EQUILIBRIUM SORPTION OF Pb(II) AND NITRATE IONS FROM AQUEOUS SOLUTION USING CHEMICALLY MODIFIED RICE HUSK

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ABSTRACT

The ability of converting a waste product, rice husk, into an economically cheap adsorbents have been investigated for Pb(II) and NO_3^- removal from aqueous solution through adsorption. The Batch experiments show that the maximum sorption was obtained at the pH between 4 and 5 and at a temperature of 35^oC for both ions. Time dependent experiments for the nitrate ions showed that the binding to the husk was rapid and occurred within 50 minutes. The adsorption data followed both the Langmuir and the Freundlich equations but fitted best into the Freundlich model. The adsorption data were analyzed using the pseudo-first-order and pseudo-second-order kinetic equations and the results showed that the adsorption process followed pseudo-second-order kinetics. The sorption data were also correlated with Dubinin-Radushkevich adsorption model and the results showed that the adsorption process is physical.

Keywords: Rice husk, adsorption, heavy metals, nitrate ions, kinetic model

INTRODUCTION

Nitrate is a wide spread contaminant of ground and surface waters world wide (Hallberg, 1989; Pucket, 1995). It is a potential threat to human health especially in infants causing a condition known as methemoglobinemia also called “blue baby syndrome” (Pucket, 1995). In this condition, nitrate is converted to nitrite which then combines with hemoglobin to form methemoglobin and tends to decrease the ability of the blood to carry oxygen. Other health problems associated with chronic consumption of high level nitrates such as cancers have also been reported (Kross *et al.*, 1993). In a recent report by the United States Environmental Protection Agency (USEPA), Bacteria and Nitrates are the only two substances for which standards have been set that pose immediate threat to health whenever the limits are exceeded (USEPA, 1991). In addition, high nitrate levels in water and feeds can results in reduced vitality and increased still birth in livestock (National Academy of Sciences, 1972).

Industrial activities such as textile manufacturing, mining operations, paint & pigment manufacturing, storage batteries production and glass production processes have also led to the pollution of wastewaters by heavy metals like cadmium, nickel, lead, chromium and copper (Ong *et al.*, 2007). These metals have been reported to be non-biodegradable and carcinogenic to aquatic life, plants and humans (Abia & Asuquo, 2006). Because of these inherent dangers and threat to life posed by the accumulation of nitrates and this heavy metal Pb(II) in the body, their concentration in the environment have to be reduced to the barest minimum. Adsorption of heavy metals unto insoluble compounds has been the major means by which their removals are being effected. Efforts to produce cheap and efficient adsorbents have become necessary due to the increasing rise in the cost of the conventional adsorbents such as activated carbon. In this regard, the use of agricultural wastes like cotton seed hulls and sugar bagasse (Marshall & Champagne, 1995), acid modified rice husk (Ong *et al.*,

2007), shea butter seed husk (Eromosele *et al.*, 1996), cassava fibre (Okorie & Egila, 2002), sawdust (Chung *et al.,* 1992), and burnt clay (Mumin *et al.,* 2007), as adsorbents have been reported. It has also been shown that chemical modifications of these materials increased their sorption capacities (Ong *et al.*, 2007) and that the complicated and often expensive regeneration process associated with the conventional adsorbents is avoided (Ghole and Nagada, 2008) The adsorption studies of Zn(II), Cu(II), Hg(II) and Pb(II) metal ions on formaldehyde and pyridine modified bean husk and wood cellulose modified with urea and thiourea have been studied in our laboratory (Adediran *et al.*, (1999, 2007). The percentage of the sorbed metal ions by the modified wood cellulose was within the range of 72.9-86.9% for urea and 76.9-89% for thiourea.

