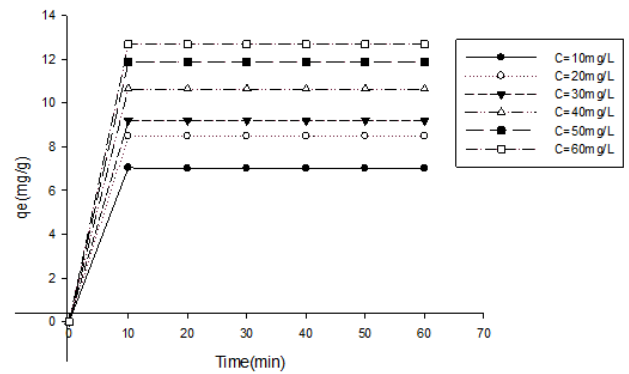


Fig 7. Effect of the initial dye concentration and contact time

Effect of initial concentration and contact time of Mo Solution

The influence of the initial concentration of MO on the dye removal capacity of activated carbon animal was carried out at a fixed adsorbent dosage (0.2 g), a pH of 3, various dye concentrations (10- 60 mg/L) and different time intervals (then intervals of 10 minutes up to 60 minutes). As is apparent in Figure 7, increasing the concentration of the dye from 10 to 60 mg/L, increases the adsorption capacity from 7.039 to 12.671 mg/g. This could be attributed to a high mass transfer driving force generated by the initial dye concentration that overcomes the mass transfer resistance of all the molecules between the aqueous solution and solid phases (Dogan *et al.*, 2006) MO exhibited a fast adsorption rate during the first 10 minutes of contact time due to a great availability of surface area/binding sites for dye molecules to be adsorbed. Generally, MO anions will bind to all the active sites until they are fully occupied. Hence with time, fewer active sites are available and thus reduce the amount of dye being adsorbed (Haddadian *et al.*, 2013 and Domga *et al.*, 2013).

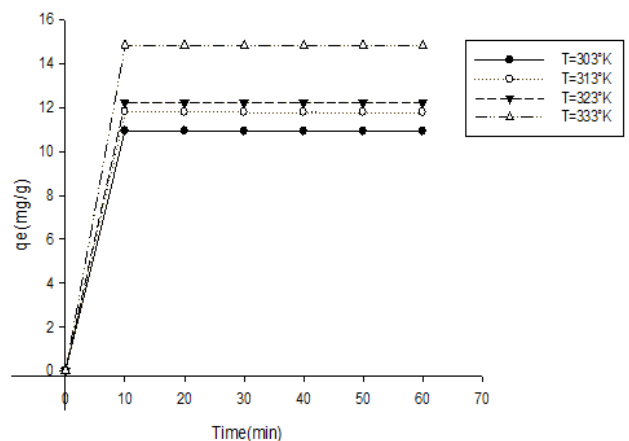


Fig 8. Effect of Temperature

The temperature is an important parameter in the adsorption process. The temperature affects the solubility of the adsorbate and the equilibrium constant for adsorption. The MO adsorption experiments were performed at different temperatures (303 K-333 K) at concentration of dye is 10mg/L. Figure 8 shows that the adsorption capacity of the dye

increased with increasing temperature. This behaviour may point out the higher mobility of the molecules at higher temperatures and a greater availability of molecules with enough energy to interact with the active sites on the surface (Asfour *et al.*, 1985) In addition, increasing the temperature resulted in the swelling of the internal structure of the activated carbon which helps to facilitate the movement of large dye molecules (Haddadian *et al.*, 2013). Similar result was obtained by Zahra *et al.* 2013 (Haddadian *et al.*, 2013) during removal methyl orange from aqueous solutions using dragon fruit foliage and Domga *et al.* 2015[3] during the removal methylene blue in aqueous solution onto activated carbon animal.

Adsorption Isotherms

Langmuir Adsorption Isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of MO ions between the solid and liquid phases (Vermeulan *et al.*, 1966 and Dada *et al.*, 2010). The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \quad (2)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (2) into linear form.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}} \quad (3)$$

Where: C_e = the equilibrium concentration of adsorbate (mg/L); q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g); q_{max} = maximum monolayer coverage capacity (mg/g); K_L = Langmuir isotherm constant (L/mg).

