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Equilibrium study on the biosorption of malachite green from aqueous solution onto thermochemically cracked groundnut shells

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ABSTRACT

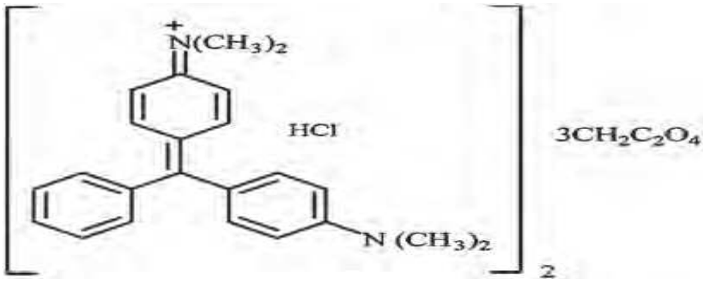
Groundnut shells (GS) was used as a precursor to study the workability of H_3PO_4 and $ZnCl_2$ treated activated carbon. Dye absorption was found to fit into Freundlich and Langmuir isotherms models. The results revealed that thermally cracked groundnut shell at 600^oC could serves as filter for the dye adsorption from water phase. Over 80 percent adsorption was reported by each adsorbent. Percentage of dye absorbed (%RE) by the absorbents, followed the trend: commercial > GS/$ZnCl_2$ > GS H_3PO_4 > GS pyrolized. This follows that the adsorption by pyrolized sample is onto a surface of least heterogeneity. The same sample present least value of adsorption intensity (n = 1/1357 or 0.734). This evidently proves the role played by activation. Furthermore, the percentage burn off, effect of carbon dose and effect of initial concentrations were also estimated. It was generally proven that the sorted biomass could be a potential precursor for generating activated carbon used for waste dye affluent treatment.

Key words: *Biosorption, Malachite Green, Groundnut shell, Activated carbon.*

INTRODUCTION

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). Malachite green which is also called basic green or victoria green is a toxic chemical primarily used as a dye. Malachite green when diluted, can be used as a typical antiseptic property to treat parasites, fungal infections, and bacterial infections in fish and fish eggs. It is also used as a bacteriological stain (Bongsup, *et al*.,2003). Malachite green and its major metabolite, leuco-malachite green had been reported to have mutagenic and carcinogenic effects. Culp, (2002) in her recent article published in Mutation Research mentions that rats fed malachite green experience "a dose-related increase in liver DNA adducts" along with lung adenomas. Leuco-malachite green causes an "increase in the number and severity of changes". As leuco-malachite green is the primary metabolite of malachite green and is retained in fish muscle much longer, most intake of malachite green would be in the leuco form. Information of this adsorbate inlude: IUPAC name: 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline Molecular formula: $C_{23}H_{25}ClN_2$ (chloride), Molar mass: 364.911 g/mol (chloride).

Malachite Green



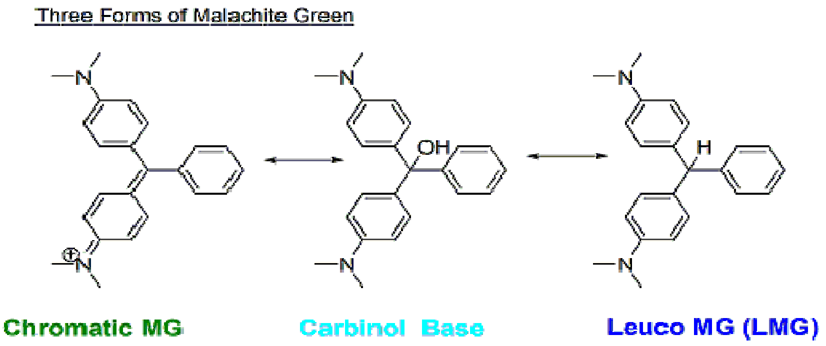


Figure 1: Malachite Green; Chemical formula = $C_{50}H_{52}N_4O_8$, MW = 927.03, Chemical IUPAC name = *N*-[4-(4-dimethylaminophenyl)phenylmethylene]-2,5-cyclohexadien-1-Ylidene-*N*- methyloxalate

