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EFFECT OF ACTIVATED CARBONS FROM RUBBER SEED SHELL ON CRYSTAL VIOLET REMOVAL

Anegbe, B.[a], Emeribe, R. C.[b] and Okuo, J. M.[b]

[a]Department of Basic and Industrial Chemistry, Western Delta University, P.M.B. 10, Oghara, Delta State. e-mail: bala.anegbe@wdu.edu.ng

[b]Environmental Analytical Research Laboratory, Department of Chemistry, University of Benin, Benin City. e-mail: james.okuo@uniben.edu

Corresponding Author's e-mail / phone no: james.okuo@uniben.edu / 08065995410

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ABSTRACT

Dyes are complex organic compounds which are used by various industries to add colour to their products. Water bodies are polluted when these industries dispose their effluents to the environment. In this study, powdered activated carbon was prepared from rubber seed shells (RSS) and was employed in the removal of crystal violet from aqueous solution. The rubber seed shell was first activated using ammonium chloride, shared into two portions and was carbonized at 500 and 300°C respectively. They were characterized in terms of bulk density, ash and moisture contents, surface area and IR Spectroscopy. Batch adsorption process which involved the use of these rubber seed shells was employed in the removal of crystal violet from aqueous solution. The effect of contact time, adsorbent dose, pH and dye concentration were investigated. The results showed that maximum adsorption capacity of 500°C carbonized rubber seed shell was 97.93 % at 75 mins. The adsorbent dose, pH and optimum concentration were respectively 5.0 g, 10 and 10 mg/l. The maximum adsorption capacity of 300 °C carbonized rubber seed shell was 96.73 % at 30 mins with an adsorbent dose of 5.0 g; pH of 10 and optimum concentration of 10 mg/l. The experimental data obtained were fitted into Freundlich, Langmuir, Temkin and Frumkin adsorption isotherms and was found to fit into the four isotherms. However, the rubber seed shell carbonized at 500 °C was found to be more effective in the removal of crystal violet from aqueous solution than that carbonized at 300°C. This might probably be due to the larger surface area.

Keywords: Activated Carbon, Rubber Seed Shell and Crystal Violet

INTRODUCTION

Dyes are one of the most hazardous chemical compounds found in industrial effluents and need to be treated since their release into aquatic environment causes reduction in the growth of algae (Da Sousa *et al*., 2012). This is due to obstruction of light required for photosynthesis, which subsequently leads to ecological imbalance in the aquatic ecosystem (Da Sousa *et al*., 2012). A large number of dyes are discharged into waste stream by industries. Many industries, such as dyestuff, textile, pharmaceutical, paper, plastic, and tannery, make use of dyes to add color to their products; of these industries; textile industry is the largest consumer of dyes (Da Sousa *et al*., 2012). It has been shown that about 10,000 different textile dyes with an estimated annual production of 7 metric tons are commercially available worldwide (Carmen and Daniela 2012). As a result of the enormous utilization of these dyes, substantial amount of dyes are frequently released as wastewater into aquatic environment. Contamination of aquatic environment by dyes has also been shown to have toxic, carcinogenic, and aesthetic effects on humans (Ratna and Padhi 2012). Due to the deleterious effects of dyes on aquatic ecosystem, different methods have been proposed for the removal of dyes in contaminated effluents and have been broadly classified as biological, chemical and physical (Adinew, 2012). Presently, there is a growing interest and concern over contamination of the aquatic environment by dyes. This is because pollution of the environment has become a serious problem worldwide and awareness of water pollution has been a major concern for environmentalists (Paul *et al*., 2011). Rubber seed shell (RSS) is a biomass waste and currently has no commercial value (Noorfidza *et al*., 2011). Huge amount of RSS are agricultural waste and become environmental problem. This carbonaceous material can be converted into useful, high-value adsorbent. Therefore, one of the solutions to this problem is to reuse this waste to produce activated carbon which can be used for many purposes. Recently, efforts are being made worldwide to invent more effective, low cost, environmental friendly and easily regenerated adsorbents from agricultural wastes (Mahmoud *et al*., 2012; Sharma *et al*., 2012 and Rashed, 2013). Activated carbon is widely used as adsorbents and also as catalysts as well as catalyst supports for gas-phase and liquid-phase application, due to its extensive surface area, well-developed micro pore structure and the presence of functional groups of different types on the surface. Commercial activated carbon is a preferred adsorbent for the removal of micro pollutants from the aqueous phase; however, its widespread use is restricted due to high costs (Joana *et al*., 2007). There has been a constant search for low cost adsorbents. This research seeks to reveal the use of rubber seed shell as a low cost adsorbent in the removal of crystal violet dye from aqueous solution which is a way of converting this agricultural waste into useful material.

MATERIALS AND METHODS

Preparation of Rubber Seed Shell Activated Carbon

In this research, the chemical activation method was used. It involved accomplishing the activation and carbonization in a single step by carrying out the thermal decomposition of the rubber seed shells that was previously impregnated with ammonium chloride as activating agent (Okieimen *et al*., 2005). The activated rubber seed shell was then divided into two portions. The first portion was carbonized in a muffle furnace at 500 °C for 2 hrs while the other portion was carbonized at 300 °C for 3 hrs. The two portions were separately ground and washed thoroughly until the pH of the water became neutral.

Characterization of Prepared Activated Carbon

In this research the bulk density, ash content, moisture content were determined using American society for testing and materials ASTM D7481-09, ASTM D2866-11, ASTM D2216-10 methods as reported by Okieimen *et al*., (2007). The pH of the activated carbon was determined as reported by Okieimen *et al*., (2007). The surface area of the activated carbon was determined as proposed by Mianowski *et al*. (2007). The I.R scan of the activated carbon was done using a Bulk Scientific, Model 500 Infra-Red Spectrophotometer. From the spectrum, the functional groups present in the activated carbon were obtained.

