Ilorin Journal of Science
Volume 3, Number 2, 2016, pp. 300 – 326 (Printed in Nigeria)
ISSN: 2408 – 4840 © 2016 Faculty of Physical Sciences, University of Ilorin
https://doi.org/10.54908/iljs.2016.03.02.009

ILORIN
JOURNAL OF SCEINCE

ILJS-15-001

A Comparative Study on the Adsorption Kinetics and Thermodynamics of Co (II) ion onto acid Modified and Activated Carbon Prepared from Groundnut Shell

Adebayo[1], G. B., Nwosu[1], F. O., Jamiu[1*], W., Balogun[1], B. B. and Jimoh[2], A. A

[1]Department of Industrial Chemistry, University of Ilorin, Ilorin, Nigeria.

[2]Department of Chemical, Geological and Physical Sciences, Kwara state University Malete, Ilorin, Nigeria.

Abstract

Acid modified (MGS) and activated carbon (GSAC) prepared from groundnut shell was used for the removal of Co (II) ion from aqueous solution. The effect of pH, contact time, adsorbent dose, metal ion concentration and temperature were studied. Some physico-chemical and Spectroscopic characterization of the adsorbents were carried out, such as moisture content, ash content, pH, bulk density, volatile matter, iodine number, point of zero charge (PZC), XRF, and FTIR. The moisture and ash content of MGS and GSAC adsorbents were found to be 15.36±0.09, 9.61 ±0.21% and 4.1 ±0.15, 4.85 ±0.05% respectively. The pH and PZC of the adsorbents has 6.8±0.1, 6.8±0.01 and 7.6, 7.4 respectively. The adsorbent samples has the bulk density of 0.32±0.01 g/m^3 and 0.46±0.02 g/m^3, iodine number of 283.10±22 mg/g and 235.36±20.3 mg/g, The XRF analysis indicate that K constitute major inorganic elements in the adsorbents while Ca, and Mg are minor element. The FTIR analysis results shows functional group such as O-H, C=O, and C=C stretching. The maximum adsorption capacity of Co (II) ions occurred at pH 7 for MGS and pH of 9 for GSAC. The experimental data were best described by Langmuir adsorption isotherm. The kinetics study revealed that the sorption of Co (II) ions could be best described by pseudo-second order kinetics models with R^2 value of 0.999. Thermodynamics result revealed the spontaneity and feasibility of the reaction for acid modified and activated carbon adsorbents.

Keywords: Groundnut shell, adsorption, heavy metals, kinetics, thermodynamics.

1. Introduction

Industrial processes are based on chemical processes involving several organic and inorganic compounds such as acid, chromium salts, dyes, auxiliaries and other chemical additives (Hammami *et al.*, 2009). Water pollution due to heavy metals has been the major cause of concern, for environmental scientists. The industrial and domestic wastewaters are responsible for several damages to the environments and adversely affect the health of the people.

---

*Corresponding Author: Jamiu, W.

Email: waschem06@gmail.com

Several episodes due to heavy metal contamination in aquatic environments increased the awareness about the heavy metal toxicity. A variety of industries are responsible for the release of heavy metals into the environment through their wastewater (Braukmann, 1990). These include iron and steel production, the non-ferrous metal industry, mining and mineral processing, pigment manufacture, the painting and photographic industries and metal working and finishing processes (electroplating).

The main techniques, which have been utilized to reduce the heavy metal ion content of effluents, include line precipitation, ion exchange, adsorption onto activated carbon (Dean *et al.,* 1972), membrane processing and electrolytic method (Braukmann, 1990). These methods have been found to be limited, since they often involved high capital and operational costs and may be associated with the generation of secondary waste which presents treatment problems, such as the large quantity of sludge generated by precipitation processes (El-Hendawy, 2003). Activated carbon has been recognized as a highly effective adsorbent for the removal of heavy metal-ion from the concentrated and dilute metal bearing effluents (Netzer and Hughes, 1984; Namasivayam and Kavitha, 2001). The process however, has not been used by small and medium scale industries for the treatment of their metal bearing effluents, because of the high manufacturing cost. The use of low cost materials as adsorbent for metal-ion removal from the wastewater has been highlighted and effort has been contributed to develop new adsorbent and improving the existing adsorbents to have an alternative to activated carbon (Alluri, 2007). These materials range from industrial products such as rubber tyres (Knocke and Hemphill, 1981), industrial waste and some natural material including agricultural product and by-product (Mattson and Mark, 1971).

The uses of low cost materials as possible media for metal removal from wastewater have been highlighted (Hogan, 2010). Agricultural product and by-product is an abundant waste material, and need proper disposal, when disposed by burning in situ, it generated carbon dioxide and other form of pollutions. This creates a need for the conversion of agricultural product and by-product to useful value added products. The heavy metals have been observed to cause different ailment in man ranging from kidney damage, bronchitis, gastro intestine disorder, bone narrow, cancer to mention few (Alluri, 2007). Cobalt and its compounds especially cobalt carbohydrates (known as Cobalt soaps) are used in paints, varnishes, and inks as drying agents through oxidation of certain compounds. They are also use to improve adhesion of steel to rubber in steel belted radial trees (Holleman *et al.,* 1985). Although minute amount of cobalt is required by living organisms to assist in eco-enzymes formation, high level of exposure to cobalt shows mutagenic and carcinogenic effects. Cobalt compounds also lead to cardiomyopathy and it also causes contact dermatitis (Lane and Morel, 2000).

The main objective of this research is to prepare chemically modified and activated carbon from agricultural waste (groundnut shell) for the removal of toxic metals from aqueous solution. However, the result obtained from this research will ascertain the unique and effectiveness of the groundnut shell in the removal of Co (II) ion from aqueous medium.

2. Materials and Methods

The Groundnut shell was obtained from Ipata market in Ilorin metropolis, Kwara state, Nigeria. The sample was then dried at 30 ^oC for some days and was later placed in an oven at 105 ^oC overnight (Fan *et al*., 2003 and, Itodo *et al*., 2009). It was crushed using laboratory mortar and pestle, followed by sieving using smallest sieve size 0.09mm.

2.1 Modified Sample Preparation

The resulting particles were divided into two; one part was carbonized and other part was chemically modified. The ground-sieved sample was soaked in excess 0.3M HNO_3 for 24hours at room temperature. It was followed by washing severally with deionized water to neutral until (pH 7) was obtained. The sample was then filtered and air dried (James *et al*., 2007). The air dried biomass was then soaked in 0.3M citric acid overnight. The citric acid modified sample was severally washed until flushing water has a pH of 7. It was finally air dried and kept in tight container (James *et al.*, 2007).

2.2 Activated Carbon Preparation

A 5 g of the groundnut shell sample was weighed into 10 different pre-weighed crucibles and was introduced into the furnace at the temperature of 500 ^oC for 20 minutes. The pyrolysed sample was cooled and ground into a granulated size (Scricharoenchaikul *et al.,* 2008). Activation of char produced was done by mixing it with 75% concentrated orthophosphoric acid in a beaker using weight ratio of H_3PO_4/ char to be 0.1. The slurry was evaporated at 60 ^oC for 24 hours, and a dried mixture consisting of activated H_3PO_4 char was obtained (Lillo-Rodenas *et al*., 2003). This was followed by washing to neutral pH of 7. The sample was then poured in a beaker containing 250 ml of 0.1M HCl for purification and stirred for 1hour. Finally the sample was rinsed with distilled water to a pH 6-7 (Strinivasan, 1999). The resulting activated carbon was kept in tightly closed container for application (Scricharoenchaikul *et al.,* 2008).

2.3 Preparation of Aqueous Solution

The 1000 ppm of Co (II) ion were prepared accordingly by weighing and dissolving 4.30 g $CoCl_2$ in 1 litre volumetric flasks and it was made to the mark with more de-ionized water. Other concentrations were prepared from the stock solution by serial dilution.

2.4 Batch Adsorption Experiments

The adsorption of Co (II) ion on MGS and GSAC was investigated by batch adsorption experiments. The optimization of adsorption parameters were done and the amount of metal ion adsorbed by the acid modified and activated carbon was calculated by using the following equation

$$Q_e = \frac{V(C_{o-}C_e)}{M}, \qquad (1)$$

where q_e is the equilibrium concentration of the adsorbed metal uptake capacity (mg/l), C_o and C_e are the initial and final concentration of metal ion in solution at any time, t (mg/l), *V is* the total volume of the metal standard solution in the flask (L), M is the mass of adsorbent used (g) (Ajmal *et al.,* 2000).

2.4.1 Effect of initial metal ion Concentration

Some different concentrations of the adsorbate were prepared: 5, 10, 15, 20, 25, and 30 (mg/l) by serial dilution of the stock solution and then contacted with a fixed dosage of the adsorbent of 0.2 g in 100 ml conical flask containing 25 ml of the adsorbate. It was then agitated for 2 hours. At the end of agitation time the mixture were filtered and analyzed using Atomic Adsorption Spectrophotometer (Jimoh *et al*., 2012).

2.4.2 Effect of Contact Time

The effect of contact time on metal adsorption was studied using metal ion concentration that gave optimal adsorption at different time intervals (30, 60, 90, 120, 150 and 180 min). A 25 ml of metal concentration (equilibrium concentration) of the adsorbate were contacted with 0.2 g dosage of the adsorbent, the mixture was shaken for 2 hours. The mixture was filtered and analyzed using Atomic Absorption spectrophotometer (Abdus-Salam and Itiola, 2012).

