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Equilibrium and kinetic modelling of adsorption of methyl orange dye on palmyra palm nut

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Abstract

The adsorption of methyl orange dye by an agro waste based activated carbon prepared from palmyra nuts was investigated in order to analyze the equilibrium and kinetic effects of the process, as well as assess its viability as an adsorbent. The activated carbon was prepared using chemical activation with phosphoric acid (H_3PO_4). The effect of various factors namely pH, initial adsorbate concentration, adsorbent dosage, contact time, and adsorbent particle size was studied to identify the adsorption capacity of palmyra nutshell. The percentage removal of dye increased with increasing adsorbent dosage and contact time, but decreased with increasing dye concentration and adsorbent particle size. The highest uptake of 97.5% was observed at a pH of 8.0.Adsorption data were modeled using Langmuir and Freundlich isotherms. The kinetic data were also applied to the pseudo-first-order and pseudo-second-order models. However, the adsorption process was well described by Langmuir isotherm and conformed well to pseudo-first-order and pseudo-second-order kinetic models. It was evident from the results that palmyra nutshell, a low-cost adsorbent can be used for the removal of dyes from aqueous solution.

Keywords: Equilibrium; kinetic; methyl orange; dye; adsorption

1. Introduction

Dyes have long been used in paper and pulp, textile, leather, cosmetics, printing and food industries. Wastewater discharged from these industries into the water bodies poses severe problems to aquatic and human lives. They are considered to be particularly dangerous compounds for the environment (Sapari, 1996; Klimiuk et al, 1999). Their presence, even in very low concentration, is highly viable and will affect aquatic life as well as food web (Rita et al, 2005).

According to Chakrabarti et al (1998), nearly 40,000 dyes and pigments are listed which consist of over 7000 different chemical structures. Most of them are completely resistant to biodegradation processes as they are generally stable to light, oxidizing agent and possess complex aromatic molecular structures (McKay et al, 1987). Most of these dyes are toxic, mutagenic and carcinogenic, hence leading to several damages to the liver and central nervous system in humans, as well as degrading the aesthetic nature of the environment (Aksu and Tezer, 2000).

The conventional methods of colour removal from industrial effluents include ion exchange, chemical oxidation, activated carbon adsorption, membrane separation, dilution, electrochemical treatment, coagulation and flocculation (Easton et al, 1995). The adsorption process, amongst all the other methods, has been shown to be one of the most efficient and versatile methods to remove dyes from effluents (Rufattulah et al, 2009). However, relatively high operating costs and problems with regeneration of the spent carbon, limit its commercial application (Charkraborty et al 2005).

Many researchers have investigated the use of cheap and efficient alternative sources derived from agricultural waste (Singh et al, 2003) for the production of activated carbon to remove dyes from wastewater. Some of these alternative sources of activated carbon are palm ash, sawdust, almond shells, rice husks, coconut shells, and many more (Ahmad et al, 2006; Robinson et al, 2002). The objective of this study is to determine the potential of palmyra palm nut as an adsorbent in the removal of methyl orange dye from wastewater effluent.

2. Materials and methods

2.1. Preparation of activated carbon

Palmyra palm nuts were obtained from Nnamdi Azikiwe University, Awka, Nigeria. The palm nuts were washed with deionized water, dried in the sun, ground into fine particles and sieved to a particle size of 300μm. 200g of sample was impregnated with concentrated orthophosphoric acid at the ratio of 1:1

(wt %). The impregnated sample was dried in a Memmert oven at 120^0C for 24hrs. The dried sample was carbonized in a Muffle furnace for 2hr at 500^0C. After cooling to the ambient temperature, the sample was washed with de-ionized water several times until pH 6-7, filtered with Whatman No.1 filter paper and then dried in the oven at 110^0C for 8hours. The sample was crushed and passed through different sieve sizes and then stored in air- tight bottle ready for use.

2.2. Characterization of activated carbon

Determination of pH of activated carbon: The pH of the carbon was determined using standard test of ASTM D 3838-80 (ASTM, 1996).

Determination of moisture content: Moisture of activated carbon and raw materials was determined using ASTM D 2867-91 (1991).

Determination of bulk density of activated carbon: The bulk density of the activated carbon was determined according to the tamping procedure by Ahmedna et al (1997).

Determination of volatile content: 1.0g of sample was weighed and placed in a partially closed crucible of known weight. It was heated in a muffle furnace at 900^0C for 10mins.

