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Application of isotherm studies on the evaluation of sorption energies for dyestuff removal onto derived thermo-cracked shea nut shells.

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ABSTRACT

This information add to database an attempt to model the adsorption of dye from dyeing wastewater in relationship to certain established energy parameters. The adsorbent is thermochemically cracked shea nut shell activated carbon, the adsorbate is textile dyestuff wastewater from Chellco textile ltd., Kaduna, Nigeria. The process is batch adsorption test while the adopted models are Rudishkevich – Dubinin and Temkin isotherms. 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 $kJmol^{-1}$) as a direct proportionality to the theoretical saturation capacities (q_D = 2.032 – 4.169mgg^{-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.

Keywords: Isotherm, Sorption, Energies, Dyestuff ,Thermo-cracked, Shea nut.

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INTRODUCTION

During the last decades, the scientific community has become increasingly concerned about the potential public health impact of new environmental contaminants originating from industrial, agricultural, and human activities. These compounds, known as emergent pollutants, include prescription and non-prescription human and veterinary pharmaceutical compounds and personal care products (PPCPs). However, little is known about the occurrence, fate, synergistic, and long-term effects of these pollutants and their metabolites following their end [1]. Recent studies in Europe and North America have reported the occurrence of PPCPs in wastewater and ambient waters. Many physicochemical methods have been proposed for removal of organic pollutants from industrial effluent [2]. Some of this method include electrochemical precipitation, ultra titration, ion exchange and reverse osmosis among others[3]. These methods are however not economically appealing because of high operational costs.

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[2] 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 [3] and animals sources [4-9]. 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 [10].

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 [4,11]. 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 [12]. 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. In a study earlier reported, dye upsets the biological activities in water and poses problem along the food chain due to their mutagenic and carcinogenic effects [13].

Isotherm Models:

Adsorption isotherms are basic requirement for the design of adsorption system[1],it is basically imported to describe how solute (dyestuff) interact with biosorbent (shea nut 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 [4-9].

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

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

Where A and B are the Temkin isotherm constant (L/g) and heat of sorption (J/mol) respectivelly. 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)

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

T is the absolute temperature in Kelvin [14]. The quantity, b has no unit as justified by the unit relationship in (3) below:

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

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 [15]. The major equation governing this model is expressed as equation (4)

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

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 (^oK) 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 (mol2 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 $KJmol^{-1}$ .This was also discussed elsewhere [15].

EXPERIMENTAL

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^oc for 5minutes dwell time [16,17]. The water and acid washed sorbents were oven dried at 110^oc overnight followed by grounding 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 (designated as SS/A/5, SS/Z/5, SS/A/15 and SS/Z/15) were 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 λmax of 540nm.

- Each experiment was carried out in triplicate under identical conditions and the result presented as mean value [17,18].

The amount of dye uptake per unit mass of sorbent (q_e) and the percent dye removal were calculated as equations 6 and 7.

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

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

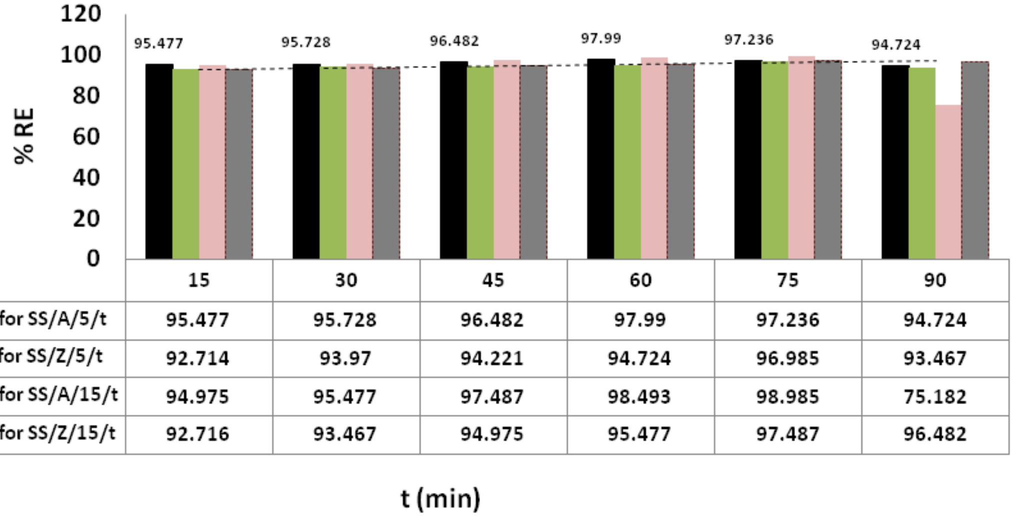
Where RE (%) is the percent dye removal, C_o and C_e are the initial and equilibrium dye concentrations (mgl^{-1}) respectively. V (dm^3) is the volume of dye solution and W (g) is the adsorbent dose [5-9, 17,19].

