

# ADSORPTIVE REMOVAL OF DYES FROM SYNTHETIC WASTEWATER USING ACTIVATED CARBON FROM TAMARIND SEED

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## Abstract

Activated carbon prepared from seed (*Tamarindus indica*) was utilized for the removal of orange G and safranin O dyes from aqueous solution. Chemical activation using orthophosphoric acid ( $H_3PO_4$ ) was employed for the preparation of activated carbon. The effect of various factors namely; particle size, pH, adsorbent dosage, ion concentration, and contact time was studied to identify the adsorption capacity of the tamarind seed. The percentage of dye adsorbed was found to be dependent on these factors. The Langmuir, Freundlich, and Temkin isotherm models are fitted into the graphs, but the Freundlich isotherm model is best-fitted into the experimental data. The pseudo-first order, pseudo-second order, Elovich, and Bhattacharya-Venkobachor kinetic models were also fitted into the graphs, but pseudo-second order is best fitted into the experimental data. The thermodynamic parameters such as enthalpy, entropy, and free energy were evaluated using the Van't Hoff equations. The negative free energy ( $\Delta G$ ) and negative enthalpy ( $\Delta H$ ) indicate the feasibility and exothermic nature of the adsorption process. The positive entropy ( $\Delta S$ ) shows the increased randomness of the solid/solution interface during the adsorption process. The chemical functional groups, crystalline nature, and the surface morphology of the carbon adsorbents were studied by Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Characteristics of the activated carbons were determined using standard methods.

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**Keywords:** Adsorption, dyes, tamarind seed, isotherms, kinetics, thermodynamics

## Introduction

Environmental pollution control has been an issue of major concern in many countries. However, air pollution and water pollution constitutes the major environmental pollution in several countries. Consequently, open burning leads to air pollution, while industrial effluent and domestic sewage leads to water pollution. Water pollution results to bad effects on public water supplies which can cause health problem, while air pollution can cause lung diseases, burning eyes, cough, and chest tightness. The environmental issues surrounding the presence of colour in effluent is a continuous problem for dye stuff manufacturers, dyers, finishers, and water companies (Kesari *et al.*, 2011). The contaminants such as dyes, heavy metal, cyanide, toxic organics, nitrogen, phosphorus, phenols, suspended solids, colour, and turbidity from industries and untreated sewage sludge from domestics, are becoming of great concern to the environmental and public health. Therefore, the treatment of these pollutions is very important (Cheremisinoff, 1993).

Dye is a natural or synthetic colouring material, whether soluble or insoluble which impact its colour to a material by staining or being imbibed by it, and which is employed from a solution of fine dispersion, sometimes with the aid of mordant. They are widely used in textile, paper, leather, and mineral processing industries to colour their product. Their presence in wastewater causes adverse effects in human and aquatic life when disposed into the environment (Wang *et al.*, 2004). Many types of dye used in textile industries are direct, reactive, acid, and basic dyes. However, these dyes are invariably left in the industrial wastes. This is because they have synthetic origin and complex aromatic molecular structures, which makes them inert and difficult to biodegrade when discharged into waste streams. Also, people overlook their undesirable nature. Some dyes and their degradation products may be carcinogens and toxins, which are important sources of water pollution. Thus, their treatment becomes a major problem to environmental managers. Some dyes are harmful to aquatic life in rivers where they are discharged, because they can reduce light penetration into water, decrease the efficiency of photosynthesis in aquatic plant, and have adverse effect on their growth (Gurses *et al.*, 2004). Furthermore, dyes can also cause severe damage to human beings such as the malfunction of kidney, reproductive system, liver, brain, and the central nervous system (Andre *et al.*, 2011). The occupational exposure of workers in the textile industry is linked to a higher bladder cancer risk. Hence, the removal of dye has become an important aspect of wastewater treatment in industries. Various processes like adsorption, coagulation, flocculation, biosorption, photo-decomposition, ultra-filtration, oxidizing

agents, membrane, and electrochemical processes have been used in the treatment of wastewater (Ho and Chiang, 2001).

Adsorption process is a process by which a gas, liquid or solid adheres to the surface of a solid, but does not penetrate it (Klaus Christmann, 2010). The adsorbing phase is the adsorbent, while the material concentrated or adsorbed at the surface of the phase is the adsorbate. Adsorption process has been found to be an efficient and economic process to remove dyes, pigments, and other colourants (Wang *et al.*, 2004). In addition, it has been found to be superior to other techniques of wastewater treatment in terms of cost, simplicity of design, ease of operation, and insensitivity to toxic substances (Garg *et al.*, 2004). Adsorbents such as activated carbon, peat, chitin, clay, and others can be used. Adsorption using activated carbon is rapidly becoming a prominent method of treating aqueous effluents and has been used in the industrial processes for variety of separation and purification techniques.

Furthermore, activated carbon is used as adsorbent for dye removal from wastewater. This could be related to their extended surface area, high adsorption capacity, microporous structure, and special surface reactivity. Therefore, the removal of dyes through activated carbon adsorption is very effective. At present, there is a growing interest in using other low cost sorbents for dye removal. Many lignocellulosic materials including coir pith, sunflower stalks, corncob and barley husk, rice husk, and other materials have been used as a low cost dye sorbents (Banat *et al.*, 2003).

The purpose of this work is to test the effectiveness of activated carbon produced from tamarind seed for the removal of Orange G and Safranin O dyes from synthetic wastewater by adsorption technique.

## **Experimental Method**

### ***Adsorbent and Adsorbates***

Tamarind seeds were obtained from Mallam Nuhu farm in Kano state. The seeds were washed thoroughly with de-ionized water to remove unwanted materials. They were dried in an air-drying oven at 110°C for 24hours. However, the dried sample was carbonized in a muffle-furnace at 500°C for 1hour. The sample was impregnated with 60% weight of orthophosphoric acid at the ratio of 1:2(wt %). Then, the resulting carbons were washed with de-ionized water until the leachate was between a pH of 6-7. They were then dried in an air-drying oven at 110°C for 6hours. Also, the sample was crushed and was made to pass through different sieve sizes. Finally, the sample was stored in a tight bottle ready for use.

All dyes were obtained from Onitsha market in Anambra state. The pH solution was adjusted by adding a small amount of 0.1M HCl or NaOH.

### ***Characterization of Activated Carbon***

The ash content was determined using ASTM E1755-01 (ASTM, 2003). The pH of the carbon was determined using standard test ASTM D 3838-80 (ASTM, 1996). Moisture content of activated carbon was determined using standard test ASTM D 2867-91 (ASTM, 1991). The specific surface area of the activated carbon was estimated using Sear's method (Gregg and Sing, 1982). In addition, the iodine number was determined based on ASTM D 4607-86 (1986) using the sodium thiosulphate volumetric method.

### ***Batch Adsorption Studies***

Batch adsorption equilibrium experiments were conducted for the adsorption of orange G dye ( $C_{16}H_{10}N_2Na_2O_7S_2$ ) and safranin O dye ( $C_{20}H_{19}ClN_4$ ) on activated carbon of tamarind seed as a function of particle size, initial pH, adsorbent dosage, ion concentration, and contact time. This was done by adding 0.5g of adsorbent to 100ml of adsorbate solution of concentration (100mg/L) having a known pH in a conical flask and mixed on a Wincom magnetic stirrer (hot plate SH85-2) at 30°C for 60mins. Based on the effect of the particle size, 0.5g of adsorbent with different adsorbent particles passing through 75 $\mu$ m sieve mesh size and retained in 1000 $\mu$ m was added to different conical flasks. These flasks contain 100ml of adsorbate solution of concentration (100mg/L) which was mixed for 60mins. Based on the effect of the pH, dye solution was measured into different conical flask and adjusted in the pH range of 2, 4, 6, 8, and 10 with dilute HCl (0.1M) and NaOH (0.1M) solutions through the use of a pH meter. Based on the effect of adsorbent dosage, different adsorbent dose of 0.3, 0.5, 1, 1.5, and 2g was added in each conical flask containing 100ml of adsorbate solution of concentration (100mg/L), and was stirred for 60mins. Based on the effect of ion concentration, 0.5g of adsorbent was added to each conical flask containing 100ml of adsorbate solutions of different concentrations of 50, 100, 150, 300, and 500mg/L which was stirred for 60mins. Based on the effect of contact time, 0.5g of adsorbent was added to 100ml of adsorbate solution of concentration (100mg/L) and was stirred at different time intervals of 3, 5, 10, 20, 30, 45, 60, 90, 120, and 150mins. Furthermore, the solution was withdrawn from the reaction mixture at a fixed time interval, and was filtered using Whatman no.1 filter paper. The amount of unadsorbed dye in the supernatant solutions was measured with the aid of a Wincom visible spectrophotometer at wavelengths of 480nm for orange G dye and 510nm for safranin O dye.

Therefore, the amount of adsorption at equilibrium ( $q_e$ ) (mg/g) and the percentage adsorption (%) were computed as follows:

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

$$\% \text{ adsorbed} = \left[ (C_o - C_e)/C_o \right] \times 100 \quad (2)$$

Where;  $C_o$  and  $C_e$  are the initial and final dye concentration respectively (mg/L) at any time (t).

V is the volume of the solution (L) and M is the mass of the adsorbent used (g).

