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Removal of Pb^{2+} onto HDTMA-Br Modified Kaolinite Clay as function of pH: Batch Sorption, Isotherms and Kinetics

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Abstract: *Adsorption removal of toxic heavy metals from wastewaters is considered as one of the most important methods of wastewater treatment due to its low maintenance cost, high efficiency and ease of operation. The adsorption capacities of some specific clay minerals have been known to improve significantly when modified with quaternary ammonium compounds (QACs).In the present study, kaolinite clay from Alkaleri LGA, Northeast-Nigeria was characterized and modified with a cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br) and applied for batch sorption of Lead (II) ion contaminant from aqueous solution at different pH values. The results showed that Lead (II) ion uptake decreased with increase in pH. The maximum Pb^{2+}removal efficiency was 99.68% at pH3 and least at pH11 with 87.10%.The Langmuir adsorption isotherm proved to be the best fit based on correlation factor R^2 ranging from 0.9630-0.9950, while pseudo-second order kinetic was found to be the best fit based on R^2 ranging from 0.9860-0.9960.The negative values of Temkin binding energy (b_T) indicated that the process was exothermic. The high values of free energy E (1.8227×10^1-1.0000×10^3 kJ/mol) from Dubinin-Radushkevich (D-R) isotherm model suggested that chemisorption was the rate controlling step.*

Keywords: *Alkaleri Kaolinite Clay, Nigeria, Cationic Surfactant, Lead (II) Sorption, Kinetic, Isotherm*

I. Introduction

Heavy metals waste are discharged into streams, rivers and lakes and the continuous enrichment of these waters with these metals waste beyond the healthy level may cause poisoning, leading to various sicknesses (Mbadcam*et al*., 2011). The removal of toxic heavy metals from wastewaters is considered as one of the most important areas of water treatments, since the excessive industrial disposal of heavy metals creates major pollution problems thus their high toxicity and harmful effect to plants, animals and humans(Georgaka and Spanos, 2010;Dawodu*et al*., 2012).

Lead (Pb) and its compound are widely used in many industries such as battery, metal plating and smelting, painting and mining industries. The wastewaters generated by these industries are usually contaminated with Pb, which spreads into the environment thereby accumulating in the food chain since they are non-biodegradable and subsequently results in serious environmental health problems(Dawodu*et al*., 2012).The outbreak of acute Pb poisoning among the rural dwellers of Zamfara State in North-west Nigeria, happened to be the worst heavy metals poisoning incident in recent time, which resulted in the death of over 500 children within seven months in 2010 (Hassan *et al*., 2015).

The current maximum Lead concentration limit, according to the US Environmental Protection Agency (EPA) for drinking water is 0.015 mg/L(Bilgin and Tulun, 2015). Lead has no biological role in the human body and can be toxic even at a very low concentration in drinking water. Thus, World Health Organisation has set the maximum permissible limit for Pb in drinking water to be 0.01ppm(WHO, 2011).

The methods which have been used to remove Pb and other heavy metals from industrial effluents include solvent extraction, membrane filtration, ion exchange, chemical precipitation, electrochemical deposition, chemical oxidation and reduction, reverse osmosis and adsorption. Among these techniques exploited, adsorption have been found to be the most successful due to its relative low maintenance cost, high efficiency and ease of operation(Dawodu*et al*., 2012). However, many techniques that have been used have their drawbacks and shortcomings(Ahmed, 2016).

Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both.The organo-kaolinite clay is formed when cationic surfactant is retained by the kaolin clay in aqueous system. The quaternary ammonium compounds (QACs) can be retained by both the outer and interlayer surfaces of kaolin clay via an ion exchange process and are not easily displaced by smaller cations such as H^+, Na^+, K^+, Ca^{2+}, Al^{3+}, and Si^+ as a result, organoclay has greatly increased capabilities to remove hydrophobic contaminants from aqueous solutions(Ahmed, 2009; Aroke and El-Nafaty, 2014).The degree of $HDTMA^+$ addition is limited to the cation exchange capacity (CEC) of the clay being modified, where $HDTMA^+$ replaces the charge-balancing cations on the surfaces.

$$M.clay + HDTMA^+ \rightarrow clayHDTMA + M^+ \quad (1)$$

Where M^+ is the metal cation. The substitution of Na^+ or Ca^{2+} by quaternary ammonium cations at the exchangeable sites of natural clays results in organoclay derivatives with organophilic properties that can act as sorbent contaminant hydrocarbons(Aroke *et al*., 2015a).

