

Adsorption of Pb^{2+} from aqueous solution by modified melon (*Citrullus lanatus*) seed husk.

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Abstract

The application of Modified Melon Seed Husk (MMH) an agricultural waste in the remediation of water contaminated with lead ions was investigated in the present study. Modification was done by soaking the melon seed husk in 0.5M NaOH solution. Batch kinetic and isotherm studies was performed to understand the ability of the adsorbents. Effect of some process variables were assessed viz: pH, initial metal ion concentration and sorbent dosage on the sorption process. The equilibrium sorption isotherm was studied using the Freundlich and Langmuir isotherm models. The results obtained showed that the process of the sorption fitted better with the Freundlich isotherm, implying that the sorption occurred on a heterogeneous surface of the MMH. The monolayer adsorption capacity determined from the Langmuir adsorption equation was found to be 52.08 mg/g which competes favourably with some other biosorbents. Data obtained from the kinetics of the sorption process via initial metal ion concentration were analyzed using pseudo second order, the pseudo first order model and intraparticle diffusion model. The sorption process obeyed the pseudo second order kinetic model better than the pseudo first order kinetic model, thus suggesting the role of chemisorption in the mechanisms of the sorption. The intraparticle diffusion model showed that intraparticle diffusion is not the singular rate limiting step in the sorption process. The kinetic parameters suggest that adsorption of lead ions by MMH was favourable. Overall, the present findings suggest that MMH, an environmentally friendly, efficient and low-cost biosorbent is useful for the removal of Pb^{2+} from aqueous media.

Key words: Adsorption, Isotherm, Kinetics, Lead, Melon seed Husk, Wastewater

Introduction

The danger of accumulation of trace metals in the various aspects of the environment has in recent times gained prominence. Numerous literatures on environmental monitoring of surface water indicated that streams and rivers in the country are showing increasing trends of water pollution due to population, industrialization and urbanisation advancement. Acid battery manufacturing industries, metal plating industries ceramic and glass industries are some of the process industries that are major sources of lead pollution in the environment (Opeolu et al., 2008). Industrial effluents when discharged directly into rivers without prior treatments have capacity of affecting water quality parameters. These waste streams consist of salts, oils, sulphides, mixtures of organic compounds and toxic metals such as Cr, Cd, Pb, Hg, Ni, Cu and Zn (Patrick et al., 1992). Heavy metals are potential threats to the environment and ecosystem due to their persistency and bioaccumulation in the food chain. Lead poisoning affects major organs in humans like the kidney, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal death (Ofomaja et al., 2005). Wastewater reuse has been made possible through the development of different wastewater treatment technologies (Oladoja et al., 2006). Current abatement and remediation procedures for lead in wastewater includes pH adjustment with lime or alkali hydroxides, coagulation /sedimentation, membrane filtration, reverse osmosis, ion –exchange, foam floatation and electrolysis. These processes however are limited in their technical and economic viability (Sciban et al., 2007). Adsorption however offers significant advantages such low cost, availability, profitability, easy operation and minimisation of chemical and efficiency in comparison with conventional methods especially from the economic and environmental points of view (Rafatullah et al., 2009). Moreover, conventional methods are not associated with problems like high cost and the inability to remove metals at low concentrations (Nasir et al., 2004). The quest for cheap and cost- effective technology for removal of heavy metals from industrial effluents has led to the use of materials of biological origins as adsorbents. The use of economically viable materials in the remediation heavy metals is more suited to a developing country like Nigeria where many of the industries are small-scale cottage – based and as such may not be able to afford expensive treatment plants. Also

to be noted is that treatment by sorption of pollutants from aqueous solution has proven to be a cheap and efficient method of water purification since it does not need huge sludge –handling processes. Some waste biomass has been reported to effectively sequester heavy metals. These include rice bran (Wang and Qui 2005), corn chaffs (Han et al., 2006), black gram husk (Saeed and Iqbal 2003) and hazel nut (Cimino et al., 2000). The adsorption capacities and the feasible removal sites of many adsorbents can be substantially boosted by modification of the sorbent with suitable techniques. For this reason, modification and impregnation techniques were often used to increase surface adsorption and removal capacity of many adsorbents with the advantage of adding selectivity to the sorbent (Mojed et al., 2008).