## Results and Discussion

### *Characteristics of Activated Carbon Derived from Tamarind Seed.*

The physico-chemical characteristics of activated carbon are shown in Table 1. The higher surface area ( $983\text{m}^2/\text{g}$ ) may be due to the restricted pore shrinkage during activation indicating high porosity. The typical range of values for commercial activation according to Haimour and Emeish (2006) is  $600\text{-}1500\text{m}^2/\text{g}$ . Thus, the low ash content value (2.35%) indicates that the activated carbons have low inorganic content and high fixed carbon. This is because ash content can reduce the efficiency of reactivation. Therefore, the lower the ash content, the better the activated carbon. Moisture content dilutes the carbon and increases the weight during treatment process. Thus, the lower the moisture contents in activated carbons, the better. The moisture content (3.00%) was found to be low, indicating that the carbon structure has extensive porosity through the activation process. The moisture content value can be compared with the value reported by Verla *et al.* (2012). As reported by Okiemmen *et al.* (2008), the pH of carbon is acceptable in the range of 6 - 8. The pH value of the activated carbon was 6.8. Bulk density is an important variable that must be considered in the design of adsorption column because it can affect the overall cost of the process. Hence, it determines the mass of carbon which can be contained in a filter by a given solids capacity. It also determines the amount of treated liquid that can be retained by the filter cake. However, it can be seen that the bulk density ( $0.51\text{ g/cm}^3$ ) will filter high liquor volume before the available cake space is filled. Iodine number can be obtained by the adsorption of iodine from solution by the activated carbons. It is a measure of the micropore content of the activated carbon, because micropores are created during activation process and are responsible for the large surface area of activated carbons. In addition, the iodine value ( $865\text{mg/g}$ ) shows high micropore content in the activated carbon.

Table 1: Physico-Chemical Characteristics of Activated Carbon Derived from Tamarind Seed

Properties	Values
Surface area (m <sup>2</sup> /g)	983
Moisture content (%)	3.00
Ash content (%)	2.35
pH	6.80
Bulk density (g/cm <sup>3</sup> )	0.51
Iodine number (mg/g)	865

### ***Fourier Transform Infrared Spectroscopy Analysis.***

Fourier Transform Infrared Spectroscopy (FTIR) study was carried out to identify the functional groups present in the adsorbents ranging from 600cm<sup>-1</sup> to 4000cm<sup>-1</sup>. The adsorption capacity of adsorbent depends upon the porosity as well as the chemical reactivity of the functional groups at the adsorbent surface (Suresh, 2013). The plot of functional groups and their peaks on the carbon adsorbent and acid impregnated carbon adsorbent are shown in Figures 1 and 2. Furthermore, the results presented in Tables 2 and 3 show the presence of alkanes (C-H stretch), alkenes (=C-H stretch), alkynes (-C≡C-), carboxylic acids (O-H bend), aromatics amines (C-N), nitrites (C≡N stretch), aromatics (C-H stretch), alkyl halides, etc. The shift in the wave number of dominant peak associated with the plots showed various surface functional groups. The presence of hydroxyl groups, carbonyl groups, ethers, and aromatic compounds is an evidence of the lignocellulosic structure of tamarind seed which was also observed in other materials such as coconut shell (Andre et al., 2011) and cotton stalks (El-Hendawy et al., 2008).

Table 2: Fourier Transform Infrared Spectrum for Acid Activated Carbon Tamarind Seed

Functional Group	Absorption Peak (cm <sup>-1</sup> )
C-Cl stretch alkyl halides	778.7686
C-H, aromatics	894.0875
C-N stretch aromatic amines	1104.074
C-N stretch aromatic amines	1287.1
N=O bend nitro compounds	1.381.824
C-C stretch (in ring) aromatics	1452.822
-C=C- stretch alkenes	1627.21
-C≡C- stretch alkynes	2176.194
Hydrogen-bonded O-H stretch carboxylic acid	2424.58
Hydrogen-bonded O-H stretch carboxylic acid	2621.008
Hydrogen-bonded O-H stretch carboxylic acid	2706.048
H-C-H stretch alkanes	2850.872
H-C-H stretch alkanes	2989.518
C=C-H stretch alkenes	3091.54
O-H stretch, carboxylic acid	3216.43
N-H stretch in amines, amides	3302.668

O-H stretch, H-bonded, phenols and alcohol	3429.882
O-H stretch, H-bonded, phenols and alcohol	3491.908
O-H stretch in phenols and alcohol	3679.638
O-H stretch in phenols and alcohol	3791.593
O-H stretch in phenols and alcohol	3899.307

Table 3: Fourier Transform Infrared Spectrum for Carbon Tamarind Seed

Functional Group	Absorption Peak (cm <sup>-1</sup> )
-C-H bending R-CH=CH <sub>2</sub>	909.1885
C-O stretch, alcohol, carboxylic acid, esters, ethers	1048.632
C-O stretch, alcohol, carboxylic acid, esters, ethers	1142.67
C-N stretch aromatic amines	1313.454
C-H stretch alkanes	1406.053
-C=C- stretch aromatics	1564.395
-C=C- stretch alkenes	1638.292
-C≡C-H stretch alkynes	2187.355
-O-H stretch carboxylic acid	2545.098
-O-H stretch carboxylic acid	2662.83
C-H stretch off C=O	2841.17
O-H stretch carboxylic acid	2964.175
-O-H stretch carboxylic acid	3143.41
N-H stretch 1°, 2° amines, amides	3335.602
Hydrogen-bonded O-H stretch phenols and alcohol	3528.681
O-H stretch, free hydroxyl, alcohol and phenols	3628.434
O-H stretch in phenols and alcohols	3828.511

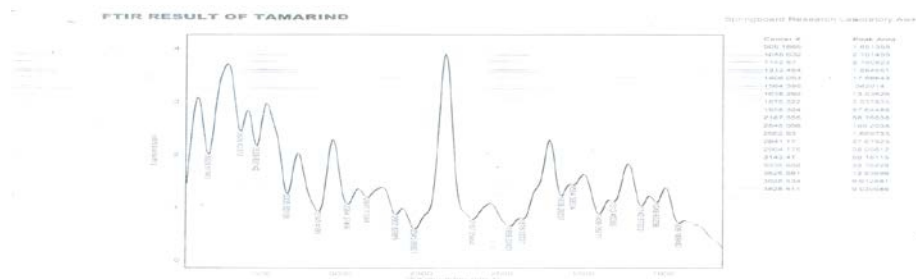


Fig 1: FTIR Spectrum for Carbon Tamarind Seed

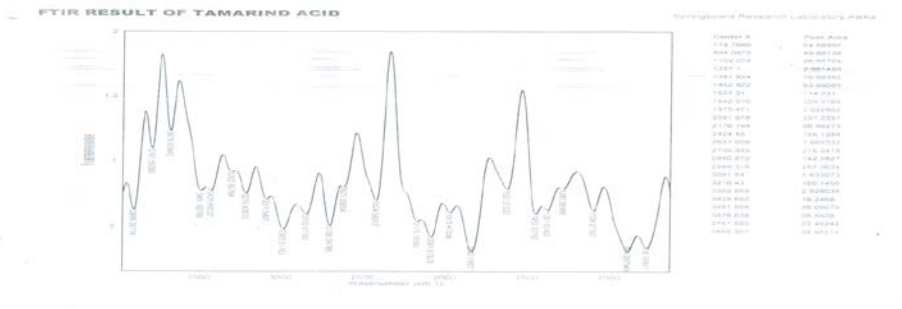


Fig 2: FTIR Spectrum for Acid Activated Carbon Tamarind Seed

**X-ray diffraction analysis**

X-ray diffraction measurement was used to determine the crystal structure of the adsorbents. The XRD patterns for acid activated tamarind seed carbon and activated tamarind seed carbon were demonstrated in Figures 3 and 4 respectively. Higher peaks and broadness were observed in acid activated samples than the non-acid activated samples. Also, the presence of high diffraction peaks and broadness are evidence of good crystallinity of the prepared powdered samples. The intensities for each samples as presented in Figures 3 and 4 are in the range of  $10^{-79} = 2\theta$ . Thus, this indicates that other low intensity peaks corresponding to other crystalline phases of carbon have also been observed.

