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Batch Equilibrium, Kinetic and Thermodynamic Studies on Adsorption of Methylene Blue in Aqueous Solution onto Activated Carbon Prepared from *Bos Indicus Gudali* Bones

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Abstract

This paper report the efficiency of carbonaceous adsorbent prepared from *Bos Gudali Inducus* bones in removing of methylene blue (MB) in aqueous solution. The experimental parameters such as pH of solution, contact time, adsorbent dose, initial concentration of MB and temperature were studied. The adsorbent showed good potential for adsorption at pH 3.0 with a maximum take up of 98.58%. Adsorption equilibrium was reached after 10min. FT-IR spectra indicated high surface functional groups present in the carbons. Experimental data were analysed by two adsorption isotherms models (Langmuir and Freundlich). Applicability of isotherm equation to describe the adsorption process was analysed by the correlation coefficients values, R^2. Langmuir model shows best fit with R^2 values of 0.999, as compared to the Freundlich model. Kinetic model of pseudo-second-order best describes the adsorption kinetics on the experimental data. The mechanism of adsorption of methylene blue is therefore based on the assumption of the kinetic model of pseudo-second order in two steps. Thermodynamic parameters such as ΔH°, ΔG° and ΔS° proved that adsorption mechanism of MB onto activated carbon prepared from *Gudali* bones is possible, physisorption, spontaneous and exothermic in the ranges of temperature of 298-333K. The results of this study show that the animal activated carbon from bones of zebu cattle *Gudali* can be used as an adsorbent for removal of methylene blue residue in aqueous solution.

Keywords

Activated Carbon, Adsorption Isotherms, Kinetics, Methylene Blue, Thermodynamic

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1. Introduction

Dyes currently occupy an important place in the industrial sector. They are widely used in the paper, cosmetic, food industry, particularly in the textile industry (Gargetal.2005). These releases, consisting surfactants, biocides compounds, suspended solids, dispersing and wetting, dyes and trace metals are toxic to most living organisms (Ndi et al. 2013). The heterogeneity of their composition makes it difficult or almost impossible to obtain pollution levels at or below those set by environmental standards, after treatment with

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traditional techniques (Dipa et al. 2002). Hence the extensive use of dyes in everyday life has created problems both in the environment and in food (Zhenwang et al. 2000). Methylene blue, cationic dye, is an organic compound belonging to the family of Xanthines (Tahiri 1992). Dissolved in water, aqueous solutions have a dark blue colour. Methylene blue has a strong adsorption affinity for solid surfaces (Aerdizzone et al. 1993, Miehretal. 2004, Leupin et al. 2005) particularly for the surfaces of opposite charge (Jones et al. 2005). This affinity is attributed to both electrostatic and hydrophobic interactions (Miehr et al. 2004). Methylene blue is used for the determination of the specific surface of clay minerals (Kaewprasit et al. 1998, Lavine et al. 2001). Methylene blue is mainly contained in industrial effluents; it is non-biodegradable and highly toxic to plants, aquatic animals and humans. Methylene blue is 1 ppm visible in water; therefore, it negatively affects the aquatic ecosystem, because it reduces light scattering, there by inhibiting photosynthesis of aquatic plants (Ndi et al. 2013). In human beings, methylene blue may cause the following annoyances: the respiratory and intestinal tract, nausea, vomiting, diarrhea, headache, dizziness and blindness (irreversible damage to the optic nerve) (Dipa et al. 2002). It is therefore important to treat effluents containing methylene blue before their release into the environment. Various physical and chemical methods have been used for the disposal of the effluent water. These include coagulation (Tunay1996), reverse osmosis (Forgacs et al. 2004), the photo-degradation (Wu et al. 2005), electrochemical oxidation (Kusvuran et al. 2004), the ozonation (Robinson et al. 2001) and adsorption (Olushola et al. 2013). Adsorption is a process less expensive and simple to implement, effective at low concentrations, and offers the possibility to regenerate the adsorbent. For this purpose several types of adsorbents were tested for the removal of dyes in water including clays, zeolites, silicate gels, iron oxides, activated charcoal, titanium oxide, sepiolite, diatomite, sludge waste rice, silica, sawdust (Alkane et al., Tsai et al. 2004, Al-Ghouti et al. 2005, Weng et al. 2006, Gupta et al. 2006, Batzias et al. 2007). From these adsorbents, activated carbons are the most widely used because of their high adsorption capacity and high stability (Wu et al. 2005). In this work, the activated carbon derived from the carbonization of *Gudali Zebu* cattle bones were used for the removal of methylene blue.