Carbinol form, spreads across cell membranes faster. When it is inside the cell, it is then metabolized into a form called leuco-malachite green. This form is known by researchers to be toxic in addition to the fact that it is retained in the body for a longer period than the chromatic form of malachite green (Plakas *et al*.,1996). Malachite green is used to dye materials like silk, leather, and paper. The chemical known as malachite green does not actually contain the mineral malachite. The name comes from the similarity of color. Malachite green is also found to be active against the fungus, which infects fish eggs in commercial aquaculture. It is also a very popular treatment against ichthyophthirius in freshwater aquaria. The principle metabolite, leuco-malachite green (LMG), is the main chemical found in fish treated with malachite green. This is due to its longer retention time inside fish muscle tissues (Plakas *et al*., 1996). The use of this substance has been banned in many countries as a suspected carcinogen. Lab tests revealed that

rats fed malachite green at the concentration of 100 ppb for longer than 2 years showed signs of tumors.
Activated carbon is usually derived from charcoal. Activated carbon are amorphous form of carbon in which a high degree of porosity and surface area has been developed, making it the most versatile adsorbent to be used for effective removal of organic contaminant (Bansode *et al*,2003) and for removal of a wide range of substances from both liquid and gases (Abram, 1973). It can be prepared from animal or agricultural waste as well as various nutshells (Bansode *et al*,2003). Agriculture wastes such as oil palm nut shells, rice husks, olive waste cakes, coconut shells and guava seeds have be reportedly used (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).Groundnut, famous by its Hausa name "Gyada", belongs to the pea and bean family and is a legume but is considered as nut because of its high nutrition value.

The most commonly used technologies for adsorption 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). Adsorption is the collection of a substance on to the surface of adsorbent solids. It is a removal process where certain particles are bound to an adsorbent surface by either physical or chemical attraction (Steve and Erika, 1998).

Isotherms are empirical relationships used to predict how much solute can be adsorbed by activated carbon (Steve and Erika, 1998). Adsorption isotherm is a graphical representation showing the relationship between the amount absorbed by a unit weight of the adsorbent and amount of the adsorbate remaining in the test medium at equilibrium (Chilton *et al*., 2002). The major factors determining the shape of an isotherm are:-The number of compound in the solution, relative adsorbability of the compounds, initial concentration in the solution, degree of competition among solute for adsorption sites and the characteristics of the activated carbon. The three well known isotherms are; (i) Freundlich (ii) Langmuir and (iii)Linear adsorption (Steve and Erika, 1998).

The Langmuir equation also called Langmuir isotherm, Langmuir adsorption equation or Hill-Langmuir equation, relates the coverage or adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. Hameed, (2009) presented a linearized form of the Langmuir equation as ;
$1/q_e = 1/k_a q_m C_e + 1/q_m$ -------------------- (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). This is the simplest theoretical model that can be used to describe monolayer adsorption. The Langmuir equation is based on a kinetic approach and assumes a uniform surface, a single layer of adsorbed material and constant temperature. The model is useful when there is a strong specific interaction between the surface and the adsorbate so that a single adsorbed layer forms and no multi-layer adsorption occur. The rate of attachment to the surface should be proportional to a driving force times an area. The driven force is the concentration in the fluid and area is the amount of bare surface (Chilton *et al*., 2002, cited in Itodo, 2008). The theoretical concept behind the langmuir isotherm is as summarized thus; The

adsorption is an equilibrium process, the adsorption may not proceed beyond mono layer coverage, all site are equivalent and surface is uniform (perfectly plat on a microscopic scale).

The Freundlich equation or Freundlich adsorption isotherm is an adsorption isotherm, which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. Freundich isotherm is the most popular model for single solute system. It is an empirical equation based on the distribution of solute between the solid phase at equilibrium (Freundich, 1928; cited by Itodo, 2008). The basic Freunlich equation is linearly expressed as equation 2 below;

$$\text{Log}\,(x/m) = \log K + 1/n \log Ce \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where 1/n = slope, Log K = intercept, It is an empirical equation with no bases in theory, which assumes an exponential variation in site energies (Chilton *et al.*, 2002; in Itodo,2008). Adsorption isotherm helps in predicting the capacities of activated carbon. Adsorption isotherm provides an indication of the functional dependence of capacity on the concentration of contaminant in solution. The steeper the isotherm, the more effective the activated carbon is. (Itodo, 2008).