Determination of percentage fixed carbon: The percentage fixed carbon is given by:
100 – (Moisture content + ash content + volatile matter) %.

Determination of iodine number of activated carbon: The iodine number was determined based on ASTM D 4607-86 (1986) by using the sodium thiosulphate volumetric method.

Determination of surface area: The specific surface area of the activated carbon was estimated using Sear's method (Al-Qadah and Shawabkah, 2009; and Alzaydien, 2009)

2.3. Adsorbate preparation and adsorption study:

A stock solution of 500mg/l of methyl orange dye was prepared by diluting 500mg of the dye in one litre of distilled water. The adsorption experiments were performed by batch method where samples of 0.5g of the produced activated carbon were equilibrated with 250ml of the solution with intermittent stirring at a speed of 120rpm for two hours.

The effect of contact time on the adsorption of the dye was observed for 10mins, 20mins, 30mins, 40mins, 60mins, 120mins, and 180mins at a concentration of 50mg/l, pH of 8.0, dosage of 0.5g, and particle size of 150µm.

Effect of adsorbent dosage was studied for dosages of 0.5g, 1.0g, 1.5g, 2.0g, 2.5g and 3.0g at a concentration of 50mg/l, pH of 8.0, and particle size of 150µm for 2 hours.

The effect of the initial dye concentration was investigated by varying the concentration (50mg/l, 100mg/l, 150mg/l, 200mg/l, 250mg/l and 300mg/l) at a pH of 8.0, particle size of 150µm, and dosage of 0.5g of activated carbon for 2 hours.

The pH of the solution was varied (2.0, 3.0, 5.0, 7.0, 8.0, 10.0, and 12.0) using 0.1M HCl and 0.1M NaOH at a concentration of 50mg/l, particle size of 150µm, and dosage of 0.5g of activated carbon for 2 hours.

Particle sizes of the activated carbon was varied (150µm, 300µm, 600µm, 850µm and 1000µm) at a dosage of 0.5g, pH of 8.0, and concentration of 50mg/l for 2 hours.

The absorbance value at each stage was estimated with a UV Visible spectrophotometer at a wavelength of 465nm. The adsorption capacity, q_e (mg/g) and percentage adsorbed were calculated from equation (1) and equation (2) respectively.

$$q_e = [(C_o - C_e)\,V/m] \quad (1)$$

$$\%\ Adsorbed = [(C_o - C_e)/C_o]\,x\,100 \quad (2)$$

where, C_o and C_e are the dye concentrations (mg/l) at initial and any time t, respectively, 7v the volume of the solution (L), and m the mass of adsorbent used (g).

3. Results and discussions

3.1. Characteristics of activated carbon derived from palmyra palm nut

The physio-chemical characteristics of activated carbon are shown in Table 1. The values of fixed carbon, bulk density, surface area, volatile matter, iodine number were similar to the values obtained by Karthikeyan et al (2008).

Table 1
Physico-chemical characteristics of activated carbon derived from nipa palm nut

Properties	Values
pH	6.8
Bulk density, g/cm3	0.61
Iodine number, mg/g	785.78
Moisture content, %	4.1
Volatile matter, %	18.14
Ash content, %	3.30
Fixed carbon, %	78.56
Surface area, m^2/g	820.37

3.2. Effect of concentration on the adsorption of methyl orange dye

From Figure 1, it is observed that the percentage removal of methyl orange dye decreased with increase

in concentration. Maximum percentage removal of 97.5% occurred at 50mg/l. The percent removal decreased from 97.5% to 59.5% as the concentration increased from 50mg/l to 300mg/l.

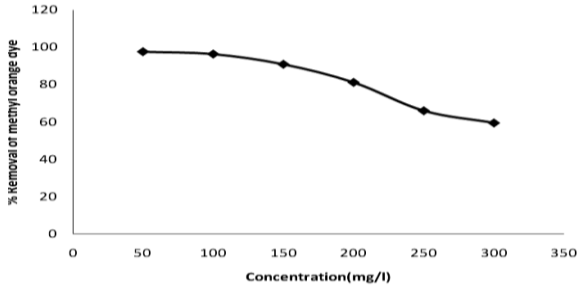

Fig.1. Effect of concentration on the adsorption of methyl orange dye.

3.3. Effect of contact time on the adsorption of methyl orange dye

Figure 2 shows that percentage removal of methyl orange increased with increase in contact time. It can be observed that there was rapid adsorption between 40mins and 60mins. Percentage removal increased steadily with time until 120mins, which is the optimum contact time. Further increase in time to 180mins resulted to just 0.3% increase in percentage removal.