ADSORPTION EXPERIMENT

The adsorption experiment was carried out as describe by Muhammad *et al*., (2012). All glasswares were thoroughly washed, rinsed with distilled water and dried in an oven. The set ups for the experiment were prepared in batches and were subjected to varying conditions and agitated in a thermostatic shaker at 180 rpm after which filtration of the adsorbent from the solutions were carried out. The batch adsorption was carried out at room temperature and the concentration of crystal violet left in the solutions were determined using a Techmel & Techmel USA, model-25 Ultraviolet/Visible Spectrophotometer and the percentage removal of crystal violet by the two adsorbents (500 and 300°C carbonized rubber seed shell) were calculated.

RESULTS AND DISCUSSION

The bulk density is an important physical parameter of activated carbon especially when the activated carbon is being investigated for its filterability. It determines the amount of carbon that can be contained in a filter of a given solid and the amount of the treated liquid that can be retained by the filter cake. According to Ahmedna *et al*., (2000), carbons with bulk densities of about 0.5 g/ml are adequate for sugar decolouration. The bulk densities of 500 and 300 °C carbonized rubber seed shells which were found to be 0.785 and 0.718 g/ml (Table 1) respectively make them suitable to be used in decolouration processes. Ash content of activated carbons is an indication of their quality. The lower the ash content, the more effective the activated carbon for adsorption. Ash content affects the overall activity of activated carbon. From the result, the ash contents of the carbonized rubber seed shells were found to be 0.5 and 0.3% respectively for 500 and 300 °C treated samples. These values are lower than 2.08, 2.21 and 2.14 % obtained for activated carbon made from cornelian cherry, apricot stone and almond shell (Demirbas, 2009), This may be an indication that the chemical activation used in this study greatly reduced the production of ash. The 500 and 300 °C carbonized rubber seed shells had moisture content of 6.8 and 5.4 % respectively.

Table 1: Physio - Chemical Properties of 500 and 300 °C Carbonized Rubber Seed Shell Activated Carbon.

Parameters	500 °C carbonized Rubber seed shell Ac	300 °C carbonized Rubber seed shell Ac
Bulk density (g/ml)	000.719	000.785
Ash content (%)	000.500	000.300
Moisture content (%)	006.800	005.400
pH	007.150	006.980
Surface area(m^2/g)	453.320	324.420

The moisture content of activated carbon is often required to define and express its properties in relation to the weight of the carbon. Since moisture impairs the adsorption capacity of activated carbons, it implies that this rubber seed shells activated carbon are good adsorbents. The pH of the carbonized rubber seed shells were found to be 7.15 and 6.98 at 500 and 300 °C. It has been reported by (Ahmedna *et al*., 2000 and Okieimen *et al*., 2007) that for most applications, activated carbon with a pH range of 6 to 8 is acceptable. The surface area of rubber seed shell (RSS) carbonized at 500 and 300 °C were respectively 453.32 and 324.42 m^2/g. This is an indication that there was better evolution and development of pore in the carbonization temperature of 500 °C compared to 300 °C. The IR spectra for 500 and 300 °C carbonized rubber seed shell are shown in Figure1a and b respectively.

The functional groups identified in the activated rubber seed shell carbons and the fragments are shown in Figs. 1a and b and Tables 2a and b.