Rice husk is a byproduct of the rice mills which consist mainly of hemicelluloses (HC), lignin (L), cellulose (C) and silica (Asian Energy Facility Project, 2004). Complete acid hydrolysis of cellulose yields D-(+) – glucose as the only monosaccharide while partial hydrolysis leads to cellobiose and higher member of the homologous series (Morrison and Boyd, 1990). The formation of various derivatives of cellulose proves that three alcoholic hydroxyl groups are free and can undergo substitution reactions. Further analysis of cellulose derivatives shows that two of the hydroxyl groups are secondary and the other one is primary (Vogel, 1961). Cellulose matrix can be modified to become positively or negatively charged by introducing acidic or basic group resulting in the formation of the cation and anion exchanger respectively. The anion exchanger ($-OCH_2CH_2-N^+(C_2H_5)_3$) in this work was produced by treating the cellulose with an amine (triethylamine) to enhance its sorption ability. Although attempts have been made by other authors to modify agricultural wastes into useful adsorbents as discussed above, but the literature is replete on the use of chemically modified rice husks as adsorbent for lead and nitrate ions removal from aqueous systems thereby necessitating this research.

MATERIALS AND METHODS

Materials: The rice husks were obtained from a local rice mill in Ilorin. The chemicals used were of analytical grade, and glass distilled and deionised water was used. The samples were washed with the deionised water after the removal of dirt and sand particles. They were then dried, grounded and sieved with a 0.6mm mesh sieve.

Modification of the samples: The method described by Vogel (1961) was adopted. 68g of anhydrous Zinc chloride and 18.5g of the sample were dissolved in 40ml of concentrated hydrochloric acid in a 200ml distillation flask. A reflux condenser was fitted into the mouth of this flask and the mixture heated gently on a wire gauge for several minutes. The solid material obtained was air dried and a mixture of 3g of this dried sample and 3ml of triethylamine was allowed to stand for 5 minutes. This modified sample was labeled **RCH** while the unmodified sample was labeled **RR**.

Adsorption procedures: 50ml of different concentrations of Pb(II) and NO_3^- were separately shaken with 1g each of the adsorbents on a thermostat shaker bath for a contact time of 6 hours. The mixtures were then allowed to stand for at least 1 hour after which the suspensions were filtered. The filtrates were analyzed for their nitrate and Pb(II) contents using the literature procedure (Vogel, 1961). Blank solutions were also shaken without adsorbent and the concentrations of the nitrates and Pb(II) determined and this was taken as initial concentration. The concentrations of the Pb(II) ions were determined using Atomic Absorption Spectrophotometer (SP-9 Unicam model) while nitrate ions concentrations were estimated using the UV-visible Spectrophotometer (Aquamate V60 model). The difference between the initial and final concentrations of the respective ions was calculated to be the amount adsorbed by the rice husks. The procedure was extended to determine the effect of contact time, temperature and pH on the adsorption capacities of the adsorbent.

RESULTS.

Adsorption Studies:

Effect of Initial adsorbate concentration: The adsorption capacities of both the RCH and RR were measured at different initial concentrations of the Pb(II) and NO_3^- ions from 13.0 to 100 mg L^{-1}. The results as presented in Figure 1 show that at higher concentrations of the adsorbates there is decrease in the amount adsorbed. This could be attributed to the greater competitions for adsorption sites on the adsorbent's surface because more molecules of NO_3^- would be involved (Gupta and Mohapatra, 2003). This same pattern was followed by the Pb(II) except that the decrease in adsorption was progressive and without a maximum as in the case of NO_3^-.

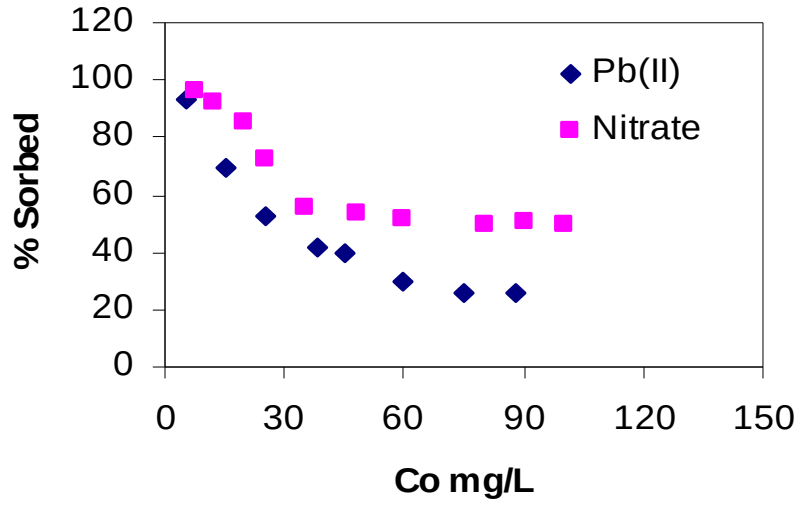


Figure 1: Effect of initial concentrations of Pb(II) and Nitrate ions at 308 K (contact time = 60 min, RCH dosage = 100 mg)