RESULTS AND DISCUSSION

In the present study percentage dye uptage, adsorption feasibility test, and the application of the sorted energy- related isotherms were made available. Other models, explaining adsorption phenomenon, surface coverage and kinetics of adsorption was earlier published [20].

Adsorption efficiency test

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.



	15	30	45	60	75	90
■ %RE for SS/A/5/t	95.477	95.728	96.482	97.99	97.236	94.724
■ %RE for SS/Z/5/t	92.714	93.97	94.221	94.724	96.985	93.467
■ %RE for SS/A/15/t	94.975	95.477	97.487	98.493	98.985	75.182
■ %RE for SS/Z/15/t	92.716	93.467	94.975	95.477	97.487	96.482

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

Adsorption feasibility test

The four series of activated carbon prepared, interact spontaneously. Figure 2 presents the effect of contact time on the thermodynamic parameter, ΔG. The Gibbs free energy values (-ΔG) 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.

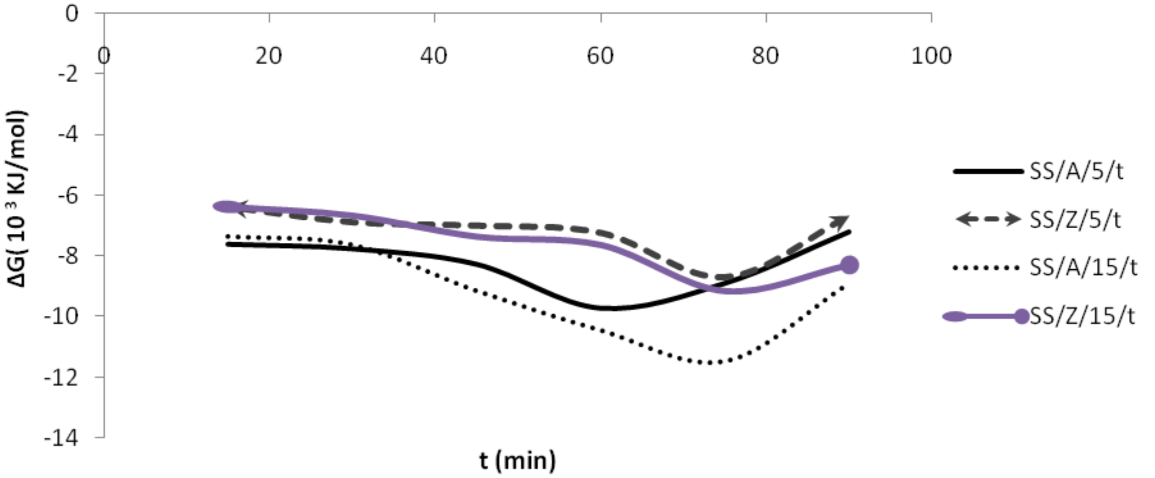


Figure 2: Effect of contact time on Gibbs free energy for dye adsorption by acid and base treated activated Shea nut shells.

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 [21].

$$\Delta G = -RT \ln Kc \qquad (8)$$

$$K_c = C_a/C_e \qquad (9)$$

Where K_c is the equilibrium constant, C_a and C_e are the solid and equilibrium phase concentrations in mg/g and mgl^{-1} respectively. T is the temperature in Kelvin while R is the gas constant.

Table (1): Thermodynamic data K_c, and (- ΔG × kJmol^{-1}) values for the sorption of dye unto chemically modified SS Biosorbent.

Equilibrium constant, Kc and Gibbs free energy (- ΔG × kJmol^{-1})						
Sorbent	15min	30min	45min		60min	75min
SS/A/5/t	3.050(2.783)	3.120(2.839)	3.311(2.988)		3.887(3.387)	3.560(3.169)
SS/Z/5/t	2.543(2.329)	2.746(2.521)	2.791(2.561)		2.888(2.647)	3.471(3.105)
SS/A/15/t	2.939(2.690)	3.050(2.783)	3.658(3.236)		4.180(3.569)	4.590(3.803)
SS/Z/15/t	2.546(2.332)	2.661(2.442)	2.939(2.690)		3.050(2.783)	3.658(3.236)

Adsorption isotherms in Energy studies

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, B and b

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

Sorbent	Linear eqn. (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 in plots type as figure (3).