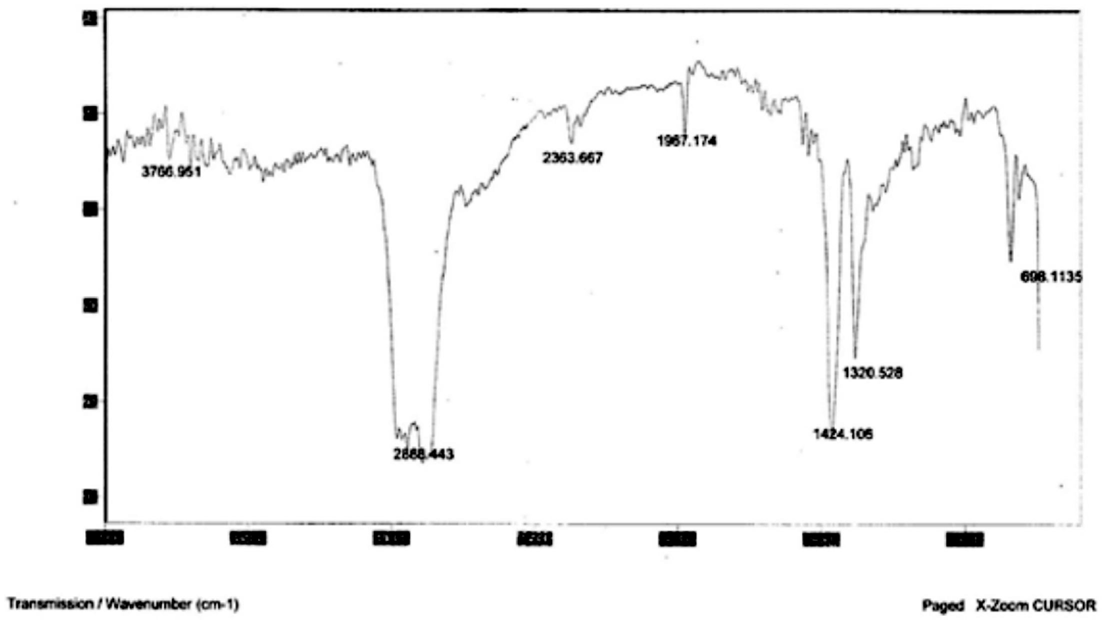

Fig. 1a. IR Spectrum of 500 °C Activated Rubber Shell Carbons

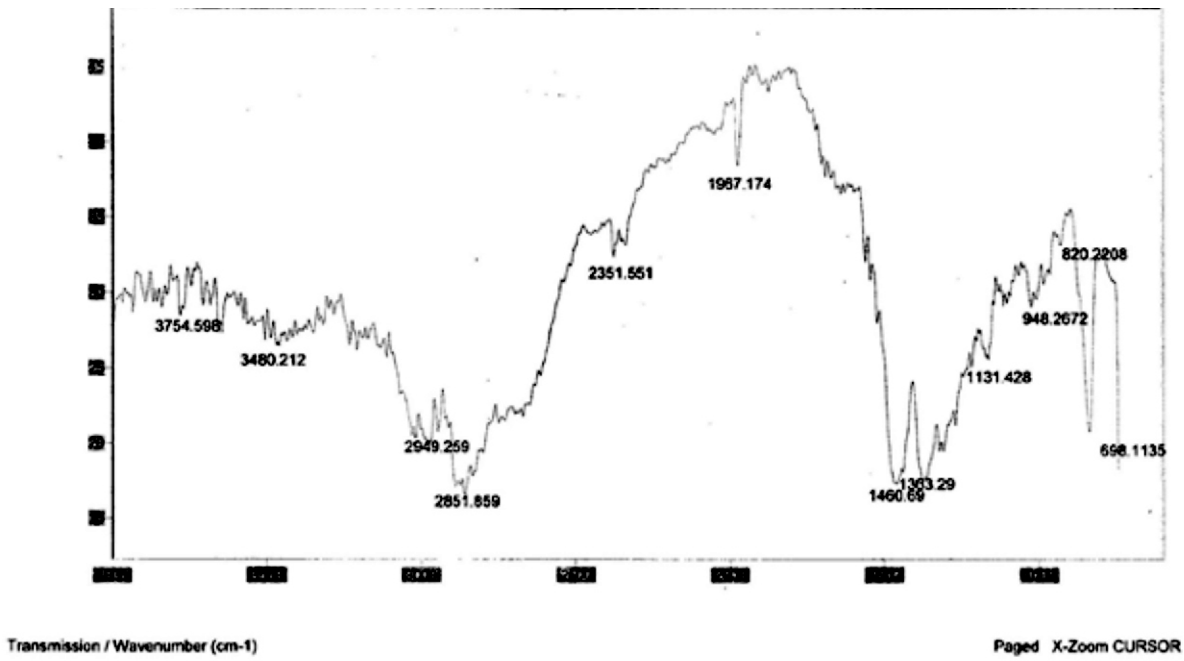

Fig. 1b IR Spectrum of 300 °C Activated Rubber Shell Carbons.

Table 2a Functional Groups which are Present in Rubber Seed Shells Carbonized at Temperatures of 500 °C and 300 °C

FREQUENCY (cm^{-1})	FREQUENCY RANGE (cm^{-1})	FUNCTIONAL GROUP
3766.9510	4000-3600	Alcohols and Phenols (OH stretch)
2888.4430	3000-2850	Alkyl groups (C-H stretch)
2363.6670	3300-2200	Alkynes, Nitriles (C=C), (C=N)
1967.1740	2260-2150	Alkynes or Nitriles R≡CH or RC≡N
1424.1060	1465-1415	Aromatic (C-H bend)
1320.5280	1300-1150	Esters, Anhydrides (C-O stretch)
0698.1135	710-690	Monosubstituted Benzene

Table 2b Additional Functional Groups Present Only in 300 °C Rubber Seed Shells Carbonized.

3480.212	3550-3000	Amine group (N-H stretch)
948.2672	955-910	Vinyl groups (C-H bend of CH_2=C)
1131.428	1150-1100	Alcohols R_2CH_2OH or R_3COH (C-O stretch)

Adsorption Studies

The results of adsorption capacity of rubber seed shells carbonized at temperatures of 500 °C and 300 °C are presented in Figs. 2 – 5

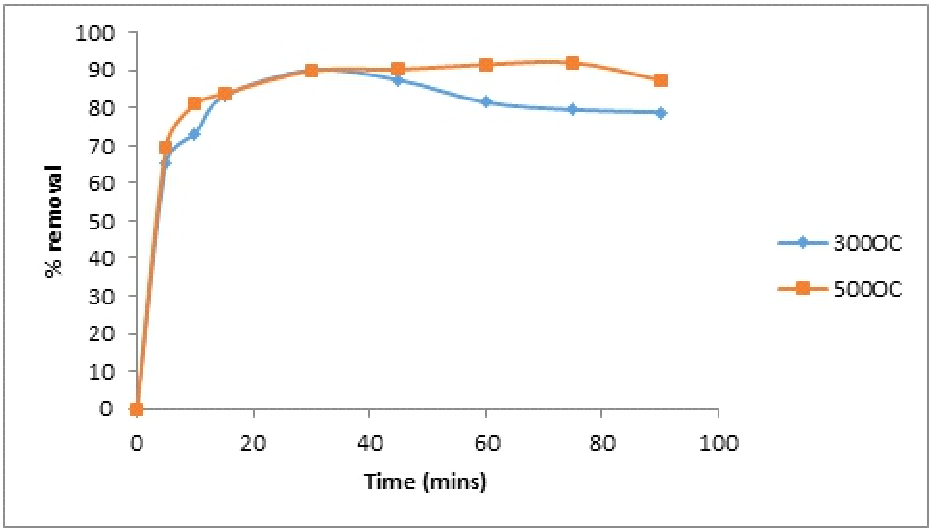

Fig 2: Percentage Removal against Time for 500 and 300 °C Activated Rubber Seed Shell Carbons.

