ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

DERIVED LOW COST BIOSORBENT AS WATER DECOLOURIZER

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ABSTRACT

This study was carried out to compare the dye adsorption capacities, intencities, efficiency and usability of biosorbent prepared from chemically treated groundnut shells. Data were tested with three isotherm models.Their trends of applicability from the R^2 values follows the order; Temkin (0.760-0.974) > Langmuir (0.598-0.949) > Freundlich (0.606-0.938).Maximum adsorption capacities' (q_m=2.188) and (K_f=0.693) were found for GS/SALT/15 by the Langmuir and Freundlich model respectively.

Key words: *Freundlich, Langmuir, Temkin, Adsorption, Groundnut shells.*

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INTRODUCTION

The risk reported on the environmental contaminant originating from textile industries cannot be overemphasized. This industry consume a large quantity of water and produces large volume of waste water from different stages in the dyeing and finishing processes (Hameed, 2009).The semi dark colouration,chlorolignin residues and toxins found in dyestuff effluent posses environmental threat on not only the receptor water bodies but on the growing porpulace.However,little is known on the occurrence,fate, synergy and long term effects of this pollutant (Anne et al.,2009).

The most widely used carbonaceous materials for the production of activated carbon are coal, wood and coconut shells (Baccar et al., 2009).These precursors are expensive and are often reserved for alternative uses, making it necessary for developing countries to find cheap and readily available precursor for generating adsorbent for industrial and domestic use as water bed filters, drinking water purification and for waste water treatment.

Equilibrium data, commonly known as adsorption isotherm are basic requirements for the design of adsorption system. Sorption capacities were reportedly enhanced by the use of oxidant agents such as $ZnCl_2$, H_3PO_4, H_2O_2/H_2O, KOH, NaOH, K_2CO_3 etc. were reported. These activant, to a greater extent redefine surface chemistry as does the activation conditions and temperature employed (Dinesh & Charles,2007).Adsorption capacities and intensities therefore depend on the activated carbon properties, adsorbate chemical compositions, temperature, pH, ionic strength,etc.

MATERILS AND METHODS

The adsorbate, an industrial dyeing waste water was obtained from the effluent discharge reservoir of Chellco textile company,Kaduna,Nigeria.The semi dried groundnut shells were procured from a local oil mill depot situated at Aliero,Kebbi State,Nigeria.The shells were washed, sundried and oven dried at 110^oc overnight. The dried shells were milled, and sieved with the < 2mm aperture Endecott sieve. Chemical activation was by the one-step activation scheme as earlier described by Turoti et al,(2007) in which about $3.0cm^3$ of each 1 molar activant is directly interacted with the raw pretreated shells, allowed to stand for one hour followed by a direct activation at 800^oc without passing through a separate stage of pyrolysis (Turoti et al.,2007) .The waste dyeing effluent was used without further purification, However, a concentration brix of 1000ppm was prepared from the dye concentrate obtained after a mild and controlled evaporation as described by Mudoga et al., (2002).The maximum wavelength of the dye is 540nm.

Batch equilibrium studies: Batch experiments of adsorption were carried out in $250cm^3$ Erlenmeyer flasks. 0.1g of adsorbent was separately mixed with $10cm^3$ each of 10,20,30,40, and 50ppm of the industrial dye solution. These fixed initial dye concentrations were in separate flasks, allowed to stand for 30 minutes contact time. Mixtures were filtered, using

Wattman filter paper (Abdulrahman et al.,2009).Absorbance of filtrates was taken, using the spectrophotometer (Jenway 6100 model, England) at an already predetermined wavelength of 630 nm.The amount of dye adsorbed was measured by difference as shown in equation 1 below:

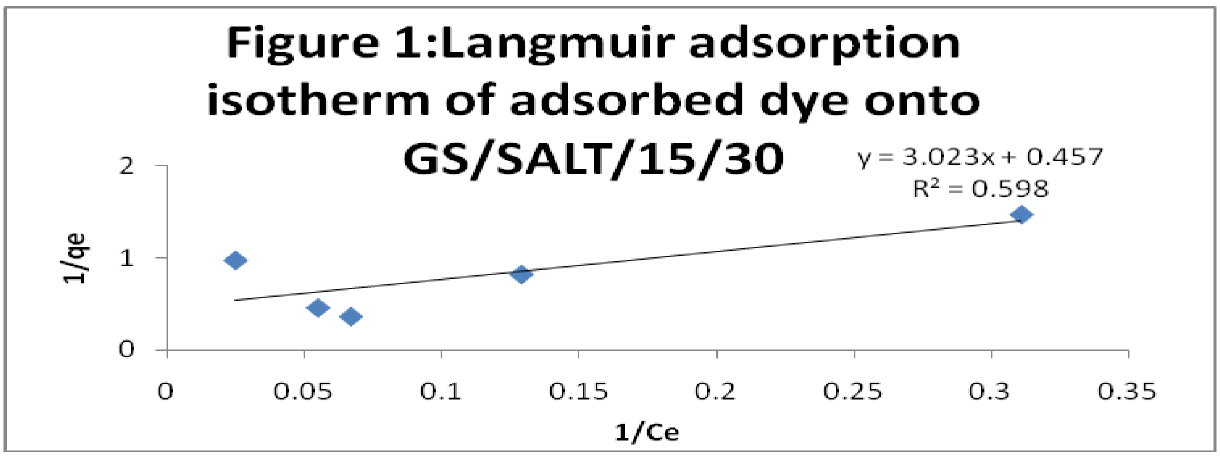
$$q_e = (C_o - C_e)V/m \qquad - \quad - \quad - \quad - \quad - \quad -(1)$$