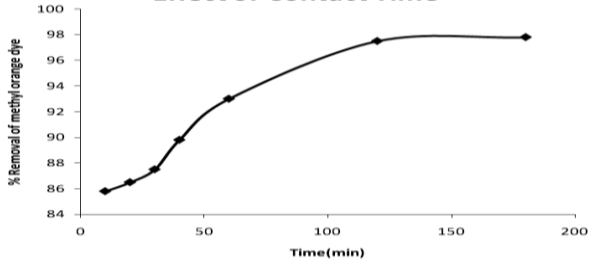

Fig. 2. Effect of contact time on the adsorption of methyl orange dye.

3.4. Effect of pH on the adsorption of methyl orange dye

The effect of pH on percentage removal is shown in Figure 3. The pH of the aqueous solution was varied from 2 to 12. The maximum adsorption efficiency was 97.5% at pH 8, and this pH value was selected as optimum pH for further studies. There was decrease in percentage removal from pH 10.

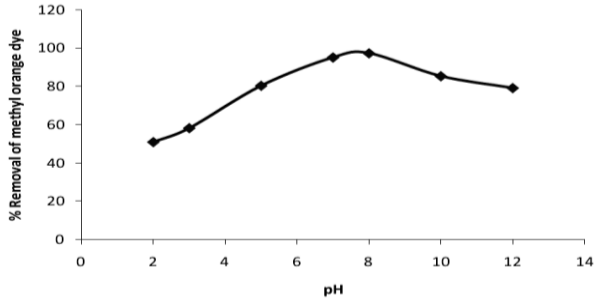

Fig. 3. Effect of pH on the adsorption of methyl orange dye.

3.5. Effect of adsorbent dosage on the adsorption of methyl orange dye

Figure 4 shows the effect of adsorbent dosage on percentage removal of methyl orange. The percentage removal increased from 97.5% to 99.5% as the adsorbent dose was increased from 0.1g to 3.0g. This is due to increase in active sites of the adsorbent as the dosage is increased, resulting to availability of more surface area for the adsorption.

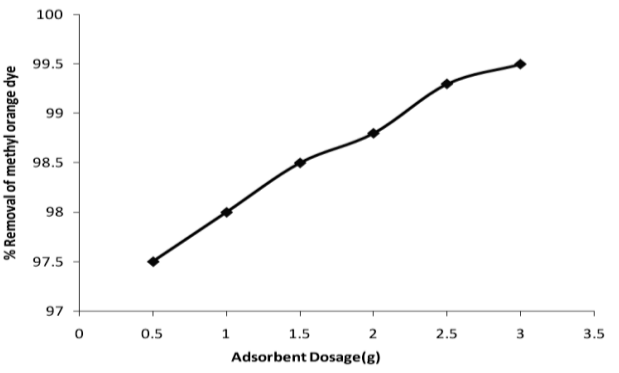

Fig. 4. Effect of adsorbent dosage on the adsorption of methyl orange dye.

3.6. Effect of adsorbent particle size on the adsorption of methyl orange dye

Figure 5 shows the effect of varying particle size on the percentage removal of methyl orange. It can be seen that the percentage removal of methyl orange dye decreased as the particle size increased from 150µm to 1000µm. The maximum percentage removal was recorded using 150µm particle size.

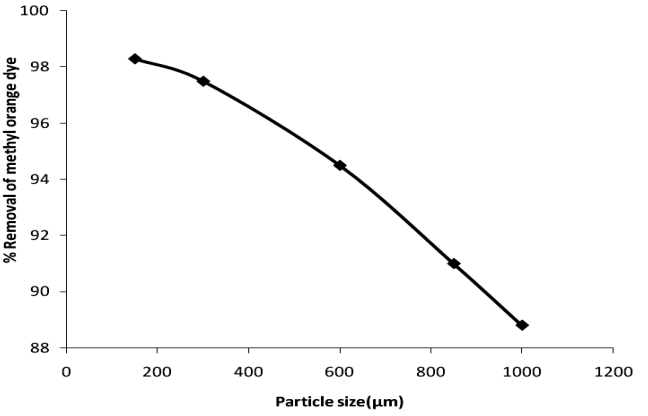

Fig. 5. Effect of adsorbent particle size on the adsorption of methyl orange dye.

3.7. Adsorption isotherm

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 (Hameed et al, 2006).