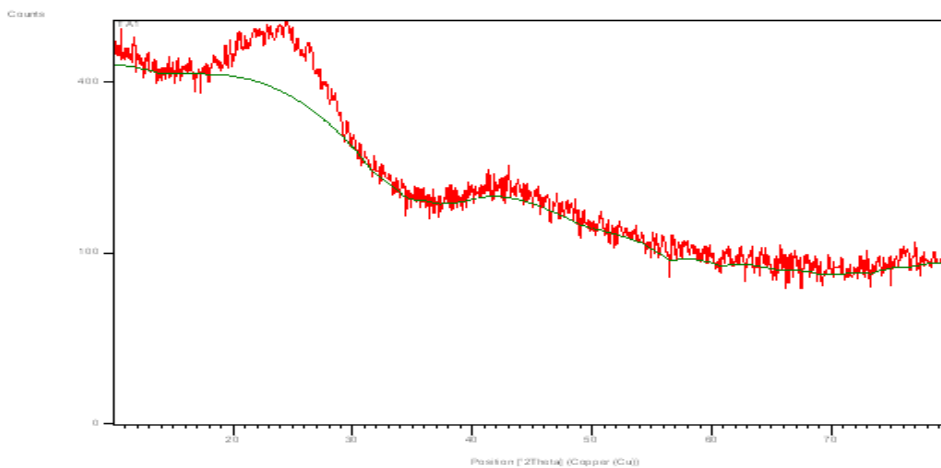


Fig 3: XRD Measurement for Acid Activated Carbon Tamarind



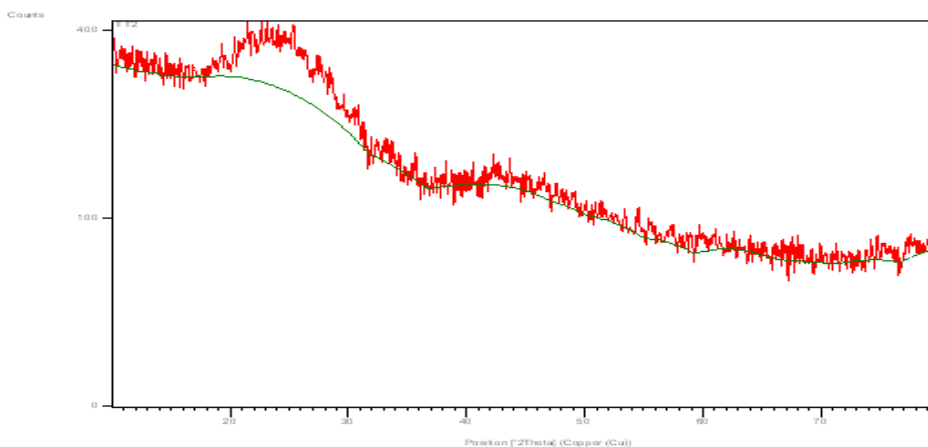


Fig 4: XRD Measurement for Carbon Tamarind Seed

### ***Scanning Electron Micrograph Analysis***

Scanning electron micrographs of activated tamarind seed carbon and acid activated tamarind seed carbon are shown in figures 5 to 8. In this work, combinations of lower and higher magnifications were used. These included magnifications of 4000X and 8000X for both samples with 15kV accelerating voltage. In the SEM image at magnification of 4000x (corresponding to specimen area of  $20\mu\text{m}^2$ ) for both samples, the micrograph displayed an irregular shape pitted canal-like structure with larger pore size. However, this was observed in the acid activated carbon than in the non-acid activated carbon. At a magnification of 8000x (corresponding to specimen area of  $10\mu\text{m}^2$ ), the micrograph for the non-acid activated carbon displayed a larger canal-like structure than those of the 4000X magnification, while the acid activated carbon displayed a net-like structure with larger pore size observed than those of 4000X.

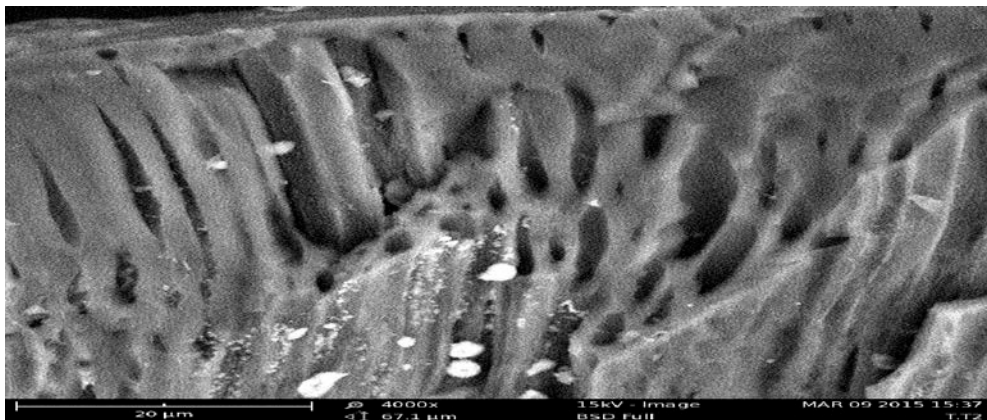


Fig 5: Scanning Micrograph for Activated Tamarind Seed Carbon at 4000X Magnification

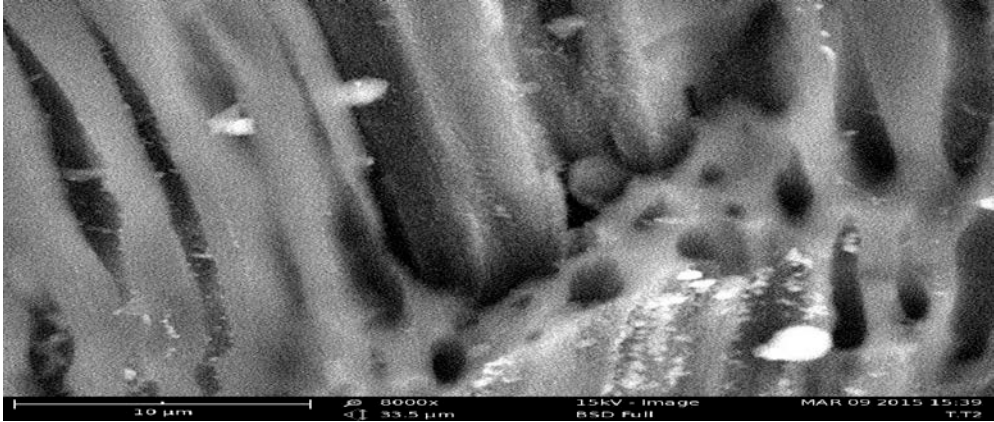


Fig 6: Scanning Micrograph for Activated Tamarind Seed Carbon at 8000X Magnification

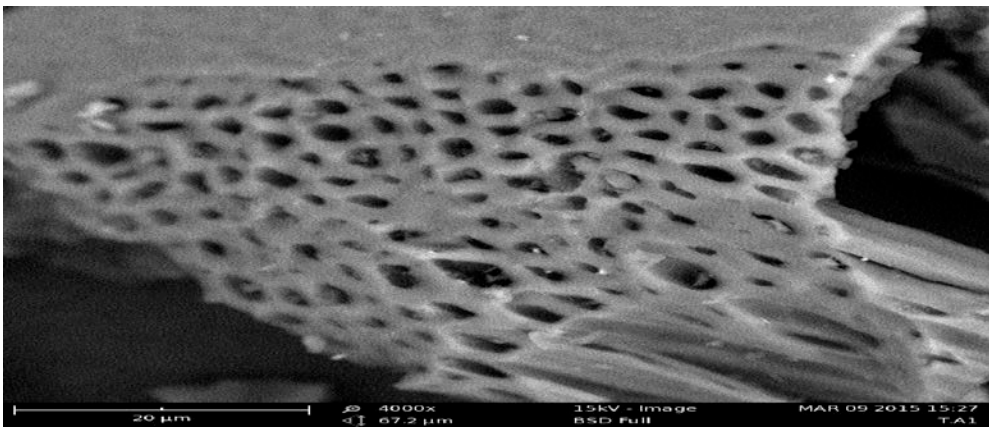


Fig 7: Scanning Micrograph for Acid Activated Tamarind Seed carbon at 4000X Magnification

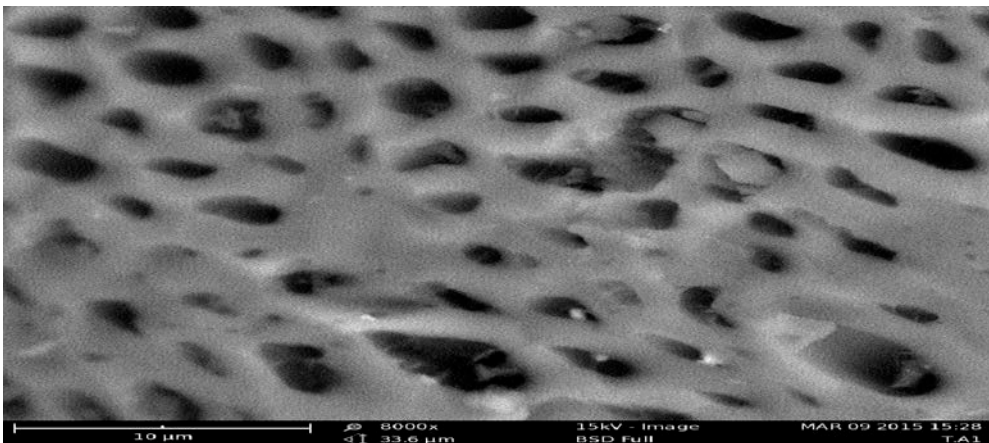


Fig 8: Scanning Micrograph for Acid Activated Tamarind Seed carbon at 8000X Magnification

### Effect of Particle Size on the Adsorption Process

The removal of orange G and safranin O dyes using activated carbon of different particle sizes showed that the removal rate decreases with increase in particle size (Figures 15 and 16). The particle sizes ranging from 75 $\mu\text{m}$  to 1000 $\mu\text{m}$  have percentages of dye adsorbed between the ranges of 68.26% to 19.27% for orange G dye and 87.13% to 34.03% for safranin O dye respectively. This shows that 75 $\mu\text{m}$  was the best particle size to be used, because it adsorbed the highest percentage of dye. The relatively higher adsorption with smaller adsorbent particle size may be attributed to the fact that smaller particle yields larger surface area. Thus this provides a greater number of sites for adsorption and implies opening of more micropores. However, similar results were obtained by Rahman *et al.* (2012).