The activated carbon largely consumed in Nigeria is imported, the demand is therefore increasing, it was also recognized that waste management and pollution are a key factor in assessing the extent of achieving the millennium development goals, therefore, a more environmental friendly and potentially profitable mean of waste management is needed (Itodo, 2008). Groundnut shell as a precursor was chosen to see the possibilities of adding more economic value to groundnut byproduct utility, and therefore boosting its farming first for profit and second for environmental protection. This present research is therefore aimed at generation of activated carbon locally available agricultural by-products, thereby adding more value to the waste and reducing solid waste from the environment and to study some physical and chemical properties of activated carbon prepared using different method such as commercial activated carbon.

EXPERIMENTAL SECTION

The groundnut shells was obtained from Kofar Atiku local groundnut oil industry, Sokoto, Nigeria. The sampling was carried out two times within two weeks, the samples were obtained in a polythene bags and stored at room temperature. Washing was carried out with plenty of water to remove the surface impurities after which it was sundried and later oven dried at 100^oC over night (Omonhenle *et al.*, 2006). The dried shells was pounded followed by sieving with a <2mm mesh size sieve, the less then 2mm samples were kept in airtight container.

AOAC, (1990) methods were used for moisture content, ash content and volatile solid determination. The pH, bulk density, burn off, carbonization and activation methods were adopted from a generally acceptable method as reviewed by National Organic Standard Board Technical Advisory panel for USDA, on activated carbon processing (USDA, 2002). For the adopted and modified one way scheme activation method, approximately 3g of the sample was separately measured in different crucibles and impregnated with 3ml of the activating agent (i.e

H_3PO_4 or $ZnCl_2$). The sample mixture was kept for 24hours after which they were subjected to the furnaces at 800°C for 5minutes, the sample were removed and poured into ice water bath. Excess water was drained (Gimba *et al*., 2004)

The activated carbon generated was washed with a 0.1M HCl (Fan *et al.*, 2003) to remove surface ash, followed by warm and cold water rinsing to remove residual acid (Rahman *et al.*, 2002). The sample was then dried in an oven at 105°C overnight.

Adsorption Study: The adsorption capacities of biosorbent produced form groundnut shells was measured under nature of activating agent and initial dye concentration. For the Stock solution preparation; 0.5grams of 100% pure Malachite green dye was dissolve in a beaker with little amount of distilled water, transferred into a 1000cm^3 volumetric flask and made up to the mark.(concentration = 500ppm or 0.5 g/L). Working standard was prepared using serial dilution to obtain 10, 20, 30, 40, 50, and 60ppm. 10 cm^3 of each dye sample was interacted with 0.1g of biosorbent and allowed to equilibrate for one hour (Itodo *et al.*, 2008). 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 617 nm.

RESULTS AND DISCUSSION

Table 1: Proximate analysis, moisture content, ash content and pH measurements

Samples	%Moisture content	%Ash content	pH
Raw sample	0.111	5.896	5.64
GS/H_3PO_4/5min	_	_	5.60
GS/ $ZnCl_2$/5min	_	_	5.26

Table 2: Bulk density, porosity and apparent density

Samples	Volume(cm^3)	Mass(g)	Bulk density(m/ cm^3)	Porosity
Raw sample	15	5.6	0.37	0.998
GS/Carbonized/5min	15	5.1	0.34	0.999
GS/ H_3PO_4 /5min	15	3.5	0.23	0.996
GS/ $ZnCl_2$ /5min	15	4.8	0.32	0.992

Table 3: Percentage yield on pyrolysis, activated carbon and activated burn off

Samples	Yield*(%)	Yield of AC (%)	Burn off (%)
GS/Carbonized/5min	37.14	_	_
GS/ H_3PO_4 /5min	_	36.06	51.66
GS/ $ZnCl_2$/5min	_	36.32	57.32

