



ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(13):9-15
(<http://derpharmachemica.com/archive.html>)

The potential of a natural clay mineral (NSU clay) for the adsorption of lead (ii) ions from aqueous stream

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ABSTRACT

The adsorption of Pb(II) from aqueous solution on Nsu clay as an adsorbent was determined. The aim of the study was the utilization of Nsu clay as a cheap alternative adsorbent for the removal of Pb(II) ions from industrial wastewaters, this is to help reduce the high cost involved in using traditional methods to treat effluents. The experiment was performed using batch technique. The batch adsorption study was carried out as a function of initial solution pH, contact time and initial Pb(II) concentration. An increase in adsorption with increase in pH was obtained. The adsorption process was found to be rapid as equilibrium was attained within 50 minutes. The result showed an increase in adsorption capacity with increase in Pb(II) concentration, although the actual percentage removal showed a decrease with increase in concentration. Among the three isotherms tested, the Langmuir isotherm gave the best fit with regression, R^2 value of (0.969) followed by the Freundlich isotherm, (0.948) and then the Dubinin-Radushkevich, (0.945). Although the isotherms studied were each appropriate in the description of the adsorption data. The constant b obtained from the Langmuir isotherm indicated a high affinity of Nsu clay for Pb(II) ions. The value of the apparent energy of adsorption, E , (100 kJ/mol) showed that the process is mainly particle diffusion controlled. These results suggested the applicability of Nsu clay as a low-cost adsorbent for Pb(II) removal from aqueous solution.

Keywords: Adsorption, Equilibrium isotherm, Lead, Nsu clay, Pb(II).

INTRODUCTION

The growth of Industries in Nigeria and most developing Nations has increased enormously industrial effluents which are highly contaminated with various heavy metals. The heavy metals are present in effluents from different industries such as ceramics, tanneries, mining, metal plating, paints, catalyst, alloy, galvanizing iron, wire conducting, pigments, dyes and wood preservation [1]. Heavy metals have been found to be hazardous to health and environment and noted to be toxic even at low concentrations. Lead is one of the most toxic and can result in kidney, reproductive system, liver and brain damages in Humans. Lead poisoning causes a range of health effect from behavioural problems and learning disabilities to seizures and death. Due to these problems scientist over the world have made use of different techniques for the removal of Lead and other heavy metals from effluents. These techniques include ion exchange, precipitation, reverse osmosis, solvent extraction and activated carbon adsorption. However, these techniques are expensive, require trained personnel and are usually ineffective especially when the metal concentration in solution is in the range 1-10 mg/l. As a result, present day researchers have worked on and are still researching on the use of cheap materials such as agricultural waste biomass, soil and clay for adsorption of Pb(II) and other metal ions from solution [2-15]. Adsorption on these materials have been found to be effective.

In the Eastern part of Nigeria, there is a large availability of clay materials which are cheap and easily accessible and thus can be used as cheaper alternatives for Lead removal. This paper reports the application of Nsu clay

obtained from Okigwe Zone, Imo State Nigeria as a cheap adsorbent for Pb(II) removal. The effect of pH, contact time and initial metal ion concentration were investigated. Langmuir, Freundlich and Dubinin-Radushkevich equilibrium isotherm models were applied to the experimental data.

MATERIALS AND METHODS

Adsorbent Preparation and Characterization

Nsu clay was obtained from Okigwe Zone, Imo State, Nigeria. The clay was soaked in excess distilled water in a pre-treated plastic container, stirred to ensure uniform dissolution and then filtered in order to get rid of unwanted particles. The filtrate was allowed to settle for 48hrs after which excess water was decanted off. The clay was sundried for several days to get rid of water molecules, then oven dried at 105°C for 2hrs. The dried clay was then crushed and passed through a mesh sieve of size 100µm and kept until use.

The chemical composition of Nsu clay was determined by classical method with the use of the Atomic Absorption spectrophotometer (AAS) (Buck Scientific Model 210VGP). The specific surface area (SSA) of the clay was determined by the methylene blue adsorption test method described elsewhere [11]. The pH point of zero charge was obtained by the method described previously [11].