RESULTS AND DISCUSSION

Isotherm studies: The relationship between mass of adsorbate per unit weight of biosorbent and liquid phase equilibrium concentration of dye were represented as Langmuir (Figure 1),Freundlich (Figure 2) and Temkin (Figure 3) adsorption isotherms.According to Hameed,(2009),The linearized form of Langmuir isotherm is given as equation 2;

$$1/q_e = 1/(K_a q_m C_e) + 1/q_m \qquad - \quad - \qquad (2)$$

Langmuir constants, K_a (Lmg-1) and q_m (mgg-1) are related to the energy of adsorption and the adsorption capacity respectively.



Langmuir model assumes that dye uptake occur on a homogenous surface by monolayer adsorption which is free from interaction by already adsorbed dye and free from transmigration of adsorbate in the plane of the surface. It assumes uniform energies of adsorption to the surface (Monika et al., 2009).The linear plot of specific adsorption ($1/q_e$) versus equilibrium concentration($1/C_e$) shows that the adsorption obeys Langmuir model (Hameed,2009).The Langmuir constant constant (q_m) and K_a were determined from the slope and intercept of the plot. The Langmuir constants value were obtained from plots, similar to Figure 1 and presented on Table 1

Table 1: Langmuir isotherm parameters for the adsorption of dye onto GS- biosorbent at room temperature.

Samples	Equations,(y =)	R^2	$q_m(mgg^{-1})$	$K_a(Lmg^{-1})$	RL
GS/ACID/5/30	33.05x-0.345	0.949	2.915	0.011	0.643
GS/ACID/15/30	30.55x+1.138	0.658	0.879	0.037	0.645
GS/SALT/5/30	16.13x-0.178	0.779	5.618	0.011	0.645
GS/SALT/15/30	3.023x+0.457	0.598	2.188	0.151	0.117

A/B/C – sample (A) modified with chemical (B) at activation time (C),interacted at time,t – for GS/salt/5/t $_{etc}$

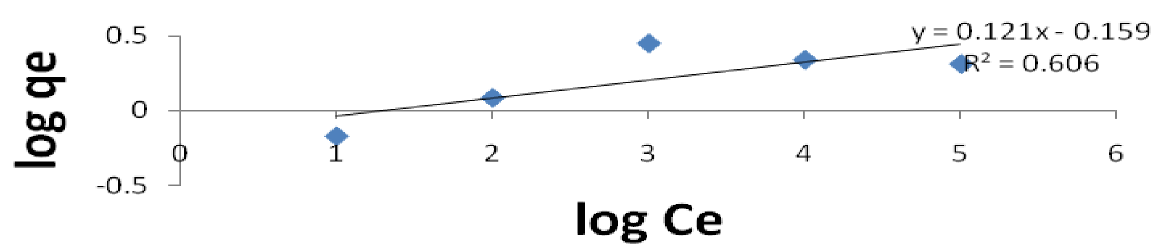
The coefficient of correlation (R^2=0.949, 0.658, 0.779 and 0.598) were obtained from the isotherms. These R^2 values, > 0.5 are indication of a good fit.