As the contact time increased (Fig. 2) the percentage removal of the dye increased significantly up to a maximum of 90.10 % for a 30 mins period in 300 °C carbonized rubber seed shell. There was also increase in percentage removal up to 92.08 % for a period of 75 mins in the case of 500 °C carbonized rubber seed shell. The rate of dye removal is higher within these periods due to large surface area of the adsorbents. This is in agreement with the observation of (Okuo *et al.*, 2014 and Muhammad *et al.*, 2012). The time variation curve is smooth and continuous which indicates formation of monolayer coverage on the outer interface of the adsorbent Okuo *et al.*, (2014). The reaction is a heterogeneous process which attained equilibrium due to exhaustion of the adsorption sites Okuo *et al.*, (2014), followed by desorption as seen in Fig 2.

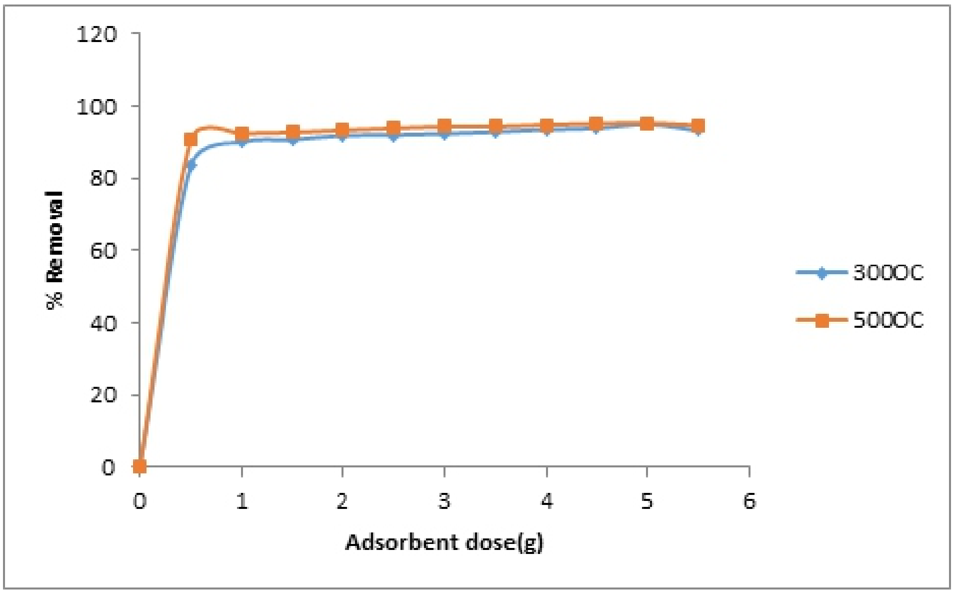

Fig. 3: Percentage Removal of Crystal Violet against Adsorbent Dose of 500 and 300 °C Activated Rubber Seed Shell Carbons.

For an effective dye removal, the dosage of adsorbent to be used should be considered. From Fig. 3, the percentage removal of crystal violet increased from 90.57 to 95.28 % and 83.41 to 94.96 % for 500 and 300 °C carbonized rubber seed shell. This is due to the greater availability of the exchangeable sites of the adsorbent. This trend has been reported by (Maley *et al.*, 2013 and Okuo *et al.*, 2014). It was also observed that further increase of the adsorbent dose to 5.5g decreased the percentage removal. This may be due to adsorbent aggregation which causes blockage of the adsorption pores.

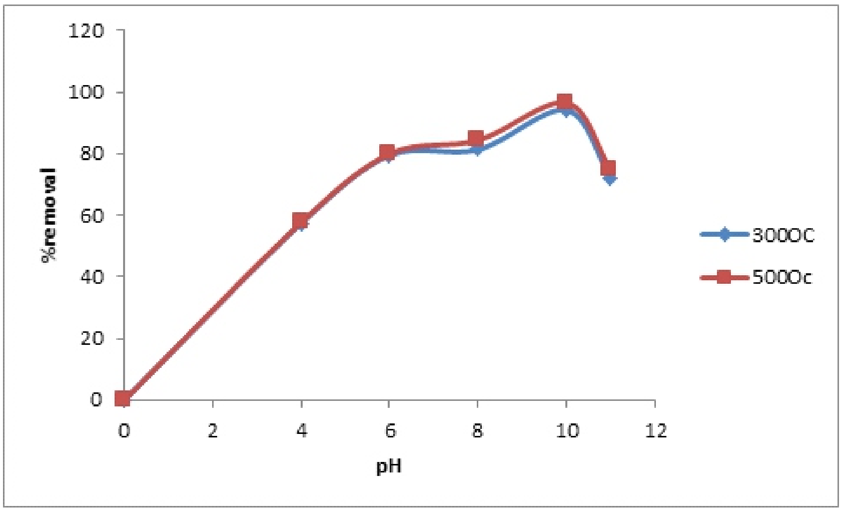

Fig.4 Percentage Removal against pH for 500 °C and 300 °C Activated Rubber Seed Shell Carbons.

In this study, the optimum pH for the adsorption capacity of crystal violet was achieved by varying the pH of the dye solution. There is an increase in the percentage removal from 57.72 to 96.43 % and 57.39 to 94.06 % for 500 and 300 °C carbonized rubber seed shell (Fig. 4) when the pH was increased from 4 to 10. The low removal of the dye at pH 4 may be associated with the competition that sets in between the excess H^+ concentration and the cationic part of the dye for the active site of the adsorbent (Okuo *et al.*, 2014). There is also clear evidence that rubber seed shell activated carbon adsorbs crystal violet better in alkaline medium. Both adsorbents showed a decrease in percentage removal at pH 11 with 74% and 71% for 500 and 300 °C carbonized adsorbents. This pattern is referred to as adsorption envelop. A similar result has been reported by (Muhammed *et al.*, 2002).