Adsorbate preparation

De-ionized water was used for preparing and dilution of all solutions, analytical grade of Pb(NO₃)₂ was used. 6 different standard solutions of Pb(II) with different concentrations ranging from 2 – 12 mg/l were prepared by dissolving appropriate amounts of Pb(NO₃)₂ in water. The pH of each solution was adjusted to the required value by the drop wise addition of 0.1M HNO₃ or 0.1M NaOH when required by the use of a pH meter. In each adsorption study freshly prepared solution was used.

Adsorption experiment

Batch adsorption method was used by contacting 2g of Nsu clay with 20ml of a given solution, at a room temperature of 27°C, the mixture was agitated and left for a given contact time. At the end of the given time, the solution was filtered and the filtrate was analyzed for the concentration of Pb(II) remaining using the AAS. The experiment was repeated and the mean value calculated. The amount of Pb(II) adsorbed and the percentage removal was calculated from equation (1) and (2) respectively.

$$q_e = V[C_o - C_e]/m \quad (1)$$

$$\%R = 100[(C_o - C_e)/C_o] \quad (2)$$

Where q_e (mg/L) is the equilibrium uptake capacity of the clay, C_o (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of Pb(II) respectively, V (L) is the volume of adsorbate and m (g) is the mass of Nsu clay used.

RESULTS AND DISCUSSION

Characterization of Nsu Clay

The result for the chemical characterization of Nsu clay is shown in Table 1. It is seen that silica and Alumina make up a large composition of the clay. Other elements are present in minute quantities. It is expected that Lead (II) ions in solution should be removed mainly by the silica and alumina groups on the clay surface.

TABLE 1: Chemical Characterization of Nsu Clay [8]

Composition	% by Weight
SiO ₂	46.25
Al ₂ O ₃	38.41
CaO	0.87
Fe ₂ O ₃	0.71
MgO	0.39
LOI	13.37
SSA (m ² /g)	=21.53
pHpzc	= 4.2

Influence of initial Solution pH on sorption

The effect of initial solution pH is an important factor to be determined because it affects the solubility of metal ions, concentration of counter ions on the active sites of the adsorbent and the degree of ionisation of the adsorbate during reaction [16]. Fig.1 depicts the effect of pH on the adsorption of Lead (II) ions by Nsu clay. The result showed that with increase in pH of the solution from 1 to 8 there was a corresponding increase in the amount of

cadmium (II) ions adsorbed. As, expected, the adsorption of lead ions decreased with decrease in pH because the aluminol and silanol groups are more protonated and hence are less available to retain the lead ions [17]. Surface complexation reactions are affected by the electrostatic attraction between the surface charge and the dissolved ions, since lead has a large ionic radius (1.20Å), it has a low charge density and is therefore affected by the protonation of the surface groups on the clay. Also, according to Badmus *et al* [16] as the solution pH increases, the onset of metal hydrolysis and precipitation begins at pH values greater than 6. Although maximum uptake was achieved at pH 8.0, sorption experiments were conducted at pH 6.0 in order to avoid metal precipitation at higher pH values. Similar results have been reported [11,12,17].

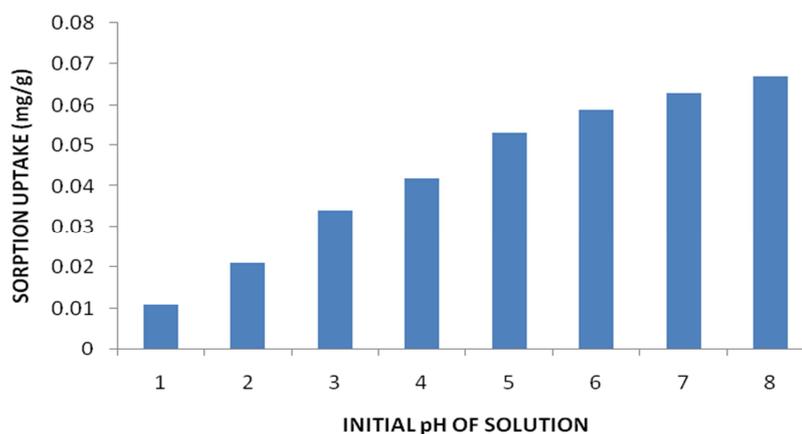


Fig.1: Effect of pH on the Adsorption of Lead (II) ions unto Nsu clay (Conc, 12mg/l, time, 2hrs, temp, 300K)

