International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2013): 4.438

Locally-Sourced Beans Husk, a Potential Adsorbent for Cd(II), Pb(II), Hg(II) Ions in Aqueous Solution

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Abstract: ***Ground beans husk(GBH) was used to remove Cd(II), Pb(II) and Hg(II) ions from their aqueous solution. FTIR analysis showed the presence of functional groups that could serve as sites for adsorption. Adsorption was carried out with the variations of metal ion concentration, contact time, temperature and pH. Results obtained showed that adsorption in all cases was better described by pseudo second order kinetics with the R^2 values of 0.999, 0.999 and 1.0 for Cd(II), Pb(II) and Hg(II) respectively. The experimental data for Cd(II) and Hg(II) were better described by Langmuir isotherm with the highest correlation co-efficient R^2 values of 0.935 and 0.990 and Pb(II) by Temkin isotherm model with R^2 value of 0.870.Thermodynamic studies showed that the reaction was spontaneous and exothermic for Cd(II) and Pb(II) ions but endothermic for Hg(II) ion. pH studies revealed that the optimum pH value for better adsorption was pH of 6 for the three metal ions.***

Keywords: Adsorption, kinetics, isotherm, Heavy metals

1. Introduction

Heavy metals are metals or metalloids of environmental concern. The term heavy metal originated with reference to the harmful effects of cadmium, mercury and lead, all of which are denser than iron. It has been used to describe the group of dense metals or their related compounds, usually associated with environmental pollution or toxicity [1].With the rapid increase in population and growth of industrialization worldwide, quality of both surface and ground water is deteriorating day by day. Water of high quality is essential to human life and water of acceptable quality is essential for agriculture, industrial, domestic and commercial uses. All these activities are also responsible for polluting the water. Billions of gallons of waste from all these sources are thrown to freshwater bodies every day. Industrial wastewater containing lead, copper, cadmium and chromium, etc can contaminate groundwater resources and thus lead to a serious groundwater pollution problem [2]. The requirement for water is increasing while slowly all the water resources are becoming unfit for use due to improper waste disposal [3-4]. High consumptions, frequent disposal and replacement of disposable items are generating diverse types of metallic wastes. These wastes are invariably discharged into the environment and thus are poisoning the biosphere [5]. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Heavy metals are toxic to aquatic flora, animals and human beings, even at relatively low concentration. The toxic metals are arsenic, cadmium, mercury, nickel, cobalt and lead [6]. Heavy metals are capable of being assimilated, stored and concentrated by organisms as they are hard to metabolize. They enter plants, animals and human tissues via air inhalation, diet and manual handling. The main threats to human health are associated with exposure to lead, cadmium, mercury and arsenic (arsenic is a metalloid, but is usually classified as a heavy metal)[7]. In the last century, lead emissions to ambient air have caused considerable pollution, mainly due to lead emissions from petrol. Children are particularly susceptible to lead exposure due to high gastrointestinal uptake and the permeable blood–brain barrier [8]. Long term exposure to heavy metals can lead to renal dysfunction, obstructive lung disease in humans and has been linked to lung cancer and bone defects [9]. Cadmium emissions have increased dramatically during the 20th century because cadmium-containing products are rarely re-cycled, but often dumped together with household waste. Cigarette smoking is a major source of cadmium exposure[7]. Chronic exposure to elevated level of cadmium is known to cause renal dysfunction (Fanconi syndrome), bone degradation (itai–itai syndrome), cancer, hypertension, liver damage, and blood damage[10]. The usage of mercury is widespread in industrial processes and in various products (e.g. batteries, lamps and thermometers). It is also widely used in dentistry as an amalgam for fillings and by the pharmaceutical industry. The presence of mercury in fish, waste water, dental amalgams, vaccine preservatives, and in the atmosphere has made this particular toxic metal an increasing focus for health authorities and interest groups [11-12]. The task of providing proper treatment facility for all polluting sources is difficult and also expensive, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient [3].

Some of the techniques which have been used in the removal of heavy metals from effluents include ion exchange, chemical precipitation, electrodialysis, electrolytic extraction, reverse osmosis, and cementation. These methods are expensive and in addition have the inability to remove metals at low concentration. Compared with the aforementioned techniques, adsorption has proved to be less expensive alternative for the removal of metals from aqueous solution[13].

Adsorption technique is good proposition for high strength and low volume of wastewater. Adsorption has advantage over other methods because the design is simple, highly efficient; it is sludge free and can involve low investment in terms of both the initial costs and land [8].

Literature has indicated the potential of some agricultural waste products as inexpensive adsorbents. Due to their low cost, after these materials have been expended, they can be disposed of without causing environmental degradation [14]. In addition, it is argued that since agricultural products and by-products are abundant waste materials that need proper disposal other than burning, which can generate carbon dioxide and other forms of pollution, the conversion of these products into useful and value-added products, is an environmental friendly decision [15]. Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as coconut shell, sawdust, mango leaves, chitosan, egg shell, and other adsorbents, which have high adsorption capacity and are locally available[3]. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry [16-17]. Of course improved adsorption capacity may compensate the cost of additional processing [18]. Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail.

The purpose of the present study was to evaluate the adsorption capacity of ground beans husk(GBH) in unmodified form for the removal of lead(II), Hg(II) and Cd(II) ions from aqueous solutions. In addition, kinetic, adsorption isotherm and thermodynamic parameters were also evaluated.