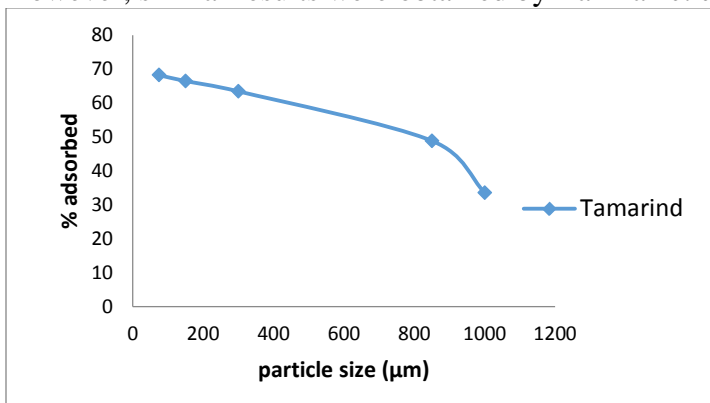


Fig 15: Effect of particle size on acid activated tamarind seed carbon using orange G dye.

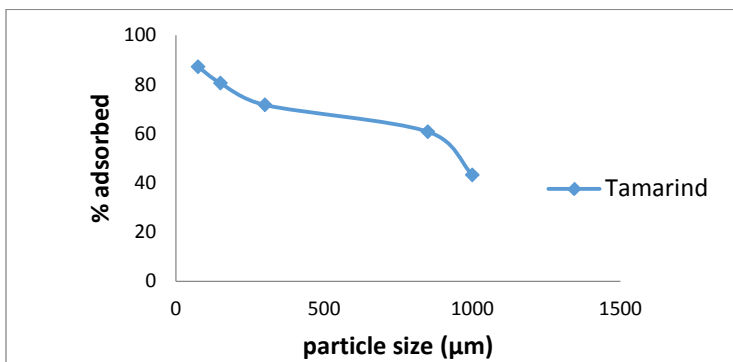


Fig 16: Effect of particle size on acid activated tamarind seed carbon using safranin O dye.

### ***Effect of pH on the Adsorption Process***

pH is an important parameter in adsorption study because it controls the degree of ionization and speciation of the adsorbate. The effect of pH on the adsorption of dye into acid activated tamarind seed carbon was studied between the ranges of 2-10. The percentages of dye adsorbed were between the range of 88.08% to 42.97% for orange G dye and 35.00% to 95.52% for safranin O dye. The result showed that the amount of dye adsorbed decreased with increase in the pH value for orange G dye (Figure 17) and increased with increase in pH value for safranin O dye as shown in (Figure 18). This indicates that a low pH was favourable for the adsorption of orange G dye by the adsorbent, because they are anionic dye (acid dye). This is due to the fact that as the pH of the system decreased, the number of negatively charged adsorbent sites decreased also, while the number of positively charged surface sites increased. These effects favoured the adsorption of the negatively charged dye anions due to electrostatic attraction. The high pH favourable for the adsorption of safranin O dye (cationic dye known as basic dye) is due to the fact that as the pH of the system increased, the number of negatively charged adsorbent sites increased also, and the number of positively charged surface sites decreased. This effect favours the adsorption of the positively charged dye cations due to electrostatic attraction. However, similar results were obtained by singh *et al.* (2011).

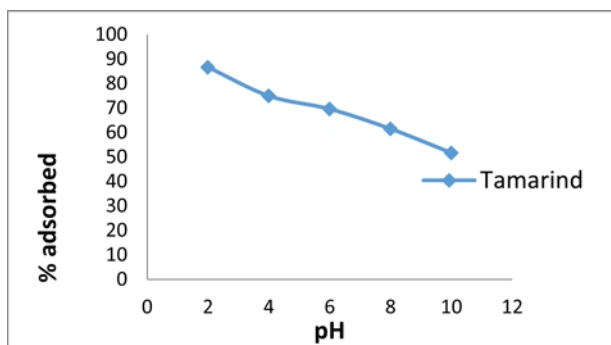


Fig 17: Effect of pH on acid activated tamarind seed carbon using orange G dye.

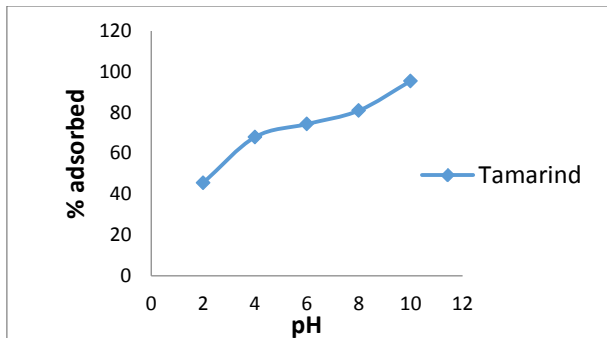


Fig 18: Effect of pH on acid activated tamarind seed carbon using safranin O dye.

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

Adsorption dosage determines the capacity of an adsorbent for a given initial concentration of the adsorbate (Joseph and Philomena, 2011). The result showed that as the adsorbent dosage increased, the percentage of dye adsorbed increased also from 0.5g to 2g. The percentage of adsorption increased up to 1.0g of adsorbent after which no significant changes in the percentages of dye was adsorbed with an increasing amount of the adsorbent (Figures 19 and 20). However, it showed that most of the adsorbents studied attained equilibrium around 1.0g of dosage. The adsorption efficiency increased due to the increased number of adsorption sites and surface area. However, similar results were obtained by Bulut and Aydin (2005).

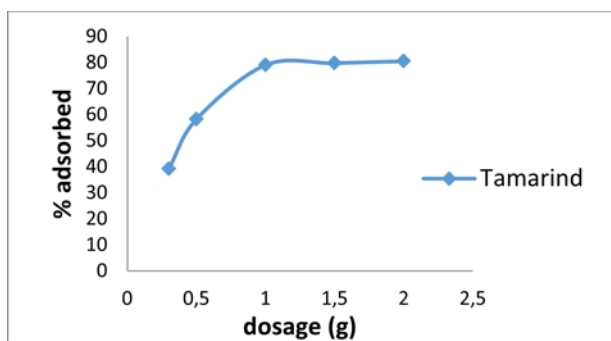


Fig 19: Effect of dosage on acid activated tamarind seed carbon using orange G dye.

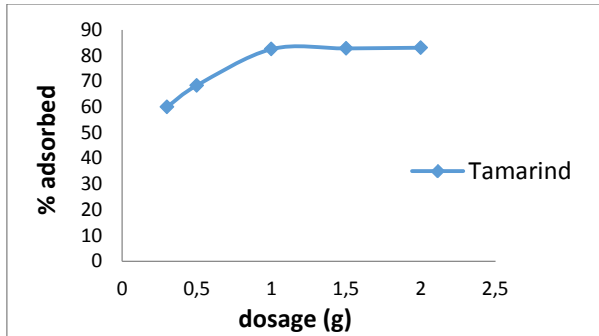


Fig 20: Effect of dosage on acid activated tamarind seed carbon using safranin O dye.

### ***Effect of Initial Concentration on the Adsorption Process***

The initial concentration of adsorbate plays an important role, as a given mass of adsorbent can adsorb only a certain amount of a solute. The concentrations ranged from 50mg/L to 500mg/L. As presented in Figures 21 and 22, the result showed that the more the concentration of the solution, the smaller the percentage of dye that a given mass of adsorbent can adsorb. In a low concentration range, the fractional adsorption is higher compared to the high concentration range. This is due to the fact that at a lower concentration, the available sites for adsorption become more, while at a higher concentration, the available sites become fewer. Thus, the percentage of dye removal was dependent upon the initial concentration. However, similar results were obtained by Khan *et al.* (2009) and Ozacar *et al.* (2003).

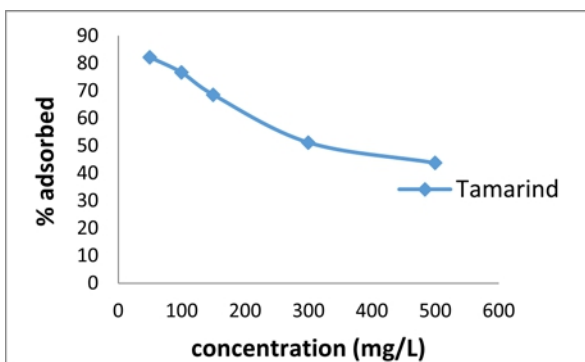


Fig 21: Effect of concentration on acid activated tamarind seed carbon using orange G dye.

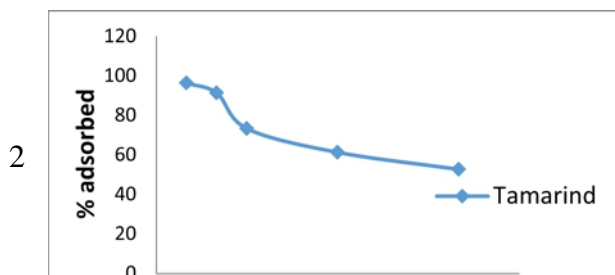


Fig 22: Effect of concentration on acid activated tamarind seed carbon using safranin O dye.

