

# Adsorption of Alizarin and Fluorescein Dyes on Adsorbent prepared from Mango Seed.

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## ABSTRACT

An activated carbon was prepared from mango seeds (MGA) using a one-step procedure with 62.27% yield, 2.23% ash content, 819.80 m<sup>2</sup>/g surface area, 762 mg/g iodine number and the CHN analysis gave 52.31% C, 3.38% H, and 1.02% N. The FTIR spectroscopy revealed N-H, C-H, C=C and C-O stretching vibrations. The adsorptions of Alizarin and Fluorescein dyes were rapid at the first 15 min of agitation with 86.90% and 85.75% removal respectively. The adsorption equilibrium was achieved in 90 min of agitation with 90.44% Alizarin dye and 91.32% Fluorescein dye removal. The correlation coefficient, R<sup>2</sup>, for a pseudo-first order and pseudo-second order kinetic models are 0.938 and 0.999, respectively. The adsorption data for alizarin and fluorescein dyes on MGA fitted well into Langmuir isotherm with correlation coefficient (R<sup>2</sup>) very close to unity and Langmuir maximum adsorption constant, q<sub>m</sub> > 1.00. The activation energy (E<sub>a</sub>) of the adsorption process of alizarin and fluorescein dyes on MGA was found to be +13.84 and 16.56 KJ/mol respectively. The evaluated thermodynamic quantities supported physical, spontaneous and endothermic adsorption process.

(Keywords: activated carbon, adsorption isotherms, alizarin dye, fluorescein dye, kinetics, mango seeds, thermodynamics)

## INTRODUCTION

In developing nations, the activated carbon (AC) requirements are met by importation in enormous quantity at a very high cost depleting their foreign reserves. Large quantities of agricultural by-products, which can be used for AC production to meet local demands, are generated annually. If AC production technology is developed to

harness these by-products it will be a value added product and resource for other industries.

An effluent from textile industries are often highly loaded with mixtures of dyes, inorganics and toxic organics, dissolved solids, acids and bases (Gupta et al., 2004) which make the removal by biological process difficult. The effluent discharged from textile industries consist essentially of dyes and such discharge into natural bodies of water is undesirable for several reasons. For example, it diminishes the aesthetic, biological and chemical qualities of water bodies and can also be devastating to the health of its consumers (man and aquatic organisms) because of its persistence and non-biodegradability characteristics (Asiagwu et al., 2012). Moreover, small concentrations of these dyes in effluent water are highly visible. Consequently, the removal of color from effluents containing various kinds of synthetic dyes becomes important (Igwe and Abia, 2003).

The conventional methods of color removal from industrial effluents include biological treatment, coagulation, floatation, adsorption, oxidation and hyper filtration (Asiagwu et al., 2012). Among the treatment options, adsorption appears to have considerable potential for the removal of color from industrial effluents. Adsorption onto activated carbons is an acceptable process for micro-pollutants removal (Faur-Brasquet et al., 2003).

Activated carbon is a solid, porous and black carbonaceous material that has an essentially graphitic structure (Norlia et al., 1999). The removal of all non-carbon impurities and the oxidation of the carbon surface distinguished it from elemental carbon. Besides that, AC contain physical characteristic such as large internal surface area and pore volume. The large surface

area results in a high capacity for absorbing chemicals from gases or liquids. The adsorptive property stems from the extensive internal pore structure that develops during the activation process. AC were prepared from mango peel using both physical and chemical activation methods (Bello and Ahmad, 2011) and was used for the removal of inkjet and helactine dyes from aqueous solutions, raw and NaOH treated mango seed integuments (Malekbalala et al., 2012) was used for the removal of Safranin, AC from mango seed shells as filters for removing dyestuff from solution was investigated in both batch and column modes (Itodo et al., 2011). Some other agricultural by-products that have been used for the preparation of AC include rubber wood sawdust (Srinivasakannan and Abu Baker, 2004), dates stone (Alhamed and Bamufleh, 2009), bamboo-based (Hameed et al., 2007).

A number of the research works were aimed at water treatments which include granulated activated carbon (GAC) prepared from pecan and almond shells for the removal of VOCs, COD,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  (Bansode, 2002), jatropha husk for the removal of anions, heavy metals, organics and dyes (Namasivayam et al., 2007), mango seed shell for colour removal (Akpen et al., 2011), Rosa canina for the removal of dye (Gurses et al., 2006), rice husk and corn-cobs for phosphate removal (Aloko and Adebayo, 2007).

