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Preparation of zinc oxide/activated carbon nano composite from agro wastes (Mango Seed) for adsorption of heavy metals

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Abstract

The treatment of wastewater generated during industrial, domestic and agricultural activities is a matter of concern worldwide. The presence of heavy metals as a major pollutant in water calls for serious attention due to its persistent, non-biodegradability, accumulative and toxic nature. This research explored the potentials in mango seed in the raw, activated carbon /zinc oxide Nano composite forms(M(raw), M(NC) for the removal of Lead from aqueous solutions. The adsorption capacities of the adsorbents were determined by the application of atomic adsorption spectrophotometric methods in a batch adsorption study under varying conditions of temperature, time, dosage, concentration and pH, and the results showed high adsorption capacities with very high percentage removal. The adsorption was favored with maximum adsorption at temperature of 45 ^{0} c, equilibrium sorption time of 180mins.In general adsorption capacities increased with increase in varying conditions except for dosage. The experimental data were sampled on different kinetic models (pseudo-first order, pseudo-second order, intra-particle diffusion a (Langmuir and Freundlich). The results indicates pseudo second order kinetic and intra particle diffusion models fitted the sorption process better than pseudo first order and liquid film diffusion models respectively. These results implied chemisorption process and pore penetration of the adsorbates. The thermodynamic studies revealed a chemisorption and spontaneous process with increased degree of disorderliness. The results obtained in this study revealed that Mango seed especially in the activated/zinc Nano composite form is an efficient and effective adsorbent in the removal of Lead from aqueous solution.

Keywords: lead, adsorption, activated carbon /zinc oxide nano composite

Introduction

Water is essential for all forms of life and as such, the role played by water to human and biological system cannot be overemphasized.

Availability and accessibility of clean and safe water is of major concern to the whole world. A Survey conducted by Nigeria's Bureau of Statistics and UNICEF shows that about 60 million Nigerians or 33 percent of the population do not have access to clean water (Press freedom, 2019) [34].

Pollution is a major cause of water scarcity in Nigeria. It has led to high level of toxic chemicals such as heavy metals and pesticides, which pose a major health risk. Pollution of water by heavy metals is a major global issue that calls for serious attention.

Although, there is no specific definition of a heavy metal, it has been defined as a naturally occurring element having a high atomic weight and high density which is five times denser than water (Masindi *et al*, 2018) [27]. Heavy metals are usually present in trace amounts in natural water but many of them are toxic even at low concentrations. In certain concentrations, some of these heavy metals are essential to plants and animals but in high concentrations can become toxic. The presence of heavy metals is a health hazard due to their persistence, non –biodegradable and non- thermo degradable characteristics in the environment (Sharna *et al*, 2007). The uptake of metals may cause diseases like lung cancer, damage to the central nervous system, kidney and liver damage among others (Verma R and Divivedi P,2013) [41]. All these negative effects of heavy metals call for its removal from natural waters as it poses threat to human lives.

Several techniques have been employed in the removal of heavy metals from aqueous solution. These techniques include Membrane filtration (Gholami *et al*,2014) [14], Ion exchange (Iqbal *et al*,2009b) [21], reverse osmosis (Kedr, 2013), Electrolysis (Deng *et al*, 2010) and others. These techniques however, are expensive and have been proved to be less effective especially in removing lower concentrations of heavy metals (Popuri *et al*, 2007; Xiangliang *et al*, 2005) [33], Another disadvantage of using these techniques is the production of metals contained sludge, which require further treatment to dispose (Ahalya *et al*., 2003; Igwe *et al*., 2005).

Besides the above-mentioned techniques, adsorption is another technique used in the removal of heavy metals from aqueous solutions and results proves it to be very effective even at low concentrations of the metals (<100mg/l) (Popuri *et al*,2007) [33]. Adsorption using activated carbon is the most widely used technique for the removal of toxic heavy metals (Ahmed *et al*,2006). The significant characteristic of the adsorbents is their high porous nature which results in larger surface area to bind the heavy metals. The use of commercial activated carbon is no longer trending because of the high-cost value associated with it (Fu and Wang, 2011) [13] and has given rise to the search and discovery of cheaper materials; agro wastes.