*Effect of Contact Time on the Adsorption Process*

The contact time was found to play significant roles in the process of dye removal from wastewater by adsorption at a particular temperature, pH, adsorbent dosage, and particle size. The batch equilibrium adsorption time of orange G, and safranin O dyes on acid activated tamarind seed were investigated at different times (3, 5, 10, 20, 30, 45, 60, 90, 120, and 150mins). As shown in Figures 23 and 24, the rapid uptake of the dyes species and the establishment of equilibrium within a short period indicated the efficiency of the adsorbent for its use in wastewater treatment. It can be seen that the removal of the dyes reaches maximum at 60mins for orange G and 45mins for safranin O dye and becomes gradual thereafter. This indicates that the rate of adsorption is very fast; and after that, no significant change in the extent of adsorption was observed (Singh *et al.*, 2011).

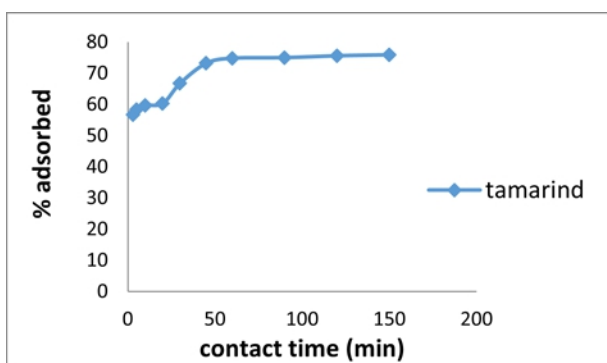


Fig 23: Effect of contact time on acid activated tamarind seed carbon using orange G dye

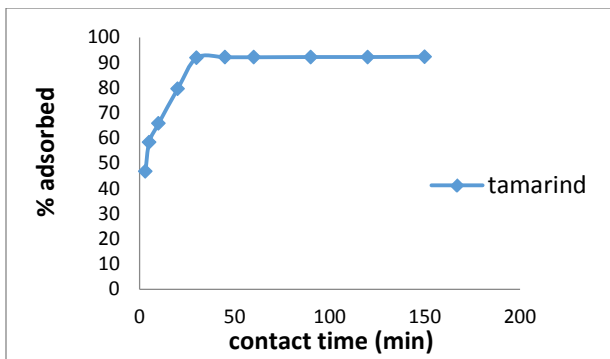


Fig 24: Effect of contact time on acid activated tamarind seed carbon using safranin O dye

*Langmuir Isotherm Model*

The Langmuir isotherm model is given by:

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{3}$$

The linearized form of the Langmuir equation can be written in the form (Sekar *et al.*, 2004):

$$C_e/q_e = 1/Q_o C_e + 1/Q_o b \tag{4}$$

Where  $q_e$  is the amount of adsorbate per unit mass of adsorbent (mg/g);  $C_e$  is the equilibrium concentration of adsorbate (mg/L); and the Langmuir constants  $b$  and  $Q_o$  represents the adsorption equilibrium constant and the maximum adsorption capacity, respectively. A straight line graph with slope of  $1/Q_o$  and intercept  $b$  was obtained when  $C_e/q_e$  was plotted against  $C_e$ . Therefore, this indicates that the adsorption follows the Langmuir isotherm as shown in figures 25 and 26.

The study of equilibrium parameter  $R_L$ , which is a dimensionless constant and is referred to as separation factor is given by:

$$R_L = \frac{1}{1 + (1 + b C_o)} \tag{5}$$

Where;  $C_o$  is the initial concentration. The  $R_L$  values indicate the adsorption to be favourable if ( $0 < R_L < 1$ ), unfavourable if ( $R_L > 1$ ), linear if ( $R_L = 1$ ) or irreversible if ( $R_L = 0$ ). The  $R_L$  values issued from this study were ranged from 0.276 to 0.301 for orange G dye and 0.225 to 0.303 for safranin O dye, while the correlation coefficients ( $R^2$ ) ranged from 0.967 to 0.970 for orange G dye and 0.904 to 0.927 for safranin O dye with the increase in temperature from 303K to 323K, respectively (Tables 4 and 5). These results have indicated that the description of adsorption process by means of



Langmuir isotherm model is favourable and also fits into the graph. However, similar results were obtained by Juang *et al.* (1997).

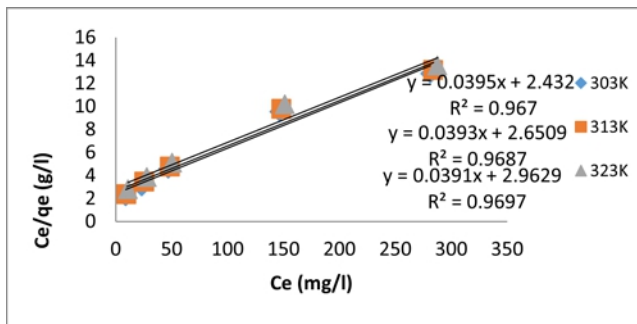


Fig 25: Langmuir isotherm plot for orange G dye on acid activated tamarind seed carbon.

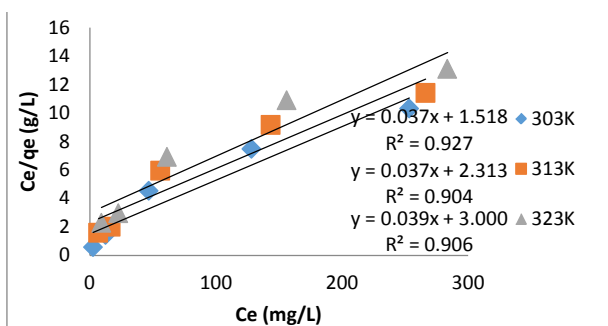


Fig 26: Langmuir isotherm plot for safranin O dye on acid activated tamarind seed carbon.

### Freundlich Isotherm Model

The Freundlich adsorption isotherm (Ozacar, 2003) is given by:

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

A linear form of the expression above is written as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

Where  $K_f$  and  $n$  are Freundlich constants.  $K_f$  and  $n$  corresponding respectively to adsorption capacity of adsorbent and adsorption intensity have been obtained from the intercepts and slopes of the linear plot of  $\log q_e$  against  $\log C_e$  as shown in Figures 27 and 28. The magnitude of adsorption intensity  $n$  gives an indication of the favourability of the adsorption process. Ho and Chang, (2001) reported that the favorability of the process is achieved if  $n$  lies in the range of 1–10. The adsorption intensity ( $n$ ) varied from 2.155 to 2.004 for orange G dye and 2.915 to 2.212 for safranin O dye with the increase in temperature from 303K to 323K respectively as shown in Tables 4 and 5. The values of the adsorption intensities obtained are in

conformity with the requirement for physical adsorption process, which characterize it to be favourable.

The correlation coefficients  $R^2$  ranged from 0.986 to 0.989 using orange G dye and 0.943 to 0.963 with safranin O dye (Table 4 and 5). This shows that the adsorption of the dyes on the adsorbent followed Freundlich isotherm. However, similar results were obtained by Ho and Chinn (2001)

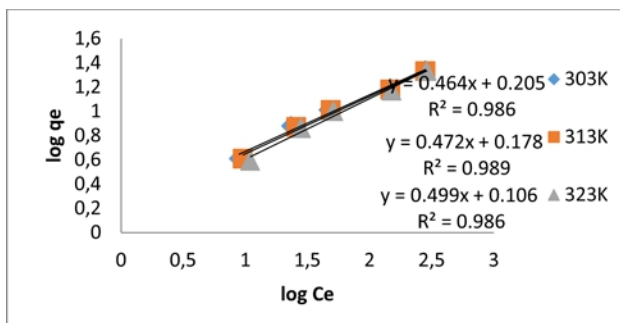


Fig 27: Freundlich isotherm plot for orange G dye on acid activated tamarind seed carbon.

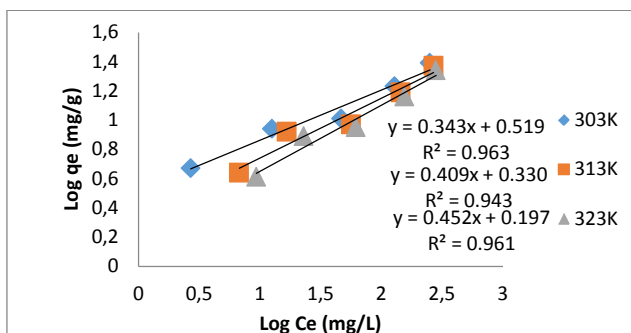


Fig 28: Freundlich isotherm plot for safranin O dye on acid activated tamarind seed carbon.

### Temkin Isotherm Model

The Temkin isotherm (Aharoni and Sparks, 1991) is given by:

$$q_e = \frac{RT}{b} \ln(A_T C_e) \tag{8}$$

The linear form of Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \tag{9}$$

Where  $A_T$  is the Temkin isotherm equilibrium binding constant (L/g);  $b_T$  is the Temkin isotherm constant;  $R$  is the universal gas constant (8.314J/mol/K);  $T$  is the temperature at 298K; and  $C_e$  is the equilibrium concentration (mg/L). Temkin isotherm constant  $b_T$  and Temkin isotherm equilibrium binding constant  $A_T$  were obtained from the intercepts and slopes of the linear plot of  $q_e$  versus  $\ln C_e$  as shown in Figures 29 and 30. The

correlation coefficients  $R^2$  ranged from 0.960 to 0.963 for orange G dye and 0.862 to 0.890 for safranin O dye as the temperature increased from 303K to 323K, respectively, as shown in Tables 4 and 5. This shows that the data for orange G dye conforms more to Temkin isotherm model than safranin O dye. However, similar results were obtained by Dada *et al.* (2012).