The use of unmodified biosorbents can bring several problems such as low adsorption capacity, increased COD, BOD and TOC of the sludge due to the release of soluble organic compounds contained in the plant materials (Gaballah et al., 1997; Nakajima and Sakaguchi 1990). Modification methods for the purpose of increasing efficiency of metal adsorption include basic treatments, acidic treatments and the use of organic compounds or oxidizing agents. An agrarian country like Nigeria is rich in many agricultural by- product, majority of which are laying waste as litters in the environment. Melon (*Citrullus lanatus*) is a cucurbit crop that belongs to the family cucurbitaceae. Melon seeds ‘Egusi’ are grown, harvested and processed by removing the seeds from the fruits followed by washing and sun –drying. The flesh is inedible but the seeds are a valuable in Africa. They found usage either as food supplement (soup condiment) or also for medicinal purposes. They are used in the treatment of urinary tract infection, hepatic congestion, intestinal worms and abnormal blood pressure. Melon husks are shells that are discarded after shelling of melon seeds. Melon husk is a lignocellulosic plant biomass and a waste product from the food industry, having proteins, celluloses and lipids coated on its surface. Adsorption process can therefore occur on these organic functional groups. Many thousands of kilograms of these are dehulled from the seeds each year their conversion as packing materials for heavy metal removal would create jobs for the unemployed (Olayinka et al., 2005). The objective of this study was to evaluate the adsorption performance of modified melon seed husk (*Citrullus lanatus*) for the removal of Pb^{2+} from aqueous solution. The Pb^{2+} adsorption equilibrium and kinetics parameters were determined. Langmuir and Freundlich isotherm equations were employed to quantify the adsorption equilibrium. The effects of solution pH, adsorbate initial concentration and amount of adsorbent on the sorption potential of the MMH were examined. An intraparticle diffusion model was used to investigate the adsorption mechanisms.

Materials and Methods

Chemicals and Reagents: All chemical used were of analytical-reagent grade. NaOH and $Pb(NO_3)_2$ were purchased from Finlab Chemicals Ltd and were used without further purification.

Preparation of Adsorbent: Melons husk used in this study was obtained from local markets in Wukari, Taraba State, Nigeria. A magnetic bar was used to remove any metallic objects which may constitute as additional source of metallic ions in the melon husk. It was washed with plenty of water to remove surface impurities, sun-dried and then milled to reduce the size. The modification of the melon husks was done by heating 500g of the melon husks (MH) for 4hrs continuously in 0.5M NaOH in the oven. This was done twice with fresh NaOH solution. The NaOH was then filtered out and the modified melon husk (MMH) was washed several times with distilled water until the supernatant became clear. The husk was then oven dried at 80°C for 8 hours, grinded to sieve size of 180-300um and stored in an air tight container pending usage as an adsorbent.

Preparation of Adsorbate: Lead nitrate $Pb(NO_3)_2$ salts were used in the preparation of the salt stock solutions. Stock solution was prepared by dissolving the accurately weighed amounts of $Pb(NO_3)_2$ in 1000ml distilled water. Working solutions of concentration ranging from 5 to 60mg/l were prepared from the stock solution by serial dilution with distilled water.

Metal Analysis: Metal ion concentrations were measured by Atomic Absorption Spectrophotometer (Model 969, Solar Unicam Series), using an air-acetylene flame and single element hollow cathode lamps. The instrument was calibrated with standard solutions of 1 to 20 mg/L. Lead absorbance was measured at 217nm. The spectrophotometer was linked to a microprocessor using SOLAR AA software.

Sorption Studies: In order to determine the sorption isotherm, 0.1g of the adsorbents was brought in contact with 50ml of the varying concentrations of the working solutions (5-60mg/l) of the sorbate. The mixture was

agitated in a mechanical shaker at ambient temperature for 120 minutes at a constant agitation speed of 200 rpm. At the end of the agitation, suspensions were separated by filtration and the supernatant was analyzed for residual lead ions via AAS. The equilibrium sorption of Pb^{2+} ion by MMH was tested with Langmuir and Freundlich isotherm models to determine the best-fit isotherm equation.