In recent decades, interest in the use of cost-effective adsorbents to reduce the high expense of water treatment processes has intensified. Attention has been focused on natural agricultural waste materials such as seeds, fruit peel (Mallampati *et al*., 2015) [26], nut shells (Taşar *et al*., 2016), crop residues (El-Said, 2010), and fruit shells (Zein *et al*., 2010) [45] as low-cost and environmentally friendly adsorbents which are highly efficient and generally available in large quantities (Ibrahim *et al*,2010) [19].

The application of nanotechnology has taken over other adsorption techniques in the recent past years. nanotechnology is gaining enormous popularity due to its ability to reduce metals, metalloids and metal oxides into their Nano size, which essentially alter their physical, chemical, and optical properties. Nano materials are efficient adsorbents for the removal of heavy metals from aqueous solution because of the unique properties they display such as large surface area, enhanced active sites and the functional groups that are present on their surface (Gopalakrishan *et al* 2015) [15]

This study presents the first outcoming results about the possible use of mango seed in its activated carbon /zinc oxide Nano composite form as heavy metal bio sorbents. This material was chosen considering its availability and cost effectiveness.

The aim of the present work was to study the adsorption capacity of the agricultural waste (mango seed) for heavy metal (Lead) removal from aqueous solution under different experimental conditions. The effect of various operating parameters on biosorption such as contacts time. Dosage of the adsorbents, initial pH and metal concentration were studied and optimal experimental conditions were decided.

Materials and methods

1. Adsorbent preparation

The adsorbent (mango seed) was thoroughly washed to remove dusts and dirt. They were dried under sunlight for 16 hours I.e. (4 hours for 4 days) and was allowed to dry in the oven at 60^0C for 4 hours to remove moisture before being ground to powdered form and was sieved to achieve the desired size of less than 300μm using British standard sieve (BSS)

2. Lead stock solution

A portion 0.5ml of 100mg/l Lead stock solution was carefully measured into a 100ml volumetric flask and made up to mark with distilled water to get 5mg/l. A working solution of 0.158, 0.315, 0.630,1.250,2.50 and 5.0mg/l was prepared by diluting 0.0158,0.0315,0.0630,0.125 and 0.250ml stock solution to mark in a 100ml volumetric flask by using the equation

$$M_1V_1=M_2V_2 \qquad (1)$$

3. Preparation of activated carbon

3.1 Carbonization and activated process

The powdered raw sample (mango seed) was impregnated with 20% $Zncl_2$ in the ratio of 1:2 for 24 hours, after which was drained and dried in the oven at 80^0C. Then transferred to a crucible and placed in the furnace at a temperature of 300^0C for 15 minutes. The resulting carbon was washed until the pH is neutralized. It was then allowed to dry in the oven for 105^0C for 4 hours.

3.2 Preparation of activated carbon / Zinc oxide Nano composite (Madha *et al*, 2018)

A portion (2g) of the activated carbon was carefully measured in a 200ml of 10%(V/V) HCl solution in order to remove impurities for 24hours and filtered. The residue was transferred into a 250ml beaker and 100mL of 0.9M Zinc acetate solution was carefully measured into it and allowed to stand for 12h and then filtered. The final product was dried at 80^0c for 18hr and then calcined in a furnace at 400^0c for 4h. The resulting product was transferred into a nylon bag and stored prior to use.