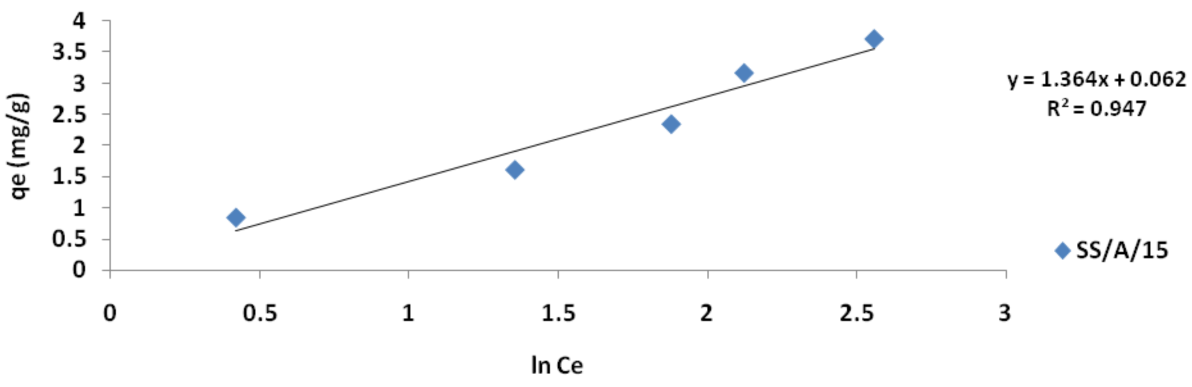


Figure 3 :Temkin isotherm for dye sorption by SS/A/15 sorbent

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 (4.169mgg^{-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^2KJ^{-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

E_D -mean free energy.

B_D is a value, related to adsorption energy [15]. Biosorbent with low B_D (0.265 and 0.272 mol^2kJ^{-2}). values on table 3 in turn, gave what is pressume 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).

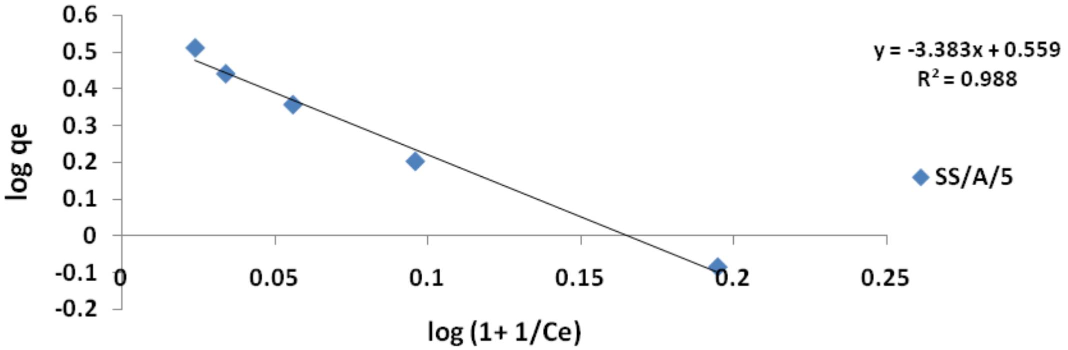


Figure 4: R-D isotherm for dye sorption by SS/A/5 sorbent

Physisorption was earlier described [15] as one in which the mean free energy value, E_D < $8KJmol^{-1}$, 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. Physical adsorption is 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. Physisorption is also referred to as ideal adsorption [21] in which the binding energy of the adsorbate is less than 20KJ/mol. 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. It occurs in minutes and the process is reversible [21].

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 < 20$KJmol^{-1}$).
- Adsorption is spontaneous with increase -ΔG values as sorbate-sorbent interaction time increases.
- Sorbent of high sorption energy (B) presented a corresponding high saturation capacity (q_D).
- 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 $ZnCl_2$ - treated activated carbon.
- Uptake of dye by shear butter shells activated carbon best fit into the Rudishkevich Dubinin (R-D) isotherm model than it does for the TEMKIN model.
- Result in this paper competes well with those of similar waste as reviewed in literatures.

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