Data Analysis: Lead uptake by the MMH during the series of batch investigation was calculated using the mass balance equation as stated below:

$$q_e = \frac{v}{m} (C_i - C_e) \quad (1)$$

where, q_e is the amount of sorbate sorbed (mg/g) at equilibrium, c_i is the initial concentration of Pb^{2+} (mg/l) in solution; c_e is the final residual Pb^{2+} concentration (mg/L) at equilibrium and, m is the mass of MMH (g), v is the volume of initial sorbate concentration (L). The removal percentage (R %) defined as the ratio of difference in metal concentration before and after adsorption ($C_i - C_e$) to the initial concentration of the Adsorbate in aqueous solution (C_i) was calculated as shown below:

$$(R\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Kinetics of Sorption Studies: The time- concentration profiles of the adsorption of the adsorbates were assessed to obtain the kinetic parameters by the addition of 0.4g of the adsorbent into a 200ml working solution of the adsorbates of varying concentrations, agitated with a shaker at 200 rpm. Solution samples were withdrawn at intervals between 2mins - 2hours of contact, filtered and the supernatant was analyzed for residual metal ions. The kinetics of Pb^{2+} sorption on the MMH was analyzed using Langeren pseudo first order and pseudo second order kinetic models and Intraparticle models.

Sorption Process variables Optimization

pH Effects : The sorption process variables were optimised by assessing the effects of pH on the sorption process varying the pH of the initial adsorbate solution of 50ml between pH2-6 with 1M HCl or 1M NaOH and fixed sorbent dosage of 0.1g at ambient temperature for 120mins and agitation speed of 200rpm.

Effects of initial metal ion concentration: The effects of initial concentration variation on the kinetic of the sorption process were assessed by varying the concentrations of the adsorbate between 25mg/l – 100mg/l, fixed sorbent dose of 0.1g and 50ml of initial adsorbate solution at ambient temperature for 120mins and agitation speed of 200rpm.

Effect of the sorbent dose: The effect of the sorbent dose on the sorption process was investigated at different adsorbent dosages of 0.05g-0.60g by contacting with 50ml of adsorbate for 120mins at ambient temperature and agitation speed of 200rpm.

Results and Discussion

Sorption Isotherm Studies: Adsorption is usually described through isotherms, the amount of adsorbate on the adsorbent as a function of its concentration (if liquid) at constant temperature and whose parameters present the surface properties and affinity of adsorbent to solute. The evaluation of a sorbate's affinity for a particular sorbent is usually obtained from the analysis of the results obtained from the equilibrium isotherm studies. Equilibrium studies are described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity for the sorbent. The results obtained in this study were tested with two isotherm equations, Langmuir and Freundlich equations. The Langmuir isotherm which hints on homogeneity

describes the monolayer coverage of a sorbate on a sorbent surface at constant temperature. The linear form of the Langmuir equation is:

$$C_e/q_e = 1/Kq_m + C_e/q_m \dots \dots \dots (3)$$

where C_e is the concentration of the sorbate at equilibrium (mg/l), q_e is the amount of sorbate sorbed at equilibrium per unit mass (mg/g), q_m is the monolayer sorption capacity at equilibrium (mg/g) and k is the Langmuir equilibrium constant (l/mg). The values of q_m and k were obtained from the slope and intercept respectively of the plot of straight line graph of C_e/q_e against C_e . The Freundlich isotherm is regarded as an empirical isotherm. It indicates the surface heterogeneity of the sorbent. The linearized form of Freundlich equation is given by:

$$\ln q_e = (1/n) \ln C_e + \ln K_f \dots \dots \dots (4)$$

where k_f and n are Freundlich adsorption constants, related to adsorption capacity and sorption intensity respectively obtained from the plot of $\ln q_e$ against $\ln C_e$ which gives a straight line graph with $1/n$ as slope and $\log k_f$ as intercept. In order to understand the mechanism of Pb^{2+} adsorption on MMH, the experimental data were fitted to the aforementioned equilibrium isotherm equations. An error function is required to evaluate the fitness of each isotherm equation to the experimental data obtained from the process employed. In the present study the linear coefficient of determinations, r^2 , was used. The values of the linear correlation, r^2 of each isotherm equation and their parameters when fitted to the experimental data are presented in Table 1. The highest values of r^2 was obtained when the experimental data were fitted into Freundlich isotherm equations (0.993). The description of the sorption of Pb^{2+} on MMH by the Freundlich isotherm equations is a pointer to the heterogeneity of the surface of the MMH and the multilayer adsorption nature of the Pb^{2+} on MMH. The equilibrium adsorption plots, relating the solid and liquid phase concentrations, for the two isotherms are presented in Fig 1 and 2.

Table 1: Sorption isotherm models constants and coefficients of determination for the sorption of Pb (II) ion by MMH.