Effect of Contact Time

The effect of contact time on adsorption was determined in order to establish the rate at which adsorption takes place and the equilibrium time. The result on the effect of contact time on the sorption of lead (II) ions by Nsu clay is shown in Fig.2. The result showed a rapid increase in adsorption at the initial stage up to 50 minutes after which there was no significant increase in the rate of adsorption. This indicated that equilibrium was established within 50 minutes and the adsorption process is a rapid one. The fast uptake at the initial stages is due to the presence of abundant active sites for sorption, but as time progresses the active sites became used up and saturated leading to the insignificant adsorption noticed with time. Sorption experiments were performed at a contact time of 2hrs hence we ensured equilibrium attainment. Similar finding on the use of clay for the adsorption of heavy metals have been reported [9, 18].

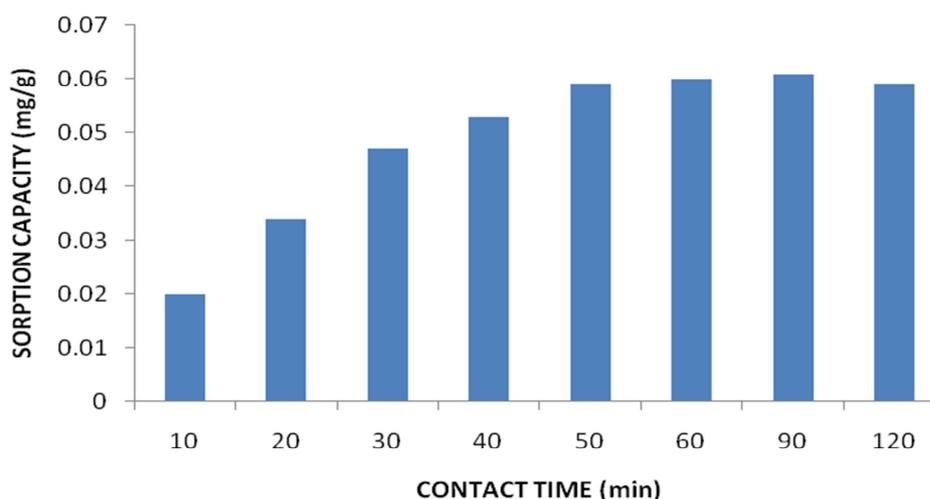


Fig.2: Effect of contact time on the adsorption of Lead (II) ions unto Nsu clay (pH, 6.0, conc, 12mg/l, temp, 300K)

Effect of initial Pb(II) ion concentration

The initial metal ion concentration of an adsorbate has been found to be an important factor in adsorption studies. The initial metal ion concentration determines the amount of metal ions adsorbed by the adsorbent in the presence of available binding sites. The effect of initial Pb(II) ion on adsorption on Nsu clay was performed at a contact time of

2hrs to ensure equilibrium was attained, the result is shown in Fig.3. As seen, an increase in adsorption capacity with increase in concentration was obtained, this is accounted for as due to higher availability for metal ions for sorption.[19]. As the concentration increases there is an increase in the collision between Pb(II) ions and the active sites on the clay, this is a major factor in kinetics for increase in the rate of chemical reaction. Also it is obvious that for higher initial concentration more efficient utilization of active sites is expected due to a greater driving force by a higher concentration gradient. However, a decrease in the percentage of Pb(II) on Nsu clay removed was seen in Fig.4, this can be explained that at lower concentrations more active sites are available for sorption, but as the concentration increased the sites became occupied hence a decrease in the percentage removed.