The increased interest in the use of agricultural based precursors for the preparation of AC is partly due to its low cost, renewable source and it is a way of recycling agricultural wastes which could otherwise constitute environmental pollution, particularly as it relates to solid waste management. There are wide variations in the adsorptive properties of AC prepared from different agricultural base materials which is essentially due to the optimization of preparation conditions (Torregrosa-Macia, et al., 1997). Activated carbon with a relatively wide pore size distribution can be obtained solely through a chemical activation process (Torregrosa-Macia et al., 1997). Physical activation can further enhance the adsorbent's pore structure due to a partial oxidation of the carbonized material by gases such as  $\text{CO}/\text{CO}_2$  or steam (Molina-Sabio et al., 1996). The focus of this research was to explore the feasibility of mango seed-based activated carbon for the removal of Alizarin dye and Fluorescein dye from aqueous solutions and also to optimize the adsorption conditions that will ensure high dyes uptake.

## **MATERIALS AND METHODS**

### **Sample Collection and Preparation of the Adsorbent**

The semi-dried mango seeds were collected within the University of Ilorin campus, the samples were washed with distilled water to remove all impurities, sun dried and cracked using hammer. The resulting cracked seeds were further sun-dried. All reagents that were used in this study were of analytical grade. Working standard solutions were prepared from analytical grade reagents and by serial dilution method from the stock solutions.

### **Production of Activated Carbon**

A single-step production method which involves carbonization and activation by thermal decomposition of the raw materials that were already impregnated with activating agent was adopted. A 65 g of the raw mango seeds (MG) was soaked in 100 ml of 50 % (v/v)  $\text{H}_3\text{PO}_4$  acid at room temperature for 48 hr, the phosphoric acid was decanted and the impregnated sample was washed thoroughly with deionized water until the pH reading was almost neutral. The impregnated raw material was carbonized in a muffle furnace at 400 °C for 90 minutes. After cooling, the carbonized material was weighed to determine percentage yield then pulverized to reduce the size and sieved using a 100  $\mu\text{m}$  sized sieve. Thereafter, samples with diameter  $\leq 100 \mu\text{m}$  were used for other determinations and experiments.

### **Characterization**

The MGA yield was determined by mass difference between the starting raw seeds (MG) and the MGA obtained (Fapetu, 2000). The MGA moisture content was determined by oven drying at 103°C (Hesse, 1997), the volatile organic matter by American society for Testing and Materials (ASTM) (Hesse, 1997), the ash content by ASTM (ASTM D2866), surface area by titration (Bhattacharyya and Gupta, 2006), Bulk density by using density bottle (Yoshiguki and Yukata, 2003), thermometric determination of pH in  $\text{CO}_2$  free water ([www.scribd](http://www.scribd.com)) and the iodine number by ASTM procedure (ASTM D4607). The carbon, hydrogen and nitrogen were analysed by CHN CE 440 analyser, the metals composition by XRF axios pw: 4400/24 model and the surface

functional groups by Perkin Elmer model 100 FTIR.

### **Determination of the Adsorption Capacity**

A 50 ml of varying concentrations of the dyes (2, 5, 10, 15, 20, 30, and 50 mg/L) were contacted with 1g of the adsorbent. The contents were agitated on an incubator shaker, KBLEE1001 for a period of 8 hr. The un-adsorbed dye was determined with Beckman Coulter, DU-730 life science UV/Vis spectrophotometer. The quantity sorbed was calculated from Eqn. 1 (Adekola et al., 2011).

$$q_e = \frac{C_i - C_f}{M} \times V \quad (1)$$

Where  $q_e$  is the quantity of dye adsorbed (mg/l),  $C_i$  and  $C_f$  are the initial and final concentration of the dyes (mg/L),  $V$  is the volume of the standard solution used (ml) and  $M$  is the mass of the adsorbent (g) used.

### **Effect of Agitation Time**

A 50ml of each of the dye solution were measured into a 100 ml flask and contacted with 1g of the adsorbent at room temperature. The flasks were labelled for time difference of 5, 10, 15, 30, 45, 60 and 90 minutes and flasks were tightly covered and agitated for the appropriate time using incubator shaker. At the end of the timing scheduled each of the flasks were brought out and suspensions were filtered using Whatman No. 1 filter paper. The un-adsorbed dye was determined with Beckman Coulter, DU-730 life science UV/Vis spectrophotometer. The quantity sorbed was calculated from Eqn. 1.