The sorption data were also tested with the Freundlich adsorption isotherm .This model assume the uptake of dye(adsorbate) to occur on a heterogeneous surface by multilayer adsorption and that the amount of dye adsorbed increases infinitely as the concentration increases. The linearized Freundlich model is expressed as shown in equation 3;

$$\text{Log } q_e = \log K_f + 1/n \log C_e \qquad (3)$$

q_e and C_e is the amount of dye at equilibrium(mgg^{-1}) and the equilibrium concentration (mgl^{-1}) respectively.K_f and n are factors which affect the adsorption process (adsorption capacity and intensity respectively).A plot of log q_e against log C_e gave a straight line as shown in Figure 2

Figure 2:Freudlich adsorption isotherm of adsorbed dye onto GS/SALT/15/30



The higher the value of K_f (intercept) and n (slope),the higher the absorption capacity. Good linearity (R^2) obtained for the Freundlich isotherm plots were of least fit compared to that of Langmuir and Temkin isotherms. The R^2 values for the two models are Temkin (Freundlich)**:** 0.770 (0.642), 0.835 (0.765), and 0.974 (0.606) values for GS/ACID/15/30, GS/SALT/5/30,and

GS/SALT/15/30 respectively. This is however not true for GS/ACID/5/30, with values: 0.760(0.938).Values of n, greater than unity n >1, are indication of favourable adsorption.

Table 2: Freundlich isotherm parameters for the adsorption of dye onto GS- biosorbent at room temperature.

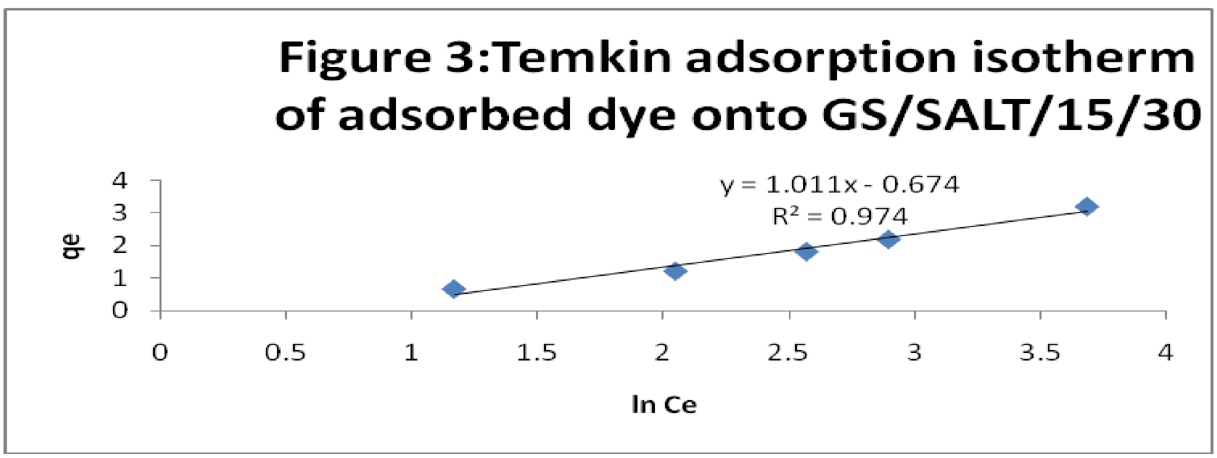
Samples	Equations,(y =)	R^2	1/n	$K_f(mg1^{-1}/n\ (dm^3)^{1/n}\ g^{-1})$	n
GS/ACID/5/30	1.334x-1.800	0.938	1.334	0.015	0.750
GS/ACID/15/30	0.797x-1.542	0.642	0.797	0.035	1.255
GS/SALT/5/30	0.883x-0.990	0.765	0.883	0.102	1.333
GS/SALT/15/30	0.121x-0.159	0.606	0.121	0.693	8.264

A/B/C – sample (A) modified with chemical (B) at activation time (C),interacted at time,t – for GS/salt/5/t $_{etc}$

Fitness of the adsorption data to Temkin adsorption model was also studied. Their R^2 values were represented on table 3 as determined from plots of type in figure 3.This model was applied in forms, given as equation 4 below;

$$q_e = B \ln A + B \ln C_e \quad - \quad -- \quad - \quad - \quad - \quad -(4)$$

Where B = RT/b or b = RT/B. By plotting q_e against ln C_e gave the constants, A and B which are the Temkin isotherm constants (Lg^{-1}) and the Temkin constant related to heat of sorption ($JMol^{-1}$) respectively. R is the gas constant ($8.318Jmol^{-1}K$), b is also a Temkin isotherm constant while T is the absolute temperature in Kelvin (Hameed, 2009).



The R^2 value range obtained for the Temkin model is high compared to those of both the Freundlich and Langmuir models..It therefore stands that for this adsorption studies, the Temkin model is most suitable and that applicability follows the order; Temkin > Langmuir >Freundlich adsorption models.

Table 3: Temkin isotherm parameters for the adsorption of dye onto GS- biosorbent at room temperature.