2.4.3 Effect of Adsorbent Dose

The metal ion concentration that gave optimal adsorption per 0.2 g was used. A 25 ml of the adsorbate was contacted with varying amounts of the adsorbent doses (0.1, 0.2, 0.3, 0.4, and 0.5 g) at the equilibrium concentration (concentration of maximum adsorption). The mixture was agitated with an orbital mechanical shaker for 2 hours. The resultant solution was filtered and the filtrates were analyzed using Atomic Absorption Spectrophotometer (AAS) (Abdus-Salam and Itiola, 2012).

2.4.4 Effect of pH

A 25ml of the optimum (equilibrium) concentration for Co (II) ion were contacted with 0.2 g of the adsorbent in a 100 ml conical flask and the pH of the solution matrix was varied with 0.1M HCl and 0.1M NaOH to obtain pH of 3, 5, 7, 9 and 11. The solution was equilibrated for 2 hours, the resultant mixture was filtered and the residual metal ion concentrations were analyzed using Atomic Absorption Spectrophotometer (Elaigwu *et al*., 2009).

2.4.5 Effect of Temperature

The various used temperature are 30, 40, 50, 60 and 70 ^{o}C. A 25 ml of the optimum concentration for Co (II) ion were contacted with 0.2 g of the adsorbent in a 100 ml conical flask. The mixtures were equilibrated for 2 hours at stated temperatures. The resultant mixtures were filtered. The filtrate was analyzed using Atomic Absorption Spectrophotometer (Abdus-Salam and Itiola, 2012).

2.5. Kinetic study profile

The experimental data were subjected to the kinetics profile such as, pseudo-first and pseudo-second order kinetics model were employed and the equations are stated as follows.

(i) Pseudo-first order kinetics

The rate law is given below:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (2)$$

where, q_e and q_t are the amount of Co (II) ion adsorbed at equilibrium and time t, respectively, k_1 is the rate constant for the pseudo first order adsorption. The integrated rate law is given as follows

$$log(q_e - qt) = logq_e - \frac{K}{2.303}. \quad (3)$$

A plot of $log(q_e - q_t)$ against t was made and the values of k_1 and q_e were obtained from the slope and intercept, respectively (Ho and Mckay, 2000).

(ii) Pseudo-second order kinetics

The linear form of pseudo-second order kinetics model is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \tag{4}$$

where, q_e and q_t are the amount of metal ion adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium and time *t*, respectively, and k_2 is the pseudo second order rate constant. A linear plot of t/q_t against t confirms the fitness of data to this model (Ho and Mckay, 2000).

2.6. Adsorption Isotherms

Three adsorption isotherms were employed in this research and their respective formula are given below.

(i) Langmuir adsorption isotherm

Langmuir adsorption isotherm equation is given below:

$$\frac{Ce}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} Ce, \tag{5}$$

where Ce is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), q_{max} is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g) and K_L is the Langmuir constant (L/mg).

(ii) Freundlich adsorption isotherm

Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$log\, q_e = log\, k_f + \frac{1}{n} log\, C_e, \tag{6}$$

where q_e is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at equilibrium, K_f and n are the empirical constants dependent on several factors and n is greater than one. (Najua *et al.*, 2008).

(iii) Temkim isotherm

Temkim isotherm is given by the following equation:

$$Q_e = \frac{RT}{b} ln\, K_T C_e. \tag{7}$$

Equation above can be linearized into the following:

$$Q_e = B\, ln\, K_T + B\, ln\, C_e, \tag{8}$$

where $B = \frac{RT}{b}$. Regression of Q_e against $\ln C_e$ enables the determination of isotherm constant K_T and B. The K_T is the equilibrium binding constant (L/mg) corresponding to maximum binding energy constant and is related to the heat of adsorption.

2.7. Thermodynamics Studies

The thermodynamics parameters such as Gibbs free energy change (ΔG), Enthalpy change (ΔH) and Entropy change (ΔS) were also studied in order to understand better the effect of temperature on the adsorption of Co (II) ions. The Gibb's free energy change (ΔG) is related to the thermodynamics equilibrium constant by the following equation:

$$K_c = \frac{C_{A_e}}{C_e}, \quad (9)$$

$$\Delta G^0 = -RT \ln K_c, \quad (10)$$

$$\log K_C = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}, \quad (11)$$

where, K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the solid-phase concentration at equilibrium (mg/L). ΔG, ΔH and ΔS are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the molar gas constant (8.314 J/mol/K) and T is the temperature (K). The values of ΔH and ΔS were determined from the slope and the intercept of Van't Hoff plots of log K_c versus 1/T (Mohan, 2002).

3. Results and Discussion

3.1 Physico-chemical Characterization of the Samples

Moisture content is the amount of water retained by the sample and suggests extensive porosity in the structure of all adsorbents. From Table 1, the moisture content of the samples is 15.36±0.21 and 9.61±0.21%. Although, moisture content of the activated carbon has no effect on its adsorptive power, it has been observed that if the moisture content of adsorbent is high its adsorptive capacity will be reduced and it would necessitate utilizing an additional weight of the carbon during treatment process. (Sugunadevi *et al*., 2002). The moisture content of the adsorbents are higher to the value reported elsewhere Salman *et al*. (2011), (4.5%) and Elnasri *et al*. (2013), (2.2%).

Table 1: Showing physico-chemical characterization of acid modified (MGS) and activated carbon groundnut shell (GSAC).

Properties	**MGS**	**GSAC**
Moisture content (%)	15.36±0.09	9.61±0.21
Ash content (%)	4.1±0.15	4.85±0.05
Bulk density (g/m^3)	0.32±0.01	0.46±0.02
%Yield	67.38±0.1	74.15±0.21
Volatile matter (%)	N.A	24.79±0.19
pH	6.8±0.1	6.8±0.01
Iodine number (mg/g)	283.10±22	235.36±20.3
Point of zero charge	7.6	6.4
Particle size (mm)	0.25	0.25

The ash content shows the amount of inorganic constituents associated with carbon. Ash content of adsorbents usually increases with increase in carbonization temperature. This was believed to be due to lowered volatile matter (Gan *et al*., 2004). The percentage ash contents for MGS and GSAC obtained were 4.1±0.15% and 4.85±0.05% respectively, lower than the value of adsorbents reported by Salman *et al.* (2011), (10.5%), Aloko and Adebayo, 2008, (29.24%), and close to the value reported elsewhere, Mane *et al.* (2005), (5.6%). The ash content of adsorbents increased with decreased percentage of volatile matter which indicates that ash is non-volatile as reported (Gan *et al.,* 2004*).*

Bulk density indicates the fiber content of the precursor. It is an important parameter when carbon is removed by filtration, because it determines the quantity of carbons that is contained in a filter of a given solid capacity and how much treated liquid is retained by the filter cake. Carbons with adequate density also help to improve the filtration rate by forming an even cake on the filter surface. It is shown that MGS and GSAC adsorbents densities are 0.32±0.01 and 0.46±0.02% which are both lower than the value reported by Itodo *et al.* (2011), (0.53g/m^3), Onundi *et al.* (2011), (0.864g/m^3). These values are moderate when compared with literature values. Generally, an adsorbent with high bulk density need not be regenerated frequently because it can hold more adsorbate per unit weight (Yang and Lua, 2003).

The percentage yield obtained for MGS and GSAC adsorbents are 67.38±0.1%, and 74.15±0.21% respectively. This is an indication of high percentage yield compared to the reported percentage yield of 40% and 51% by Faust and Aly (1983); Sahu *et al*. (2010), (46.08%), Hameed *et al.* (2009), (17.96%). The activated carbon adsorbent obtained have good percentage yield, Ash content and volatile matter than the acid modified adsorbent as reported elsewhere, Raffiea *et al.* (2012).

Volatile matter is due to the presence of organic compounds present in the raw material. It was evident that at longer carbonization period, more volatiles are released from the char, thereby resulting to a higher burn off and a corresponding lower yield (Itodo *et al.*, 2011). The volatile matter obtained for the GSAC adsorbent is 24.79±0.19%, which is higher than the value reported by Raffiea *et al*. (2012), (20.9%).

The pH of adsorbent is the degree of acidity or basicity of that adsorbent and this depends on number of factors which include preparation methodology, inorganic matter content, chemically active oxygen groups on its surface as well as the kind of treatment to which the adsorbent was subjected (Elnasri *et al.*, 2013). The pH of both MGS and GSAC adsorbents is approximately the same, 6.8±0.1 and 6.8±0.01. These values were lower than the one reported elsewhere, Elnasri *et al*. (2013), (7.8±0.01), Mane *et al.* (2005), (7.7±0.01), and higher than the one reported by Idris *et al.* (2012), 6.32 ± 0.12.

The Iodine number is the most fundamental parameter used to characterize activated carbon performance (Raffiea *et al*., 2012). It is measure of activity level, the higher the number, the higher the degree of activation and the development of the microporous structure. It is often reported as mg/g. Iodine number may also be used as an approximation of surface area for some types of carbons between 600mg/g and 1100mg/g (Aziz *et al.*, 2009; Baccar *et al*., 2009). The iodine number of MGS and GSAC adsorbents were 283.10±22mg/g and 235.36±20.3mg/g respectively, which are lower than the one reported elsewhere, Raffiea *et al*. (2012), (798 mg/g). Both adsorbents have high iodine number which implies high degree of micropore, and it is an indication of better performance as adsorbents (Raffiea *et al*., 2012).