### **Effect of Adsorbent Dosage on Adsorption**

The effect of adsorbent dosage on the adsorption of dye ions by the MGA was performed according to a literature work (Asiagwu et al., 2012). A variable mass, 0.25, 0.5, 1, 2, 3 and 4 g of the adsorbent were weighed into five different conical flasks. A 50 ml of the 30 mg/l of each dye solutions were measured into the two (2) sets of the five conical flasks (i.e., experiment was performed on duplicate samples). The flask was labelled for dosage differences. The flasks were

tightly covered, agitated for 90 min and thereafter, the suspensions were filtered using Whatman No. 1 filter paper. The un-adsorbed dye was determined with Beckman Coulter, DU-730 life science UV/Vis spectrophotometer. The quantity sorbed was calculated from Eqn. 1.

### **Effect of Temperature on Adsorption**

The effect of temperature on adsorption was performed according to a literature work (Mishra et al., 2009). A 2 g of the adsorbent was weighed into two sets of five conical flasks and 50 ml of the dye solutions (30 mg/L) were measured into the flasks. The flasks were labelled for temperature difference of 35, 40, 50, 60, and 70 °C. The flasks were tightly covered and heated at the appropriate temperatures using KBLEE1001 thermostated incubator shaker for the time interval of 5, 10, 15, 30, 45, 60 and 90 minutes at every temperature. At the end of the timing schedule, each of the flasks was brought out and the suspensions were filtered using Whatman No. 1 filter paper. The un-adsorbed dye was determined with Beckman Coulter, DU-730 life science UV/Vis spectrophotometer. The quantity sorbed was calculated from Eqn. 1.

### **Adsorption Isotherms**

Three isotherm equations were used to find out the relationship between the equilibrium concentration of the adsorbate in the liquid phase and in the solid phase. More importantly, to determine which of the isotherms best describes the adsorption process. Experimental data were substituted into the equations and appropriate graphs, constants and other variables were generated for each of the following equations:

a) Langmuir:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \left\{ \frac{1}{q_m} \right\} C_e \quad (2)$$

Where  $b$  (L/mg) and  $q_m$  (mg/g) are Langmuir coefficient representing the equilibrium constant for the Adsorbate-Adsorbent equilibrium and the monolayer capacity,  $C_e$  is the equilibrium concentration of the solute in the bulk solution (mg/l) and  $q_e$  is the amount of solute sorbed per unit weight of adsorbent at equilibrium (mg/g).

The plot of  $\frac{C_s}{q_e}$  versus  $C_e$  was plotted, the slope and the intercept are  $\frac{1}{q_m}$  and  $\frac{1}{bq_m}$ , respectively.

$$b) \text{ Freundlich:- } q_e = K_f C_e^{1/n} \quad (3)$$

The linearized form of Freundlich equation is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where  $C_e$  and  $q_e$  are the equilibrium concentration of the dyes in liquid phase and in solid phase respectively,  $K_f$  and  $n$  are Freundlich coefficients relating to overall adsorption capacity (mg/g) and surface heterogeneity (dimensionless) respectively. The plot of  $\log q_e$  versus  $C_e$ , the intercept of the graph is  $\log K_f$  while the gradient is  $1/n$ .

c) Temkin:

$$-q_e = B \ln A + B \ln C_e \quad (5)$$

Where  $B = RT/b$ ,  $b$  is the Temkin constant related to heat of sorption (J/mol);  $A$  is the Temkin isotherm constant (L/g),  $R$  is the gas constant (8.314 J/mol K) and  $T$  is the absolute temperature (K). The linearized Langmuir, Freundlich and Temkin forms were used for graphical plots and the corresponding constants were obtained.

## RESULTS AND DISCUSSION

The Table 1 summarized some of the characteristics of MGA. The % efficiency of MGA was 62.27 %, this value was relatively higher compared to the reported yield of 46.08 % and 51% by Faust and Aly, (1983) and Sahu et al., 2010.

The Ash content is a reflection of the amount of inorganic substituent present and was obtained as 2.33 %. The ash content of most AC from agricultural products is within 0.2-13.4 % (Ioannidou and Zabaniotou, 2007).

Volatile matter is due to the residual organic compounds in the prepared MGA. The volatile matter obtained was 26.79 %, which is higher than the value reported by Raffiea et al., 2012, (20.9 %).

Bulk density indicates the fiber content of the precursor, the lower the value the better for its regeneration upon use (Yang et al., 2003). The MGA bulk density was 0.67 g/ml which is within the values reported by Nale et al., 2012 (0.45 g/ml) and Onundi et al., 2011 (0.864 g/ml).

The moisture content of the MGA is 15.47 % which is slightly higher than the value reported elsewhere by Raffiea et al., 2012, (13.2%).

