



Evaluation of Dyestuff Removal by Shea Nut (*Vitellaria paradoxa*) shells

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ABSTRACT: The removal of textile dyestuff from waste water was investigated in a batch sorption process using shea nut (*Vitellaria paradoxa*) shell activated carbon. The data were tested using the Rudishkevich – Dubinin and Temkin isotherm models. The result showed that removal efficiency increases with increase in contact time. This critical study which utilizes these more recent adsorption isotherms was found to present the mean free energy values ($E_D = 1.036 - 1.406 \text{ kJmol}^{-1}$) as a direct proportionality to the theoretical saturation capacities ($q_D = 2.032 - 4.169 \text{ mgg}^{-1}$). Sorption energy values proves to be higher for biosorbent, SS/A/15 (1.364 kJmol^{-1}), which also gave the corresponding higher adsorption capacity (4.169 mgg^{-1}) than the other three biosorbent in the series. A thermodynamic parameter (ΔG) was investigated to be more negative with sorbent – dye contact time, within the equilibration limit. The Close similarities of analytical results to those reported in reviewed literature, and the good degree of adsorption is an indication that using shea nut shells as a low cost biomass for generating activated carbon could be a feasible outlet in bioremediation. @JASEM

Adsorption using activated carbon is an effective separation and purification technique used in waste water treatment. This is linked to (i) the pore size that determines its adsorption capacities (ii) chemical structure that influences its interaction with polar and non polar adsorbents, (iii) active sites which determine the type of chemical reaction with other molecules (Maryam *et al.*, 2008) and probably (iv) the sorption energy which account for spontaneity, feasibility and the degree of phase interaction. There are many studies in the literature relating the preparation of biosorbant from agricultural waste. However there is only limited research on the preparation of activated carbon from shear butter shells, for dye removal. Normally, these shells are used as boiler fuels or in landfills.

Activation carbon have been produced from a large number of carbonaceous raw materials such as coal, lignite, wood, coconut shell and some agricultural waste products (Guo and Lua, 1998) and animals sources (Itodo *et al.*, 2008). The effectiveness of activated carbon as an adsorbent is attributed to its unique properties including large surface area, high degree of surface reactivity, universal adsorption effect, and favorable pore size (Zahangir *et al.*, 2008; Ozer *et al.*, 2005).

The adsorption by activated carbon depends not only on its surface area, but also on the internal pore structure, surface characteristics and the sorption energies (Ismadji *et al.*, 2005, Itodo *et al.*, 2008). Although there are many studies in the literature relating to the preparation and characterization of Activated Carbon from agricultural wastes, no such information on the preceding sorption energies and how it affects the adsorption capacities especially for

dye uptake and by chemically catalyzed shea nut shells. In this present study, 3 sorption energies parameters, namely; mean free energy (E_D), sorption energy (B) and Gibbs free energy (ΔG) were evaluated in relationship to adsorption capacities, using the R-D and Temkin sorption models.

One of the major environmental pollutants is the textile dyeing industry wastewater. Treatment of dye effluent is difficult because of the presence of the large amount of suspended solids with high chemical oxygen demand (COD) concentration accompanied by a fluctuating pH (Kardirvelu *et al.*, 1999). Colour is the most obvious evidence of water pollution. Its discharge damages the aesthetic nature of receiving water bodies and imposed aqua toxicity. This colour impede light transmission and penetration into streams, thereby reducing photosynthesis action. According to Lee *et al.*, 1999), dye upsets the biological activities in water and poses problem along the food chain due to their mutagenic and carcinogenic effects (Lee *et al.*, 1999). This present study utilizes more recent adsorption isotherms to predict the mean free energy and sorption energy values for dye uptake by activated *Vitellaria paradoxa*.

Isotherm Models: Adsorption isotherms are basic requirement for the design of adsorption system (Ozer *et al.*, 2007), it is basically imported to describe how solute (dyestuff) interact with biosorbent (shear butter shell activated carbon), and it is critical for optimizing the use of adsorbent. More recent and less regularly applied models (which predominately deals with energy quantities) were employed in this work, (Itodo *et al.*, 2008).