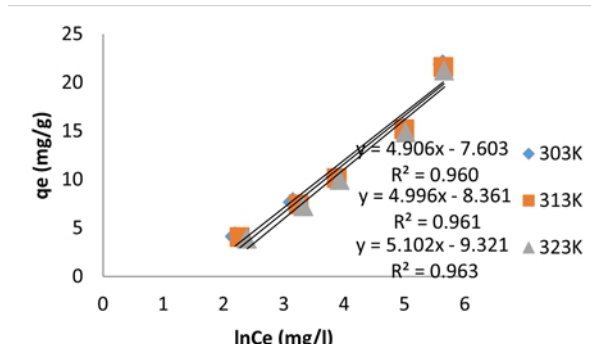


Fig 29: Temkin isotherm plot for orange G dye on acid activated tamarind seed carbon.

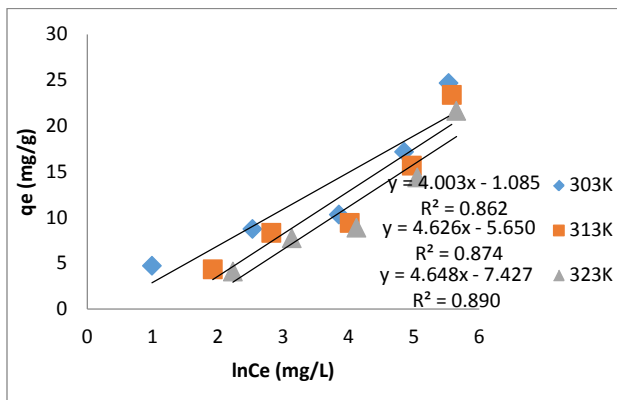


Fig 30: Temkin isotherm plot for safranin O dye on acid activated tamarind seed carbon.

The Dubinin-Radushkevich equation (Masany and Chaudhary, 1996) is given by:

$$q_e = (q_D) \exp(-B_D \varepsilon^2) \quad (10)$$

The linear form of Dubinin-Radushkevich equation is given by:

$$\ln q_e = \ln q_D - (B_D \varepsilon^2) \quad (11)$$

Where  $q_D$  is the theoretical isotherm saturation capacity (mg/g),  $B_D$  is the Dubinin-Radushkevich isotherm constant ( $\text{mol}^2/\text{kJ}^2$ ), and  $\varepsilon$  is the Polanyi potential.

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (12)$$

Where  $R$  is the universal gas constant (8.314J/mol/K);  $T$  is the temperature at 298K; and  $C_e$  is the equilibrium concentration (mg/L). The constant  $B_D$  gives the mean free energy  $E$  of sorption per molecule of the sorbates when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship;

$$E = 1/\sqrt{2}B_D \tag{13}$$

The Dubinin-Radushkevich parameters  $B_D$  and  $q_D$  (theoretical isotherm saturation capacity) were calculated from the slopes and intercepts of the linear plots of  $\ln q_e$  versus  $\epsilon^2$  as shown in Figures 31 and 32. The correlation coefficients  $R^2$  using orange G dye ranged from 0.727 to 0.738 and 0.619 to 0.695 for safranin O dye as temperature increased from 303K to 323K (Tables 4 and 5). This shows that the graph did not conform to the Dubinin-Radushkevich isotherm.

The mean free energy  $E$  reveals the nature of adsorption. Thus, if the value of adsorption energy  $E$  is less than 8KJ/mol, adsorption process is physical; but if it is ranged from 8 to 16KJ/mol, it is a chemical adsorption. The  $E$  values obtained ranged from 0.158 to 0.129KJ/mol using orange G dye and 0.500 to 0.224KJ/mol using safranin O dye. The  $E$  values obtained are less than 8KJ/mol, indicating that it is a physio-sorption process. However, similar results were obtained by Dada *et al.* (2012).

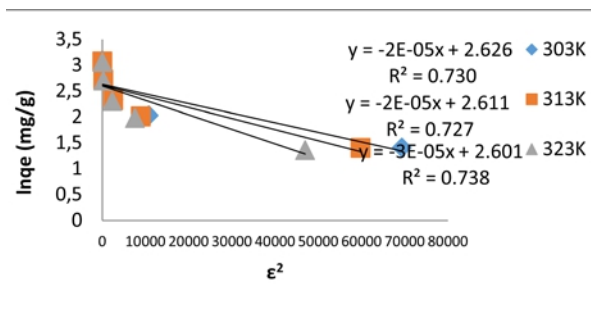


Fig 31: Dubinin-Radushkevich isotherm plot for orange G dye on acid activated tamarind seed carbon.

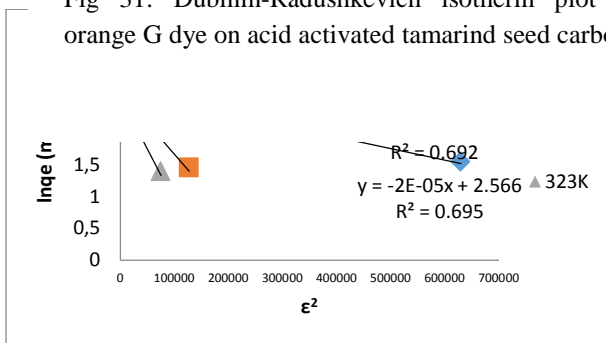


Fig 32: Dubinin-Radushkevich isotherm plot for safranin O dye on acid activated tamarind seed carbon.

Table 4: Adsorption Isotherm Studies Parameters for Acid Activated Tamarind Seed Using Orange G Dye

Models	Parameters	303K	313K	323K
Langmuir	Q (mg/g)	25.316	25.445	25.575
	b (L/mg)	0.016	0.015	0.013
	R <sub>L</sub>	0.276	0.287	0.301
	R <sup>2</sup>	0.967	0.969	0.970
Freundlich	n	2.155	2.119	2.004
	K <sub>f</sub> (L/g)	1.603	1.507	1.276
	R <sup>2</sup>	0.986	0.989	0.986
Temkin	b <sub>T</sub> (J/mg)	505.009	495.911	485.608
	A <sub>T</sub> (L/g)	0.212	0.188	0.161
	R <sup>2</sup>	0.960	0.961	0.963
Dubinin-Radushkevich	B (mol <sup>2</sup> /J <sup>2</sup> )	-2x10 <sup>-5</sup>	-2x10 <sup>-5</sup>	-3x10 <sup>-5</sup>
	q <sub>s</sub> (mg/g)	13.818	13.613	13.477
	E (KJ/mol)	0.158	0.158	0.129
	R <sup>2</sup>	0.730	0.727	0.738

Table 5: Adsorption Isotherm Studies Parameters for Acid Activated Tamarind Seed Using Safranin O Dye

Models	Parameters	303K	313K	323K
Langmuir	Q (mg/g)	27.027	27.027	25.641
	b (L/mg)	0.024	0.016	0.013
	R <sub>L</sub>	0.225	0.278	0.303
	R <sup>2</sup>	0.927	0.904	0.906
Freundlich	n	2.915	2.445	2.212
	k <sub>f</sub>	3.304	2.138	1.574
	R <sup>2</sup>	0.963	0.943	0.961
Temkin	b <sub>T</sub> (J/mg)	618.929	535.575	533.04
	A <sub>T</sub> (L/g)	0.763	0.295	0.202
	R <sup>2</sup>	0.862	0.874	0.890
Dubinin-Radushkevich	B (mol <sup>2</sup> /J <sup>2</sup> )	-2x10 <sup>-6</sup>	-1x10 <sup>-5</sup>	--2x10 <sup>-5</sup>
	q <sub>s</sub> (mg/g)	14.325	14.041	13.014
	E (KJ/mol)	0.500	0.224	0.158
	R <sup>2</sup>	0.619	0.692	0.695

**Adsorption Kinetics**  
**Pseudo-First Order Kinetic Model**

The pseudo-first order rate expression popularly known as Lagergren equation is generally expressed by this equation (Lagergren 1898):

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{14}$$

Where  $q_e$  and  $q_t$  are the amount of dye adsorbed at equilibrium time and at any time  $t$ , respectively (mg/g);  $K_1$  is the pseudo-first order adsorption rate constant ( $\text{min}^{-1}$ ); and  $t$  is the contact time (min). The Pseudo-first order rate constants,  $K_1$  and  $q_e$  at different temperatures were determined from the slope and intercept of the plot of  $\ln(q_e - q_t)$  versus  $t$  as presented in figures 33 and 34 . The results of the  $q_e$  and  $K_1$  were evaluated and listed in Tables 6 and 7. The values of the correlation coefficient  $R^2$  ranged from 0.940 to 0.972 for orange G dye and 0.763 to 0.910 for safranin O dye. The values for orange G dye was high showing that Pseudo-first order kinetic model describes the adsorption process, but was not applicable to safranin O dye. However, similar results were obtained by Ho and Mckay (1998).

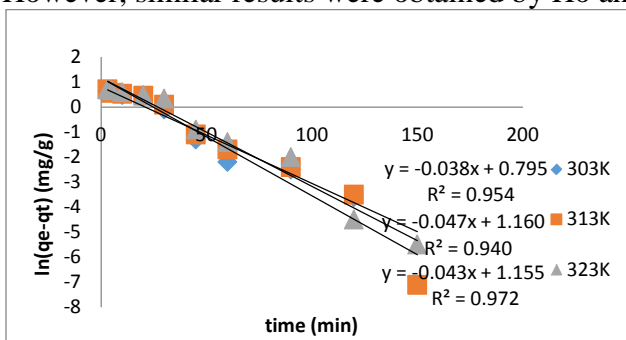


Fig 33: Pseudo-First order kinetics plot for orange G dye on acid activated tamarind seed carbon.