Langmuir	Freundlich
$K_L (dm^3/mg) = 0.88$	$K_f (l/mg) = 1.9089$
$q_m (mg/g) = 52.08$	$n = 1.618$
$r^2 = 0.968$	$r^2 = 0.993$

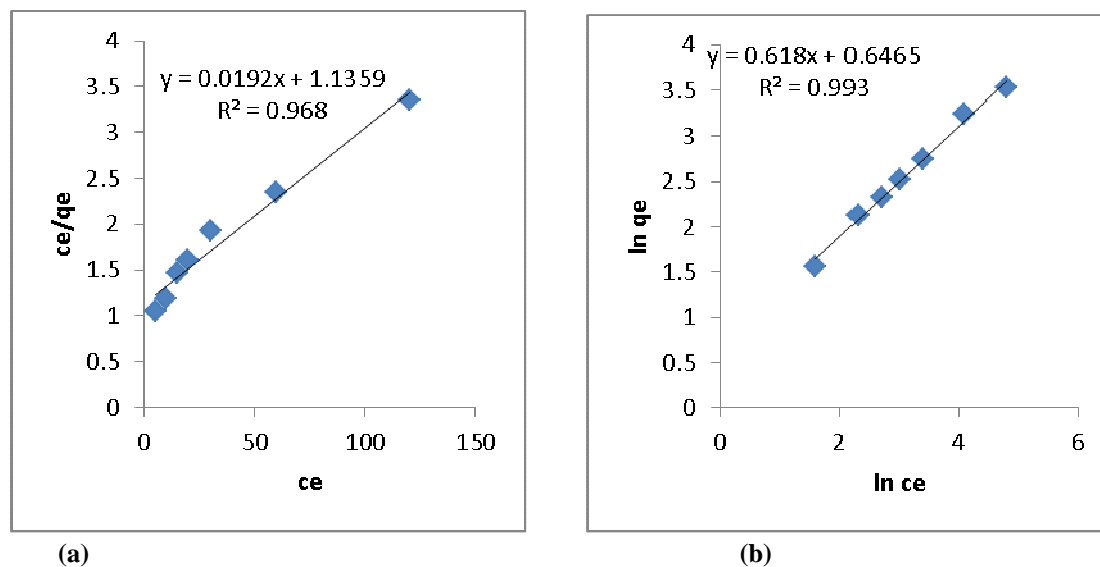


Fig 1: (a) Langmuir plot of Pb²⁺ sorption by MMH (b) Freundlich plot of Pb²⁺ sorption by MMH

The value of n (1.618) the sorption intensity is a pointer to a favorable adsorption process. The maximum adsorption value, 52.08 mg/g, obtained in the present study indicated a good uptake of Pb²⁺ in aqueous solution. Comparison of the potential of MMH as a sorbent for Pb²⁺ uptake in aqueous systems showed that MMH can compete favourably with other sorbents (Poplar 21.05 mg/g, Walnut 6.54 mg/g, Pinussylvestris 9.71 mg/g (Li et al., 2007; Yasemin and Zek 2007 and TatyCostodes et al., 2003).

Effects of Solution pH: Organic functional groups such as alcohol, aldehydes, ketones, carboxylic, phenolic and ether group usually present on the surface of biosorbents have been found to participate in cation binding due to their ability to ionize in aqueous solution (Kapoor et al,1999; Ofomaja and Ho, 2005). pH is an important factor controlling the process of adsorption. The ability to form electrical charges on the biosorbent surface is dependent on solution pH. At lower pH most of these functional groups are dissociated and can readily exchange H⁺ with metal ions in solution. In the present study, biosorption of Pb could not be carried out beyond pH6 due to the precipitation of Pb(OH)₂ at higher pHs and therefore the experiments were done in the pH range 2-6. The effect of solution pH on the uptake of lead ions from aqueous solution showed an increase in percentage removal from 30-92%, 43-90% and 39-90 % for 30, 60 and 90 mg/l of Pb ion in solution shown in Fig 2a. As solution pH increases, the amount of metal sorbed increases. The presence of positively charged sites on the biosorbent surface may be responsible for the low metal ion uptake at low solution pH. Increasing the pH reduces the competition between the H⁺ and Pb²⁺ leading to interaction between the surface functional groups of the sorbent and Pb²⁺. It should be noted that there is only a slight variation in the % removal between the different concentrations used. For the study an optimum pH of 5 was chosen.