The point of zero charge is a phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero (Lyklema 1995; Kirby 2010). The PZC is located at the point of interception of the curves when traced to the pH axis. The PZC is (usually) the pH value at which a solid submerged in an electrolyte exhibit zero net electrical charge on the surface. The pHpzc of MGS and GSAC is 7.6 and 6.4 which are within the range as reported by Elnasri *et al.* (2013), (7.3).

3.2 Spectroscopic Characterization

Table 2: Showing X-ray fluorescence (XRF) analysis of MGS and GSAC adsorbents.

Elements	MGS (*conc*)	GSAC (*conc*)
K	20.772±1.1	19.89±1.2
Ca	7.18±2.01	9.639±2.64
Ti	1.232±0.12	1.965±0.17
Cr	0.011±3.4	0.011±0.02
Mn	0.315±0.15	0.39±0.10
Fe	0.772±0.04	0.432±0.01
Cu	1.501±0.4	1.12±1
Na	1.326±11.2	1.13±2
Mg	5.290±11.2	5.61±2

The XRF data indicates various elemental concentrations in MGS and GSAC adsorbents. From Table 2 above, K constitute major inorganic elements in the adsorbents while Ca, and Mg are minor elements, while Cr, Mn and Fe were found in trace level. This shows that MGS and GSAC cannot be used as adsorbent in the removal of metals like K, Cr, Mn and Fe. It will serve better purpose for the removal of metals such as Co, Pb, Cd and As, among others. Many catalytic processes, especially those used in organic synthesis required transition metals which include Fe, Ti and Zn and so on. The prepared MGS and GSAC adsorbents contain some various concentrations of transition metals which may be useful in catalytic processes and during adsorption process (Mishra *et al.,* 2009).

3.3 Fourier Transform Infra-Red Spectroscopy

The FTIR spectra of MGS and GSAC were taken to obtain information on the nature of possible interactions between the functional group of the adsorbent and the metal ions as presented in Figure 1 and 2.

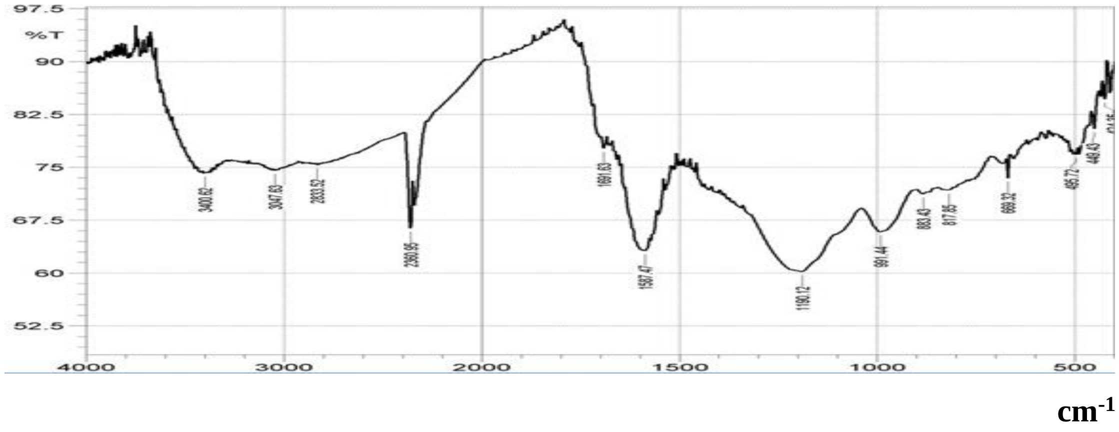

Figure 1: FTIR spectrum of GSAC adsorbent.

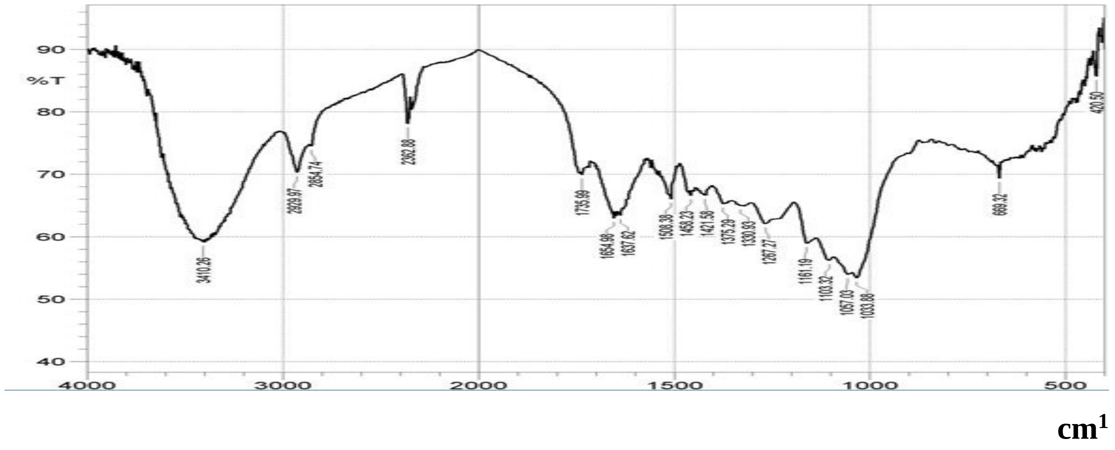

Figure 2: FTIR spectrum of MGS adsorbent.

The FTIR analysis was carried out in order to identify the different functional groups present in MGS and GSAC sample which contributed to adsorption process. The IR pattern of the biomass showed distinct and sharp absorptions indicative of the existence of the –OH and C=O groups as shown in Figure 1and 2. The bands are due to the functional groups of the groundnut shell that participated in the biosorption of Co (II). On comparism, there are clear band shifts and decrease in intensity. Peaks appearing in the FTIR spectra were assigned to various functional groups according to their respective wave number (Das and Mondal, 2011).

The FT-IR spectra of the groundnut shell indicated slight changes in the absorption peak frequencies due to the fact that the binding of the metal ions causes reduction in absorption frequencies. This shift in absorbance observed implies that there were metal binding processes taking place on the active sites of the biomass (Das and Mondal, 2011).

3.4. Adsorption Experiments

3.4.1 Effect of Initial Concentration

The adsorption of metal ions by an adsorbent is strongly dependent on the initial concentration of metal ions in solution. This makes it an important parameter to be determined in adsorption studies. The result on effect of initial Co (II) ion concentration on its adsorption by MGS and GSAC are shown in figure 3. It is seen that increases in adsorption capacities with increases in metal ion concentrations were obtained, as initial concentration of metal ions were increased from 5 ppm to 30 ppm. It was also observed that corresponding increases in the adsorption capacities also occurred until the curves attained optimum adsorption capacity at initial concentration of 20 ppm after which the adsorption dropped. The actual amount of Co (II) ion adsorbed per unit mass of groundnut shell activated carbon increased with increase in metal ion concentration. It has been reported that as the metal ion concentration is increasing, more ions are available for adsorption on the adsorbent (Adegoke *et al.*, 2014). The rapid increase in the rate of adsorption have also been attributed to the sufficient surface area to accommodate more metal available in the solution due to the effect of concentration gradient which is the main driving force for the adsorption process (Mishra *et al.*, 2009). These results has been observed to be that the binding sites became exhausted and the uptake rate slowed down due to competition for decreasing availability of active sites by metal ions (Gupta and Gaur, 2008).

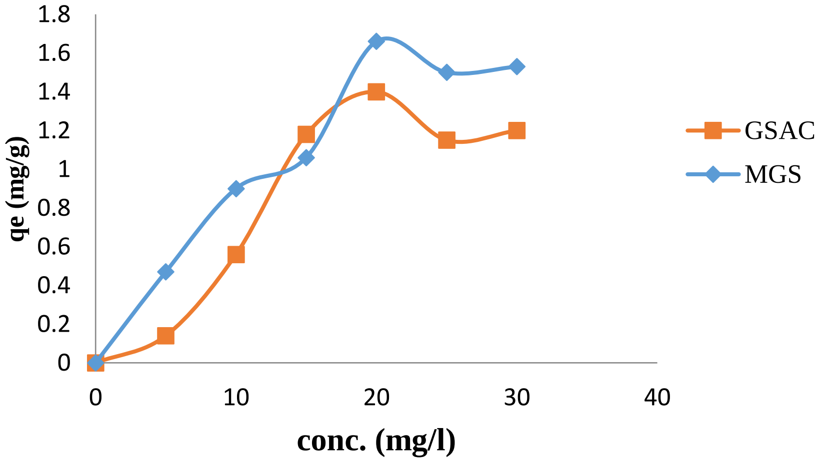

Figure 3: Effect of initial metal ion concentration on the adsorption of Co (II) ion by MGS and GSAC.