4. Adsorption Studies

4.1 Adsorption experiment

The batch adsorption experiment was carried out in 100ml Erlenmeyer flasks where 0.1g of the adsorbents and 20 ml of the metal stock solution of (100-300mg/L) concentrations. This was added at a pH of 6 for the solution. The flasks were placed on a shaker at 120rpm at 30^0C for 60 minutes, After the equilibrium was attained, each sample was filtered to obtain solution containing un-adsorbed Pb^{2+} that is free from adsorbent and the concentration of the metal ion was analyzed by Atomic Absorption Spectrophotometer (AAS) model AA500 at the specific wavelength of the metal (Lead). The amount of adsorption at equilibrium q_e (mg/g), then calculated by

$$q_e = \frac{(Co-Ce)\,V}{W} \qquad (2)$$

Where C_0= initial concentration, C_e= concentration at equilibrium, V= volume of solution in L,
W=weight of dry adsorbent in g, q_e= adsorption capacity

$$\text{and \% Removal} = \frac{(Co-Ce)\,V}{W} \qquad (3)$$

To study the effect of time, the adsorbent with weight (0.1g), temperature (30^0c), time (60 mins) concentration (150 mg/L) and pH (2) were kept constant and the experiments were carried by varying time between 30-180mins. In the same way, the effect of dosage, temperature concentration and pH were studied by varying weights between (0.1-0.5g), concentration between (100-300 mg/ L) and pH (2-10) respectively while leaving other variables constant.

Results and discussion

1. Study of variables

1.1 Effect of adsorbent dosage

Adsorbent dosage is a very important parameter which can affect the adsorption of heavy metals on adsorbents (Li *et al*., 2013) [24]. A decrease in the adsorption capacity of metal ions with increase in adsorbent dosage was obtained as shown in Figure 3.1.1. This decrease in adsorption capacity per unit mass of adsorbent may be due to the higher adsorbent dose providing more active adsorption sites, which results in the adsorption sites remaining unsaturated during the adsorption reaction (Li *et al*., 2013) [24]. This decrease can also be attributed to a decrease in the total adsorption surface area and increase in diffusion path length resulting from overlapping or aggregation of adsorption sites (Dawodu and Akpomie, 2014) [9]. The effect of adsorbent dosage on the percentage removal of Pb (II) onto the adsorbents was also determined. An increase in the percentage removal of the metal ions with increase in adsorbent dose was obtained. The increase in percentage removal of metal ions with increase in adsorbent dosage may be attributed to an increase in the number of available active sites with increasing adsorbent dose (Unuabonah, 2007). In this study the M(NC) had a higher percentage removal (97.62) compared to M(raw) with % removal (94.64)

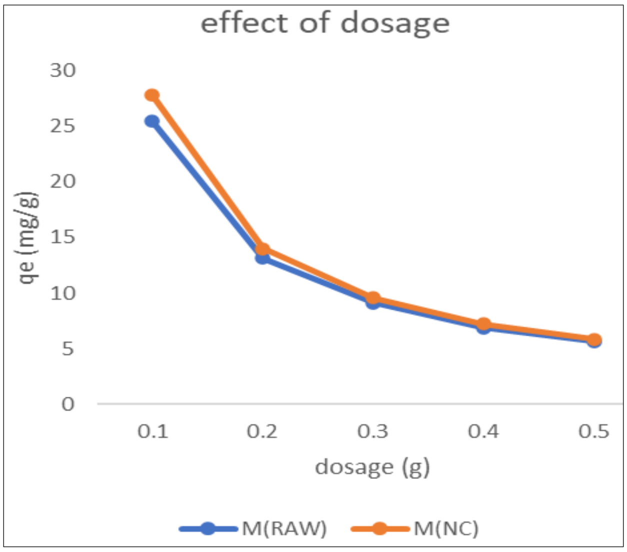

Fig 1: Effect of adsorbent dosage on adsorption capacity

1.2 Effect of contact time

Contact time is an important factor in designing the adsorption process. Fig.3.1 2 shows the results for the effect of time on Lead removal. As shown, the adsorption capacity increased as the sorption time increased from 30 -180 mins. The adsorbents (M(raw) and M(NC) were seen performing very well as contact time increased. However, M(NC) performed better with maximum adsorption capacity qe (29.93) as opposed to (28.30) of M(raw). In the same vein, the percentage removal increased as contact time increased with M(NC) having a greater percentage removal than the raw adsorbent.