**Table 1:** Physico-Chemical Characterization of MGA.

| Properties                       |        | Element    | (%)    |
|----------------------------------|--------|------------|--------|
| Moisture content (%)             | 15.47  | Sodium     | 0.044  |
| Ash content (%)                  | 2.33   | Sulphur    | 0.315  |
| Volatile matter (%)              | 26.79  | Silicon    | 2.016  |
| Surface area (m <sup>2</sup> /g) | 819.80 | Calcium    | 9.230  |
| Iodine number (mg/g)             | 762    | Aluminum   | 0.819  |
| Bulk density (g/ml)              | 0.67   | Iron       | 0.815  |
| pH                               | 6.30   | Potassium  | 1.186  |
| % Yield                          | 62.27  | Titanium   | 0.084  |
| C                                | 52.31  | Manganese  | 0.179  |
| H                                | 3.38   | Magnesium  | 0.030  |
| N                                | 1.02   | Phosphorus | 28.512 |

The MGA has a moderately high surface area of 819.80 m<sup>2</sup>/g and is comparable to 760 m<sup>2</sup>/g for commercial activated carbon (AC-a) (Ionannou and Simitzis, 2013). The value obtained is lower than 862.39 m<sup>2</sup>/g reported by Raffiea et al., 2012 and 1141 m<sup>2</sup>/g by Hameed et al., 2009. Iodine number is the most fundamental parameter used to characterize activated carbon performance and it is a measure of activity level, the higher the number the higher the degree of activation. It is often reported in mg/g and typical values range between 500-1200 mg/g, (Raffiea et al., 2012). The MGA has moderate iodine number (762.0 mg/g) and it is an indication of better performance as an adsorbent.

The result of CHN analysis (Table 1) showed that it contains 52.31% C, 3.38% H, and 1.02% N and for most agricultural materials the values range between 41.23-84.50% C, 4.63-6.26% H, and 0.7-4.10% N (Ioannidou and Zabaniotou, 2007). The results of elemental analysis by XRF (Table 1) showed that P, Ca, Si, and K occurred as major constituents while Al, Fe, S and Mn as minor constituents.

The FTIR spectra obtained (Table 2) was interpreted based upon similar researches (Jung, et al., 2001, Olivares-Mar'in et al., 2006, Tan et al., 2008, Depci et al., 2012). The FTIR spectra showed a prominent peak at 3435.54 cm<sup>-1</sup> that was attributed to the stretching frequency of N-H due to primary or secondary amines. The peak observed at 2925.77 cm<sup>-1</sup> was associated with the stretching vibrations of C-H bond of methyl, methylene or methoxy group. For most

carbonaceous materials, C=C stretching absorption frequently occurs at ≈1600 cm<sup>-1</sup> region (Florida *et al.*, 2009). The spectrum in the region of 1168.54 cm<sup>-1</sup> and 1080.25 cm<sup>-1</sup> represented C-O stretching vibrations of functional groups such as alcohols, ethers, carboxylic acids or esters.

### Effect of Adsorbate Concentration

The influence of equilibrium concentration of the alizarin and fluorescein dyes followed similar trend (Figure1). There was a general initial increase in adsorption of alizarin and fluorescein dyes with increase in the equilibrium concentrations onto MGA up to a concentration of 30 mg/L with 0.131 and 1.149 g/g MGA respectively as the maximum quantity adsorbed when adsorption curves formed plateau after which the adsorption dropped. At lower initial concentrations, the metal concentration provides the necessary driving force to overcome the resistance to the mass transfer of the dye molecules between the aqueous phase and the solid phase. The initial increase also enhances the interactions between the MGA surface and the dye molecules. These combine factors enhances the uptake of dye molecule from aqueous phase onto the MGA. Since the adsorption was carried out against fixed number of active sites, there was decrease in the % removal (Mishra *et al.*, 2009). As the binding sites became exhausted, the uptake rate slowed down due to competition between dyes molecules for decreasing available actives sites (Gupta et al., 2008).