3.4.2 Effect of Contact Time

The biosorption of metal ions from aqueous solution is controlled by the rate of adsorption which determines the equilibrium time. It is one of the important characteristics defining the efficiency of an adsorbent (Krishnan and Anirudhan, 2003). The time of the adsorbent-adsorbate is of great importance in adsorption, because it depends on the nature of the system used. The fastest adsorption capacity was observed by Co (II) onto MGS and GSAC at 30 minutes of experiment (fig. 4). The longer agitation time might have exposed the inaccessible adsorption sites which accounted for increased adsorption with time. The rapid initial biosorption may be attributed to the accumulation of metals onto the surface of biosorbent due to its large surface area. With the progressive occupation of these sites, process became slower in the second stage. Moreover, the initial deposited metal ions penetrated to the interior of the biosorbent through intra-particle diffusion which was slower process. This is in accordance with the observation of other similar studies (Sanji *et al.*, 2008 and Qaiser *et al.*, 2009).

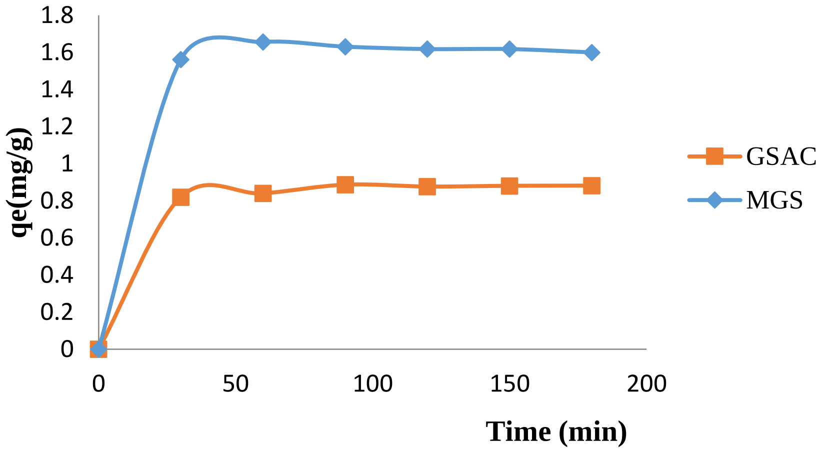

Figure 4: Effect of contact time on adsorption of Co (II) ion by MGS and GSAC.

3.4.3 Effect of pH

The initial pH of a solution is a very important factor to be considered in adsorption studies as it has been observed to play a major role in the adsorption of metal ions by various adsorbents, because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Badmus *et al.*, 2007). The removal of metal ions from aqueous solution by adsorption is related to the pH of the solution, as the pH affects the surface charge of adsorbents and the degree of ionization of the adsorbate species. In this study, the effect of pH on the Co (II) ions adsorption capacities of all the adsorbents was conducted at various pH ranging 3-11 with 20mg/L fixed initial metal ion concentrations and contact time of 2hours as can be seen from Fig.5. The role of H^+ concentration was examined from the samples at different pH. The result shows that the maximum adsorption was observed between pH 7 and 9 for both samples, while the amount adsorbed increases with increases in pH. Similar trend were report in literature elsewhere (Kobya *et al.*, 2005). This might be due to precipitation of the Co (II) hydroxides at pH 9 (Zahangri *et al.*, 2008).

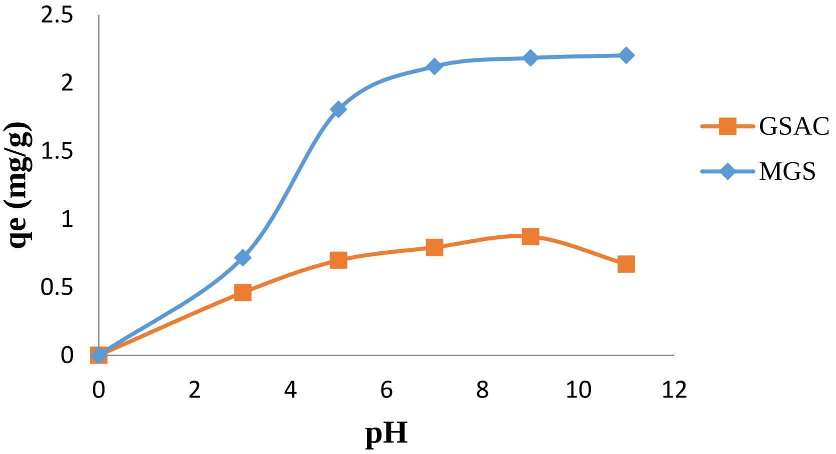

Figure 5: Effect of pH on the sorption of Co (II) onto MGS and GSAC.

3.4.4 Effect of adsorbent dose

The influence of different amounts of adsorbents dose 0.1-0.5g on Co (II) ions adsorption at constant initial metal ion concentration of 20 mg/L, contact time of 2hours and the temperature of 298k, showed decrease in the quantity adsorbed with increase in adsorbent dosage as the number of sorbate ions concentration decreases per active site available for sorption on the surface (Yu *et al.*, 2000). It has been reported that higher adsorbent dose creates particle aggregation resulting in a decrease in a total surface area and an increase in diffusional path length both of which contribute to the decrease in amount adsorbed per unit mass (Shukla, 2002).

Fig.6 shows the effect of adsorbent dose on adsorption of Co (II) ions on MGS and GSAC, and maximum adsorption was observed at 0.1g for both adsorbents. The net equilibrium amount adsorbed however is an expression of the efficiency of an adsorbent which may not show increase in amount adsorbed per unit mass as the adsorbate dose increases. The observation shows that small amount of adsorbent gave maximum adsorption, which may be due to the high surface area and pore volume of the samples (Yu *et al.*, 2000).

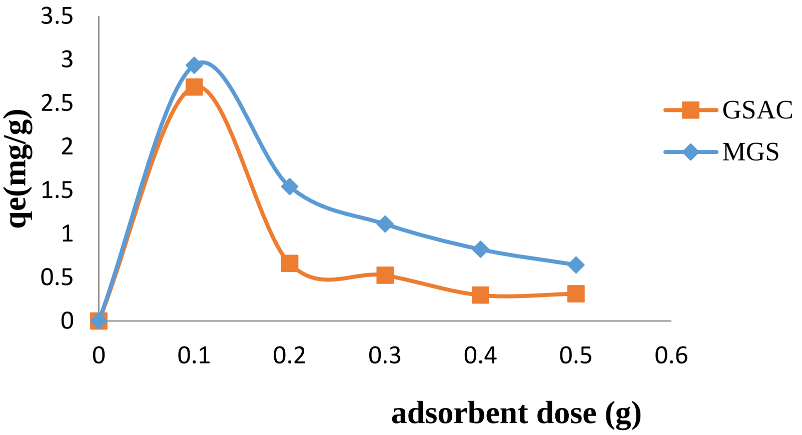

Figure 6: Effect of adsorbent dose on the sorption of Co (II) onto MGS and GSAC.

3.4.5 Effect of temperature

From the Fig.7, it showed that there was gradual increase in the quantity of Co(II) ion removed as temperature increased from 303 to 343K. The increase in the amount of Co(II) ions adsorbed as temperature increased might be attributed to the fact that the adsorption by MGS and GSAC adsorbents may involve not only be physical but also chemical adsorption, and sometimes bond rupture. The increasing temperatures had a remarkable action on swelling effect within the internal structure of the adsorbents enabling Co (II) cation to penetrate further thereby increasing the adsorption rate (Jimoh *et al.*, 2013). From the result obtained, it can be seen that the number of adsorption sites tend to increase with increase in temperature which may be an indication of possible chemical interactions between the adsorbate and the adsorbent (Ekop and Eddy, 2010).

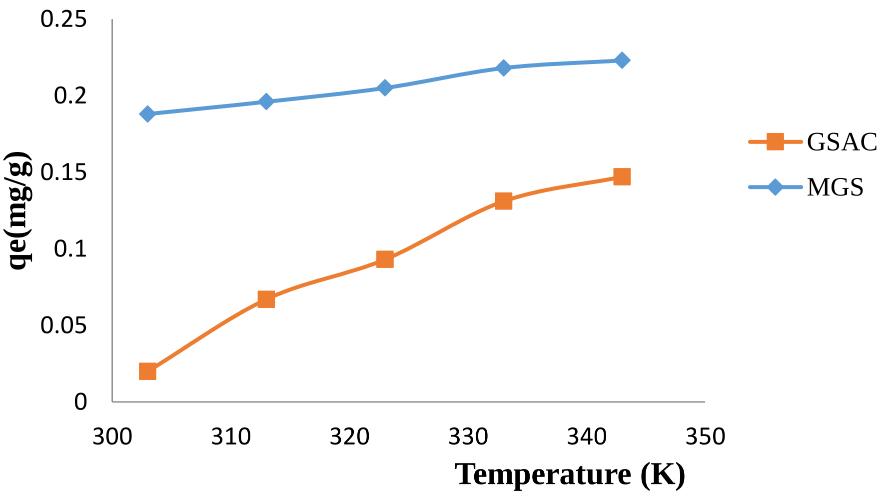

Figure 7: Effect of temperature on the sorption of Co (II) onto MGS and GSAC.