The Temkin model is linearly represented as equation (1) and generally applied in the form:

$$q_e = B \ln A + B \ln C_e \quad (1)$$

Where A and B are the Temkin isotherm constant (L/g) and heat of sorption (J/mol) respectively. R is the gas constant (J/mol.k), b is the Temkin isotherm constant linked to the energy parameter, B, as shown on equation (2)

$$b = RT/B \quad (2)$$

T is the absolute temperature in Kelvin (Hameed, 2009). The quantity, b has no unit as justified by the unit relationship in (3) below:

$$b = (Jmol^{-1}.K^{-1}.K)/Jmol^{-1} \quad (3)$$

The Rudishkevich – Dubinin, (R-D) sorption isotherm is more general than the famous Langmuir model as its deviation is not based on ideal assumption such as equal sorption site potentials, absence of steric hindrance between sorbed and incoming sorbate and the surface homogeneity at a microscope scale (Monika *et al.*, 2009). The major equation governing this model is expressed as equation (4)

$$\log q_e = \log q_D - 2B_D R^2 T^2 (\log(1+1/C_e)) \quad (4)$$

Subjecting sorption data into this model equation as plot of $\log q_e$ versus $\log(1+1/C_e)$ will give a straight line with slope $(-2B_D R^2 T^2)$ from which the mean free energy (E_D) is obtained. R is the gas constant in $KJmol^{-1}K^{-1}$, T is temperature ($^{\circ}K$) while q_D is the theoretical saturation capacity obtained from intercept ($\log q_D$). The B_D is a constant which is an indication of adsorption energy ($mol^2 KJ-2$). The constant B_D gives an idea about the mean free energy E_D ($KJmol^{-1}$) of adsorption per molecule of adsorbate when it was transferred in the solution. Calculation of E_D is expressed as equation (5)

$$E_D = 1/\sqrt{2B_D} \quad (5)$$

Adsorption process is termed as “physical adsorption” if the value of E_D is less than 8 $KJmol^{-1}$ (Monika *et al.*, 2009).

MATERIALS AND METHODS

Deseeded shear butter shells, collected from Rikoto village at Zuru, Kebbi state – Nigeria were washed, sundried and chopped into small pieces. 3g of the chopped pieces were treated with $3cm^3$ of 1M activating agent (H_3PO_4 as A and $ZnCl_2$ as Z). The

semi glued mixture, upon a one hour standing was introduced into the Carbolite furnace and fired at $800^{\circ}C$ for 5minutes dwell time (Turoti *et al.*, 2007; Abdulrahman *et al.*, 2008; Itodo *et al.*,2008). The water and acid washed sorbents were oven dried at $110^{\circ}C$ overnight followed by grinding and sieving with a $<2mm$ aperture sieve. The textile dyeing effluent was collected from the dye wastewater reservoir of Chellco textile ltd., Kaduna , Nigeria. A 1000 mg/l concentration brix was prepared from the dye concentrate. Series of working concentrations (10 – 50 mg/l) in $100cm^3$ flask were prepared from the stock.

Adsorption Experiment: 0.1g of each biosorbent was integrated with $10cm^3$ of dye solution in a $25cm^3$ Erlenmeyer flask. The Erlenmeyer flask containing the mixture were capped and mixture allowed to equilibrate for one hour. The separately interacted samples were filtered after one hour, using watt man filter paper number 42 and absorbance was taken using the Jenway 610 model spectrophotometer at predetermined λ_{max} of 540nm.

- Each experiment was carried out in triplicate under identical conditions and the result presented as mean value (Omonhenle *et al.*, 2006; Abdulrahman *et al.*, 2008; Itodo *et al.*,2010; Itodo and Itodo,2010). The amount of dye uptake per unit mass of sorbent (q_e) and the percent dye removal were calculated as equations 6 and 7.

$$q_e = (c_o - c_e) \times v/w \quad (6)$$

$$\% RE = C_o - C_e / C_o \times 100 \quad (7)$$

Where RE (%) is the percent dye removal, C_o and C_e are the initial and equilibrium dye concentrations ($mg\ l^{-1}$) respectively. V (dm^3) is the volume of dye solution and W (g) is the adsorbent dose (Hameed *et al.*, 2006; Abdulrahman *et al.*, 2008; Itodo and Aminu,2010; Itodo *et al.*,2009).

RESULTS AND DISCUSSION

Figure 1 shows the effects of contact time on sorbent-sorbate interaction time. The auto appended table revealed only a gradual increase in % adsorption with time. The 90 minutes equilibration however deviates from the trend. This is an indication that above the equilibration time(75 minutes),there could be a possibility of desorption.