2. Experimental

2.1. Preparation and characterization of adsorbent

The bean husks used in this research work were collected from a local market at Alafia in Lagos State, Nigeria. These were washed in de-ionized water to remove sand and other debris. The cleaned bean husks were then sundried, and ground to fine powder which was used in the whole experiment. 5g of GBH was weighed and put in sample bags for subsequent use. Spectra of GBH before and after adsorption were obtained using FT-IR spectrophotometer (FTIR RX-1,Perkin Elmer, USA)

2.2. Materials and instruments

All the primary chemicals used in this study were of analytical grade and were used without further purification. $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2$, $Hg(NO_3).H_2O$ were purchased from Onitsha market. The stock solution of 1000 mg/L Cd(II), Pb(II) and Hg(II) was prepared by dissolving 2.74g, 1.6g , 1.71g of $Cd(NO_3).4H_2O$, $Pb(NO_3)$ and $Hg(NO_3).H_2O$ respectively in 1000mL of distilled water. All required concentrations were prepared by appropriately diluting of the stock standard solution. Solutions of 0.5M sulfuric acid (H_2SO_4) and 0.5M caustic soda (NaOH) were used for pH adjustment. The concentrations of the metal ions were determined using atomic adsorption spectrophotometer AAS (240 FS AA.)

2.3. Adsorption Experiments

Already weighed out 5g of GBH was introduced into five different beakers containing 100ml of $Pb(NO_3)_2$ solution in varying concentrations of 10mg/l, 20mg/l, 30mg/l, 40mg/l and 50mg/l. These were stirred mechanically and the mixtures were allowed to stand for 45 minutes, after which 10ml of the mixture was drawn out, filtered into sample bottles and the filtrates were analysed with (AAS) , for residual metal ion concentration. The above procedure was repeated using $Cd(NO_3)_2.4H_2O$ and $Hg(NO_3).H_2O$solutions. Results obtained were fitted into Langmuir, Freundlich, Dubinin-Radushkevic (DR) and Temkin models.

5g each of the adsorbent was added to five different beakers respectively, each containing 100ml of 40mg/l of .$Pb(NO_3)_2$. The mixtures were stirred mechanically and allowed to stand. At time intervals of 5, 10, 60, 90 and 120 minutes, 10 ml of the mixture was drawn out in successive order and filtered. The filtrate was analysed for the metal ion concentration. This procedure was repeated using $Cd(NO_3)_2.4H_2O$ and $Hg(NO_3).H_2O$solutions. Results obtained were analysed using three models namely: Lagrgren first order, Pseudo second order and Weber-Moris(WM) kinetic models. Thermodynamic experiments were carried at temperatures of 50℃, 70℃ and 90℃ to check for the effect of temperature on the adsorption of Cd(II), Pb(II) and Hg(II) ions from their aqueous solutions. 100ml of 40mg/l of $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2$, $Hg(NO_3).H_2O$ solutions was put into three different beakers respectively. 5g of bean husk was added to each beaker and stirred thoroughly. The beakers were placed on a thermostat water bath which was set to 50℃ and the beaker was allowed to stand in the water bath for 45 minutes after 10ml of the mixture each was drawn out and filtered for analysis.. This procedure was repeated at temperatures of 70℃ and 90℃. Thermodynamic parameters such as Gibb's free energy changes (ΔG), enthalpy change(ΔH), and entropy change(ΔS) were determined.

The effect of pH on adsorption of metal ions was studied over the pH range of 2-8. 100 ml of 40mg/l of $Pb(NO_3)$ solution was measured into different beakers. The pH was adjusted from 2-8 using 0.5M H_2SO_4 and 0.5M NaOH. 5g of bean husk was added into each beaker and stirred. The mixture was allowed to stand for 45 minutes after which 10ml was drawn out and filtered for analysis. This procedure was repeated using $Cd(NO_3)_2.4H_2O$ and $Hg(NO_3).H_2O$ solutions.

In all cases the amount of ions q adsorbed per unit weight of adsorbent at time t and removal efficiency (R) were calculated as:

$$q = \frac{V(C_0 - C_t)}{W} \quad (20)$$

$$R = \frac{V(C_0 - C_t)}{c_o} \times 100 \quad (21)$$

where, C_o is the initial concentration (mg/L), C_t is the concentration at any time t, V is the volume of solution in L and m is the mass in g of adsorbent

3. Data Analysis

3.1 Adsorption Isotherm

Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites[19]. It is represented as follows:

$$\frac{1}{q} = \frac{1}{q_{max} k_L C_e} + \frac{1}{q_{max}} \tag{1}$$

Where C_e is the equilibrium concentration in mg/l of metal ion in the liquid phase. Langmuir constant k_L and maximum adsorption capacity q_{max} in mg/g are evaluated from the plot of 1/q against $1/C_e$.(figs 5-7)

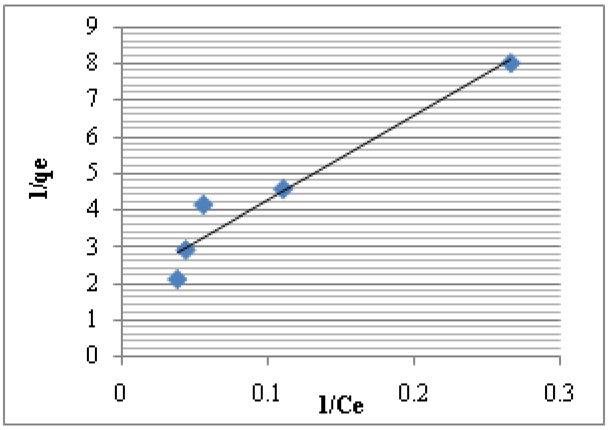


Figure 5: Langmuir isotherm plot for the adsorption of Cd(II)

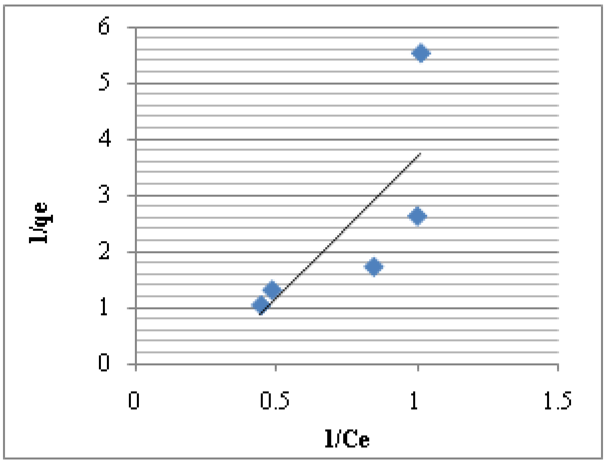


Figure 6: Langmuir lot for the adsorption of Pb(II)