2. Material and Methods

2.1. 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 H_3PO_4 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 the pyrolysis was conducted in the muffle furnace Heraeus, MR model 260E with a heating rate of 5°C. min^{-1}.

2.2. Preparation of Methylene Blue Solutions

Methylene blue (MB) is a cationic dye with a molecular formula $C_{16}H_{18}N_3SCl$ (Figure 1) was purchased without any treatment from Merck. The dye stock solution was prepared by dissolving accurately weighted MB in distilled water to the concentration of 100 mg/L. Experimental solutions were obtained by diluting MB in accurate proportions to required initial concentrations.

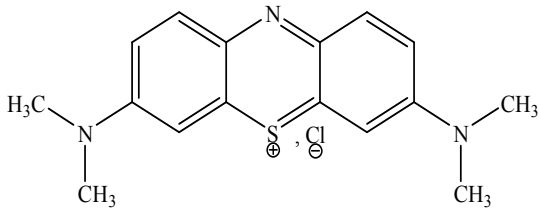

Figure 1. Chemical structure of methylene blue.

2.3. Determination of MB Concentration

UV-visible spectrum of MB 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 664 nm. The concentrations of MB solution are obtained by measuring the absorbance at 664.5 nm by a spectrophotometer "Pharo 100".

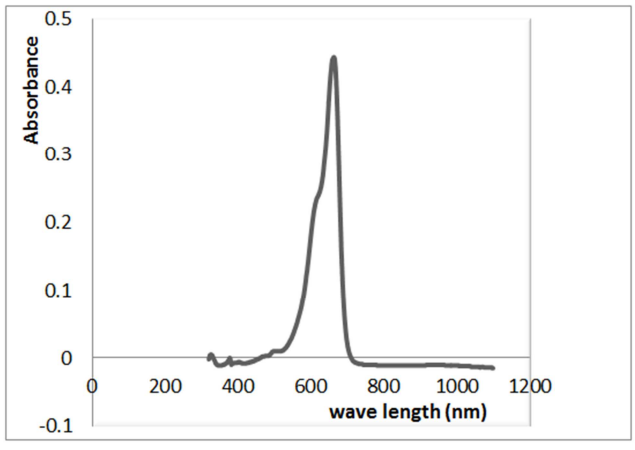

Figure 2. Absorption spectrum of methylene blue.

2.4. Batch Equilibrium Adsorption Studies

Adsorption studies were carried out at room temperature in a 250 ml reactor. For each experiment, dose of 0.2-0.6 g of adsorbent was weighed and put in reactors containing 50 mL

of concentration ranging from 10-70 ppm, pH increasing from 3 to11. The mixture was subjected to magnetic stirring over the interval of time between 10 to 60 minutes, using a magnetic stirrer. The suspension was filtered and the residual concentration was determined by UV-visible spectrophotometry. Concentration of remaining BM in the solution was calculated by the difference of the initial and the final BM concentrations. Adsorption capacities were obtained using a mass balance equation (Ayanda et al. 2012):

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

Where q_e is the equilibrium adsorption capacity per gram dry weight of the adsorbent (mg/g), C_0 is the initial concentration of BM in the solution (mg/l), C_e is the final or equilibrium concentration of BM in the solution (mg/L), V is the volume of the solution (L), and m is the dry weight of the adsorbent (g). Similarly, adsorption capacity at a specific time (q_t) during the experiment was calculated by taking the difference of the initial BM concentration (C) and the BM concentration at a specific time (C_t):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

2.5. Adsorption Kinetics Studies

Pseudo first-order, pseudo second-order, intraparticle and fractional power rate equations have been used to model the kinetics adsorption of BM (Olushola et al. 2013). A non-linear regression was used for all these models. It must be noted that all analyses were repeated in triplicate.

The pseudo first-order equation is generally expressed as (Lagergren et al. 1898):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Where q_e is the amount of As adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_t is the amount of As adsorbed at any time (mg/g) and k_1 is the pseudo first-order rate (constant/min). The values of $\log(q_e - q_t)$ were correlated with t. From the plot of $\log(q_e - q_t)$ versus t, k_1 and q_e can be determined from the slope and intercept respectively.