The values of LK and q_{max} were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$ [40]. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter (Weng *et al.*, 2013 and Dada *et al.*, 2012)

$$R_L = \frac{1}{1 + (1 + K_L C_o)} \quad (4)$$

Where: C_o = initial concentration, K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$. From the data calculated in table 1, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favorable. From this research work, the maximum monolayer coverage capacity (q_{max}) from Langmuir Isotherm model was determined to be 7.045 mg/g, K_L (Langmuir isotherm constant) is 0.165 L/mg, R_L (the separation factor) is 0.274 indicating that the equilibrium adsorption was favorable and the R^2 value is 0.999 proving that the adsorption data fitted well to Langmuir Isotherm model.

Freundlich Adsorption Isotherm

This is commonly used to describe the adsorption characteristics for the heterogeneous surface (Eofomaja *et al.* 2006). These data often fit the empirical equation proposed by Freundlich:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

Where: K_F = Freundlich isotherm constant (mg/g); n = adsorption intensity; C_e = the equilibrium concentration of adsorbate (mg/L); q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing equation 5, we have:

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

The constant K_F is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in

Table 1. Isotherm constants and correlation coefficients for the adsorption of MO on activated carbon animal at different mass

Model	Parameters	m=0.2g	m=0.3g	m=0.4g	m=0.5g	m=0.6g
Langmuir	K_L (L/mg)	0.165	0.218	0.373	1.432	3.697
	q_{max} (mg/g)	7.045	5.152	4.310	3.620	2.755
	R_L	0.274	0.240	0.175	0.063	0.025
	R^2	0.999	0.999	0.999	0.999	0.999
Freundlich	K_F	46.866	22.851	17.392	9.061	9.422
	$1/n$	1.136	0.943	0.741	0.666	1.221
	R^2	0.999	0.999	0.999	0.999	0.999

Table 2. Pseudo-first order, pseudo-second and intra-particle diffusion kinetic parameters for MO adsorbed on activated carbon animal

Model	Parameters	m=0.2g	m=0.3g	m=0.4g	m=0.5g	m=0.6g
Pseudo-first-order	K_1 (min ⁻¹)	0.061	0.092	0.098	0.098	0.088
	q_e (mg/g)	1.747	2.630	1.944	1.944	2.678
	R^2	0.652	0.597	0.681	0.681	0.581
Pseudo-second-order	K_2 (g.mg ⁻¹ .min ⁻¹)	20.165	37.631	54.286	9.661	33.130
	q_e (mg/g)	7.042	5.155	4.292	3.597	2.747
	R^2	0.999	0.999	0.999	0.999	0.986
Intra-particulatediffusion	K_{in} (mg.g ⁻¹ .m ^{-1/2})	0.807	0.593	0.493	0.414	0.316
	C (m ² .S ⁻¹)	2.057	1.505	1.250	1.056	0.805
	R^2	0.656	0.658	0.658	0.658	0.657

the adsorption process (Mohan *et al.*, 1997; Hutson *et al.*, 200 and Dada *et al.*, 2012). If $n = 1$ then the partition between the two phases are independent of the concentration. If value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption (Guadalupe, 2003 and Dada *et al.*, 2012) However, K_F and n are parameters characteristic of the adsorbent-adsorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models (Guadalupe *et al.*, 2008). Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate adsorption data where $1/n$ is a heterogeneity parameter, the smaller $1/n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between one and ten, this indicates a favorable adsorption process (Goldberg Equations and Models Describing Adsorption Processes in Soil s, 2005 and Dada *et al.*, 2012) From the data in table 3, that value of $1/n = 1.136$ while $n=0.880$ indicating that the adsorption of MO onto activated carbon animal is favorable and the R^2 value is 0.999.

Table 3. Thermodynamic parameters for the adsorption of MO onto the activated carbon animal

T(K)	$\Delta G^\circ(\text{KJ.mol}^{-1})$	$\Delta H^\circ(\text{KJ.mol}^{-1})$	$\Delta S^\circ(\text{Kj.mol}^{-1}.\text{K}^{-1})$	R^2
303	-118.081			
313	-120.066	-57.924	198.538	0.996
323	-122.052			
333	-124.037			

Kinetics Studies

Three simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the Lagergren pseudo-first-order equation (Ho *et al.*, 2004 and Domga *et al.*, 2015) as depicted in equation (7). The adsorption data can be presented by the following equation (Tunali *et al.*, 2006 and Chakkrit *et al.*, 2013).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

$$q_t = k_{int} \sqrt{t} + C \quad (8)$$

Where: q_e and q_t are the amounts of MO adsorbed (mg/g) at equilibrium and at time t (min), respectively, and $k_1(\text{min}^{-1})$ is the rate constant. Values of k_1 at ambient temperature were calculated from the plots of $\log(q_e - q_t)$ versus t for initial concentrations of MO $k_{int}(\text{mg}/(\text{g}.\text{min}^{1/2}))$ represents the intra-particle diffusion rate constant and C is a constant (mg/g) which gives information about the thickness of the boundary layer. The plot of q_t versus $t^{1/2}$ yields a straight line passing through the origin in the case of intra-particle diffusion. The set of R^2 values obtained were poor for two models kinetics (Table 2). On the other hand, the pseudo-second-order equation based on equilibrium adsorption (Ho *et al.*, 2004) is expressed as equation (9):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