Yield- yield on pyrolysis, AC- Activated carbon.*

Table 4; Result of absorbance for different initial malachite green concentrations (Before interaction with AC)

Concentration mg/l	Absorbance (working standards)
10	1.415
20	2.279

30	2.567
40	2.591
50	6.616
60	6.901

Table 5; Result of absorbance of the 10ml Malachite Green Solution after Interaction with 0.5g Generated Carbon

Conc mg/l	Absorbance readings at 617nm			
	Comm AC	H_3PO_3 AC	$ZnCl_2$ AC	Pyrolized sample
10	0.052	0.077	0.019	0.073
20	0.060	0.131	0.016	0.074
30	0.065	0.253	0.025	0.075
40	0.065	0.279	0.055	0.085
50	0.067	0.292	0.075	0.124
60	0.074	0.311	0.095	0.201

Table 6; investigation of absorbance readings of different carbon dose

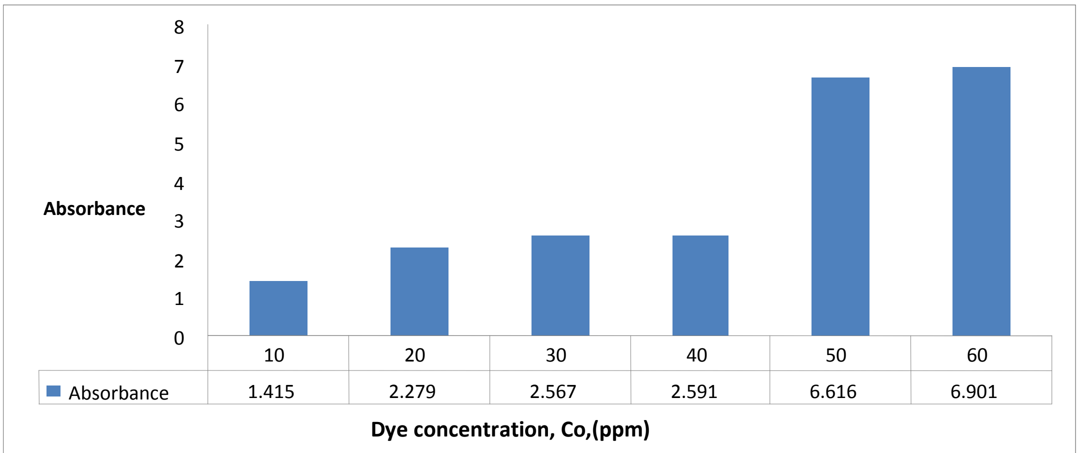
Mass of carbon(g)	Absorbance
0.5	0.129
1.0	0.101
1.5	0.067
2.0	0.063
2.5	0.063

Table 7:Freundlich isotherm experimental constants for the malachite green dye absorption

Samples	Equation	R^2	K_f	1/n
Comm. AC	1.154x+0.025	0.360	1.0495	0.154
GS/H3PO4/5	0.732x-0.458	0.692	0.548	0.732
GS/$ZnCl_2$/5	0.709x+0.086	0.812	1.216	0.709
GS/pyrolized/5	1.352x-0.192	0.806	0.643	1.357