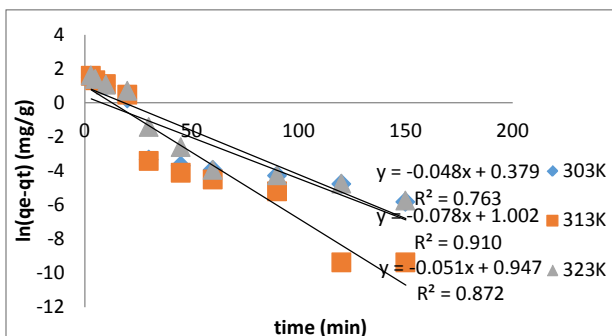


Fig 34: Pseudo-First order kinetics plot for safranin O dye on acid activated tamarind seed carbon.

**Pseudo-First Order Kinetic Model**

The pseudo-second order equation is expressed as (Ho and Mckay, 1998):

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \tag{15}$$

The integrated form of the expression gives:

$$t/q_t = 1/K_2q_e + t(1/q_e) \tag{16}$$

Where;  $K_2$  is the pseudo-second adsorption rate constant (g/mgmin). The pseudo-second order rate constants,  $K_2$  and  $q_e$  at different temperatures were determined from the slope and intercept of the plot of  $t/q_t$  versus  $t$  as presented in Figures 35 and 36. The results of  $K_2$  and  $q_e$  were evaluated and listed in Tables 6 and 7. The calculated  $q_e$  values agree with the experimental  $q_e$  values. The correlation coefficient values  $R^2$  was 0.999 for orange G dye and 0.999 for safranin O dye. These results show that the correlation coefficient of pseudo-second order was higher than that of pseudo-first order, which implies that the adsorption system studied follows the pseudo-second order kinetics model better. However, similar results were obtained by Horsfall *et al.* (2004).

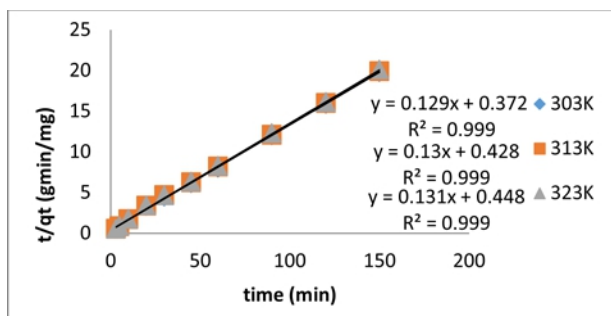


Fig 35: Pseudo-second order kinetic plot for orange G dye on acid activated tamarind seed carbon.

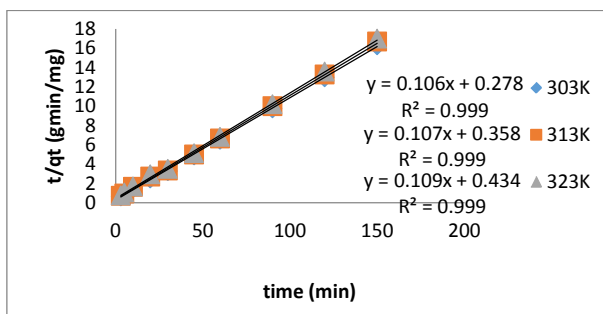


Fig 36: Pseudo-second order kinetic plot for safranin O dye on acid activated tamarind seed carbon.

### ***Elovich Kinetic Model***

The Elovich equation is expressed as (Oladoja *et al.*, 2008):

$$dq/dt = \alpha e^{-\beta q t} \quad (17)$$

Integrating this equation for the boundary conditions gives:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (18)$$

Where  $q_t$  is the quantity of gas adsorbed during the time  $t$  (mg/g);  $\alpha$  is the initial adsorption rate (mg/min);  $\beta$  is the extent of surface coverage and activated energy (g/mg); and  $t$  is the contact time (min). The Elovich constants,  $\alpha$  and  $\beta$  at different temperatures were determined from the slope and intercept of the plot of  $q_t$  versus  $\ln(t)$  as presented in Figures 37 and 38. The results of  $\alpha$  and  $\beta$  were evaluated and listed in Tables 6 and 7. The values  $\alpha$  for both dyes decreased with increase in temperature from 303K to 323K. This shows that as adsorption rate decreased, desorption rate increased with increased temperature. The values of the correlation coefficient  $R^2$  ranged from 0.903 to 0.922 for orange G dye and 0.878 to 0.902 for safranin O dye as temperature of adsorption varied from 303K to 323K. This shows that the graphs conform to the model. However, similar results were obtained by Oladoja *et al.* (2008).

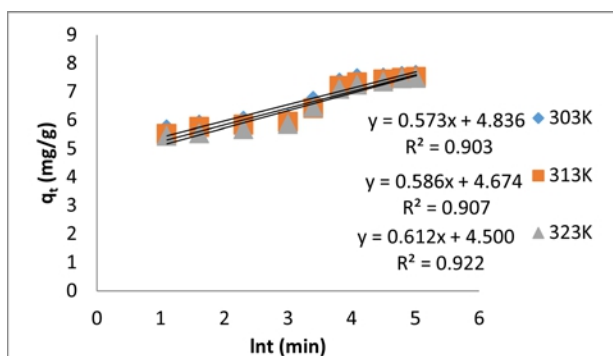


Fig 37: Elovich model kinetic plot for orange G dye on acid activated tamarind seed carbon.



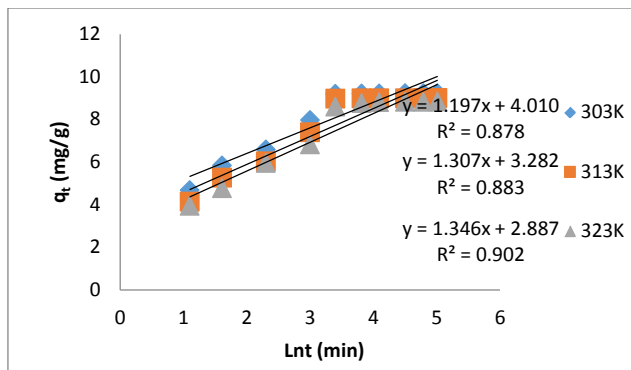


Fig 38: Elovich model kinetic plot for safranin O dye on acid activated tamarind seed carbon.

The Bhattacharya-Venkobachar model (Goswami and Ghosh, 2005) is expressed as:

$$\ln(1 - U_t) = K_B t \tag{19}$$

$$U_t = \frac{C_o - C_t}{C_o - C_e} \tag{20}$$

Effective diffusion Coefficient  $D_2$  is obtained from the equation;

$$D_2 = \frac{K_B r^2}{\pi^2} \tag{21}$$

Where  $r$  is the particle radius (m);  $K_B$  is the Bhattacharya-Venkobachar rate constant;  $C_o$  is the initial concentration (mg/L);  $C_e$  is the equilibrium concentration (mg/L);  $C_t$  is the equilibrium concentration at time,  $t$  (mg/L);  $U_t$  is the Bhattacharya-Venkobachar constant; and  $t$  is contact time (min).

The Bhattacharya-Venkobachar rate constants,  $K_B$  for all adsorbents at different temperatures were determined from the slope of the plot of  $\ln(1-U_t)$  versus  $t$  as presented in figures 39 and 40. The results of  $K_B$  and  $D_2$  were evaluated and listed in Tables 6 and 7. The correlation coefficient values  $R^2$  ranged from 0.954 to 0.976 for orange G dye and 0.866 to 0.937 for safranin O dye, as temperature of adsorption varied from 303K to 323K. Thus, this indicates that the kinetic data followed Bhattacharya-Venkobachar model.

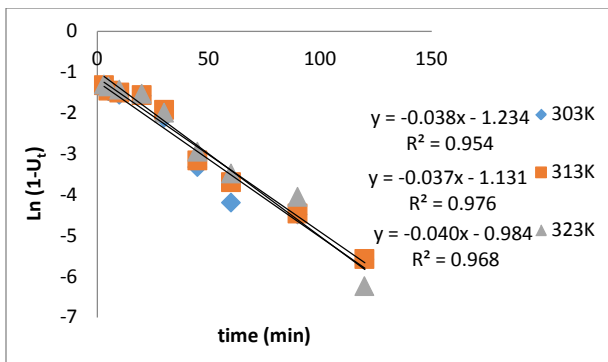


Fig 39: Bhattacharya-Venkobachar kinetic model plot for orange G dye on acid activated tamarind seed carbon.

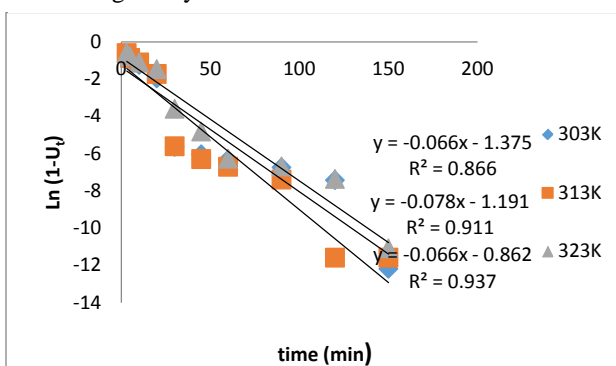


Fig 40: Bhattacharya-Venkobachar kinetic model plot for safranin O dye on acid activated tamarind seed carbon.