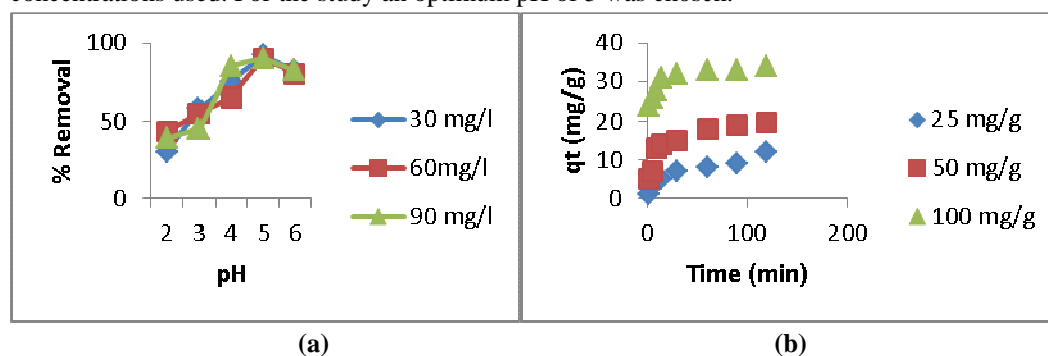


Fig 2: (a) Effect of Solution pH on Pb²⁺ uptake by MMH (b) Effect of Initial Metal ion concentration on Pb²⁺ uptake by MMH

Studies on Sorption kinetics: Sorption kinetic parameters of adsorbate uptake are important for choosing optimum operating conditions for the full scale batch process (Gupta *et al.*, 1997). These parameters which give information for the designing and modeling of the adsorption processes are also essential tools for the prediction of adsorption rate. In order to understand the underlying mechanism of any sorption process, different kinetic models have been proposed and used to analyze data obtained from different sorption experiments. Consequent upon this, data obtained from study of the effect of initial Pb²⁺ ion concentration effects were analyzed using Lagergren Pseudo first order, Pseudo second order (Ho, 1998) and Intraparticle diffusion kinetic models to explicate the mechanism guiding the sorption of Pb²⁺ by MMH. The linearized form of the pseudo –first order equation of Lagergren is generally expressed as follows:

$$\log (q_e - q_t) = \log(q_e) - \frac{t k_1}{2.303} \quad (5)$$

where q_e and q_t are the sorption capacity at equilibrium and time t respectively (mg/g). k_1 is the rate constant of pseudo – first order adsorption. A plot of $\log (q_e - q_t)$ against t gives a linear relationship from which the pseudo - first order parameters can be determined from the slope and intercept of the plot. The pseudo-second order kinetics represented by the linear equation presented below was also used to test the experimental data:

$$t/q_t = i/k_2q_e + 1/q_e t \quad (6)$$

where q_e , q_t and t have the same meaning as explained above. k_2 is the overall rate constants of pseudo-second order sorption ((g/mg)/min) . The plot of t/q_t against t of equation (6) should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot. The initial sorption rate (h) can be obtained from the pseudo-second order linear plots, as q_t/t approaches zero:

$$h = k_2 q_e^2 \quad (7)$$

Effect of initial Pb²⁺ concentration: Different concentrations of the adsorbate from 25 to 100 mg/L were used to study the effect of initial pb²⁺ concentration on the kinetics of adsorption by MMH. Agitation was carried out at 200 rpm for 120 min. The effect of initial concentration on the sorption of Pb ion is presented in Fig.2b. The plot obtained when the amount of Pb²⁺ adsorbed per gram of MMH was plotted against time showed that the rate of sorption was fast at the inception of the sorption studies and reduced as equilibrium was being approached. The sorbate removal increased with the increase in the initial concentration. This could be assumed to be due to the fact that resistance to the uptake of the sorbate decreased with the increase in sorbate concentration. This trend was common for all initial concentrations used. In order to understand the underlying mechanism of the sorption process under the influence of varying initial Pb²⁺ concentration, the data obtained from the sorption process were tested with different kinetic models as previously highlighted. When the data obtained from the adsorption experiment were interpreted with these kinetic models, the Lagergren pseudo-first order kinetic model was the least to conform to the description of the sorption of lead ion by MMH (Table 2).