3.5 Adsorption Isotherms

Langmuir, Freundlich and Temkim isotherms were used to describe experimental data obtained. The Langmuir, Freundlich and Temkim isotherm plots are presented in Figs. 8-13. The various parameters are shown in Tables 3. From Table 3, the adsorption of Co (II) ions onto MGS and GSAC can best be described by Langmuir isotherm based on the correlation coefficient values obtained. Comparative examination of the data as shown in Table 3 indicated that Langmuir model better described the adsorption of metal ions than Freundlich and Temkin model. The order of fitness was Langmuir>Freundlich > Temkin. The low values of R^2, correlation coefficient obtained for freundlich and temkin adsorption isotherms are due to much scattered of the plot. The 1/n value of o.651 indicates favourable adsorption process for MGS adsorbents while that of GSAC is unfavourable. The freundlich adsorption constant of 0.324 mg/g was obtained for MGS and 0.054 mg/g for GSAC. The monolayer capacity q_m is 1.953 for MGS and negative was obtained for GSAC.

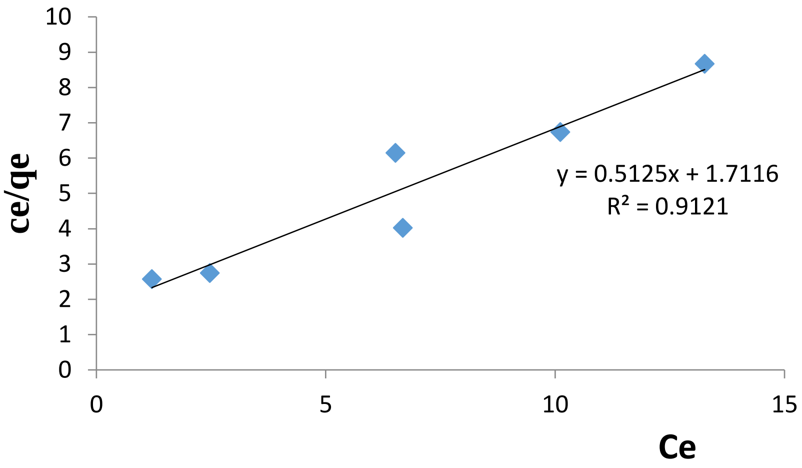

Figure 8.: Langmuir plot of Co (II) onto MGS.

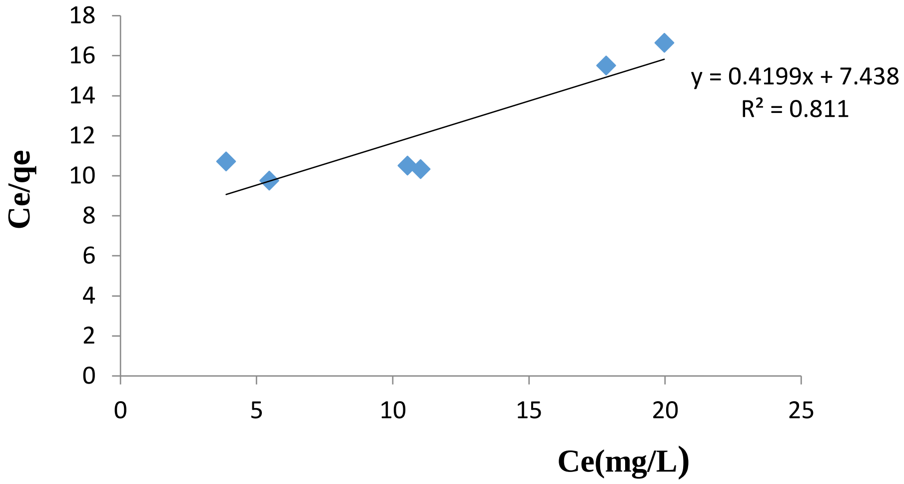

Figure 9.: Langmuir plot of Co (II) onto GSAC.

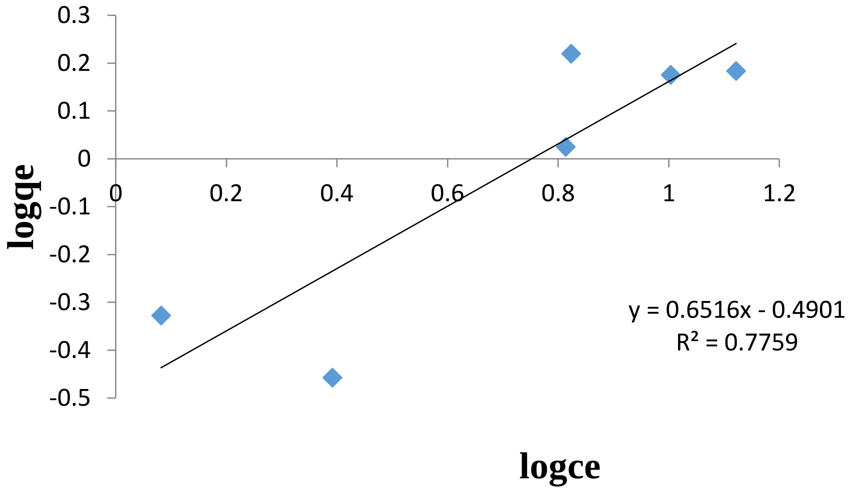

Figure 10.: Freundlich plot of Co (II) onto MGS.

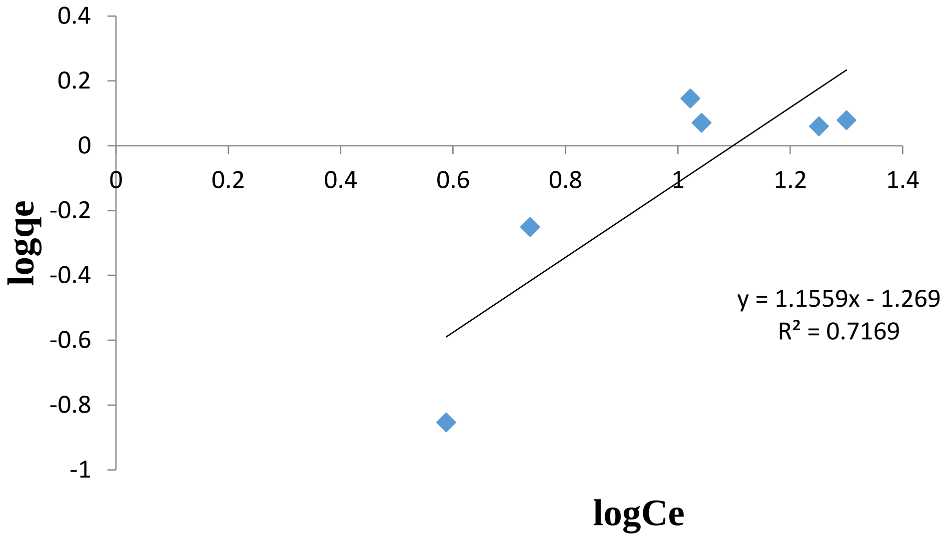

Figure 11.: Freundlich plot of Co (II) onto GSAC.

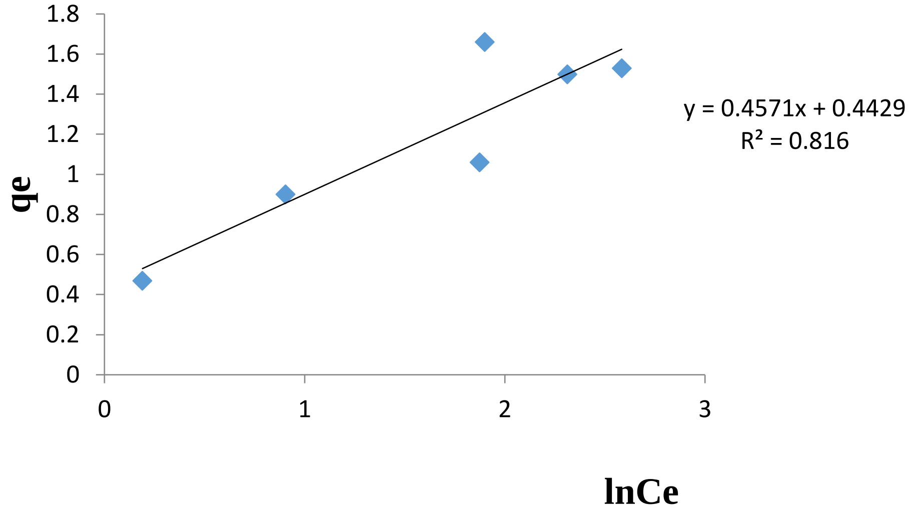

Figure 12.: Temkin plot of Co (II) onto MGS.

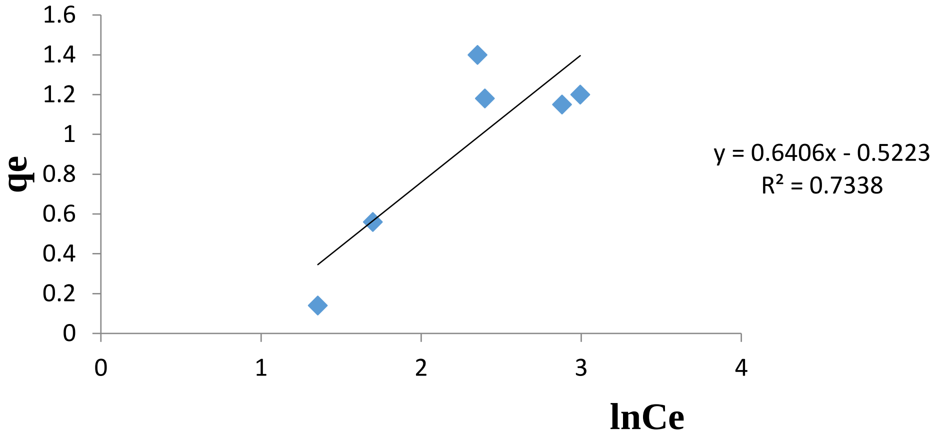

Figure 13. : Temkin plot of Co (II) onto GSAC.