Where: $k_2(\text{g}/\text{mg}.\text{min})$ is the rate constant of second order adsorption. The linear plot of t/q_t versus t at ambient

temperature, yielded set of R^2 values that are greater than 0.999 for initial concentrations of MO as shown in Table 2, indicating the applicability of this model to describe the adsorption process of MO onto the activated carbon animal.

Thermodynamic Parameters

In the practical application of a process, the thermodynamic parameters including change in the enthalpy (H°), entropy (S°), and Gibbs free energy (G°) are essential for a further understanding of the effect of temperature on adsorption indicating whether the adsorption processes occurs spontaneously. The effect of temperature on adsorption in this study was investigated at four temperatures (303, 313, 323 and 333 °K). The values of H° and S° were estimated from the slope and intercept of the van't Hoff plot of $\ln(K_c)$ versus $1/T$ according to Equation 10. The value of G° can be determined by Equation 11:

$$\ln K_c = \frac{S^\circ}{R} - \frac{H^\circ}{RT} \quad (10)$$

$$G^\circ = RT \ln k_c \quad (11)$$

Where: R (8.314 J/(mol.K)) is the universal gas constant and T (°K) is the absolute solution temperature. As seen in Table 3, the G° values are negative for all the experimental temperatures indicating that MO adsorbed onto activated carbon animal was spontaneous and that the system did not gain energy from an external source. When the temperature increased, the magnitude of G° shifted to a high negative value suggesting that the adsorption was more spontaneous at a higher temperature. Therefore, the magnitude of H° and G° gives some information about the nature of adsorption process (Suteu *et al.*, 2011). The literature data show that a physical adsorption is characterized by values of H° no more than 4.2 KJ/mol and G° lower than 40 kJ/mol. According to the calculated data from Table 3, the adsorption of MO onto activated carbon animal is rather physical adsorption than chemisorption. These observations are confirmed by the other research results included in one of our previous study (Domga *et al.*, 2015).

Finally, it can be said that the sorption mechanism of adsorption of MO dye onto activated carbon animal is a combined one of adsorption and ionic exchange. The links and forces involved in adsorption can range from weak van der Waals forces to electrostatic attractions between the ionized sulfonyl groups of the dye molecule and positively charged surface of adsorbent. As G° changed from -118.081 to -124.037 kJ/mol when the temperature increased from 303 to 333°K, it can be concluded that the adsorption mechanism is dominated by physisorption (Seki *et al.*, 2006 and Chakkrit *et al.*, 2013) A negative value of H° indicates that the adsorption reaction of MO is an exothermic process, as has been found in most cases (Seki and Yurdakoç, 2006; Almeida *et al.*, 2009 and Chakkrit *et al.*, 2013). This also suggests that a large amount of heat is consumed to transfer MO from an aqueous into a solid phase. The positive value of entropy change (S°) corresponds to an increase in the degree of freedom of the adsorbed species. A small change in the entropy shows that activated carbon does not significantly change.

Conclusion

The activated carbon animal exhibited good adsorption capacity for the removal of MO from aqueous solutions. The adsorption was depending on contact time, initial solution pH, and temperature. The adsorption equilibrium was attained a 10 min and the maximum adsorption was obtained at the initial solution pH of 3.0 and temperature at 298.23 °K. The equilibrium data obtained at different mass fitted well with the Langmuir model. The maximum monolayer capacity of MO adsorbed onto activated carbon animal decreased from 7.045 to 2.755 mg/g when the mass increased from 0.2 to 0.6 g, showing that the uptake of MO decreased with operating mass. The calculated values of ΔH° , ΔS° and ΔG° suggested that the adsorption was exothermic, random, and spontaneous. Regarding kinetic studies, the pseudo second order kinetic model agreed with the dynamic behavior for the adsorption of MO onto activated carbon animal. Though the results from the effect of initial solution pH and kinetic experiments reveal the adsorption process is chemisorption. These results suggested that activated carbon animal is a potential adsorbent for the reduction of dye accumulations normally found in the effluent of various industries.

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