SORBENT CAPACITIES AND INTENSITIES OF THERMOCHEMICALLY CRACKED SHEA NUT SHELLS FOR THE REMOVAL OF WASTE WATER DYESTUFF

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Abstract: The sorbent capacities and intensities of activated carbon by one-way thermochemical pyrolysis of shea nut shells were studied on waste water dye removal and the results are presented in this paper. The relationship between the ordinary (k_f), maximum (q_m) ,and theoretical saturation capacities (q_D) were also investigated to follow the order ; $q_m > q_D > k_f$. H_3PO_4 catalyzed sorbent at a longer activation dwell time, SS/A/15 presented a higher adsorption capacities (q_m=6.024 mgg^{-1},q_D=4.189 mgg^{-1} and k_f = 0.628) and higher sorption intensity (1/n =0.714) ,than the other 3 series.The high % dye removal (%RE up to 84.80%), adsorption normalcy (1/n <1 and R_L<1) and good applicability (R^2 >0.869) are critical for considering shea nut shells as precursor for generating low cost active biosorbents. [Academia Arena 2010;2(3):41-50]. (ISSN 1553-992X).

Keywords: Adsorption capacities, intensities, Dye, Shea nut shells, waste water

1. INTRODUCTION

Textile, just like plastic and paint industries is known to utilize a great deal of water and thus releases large quantities of waste water from different stages in the dyeing process (Hameed and Hakimi,2008) some stages requiring water utilization includes scouring and rinsing, bleaching, dyeing and printing (USEPA, 1991). Effluent derived from the textile and dyestuff activities can provoke serious environmental damage on neighboring water receptor bodies and the ever increasing populace. The main threat is the toxin, chlorolignin and dark coloration (Hameed, 2009)

Various treatment technologies have been developed for purification of waste water. The most commonly used methods includes chemical precipitation, solvent extraction, oxidation reduction, electro dialysis, electrolyte extraction, reverse osmoses, ion exchange, evaporation concentration adsorption, filtration etc. Among these methods, adsorption has evolved as the optimum choice (Mohan and Signh, 2001). Activated carbon includes wide range of amorphous carbon based material prepared to exhibit a high degree of porosity and an extended inter-particulate surface area (Zahangir *et al*., 2008). These qualities impart activated carbon with excellent adsorbent characteristics that make it useful for filtration, purification, deodorization, decolorization and separation (Zahangir *et al.,* 2008).

Adsorption on activated carbon has long been recognized to be one of the most effective methods for removal of organic compounds, including dyestuff from aqueous solutions. Agriculture waste

such as oil palm nut shells, rice husks, olive waste cakes, coconut shells and guava seeds have be reportedly used (Rahman *et al*., 1997 Rahman *et al* ., 2000; Rahman *et al* 2002) .wastes of animal origin such as human hair, cow biosolids, poultry litter, blood, Fish, etc. were also reported (Itodo *et al*.,2008).

Adsorption isotherms can be generated based on numerous theoretical explanations. The simplest model that can be used to describe monolayer adsorption is the Langmuir equation (Meghea *et al.*, 1998). The Langmuir equation is based on kinetic approach and assumes a uniform surface, a single layer of adsorbed material and constant temperature. This model is useful when there is a strong specific interaction between the surface and the adsorbate so that a single adsorbed layers forms and no indication of formation of multilayer adsorption. The driving force is the concentration of adsorbate in the fluid and the area or amount of bare surface (Chilton *et al*., 2002). Hameed, 2009 presented a linearized form of the Langmuir equation as ;

$$1/q_e = 1/k_a q_m C_e + 1/q_m \quad \text{--- -------- ----(1)}$$

Where q_m (mgg^{-1}) and k_a (L/mg) are Langmuir constant related to the maximum adsorption capacity and energy of adsorption respectively. These constants are calculated from the plot of $1/q_e$ verses $1/C_e$ (Hameed,2009).