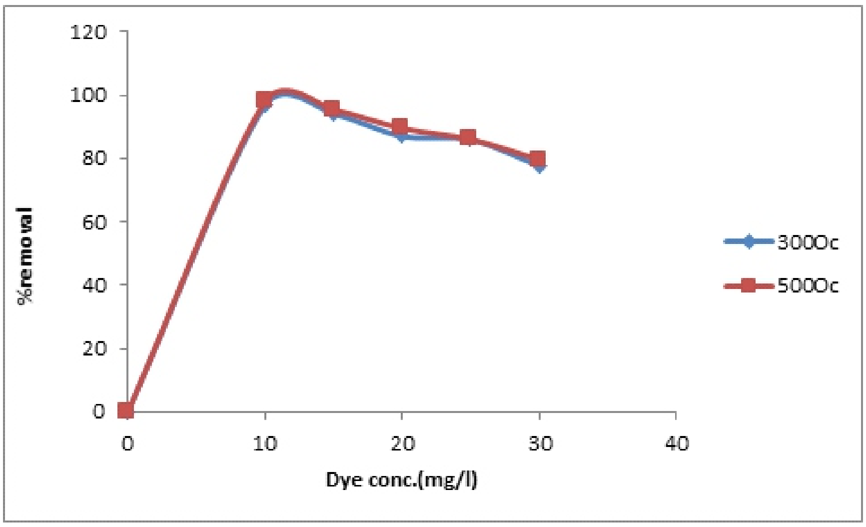

Fig. 5. Percentage Removal against Dye Concentration for 500 and 300°C Activated Rubber Seed Shell Carbons.

An increase in dye concentration from 10 to 30 mg/l with adsorbent dose of 5 g at pH 10 caused a decrease in percentage removal of the dye from 97.93 to 79.58 % and 96.73 to 77.68 % in 500 and 300 °C activated adsorbents (Fig. 5). This may be attributed to the fact that most of the adsorption sites have been occupied by the adsorbate followed by possible desorption (Okuo *et al.*, 2014).

Adsorption Isotherms

Various isotherm models have been used for equilibrium modeling of adsorption systems. The Freundlich and Langmuir models which are most widely acceptable are used in this study together with Temkin and Frumkin isotherms.

Freundlich Adsorption Isotherm: This is used to describe the adsorption characteristics for a heterogeneous surface (Ho *et al.*, 2005). The equation proposed by Freundlich encompasses the heterogeneity of sites and the exponential distribution of sites and their energies. The Freundlich isotherm equation is given by equation 1.

$$\frac{x}{m} = KC^{1/n} \qquad (1)$$

Where K is the Freundlich isotherm constant, n is the adsorption intensity, C is the concentration

$\frac{x}{m}$ = quantity adsorbed (q_e)

Linearizing equation (1) gives:

$$log_{q_e} = logk_f + \frac{1}{n}logC_e \qquad (2)$$

Where, k_f and n are the Freundlich constants related to the adsorption capacity of the sorbent and the adsorption intensity. A plot of the logarithm of quantity adsorbed against the logarithm of the concentration enabled the estimation of the correlation coefficients as shown in the Figures 6a and 6b for 300 and 500 °C activated rubber seed shell carbons.

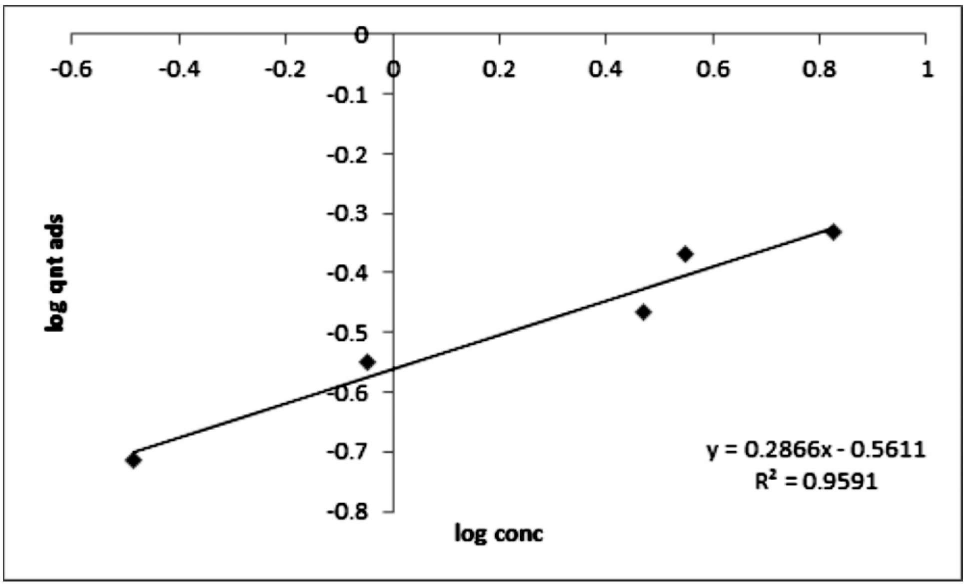

Fig: 6a) Freundlich Isotherm of 300 °C Activated Rubber Seed Shell Carbons.