The pseudo second-order kinetic rate equation is expressed as (HoandMckay1998):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

Where k_2 is the rate constant of the pseudo second-order adsorption equation (g/mg.min). The constants q_e and K_2can be obtained by plotting t/q versus t in equation (4).

Intraparticle diffusion model equation is generally expressed as:

$$q_t = k_{int}\sqrt{t} + C \quad (5)$$

Where q_t (mg/g) is the amount adsorbed at time t and K_{int} is the intraparticle rate constant (mg/gmin$^{1/2}$), whereas the larger K_{int} values illustrate a better adsorption mechanism which is related to an improved bonding between ions and the adsorbent particles.

2.6. 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 (Haghseresht and Lu 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 (Weber and Chakkravorti 1974).The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

- *Langmuir isotherm*

The linear form of the Langmuir isotherm model is given by the following equation:

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

Where C_e is the equilibrium concentration of the adsorbate (MB) (mg/L), q_e, the amount of adsorbate adsorbed per unit mass of adsorbate (mgg^{-1}), and q_{max} and K_L are the Langmuir constants related to the monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. When C_e/q_e was plotted against C_e, a straight line with slope of $1/q_{max}$ was obtained, indicating that the adsorption of the MB on treated cattle bones Gudali Zebu produced from treated cattle bones follows the Langmuir isotherm. The Langmuir constants K_L and q_{max} were calculated from this isotherm and their values are given in Table 1.

- *Freundlich isotherm*

The well-known logarithmic form of the Freundlich model is given by the following equation:

$$Lnq_e = LnK_F + \frac{1}{n}LnC_e \quad (7)$$

Where q_e is the amount adsorbedate quilibrium (mg.g^{-1}), C_e the equilibrium concentration of the adsorbate (MB) and K_F and n are the Freundlich constants, n giving an indication of

how favourable the adsorption process and K_F (mgg^{-1} ($l\ mg^{-1}$)^n) is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or a distribution coefficient and represents the quantity of dye adsorbed onto treated cattle bone adsorbent for a unit equilibrium concentration.

The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghseresht and Lu 1998). A value for 1/n be low one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption. The plot of $\log q_e$ versus $\log C_e$ gives straight lines with slope of 1/n which shows that the adsorption of the MB also follows the Freundlich isotherm. Accordingly, the constants (K_F and n) were calculated and recorded in Table 1.

3. Results and Discussion

3.1. Infrared Spectroscopy of Adsorbent

Figure 2 shows at $3224cm^{-1}$ a band that corresponds to the –OH stretching vibration of alcohols. There is also a band between $201-1943cm^{-1}$ 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=CH_2), 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.