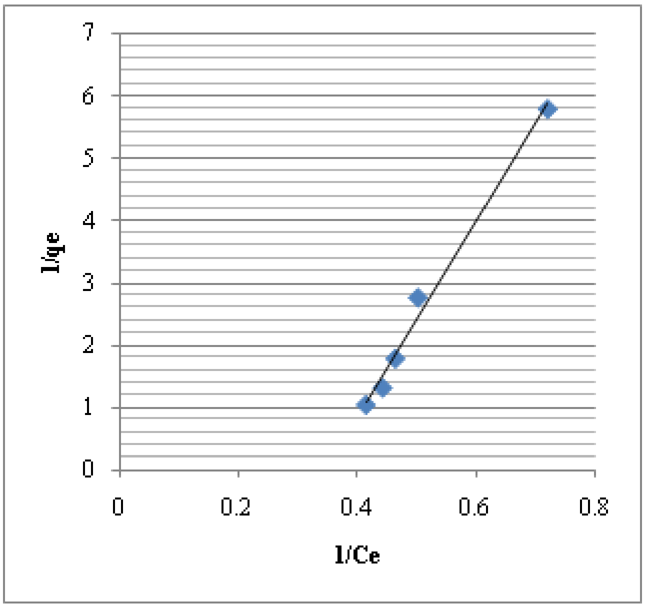


Figure 7: Langmuir lot for the adsorption of Hg(II)

Freundlich isotherm describes adsorption on heterogeneous surfaces. The expression for the Freundlich isotherm model [20] is given as:

$$lnq = lnk_F + \frac{1}{n} lnC_e \tag{2}$$

k_F inmg/l and n are Freundlich constants related to sorption capacity of the adsorbent and energy of adsorption respectively. These constants are evaluated from the plot of lnq versus lnC_e (figs 8-10).

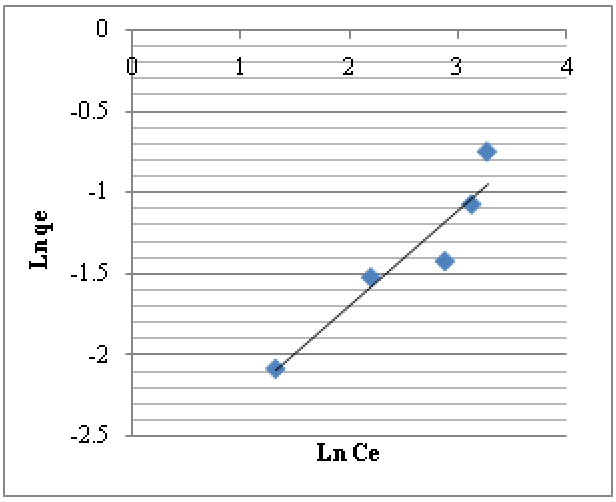


Figure 8: Freundlich plot for the adsorption of Cd(II)

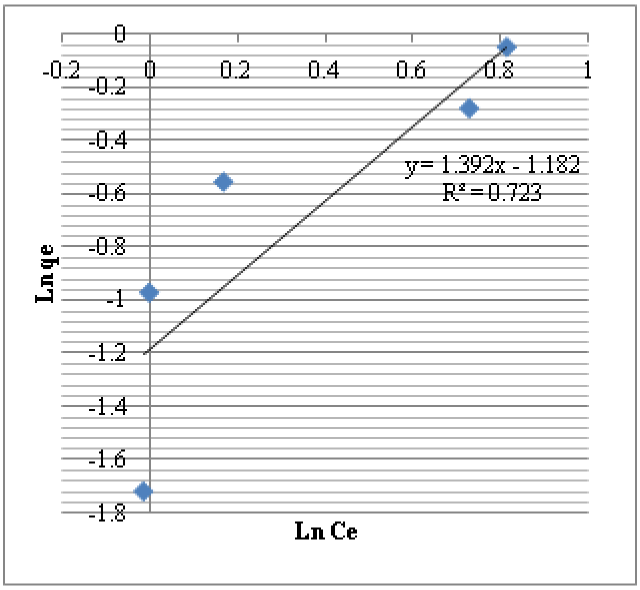


Figure 9: Freundlich plot for the adsorption of Pb(II)

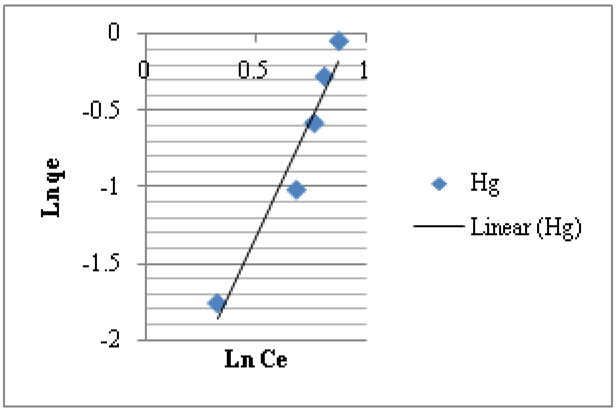


Figure 10: Freundlich plot for the adsorption of Hg(II)

Dubinin–Radushkevich(D-R) isotherm model was also used to evaluate the mean energy of sorption. It is represented in the linear form by the equation [21].