The effect of contact time: Figure 2 shows the effect of contact time on the rate of adsorption of NO_3^- and Pb(II) unto the modified rice husk. The adsorption rate increased from 44.8% to 94.7% for Pb(II) and from 38% to 78% for the NO_3^- with increase in contact time from 10 to 120 minutes. After this range, the concentrations of both ions in the test solution became constant. This trend could be attributed to the fact that at the initial time between 10-50 minutes there exist a large number of vacant sites on the adsorbent but after 50 minutes these sites became filled with the adsorbate molecules which at a point between 50 and 80 minutes the repulsive force between solute molecules and bulk phase becomes significant (Saravanane *et al.*, 2002).

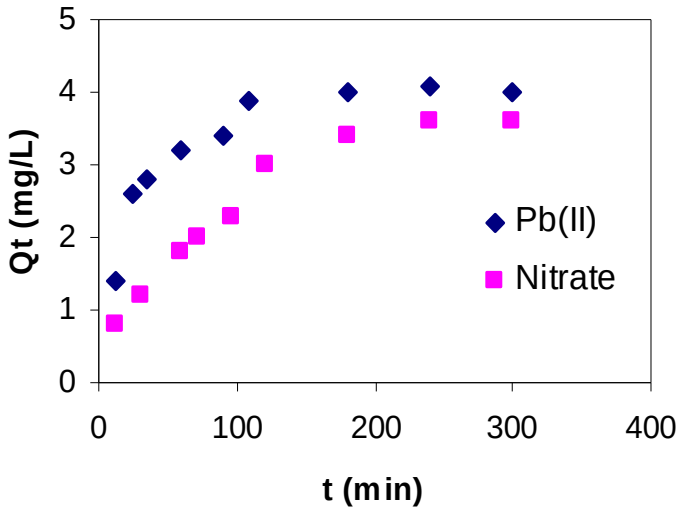


Figure 2: Effect of contact time on Pb(II) and NO_3^- adsorptions at 308 K ([Pb(II)] = [NO_3^-] = 100 mg L^{-1})

The effect of pH: As observed in Figure 3, the rate of adsorption increased with pH reaching a maximum and tends to decrease at pH above the maximum in both cases. This trend of pH

dependence of the adsorption rate is consistent with an ion exchange adsorption mechanism. The ionization constants reported for a number of COOH groups range between 3 and 5, thus at lower pH values the COOH retains their protons which reduced the probability of binding positively charged Pb(II) ions but at pH very close to 4, the ionized COO^- will attract readily Pb(II) thereby leading to faster rate of adsorption. The nitrates ion adsorption with respect to the pH could also be explained in the same manner except that binding to the rice husk is expected to be through the amino groups on the adsorbent surface. These results thus indicate that binding of these ions to the adsorbent follows an ion-exchange mechanism involving electrostatic interaction between the appropriate groups on the adsorbent and the ions of the adsorbates. This observation agrees with the literature reports (Leo *et al.*, 1995).