Table 2: Kinetic Parameters for the sorption of Pb²⁺ by MMH at varying initial concentrations

Conc (mg/l)	Pseudo First Order					Pseudo Second Order					
	R ²	q _{e-cal}	q _{e-exp}	K ₁	SSE	R ²	K ²	q _{e-cal}	q _{e-exp}	h	SSE
25	0.9935	8.033	9.011	0.0466	0.2	0.983	0.0072	10.05	9.011	0.7272	0.2
50	0.8064	11.69	18.03	0.0522	1.2	0.979	0.0098	18.18	18.0	3.238	0.036
100	0.9435	20.45	33.021	0.0811	2.5	0.999	0.0240	33.22	33.021	26.486	0.044

q_{e-exp} : Experimental amount adsorbed per unit gram of MMH, q_{e-cal}- calculated amount adsorbed per unit gram of MMH, K₁,K₂- First and Second order rate constant, h- initial sorption rate , SSE-Statistical Sum of Error Square, Correlation coefficient –R²

Table 2 showed the kinetic experimental data for Pb²⁺ sorption onto MMH. Accepted kinetic model for a given adsorption is characterized by a good and high correlation coefficient, R² which is an indication of the

applicability and reliability of a given model, close agreement between the calculated and experimental qe values (precision test) and least values for error analysis squares for N number of data points which is determined as:

$$SSE (\%) = \frac{\sqrt{\sum (qe_{exp} - qe_{cal})^2}}{N} \quad (8)$$

Comparing the two models used, (Table 2) the deviations between the calculated qe values and the experimental qe values were relatively lower for pseudo second order than for Langeren Pseudo first order model and the pseudo second order gave a lower value for the SSE than Langeren pseudo first order. The regression coefficient values of the pseudo first order were found to be in the range of 0.9935–0.8064 which shows that the model can be applied but are not appropriate to describe the entire process. The Pseudo first order adsorption rate constant were in the range 0.0466–0.0811 (min^{-1}) for initial Pb^{2+} concentration of 25–100 mg/L. Ho *et al.*, (2000) considered pseudo second order equation to be appropriate for studying metal ion sorption. Sequel to this, the data obtained from the sorption experiment was tested with the pseudo second order kinetic model. The pseudo second order kinetic model considers the rate limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent and predicts the behaviour over the whole range of studies supporting a pseudo second order equation (Ho and McKay, 1998). The applicability of the pseudo second order kinetic model to experimental data is presented in Fig. 2a. The pseudo-second-order rate constant (k_2), the initial sorption rate (h) and the equilibrium sorption capacity (qe) were obtained from the slope and intercept of Eq. (6). The h and qe values of the MMH increased with increase in the initial concentration of the lead ion.

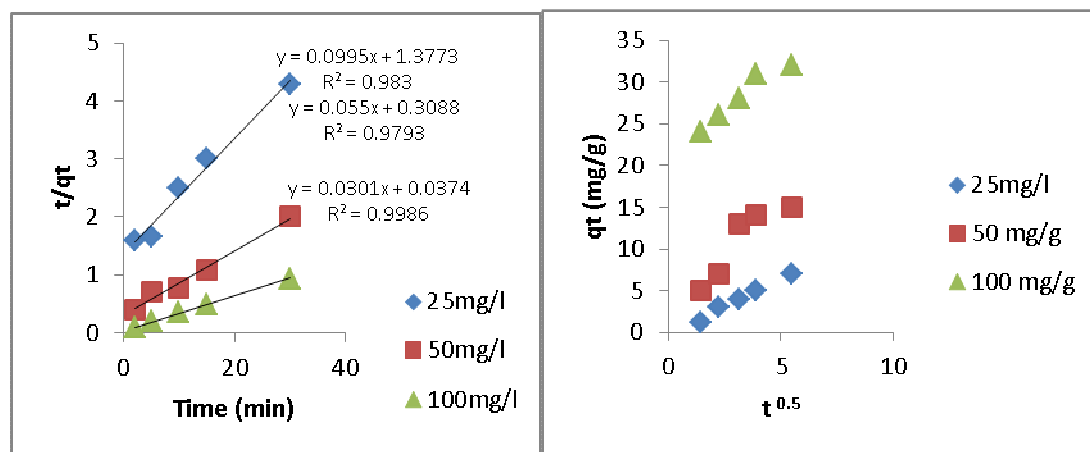


Fig. 3: (a) Applicability of pseudo-second-order kinetic model to experimental data at different initial Pb^{2+} concentration. (b) Intraparticle diffusion model