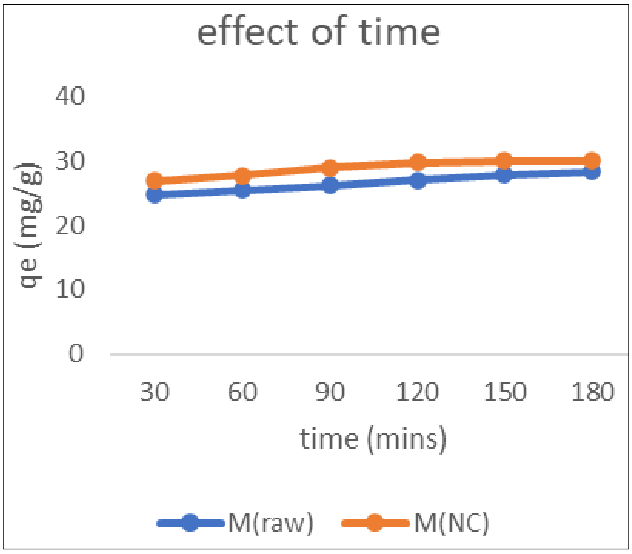

Fig 2: Effect of time on adsorption capacity

1.3 Effect of temperature

Keeping all other parameters constant temperature was varied from 30ºC to 50ºC. The sorption of Lead increased slightly with the increase in temperature up to 45ºC and then started decreasing (Figure 3.1.3). The temperature higher than 45ºC caused a change in the texture of the biomass and thus reduced its sorption capacity as such the optimal temperature for this reaction was recorded as 45^0 c.

The percentage removal also increased as the temperature increased from 30 to 45^{0}c.The adsorbents followed the trend M(NC)>M(raw) with 96.98%>92.59%

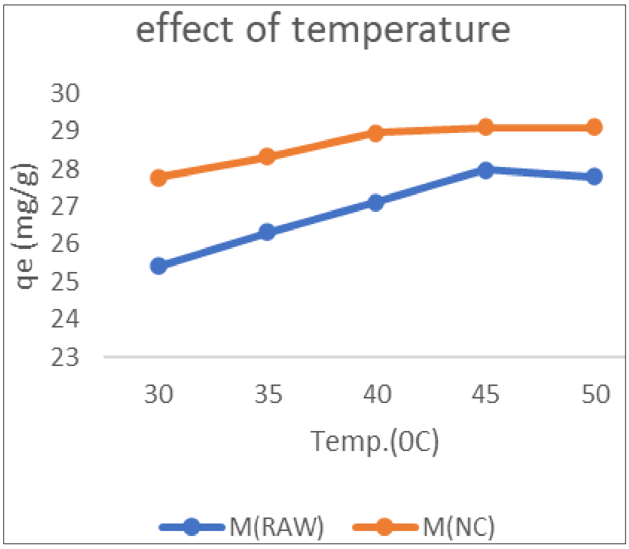

Fig 3: Effect of temperature on adsorption capacity

2. Kinetics study

Adsorption kinetics is the measure of the adsorption uptake with respect to time at a constant pressure or concentration and is employed to measure the diffusion of adsorbate in the pores.it gives insight into the reaction rate and the sorption mechanism. For an effective sorption system to be designed, investigations should be carried out to determine the rate of sorption by implementing the experimental data on several kinetic models (Senthilkumaar *et al.*, 2005) [35]

Table 1: Adsorption kinetic models

Kinetic model	M(raw)	M(NC)
qe$_{max}$ exp (mg/g)	28.30	29.93
Pseudo first order qe$_{cal}$ (mg/g)	6.89	23.24
$K_{1\,=}$ (min^{-1})	0.015	0.044
R^2	0.907	0.891
Pseudo second order qe$_{cal}$ (mg/g)	29.41	31.25
$K_{2\,=}$ (min^{-1})	0.00006	0.00004
R^2	0.998	0.999
Intra particle diffusion Kd (meg g^{-1} min^{-1})	0.728	0.639
R^2	0.996	0.889
C (intercept)	24.02	26.62
Liquid Film diffusion K$_{ed}$	0.466	1.309
R^2	0.909	0.892

The adsorption kinetic models were applied to the experimental data to analyze the rate and mechanism of the Lead sorption onto M(raw) and M(NC). The kinetic models applied to the study are the pseudo- first order, pseudo-second order, intra particle diffusion and Liquid film diffusion models.