Surfactant modified clays can provide selectivity and are produced from inexpensive base material and are chemically regenerable. The adsorption capacities of clay mineral have been shown to improve significantly due to the modification with QACs. The molecular structure of the modifying cations was also shown to play an important role in controlling the preference adsorption. Therefore, modification of a specific clay mineral with a quaternary ammonium salt can produce a sorbent that is capable of sorbing inorganic from aqueous solutions(Aroke *et al*., 2015a).

In the present study, well-characterized 'Alkaleri' kaolinite clay modified with hexadecyltrimethylammonium bromide (HDTMA-Br) was used for batch sorption of Pb^{2+} contaminant at different pH values. The work further involved the determination of optimum pH for the adsorption of Pb^{2+} in aqueous solution onto organically modified kaolinite clay, prediction of the adsorption isotherm andkinetic models that fitted the experimental data.

II. Experimental Section

Materials and Chemicals

Kaolinite clay was obtained directly from a mine site in Alkaleri LGA of Bauchi State, Northeast-Nigeria. It was subjected to preliminary treatment, physical beneficiation, well characterized and reported in a separate publication (Aroke *et al*., 2016). The chemicals and reagents used were of analytical grade manufactured by Aldrich Chemical Company Ltd. UK and purchased in a local chemicals shop in Bauchi Metropolis, Northeast-Nigeria except cationic surfactant HDTMA-Br imported from Xiamen Xm-innovation Chemical Co. Ltd. China.

Preparation of bilayer modified clay (BMC)

Appropriate concentration of 0.190 mol of cationic surfactant HDTMA-Br was prepared in 1-litre beaker. 100 g of kaolinite clay was accurately weighed into a petri dish and vigorously stirred to dissolve in the cationic surfactant HDTMA-Br. The aqueous mixture was charged into a batch reactor and stirred continuously for 24 hours at 740rpm and 298 K, time enough to achieve equilibrium (Aroke *et al*., 2014). The content was discharged and further centrifuged at 3000rpm for 30 minutes and the supernatant was decanted. The solid part (organoclay) was washed four times with deionised water and dried in an oven at 60^oC for 20 hours. The final organoclay was ground, sieved with 75µm mesh size and stored in a desiccator for further use.

Preparation of Pb^{2+} contaminant

A stock solution containing 4.8266mMPb^{2+}prepared by dissolving 1.0771g of PbO into volumetric flask contain 1000mL of deionised water and the mixture was vigorously stirred until complete dissolution. The concentration was verified by using atomic absorption spectrophotometer (Buck scientific, model: VGB 210)and the pH values adjusted accordingly using dilute HCl&NaOHand also verified by using pH meter (Hanna Italia, model: 800-276868).

Batch adsorption Study

An adsorbent (BMC) dosage of 100g/L was contacted with appropriate contaminant (Pb^{2+}), the mixture was transferred into an orbital shaker and operated at stirring speed of 400rpm while samples collected at 30 minutes interval for 180 minutes at constant temperature of 298K for analyses. The two phases was separated by centrifugation and supernatant analysed using AAS to determine the amount of Pb^{2+}unadsorbed where the equilibrium relationship curve was established to know the trend of sorption at pH values ranging from 3 to 11.

The adsorption capacities of BMC equilibrium studies at different pH values and time with constant adsorbent dosage and temperature was calculated from mass balance relationship Eq. (2)(Farouq and Yousef, 2015).

$$q_e = (C_o - C_e)\frac{v}{m} \tag{2}$$

The removal efficiency of Pb^{2+} by BMC was evaluated using the relationshipEq. (3):

$$removalefficiencyPb^{2+}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{3}$$

Where q_e (mg/g) is the amount of solute adsorbed at equilibrium per unit mass of adsorbent, C_0 (mg/L) is the initial concentration, C_e (mg/L) is the final or equilibrium concentration, v is the experimental solution volume (L), and m is the adsorbent dosage (g).