**Table 2:** FTIR Spectrum of MGA and their Assignments.

| Band Position (cm <sup>-1</sup> ) | Assignment  |
|-----------------------------------|---|
| 3435.54                           | N-H stretching vibration                                      |
| 2925.77                           | C-H asymmetric stretching vibration of CH <sub>2</sub>        |
| 2853.70                           | C-H stretching vibration of CH <sub>3</sub> , CH <sub>2</sub> |
| 2361.37                           | C≡C stretching vibration                                      |
| 1633.67                           | C=C stretching vibration                                      |
| 1168.54, 1080.25                  | C-O-H stretching vibrations                                   |
| 992.50                            | M-O (Metal-Oxygen) stretching vibrations                      |
| 875.59, 721.10                    | C-H bending (out-of-plane) vibration                          |
| 507.80                            | C-O-H twist   |

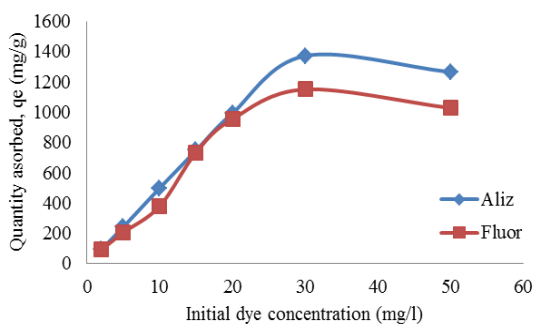


Fig. 1: Effect of initial on adsorption of dyes

### The Effect of Agitation Time

The plot of the effects of agitation time on the adsorption of the alizarin and fluorescein on MGA are depicted in Figure 2. A biphasic kinetic was observed: an initial fast phase (0 – 15 min) where adsorption was rapid and contributed essentially to the equilibrium uptake of the Alizarin and Fluorescein dyes (86.90 % and 85.75% respectively); and a second slow phase (15 – 90 min) whose contribution to equilibrium was relatively smaller with total amount of Alizarin and Fluorescein dyes adsorbed as 90.44% and 91.32%, respectively. The first phase is an instantaneous phase which is caused by external adsorption on to MGA. This was followed by slow phase which was diffusion controlled phase. The process of agitation of the adsorbate-adsorbent phase has the tendency of exposing active surfaces which otherwise, may be inaccessible. Similar observation was earlier reported. The optimum time for adsorption of these dyes onto MGA is 90 min.

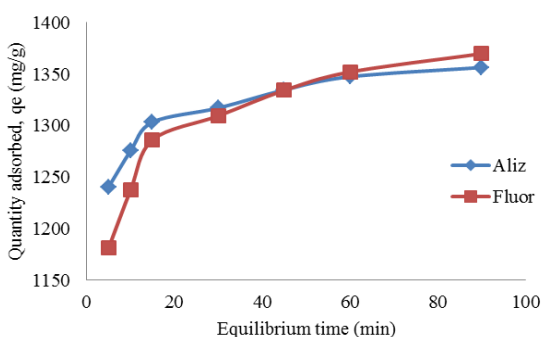


Fig . 2: Effect of agitaion time

### The Effect of Adsorbents Dose

The effect of the quantity of MGA used on the adsorption of alizarin and fluorescein dyes were studied, in which the amount of adsorbent was varied from 0.25 to 4 g while the dyes concentration were fixed at 30 mg/L. The net quantity of adsorbate removed increased with increasing mass of MGA which is attributed to an increase in the sorptive surface area and the availability of more active binding sites (Figure 3).

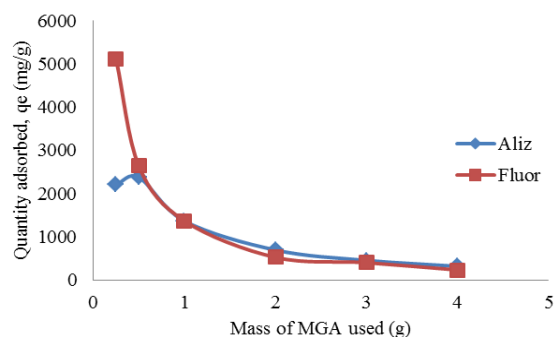


Fig. 3: Effect of adsorbate dose on adsorption

The net equilibrium amount adsorbed however is an expression of the efficiency of an adsorbent which may not show increase in the amount adsorbed per unit mass as the adsorbate dose increases (Nasuha et al., 2010). The amount of alizarin dye and Fluorescein dye adsorbed per unit mass of MGA decreased as the MGA dosage was increased from 0.25 - 4 g. This may be due partly to the inaccessibility of the active sites and partly to overlapping or aggregation of adsorption sites as the adsorbate dose increases (Akar and Ozcan, 2009). Thus with increasing adsorbent mass, the amount of dye adsorbed onto unit mass of adsorbent gets reduced, thus causing a decrease in  $q_e$  value with increasing adsorbent mass concentration.

### The Effect of Temperature

The dependence of dye adsorption on temperature was studied within the temperature range of 35 - 70°C. The effect of temperature on the adsorption of Alizarin and Fluorescein dyes followed the same trend and gave an S-like curve (Figure 4).