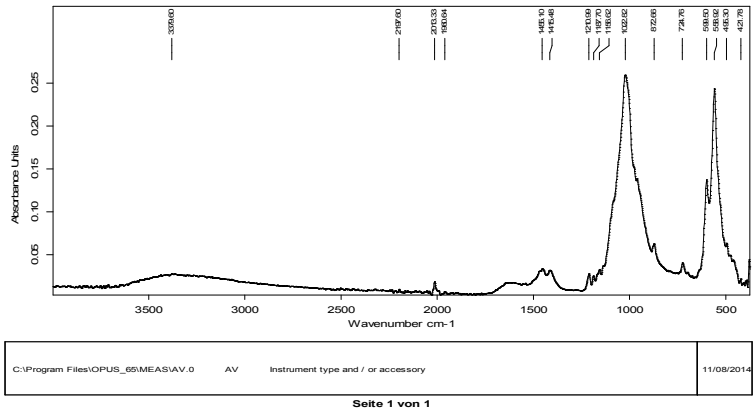

Figure 3. FTIR spectrum of activated carbon from bones of *Gudali zebu.*

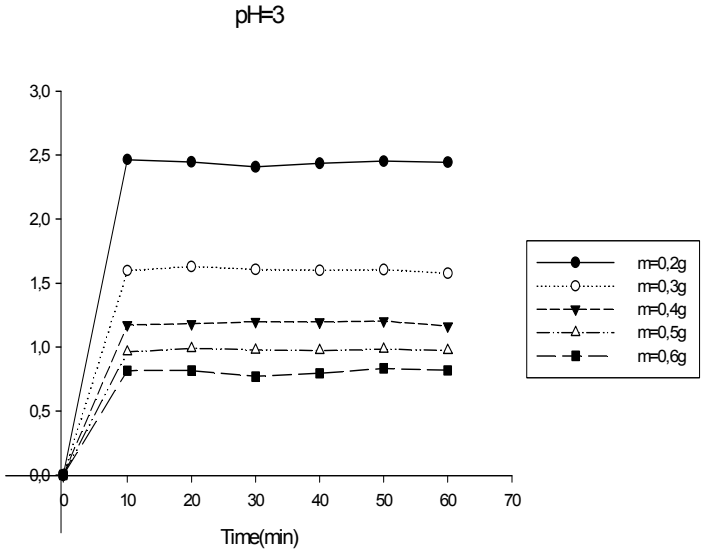

Figure 4. Kinetics study of MB adsorption at pH = 3.

3.2. Kinetics Studies

The influence of stirring time on the adsorption of on activated carbon is a very important step because it determines the time required to reach equilibrium. All studies were carried out at temperature of 25°C and initial MB concentration of 10 mg/L The results obtained are illustrated in figures 4, 5, 6 and 7 which show the variation of the amount of adsorbed on animal charcoal expressed in mg/g depending on the contact time. It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stage still saturation is allowed. The final dye concentration did not vary significantly after 10 min from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 10 min. It is basically due to saturation of the active sites which do not allow further adsorption to take place. These curves, shows that the adsorption kinetics is relatively fast. The maximum adsorption is reached after 10 minutes of contact, with a percentage of adsorption of the order of 98.58%. After this time, the adsorbed amount is constant, which shows that the equilibrium is reached between the adsorbate and the adsorbent.

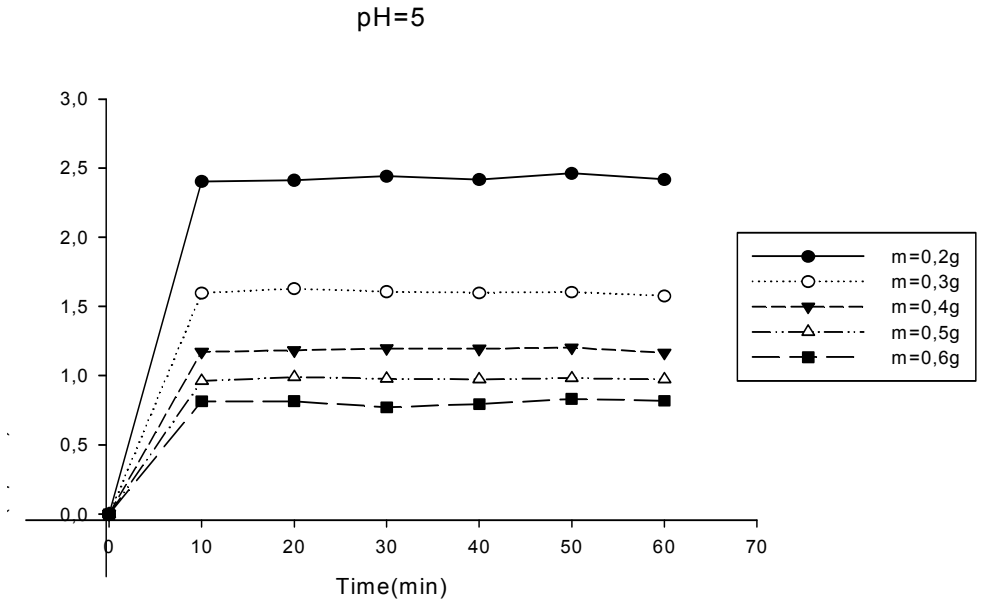

Figure 5. Kinetics study of MB adsorption at pH = 4.