An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH (Foo and Hameed, 2010).Five adsorption isotherm models were tested by applying their linearized form for the best fit of experimental data, such as:

The Freundlich isotherm model can be expressed as(Foo and Hameed, 2010;Shahbeig*et al*., 2013; Anguile*et al*., 2013):

$$q_e = K_F C_e^{1/n} \tag{4}$$

The linear form of the equation or the log form is:

$$log q_e = log K_F + \frac{1}{n} log C_e \tag{5}$$

Where K_F and n are Freundlich constants related to the capacity of the adsorbent (mg/g) and adsorption intensity respectively.

The Langmuir isotherm model can be described by the equation(Foo and Hameed, 2010; Anguile*et al*., 2013;Dada *et al*., 2012).

$$\frac{q_0(bC_e)}{(1 + (bC_e))} \tag{6}$$

The linear form of the equation can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{7}$$

Where q_o(mg/g) and b(L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively(Emmanuel and Odigie, 2014).The essential characteristics of a Langmuir isotherm expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, defined by:

$$R_L = \frac{1}{(1 + bC_0)} \tag{8}$$

There are four probabilities for the R_L value indicating the adsorption nature to be unfavourable (R_L>1), linear (R_L = 1), favourable (0 < R_L< 1) or irreversible (R_L = 0)(Aroke *et al*., 2015a;Zheng *et al*., 2009).

The Temkin isotherm equation is given as(Foo and Hameed, 2010;Sampranpiboon*et al*., 2014):

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{9}$$

The linear form of the equation is written as:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \tag{10}$$

Where A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant (kJ/mol), R is universal gas constant (8.314 J/mol-K) and T is absolute temperature (K).

The general form of Dubinin–Radushkevich (D-R) isotherm is given by(Foo and Hameed, 2010;Dada *et al*., 2012;Dabrowski, 2001; Chen, 2015):

$$q_e = q_s \exp(-K_{ad}\, \varepsilon^2) \tag{11}$$

The linear form is given as:

$$ln(q_e) = ln(q_s) - (K_{ad})\varepsilon^2 \tag{12}$$

The mean free energy E per molecule of adsorbate can be computed by the relationship:

$$\mathrm{E} = \frac{1}{\sqrt{2B_{DR}}} \tag{13}$$

Meanwhile, the parameter ε can be correlated as:

$$\varepsilon = \mathrm{RT} \ln(1 + \frac{1}{\mathrm{C_e}}) \tag{14}$$

Where B_{DR} is D-R is isotherm constant, q_s is theoretical isotherm saturation capacity (mg/g) and K_{ad} is D-R isotherm constant (mol^2/kJ) (Foo and Hameed, 2010).

Brunauer–Emmett–Teller (BET) isotherm extinction model related to liquid–solid interface is exhibited as(Foo and Hameed, 2010; Samiey and Abdollahi, 2015):

$$q_e = \frac{q_s K_B C_e}{(C_s - C_e)[1 + (K_B - 1)\left({C_e}/{C_s}\right)]} \tag{15}$$

The BET isotherm in linearized form for solid-solution system is given as [28];

$$\frac{C_e}{(C_e - C_s) q_e} = \frac{1}{K_B q_s} + \left(\frac{K_B - 1}{K_B q_s}\right)\left(\frac{C_e}{C_s}\right) \tag{16}$$

Where K_B and C_s are the BET adsorption isotherm relating to the energy of surface interaction (L/mg) and adsorbate monolayer saturation concentration (mg/L) respectively (Khan and Ho, 2015).

The rate of sorption is of particular importance for the practical application of suggested sorption material and has great significance since it will facilitate the scale-up of the treatment process to smaller reactor volumes ensuring efficiency and economy(Aroke *et al*., 2014). Thus, three adsorption kinetic models was applied in its linearized form to determine therate equation that will best fit the experimental data, such as:

The pseudo-first order equation was expressed according to Lagergren(Khan *et al*., 2015):

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{17}$$

By using the boundary conditions t = 0 to t = t and q_t = 0 to q_t = $q_t$the linearized formbecomes(Bilgin and Tulun, 2015).