Mattson and mark (1971): in Chilton *et al*., 2002 described Freundlich model as the most popular adsorption model for a single solute system. This model is an empirical equation based on the distribution of solute between the solid phase and the aqueous phase at equilibrium. The bases of the Freundlich equation is given as equation (2)

$$x/m = kC_e^{1/n} \quad \text{------- ---------- ------ (2)}$$

where, for the purpose of this research, x is the amount of dye adsorbed (mg), m is the weight of sorbent or sorbent dose (g) , $x/m = q_e$ is the amount of dye adsorbed by a unit mass of sorbent, C_e (mgl^{-1}) is the equilibrium concentration of dye in solution while k and n are empirical constant equation 2 can further be rearranged as equation 3

$$\log q_e = \log k_f + (1/n) \log C_e \text{ --------(3)}$$

this empirical equation has no bases in theory but made two assumptions which are (i) it assume heterogeneous surface energies (Hameed *et al*., 2006) that is, exponential variation in site energies (ii) it assumed that surface adsorption is not the rate limiting step. (Chilton *et al*., 2002). k_f ($mgg^{-1}(1mg^{-1})^n$ is the Freundlich constant implying the adsorption capacity (Hameed et al, 2006) one most important parameters in equation (3) above is the 1/n value. 1/n ranging between 0 and 1 is the measure of the adsorption intensity or surface heterogeneity. surface becomes more heterogeneous as 1/n gets closer to zero. It describe adsorption as either normal (1/n <1) or as a cooperate adsorption (1/n >1) (Hameed *et al*., 2006). Chilton *et al*., 2002 argued that large values for 1/n indicate a larger change in effectiveness over different equilibrium concentrations and that when 1/n > 1.0 the change in adsorbed concentration is greater than the change in solute concentration. Generally the higher the q_e value at a specified concentration, the more preferred is the biosorbent for that application (Chilton *et al*., 2002).Chen *et al* .,(1997) added that adsorption isotherms expressed as Freundlich isotherm constant are a better measure of the adsorption properties of biosorbent than the one –

point tests , such as iodine, molasses or tannin numbers (chen *et al* ., 1997).

Other types of commercial dyes have been worked upon. The removal of methylene blue and malachite green by agro waste was reported by Guo *et al*., (2003), Garg *et al*., (2004), however, relatively little or no work has been reported on the adsorption of industrial dye from dyeing waste water onto chemically catalyzed shear butter shells. In this present work, we reported our evaluation on the feasibility of using shea nut shell activated carbon, studying its adsorption properties for removal of industrial dyestuffs from waste water. This paper therefore, presents three adsorption isotherms (R-D, Langmuir and Freundlich isotherms) generated for shea nut shells (sorbent) and dyeing waste water (sorbate) system. The purpose of the study was to evaluate their adsorption capacities which are quantified as saturated (q_D), maximum (q_m) and ordinary Freundlich (K_f) adsorption capacities, with the adsorption intensity (1/n) as it relates to the use of shea nut shells bio adsorbent for industrial waste water treatment.

2. Materials and Methods

Exhausted and deseeded shea nut shells, obtained from Rikoto, zuru in Kebbi state, Nigeria was used as raw material for the production of activated carbons via thermochemical activation.

Industrial dyeing waste water was procured in plastic container from Chellco textile industries, Kaduna without further treatment. 1000 mgg^{-1} concentration brix was prepared from the dye waste water concentrate from which working standard were prepared.

The apparatus and experimental methods in this work are similar to those for chemical activated with $ZnCl_2$ as reported previously by Tsai *et al*., 2001) for thermochemical activation. Initial weight of the grinded pretreated shear butter shell was measured into crucibles and mixed with $3cm^3$ of 1M activating agent (H_3PO_4 and $ZnCl_2$). The mixture was allowed to stand for one hour and then fired in a furnace at 800^o C for 5 minutes and 15 minutes series, (Alam *et al* .,2007) the samples were both acid and water washed to remove residual ash and chemicals respectively (Itodo *et al*., 2008).This is followed by oven drying at 110^oC overnight and stored for further analysis (Tsai et al, 2001)The generated samples (biosorbents) were separately labeled as SS/A/5, SS/A/15, SS/Z/5 and SS/Z/15 implying shea nut shell, activated with either H_3PO_4 (A) or $Zncl_2$ (Z) at 5 minutes or 10 minutes dwell time.