$$\ln q = \ln q_m - \beta \varepsilon^2 \qquad (4)$$

Where

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \qquad (5)$$

where q is amount adsorbed per gram of the adsorbent (mg/g), q_m is equilibrium adsorption capacity (mg/g) using model, β is Polanyi potential, ε is activity coefficient, C_e is concentration of metal ion in solution at equilibrium(mg/L), R is universal gas constant (8.314J/K/mol) and T is temperature in Kelvin. The values of β and q_m are evaluated from the slope and intercept of the graph of lnq versus ε^2 (figs 11-3). The mean energy of sorption E (kJ mol^{-1}) is calculated from the relation [22]:

$$E = \frac{1}{\sqrt{2\beta}} \qquad (6)$$

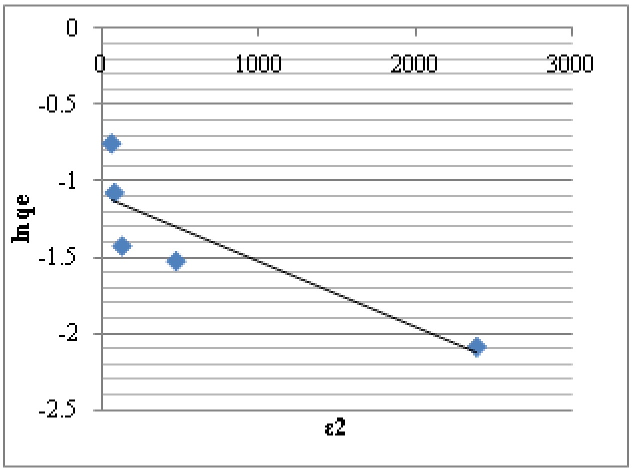


Figure 11: Dubinin-Radushkevich plot for Cd(II)

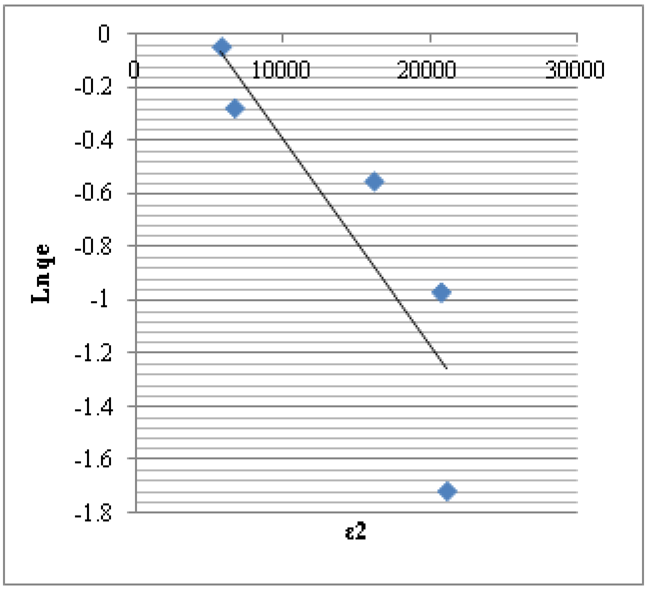


Figure 12: Dubinin-Radushkevich plot for Pb(II)

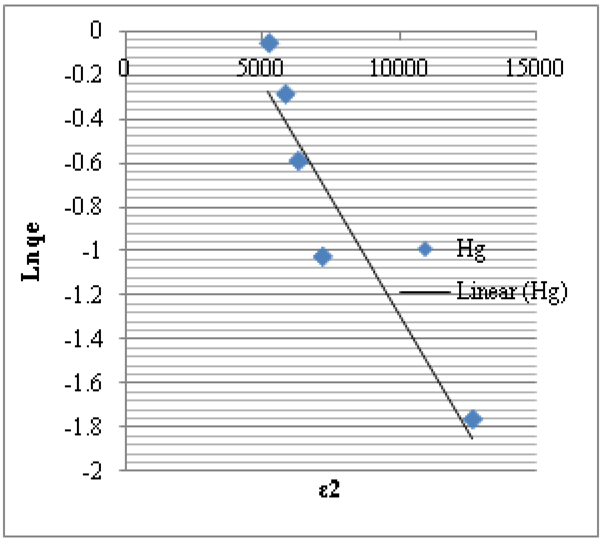


Figure 13: Dubinin-Radushkevich plot for Hg(II)

The derivation of the Temkin isotherm assumes that fall in the heat of sorption is linear. The equation for the model is given as;

$$q = \frac{RT}{b}\ln k_T + \frac{RT}{b}\ln C \qquad (3)$$

K_T and b are Temkin constants, R is universal gas constant (8.314J/K/mol) and T is temperature in Kelvin. A plot of q vs. lnC (figs 14-16), will give a slope and an intercept from which b and k_T are evaluated [23-24].

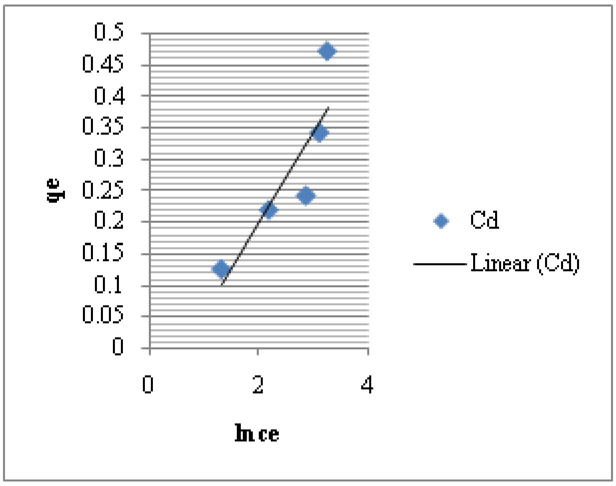


Figure 14: Temkin plot for the adsorption of Cd(II)