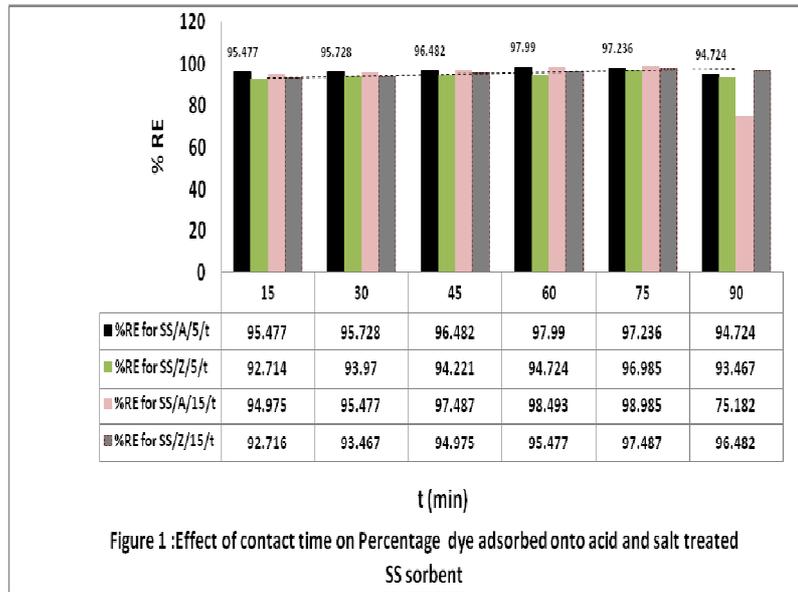


Figure 1 :Effect of contact time on Percentage dye adsorbed onto acid and salt treated SS sorbent

The four series of activated carbon prepared, interact spontaneously. Figure 1 presents the effect of contact time on the thermodynamic parameter, ΔG . The Gibbs free energy values ($-\Delta G$) increases with time

as the sorbent phases tends to equilibrium (between 15 – 75minutes) and decreases at 90 minutes after equilibrium time is exceeded. The former is an indication of spontaneity.

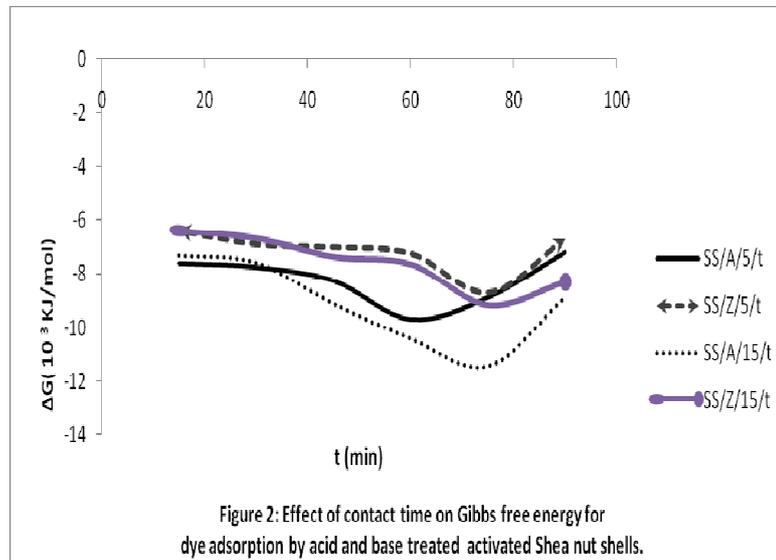


Figure 2: Effect of contact time on Gibbs free energy for dye adsorption by acid and base treated activated Shea nut shells.

The extent of spontaneity with time is more rapid for the sorbent series, SS/A/15 with values ranging between 2.32 and 3.803KJmol⁻¹. This change in Gibbs free energy was investigated, using equation 8 and 9 below (Dakiky *et al.*, 2002)

$$\Delta G = -RT \ln K_c \tag{8}$$

$$K_c = c_a/c_e \tag{9}$$

Where K_c is the equilibrium constant, C_a and C_e are the solid and equilibrium phase concentrations in mg/g and mg l⁻¹ respectively. T is the temperature in Kelvin while R is the gas constant.