2.1**Adsorption Study**

The adsorption capacities of biosorbent produced form shea nut shells was measured under the effect of contact time, nature of activating agent and initial dye concentration. A concentrate which was obtained from mild temperature evaporation of the dye waste water in an oven to a constant weight was used to prepare a $1000mgl^{-1}$ stock from which 10- 50 mgl^{-1} working dye standard solutions were prepared. 10 cm^3 of each dye sample was interacted with 0.1g of biosorbent and allowed to equilibrate for one hour (Turoti *et al.,* 2007). The mixture was then filtered, using a Wattman number 42 filter paper after which the residual dye concentration (c_e) in the filtrates were measured using Jenway 1600 spectrophotometer at room temperature (300.15k) which was set at a predetermined wavelength of 640 nm.

The amount of dye absorbed and % dye removal were calculated form the difference between the initial concentration and equilibrium concentration as shown in equation(4) and (5) respectively

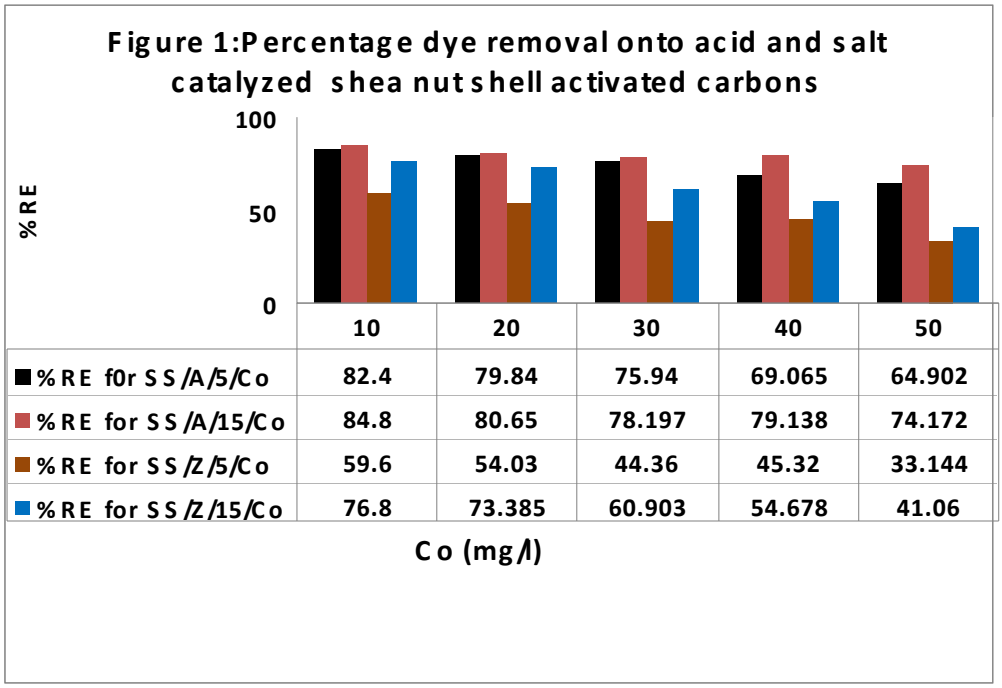
$q_e=(C_o-C_e)$ v/m ------- --------- ------ (4)

% RE = (C_o-C_e /C_o) x 100 -- ------- ---------- ---- (5)

Where q_e is the amount of dye adsorbed per unit mass of adsorbate (mgg^{-1}).It is a measure of adsorption capacity. C_o and C_e are the initial and equilibrium dye concentration respectively (g) and v (L) is the adsorbent dosage and volume of dye solution respectively (Zahangir *et al*., 2008).

3.Results and Discussions

Figure (1) present the percent dye removal at different initial dye concentration for one hour equilibration time.