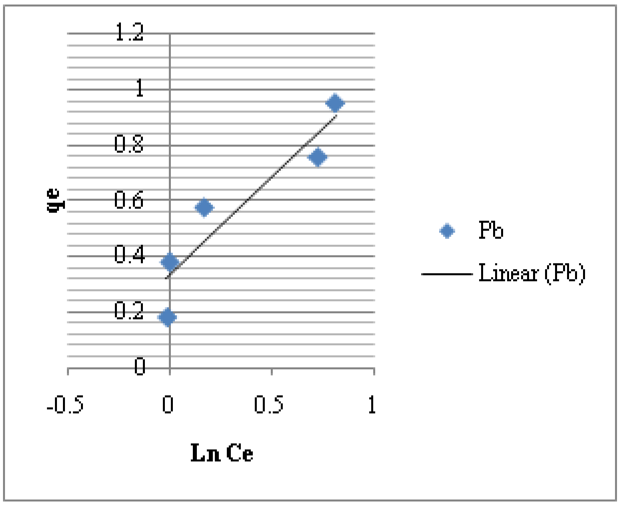


Figure 15: Temkin plot for the adsorption of Pb(II)

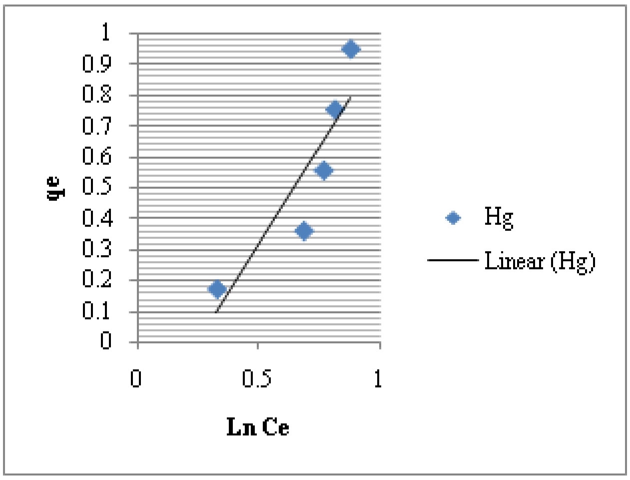


Figure 16: Temkin plot for the adsorption of Hg(II)

3.2 Kinetics Studies

Kinetics Models

In pseudo-first-order kinetic model, it is assumed that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solute uptake with time[25].

$$\frac{dq}{dt} = k_1\left(q_e - q_t\right) \qquad (7)$$

Integrating with the boundary conditions at initial time (t = 0), qt = 0 and at any time (t > 0), the amount of ion adsorbed is q_t and rearranging the rate law for a pseudo-first-order reaction becomes

$$\ln\left(q_{e(expt)} - q_t\right) = \ln q_{e(theo)} - k_1 t \qquad (8)$$

Where $q_{e\ (expt)}$ and $q_{e\ (theo)}$ are the experimental and theoretical equilibrium adsorption and q_t is experimental amount of metal ion adsorbed (mg/g of adsorbent) at any time t(min) The plot of $\ln(q_e - q_t)$ as a function of time (Fig.17) gives a straight line with slope of $-k_1$.

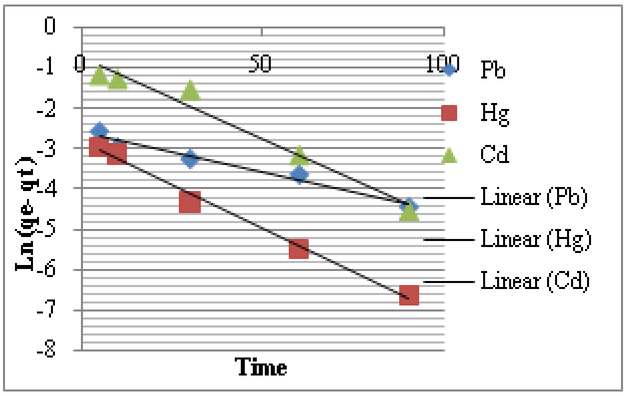


Figure 17: Largergren first order kinetics plot

The kinetics of adsorption process as described by the pseudo-second-order rate equation is expressed by as[26]:

$$\frac{dq}{dt} = k_2\left(q_{e(theo)} - q_t\right)^2 \qquad (9)$$

Separating the variables in equation 9a gives;

$$\frac{dq}{\left(q_{e(theo)} - q_t\right)^2} = k_2\,dt \ldots\ldots\ldots\ldots\ldots..(10)$$

Integrating Equation 9b for the boundary conditions t_0 to $t_t$and q_0 and $q_{e(theo)}$gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e(theo)}{}^2} + \frac{t}{q_{e(theo)}} \qquad (11)$$

A plot of t/q_t versus t (figs 18) gives a slope and an intercept, from which the values of $q_{e(theo)}$ (mg/g), and the pseudo-second order rate constant $k_2(gmg^{-1}min^{-1})$,can be calculated respectively.

At time 0, the initial rate denoted as h_0 is given as

$$h_0 = k_2 C_0^2 \qquad (12)$$

where C_0 is the initial concentration before adsorption. h_0 is then evaluated from already determined k_2