2.1 Pseudo first order kinetic model

Lagergren pseudo- first order model is expressed as (Aharoni and Sparks,1991) [2], thus:

$$\log (qe-qt) = \log qe\ K1 \frac{t}{2.303} \qquad (4)$$

where qe and qt are the amounts of adsorbate adsorbed (mg/g) at equilibrium and at time t (minute) respectively, and k1 (l/min.) is the adsorption rate constant. The plot of ln (qe-qt) versus t gives the slope of k1, and intercept of lnqe and the values are listed in Table 1. The R^2 values for all initial concentrations of Lead ions considered within the operating limit of experimental conditions are generally lower than 0.982 as can be seen in Table 1. In that case, the kinetic data of Pb^{2+} cannot be well predicted by pseudo-first-order model. This outcome is actually expected, because many researchers have reported similar results (Oyedoh and Ekwonu,2016) [32]

2.2 Pseudo second order kinetic model

Similarly, the Pseudo -second order kinetic model can be expressed as (Ho and Mckay,1998) [17] thus;

$$\frac{1}{qt} = \frac{1}{K2qe2} + \frac{1}{qe}t \qquad (5)$$

where, k2 (g/mg min^{-1}) is the rate constant of second-order adsorption and can be obtained from the linear plot of t/qt, versus t.

Table 1 compares the kinetic parameters for Lead sorption onto M(raw) and M(NC). Comparing the theoretical (qe_{cal}) values to the experimental (qe_{exp}) values, the qe_{cal} for pseudo-second order kinetic model best fitted the qe_{exp} than the qe_{cal} of the pseudo first order model. The Pseudo second order kinetic model revealed higher coefficient of regression (R^2) values which are closer to unity (1). than pseudo first order model. Based on these results, the Pseudo second order kinetic model is the best kinetic model to explain the sorption rate of Lead ion onto M(raw) and M(NC) and this agrees with previous results by Badmus *et al*,2007 [6].

2.3 intra particle diffusion model

The intra particle diffusion model can be expressed as (Weber and Morris,1963)

$$qt = K_{id}t^{1/2} + C \qquad (6)$$

Where K_{id} (mg/g min), the intraparticle diffusion rate constant is obtained from the slope of straight line of qt versus $t^{1/2}$, C gives an idea about the thickness of boundary layer i.e. the larger the intercept, the greater the boundary layer effect (Tan *et al*,2008). If the plot of qt versus t1/2 gives a straight line passing through the origin, then the sorption process was controlled by intra-particle diffusion only and the slope gives the rate constant, Kid. However, if the data exhibit multilinear plots, then two or more steps influence the sorption process, also a very large intercept would suggest that surface sorption contributes more to the rate determining step (Nwadiogbu *et al*,2015). From the results in Table 1, a high regression coefficient (R^2) and a non-zero intercept were obtained. The deviation from the origin may be due to the difference in mass transfer between the initial and final stages of the sorption process (Das and Mondal, 2011) [8]. The high regression coefficient indicates the existence of an intra particle diffusion mechanism for the sorption of Lead ion onto M (raw) and M (NC). Furthermore, the presence of the boundary layer effect confirmed the existence of surface sorption, indicating that intra particle diffusion mechanism was not the only rate - determining step. However, with the moderate value of intercept, penetration of the adsorbate into the pores of the adsorbent was more predominant than surface sorption.