Table 3.: Adsorption isotherm constants and parameters for Co (II) adsorption.

Sample	Langmuir coefficient			Freundlich coefficient			Temkin coefficient		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	1/n (L/mg)	R^2	B (kj/mol)	K_T (L/mg)	R^2
MGS	1.953	0.299	0.912	0.324	0.651	0.775	0.457	2.631	0.457
GSAC	-5.376	-0.011	0.825	0.054	1.155	0.716	0.640	0.442	0.640

3.6. Adsorption Kinetics

The kinetics of an adsorption is probably the most important factor in predicting the rate at which adsorption takes place for a given system. Kinetics of adsorption is the tool used to examine the rate of adsorption process such as chemical reaction and mass transfer, a suitable model is needed to analyze the rate data. The Lagergren's first-order kinetic model and the Ho's pseudo-second-order model are the most frequently kinetics used in the literature to predict the mechanism involved in the sorption process (Ho and McKay, 1998). They were both used to test the adsorption kinetic model of Co (II) onto MGS and GSAC adsorbents. Both models are examined for suitability using their correlation coefficient, R^2 values (Jimoh *et al.*, 2013).

The kinetics model plots are indicated in Figs. 14-17 and the various constant are displayed in Table 4. Comparison of the two model revealed that the adsorption of the metal ions could be best explained using the pseudo-second order. This was due to the fact that correlation regression coefficient of MGS and GSAC sample for the pseudo-second order were greater than that of pseudo-first order, which is the same reported by Babarinde *et al*., (2012).

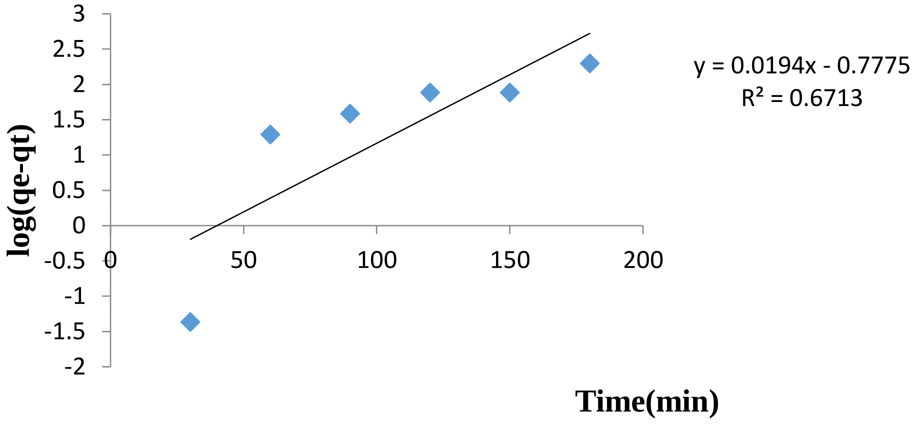

Figure 14.: pseudo first order plot of Co(II) onto MGS.

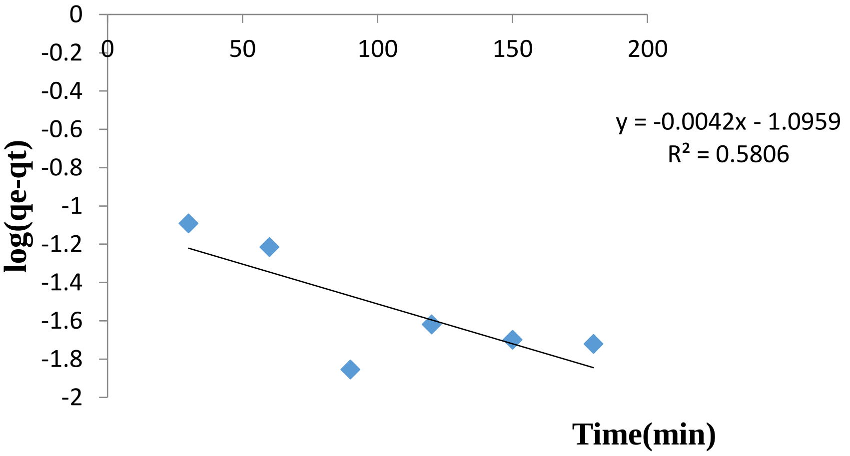

Figure 15.: Pseudo first order plot of Co(II) onto GSAC.

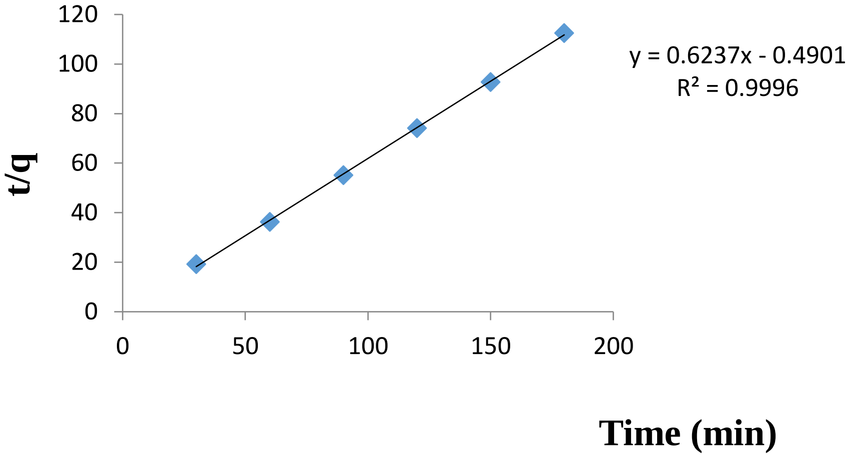

Figure 16.: Pseudo second order plot of Co (II) onto MGS.

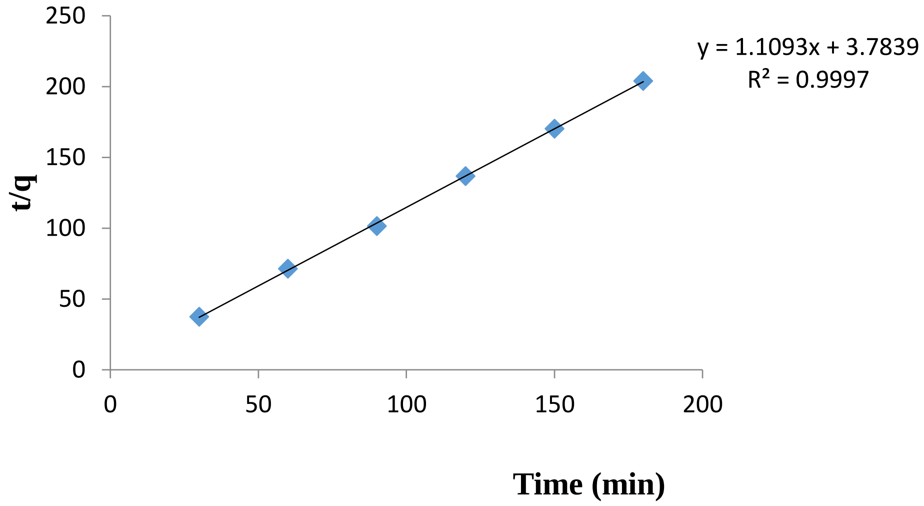

Figure 17.: Pseudo second order plot of Co (II) onto GSAC.

Table 4.: Adsorption kinetics constants for Co (II) adsorption onto MGS and GSAC.

Sample	Pseudo first order			Pseudo second order		
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2(gmg^{-1}m^{-1})	q_e (mg/g)	R^2
MGS	0.044	0.525	0.671	-0.190	1.605	0.999
GSAC	0.009	-0.091	0.580	0.325	0.901	0.999

3.7. Thermodynamics Studies

The values of enthalpy change (ΔH) and entropy change (ΔS) were obtained from the slopes and intercepts respectively, from the graph of ΔG against T in (^{o}C). From Table 5, it could be observed that Gibb's free energy change (ΔG) were negative for both adsorbents while entropy change (ΔS) and enthalpy change (ΔH) was positive in the same way. The negative values of Gibb's free energy change (ΔG) at all temperatures examined indicated that the adsorption of Co (II) ions by groundnut shell was feasible and corresponds to a spontaneous physical adsorption of the Co(II) ion, which indicate that this biosorption process does not gain external energy (vimonses *et al*., 2009). The positive values of enthalpy change (ΔH) revealed that the adsorption process was endothermic and non-physical in nature. Furthermore, a positive value of entropy change (ΔS) was an indication of an irregular increase in the degree of the randomness at the adsorbent-adsorbate interface during the adsorption process. The decrease in ΔG despite increase in temperature indicates more efficient biosorption at higher temperature, which was contrary to the findings reported for the biosorption of this metal ion with banana leaf by Babarinde *et al.*, (2012).