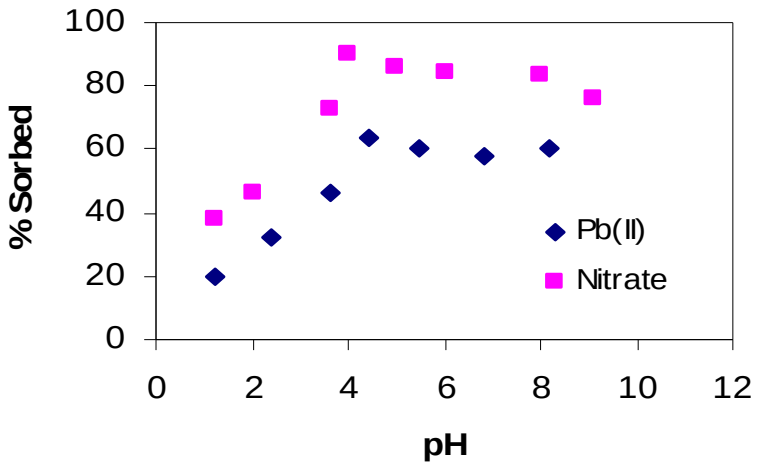


Figure 3: Effect of pH on the adsorption of Pb(II) and Nitrate ions on RCH at 308 K (RCH dose = 20 g L^{-1}, contact time = 60 min, [Pb(II)] = [NO_3^-] = 100 mg L^{-1})

Effect of temperature on the adsorption: The adsorption capacities of the modified rice husk for both Pb(II) and NO_3^- were measured at different temperatures between 303 and 333 K. The results shows that there is a gradual increase in the % removal from 42.63 to 69.76 which indicate that the adsorption process may be diffusion controlled and also an

endothermic process since the rise in temperatures favours the adsorbate transport within the pores of the modified rice husk (El-Shafey, 2005).

DISCUSSIONS.

Adsorption isotherms: The above results were analyzed using the following adsorption isotherms.

The Freundlich isotherm: The results obtained from the adsorption of Pb(II) and nitrates ions onto the modified rice husks were subjected to Seller's version of the Freundlich adsorption equation (Sellers *et al*., 1980), as

$$\text{Log } Q_e = \log k_f + {}^{1}/_{n} \log C_e \qquad (1)$$

Where k_f is Freundlich constant indicating adsorption capacity, n is a constant usually greater than unity, C_e is the equilibrium concentration of the nitrate in mg/L and q_e is the amount of nitrate adsorbed per unit amount of adsorbent given by

$$Q_e = \frac{(C_o - C_e)V}{m} \qquad (2)$$

Where C_o and C_e is the initial and equilibrium concentrations of the nitrate solution in mg/L respectively, V is the volume of the nitrate in liters (L) and m is the mass of the adsorbent in gramme (g).

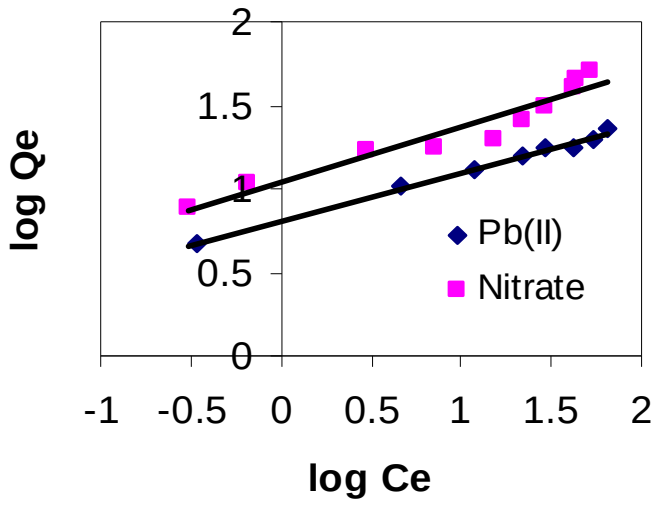


Figure 4: Freundlich adsorption isotherm for the adsorption of Pb(II) and Nitrate ions on RCH at 308 K (RCH dose = 100 mg, contact time = 60 min)

The plots of log Q_e against log C_e (Figure 4) were linear in both cases, values of Freundlich exponent n and adsorption capacities k_f determined from the slopes and intercept of these plots are recorded in Table 1. The value of n in both cases lies between 2 and 10 which indicate a favourable adsorption (Treybal, 1980).