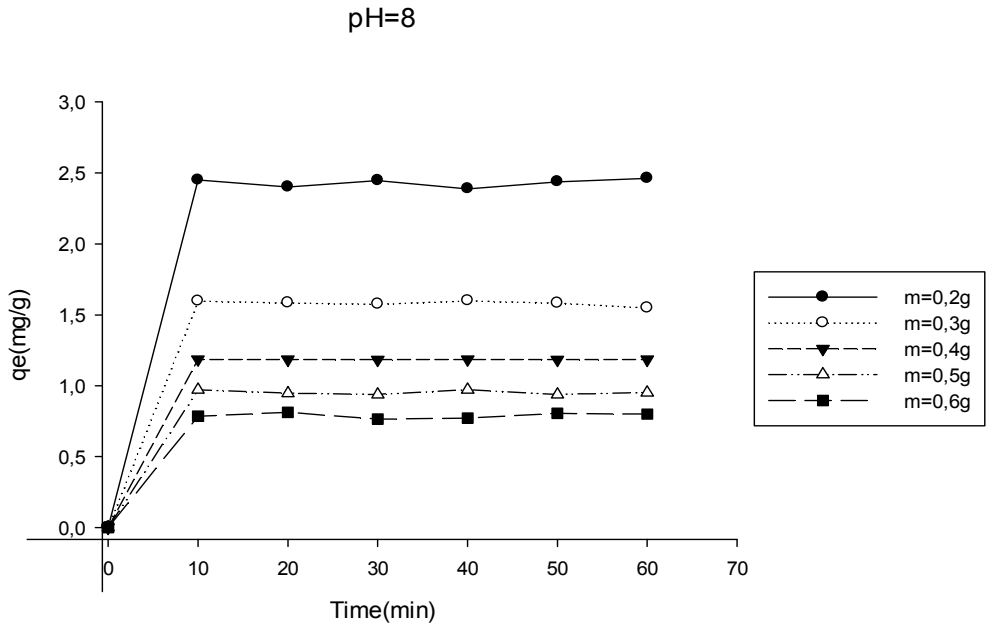

Figure 6. Kinetics study of MB adsorption at pH = 8.

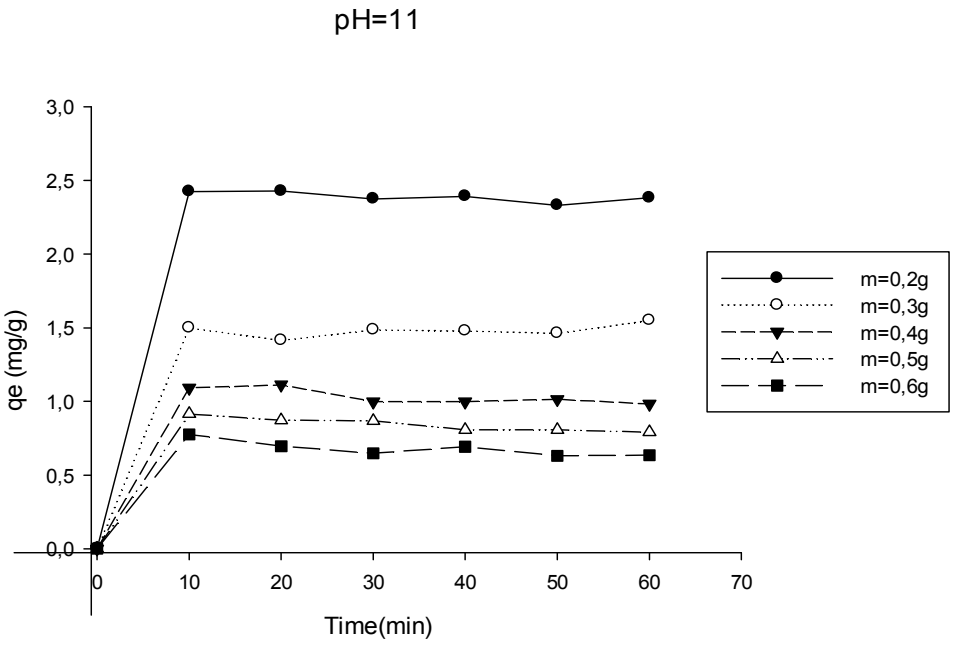

Figure 7. Kinetics study of MB adsorption at pH = 11

3.3. Effects of Adsorbent Mass

Fig. 3, 4, 5 and 6, respectively, we have shown the variations in the amounts of adsorbed mass based activated carbon. The initial concentration of adsorbate used is 10 mg/L. We find that the amount adsorbed decreases as the mass of activated carbon increases. It is known that the increase of the amount adsorbed increases with increase in the mass of adsorbent. The decrease in the amount adsorbed with increasing the dose of adsorbent is mainly due to the unsaturation of the adsorption sites. Another reason may be due to aggregation/agglomeration of the adsorbent particles on the surface of activated carbon animal which causes a decrease in the surface area available for adsorption (Madhava et al. 2008, Baliti et al. 2014). The decrease in adsorption capacity with an increase in the adsorbent concentration could be ascribed to the fact that some of the adsorption sites remained unsaturated during the process.