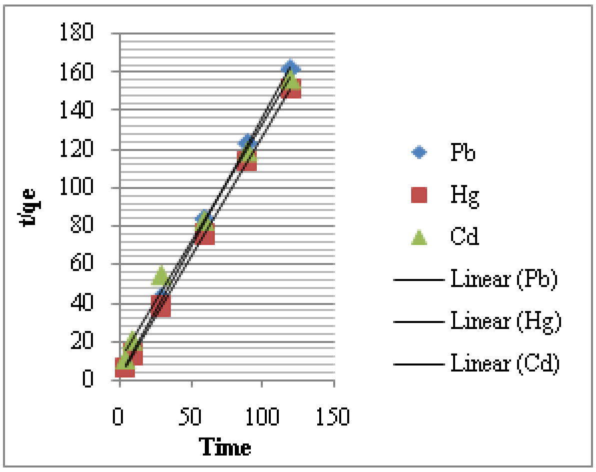


Figure 18: Pseudo-second order plot

The intra-particle diffusion model is based on the theory proposed by Weber and Morris. According to this theory,

$$q_t = k_{id} t^{0.5} + C \qquad (13)$$

Where q_t is adsorption capacity at time t, k_{id} is intra-particle diffusion rate constant in mg/g/min$^{1/2}$. A graph of qt as a function of time (fig 19) is used to shows whether the rate determining step is by the boundary film diffusion or by intra-particle diffusion

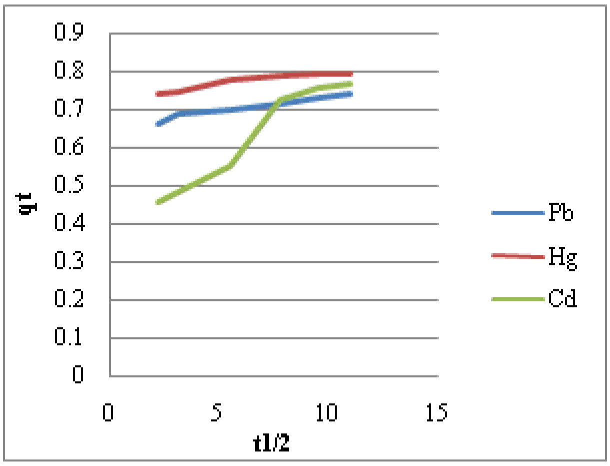


Figure 19: Weber Morris kinetics plot for the adsorption

3.3 Thermodynamic Studies

Gibb's free energy of adsorption was computed from the equation [27]:

$$\Delta G = -RT\ln K_C \qquad (14)$$

where ΔG is standard free energy change , R is universal gas constant(8.314 J/mol/ K), T is absolute temperature in K, and K_C is the equilibrium constant.The apparent equilibrium constant, K_C, is defined as

$$K_c = \frac{q}{C} \qquad (15)$$

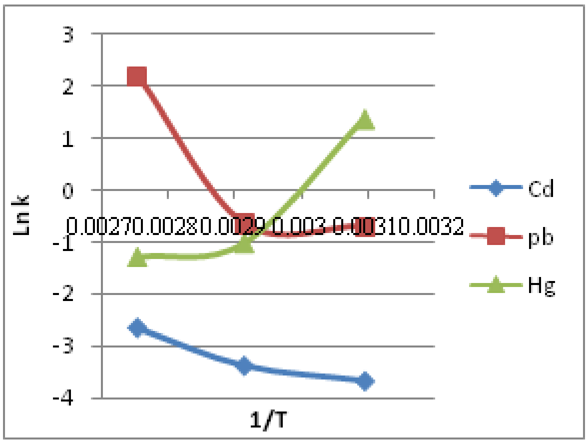
Where q is the concentration of adsorbed metal in mg/g, C is concentration in mg/l of Pb(II) solution after adsorption. The values of ΔH and ΔS are estimated from the relationships:

$$\Delta G = \Delta H - T\Delta S \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

Substituting equation 14 into equation 16 and making $\ln K_C$ the subject of the formulae, yields:

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 17$$

The values of ΔS and ΔH can be calculated from the intercept and slope of the plot of $\ln K_d$ versus 1/T(fig 20).



4. Results and Discussion

4.1. FT-IR Analysis

Figs. 1- 4 show the FTIR analysis for GBH before and after adsorption. Fig 1 showed the presence of a large number of functional groups, notably $-NH_2$ (3388.33cm-^{1}), -OH(2488.41cm^{-1}), C=C (2169.84), -C=O (1611.53cm^{-1}). Other peaks are due to the presence of complex organic framework and bending vibration of GBH. Table 1, shows the wave numbers of functional groups before and after adsorption. In comparing between fresh GBH and metal loaded GBH, it is observed that there were shifts in wave numbers of dominant peaks associated with the loaded metal. The wave number of the C=O of COOH group shifted with as much as 86.26, 16.09 and 45.02 units in GBH loaded with Cd(II), Pb(II) and Hg(II) respectively. OH group wave number shifted with 85.89, 41.6 and 35.86 units in GBH-Cd(II), GBH-Pb(II) and GBH-Hg(II) systems respectively. Wave numbers of N–H stretching shifted with units of 7.46, 92.08 and 4.73 while changes in the wave numbers of C=C group were the least with units of 6.92 and 2.8 for GBH-Cd(II) and GBH-Hg(II) systems respectively. These shifts in the wave number showed that metal binding process took place on the surface of GBH. Similar observations have also been reported [28].

Table 1. Wavenumbers for dominant peaks

Metal	*Pre-adsorption (cm^{-1})*	*Post-adsorption (cm^{-1})*	*Change in wavenumber (cm^{-1})*	*Assigned functional group*
Cd$^{(II)}$	1611.536	1697.803	86.267	C=O of COOH
	2488.418	2402.528	85.89	OH of COOH
	3388.333	3380.871	7.462	NH of COOH
	1156.886	1128.269	28.618	C-O of COOH
	2169.847	2162.919	6.928	C≡C
Pb$^{(II)}$	1611.536	1627.627	16.091	C=O of COOH
	2488.418	2446.809	41.609	OH of COOH
	3388.333	3480.418	92.085	NH of COOH
	1156.886	1202.441	45.555	C-O of COOH
Hg$^{(II)}$	1611.536	1656.562	45.026	C=O of COOH
	2488.418	2452.551	35.867	OH of COOH
	3388.333	3383.603	4.73	NH of COOH
	1007.242	1003.55	3.692	C-O of COOH
	2169.847	2172.652	2.805	C≡C