Table 5: Thermodynamic parameters for the adsorption of Co (II) onto MGS and GSAC.

Sample	**ΔH**	**ΔS**	**ΔG (KJ/mol)**				
	(KJ/mol)	**(J/molK^{l})**	303K	313K	323K	333K	343K
MGS	+4.389	+0.656	-0.194	-0.201	-0.207	-0.214	-0.221
GSAC	+42.068	+110.576	-33.462	-34.568	-35.506	-36.779	-37.885

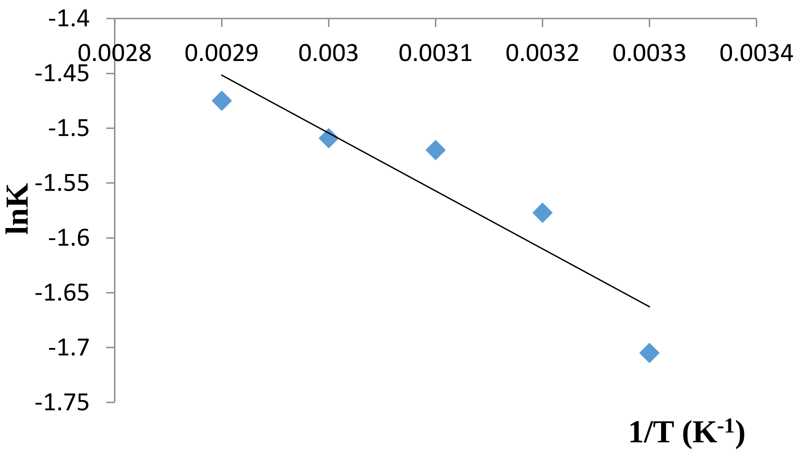

Figure 18.: Thermodynamic plot of Co (II) onto MGS.

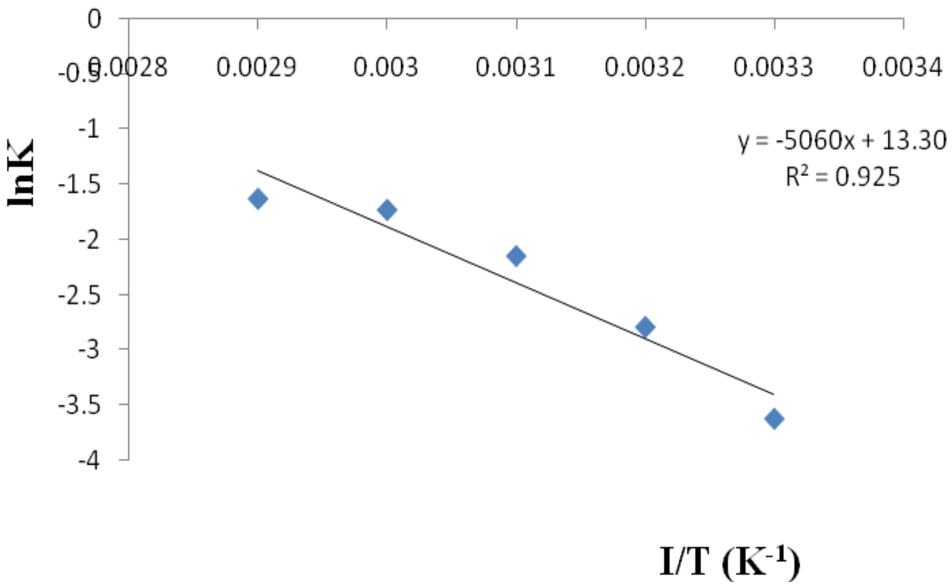

Figure 19.: Thermodynamic plot of Co (II) onto GSAC.

4. Conclusion

Based on the above study the following conclusions were drawn: (i) pH, contact time, metal ions concentration and temperature had optimum condition for effective metal uptake by the substrate. (ii) The biosorption process of the metal ions was best described by a pseudo-second order. (iii) The equilibrium data could be best explained by Langmuir than Freundlich and Temkin isotherms. (iv) Thermodynamics investigation showed that Gibb's free energy change (ΔG) was negative indicating that the adsorption of Co (II) ions by acid modified and activated carbon groundnut shell were feasible and spontaneous. The positive value of standard enthalpy change (ΔH) implies that the reaction was endothermic and non-physical in nature while positive value of standard entropy change (ΔS) implies an irregular increase in the randomness at the solid/solution interface of the adsorbent during the adsorption process.

ACKNOWLEDGMENT

The author is grateful to the entire laboratory Technologist, Department of Industrial chemistry, University of Ilorin, Ilorin, Kwara state, Nigeria, for their support during the research period.

References

Abdus-salam, N. and Itiola, A.D. (2012): Potential Application of Termite Mound for Adsorption and Removal of Pb (II) from aqueous Solutions. *Journal of Iranian chemical Society*. **9**, 373-382.

Adegoke, H. I., Adekola, F. A., Fatoki O. S. and Ximba B. J. (2014): Adsorption of Cr (VI) on synthetic Hematite nanoparticles of different morphologies. *Korean Journal Chemical Engineering.* **2**(1), 142-154.

Ajmal, M., Rao, B., Ahmad, R. A. and Ahmad, J. (2000): Adsorption studies on Citrus reticulate (fruit peel of orange): Removal and recovery of Ni (II) from electroplating wastewater. *Journal Hazardous Materials.* **79**, 117-131.

Alluri, H. K. (2007): Biosorption, an ecofriendly alternative for heavy metal removal. African *Journal of Biotechnology*. **6** (25), 2924-2931.

Aloko, D. F. and Adebayo G. A. (2008): Production and Characterization of Activated carbons from Agricultural waste. *Journal of Engineering and Applied Sciences*. **2** (2), 440-444.

Aziz, A., Ovali, M. S. and Elanduloussi, E. H. (2009): Chemically modified olive stone a low cost sorbent for heavy metals and basic dyes removal from aqueous solution. *Journal of Hazardous Materials.* **163**, 441-447.

Babarinde, N. A. A., Babalola, J. O., Adegoke, J., Muraizu, U., Ogunbanwo, T. and Ogunjinrin, F. (2012): Kinetic, equilibrium and thermodynamics studies of the biosorption of Ni (II), Cr (III) and Co (II) from aqueous solutions using banana (Musa acuminata) leaf. *International of Journal of Physical Sciences*. **7**, 1376-1385.

Baccar, R., Bouzid, J., Feki, M. and Montel, A. (2009): Preparation of activated carbon from Tunisian olive waste cakes and its application for adsorption of heavy metal ions. *Journal of Hazardous Materials.* **162**, 1522-1529.

Badmus, M. A. O., Audu, T. O. K. and Anyata B. U. (2007): Removal of Lead ion from Industrial Waste waters by Activated carbon from Periwinkle shells. *Turkish Journal Of Engineering and Environmental Sciences.* **31**, 251-263.

Braukmann, P. N. (1990): *Handbook of Water and Waste water treatment Technology*, Marcel Dekker Inc. New York. 45pp.

Das, B. and Mondal, N. K. (2011): Calcareous soil as new adsorbent to remove Lead from aqueous solution: Equilibrium, Kinetics and Thermodynamic Study. *Universal Journal of Environmental Research and Technology.* **1** (4), 515-518.

Dean, H., Volesky, B. and Mucci, A. (1972): A Review of Biochemistry of Heavy metal Biosorption by brown algae. *Water Resources*. **37**, 3147-3152.

Ekop, A. S. and Eddy, N. O. (2010): Thermodynamic Study on the Adsorption of Pb^{2+} and Zn^{2+} from aqueous solution by human hair. *E- Journal of Chemistry*. **7** (4), 1296 – 1303.

Elaigwu, S. E., Usman, L. A., Awolola, G. V., Adebayo, G. B. and Ajayi, R. M. K. (2009): Adsorption of Pb (II) from aqueous solution by activated carbon prepared from cow dung. *Environmental Research Journal*. **4**(4), 257-260.

El-Hendawy, A. A. (2003): Influence of HNO_3 Oxidation on the Structure and Adsorptive Properties of Corncob-Based Activated Carbon. *Carbon*, **41**, 713-722.

Elnasri N. A, Mutaz A. E, and Mohammed A. E (2013). Physico-chemical Characterization and Freundlich isotherms of Adsorption of Fe (II) from aqueous solution by using Activated carbon prepared from Doum fruit waste. *Archieves of Applied Science Research.* **5** (5), 149-158.

Fan, M., Marshall, W., Daugaard, D. and Brown C. (2003): Steam activation of chars produced

From oat hulls. *Bioresources Technology*. **93** (1), 103-107.

Faust, S. D. and Aly, O. M. (1983): *Chemistry of water treatment*. Butterworths publishers: Boston, London Wellington. 211pp.

Gan, Q., Allen, S. and Matthews, R. (2004): Activation of waste MDF sawdust charcoal and its reactive dye adsorption characteristics. *Waste Manage*. **24**, 841-846.

Gupta, S. and Gaur, J. P. (2008): Kinetic and Isotherm modelling of Lead (II) Sorption onto some Waste plant materials. *Chemical Engineering Journal*. **148**, 226-233.

Hameed, B. H., Tan, I. A. W. and Ahmad, A. L. (2009): Preparation of oil palm empty fruit bunch- based activated carbon for the removal of 2, 4, 6- tricholorophenol: Optimization using response surface methodology. *Journal of hazardous Materials.* **164**, 1316-1324.