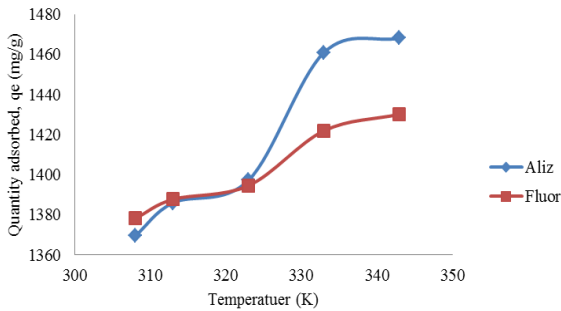


Fig. 4: Effect of Temperature on adsorption of dyes

The S-like curve had two stages of fast and slow adsorption processes. The temperatures between 35 – 40 and 50 – 60 °C represent sharp rise in the quantity adsorbed while curve between 40 – 50 °C represents slow rise in the quantity of dye molecules adsorbed. The higher removal due to increasing temperature may be attributed to chemical reaction taking place between the functional groups of the adsorbent and the dye (Sumanjit and Ishu, 2007). Moreover, at higher temperatures there would be an increase in the mobility of the dye molecules thereby producing a swelling effect within the internal structure of the adsorbent. The increase in the quantity adsorbed with increasing temperature may suggest an increasing accessibility to the MGA active sites and possibly chemical interactions between the surface functional groups of MGA and the dyes molecules.

### Adsorption Isotherms

An adsorption isotherm expresses the specific relation between adsorbate concentration in the bulk and the adsorbate amount at the aqueous/solid interface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir, Freundlich and Temkin models were used to describe the equilibrium data. These data fitted well into Langmuir isotherm for Alizarin dye (Figure 5a) with regression coefficient,  $R^2$ , of 0.994 and for Fluorescein dye (Figure 5b) with  $R^2$  0.962 while Freundlich and Temkin models yielded poor  $R^2$  values for Alizarin and Fluorescein dyes (Table 3). The fitting of Langmuir isotherm model indicates monolayer coverage of dyes molecules at the outer surface of MGA. A further analysis of the Langmuir equation was made on the basis of a dimensionless equilibrium parameter,  $K_L$

(separation factor). The  $K_L$  is an indication of the level of interaction between the adsorbate and adsorbent. The adsorption of a molecule onto an adsorbent is described as unfavorable if  $K_L > 1$ , linear when  $K_L = 1$ , favorable for  $0 < K_L < 1$  or irreversible for  $K_L < 0$  based on the calculated  $K_L$  value from eqn.6 (Bhattacharyya and Gupta, 2006).

$$K_L = \frac{1}{1 + bC_0} \quad (6)$$

The  $K_L$  values for the dyes are less than unity which is an indication that the MGA is an excellent adsorbent for Alizarin and Fluorescein. The isothermal constants and regression coefficients are summarized in Table 3.

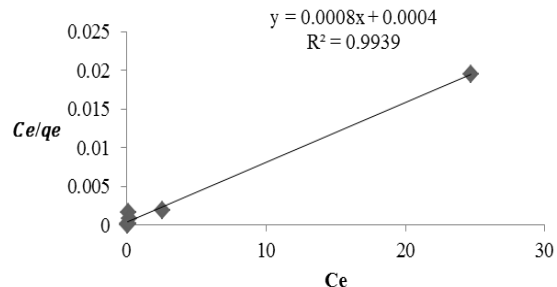


Fig. 5a: Langmuir isotherm plot of alizarin onto MGA

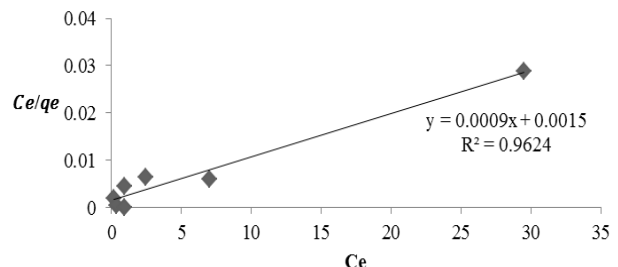


Fig. 5b: Langmuir isotherm for fluorescein onto MGA

### Adsorption Kinetics

Adsorption kinetics describes the solute uptake rate which in turns controls the residence time of the adsorbate at the aqueous-adsorbate interface including the diffusion process (Naiya et al., 2009). The data obtained from the influence of time on the adsorption of alizarin and fluorescein dyes onto MGA were subjected to the pseudo-first order (Figure 6) and pseudo-second order (Figure 7) kinetics equations for a test of fitness of data.