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{18}$$

Where $q_t$is the amount of solute adsorbed at any given time t, (mg/g) and K_1 is the rate constant of pseudo-first order sorption (min^{-1}).

The sorption kinetics can also be described by pseudo-second order rate equation(Aroke *et al*., 2014).

$$q_e = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \tag{19}$$

Equation (19) can be rearranged and linearized to obtain Eq.(20)

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \frac{1}{q_e}t \tag{20}$$

Where K_2 is the equilibrium rate constant of pseudo-second order sorption (g/mg-hr).

The linear form of the Elovich kinetic model is presented by the following equation(Yakout and Elsherif, 2010; Farouq and Yousef, 2015):

$$q_t = \frac{1}{B}\ln(AB) + \frac{1}{B}\ln t \tag{21}$$

Where A is the initial adsorption rate (mg/g-min) and B is related to the extent of surface coverage and activation energy for chemisorption (g/mg)(Badmus*et al*., 2007; Rudzinski and Panczyk, 2000; Heimberg*et al*., 2001).

III. Results And Discussion

Equilibrium adsorptivecapacity

A given mass of sorbent can sorb only a fixed amount of sorbate. Thus, the initial concentration of sorbate is very important. The adsorption capacities of BMC equilibrium studies at different pH values and time with constant adsorbent dosage and temperature was calculated from mass balance relationship Eq. (2).

Figure 1 representsthe equilibrium adsorptive capacities for contact time ranging from 0 to 180 min. It was observed that at 120 min all pH values except pH5 were at equilibrium, that is, no significant adsorption recorded, but at 150min pH5 converged with pH3 and exhibit no further significant adsorption.The maximum amount of Pb^{2+} was adsorbed within the first 120 min and thereafter the adsorption proceeded at a slower rate until 180 min.

Figure 2 depicts the percentage removal efficiency at pH3-pH11 for a time period of 180 min. Maximum removal occurred at pH3 and pH5 (acidic medium) and continue to decrease as pH increases (alkalinemedium), this was evaluated using the relationshipEq. (3).

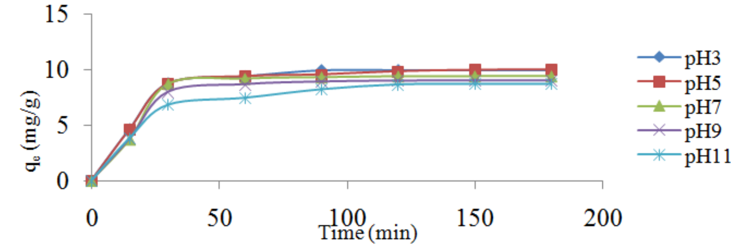

Figure 1: Equilibrium adsorptive capacity of Lead (II) ion sorption

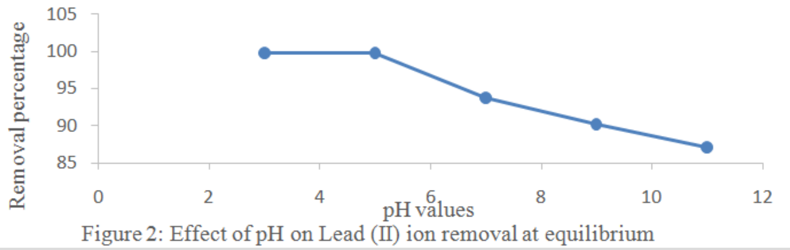

Figure 2: Effect of pH on Lead (II) ion removal at equilibrium

Sorption isotherm and parameters
Freundlich isotherm

The linearized plot of Freundlich isotherm model (Eq.5) at different pH valuesis shown in Fig. 3. The slope (1/n) ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value of 1/n below unity implies chemisorption process, where 1/n (slope) value above one is an indicative of cooperative adsorption(Shahbeig*et al.*, 2013). Since the values of (n and 1/n) are negative which are below unity implies chemisorption. The experimental adsorptive capacity shows that there is maximum adsorption at lower pH and decreases as pH increases which gives the same trend with empirical adsorptive capacity. $K_f$are very high and increases with pH, showing that adsorption ofPb^{2+} contaminant onto modified clay is higher and more favourable at lower pH with corresponding value of R^2=0.6520 but the highest R^2=0.9420 at pH7. The evaluated parameters is presented in Table 1.