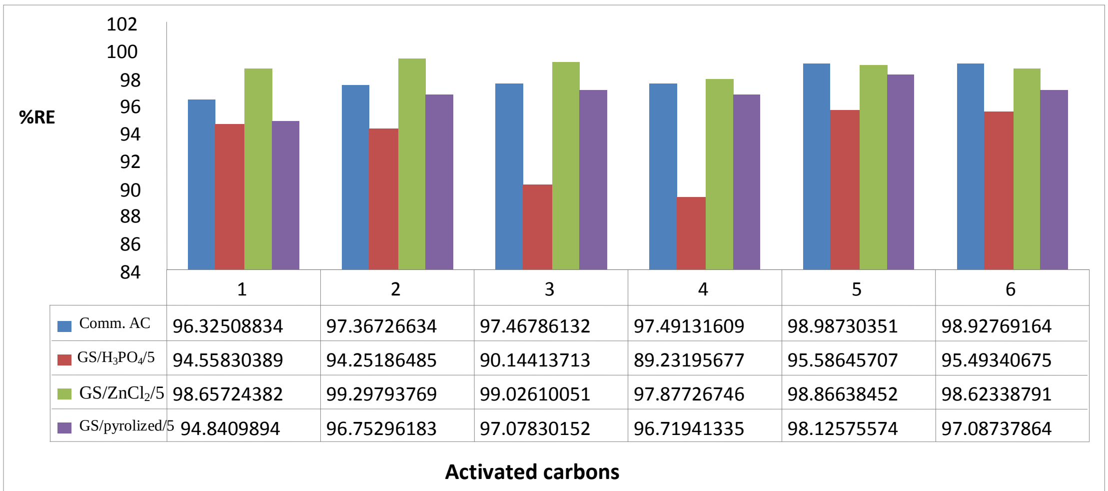
Table 8: Langmuir isotherm experimental constants for the malachite green dye absorption

Samples	Equation	R^2	Ka	qm
Comm. AC	2.131x-1.616	0.615	-0.2904	-0.6188
GS/H_3PO_4/5	2.613x+0.398	0.925	0.9616	2.5126
GS/$ZnCl_2$/5	0.474x+0.317	0.752	6.6552	3.1546
GS/pyrolized/5	3.018x-1.408	0.833	-0.2353	-0.7102



	10	20	30	40	50	60
🟦 Absorbance	1.415	2.279	2.567	2.591	6.616	6.901

Figure 1: Effect of initial dye concentration on absorbance



	1	2	3	4	5	6
🟦 Comm. AC	96.32508834	97.36726634	97.46786132	97.49131609	98.98730351	98.92769164
🟥 GS/H_3PO_4/5	94.55830389	94.25186485	90.14413713	89.23195677	95.58645707	95.49340675
🟩 GS/$ZnCl_2$/5	98.65724382	99.29793769	99.02610051	97.87726746	98.86638452	98.62338791
🟪 GS/pyrolized/5	94.8409894	96.75296183	97.07830152	96.71941335	98.12575574	97.08737864

Figure 2:Extimation of % MG removal by Commercial (C),Acid treated(A),Salt treated Activated carbons(S) and Pyrolysed Char

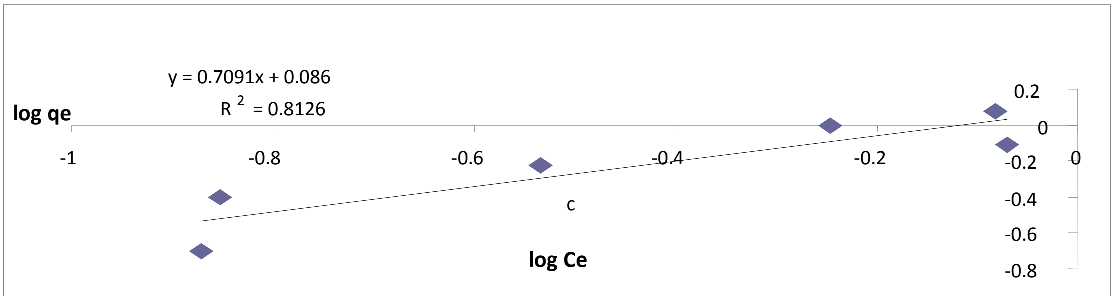


Figure 3: Freundlich adsorption isotherm of MG adsorption onto Salt treated activated carbon