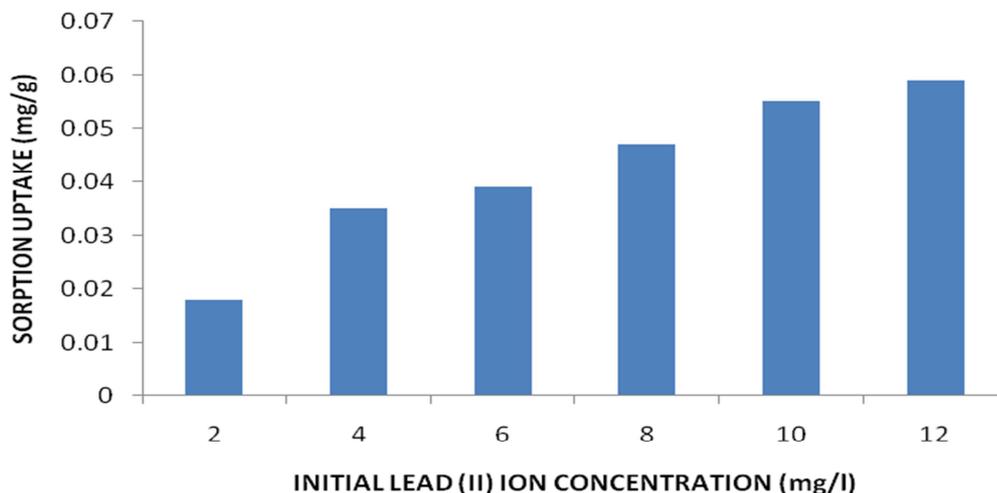


Fig.3: Effect of initial Lead (II) ion Concentration on the adsorption capacity of Nsu clay (pH 6.0, time, 2hrs, temp, 300K)

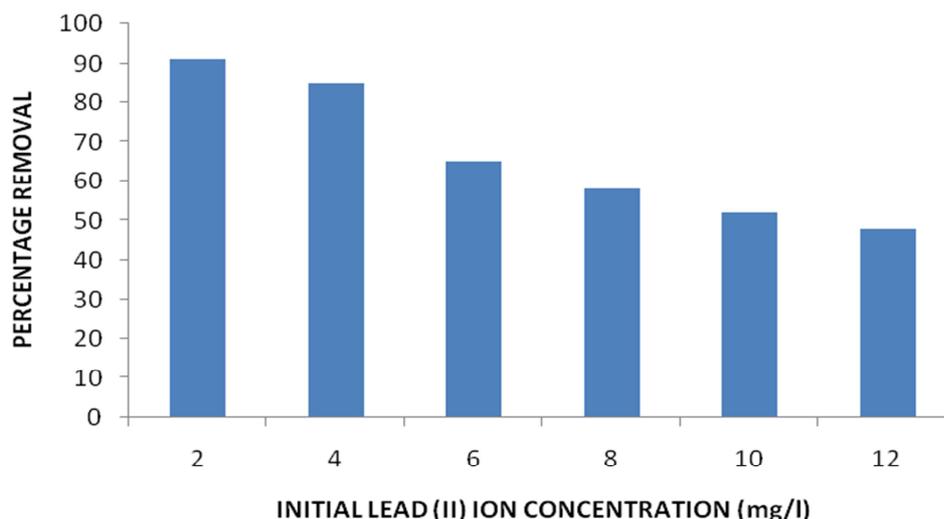


Fig.4: Effect of Initial Lead (II) ion Concentration on Its Percentage removal by Nsu clay (pH 6.0, time, 2hrs, temp, 300K)

Table 2: Langmuir, Freundlich and Dubinin-Radushkevich Isotherm Parameters

Langmuir isotherm			Freundlich Isotherm				Dubinin-Radushkevich isotherm			
qm	b	R ²	n	1/n	Kf	R ²	qD	BD (mol ² /kJ ²)	E(KJ/mol)	R ²
0.066	1.19	0.969	3.044	0.329	0.033	0.948	0.051	0.00005	100	0.912

Equilibrium Isotherms

Equilibrium adsorption isotherms are generally used to describe the relationship between the amount of metal ion adsorbed and its equilibrium concentration in solution. Among different isotherms used to explain the nature of adsorption, the most common are the Freundlich and Langmuir isotherms. These two isotherms and the Dubinin-Radushkevich isotherm were applied in this study. The isotherms were gotten from the data obtained on the effect of initial Pb(II) ion concentration on sorption. These isotherms even though do not explain the mechanism of sorption, they are useful for comparing results on a quantitative basis and have easily interpretable constants which provides information on the adsorption ability of a material.