The % dye removal by the four sorbent series follows the order, SS/A/15 > SS/A/5 > SS/Z/15 >SS/Z/15. Results in this study revealed that biomass activated at a longer dwell time (15 minutes) gave higher percents dye uptake (74.172-84.800 %). $ZnCl_2$ is a less favorable activating agent especially when cracking or pyrolysis is done at short dwell time. This however could be linked to a lesser developed pore size associated to short activation time and also due to steric hindrance, which may results from the nature of activating agent as well as activation time. Values obtained for SS/Z/5 (33.144-59.600%) are lower compared to the values (41.06-76.80%) of the same sample (SS/Z/15) activated at longer time.

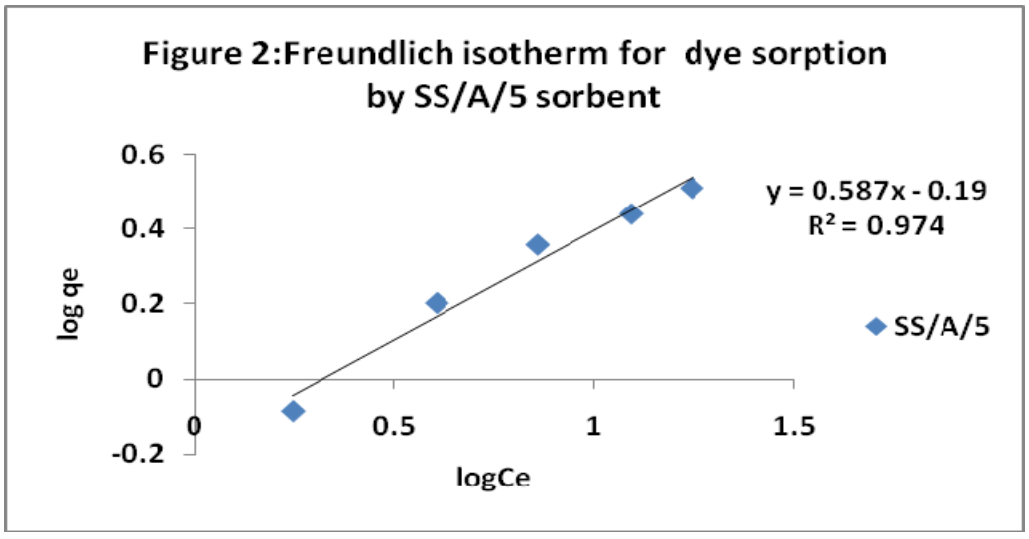
Table 1: Freundlich adsorption experimental data of dye sorption by SS biosorbent.

Biosorbent	Equation (y=)	Linearity (R^2)	1/n	K_f ($mgg^{-1}(mg^{-1})^n$)	positions R^2	1/n
SS/A//5/	0.587x-0.190	0.974	0.587	0.646	Second	Second
SS/Z,5	0.519x-0.506	0.918	0.519	0.312	Third	Third
SS/A/15	0.714x-0.202	0.989	0.714	0.628	First	First
SS/Z/15	0.392x-0.190	0.869	0.392	0.646	fourth	fourth

SS/Z/5 – shea nut shells, treated with $ZnCl_2$, activation for 5 minute dwell time.A-H_3PO_4, 15-activation dwell time of 15 minutes

3.1. Freundlich Isotherm

The data in the above Table 1 were generated from figure type represented as figure 2. The Table shows that the modeling of data generated using Freundlich isotherm gave a good linearity and applicability (R^2>0.869) for all the sorbent. The trend of best fit follows the order; SS/A/15/C_o (0.869) > SS/A/5/C_o (0.974)...The extent of applicability for this acid modified sorbent is greater than those catalyzed by salt… > SS/A/5/C_o (0.918) > SS/Z/15/C_o (0.869). It was also conveniently justified that the ranking based on the adsorption intensity (1/n) follows the same trend as does, the applicability test displayed earlier. Thus, the adsorption intensity of sorbent SS/Z/15 (0.392) is least among the series. 1/n <1 is an indication of normal adsorption (Hameed, 2009).