3.8.1. Langmuir isotherm model

The Langmuir adsorption model is given by:

$$q_e = Q \quad \frac{b\,C_e}{1+b\,C_e} \tag{3}$$

The Langmuir equation can be described by the linearized form (Sivakumar and Palanisamy, 2009; Sekar et al,2004; Nwabanne, 2008).

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o}\right) C_e \tag{4}$$

Where C_e is the equilibrium concentration of the adsorbate, q_e the amount of adsorbate per unit mass of adsorbent (mg/g), and Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When C_e / q_e is plotted against C_e, straight line with slope $1/Q_0$ indicates that adsorption follows the Langmuir isotherm.

The Langmuir constants, Q and b were evaluated from the intercept and the slope of the linear plot of experimental data of $^1/q_e$ versus $^1/c_e$ (Figure 6) and presented in Table 2. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L, defined as (Ahmed et al, 2006).

$$R_L = \frac{1}{1+bC_O} \tag{5}$$

Where, C_o is the initial dye concentration. The R_L value implies the adsorption to be unfavourable (R_L > 1), Linear (R_L =1), favourable (O<R_L<1), or irreversible (R_L=0). $R_L$value for dye adsorption is less than 1 and greater than zero indicating favourable adsorption under conditions used in this study. The correlation coefficient showed that adsorption of the dye followed Langmuir model.

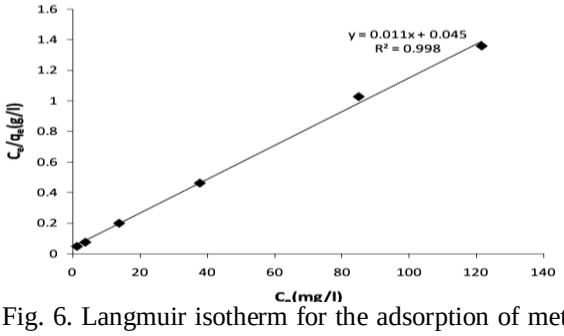

Fig. 6. Langmuir isotherm for the adsorption of methyl orange dye.

3.8.2. Freundlich isotherm

The Freundlich adsorption isotherm (Ozacar, 2003) is

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

A linear form of this expression is:

$$\log\ q_e = \log K_F + {}^1/_n \log C_e \tag{7}$$

where K_F and n are Freundlich constants, n giving an indication of how favourable the adsorption process is and K_F is the adsorption capacity of the adsorbent. K_F and n are determined from the linear plot of $\log q_e$ *versus* $\log C_e$. From the linear plots of Inq_e versus InC_e, (Figures 7) values of Freundlich constants K_F and n were calculated from the intercept and slope, respectively, and are presented in Table 2. The magnitude of the exponent, n gives an indication of the favourability and capacity of the adsorbent/adsorbate system. Karthikeyan et al (2004) has reported that n values between 1 and 10 represent favourable adsorption conditions. In this work, the exponent is 1<n<4, showing beneficial adsorption for the system. The correlation coefficient of 0.909 indicated the dye adsorption did not follow Freundlich model.

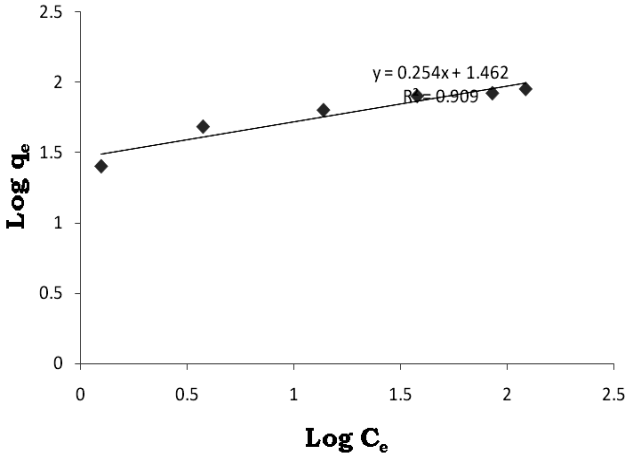

Fig. 7. Freundlich isotherm for the adsorption of methyl orange.

Table 2
Langmuir and Freundlich parameters for the adsorption of methyl orange dye

Parameters	Value
Langmuir	
Q (mg/g)	90.91
b (L/mg)	0.24
R_L	0.1
R^2	0.998
Freundlich	
1/n	0.254
K_f (L/g)	28.97
R^2	0.909

3.9. Kinetic models

3.9.1. Pseudo first-order kinetic model

The Pseudo first-order kinetic model was proposed by Lagergren (Maniatis and Nurmala, 1992). The equation is generally expressed as

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (8)$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mgg^{-1}), K_1 is the rate constant of pseudo first -order adsorption ($L\ min^{-1}$).