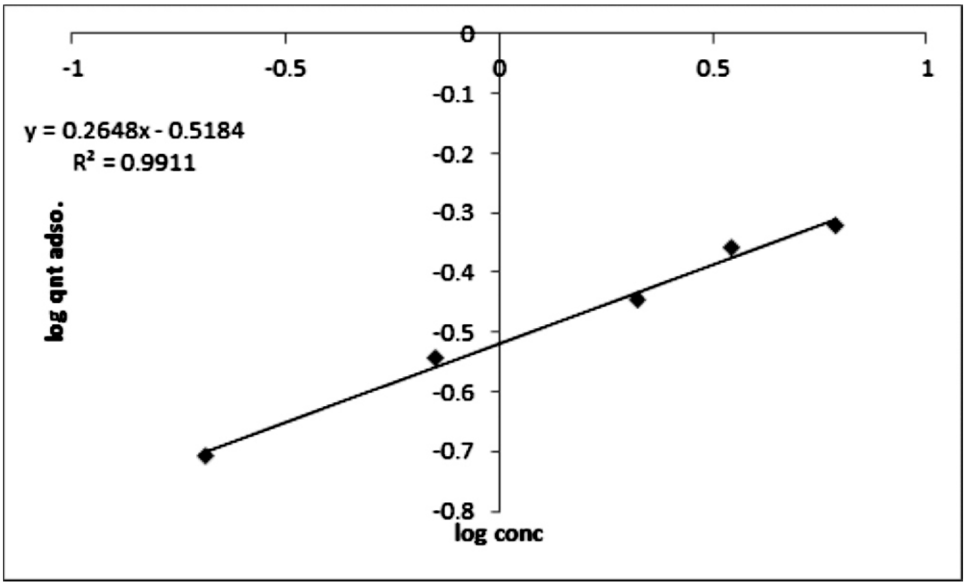

Fig. 6b: Freundlich Isotherm of 500 °C Activated Rubber Seed Shell Carbons.

The correlation coefficients (R^2) obtained from the Freundlich isotherms for 300 and 500°C carbonized rubber seed shells are 0.9591 and 0.9911 respectively. This indicates that the two adsorption processes are characteristic of heterogeneous surfaces and fitted well into the Freundlich isotherm.

Langmuir adsorption isotherm: Langmuir isotherm is an ideal one for physical and chemical adsorption. This isotherm equation gives the fractional coverage q in the form of;

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

Where, q_e is the quantity adsorbed, q_m is the maximum adsorbate uptake, K_a is the Langmuir constant related to energy of adsorption, which quantitatively reflects the affinity between the adsorbent and the adsorbate. C_e is the concentration of the solution at equilibrium. Linearizing the equation gives:

$$C_e/q_e = 1/q_m K + 1/q_m \times C_e \quad (4)$$

The langmiur parameters were obtained by fitting the experimental data to linearized equation derived from equation 5.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_a q_m C_e} \quad (5)$$

A plot of $\frac{1}{q_e}$ versus $\frac{1}{Ce}$ resulted in straight lie graph of slope $1/K_a q_m$ and an intercept of $1/q_m$

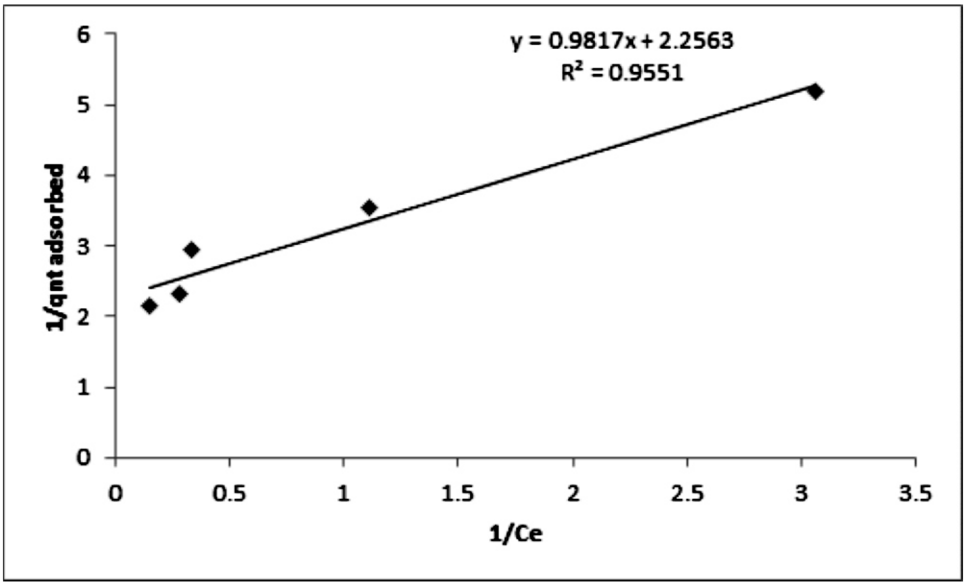

Fig. 7a. Langmuir Isotherm of 300 °C Activated Rubber Seed Shell Carbons.