Table 1: Adsorption isotherm parameters for Pb(II) and NO_3^- ions adsorption on RCH (temp = 303 K, RCH dose = 100 mg,)

	Langmuir				Freundlich			D-R			
	Q_o (mg g^{-1})	R_L	b (L mg^{-1})	R^2	k_f (mg g^{-1})	n (L mg^{-1})	R^2	q_D (mg g^{-1})	B_D (mol^2 kJ^{-2})	E_D (kJ mol^{-1})	R^2
Pb(II)	22.73	0.06	0.16	0.9716	6.47	3.46	0.9920	26.74	0.015	5.73	0.8218
NO_3^-	51.55	0.10	0.09	0.8196	11.01	3.06	0.9210	47.08	0.16	5.53	0.6078

The Langmuir isotherm: The experimental data were also fitted into the Langmuir adsorption isotherm equation of the form (Guo *et al.*, 2009),

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \qquad (3)$$

Where Q_e is the amount of solute adsorbed per amount of adsorbent, Q_m and b are Langmuir constants indicating adsorption capacity and energy of adsorption respectively. The values of Q_m and b for the adsorption of each ion were determined from the slopes and intercepts of the linear graphs obtained from the plots of C_e/Q_e against C_e (Figure 5).

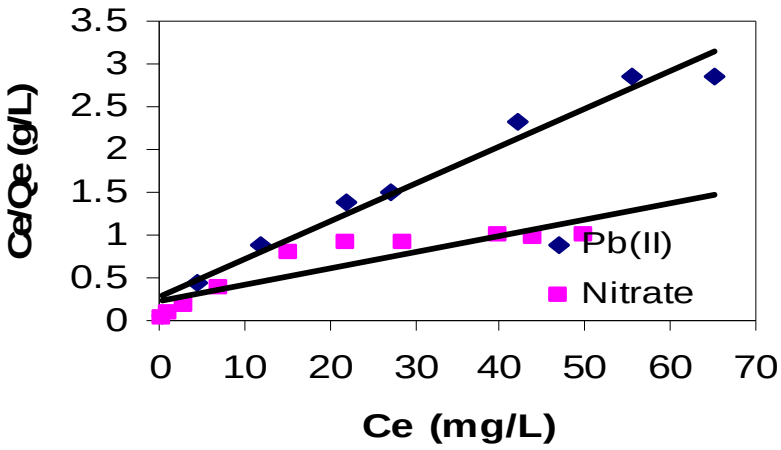


Figure 5: Langmuir adsorption isotherm for the adsorption of Pb(II) and NO_3^- on RCH at 308 K (RCH dose = 100 mg, contact time = 60 min)

The favourability of the adsorption process in terms of the Langmuir model can be determined by the value of a dimensionless constant R_L (Hall *et al.*, 1966), or otherwise known as separation factor given by the equation below:

$$R_L = 1/(1 + bC_o) \quad (4)$$

Where b is the Langmuir constant (L mg^{-1}) and C_o (mg L^{-1}) is the initial concentration of Pb(II) and NO_3^-. The value of R_L can take any of the following four possibilities, for favourable adsorption, $0 < R_L < 1$, unfavourable adsorption $R_L > 1$, linear adsorption $R_L = 1$ and irreversible adsorption, $R_L = 0$. In all cases in this present study, the value of $R_L$is greater than 0 but less than 1 (Table 1), therefore the adsorption process is favourable.

Dubinin-Radushkeevich adsorption model: To determine whether the adsorption of these ions had occurred through physical or chemical processes, the equilibrium data were fitted into the Dubinin-Radushkevich (D-R) model (Bansal *et al*., 2009). The D-R equation is given by

$$Log_{10}q_e = \log_{10}q_D - 2B_DR^2T^2\log_{10}(1 + 1/C_e) \quad (4)$$

Where q_D is the theoretical saturation capacity (mg g^{-1}), B_D is a constant related to adsorption energy ($mol^2\ kJ^{-2}$), R is the gas constant (kJ $mol^{-1}\ K^{-1}$) and T is the absolute temperature (K). From equation 4 above, a plot of $\log_{10}q_e$ against $\log_{10}(1 + 1/C_e)$ is expected to give a straight line as obtained in this study (Figure 6).