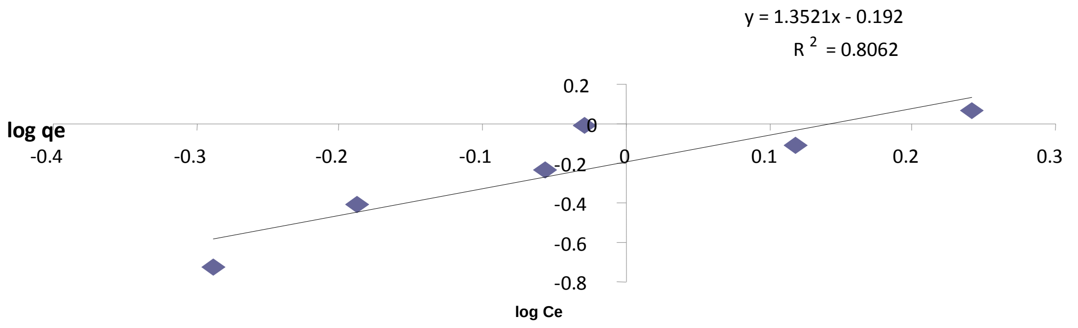


Figure 4: Freundlich adsorption isotherm of MG adsorption onto Pyrolized Char

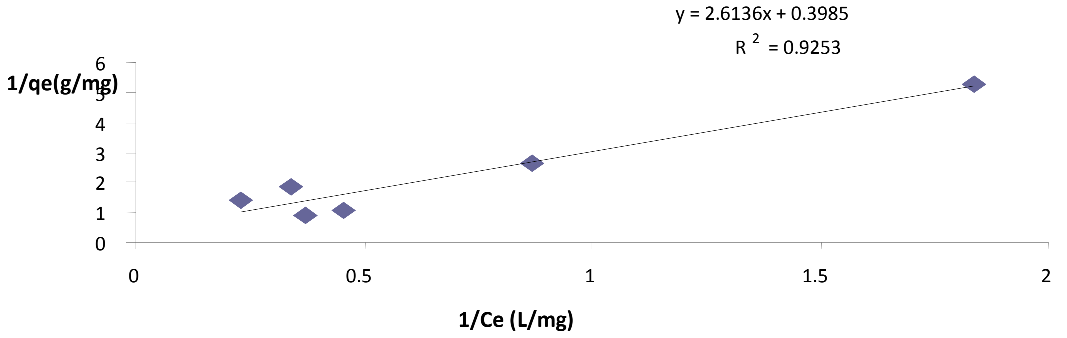


Figure 5: Langmuir adsorption isotherm of MG adsorption onto Acid treated activated carbon

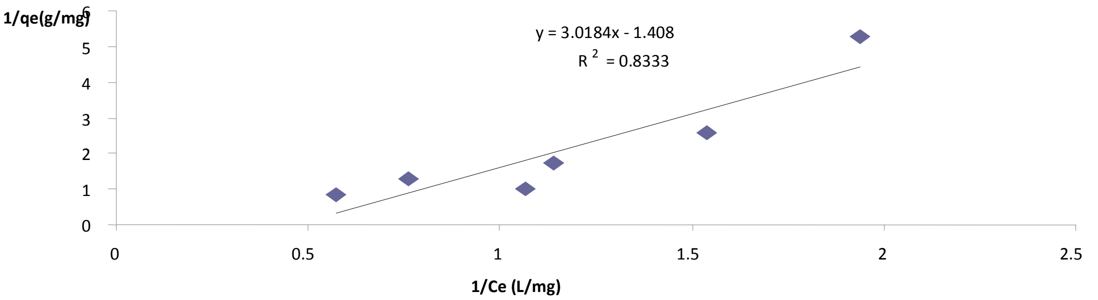


Figure 6: Langmuir adsorption isotherm of MG adsorption onto pyrolysed char activated carbon

Control analysis: A control test was conducted, using the unactivated carbon or pyrolysed carbon at a temperature of 600^{o}C from the same precursors at the same condition, this study reveals that, adsorption test using malachite green by the uninteracted carbon presented up to 94% dye removal. This value is only slightly lower than the 97-99% RE presented by the activated carbon generated.

Nature of activating agent: Impregnation using $ZnCl_2$ followed by activation, dehydrate the cellulose material, resulting in activation, $ZnCl_2$ is responsible for the decomposition of organic materials to release volatile and development of micro porous structure. The space occupied by the $ZnCl_2$ in the carbon structure becomes the pore as the $ZnCl_2$ is removed after intense washing (Malik *et al.,* 2006). Zinc impregnated carbon gave a higher yield of 36.32% compare to phosphoric acid that give 36.06%.