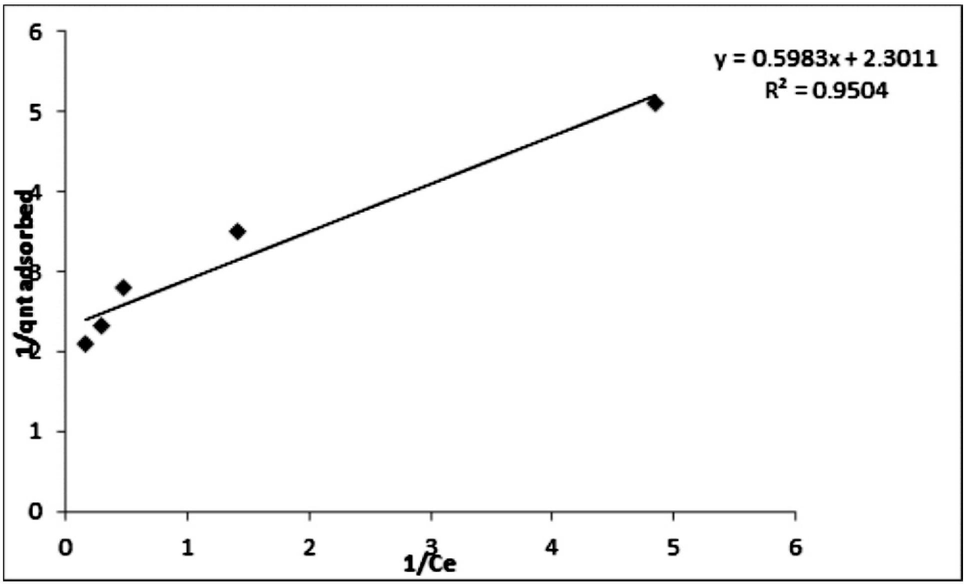

Fig. 7b. Langmuir Isotherm of 500 °C Activated Rubber Seed Shell Carbons

From Figures 7a and 7b, the R^2 values for 300 and 500 °C carbonized rubber seed shells are 0.9551 and 0.9504 respectively. This means that both of them fitted well into Langmuir isotherm indicating that the adsorption processes are more of chemisorption and monolayer coverage.

Temkin Adsorption Isotherm: This isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with quantity adsorbed due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies (Oladoja *et al.*, 2008).

The Temkin isotherm is given by:

$$q_e = b \log A + b \log C \qquad (6)$$

q_e = quantity adsorbed

A plot of quantity adsorbed against the logarithm of concentration enables the determination of the isotherm constants b and A from the slope and the intercept of the linear plot. The fitness of the adsorption into this isotherm is determined by the R^2 value obtained from the plot.

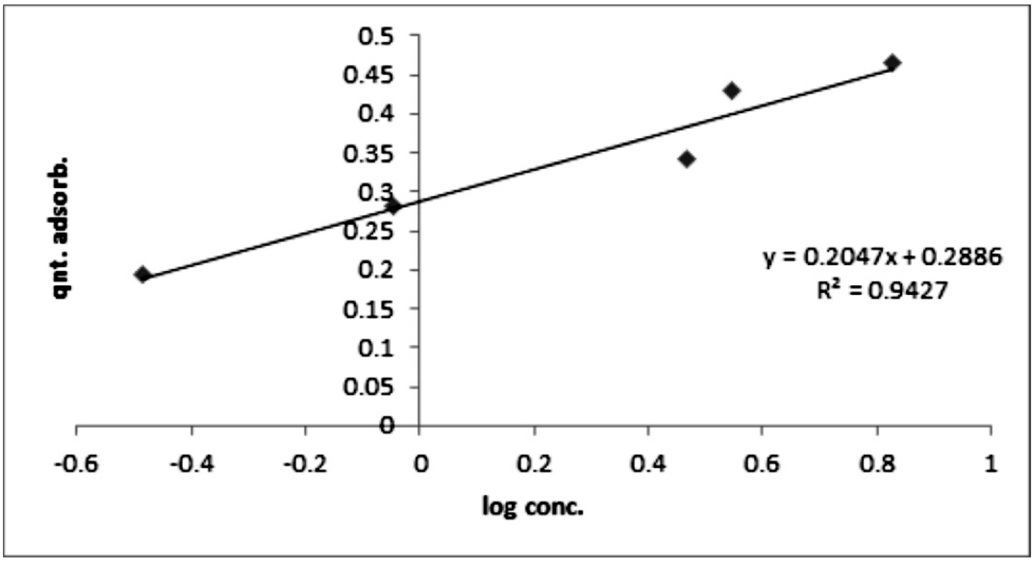

Fig. (8a) Temkin Isotherm of 300 °C Activated Rubber Seed Shell Carbons

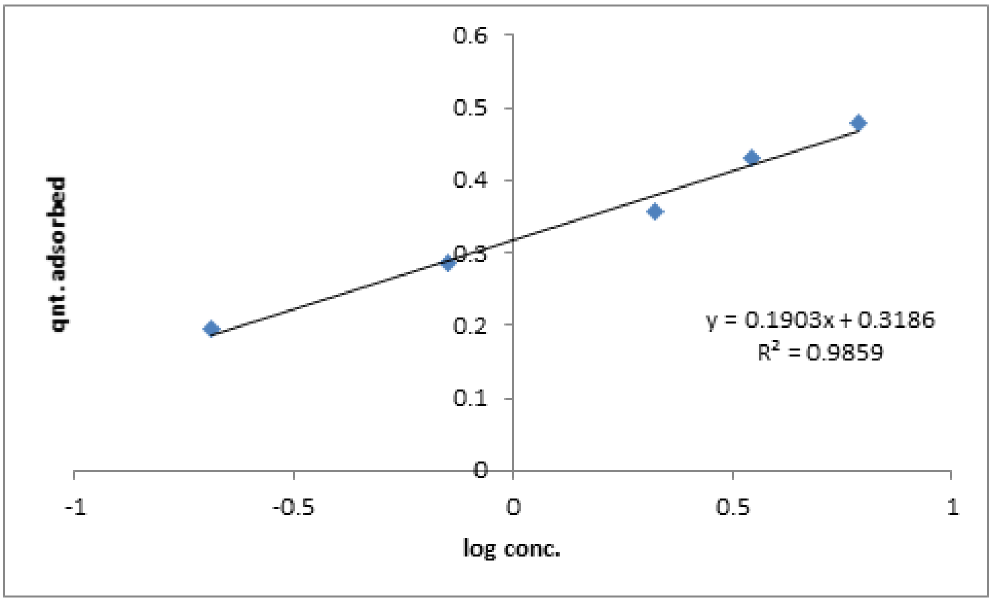

Fig. (8b) Temkin Isotherm of 500 °C Activated Rubber Seed Shell Carbons.