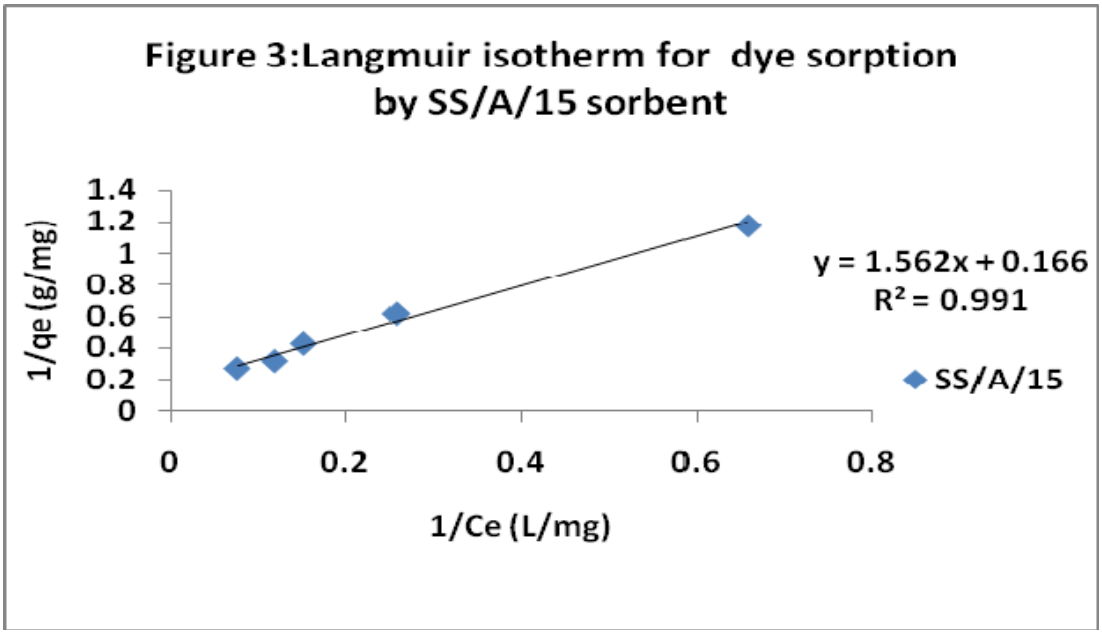
The degree of heterogeneity of adsorption surface was also measured from the 1/n values. According to Hameed *et al*., (2006) the Freundlich equation slope (1/n), ranging between 0 and 1 is a measure of surface heterogeneity. Surface become more heterogeneous as 1/n values get closer to zero (Hameed *et al*.,2006). Based on this, Sorbents, activated at longer dwell time, 15 minutes presented a

more heterogeneous surface. This finding could be linked to the nature of activating agent, since SS/Z/5 is next to SS/Z/15 in surface heterogeneity.

K_f, is the Freundlich constant which denote or depicts the adsorption capacity, unit in mgg^{-1} $(1mg^{-1})^n$ of adsorbent. It is defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the sorbent for the a unit equilibrium concentration. Biomass, activated with $ZnCl_2$ at a longer dwell time presented a higher adsorption capacity, SS/Z/15 (0.646) as does the sample with H_3PO_4 at shorter dwell time SS/A/5 (0.646). It thus, follows that for acid and salt catalysis in generation of high capacity biosorbent, biomass require a shorter and longer activation dwell time respectively.

3.2. Langmuir Isotherm

Good linearity and applicability of the Langmuir model was evidenced by high R^2 values (≤ 0.979) for all the samples as shown on figure 3 and presented on table 2.