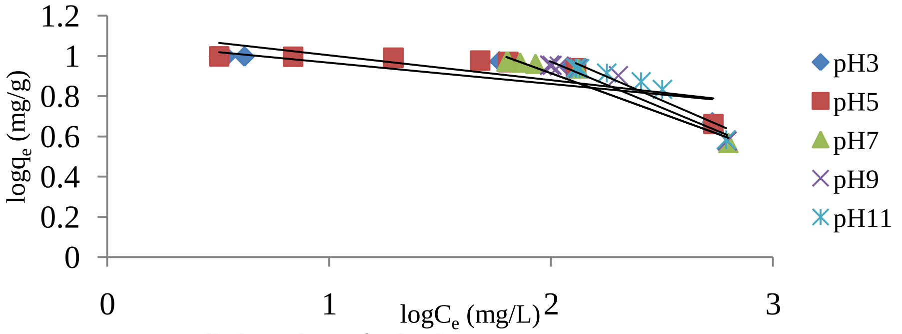

Figure 3: Freundlich isotherm for lead (II) ion sorption

Table 1: Isotherm parameters and constants for Lead (II) ion sorption onto BMC

Isotherms	Parameters	pH				
		3	5	7	9	11
Freundlich	$q_e(mg/g)_{exp}$ $K_f(mg/g)_{cal}$ N R^2	9.9681 11.77601 -9.5238 0.6520	9.9680 13.4276 -8.1301 0.6020	9.3700 51.7607 -2.5000 0.9420	9.0127 77.8037 -2.1786 0.9360	8.7100 93.1108 -2.1008 0.8930
Langmuir	$q_0(mg/g)_{cal}$ $q_e(mg/g)_{exp}$ b(L/mg) R_L R^2	4.6512 9.9681 -0.0723 -0.0140 0.9870	4.5249 9.9680 -0.0472 -0.0216 0.9870	3.4364 9.3700 -0.0203 -0.0520 0.9950	3.3898 9.0127 -0.0135 -0.0798 0.9890	3.4130 8.7100 -0.0098 -0.1133 0.9630
Temkin	b_T(kJ/mol) A_T(L/g) R^2	-3.2429×10^3 4.5302×10^{-7} 0.7040	-2.7964×10^3 1.2540×10^{-6} 0.6530	-1.0117×10^3 3.1100×10^{-4} 0.9580	-8.8834×10^2 3.7000×10^{-4} 0.9610	-6.3642×10^2 7.2000×10^{-4} 0.9470
D-R	$q_e(mg/g)_{exp}$ q_s $(mg/g)_{cal}$ K_{ad} (mol^2/kJ^2) E (kJ/mol) R^2	9.9681 7.3596 -7.3000×10^{-7} 8.2761×10^2 0.3390	9.9680 8.2318 -5.0000×10^{-7} 1.0000×10^3 0.0930	9.3700 5.2910 -4.3000×10^{-4} 3.4044×10^1 0.5690	9.0127 5.0886 -1.0300×10^{-3} 2.2001×10^1 0.6260	8.7100 5.3335 -1.5100×10^{-3} 1.8227×10^1 0.5910
BET	$q_e(mg/g)_{exp}$ $q_s(mg/g)_{cal}$ K_B(L/mg) R^2	9.9681 2.2124 -50.2222 0.9710	9.9680 2.1277 -31.3333 0.9710	9.3700 1.3228 -14.0000 0.9900	9.0127 1.3624 -8.95122 0.9780	8.7100 1.4577 -6.0708 0.9170