3.4. Effect of pH

The pH is an important factor in any adsorption study, because it may influence both the structure of the adsorbent and adsorbate, and the mechanism of adsorption. So it is wise to know the efficiency of adsorption at different pH. For this, we have shown in Fig. 4, 5, 6 and 7, the variations of the amount adsorbed versus pH of the medium, from an initial concentration of 10 mg/L for BM pH values ranging between 3 and 11.

As showed in figure 4, 5, 6 and 7, the maximum capacity and speed retention have not undergone significant changes, whether basic or acid medium. The little quantity variation of the adsorbed methylene blue at the equilibrium dependently of the pH of the solution shows that the electrostatic interactions are insignificant during the adsorption process despite the present of −COOH group at the adsorbent surface, the −COOH group that can produce H^+ ion depending of the pH of the solution. The progression of the quantity adsorbed suggests that the adsorption proceeds by an exchange reaction the methylene blue molecules and the chemical functions present at the contact surface. The results obtained show that the discoloration is not significantly influenced by varying the pH (Aarfane et al. 2014). The maximum adsorption is achieved with a percentage of adsorption of about 98.58; 98.51; 98.48 and 97.13% respectively for pH ranges of 3, 5, 8 and 11. There has been as light increase in the percentage of adsorption in acidic environments. Several authors found the opposite effect of pH on the adsorption of other cationic or anionic dyes on other types of activated carbon (Khare et al. 1988, Gupta et al. 1988, Gupta et al. 1990). The increasing trend of removal of the methylene blue with increasing pH is dependent on the nature of the adsorbent (Mohammad Arifur Rahman et al. 2012).

3.5. Effect of Initial Concentration of MB

Fig. 7 shows the adsorption percentage of methylene blue as a function of the concentration of the solution. It is apparent from Fig. 7 that the adsorption percentage increases with the concentration of methylene blue. The saturation of adsorption sites is gradually until a saturation level indicating saturation of the surface sites and thus formation of the monolayer. This result is explained by the fact that in addition to adsorption on the outer surface, there is also a possibility of transportation of the dye molecules within the pores of the

activated carbon animal; this can also be attributed to a gradient increase of the driving force with the increase of the initial concentration of dye. These results are in agreement with other studies (Al-Ghouti et al. 2005, Tsai et al. 2002, Erena and Afsin 2009, Kalavathy Helen and Miranda 2010). This coal has an interesting feature: it is effective even at low concentrations.

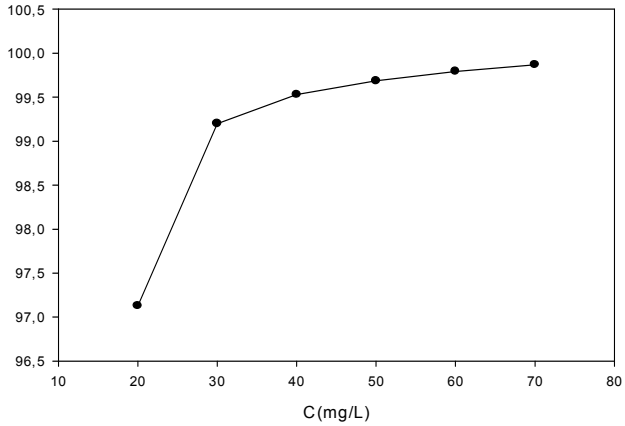

Figure 8. Effect of initial concentration on the adsorption of MB by the animal activated carbon.

The percentage removal of dye is highly dependent on the initial amount of dye concentration. The effect of the initial concentration of dye factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface. Figure 7 shows the progress of the MB removal with different initial MB concentrations. It is clear that the Yield of MB adsorption increased from 97.39% to 99.88% as the Methylene blue concentration was increased from 20 mg/L to 70 mg/L. The increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force of mass transfer at a high initial dye concentration (Bulutand AydIn, 2006). Though, further increase in dye concentration, don't affect adsorption yield. This will be attributed to the saturation of adsorption sites on the adsorbent surface (Erenand Acar, 2006).