The Langmuir constant, relating to the maximum adsorption capacity (q_m) was investigated. Sorbent, SS/A/15 gave the highest value for maximum adsorption capacity (6.124 mgg^{-1}). This is in agreement with the highest adsorption capacity value present by acidic sorbents from the Freundlich constants (k_f = 0.646). This work uncovered the fact that the maximum adsorption capacity of any series (obtained from the Langmuir relationship) should be higher than their corresponding adsorption capacities values (k_f) from the Freundlich isotherm. This can be recalled by comparing table 1 and 2 with q_m and (k_f) values as; 5. 102 (0.646), 2.611 (0.312), 2.801(0.626) and 6.024 (0.646) for sorbents SS/A/5, SS/Z/5, SS/A/15 and SS/Z/15 respectively.

Table 2: Langmuir isotherm experimental data for dye uptake by SS biosorbent

Biosorbent	Equation (y=)	Linearity (R^2)	$q_m(mgg^{-1})$	$K_a(Lmg^{-1})$	R_L	position q_m
SS/A//5/	1.743x+0.196	0.989	5.102	0.112	0.152	second
SS/Z,5	5.348x+0.383	0.983	2.611	0.072	0.217	fourth
SS/A/15	1.562x+0.166	0.991	6.024	0.106	0.158	First
SS/Z/15	2.123x+0.357	0.979	2.801	0.168	0.106	third

SS/Z/5 – shea nut shells, treated with $ZnCl_2$, activation for 5 minute dwell time.A-H_3PO_4, 15-activation dwell time of 15 minutes

Table 2 also revealed the values of the Langmuir constants, k_a (Lmg^{-1}) which directly affects the energy of adsorption (Hameed, 2009). Sorbent with high energy related value, k_a on table 2 presented low adsorption intensity as it was deduced from the Freundlich constant on table 1. The K_a and (k_f) values include 0.168 (0.628) and 0.112 (0.646) for SS/A/15 and SS/A/5 respectively.

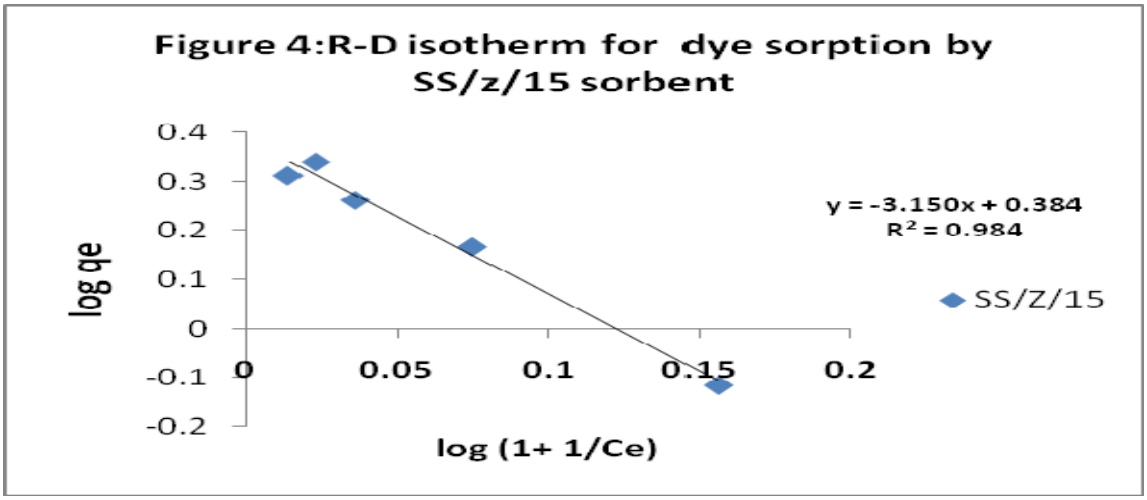
The feasibility of the adsorption process was tested from the R_L magnitude given as equation 6 as;

$$R_L = 1/ (1+K_a C_o) \text{ ------- ------ -----} \quad (6)$$

Where R_L is the essential of the Langmuir equation used in testing adsorption feasibility. K_a is the Langmuir constant related to energy of adsorption (Lmg^{-1}) and C_o is the highest initial dye concentration among the series of different sorbents concentrations (Monika *et al*., 2009) adsorption could be linear, unfavourable, favorable or irreversible depending on whether the values of R_L = 1, >1, <1 and R_L = 0 respectively. (Monika *et al*., 2009). This research presented values (0.106-0.257) which justifies favorable adsorption ($0 < R_L < 1$).