Langmuir Isotherm

The Langmuir isotherm is applied to a monolayer sorption onto a surface containing a finite number of identical binding sites on the adsorbent [20]. It is used to estimate the maximum adsorption capacity as a result of complete monolayer coverage. The linear form of the Langmuir isotherm model is given in equation (3).

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

Where b is a constant related to the affinity between the sorbate and the sorbent and q_m is the maximum adsorption capacity under the given condition. The Langmuir isotherm plot for the sorption of Pb(II) ion on Nsu clay is shown in Fig.5 and the isotherm parameters are given in Table 2. The value of the linear regression coefficient (R^2) obtained showed that this isotherm gave a good fit to the adsorption data. The value of b shows the affinity between the adsorbent and adsorbate, a low value of b indicates a high affinity of the adsorbent for the adsorbate in the adsorption process [21]. The low value of b obtained in this experiment suggested that Nsu clay has a high affinity for Lead ions.

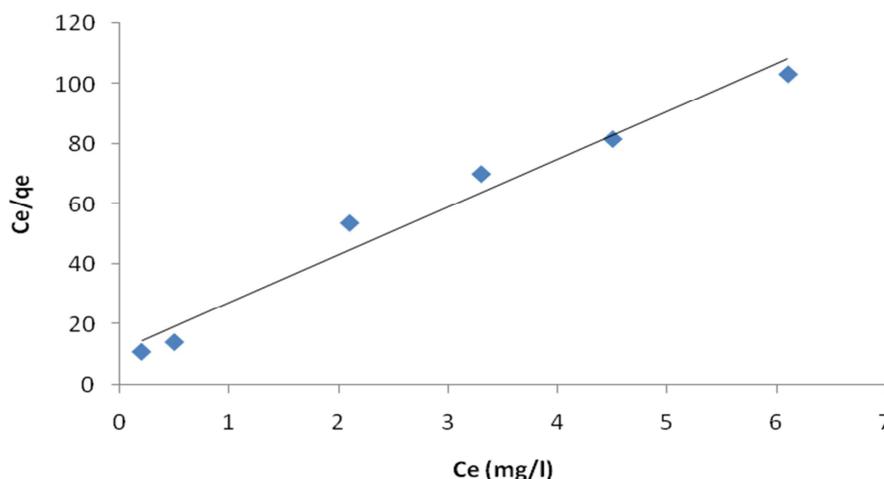


Fig.5: Langmuir Isotherm model on the sorption of Lead (II) ions unto Nsu Clay (pH 6.0, time 2hrs, temp 300K)

Freundlich Isotherm

The Freundlich isotherm unlike the Langmuir isotherm assumes that the removal of metal ions occurs on a heterogeneous adsorbent surface and can be applied to multilayer adsorption of metal ions [22]. This isotherm usually gives an appropriate description of experimental data over a restricted range of concentration. The linear form of the Freundlich isotherm is given in equation (4)

$$\ln q_e = [1/n] \ln C_e + \ln k_f \quad (4)$$

where n is an empirical parameter related to the adsorption intensity and k_f is a constant related to the adsorption capacity (mg/g). The Freundlich isotherm for the adsorption of Pb(II) on Nsu clay is shown in Fig.6 and the isotherm parameters are given in Table 2. The R^2 value obtained clearly suggest the applicability of this isotherm to the adsorption process. When the value of n is greater than unity it indicates a favourable adsorption [23]. The value of n obtained in this study is greater than unity which indicates that the adsorption of Pb(II) on Nsu clay is a favourable adsorption. Also, when the value of $1/n$ is less than unity it indicates that significant adsorption takes place at low concentration but becomes less significant at higher concentrations. This value obtained in our experiment is less than unity which accounts for the decrease in percentage adsorbed with increase in concentration observed in Fig.4.