**Table 3:** Isothermal Constants and Regression Coefficients.

| Adsorption isotherm |                       | Alizarin | Fluorescein |
|---------------------|-----------------------|----------|-------------|
| Langmuir            | R <sup>2</sup>        | 0.994    | 0.962       |
|                     | K <sub>L</sub> (L/g)  | 2.000    | 0.600       |
|                     | q <sub>m</sub> (mg/g) | 1.250    | 1.111       |
| Freundlich          | R <sup>2</sup>        | 0.234    | 0.406       |
|                     | K <sub>F</sub> (mg/g) | 673.13   | 408.60      |
|                     | n                     | 4.830    | 2.89        |
| Temkin              | R <sup>2</sup>        | 0.471    | 0.484       |
|                     | A (L/min)             | 430.99   | 34.17       |
|                     | B                     | 147.86   | 167.08      |

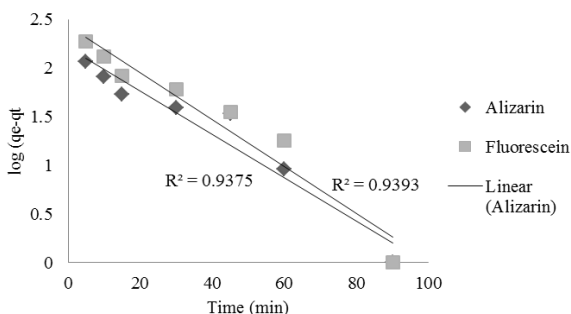


Fig. 6: Pseudo first order plot of dyes onto MGA

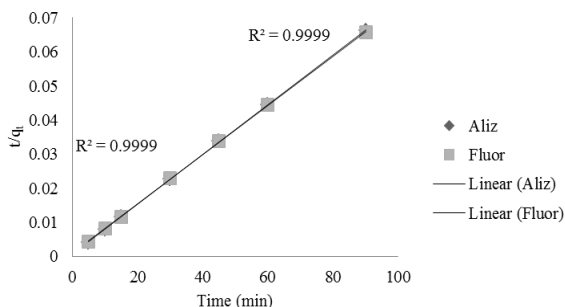


Fig. 7: Pseudo - second order plot of dyes onto MGA

The linearity of the plots with R<sup>2</sup> values that are very close to unity is an indication that the adsorption process followed both pseudo-first order and pseudo-second order kinetic models. The Table 4 summarizes the kinetics parameters for pseudo-first and second order models.

### Adsorption Thermodynamics

This study gives general information about the influence of temperature on the adsorption and particularly useful to predict the feasibility of the adsorption process. The standard free energy ( $\Delta G$ ), the enthalpy ( $\Delta H$ ) and the entropy ( $\Delta S$ ) were calculated from the Gibb's free energy and Van't Hoff equations (Sujana *et al.*, 2009)

$$K = \frac{C_{Ae}}{C_e} \quad (7)$$

$$\Delta G = -RT \ln K \quad (8)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

Where  $C_e$  is the equilibrium concentration in solution (mg/L) and  $C_{Ae}$  is the equilibrium concentration on the sorbent (mg/L) or equilibrium concentration of adsorbate A on the adsorbent and K is the equilibrium constant. The thermodynamic parameters are presented in Table 5.



**Table 4:** Kinetics Constants and Regression Coefficients.

| Adsorption kinetics |                                     | Alizarin | Fluorescein |
|---------------------|-------------------------------------|----------|-------------|
| Pseudo-first order  | R <sup>2</sup>                      | 0.938    | 0.939       |
|                     | k <sub>1</sub> (min <sup>-1</sup> ) | 0.052    | 0.056       |
|                     | q <sub>e</sub> (g/g)                | 0.156    | 0.274       |
| Pseudo-second order | R <sup>2</sup>                      | 0.999    | 0.999       |
|                     | k <sub>2</sub> (g/mg/min)           | 0.0008   | 0.0005      |
|                     | q <sub>e</sub> (g/g)                | 1.429    | 1.429       |