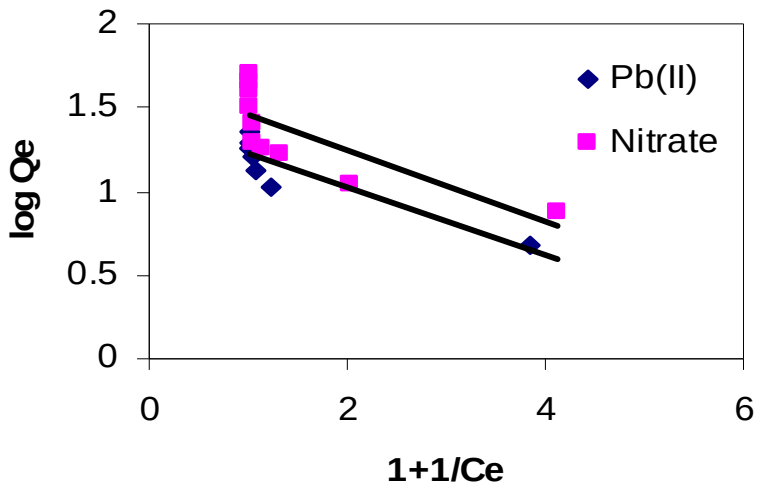


Figure 6: The Dubinin-Radushkeevich adsorption isotherm for the adsorption of Pb(II) and Nitrate ions on RCH at 308 K (RCH dose = 100 mg, contact time = 60 min

The values of q_D and B_D have been estimated from the values of the slope and intercept for both ions and the results are recorded in Table 1 above. The mean free energy of adsorption per molecule of the adsorbate E_D (kJ mol^{-1}) (Hall *et al*., 1966), when transported to the

surface of the solid adsorbent in the solution is related to the constant B_D in the D-R model equation by

$$E_D = 1/\sqrt{2B_D} \quad (5)$$

The mean free energy E_D which is also known as the sorption energy depends on the nature of the adsorbent and adsorbate and also is independent of the temperature of the system. According to the literature reports (Bansal *et al.*, 2009), if the value of E_D falls between 1-8 kJ mol^{-1} then the adsorption process is physical while the E_D values between 9-16 kJ mol^{-1} correspond to chemisorptions. In the present study, the calculated values of E_D for Pb(II) and NO_3^- ions are 5.6 and 5.27 respectively which indicates a physical adsorption process for the adsorption of both ions unto the modified rice husk.

Adsorption kinetics: The mechanism of NO_3^- and Pb(II) adsorptions on the modified rice husk was further examined by subjecting the experimental data to pseudo-first-order and the pseudo-second-order kinetic models.

Pseudo-first-order kinetic model: The linear form of Langergren's pseudo-first-order kinetic equation (Guo *et al.*, 2009), was adopted. This equation is given by

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

Where q_e and q_t are the amount of Pb(II) and NO_3^- adsorbed (mg g^{-1}) at equilibrium and at time t respectively and k_1 is the pseudo-first-order rate constant (min^{-1}) of the adsorption process. From the above equation it is expected that the plot of $\log(q_e - q_t)$ against t should be linear with a slope of $-k_1/2.303$ (Figure 7). The values of k_1 and q_e calculated from the plots are recorded in Table2.

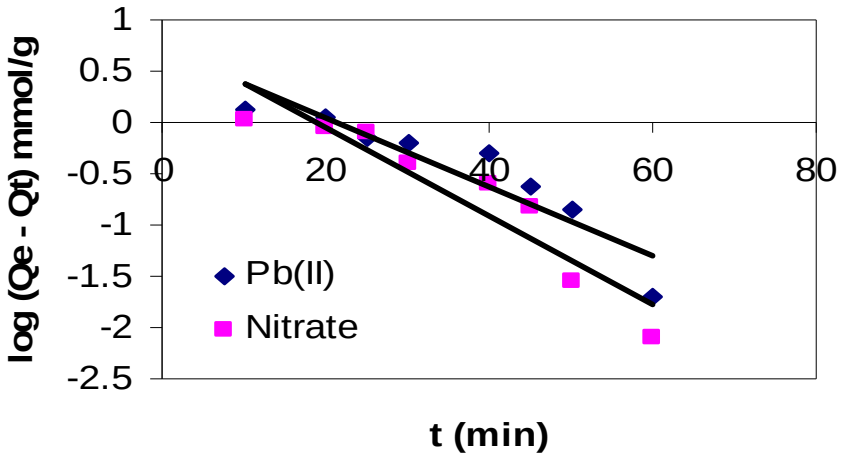


Figure 7: The Lagergren's pseudo-first-order kinetic plot for the adsorption of Pb(II) and Nitrate ions on RCH at 308 K (RCH dose = 100 mg L^{-1}, contact time = 60 min)