Table (1): Thermodynamic data K_c , and $(-\Delta G \times \text{kJmol}^{-1})$ values for the sorption of dye unto chemically modified SS Biosorbent. Equilibrium constant, K_c , and Gibbs free energy $(-\Delta G \times \text{kJmol}^{-1})$

sorbent	15min	30min	45min	60min	75min
SS/A/5	3.050(2.783)	3.120(2.839)	3.311(2.988)	3.887(3.387)	3.560(3.169)
SS/Z/5	2.543(2.329)	2.746(2.521)	2.791(2.561)	2.888(2.647)	3.471(3.105)
SS/A/15	2.939(2.690)	3.050(2.783)	3.658(3.236)	4.180(3.569)	4.590(3.803)
SS/Z/15	2.546(2.332)	2.661(2.442)	2.939(2.690)	3.050(2.783)	3.658(3.236)

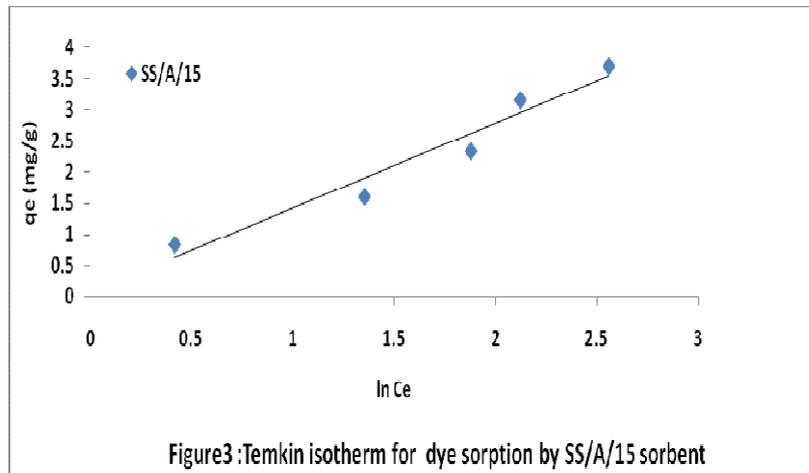
Values of ΔG in parenthesis; SS/A/5/t –Shea nut shell treated with Acid,A, activated for 5 minutes, SS/Z/15- Shea nut shell treated with salt,ZnCl₂, activated for 15 minutes

Table 2 presents the Temkin constant B, related to heat of sorption (Jmol^{-1}) biosorbent catalyzed by acid at a longer dwell time SS/A/15 gave the highest value 1.364 Jmol^{-1} with a corresponding least b value (1829.507). Since the series, SS/A/5 is next to this trend, it therefore implies that the nature of activating agent and activation dwell time affects the sorption energies.

Table 2: Sorption energy B) from the Temkin isotherm constant for dye sorption onto chemically catalyzed SS – Biosorbent.

Sorbent	Lineareqn. (y=)	R ²	B(Jmol ⁻¹)	A(Lg ⁻¹)	b
SS/A/5	1.042x + 0.917	0.996	0.042	1.208	2394.863
SS/Z/5	0.561x – 0.167	0.902	0.561	0.743	4448.212
SS/A/15	1.364x + 0.062	0.947	1.364	1.047	1829.507
SS/Z/15	0.538x + 0.448	0.912	0.538	2.300	4638.377

The above data on Table (2) were experimental values obtained from the Temkin plot shown on figure (3).



To generate data for the mean free energy (E_D) and theoretical saturation capacity (q_D), the sorption data was subjected to the Rudishkevich-Dubinin model as earlier described in equation 4 and 5. It was obvious that SS/A/15 Biosorbent has a higher saturation

capacity (4.169 mgg^{-1}). That is, it may seldom desorbs the sorbate as it may applies to the other three series. (Table 3). A critical comparison of table 2 and 3 revealed that the sorption energy B is directly proportional to the saturation capacity, q_D sorbent.