Adsorption process is usually controlled by three different steps: (i) transport of solute from the bulk solution to the film surrounding the adsorbent (ii) transfer from the film to the adsorbent surface leading to surface adsorption and (ii) diffusion from the surface to the internal sites followed by binding of the adsorbate to the active sites (Bhattacharyya *et al.*, 2004). The overall rate of the adsorption process is determined by the slowest steps. The intraparticle diffusion model was used to determine the rate determining step. According to the model, fractional uptake will vary with the function $(\Delta t/r2)^{1/2}$. For the intraparticle diffusion model, a plot of the amount of sorbate sorbed per unit weight of sorbent, (qt), versus square root of contact time, \sqrt{t} , gives a linear plot which indicate that intraparticle/pore diffusion is the rate limiting step in the sorption process. The results obtained when the intraparticle diffusion model was used to interpret the results of the effect of initial concentration of lead ion on the sorption process are presented in Fig 2b. The plots obtained indicated multilinear plots instead of a linear plot thus suggesting that intraparticle/pore diffusion is not the singular rate limiting step in the adsorption process but rather two or more steps influenced the adsorption process according to Weber and Morris (1963).

The plots showed that the data points can be related by two straight lines. The first straight line portion depicts macropore diffusion and the second represents micropore diffusion (Oladoja et al., 2010).

Effects of Dosage Amount: The variation in the extent of adsorption with the amount of adsorbent expressed in % removal is presented in Table 3. The adsorption increased rapidly as more and more of the adsorbent was added. The adsorption increased from 21.1% to 27.9% when the adsorbent amount was increased from 0.2g to 1.0g for a contact time of 2mins. Increasing the sorbent dosage makes a large number of sites available leading to an increase in adsorption.

Table 3: Variation in the extent Percentage Removal of Pb²⁺ on different dosages of MMH

Time (Mins)	0.2g	0.4g	0.6g	0.8g	1.0g
2	21.2	24.3	25.4	26.4	27.9
5	29.1	35.4	39.3	40.5	42.2
10	48.0	52.1	65.6	65.4	67.1
15	86.3	89.3	92.5	96.2	98.4
20	88.4	90.1	93.4	96.6	98.3
30	92.2	93.2	95.3	96.8	98.4
40	91.3	94.2	95.2	97.4	98.5
50	92.2	95.1	96.1	98.3	98.6
60	93.4	96.4	96.5	98.6	98.7
120	94.4	97.2	98.3	98.8	98.9

The results indicated that the amount of Pb²⁺ (q_t, mg/g) sorbed per gram of the MMH increased with time (Fig.3). When the values of q_t obtained for each MMH dosage were compared, the q_t values reduced with increase in sorbent dosage while the extent of adsorption (%) increased with increase in sorbent dosage. Similar trend have been previously reported (Ho, 1995, Ho and Ofomaja, 2005). Implying that the equilibrium adsorption capacity of the MMH is a function of the dosage used.

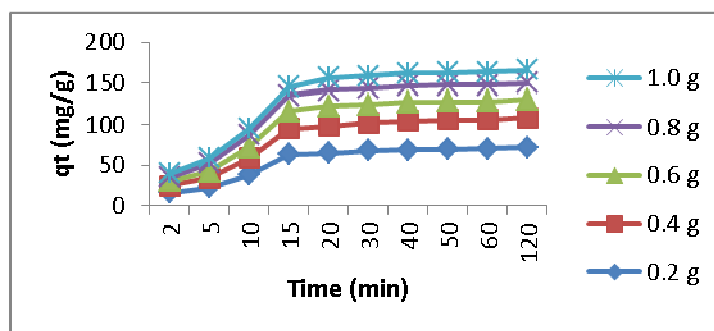


Fig 5. Plot of Amount of Pb²⁺ sorbed versus time at various initial MMH dosages.

CONCLUSION

The results obtained from the equilibrium adsorption isotherm studies showed that the capacity of MMH for lead ion was 52.08mg/g which competes very well with some other biosorbents for lead removal from aqueous system and that the sorption took place on heterogeneous surface of the MMH. The kinetic of the sorption was better described with pseudo second order models suggesting chemisorption mechanism of the sorption process. The intraparticle diffusion model might also play a significant role in the adsorption process slowing down the approach towards equilibrium. Optimum pH for lead sorption by MMH was 5 with a contact time of 30 mins

.This study showed that MMH is a promising low cost biosorbent for lead ions in aqueous system and a removal of 98% was possible at optimum conditions.

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