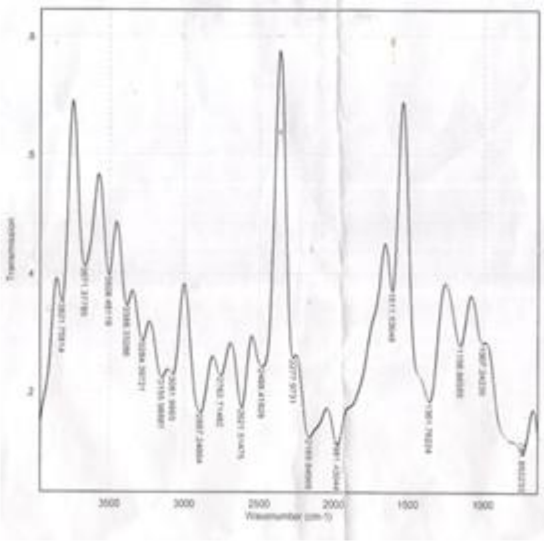


Figure 1: IR spectra of GBH before adsorption

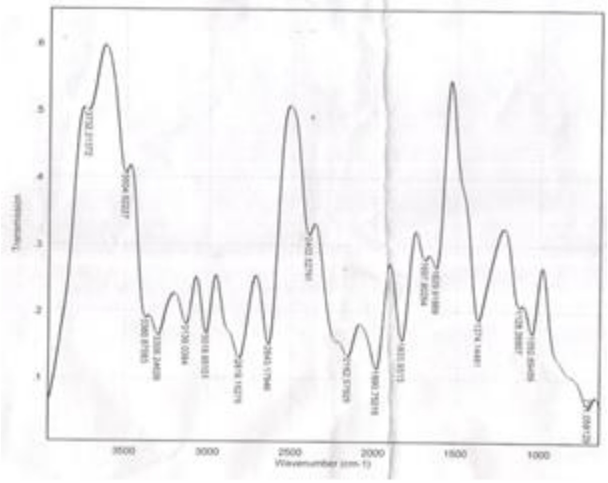


Figure 2: IR spectra of GBH after Cd(II) adsorption

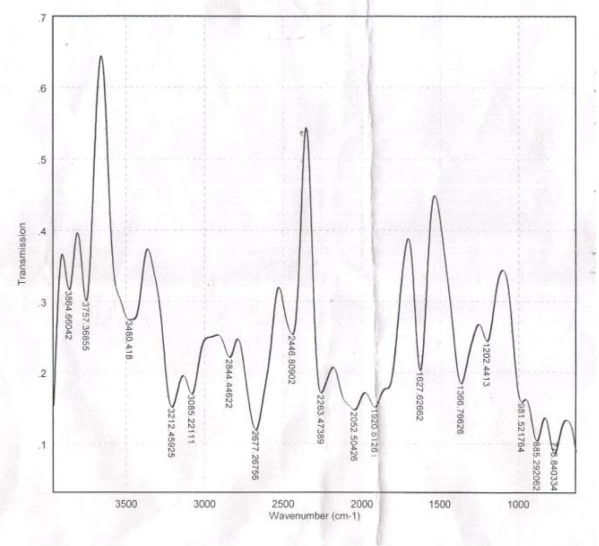


Figure 3: IR spectra of GBH after Pb(II) adsorption

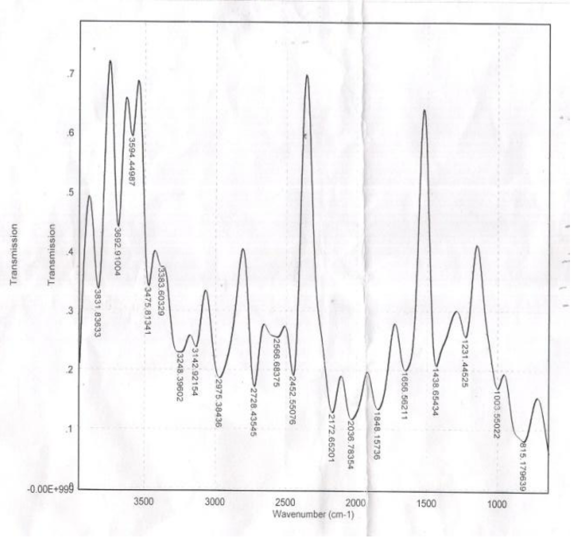


Figure 4: IR spectra of GBH after Hg(II) adsorption

4.2. Adsorption Isotherm Models

Table 2 shows the adsorption isotherm parameters for adsorption. Adsorption of Cd(II) and Hg(II) were better described by the Langmuir isotherm with R^2 values of 0.935 and 0.990. Pb(II) was best described by the Temkin isotherm with R^2 value of 0.870. Maximum adsorption capacity qm obtained with DR isotherms were higher than those obtained with Langmuir isotherm for Pb(II) and Hg(II) adsorption while qm for Cd(II) adsorption was higher in Langmuir isotherm than in DR isotherm. n values for Cd(II) and Pb(II) adsorption were between 1 and 10; this indicates that the process of adsorption was favorable. However n values for Hg(II) adsorption was less than 1, indicating unfavorable adsorption. K_F sorption capacity values according to Freundlich was less than the sorption capacity Qm obtained from both Langmuir and DR isotherms. In fact it was least with the adsorption of Cd(II). Sorption energy E, the energy required to transport one mole of the adsorbate from the liquid phase to the surface of the adsorbent was greater than 8kJ/mol in all cases. This implies that sorption processes were all by chemisorption where covalent bonds were formed between the Hg(II) Cd(II) and Pb(II) ions and the surface of GBH. E values less than 8kJ/mol indicate physiosorption, those slightly above 8kJ/mol indicate ion exchange while values much greater than 8kJ/mol indicate chemisorption[29].