3.3. Rudishkevich Dubinin Isotherm

A third capacity parameter called theoretical adsorption capacity (q_D) was evaluated from the Rudishkevich Dubinin isotherm model, simply denoted as R-D model (figure 4) and known to be more general than both the Langmuir isotherm as its deviation is not based on ideal assumption such as equipotential of sorption sites, absences of steric hindrance between sorbed and incoming particles and surface homogeneity (Monika *et al*., 2009).



Just like the Freundlich adsorption capacities (k_f), it was revealed that the theoretical adsorption capacity (q_D) from the R-D isotherm were also lower in magnitude than the Langmuir maximum adsorption capacity (q_m). Table 3 presented a higher q_D values (4.169 mgg^{-1}) for SS/A/15. This value is higher as does its corresponding q_m value (6.024 mgg^{-1}) for the same sorbent on Table 2.

Table (3): Rudishkevich Dubinin adsorption experimental data of dye sorption by SS biosorbent.

Biosorbent	Equation (y=)	Linearity (R^2)	$q_D(mgg^{-1})$	positions	
				R^2	q_D
SS/A//5/	-3.383x+0.539	0.988	3.622	first	second
SS/Z,5	-5.808x+0.308	0.962	2.032	third	fourth
SS/A/15	-3.300x+0.620	0.944	4.189	Fourth	First
SS/Z/15	-3.150x+0.384	0.984	2.421	second	third

SS/z/5 – shea nut shells, treated with $ZnCl_2$, activation for 5 minute dwell time.A-H_3PO_4, 15-activation dwell time of 15 minutes

The other q_m values were also higher than their corresponding q_D and k_f evaluated for the entire sorbent series. A summary of the 3 types of sorption capacities obtained from different isotherms and their quantitative trend in this analysis is as represented on Table 4.

Table 4: comparison of the normal; theoretical saturation and maximum adsorption capacities of dye uptake by SS Biosorbent.

Biosorbent	$K_f(mgg^{-1}(mg^{-1})^n)$	$q_D(mgg^{-1})$	$q_m(mgg^{-1})$	Trend	position
SS/A//5/	0.646	3.622	5.102	$q_m > q_D > K_f$	second
SS/Z,5	0.312	2.032	2.611	$q_m > q_D > K_f$	fourth
SS/A/15	0.628	4.189	6.024	$q_m > q_D > K_f$	First
SS/Z/15	0.646	2.421	2.801	$q_m > q_D > K_f$	third

K_f= Freundlich normal adsorption capacity, q_D = R-D theoretically saturation adsorption capacity, q_m = Langmuir maximum adsorption capacities. **SS/z/5** – shea nut shells, treated with $ZnCl_2$, activation for 5 minute dwell time.A-H_3PO_4, 15-activation dwell time of 15 minutes

Conclusion

Highlights of results presented in this works shows that shea nut shell is a potentially low cost precursor for generation of activated biosorbent, giving up to 84% dye removal. The isothermal evaluation gave isotherm experimental data that agrees with those of researches reviewed earlier. To this regards, adsorption falls within favorable limits as confirmed from the Freundlich constants (1/n <1) and the essentials of Langmuir model (R_L<1). Applicability of the three models follows the trend; Langmuir (R^2= 0.979-0.991) > R-D (R^2 = 0.944 – 0.988) > Freundlich (0.869-0.989). Both capacities, the normal Freundlich, Langmuir maximum and R-D theoretical adsorption capacities as well as the adsorption intensities also agrees well with those if similar research. A critical comparative study showed that for all the series of the adsorption study, the values of the maximum saturation capacity (q_m) > theoretical adsorption capacities > normal adsorption capacity (k_f). The three values for SS/A/15 include 6.024mgg^{-}

^{1}, 4.189mgg^{-1} and 0.628 mgg^{-1} respectively. The same trend is applicable to the other biosorbent series.

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