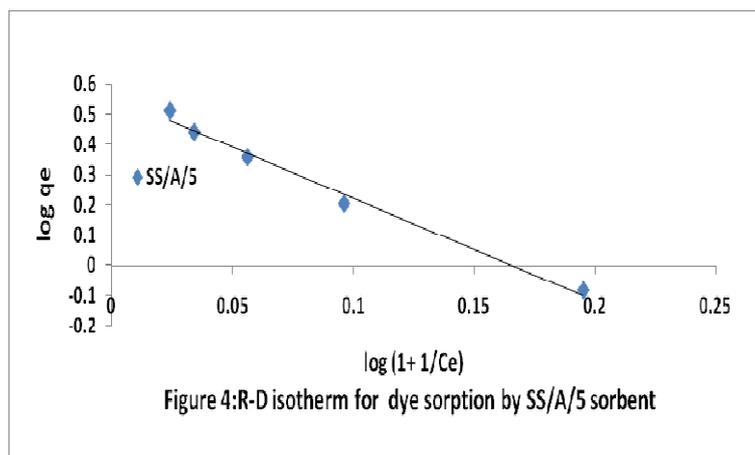
Table 3: The mean free energy (E_D) and sorbent saturation capacity from R-D isotherm constant for dye uptake by chemically catalyzed SS- sorbent

Biosorbent	Linear eqn. (y=)	Linearity (R ²)	q _D (mgg ⁻¹)	B _D (Mol ² KJ ⁻²)	E _D (KJmol ⁻¹)
SS/A/5	-3.383x + 0.559	0.988	3.622	0.272	1.356
SS/Z/5	-5.808x + 0.308	0.962	2.032	0.466	1.036
SS/A/15	-3.300x + 0.620	0.944	4.169	0.265	1.374
SS/Z/15	-3.150x + 0.384	0.984	2.421	0.253	1.406

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E_D -mean free energy. B_D is a value, related to adsorption energy (Monika *et al.*, 2009). Biosorbent with low B_D (0.265 and 0.272 mol²kJ⁻²). values on table 3 in turn, gave what is presume to be a better quality sorbent with high q_D (4.169 and 3.622mgg⁻¹). This is however, only true for the acid treated biosorbent. Mean free energy E_D is higher for the longer time (15 minutes) activation dwell time carbon. It thus, follows that activation dwell time affects the mean free energy values, thus, giving the

trend SS/Z/15 (1.406) > SS/A/15 (1.374) > SS/A/5 (1.356) > SS/Z/5 (1.036) units in KJmol⁻¹. The applicability of the two isotherm models was also investigated from the coefficient (R^2) values. Based on this, the sorption data were best modeled by the R-D isotherm (R^2 range of 0.944 – 9.984 such as in figure 4) than the Temkin isotherm model (R^2 , 0.902 – 0.947). An exception to this is the SS/A/5 series which is best fitted by the Temkin isotherm model ($R^2 = 0.996$) than the RD isotherm (R^2 , 0.988).



According to Monika *et al.*, 2009, physisorption is one where the mean free energy value $E_D < 8$ KJmol⁻¹, this paper presented E_D values of the range, 1.035 – 1.406 KJmol⁻¹. It therefore implies that the adsorption process is governed by physical adsorption. Atkins, 1999, define physical adsorption as a non specific adsorption which occur as a result of long range weak Vander waal forces between adsorbate and adsorbent. The energy released when a particle is physisorbed is of the same magnitude as the enthalpy of condensation. (Atkins, 1999). Physisorption is also referred to as ideal adsorption in which the binding energy of the adsorbate is less than 20KJ/mol (Atkins, 2003). It was argued that for physisorption, the adsorbed molecules are not affixed to a specific site at the surface but are rather free to undergo translational movement with interface (Weber, 1972). It occurs in minutes and the process is reversible (Atkins, 2003).

Conclusions: Highlights of results presented in this paper clearly shows that shear butter shells are economically valuable adsorbent for industrial dyestuff with relatively high % dye removal. Reports in this study also shows that: Adsorption is governed by physisorption ($E_D < 8$ KJmol⁻¹ and can be referred to as ideal adsorption with binding energy < 20KJmol⁻¹). Adsorption is spontaneous with increase

$-\Delta G$ values as sorbate-sorbent interaction time increases. This study also revealed that sorbent of high sorption energy (B) presented a corresponding high saturation capacity (q_D) while carbon, activated at longer dwell time gave Biosorbents of high mean free energy values. Acid catalyzed Bio-adsorbent, SS/Z/15 and SS/Z/5 proves to be a better quality adsorbent compared to the ZnCl₂ - treated activated carbon. Uptake of dye by shea butter nut shells activated carbon best fit into the Rudishkevich Dubinin (R-D) isotherm model than it does for the Temkin model. Generally, results in this paper competes well with those of similar waste as reviewed in literatures.

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