Table 2: Isotherm parameters for adsorption on GBH

Metal	*Isotherm*	*R^2*	*q_m mg/g*	*N*	*E kJ/mol*	*K_F, K_L, K_T*
Cd	Langmuir	0.935	0.501			0.087
	Freundlich	0.895		1.672		0.056mg/g
	DR	0.735	0.333		35.355	
	Temkin	0.766				0.535
Pb	Langmuir	0.568	0.759			0.026
	Freundlich	0.723		2.543		0.307mg/g
	DR	0.769	1.465		79.057	
	Temkin	0.870				1.594
Hg	Langmuir	0.990	0.181			-0.348
	Freundlich	0.941		0.328		0.058mg/g
	DR	0.894	2.309		50.0	
	Temkin	0.795				0.773

4.3. Adsorption Kinetics

Table 3 shows the kinetics parameters for the adsorption of Cd(II) and Pb(II) and Hg(II) ions. The R^2 and the rate constant (K_{ad}) obtained from the second order kinetics were higher than those of other models, showing that experimental data fitted more into the pseudo second order kinetics. This is confirmed from the calculated q_{theo}values which are greater in second order than in the first order and are also closer to $q_{exp.}$ The initial adsorption rate h_0 calculated from pseudo second order rate equation showed that Hg(II) ion has a higher adsorption rate than the other metal ions. The Weber Morris plot fig() was multi-linear with none of the intercepts of the many lines passing through the origin. This indicates that intra particle diffusion is not the only rate limiting step for adsorption of the metal ions onto bean husk. The mechanism of Cd(II) and Pb(II) and Hg(II) adsorption on GBH is complex and both the surface adsorption and intra-particle diffusion contributed to the rate determining step[30].

Table 3: Kinetics parameter for adsorption

Metal	Model	R^2	h_0	K_{ad}	q_{exp}	q_{theo}
Cd	First order	0.968		0.040	0.7427	0.472
	Second order	0.999	0.105	0.159		0.8413
	Weber Morris	0.950		0.039		
Pb	First order	0.964		0.019	0.7941	0.0740
	Second order	0.999	0.745	1.094		0.7446
	Weber Morris	0.954		0.007		
Hg	First order	0.992		0.043	0.7678	0.0593
	Second order	1.0	1.488	2.340		0.7974
	Weber Morris	0.736		0.006		

4.4. Thermodynamics Studies

Thermodynamics parameters are shown in table 4. The negative values of ΔH for the adsorption of Cd(II),Pb (II), show exothermic nature of the adsorption process, while the positive value of ΔH for the adsorption of Hg(II) shows the endothermic nature of the adsorption process.

The negative value of ΔS for the adsorption of Hg(II) corresponds to a decrease in degree of freedom of the adsorbed specie and suggests a decrease in the concentration of adsorbate in solid-solution interface, thus indicating an increase in adsorbate concentration onto the solid phase. On the contrary, the positive values of ΔS, corresponds to an increase in the randomness at the solid/solution interface during the adsorption of Cd(II) and Pb(II) onto bean husk. The negative values of ΔG for the adsorption of Cd(II) and Pb(II) signifies the spontaneity and feasibility of adsorption process at lower temperature whereas the positive values of ΔG for the adsorption of Hg(II) signifies the non-spontaneous nature of its adsorption onto GBH.

Table 4: Thermodynamic parameters

Metals	ΔH kJ/mol	ΔS kJ/mol	ΔG(kJ/mol)		
			323k	343k	363k
Cd	-24.34	44.23	-38.63	-39.51	-40.39
Pb	-68.86	203.53	-134.60	-138.67	-142.75
Hg	65.94	-195.21	128.99	132.89	136.80

4.5. Effect of pH on Adsorption

Fig. 21 shows the effect of pH on the adsorption of the metal ions. From the result the percentage removal for the adsorption of the metal ions increased with increase in pH from 2-6. However the uptake of metal ion decreased slightly from pH of 6-8. The minimum percentage removal observed at low pH was due to large amount of hydroxonium ion (H_30^+) which competed with the positively charged metal ions(Cd(II), Pb(II),Hg(II)) for the adsorbent surface sites, therefore, the available surface area and subsequent adsorption of the metal ion was reduced. Maximum percentage adsorption observed at pH of 6 follows the trend Cd(66.492) < Hg (80) < (99.475). Furthermore, the pH dependency on the metal ions uptake by biomasses can also be justified by the association–dissociation of certain functional groups, such as the carboxyl and hydroxyl groups present on the biomass. Most of the carboxylic groups is not dissociated at low pH and cannot bind the metal ions in solution[31].

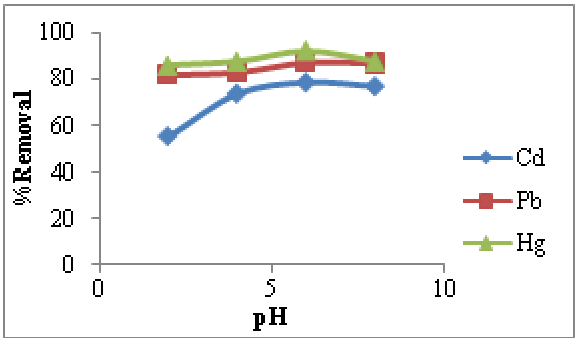


Figure 21: Effect of pH on adsorption

5. Conclusion and Recommendations

The ground beans husk used in this research possessed active functional groups onto which Cd(II), Pb(II), Hg(II) ions adsorbed. Removal of these ions was affected by the pH of the solutions. Maximum adsorptions occurred at pH values at pH 6. Second order kinetic model better described all the adsorption processes than the first order model. ground beans husk is a readily available agricultural waste Hence it can be used commercially to treat industrial and laboratory effluents before the latter are discharged into the environment to make for a cleaner and healthier environment

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