2.4 Liquid film diffusion model

Liquid film diffusion model was also used in this study to investigate if transport of metal ions from the liquid phase up to the solid phase boundary also plays a role in the adsorption process. (Issabayeva *et al*,2007) [22]

$$\ln(1-F) = -Kfd. \qquad (7)$$

where F is the fractional attainment of equilibrium (F = qt/qe), Kfd is liquid film diffusion constant. A linear plot of ln (1−F) versus t with zero intercept would suggest that the kinetics of the sorption process was controlled by diffusion through the liquid film surface surrounding the solid sorbent. qe is the adsorption capacity of the sorbent at equilibrium (mg g-1). The liquid film diffusion mechanism produced a good regression (R^2) value indicating that surface sorption also played a role in the rate determining step. However, intra particle diffusion mechanism produced a better R^2 value for all adsorbents in this study than the liquid film diffusion model.

3. Adsorption isotherm

Adsorption isotherms express the relation between the amount of adsorbed metal ions per unit mass of adsorbent (Qe) and the metal concentration in solution (Ce) at equilibrium. The equilibrium relationships between the adsorbents and adsorbate at constant temperature are described by adsorption isotherms, i.e. the ratio between the amount of solute adsorbed and the remaining portion in the solution at equilibrium. Experimental data is fitted with different isotherm models to determine the model which is most suitable regarding their correlation coefficients and can be used to design the process (Arami *et al*., 2005) [5]

In this study the experimental data was fitted into Langmuir and Freundlich models. The adsorption model constants values express the surface properties and affinity of the adsorbents for the adsorption of the metal ions.

Table 2: Batch adsorption isotherm models

Isotherm models	M(raw)	M(NC)
LANGMUIR		
Qmax	2.5253	3.7879
KL	15.8497	11.0011
RL	0.0004	0.0006
R^2	0.998	0.990
FREUNDLINCH		
KF	13.224	9.116
1/n	0.288	0.234
R^2	0.992	0.828

3.1 Langmuir Isotherm

This isotherm model assumes a monolayer homogenous coverage on the sorbent surface (Huang *et al*., 2018) [18]. The linearized expression is given by the equation

$$\frac{Ce}{qe} = \frac{1}{qemax.k} + Ce/qmax \qquad (8)$$

Where Ce: residual metal ions concentration (mg/L) at equilibrium, qe is the amount of metal ions (mg/g) adsorbed at equilibrium and qmax the adsorption capacity (mg/g) respectively. A graph obtained by plotting Ce /qe against Ce is used to get Langmuir constants (Mushtaq *et al*., 2016) [29] and will generate a straight line with a slope of $1/q_{max}$ and an intercept equals to $1/K_L q_{max}$.

The separation factor, R_L, is an Important parameter related to Langmuir isotherm which is used to check if adsorption is favorable or unfavorable. Mathematically, it can be shown as

$$R_L = \frac{1}{1 + K_L C_o} \quad (9)$$

where K_L and C_o are the Langmuir constant and highest initial concentration respectively

In general, $R_L < 1$ indicates that adsorption is favorable; $R_L \sim 0$ indicates that adsorption is irreversible; $R_L = 1$ indicates that the adsorption isotherm is linear, and $R_L > 1$ corresponds to unfavorable adsorption.

3.2 Freundlich isotherm

The model assumes a multilayer coverage of metal ions associated with different adsorption energies (Ali *et al*., 2016) [4]. The Freundlich isotherm linearized equation is expressed by the equation

$$\ln qe = \ln KF + 1/n \ln Ce \quad (10)$$

Where Ce: concentration of metal ions (mg/L) at equilibrium, qe: amount of metal ions removed (mg/g) at equilibrium. KF is adsorption capacity and n is adsorption intensity or surface heterogeneity. The values of KF and n are calculated by plotting a graph of lnqe against lnce (Nthiga *et al*., 2016) [30]. When $0 < 1/n < 1$, adsorption is considered favorable. Unfavorable adsorption occurs when $1/n > 1$ and is irreversible at $1/n = 1$.

In this work, the sorbents showed better linearity for Langmuir model with high correlation coefficients. The results showed that the formation of monolayer surface loading of Pb (II) ions are at the outer surface of the adsorbents. As seen in Table 2, the equilibrium data fits the Langmuir model better compared to Freundlich for all the adsorbents M(raw) and M(NC). This data showed specific sorption characteristic on the surface of the adsorbents i.e Monolayer adsorption on homogenous surface.