Hammami, H., Ouejhani, A., Bellakhal, N. and Dachraoui, M. (2009): Application of Doehlert matrix to determine the optimal conditions of electrochemical treatment of tannery effluents. *Journal of Hazardous Materials*. **196**, 251-258.

Ho, Y. S. and Mckay, G. (1998): A Comparison of Chemisorption Kinetic, Model Applied to Pollutant removal on various sorbents. *Process Safety and Environmental Protection.* **76** (4), 332-340.

Ho, Y. S. and McKay, G. (2000): Pseudo-second order model for sorption process. *Process Biochemistry.* **34**, 451-465.

Holleman, Arnold F., Wiberg, Egon; Wiberg, Nils; (1985). “Mangan” (in German). Lehrbuch der Anorganischen Chemie (91–100 ed.). de Gruyter. 1110–1117.

Idris, S., Iyaka, Y. A., Dauda, B. E. N., Ndamitso, M. M. and Umar M. T. (2012): Kinetic Study of Utilizing Groundnut Shell as an Adsorbent in Removing Chromium and Nickel from dye effluent. *American Chemical Science Journal.* **2** (1), 12-24.

Itodo, A. U, Itodo H. U., Atiku F. A, Kolo, R. A. and Kwaido, A. A. (2011): Dyes Uptake onto Processed Raw Mango Seed back. *Asian Journal of Plant Science and Research.* **1** (1), 57-66.

Itodo, A. U., Abdulrahman, F. W., Hassan, L. G., Maigandi, S. A. and Happiness, U. O. (2009): Thermodynamic, equilibrium, kinetics and adsorption mechanism of industrial dye removal by chemically modified poultry droppings activated carbon. *Nigerian Journal Basic and Applied Sciences.* **17** (1), 38-43.

James, M., Okun, M. E. and Oviawe, A. P. (2007): Selective sorption of mixed heavy metal ions using cassava fiber modified with citric acid. *Journal of Chemical Society of Nigeria*. **32** (2), 247-253.

Jimoh, T. O., Yisa, J., Ajai, A. I. and Musa A. (2013): Kinetics and Thermodynamics Studies of the Biosorption of Pb(II), Cd(II) and Zn(II) Ions from Aqueous Solution by Sweet Orange (Citrus sinensis) Seeds. *International Journal of Modern Chemistry*. **4** (1), 19-37.

Jimoh, T. O., Buoro, A. T. and Muriana, M. (2012): Utilization of Blighia sapida (Akee apple) pod in the removal of lead, cadmium and cobalt ions from aqueous solution. *Journal of Environmental Chemistry and Ecotoxicology*. **4** (10), 178- 187.

Kirby, B. J. (2010): *Micro and Nanoscale Fluid Mechanics: Transport in Microfluidic Devices*. Cambridge University Press, New York.

Knocke, R. L. and Hemphil, T. S. (1981): Hydrogen adsorption states on silica-supported Ru-Ag and Ru-Cu bimetallic catalyst investigated via microcalorimetry. *Thermochimica Acta*. **312** (1-2), 105-114.

Kobya, M. E., Demirbas, E. and Senturk, M. I. (2005): Adsorption of Heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresources Technology*. **96**, 1518-1521.

Krishnan, K. A. and Anirudhan, T. S. (2003): Removal of cadmium (II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar cane bagasse pith: Kinetics and equilibrium studies. *Water SA*. **29** (2), 147-156.

Lane, T. W. and Morel, F. M. M. (2000): A biological function of cadmium in marine diatoms. *Proceedings of National Academy of Science*s. **97** (9), 4627-4631.

Lillo-Rodenas, M. A., Cazorla A. D. and Linares-Solono, A. (2003): Behaviour of Activated carbons with different pore size distribution and surface oxygen groups for Benzene and Toluene Adsorption at low concentration carbon. *African Journal of biotechnology*. **43**, 1758-1767.

Lyklema, J. (1995): *Fundamental of interface and colloid science*. Academic press, New York, 23-24.

Mane, S. W., Vanjara, A. K. and Sawant, M. R. (2005): Removal of Phenol from Wastewater using Date seed carbon. *Journal of Chinese Chemical Society*. **52**, 1117-1122.

Mattson, J.S. and Mark, H.B., (1971): *Activated Carbon: Surface chemistry and Adsorption from Solution*. New York; Marcell Dekker, 169-225.

Hogan, C. M. (2010): *Heavy metal. Encyclopedia of Earth*. In National Council for Science and the Environment. eds. E. Monosson & C. Cleveland. Washington, D.C. 220-300.

Mishra, S., Prakash, D. J. and Ramakrishna, G. (2009): Characterization and Utilization of Mahua oil cake- A new adsorbent for the removal of Congo red Dye from Aqueous phase. *Electronic Journal of Environmental, Agricultural and Food Chemistry*. **8**, 425-436.

Mohan, D. and Singh, K. P. (2002): Single component and multicomponent Adsorption of cadmium and zinc using activated carbon derived from bagasse agricultural waste. *Water Research*. **36**, 2304-2318.

Najua, D. T., Luqman, C. Z. and Zawani S. A. (2008): Adsorption of copper from aqueous solution by Elais Guineensis Kernel activated carbon. *Journal of Engineering Science and Technology*. **5**, 180-189.

Nale, B. Y., Kagbu, J. A., Uzairu, A., Nwakwere, E. T., Saidu, S. and Musa, H. (2012): Kinetic and Equilibrium Studies of the Adsorption of Lead (II) and Nickel (II) ions from aqueous solutions on Activated carbon Prepared from Maize cob. *Der Chemica Sinica*. **3** (2), 302-312.

Netzer, C. and Hughes, D. (1984). Adsorptive removal of 2-chlorophenol by low-cost coir pith carbon. *Journal of Hazardous Materials*. **98,** 257-274.

Onundi, Y. B., Mamun, A. A., Al-Khatib, M. F., Al-Saadi, M. A. and Suleyman, A. M. (2011): Heavy metals Removal from Synthetic Wastewater by a novel nano-size composite adsorbent. *International Journal of Environmental Science and Technology*. **8** (4), 799-806.

Qaiser, S., Anwar, R. S. and Muhammad U. (2009): Biosorption of lead (II) and chromium (VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study. *Journal of Biotechnol*ogy. **12** (4), 0717-3458.

Raffiea, B. J., Palanisamy, P. N. and Sivakumar, P. (2012): Preparation and Characterization of Activated carbon from thevetia peruviana for the removal of dyes from textile waste water. *Advances in Applied Science Research*. **3** (1), 377-383.

Namasivayam, C. and Kavitha, D. (2001): Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, and pigments. *Dye and Pigments* **54,** 47-48.

Sahu, J. N., Achrya, J. and Meikap, B. C. (2010): Optimization of Production conditions for activated carbons from Tamarind wood by zinc chloride using response surface methodology. *Bioresources Technology*. **101,** 1974-1982.

Salman, M., Athar, M., Shafique, U., Din, M. I., Rehman, R., Akram, A. and Ali, S. Z. (2011): Adsorption modelling of alizarin yellow on untreated and treated charcoal. *Turkish Journal of Engineering and Environmental Science.* **35,** 209-216.

Sanji, M. R., Shahmoradi, A., Zolgharnein, J., Azimi, G. H. and Ghorbandoost, M. (2008): Removal and recovery of heavy metals from aqueous solution using Ulmus carpinifolia and Fraxinus excelsior tree leaves. *Journal of Hazardous Materials*. **155**, 513-522.

Shukla, A. Zhang, Y. H. Dubey, P. and Shukla, S. S. (2002). The role of saw dust in the removal of unwanted materials from water. *Journal of Hazardous Materials.* **95** (12), 137-152.

Strinivassan, S. K. Tyagi, R. and Pant, N. (1999), Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plant. *Water Research*. **23,** 111-161.

Sugunadevi, S. R., Sathishkumar M., Shanthi, K., Kadiruvelu, K. and Pattabhi, S. (2002): The adsorption of Cd (II) ions on sulphuric acid treated wheat bran. *Journal of Hazardous Materials*. **137** (2), 849-855.

Sricharoenchaikul, V., Pechyen, C., Aht-ong, D. and Atong, D. (2008): Preparation and Characterization of activated carbon from the pyrolysis of physic nut (Jatropha curcas L.) waste. *Energy and Fuels*. 22 (1), 31-37

Vimonses, V., Lei, S., Jin, B., Chow, C. W. K. and Saint, C. (2009**)**: Kinetic study and equilibrium analysis of Congo red adsorption by clay materials. *Chemical Engineering Journal*. **148,** 354-364.

Wasewar, K. L., Mohammad, A., Prasad, B. and Mishra, I. M. (2009): Batch adsorption of Zn (II) ion using tea factory waste as an adsorbent. *Desalination*. **244**, 66-71.

Yang, T. and Lua, A. (2003): Characteristics of activated carbons prepared from pistachio-nut shells by physical activation. *Journal of Colloid and Interface Science*. **267**, 408-417.

Yu, Z. Y., Shukla, A. and Doris, K. L. (2000): The removal of heavy metal from aqueous solutions by saw dust adsorption. *Journal of Hazardous Materials*. **80**, 33-42.