Samples	Equations,(y =)	R^2	A(Lg^{-1})	B ($Jmol^{-1}$)	b at 300K
GS/ACID/5/30	0.881x-1.659	0.760	0.152	0.881	2831.100
GS/ACID/15/30	0.415x-0.755	0.770	0.162	0.415	6010.120
GS/SALT/5/30	0.859x-1.049	0.835	0.295	0.859	2903.609
GS/SALT/15/30	1.011x-0.674	0.974	0.513	1.011	2467.063

A/B/C – sample (A) modified with chemical (B) at activation time (C),interacted at time,t – for GS/salt/5/t_{etc}

Isotherm analysis

Explanations based on the nature of surface coverage is best described by comparing the correlation coefficient,R^2 values of the Langmuir and Freundlich isotherm. The results obtained in this research support a better fit for the Langmuir over the Freundlich isotherm. This implies that a monolayer sorption proceeds over a surface containing a finite number of adsorption sites and uniform strategies of adsorption with no transmigration of adsorbate in the plane of the surface (Hameed et al.,2006). The R^2 values for the two isotherms include, Freundlich (Langmuir)**:** 0.939 (0.949), 0.642 (0.658), and 0.765 (0.779) for GS/ACID/5/30 , GS/ACID/15/30, and GS/SALT/5/30 respectively. This is however not true for GS/SALT/15/30, with values: 0.606 (0.598) respectively and in favour of Freundlich isotherm which is an indication of heterogeneous surface energy that varies with surface coverage.

Dinesh and Charles, (2007), reported the difficulties of comparing adsorption intensities. This, according to the Authors is due to the lack of consistencies in literature data (Dinesh and Charles,2007). 1/n, which is a measure of surface heterogeneity, is also a measure of adsorption intensities. Adsorption onto the surface becomes more heterogeneous as 1/n values get closer to zero. It thus, follows that adsorption is normal (when $1/n < 1$) and cooperative (when $1/n > 1$). Tables 2 shows that GS/ACID/5/30 gave corporative adsorption, unlike the normal cases of the other three samples.

Adsorption capacities for Freundlich isotherm (K_f) and for Langmuir isotherm (q_m) were investigated. GS/SALT/15/30 gave a higher capacity of its adsorbent nature for the adsorbate in both cases. Thus, groundnut shells activated with $ZnCl_2$ at 15 minutes residual time gave biosorbent with high capacity for the adsorbate.

The magnitude of the sorption energies in $Jmol^{-1}$ were represented by the slope of Temkin isotherm. The Temkin constants related to the heat of sorption (B) is higher for GS/SALT/15/30 (1.011$Jmol^{-1}$) which corresponds to the most favorable R^2 value (0.974) in the analysis.

The Langmuir based adsorption capacity (q_m) of several adsorbent was reported in mgg^{-1} for apricot stone (4.1), walnut shell (3.5), petrified sediment (2.4) and almond shell (1.3) (Anne et al.,2009).These values were in agreement with the data reported in this research, with q_m values of 2.94, 0.879, 5.618 and 2.188 respectively for GS/ACID/5/30, GS/ACID/15/30, GS/SALT/5/30,and GS/SALT/15/30.This implies that groundnut shell is an effective potentially low cost adsorbent especially when its preparation involve the use of $ZnCl_2$.

The K_a values for papaya seed was reported as 0.0028 Lmg^{-1} (Hameed,2009), sunflower stem waste gave 0.109 Lmg^{-1} and 0.071 Lmg^{-1} (Monika et al,2009).This values were all in agreement with the data obtained for GS in this work (Table 1).

The essential characteristics of the Langmuir isotherm was expressed in terms of dimensionless equilibrium parameters, R_L, whose magnitude defines the feasibility of the adsorption process(Monika et al.,2009).It is represented by the equation 5 as;

$$R_L = 1/(1 + K_a C_o) \qquad - \quad - \quad - \quad - \quad - \quad -(5)$$

K_a is the Langmuir constant, C_o is the highest dye initial concentration (mgl^{-1}) while R_L is an indication of the type of isotherm as either linear (R_L=1),favorable(R_L<1),unfavorable(R_L>1), or irreversible(R_L=0) (Hameed et al.,2006).Table 1 revealed that the Langmuir isotherms are all favorable with R_L values between 0.117 and 0.645 but more favourable for GS/ACID/5/30 with R_L=0.645andR^2=0.9471.

CONCLUSSION

Data generated in this present research are in close agreement with those presented in literatures. This revealed that the precursor, groundnut shell is good for biosorbent production with a high sorption ability, especially when catalyzed with salt ($ZnCl_2$).It also follows that adsorption onto carbon surface is more homogenous, as predicted by the Langmuir over the Freundlich isotherm. The applicability of the isotherms follows the trends: Temkin>Langmuir>Freundlich as disclosed by their coefficient of correlations *(R^2) values.*

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