The separation factor, RL, from the Langmuir model and 1/n from Freundlich model are all below the value one (1), confirming that Lead is favorably adsorbed onto all the adsorbents.

Langmuir isotherm models were reported to be followed in the adsorption of Pb (II) ions onto bagasse fly ash (Gupta and Ali,2004) [16], saw dust (Ezeh *et al*,2017) [12]

4. Thermodynamics study

Thermodynamic parameters can improve our understanding on the energy changes involved in adsorption processes (Yu-Feng *et al*, 2014) [44]. The thermodynamic parameters are therefore tools for proper understanding of adsorption phenomena**.**

The thermodynamic behavior for Pb (II) ions removal by the adsorbents in this study was investigated in temperature range of 303-323 K, and the influence of temperature on the adsorption capacity is shown in Fig.3.1.3. It can be seen that there is an increase in the adsorption capacity of the adsorbents M (raw) and M (NC) as the temperature increased.

The thermodynamic functions can be obtained from the van’t Hoff equation, and the integrated form of vant’ Hoff equation is expressed as:

$$\boldsymbol{InK} = -\boldsymbol{\Delta H}^{0/} \quad (11)$$

Thermodynamic parameters such as change in enthalpy (ΔH) and entropy (ΔS) were calculated respectively from the slope and intercept of the plot of ln K versus 1/T, where KL (l/mg) is the Langmuir isotherm constant and T is absolute temperature in Kelvin. The change in Gibb’s free energy determined using the following equation (Gupta and Ali,2004) [16]

$$\Delta G = - RT \ln k \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

Where: R= Universal gas constant (8.314J/mol), T = Temperature K = Distribution coefficient, ΔG= Change in Gibb’s free energy (kj/mol, ΔH = change in enthalpy, ΔS =entropy change = degree of randomness or disorderliness of a system

Table 3: Thermodynamic parameters

Adsorbents	**Enthalpy Of reaction ΔH (kj/mol)**	**Entropy of Reaction ΔS(Kj/mol)**	**Gibb’s free energy ΔG**					
			303K	**308K**	**313 K**	**318K**	**323K**	**R^2**
M(raw)	36.4062	0.1342	-4.2564	-4.9274	-5.5984’	-6.2694	-6.2694	0.9922
M(NC)	38.7923	0.1493	-6.4456	-7.1921	-7.9386	-8.6851	-8.6851	0.823

From Table 3, the ΔH values obtained for the adsorption of lead onto all the adsorbents showed positive values, this indicates that the adsorption process is endothermic in nature.

Physisorption is characterized by enthalpy value in the range of 5-20 kJ mol-1 while that of chemisorption is greater and in the region of that of chemical bonding (Vasu, 2008). Table 3 shows all the ΔH (change in enthalpy) values for all the adsorbates sorbed onto the adsorbents in this study to be greater than 20 kj/mol, meaning that all the sorption process in this study followed chemisorption mechanism. Similar results were reported for the adsorption of methylene blue onto activated carbon (Abechi, 2008)

The entropy change (ΔS) values for lead onto M(raw) and M(NC) were all positive. The positive values imply increased randomness at the solid- solution interface. It also shows the affinity of the adsorbents for the adsorbates in this study. Before adsorption occurs, the metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free metal ions interacting with the adsorbent will; be higher in the adsorbed state. similar results of positive entropy values were reported for the sorption of copper and lead onto KFAC, MFSAC and AOPA by Chowdhury, 2013.

The Gibb’s free energy values (ΔG) obtained for the adsorption of Lead onto all the sorbents were all negative for the temperature range showing thermodynamic feasibility and spontaneity (Emene,2018) [11], it also indicates that the reaction can proceed without any energy input(spontaneous) and it further indicates that the degree of spontaneity increases with increasing temperature. Similar results were reported for adsorption of lead onto china clay and wollastonite (Yadava *et al*., 1991) [43].

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