3.6. Effect of Temperature

Fig.8 shows the adsorbed amount of methylene blue as a function of temperature. The temperature is an important variable in the adsorption process. The temperature affects the solubility of the adsorbate and the equilibrium constant for adsorption. As the adsorption is an exothermic phenomenon, an increase in temperature tends to reduce the adsorption capacity of the adsorbent. It is noted that the increase in temperature from 30 to 60°C induces an increase in the adsorption capacity. The experimental results show that this parameter positively affects this process by high energy contribution, and to overcome the repulsive forces located at the interfaces of liquid and solid media. So, it is interesting to note that the contribution of the heating has an important role in the kinetics of retention of the colorant irrespective of their affinity for the support (Baliti et al. 2014, Djamel Belaid and Kacha 2011). It can be concluded that there is an optimum temperature value to promote the adsorption of the dye and the mixture. Result indicates that the adsorption capacity of activated carbon of methylene blue increased with temperature. This may be a result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the activated carbon enabling large dyes to penetrate further (Emad et al., 2006).

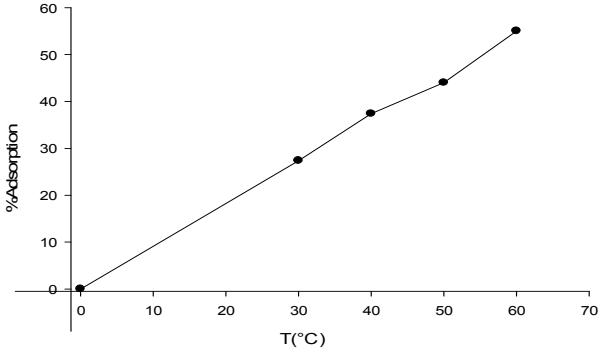

Figure 9. Effect of temperature on the adsorption of methylene blue by the animal activated carbon.

3.7. Adsorption Isotherms

The experimental results were compared with two isothermal theoretical models to describe the equilibrium adsorption process: models of Langmuir and Freundlich. It is clear from Table 1 that the values of the coefficient R^2 Langmuir and Freundlich are greater than 0.95 except m = 0.6g (R^2 = 0.606). This shows that these two models are applicable for explaining the adsorption of methylene blue on animal charcoal. Indeed, the Langmuir model indicates that we have a uniform distribution of adsorption sites while the model shows that our Freundlich adsorbent has a surface heterogeneity. As also illustrated in Table I, the value of 1/n includes the following values 0.041, 0.034, 0.053, 0.02 and 0.024 which indicates favourable adsorption (Adamson et al. 2001). This work has shown that utilization of treated animal charcoal will be useful in the treatment of methylene blue dyes from industrial waste effluents; it will also eliminate various ecological problems that these waste effluents could cause.

Table 1. Constants of Langmuir and Freundlich isotherms.

Model	Parameters	m=0.2g	m=0.3g	m=0.4g	m=0.5g	m=0.6g
Langmuir	K_L(L/mg)	73.5	80.87	38.82	209.8	118.45
	q_{max}(mg/g)	2.27	1.55	1.12	0.95	0.77
	R^2	0.999	0.999	0.999	0.999	0.999
Freundlich	K_F	2.29	1.55	1.14	1.06	1.22
	1/n	0.041	0.034	0.053	0.02	0.024
	R^2	0.964	0.953	0.992	0.958	0.606

3.8. Adsorption Kinetics

From Table 2 above that pattern of pseudo-first-order and intraparticle diffusion cannot be applied to explain the adsorption of MB because of their low values of correlation coefficients R^2 are less than 0.90. However, the coefficient correlation calculating kinetic model for the pseudo-second order is closer to unity. This indicates that the kinetic model of the second-order describes the experimental results of the adsorption of MB on activated carbon animal. We also note that the calculated amounts adsorbed theoretically (2.456 mg/g) of the kinetic model of pseudo-second order are very similar adsorbed amounts obtained experimentally (2.464 mg/g). The mechanism of adsorption of methylene blue is therefore based on the assumption of the kinetic model of pseudo-second order in two steps. The first step is the diffusion of methylene blue molecules to the surface of activated carbon animal. The second step is the interaction of the methylene blue molecules to the surface of animal charcoal.