### ***Intra Particle Diffusion Kinetic Model***

The intra-particle diffusion equation is expressed as (Weber et al., 1972):

$$q_t = Kt^{0.5} + C_t \tag{22}$$

Where  $q_t$  is the amount of dye adsorbed at time  $t$  (mg/g);  $K$  is the rate constant of the intra particle transport (g/mg/min);  $C_t$  is the equilibrium concentration (mg/L); and  $t$  is the contact time (min). The intra-particle diffusion rate constants,  $K$  and  $C_t$  at different temperatures were determined from the slope and intercept of the plot of  $q_t$  versus  $t^{0.5}$  as presented in Figures 41 and 42. The results of  $K$  and  $C_t$  were evaluated and listed in Tables 6 and 7. The values of the correlation coefficient  $R^2$  ranged from 0.926 to 0.948 for orange G dye, and 0.943 to 0.961 for safranin O dye, as temperature of adsorption varied from 303K to 323K. The high correlation coefficients for both dyes indicate the presence of intra-particle diffusion as the rate determining step. The rate limiting step that is the slowest step of the

reaction may be the intra-particle diffusion or the boundary layer of solute on the solid surface from the bulk of the solution in a batch process (Goswami and Ghosh, 2005). As shown in Figures 41 and 42, the linear lines did not pass through the origin due to the difference in mass transfer rate from the initial to the final stage of adsorption. The deviation of the linear lines from the origin indicates that intra-particle transport is not the sole rate limiting step, but other kinetic models may control the rate of adsorption simultaneously (Abechi *et al.*, 2011).

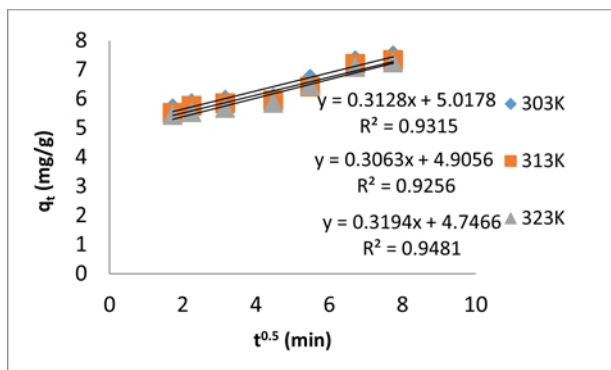


Fig 41: Intra particle diffusion kinetic model plot for orange G dye on acid activated tamarind seed carbon.

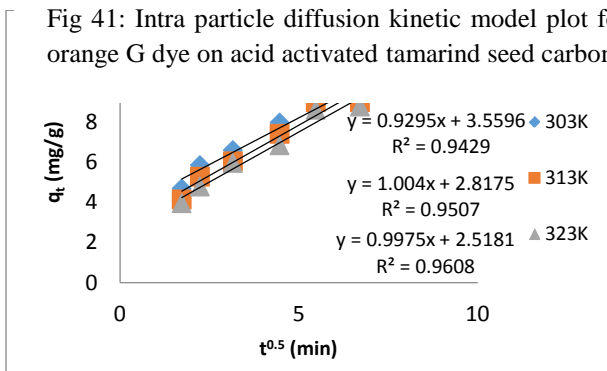


Fig 42: Intra particle diffusion kinetic model plot for safranin o dye on acid activated tamarind seed carbon.

TABLE 6: Kinetics Studies for Acid Activated Tamarind Seed Using Orange G Dye

Models	Parameters	303K	313K	323K
Pseudo-first order	$K_1$ (min <sup>-1</sup> )	-0.038	-0.047	-0.043
$q_e$ (mg/g)	2.214	3.190	3.174	
$R^2$	0.954	0.940	0.972	
Pseudo-second order	$K_2$ (g/mgmin)	0.045	0.039	0.038
$q_e$ (mg/g)	7.752	7.692	7.634	
$R^2$	0.999	0.999	0.999	
Elovich	$\alpha$ (mg/gmin)	2651.607	1705.603	955.198
$\beta$ (g/mg)	1.745	1.706	1.634	
$R^2$	0.903	0.907	0.922	
Intra particle diffusion	$K$ (g/mg/min)	0.313	0.306	0.319
$C_1$ (mg/L)	5.018	4.906	4.747	
$R^2$	0.932	0.926	0.948	
Bhattacharya-Venkobachor	$K_B$	-0.038	-0.037	-0.040
$D_2$ (m <sup>2</sup> /g)	$-2.17 \times 10^{-11}$	$-2.11 \times 10^{-11}$	$-2.28 \times 10^{-11}$	
$R^2$	0.954	0.976	0.968	

TABLE 7: Kinetics Studies for Acid Activated Tamarind Seed Using Safranin O Dye

Models	Parameters	303K	313K	323K
Pseudo-first order	$K_1$ (min <sup>-1</sup> )	-0.048	-0.078	-0.051
$q_e$ (mg/g)		1.461	2.724	2.578
$R^2$		0.763	0.91	0.872
Pseudo-second order	$K_2$ (min <sup>-1</sup> )	0.040	0.032	0.027
$q_e$ (mg/g)		9.434	9.346	9.179
$R^2$		0.999	0.999	0.999
Elovich	$\alpha$ (mg/gmin)	34.119	16.100	11.496
$\beta$ (g/mg)		0.835	0.765	0.743
$R^2$		0.878	0.883	0.902
Intra particle diffusion	$K$ (g/mg/min)	0.930	1.004	0.998
$C_1$ (mg/L)		3.560	2.818	2.518
$R^2$		0.943	0.951	0.961
Bhattacharya-Venkobachor	$K_B$	-0.066	-0.078	-0.066
$D_2$ (m <sup>2</sup> /g)		$-3.76 \times 10^{-11}$	$-4.44 \times 10^{-11}$	$-3.76 \times 10^{-11}$
$R^2$		0.866	0.911	0.937

### Thermodynamics Study

The aim of thermodynamic study is to determine the spontaneity of the adsorption process by the use of thermodynamic parameters such as free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ), and entropy change ( $\Delta S^0$ ).  $\Delta G^0$  determines if the process is feasible and spontaneous or not;  $\Delta H^0$  determines if the process is exothermic or endothermic; and  $\Delta S^0$  determines the increase or decrease in randomness of the process at the solid/solution interface. Reactions occur spontaneously at a given temperature if  $\Delta G^0$  is a negative quantity (Abdessalem *et al.*, 2012). The temperatures used in the thermodynamic study were 303K, 313K, and 323K. The thermodynamic parameters were calculated based on the following equations:

$$\Delta G^{\circ} = -RT \ln(K) \tag{23}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{24}$$

Where T is the absolute temperature (K), R is the universal gas constant (8.314J/mol/K) and K is the Langmuir constant. The Gibbs free energy of adsorption ( $\Delta G^0$ ) can be related with the equilibrium constant K (L/mol), corresponding to the reciprocal of the Langmuir constant b (Oladoja *et al*, 2008). The values of the thermodynamic parameters using orange G and safranin O dye are listed in Table 8. The negative  $\Delta G^0$  values indicate that the process is thermodynamically feasible and spontaneous. The negative  $\Delta H^0$  values indicate that the nature of adsorption process is exothermic. This is also supported by the decrease in the value of adsorbed capacity of the sorbent with the increase in temperature. The positive values of  $\Delta S^0$  pointed to an increased disorder of the solid/solution interface during the adsorption process. However, similar results were obtained by Gunasekar and Ponnusami (2012).

Table 8: Thermodynamics Studies for Acid Activated Tamarind Seed

Dyes (KJ/mol)	T(K)	$\Delta G$ (KJ/mol)	$\Delta S$ (J/mol K)	$\Delta H$
Orange G	303	-22.39		
313	-22.96	0.046	-8.488	
323	-23.31			
Safranin O	303	-22.77		
313	-22.47	0.007	-24.87	
323	-22.63			

## Conclusion

Adsorption process has been successfully used in the dye-based wastewater treatment using activated carbons obtained from tamarind seeds. The proximate analysis carried out on the activated carbon show that each property value was in good range. The Fourier transform infrared spectroscopic analysis done on the non-acid activated adsorbent and acid activated adsorbent shows the presence of functional groups (alkanes, alkenes, alkynes, carboxyl, phenols, etc.) which are very important adsorption sites. The X-ray Diffraction analysis shows the presence of high diffraction peaks and broadness which are evidence of good crystallinity of the prepared powdered samples. The Scanning Electron Microscopy images show various shape and pore sizes at different magnifications. The batch adsorptive studies carried out shows that particle size, pH, adsorbent dosage, ion concentration, and contact time are effective on the adsorption of dyes from wastewater using tamarind seed adsorbents. The Freundlich isotherm model best fitted the equilibrium data obtained. Pseudo-Second order kinetic model best describes the adsorption kinetics carried out. Thus, the thermodynamic parameters calculated which shows that the adsorption

process is feasible, has an increased disorder of solid-solute interface, and is also exothermic in nature.

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