Table 2: Kinetic parameters for the adsorption of Pb(II) and NO_3^- on RCH at 308 K

Pseudo-first-order					**Pseudo-second-order**				
	Q_e(exptal)	Q_e(theor)	k_1(min^{-1})	R^2		Q_e(exptal)	Q_e(theor)	k_2(g mol^{-1} min^{-1})	R^2
Pb(II)	3.65	4.98	0.076	0.8464	Pb(II)	4.18	4.36	0.012	0.9974
NO_3^-	5.46	6.48	0.10	0.8781	NO_3^-	5.02	4.71	0.0026	0.9759

Pseudo-second-order kinetic model: The experimental data were also analyzed using the second-order kinetic model equation of the form (Ho, 2006),

$$\frac{t}{Qt} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (5)$$

where Q_t is the amount of Pb(II) and NO_3^- adsorbed per unit mass of adsorbent (mg g^{-1}) at time t (min), Q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}) at

equilibrium, k_2 is the pseudo-second-order rate constant. The values of k_2 and q_e are determined from the values of the slopes of the plots of t/q_t against t (Figure 8) and are recorded in Table 2. From the R^2 values in table 2, it is observed that the experimental data fitted well into the second-order kinetic equation better than the first-order equation. This suggests that the adsorption process followed the pseudo-second-order kinetics. The value of q_e determined from the experiment and the theoretical value of q_e calculated from the slopes of these plots are almost the same, which lend further support to the fact that the adsorption process followed a pseudo-second-order kinetic model (Ho, 2006).

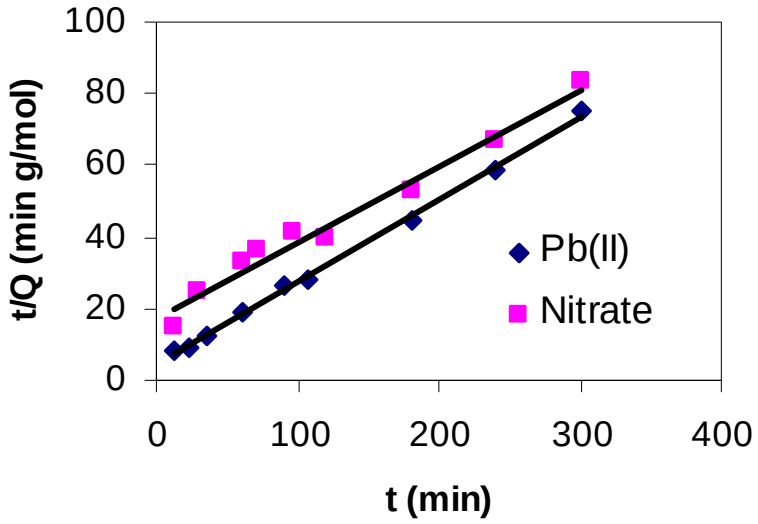


Figure 8: The pseudo-second-order plots for the adsorption of Pb(II) and Nitrate ions on RCH at 308 K (RCH dose = 100 mg L^{-1}, contact time = 60 min)