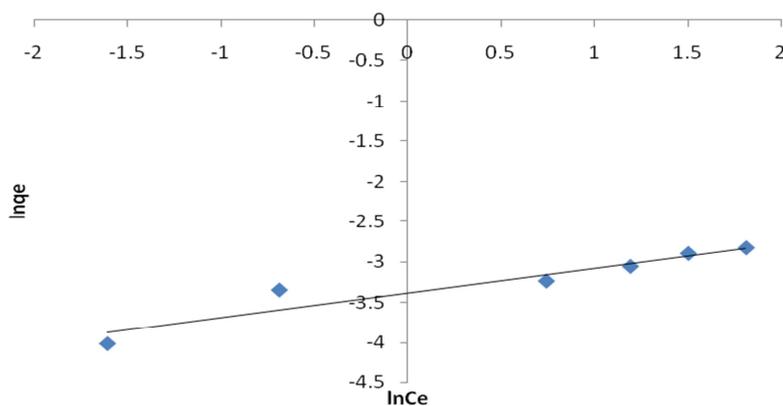


Fig.6: Freundlich Isotherm model on the sorption of Lead (II) ions unto Nsu Clay (pH 6.0, time 2hrs, temp 300K)

Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich isotherm was applied in this study to deduce the apparent energy of adsorption, E [24]. The linear form of the equation is given in equation (5) and the apparent energy of adsorption in equation (6).

$$\ln q_e = \ln q_D - B_D [RT \ln(1 + 1/C_e)]^2 \quad (5)$$

$$E = 1/(2B_D)^{1/2} \quad (6)$$

Where the constant q_D (mg/g) represents the Dubinin-Radushkevich constant related to the adsorption capacity and B_D (mol^2/J^2) is a constant related to the mean free energy of adsorption per molecule of adsorbate, T (K) and R represents the temperature and ideal gas constant respectively. The Dubinin-Radushkevich isotherm plot is shown in Fig.7 while the isotherm parameters are recorded in Table 2. The R^2 value obtained also showed that this isotherm provided a good fit to the experimental data. Furthermore, if the magnitude of the Energy of adsorption lies between 8 and 16 kJ/mol the adsorption process is said to be a chemisorptions, if the value of E is below (kJ/mol) physisorption dominates the adsorption mechanism and if $E > 16$ kJ/mol the process is dominated by particle diffusion [25]. The value of the apparent energy of adsorption indicated that the adsorption of lead (II) ions unto Nsu clay is dominated by particle diffusion mechanism.

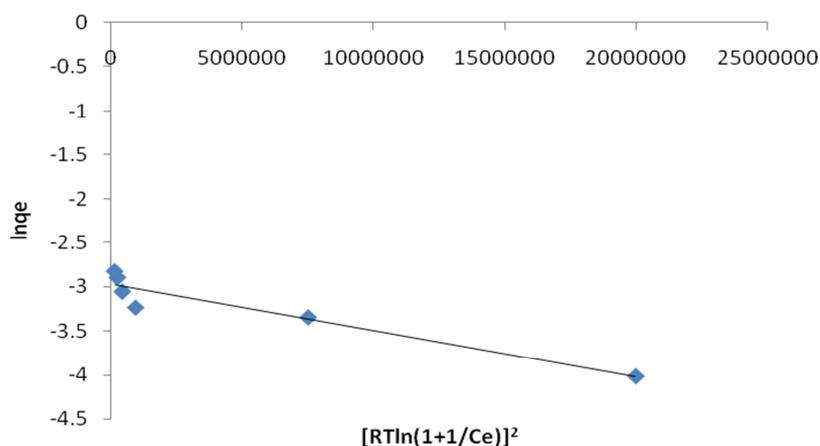


Fig.7: Dubinin-Radushkevich Isotherm model on the sorption of Lead (II) ions unto Nsu Clay (pH 6.0, time 2hrs, temp 300K)

CONCLUSION

The experimental results obtained showed that Nsu clay can be used as a good and cheap adsorbent for Pb(II) removal from effluents. The Langmuir, Freundlich and Dubinin-Radushkevich isotherm all gave a good description of the adsorption process.

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