Effect of carbon dose: From the Table 6 above, absorbance reduces as the carbon dose increases up to the 1.5g after which it became steady at 2.0 and 2.5g carbon dose. This implies that the adsorption increases with carbon dose and stabilizes at 2.0g. Note, the higher the adsorbent's dose, the lower the absorbance with a resultant high adsorption.

Effect of initial dye concentration: Table 4 above shows that absorbance increases with increase in the concentration of the dye solution. Hence, adsoption by activated carbon is expected to decrease with increase dye concentration, this is due to the competition for the adsorption site as concentration increases. There is possible desorption at high concentration.

Batch equilibrium test : Equilibrium data were fitted into the Freundlich adsorption isotherm as expressed earlier by Malik *et al.*,2006 and Itodo *et al*., 2009. The value of 1/n (slope) is a measure of surface heterogeneity. As 1/n gets closer to zero, surface heterogeneity becomes more pronounce. n values are also indication of the adsorption intensity. The higher the value the higher the intensity (Malik et al., 2006). The extent of surface heterogeneity follow the trend: commercial > GS/ZnCl2 > GS H3PO4 > GS pyrolized. If thus follows that the adsorption by pyrolized sample is onto a surface of least heterogeneity. The same sample present least value for adsorption intensity (n = 1/1357 or 0.734). This evidently proves the role played by activation.

The intercept (Kf) is roughly a measure of adsorption capacity (Itodo *et al.*, 2009). From the Table 7 above, commercial activated carbon and $ZnCl_2$ treated GS gan almost the same Kf values of 1.0495 and 1.216 to mark high absoption capacities carbon.

Table 8, shows the Langmuir exponential constants for the adsorption of malachite green dye. The values representing adsorption capacity (qm) was obtained from the equation above. A plot of 1/qe against 1/Ce give the slope, $1/(Kaq_m)$ and intercept, 1/qm

The model assumes monolayer adsorption (Hameed et al., 2006). qm value for GS/$ZnCl_2$ (3.154) is higher in the series. Thus, both isotherms present GS/$ZnCl_2$ as absorbent of highest adsorption capacity. The negative qm value obtain for the commercial activated carbon and pyrolized sample could be linked to abnormalities such as desorption, poor absorption and other irregularities. The extents of applicabilities of the two modes were investigation from the coefficient of determination, R^2. The Langmuir isotherm gives a position and fairly high R^2 values than the Freundlich isotherm. The highest, being R^2 =0.925 for the acid treated carbon of the Langmuir isotherm and R^2 = 0.812 for the Zinc chlorite of Freundlich isotherm plot.

This implies that the Langmuir isotherm best describe sorption by acid treated sorbent as does the Freundlich isotherm for the salt treated carbon. Low R^2 values for commercial carbon and pyrolized char may be link to irregularities such as data point error or desorption

The amount of dye at equilibrium (qe) was calculated from the mass balance aquation

$$Qe = (Co - Ce) V/W \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad 3$$

Where, Co and Ce are initial and final dye concentrations. W is the mass of the absorbent.

The % dye removal RE(%) was calculated for each equilibrium state, as:

RE(%) = (Co – Ce)/Co × 100 ……………………………………… 14

From the analysis (Fig 2) it is evidence that the entire sorbate gives 89% adsorption value, uptake by the GS/ZnCl2/5 proves higher then others in the series with over 97% absorption value. Effect of activating agent and activation could not be establish since the pyrolized sample gave unexpected adsorption (> 94%). It however also implies that the extent thermal decomposition of groundnut shell at the chosen temperature (600°C) was high enough to create pore size on the selected biomass.

CONCLUSION

The use of acid treated groundnut shell activated carbon for uptake of malachite green dye was evidently proven. Monolayer adsorption was reported for the treated sorbent via Langmuuir isotherm as does the heterogeneous surface absorption by salt treated sorbent.This work also present the fact that thermally cracked groundnut shell at 600°C could serve as filter for the dye adsorption from water phase. Generally the generated adsorbent competes well with the commercially available reference carbon.

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