Adsorption thermodynamic studies: Thermodynamic activation parameters for the adsorption of Pb(II) and NO_3^- ions on RCH were estimated in the temperature range of 303-338 K. These parameters include the Gibb's free energy change (ΔG^o), standard entropy change (ΔS^o) and the standard enthalpy change for the adsorption process (ΔH^o). The

equilibrium constant K_D for the adsorption process is related to the Gibb's free energy change, ΔG^o, by the relation:

$$\Delta G^o = -RT\ln K_D \quad (6)$$

And K_D in this case is estimated using the equation below (Guo *et al.*, 2009):

$$K_D = \frac{Q_e}{C_e} \quad (7)$$

Where Q_e is the amount of adsorbate (mg L^{-1}) adsorbed per Litre of the adsorbent and C_e is the equilibrium concentration of the adsorbates in the solution (mg L^{-1}). The K_D, ΔS^o, and ΔH^o according to equation 6 above will be related by:

$$\log K_D = \frac{-\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R} \quad (8)$$

Since $\Delta G^o = \Delta H^o - T\,\Delta S^o$ (9)

From equation 8 above, the values of ΔH^o and ΔS^o can be estimated from the values of the slopes and intercept of the linear plot of $\log K_D$ versus 1/T (Figure 9). The calculated values are recorded in Table 3.

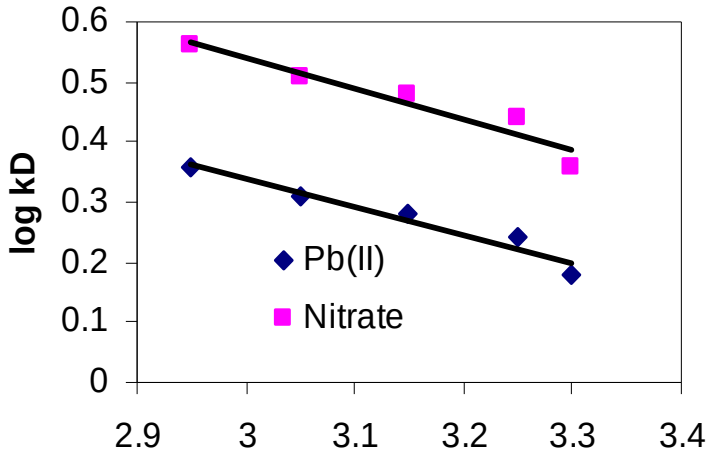


Figure 9: Effect of temperature on the adsorption of Pb(II) and Nitrate ions on RCH (RCH dose = 100 mg, contact time = 60 min, [Pb(II)] = [NO_3^-] = 100 mg L^{-1})

Table 3: Thermodynamic activation parameters for the adsorption of Pb(II) and NO_3^- on RCH.

Temp. (K)	K_D		ΔG^o (kJ mol^{-1})		ΔH^o (kJ mol^{-1})		ΔS^o (J mol^{-1} K^{-1})	
	Pb(II)	NO_3^-	Pb(II)	NO_3^-	Pb(II)	NO_3^-	Pb(II)	NO_3^-
303	1.51	2.30	-1.04	-2.08	9.48	8.94	38.7	33.3
308	1.74	2.75	-1.42	-2.59				
318	1.91	3.02	-1.70	-2.92				
328	2.04	3.16	-1.90	-3.14				
338	2.29	3.63	-2.33	-3.62				

The negative values of ΔG^o indicate that the adsorption process is very feasible and that the adsorption processes occurred spontaneously.[30] Positive values of ΔS^o in both adsorptions indicate that there is increase in randomness in the RCH-Pb(II) and RCH-NO_3^- interface during adsorption while positive ΔH^o values also supports the earlier assertion that the

adsorption process is endothermic. The physical adsorption process proposed in section 3.2.3 is further supported by the value of ΔH^o that falls between -20 and 40 kJ mol^{-1} i.e. the range for a physisorption process of adsorption (Lian *et al.*, 2009).

CONCLUSION

The results from this study showed that the chemically modified rice husk has considerable potentials for the removal of nitrate and Pb(II) ions from aqueous solutions over a wide range of experimental conditions through adsorption. The rate of adsorption decreased with adsorbate concentration and the equilibrium experiments showed that maximum adsorption occurs at the pH of 4.5 and temperature dependent. The adsorption process followed the Langmuir and Freundlich model but fitted more to the Freundlich model. The kinetic studies also revealed that the adsorption process followed a pseudo-second-order kinetics. Hence, the rice husks which are readily available and cheap could be good candidate for Pb(II) and nitrate ions removal from contaminated waters.

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