After integration and applying boundary conditions, t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the integrated form of equation 8 becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \quad (9)$$

The values of log ($q_e - q_t$) are linearly correlated with t. The slope and intercept of plots of log (q_e-q_t) versus t were used to determine the pseudo-first order rate constants, K_1 and q_e at different temperatures. The results of the q_e and K_1 were evaluated and listed in Table3 .The correlation coefficients ranged of 0.995 indicated that dye adsorption fitted well to pseudo first-order kinetic equation.

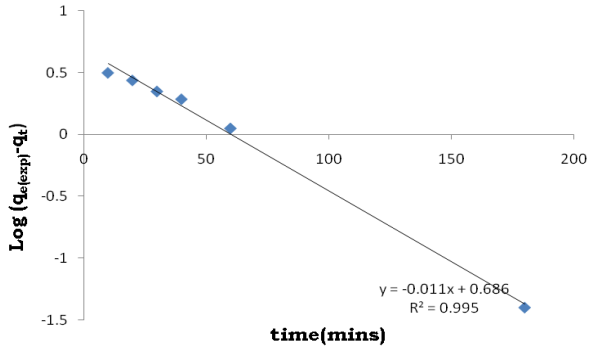

Fig. 8. Pseudo-first-order plot for the adsorption of methyl orange dye.

3.9.2. Pseudo second- order model

The adsorption kinetics may also be described by a pseudo second-order equation (Chiou and Li, 2002; Nwabanne and Igbokwe, 2008; Ho and Chiang, 2001).

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (10)$$

Integrating equation 10 and applying the boundary condition

$$t = 0\ to\ t = t\ and\ q_t = 0\ to\ q_t = q_t,\ gives \quad (11)$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2\ t$$

Equation 11 can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\ 2}} + \frac{1}{q_e}t \quad (12)$$

where K_2 is the rate constant t of pseudo second-order adsorption ($gmg^{-1}\ min^{-1}$). The slope and intercept of plot of t/q_t versus t were used to calculate the pseudo second-order rate constant, K_2 at different temperatures. Table 3 shows the results of the rate constant and q_e by pseudo second-order models. The correlation coefficient for the pseudo second-order adsorption model has high value (.999). Its calculated equilibrium adsorption capacity, q_e is consistent with experimental data. These facts suggest that the pseudo second-order adsorption mechanism is predominant. Similar phenomena have also been observed in the adsorption of direct dye on palm ash (Ahmad et al, 2006).

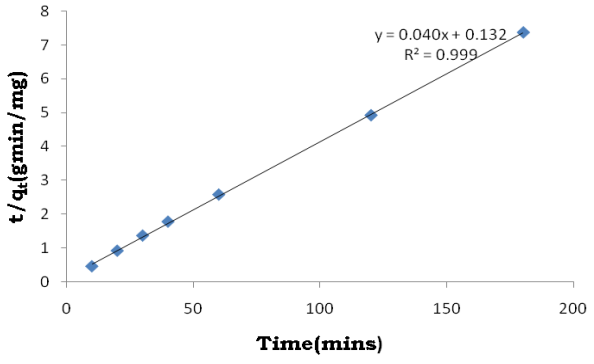

Fig. 9. Pseudo second-order plot for the adsorption of methyl orange dye.

Table 3
Adsorption kinetic parameters for methyl orange dye adsorption

Parameters	Values
Pseudo first-order	
K_1 (min^{-1})	0.025
q_e (mg/g)	4.853
R^2	0.995
Pseudo second-order	
K_2 (g/mg min)	0.012
q_e (mg/g)	25.0
R^2	0.999

4. Conclusion

The equilibrium and kinetic study of the removal of methyl orange dye contaminant from aqueous solution using activated carbon derived from palmyra palm-nut has been investigated in this work. The adsorption experiment indicated that palmyra palm nut was effective in removing methyl orange from aqueous solution. The amount of dye adsorbed was found to vary with time, pH, initial dye concentration, particle size and adsorbent dosage. The linear Langmuir and Freundlich isotherm models were applied to describe equilibrium isotherms for the adsorption. The adsorption data conformed to the Langmuir isotherm. The adsorption data also conformed to the pseudo-first-order and pseudo-second-order kinetic models.

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