Table 2. Kinetics parameters.

Model	Parameters	m=0.2g	m=0.3g	m=0.4g	m=0.5g	m=0.6g
Pseudo first-order	K_1(min^{-1})	0.071	0.061	0.076	0.083	0.067
	q_e(mg/g)	1.47	1.96	1.98	1.81	2.41
	R^2	0.652	0.571	0.588	0.697	0.375
Pseudo second-order	K_2(g.mg^{-1}.min^{-1})	1.75	3.63	5.75	56.85	4.24
	q_e(mg/g)	2.44	1.59	1.18	0.98	0.77
	R^2	0.999	0.999	0.999	0.999	0.986
Intra-particulate diffusion	K_{int}(mg.g^{-1}.m-$^{1/2}$)	0.279	0.182	0.135	0.112	0.086
	C(m^2.S^{-1})	0.71	0.479	0.353	0.287	0.249
	R^2	0.654	0.643	0.645	0.655	0.59

3.9. Calculation of Thermodynamic Parameters Related to Adsorption Process

Thermodynamic parameters, namely free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have an important role to determine spontaneity and heat change of the adsorption process. Thermodynamic parameters were calculated using the following relations (Karago et al.):

$$\Delta G^o = -RTLnk_c \quad (8)$$

The equilibrium constant K_c was calculated using the ratio:

$$K_C = \frac{q_e}{C_e}. \quad (9)$$

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

Where; K_c is the equilibrium constant, q_e and C_e are amount adsorbed (mg/g) and concentration of solution (mg/L) at equilibrium respectively. R is the universal gas constant (8.314J /mol/K) and T is the temperature (K). ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot LnK_c vs. 1/T, respectively (From equation 10), ΔG° were determined using LnK_c values for different temperatures. The Results were summarized in Table. 3.

Table 3. Thermodynamic parameters of adsorption of methylene blue on activated carbon at different temperatures.

T(K)	ΔG°(Kj.mol^{-1})	ΔH°(Kj.mol^{-1})	ΔS°(Kj.mol^{-1}.K^{-1})	R^2
303	-35.62			
313	-36.425	-12.95	0.075	0.975
323	-37.175			
333	-37.925			

The thermodynamic parameters, the standard Gibbs energy (ΔG°), standard enthalpy (ΔH°) and entropy (ΔS°) for methylene blue at various temperatures are shown in Table 3. As shown in Table 3, the negative values of the standard Gibbs energy (ΔG°) methylene blue indicate that the adsorption is possible and thermodynamically spontaneous. We note also that, for the activated carbon of the *Zebu Gudali* cattle bones, ΔG° decreases with increasing temperature of the solution. This can be explained by the fact that adsorption becomes easier, thus indicating the presence of a high drive strength. The value of the standard enthalpy (ΔH°) is negative, and this indicates that the adsorption of methylene blue on activated carbon reaction bones *zebu* cattle *Gudali* is exothermic. Furthermore, examination of the values of the standard enthalpy of adsorption (<40 kJ/mol) shows that it is a physisorption (Gherbi 2008). The positive value of standard entropy (ΔS°) shows decreasing appearance at the solid/liquid interface during the adsorption of methylene blue

on animal activated carbon.

4. Conclusion

This study revealed that the activated carbon prepared from the bones of *Gudali zebu* cattle (*Bos Indicus*) could be used as an effective adsorbent material for the treatment of methylene blue in waste water. It also shows that the adsorption of methylene blue on activated carbon depends on the contact time, initial concentration, pH, temperature and adsorbent dose. In the study of the adsorption kinetics, the model of pseudo-second order allows a better or relation between the adsorption data model of pseudo-first order; this suggests that the rate limiting step may be a physical adsorption rather than diffusion. Modeling the adsorption process mounted it in all the cases studied follows the model of pseudo-second order, the time that the isotherm follows the Langmuir model. The material (bones of zebu cattle Gudali) for the study of the adsorption is not only available, but also a product of animal waste. An activated carbon prepared from the bones of cattle zebu Gudali is economic in the treatment of waste water containing methylene blue.

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