**Table 5:** Thermodynamic Parameters for Adsorption of Alizarin and Fluorescein on MGA.

| Temp. K | MGA         |             |             |                         |             |             |             |                         |
|---------|-------------|-------------|-------------|-------------------------|-------------|-------------|-------------|-------------------------|
|         | Alizarin    |             |             |                         | Fluorescein |             |             |                         |
|         | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (KJ/mol) | E <sub>a</sub> (KJ/mol) | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (KJ/mol) | E <sub>a</sub> (KJ/mol) |
| 308     | -6.02       | +37.87      | +0.14       | +13.84                  | -6.21       | +16.81      | +0.074      | 16.56                   |
| 313     | -6.49       |             |             |                         | -6.28       |             |             |                         |
| 323     | -7.01       |             |             |                         | -7.79       |             |             |                         |
| 333     | -9.34       |             |             |                         | -8.64       |             |             |                         |
| 343     | -10.92      |             |             |                         | -9.38       |             |             |                         |

The values of ΔH and ΔS were obtained from the slope and intercept of Van Hoff's plot of lnK versus 1/T. From the pseudo-second order rate constant k<sub>2</sub>, the activation energy E<sub>a</sub> for the adsorption of alizarin and fluorescein on MGA surface were determined using the Arrhenius equation

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (11)$$

Where, k is the rate constant, A is the Arrhenius constant, E<sub>a</sub> is the activation energy (KJ mol<sup>-1</sup>), R is the gas constant (8.314 J/mol/K) and T is the temperature (K). The E<sub>a</sub> was obtained from a plot of lnk<sub>2</sub> versus 1/T (Figure 8). The negativity of ΔG which becomes more negative with increase in temperature reflects the feasibility of the adsorption process for fluorescein and alizarin but more efficient adsorption at higher temperature. Generally, ΔG for physisorption processes ranges between -20 and 0 KJ/mol while the chemisorptions is between -80 and -400 KJ/mol (Sen et al., 2011).

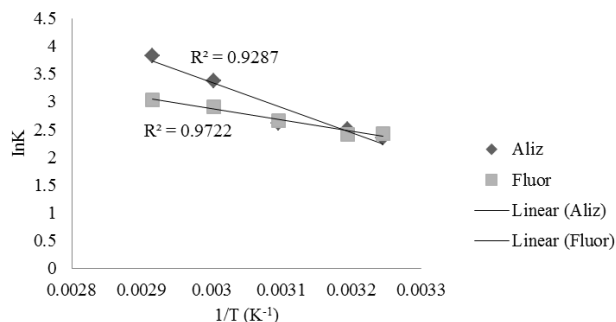


Fig. 8: A graph of lnK against 1/T for the dyes

Therefore, the adsorption of Alizarin and Fluorescein onto MGA is by physisorption process. Energies of activation, E<sub>a</sub> < 42 KJ/mol indicates diffusion-controlled process while higher values support chemisorption (Babarinde et al., 2013). The lower the E<sub>a</sub> value of a reaction process, the more probable it occurs spontaneously. Therefore, the adsorption process is physisorption for the two dyes since E<sub>a</sub> obtained was lower than 42 KJ/mol. The type of a sorption process can be explained in terms

of the magnitude of  $\Delta H$ . Generally, the  $\Delta H$  values for physisorption and chemisorption are within the range of 2.1 - 20.9 KJ/mol and 80 - 200 KJ/mol respectively (Liu and Liu, 2008). The positivity and the magnitude of  $\Delta H$  values obtained for the adsorption of Alizarin dye ( $\Delta H = 37.87$ ) and Fluorescein dye ( $\Delta H = 16.81$ ) suggest an endothermic and physisorption process (Table 4). The positive value of  $\Delta S$  shows that there was increases randomness at the aqueous-MGA interface during adsorption of the dyes.

## CONCLUSION

The preparation of MGA was achieved through one step process of carbonization and activation with 62.27% yield and moderately high surface area 819.80 m<sup>2</sup>/g. The dyes uptake increased with increasing agitation time, concentration and temperature. A fast kinetics was observed for Alizarin and Fluorescein dyes with 90.44 and 91.32% adsorption respectively at the equilibrium time of 90 min. The kinetic data obtained from this study showed good correlation coefficient for a pseudo-first and pseudo-second order kinetic models.

The equilibrium data conformed well to the Langmuir isotherm with a high correlation coefficient close to unity, indicating that the adsorption of single dye solution onto surface of MGA followed a monolayer pattern. The activation energy  $E_a$  of the adsorption process for alizarin and fluorescein on MGA were 13.84 and 16.56 KJ/mol respectively. The negative values of  $\Delta G$ , positive  $\Delta H$  and positive  $\Delta S$  indicate spontaneous, endothermic and an increased randomness at the aqueous-MGA interface during adsorption. Therefore, MGA can be considered as alternative biomass for the removal of single dye solution of alizarin and fluorescein dyes since it was not only effective but abundant, can be sourced locally and at low cost.

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