Figures 8a and b, the R^2 values for 300 and 500 °C carbonized rubber seed shells are 0.9427 and 0.9859. This clearly indicates that the adsorption processes fitted well into Temkin isotherm. This means that the adsorption is characterized by uniform distribution of the binding energies which are associated with the adsorption.

FrumkinAdsorption Isotherm:

This isotherm was deduced according to equation (7)

$$\ln [q_e/C_e (1-q_e)] = \ln K + 2a\, q_e \quad (7)$$

where, a is the lateral interaction describing the molecular interaction in the adsorbed layer, q_e is the quantity adsorbed, k is the equilibrium constant of the adsorption process and C_e is the concentration

The plot of Frumkin adsorption isotherm is q_e Vs $\ln [q_e/ C_e(1- q_e)]$

Where, Slope =2a and ln K=intercept.

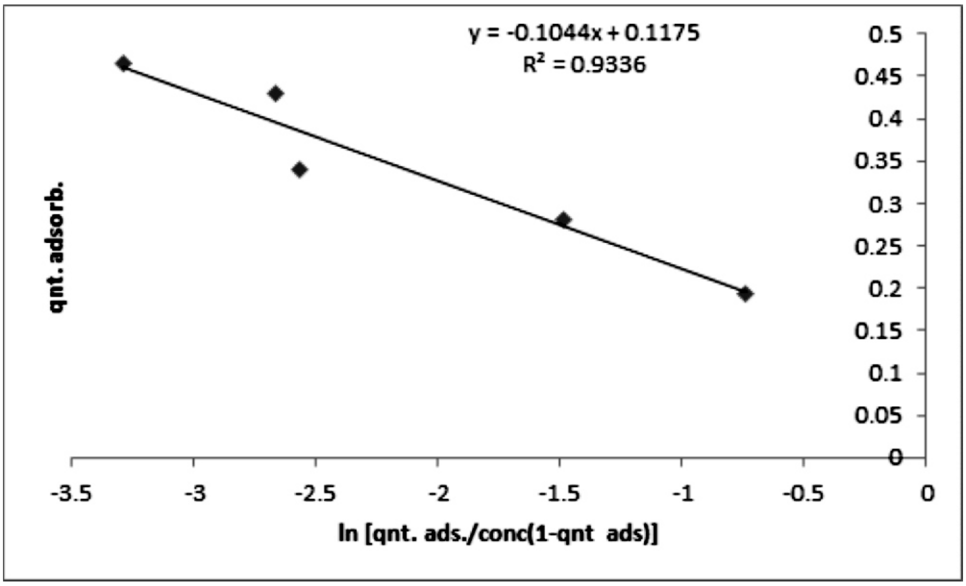

Fig. (9a) Frumkin Isotherm of 300 °C Activated Rubber Seed Shell Carbons

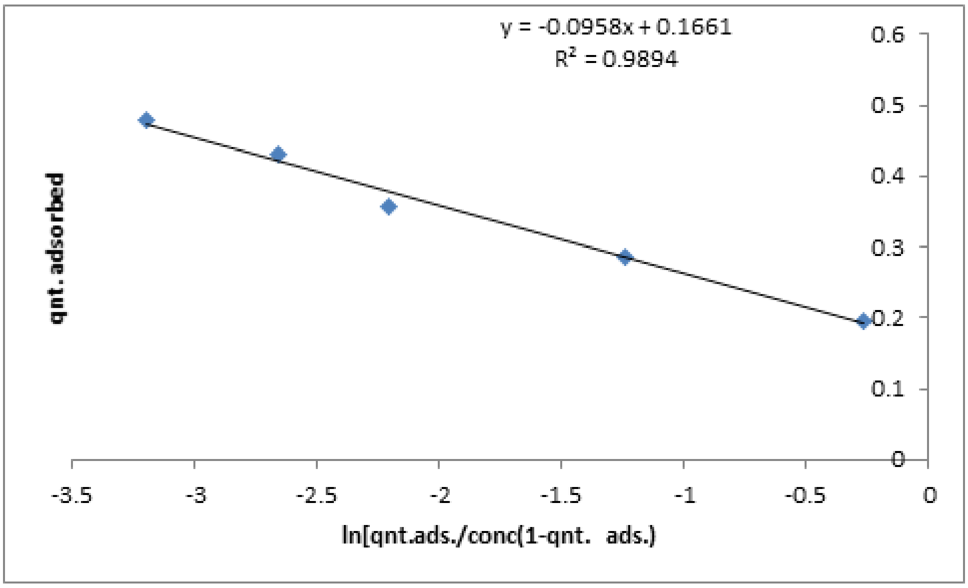

Fig. (9b) Frumkin Isotherm of 500 °C Activated Rubber Seed Shell Carbons

As can be seen from the R^2 values obtained for 300 and 500 °C carbonized rubber seed shells for Fumkin isotherm which are 0.9336 and 0.9894. The adsorptions also fitted well into this isotherm.

CONCLUSION:

This study established that activated carbon produced from rubber seed shell is effective in the removal of crystal violet from aqueous solution. However, the physical and chemical characteristics of the activated carbons showed that 500 °C carbonized rubber seed shell is more efficient than 300 °C carbonized one owing to larger surface area which contributed to its better adsorption capacity.

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