Langmuir isotherm

The linear plots of Langmuir isotherm model (Eq.7) is shown in Fig. 4for different pH values. The maximum adsorption capacity, q_0=4.6512 mg/g at pH3 with corresponding correlation factor R^2=0.9870, also experimental maximum adsorption capacity q_e=9.9681 mg/g. The values of 'b' are negative showing that the energy of sorption may be exothermic(Aroke *et al.*, 2015b). The dimensionless constant R_L referred to as separation factor was used to evaluate the whether or not the sorption is favourable and acceptable(Sampranpiboon*et al.*, 2014). Since the R_L values was out of range, it can be inferred that the adsorption of Pb^{2+} is undefined, but the correlation factor R^2 values (0.9630-0.9950) shows best fit compared with Freundlich isotherm model. The evaluated parameters from the model is presented in Table 1.

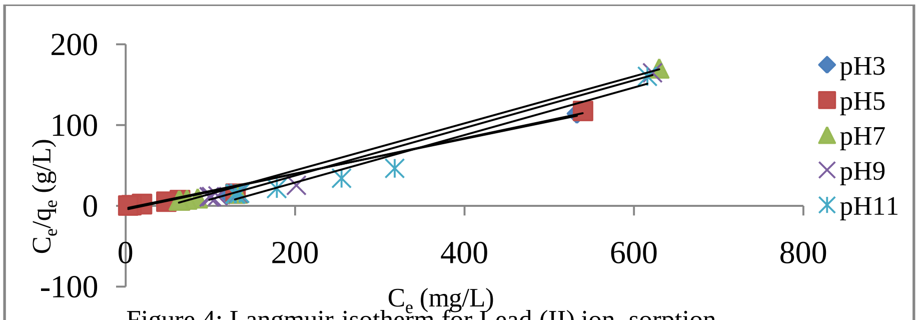

Figure 4: Langmuir isotherm for Lead (II) ion sorption

Temkin isotherm

The linear plots of Temkin isotherm model (Eq.10) is shown in Fig. 5for different pH values. The equilibrium sorption parameters were evaluated and presented in Table 1. Temkin isotherm equilibrium binding constant A_T (L/g) were irregular while Temkin isotherm constant $b_T$relating to energy of adsorption the values were negative which implies that the adsorption process is exothermic. The highest correlation factor R^2=0.9610 at pH9 with corresponding A_T=3.7000×10^{-4} L/g and the lowest R^2=0.6530 at pH5 with corresponding A_T= 1.2540×10^{-6}L/g. The ranges of correlation factors were higher than that of Freundlich but lower than that of Langmuir and BET isotherm respectively.

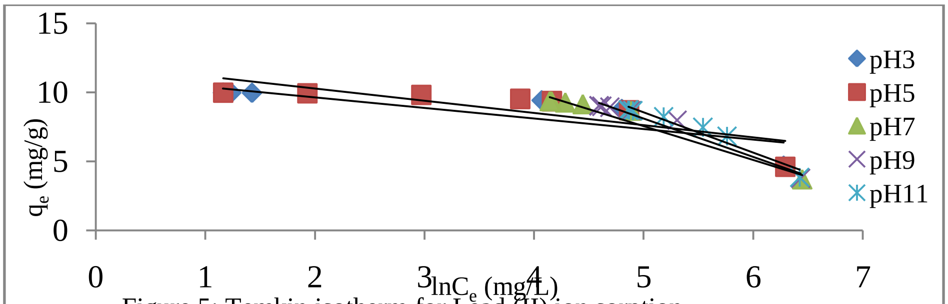

Figure 5: Temkin isotherm for Lead (II) ion sorption

Dubinin–Radushkevich (D-R) isotherm

The linearized plots of D-R isotherm model (Eq. 12) at different pHis shownin Fig. 6. The equilibrium sorption isotherm model parameters were evaluated and presented in Table 1. The free energy is an indicator of the mechanism of the ion exchange process: if E is less than 4 kcal/mol (16.74kJ/mol), the limiting step of adsorption rate is the inter-particle diffusion; if E is between 5 and 9 kcal/mol (20.93 and 37.67kJ/mol), the limiting step isintra-particle diffusion; if E is greater than 12kcal/ mol (50.23kJ/mol), the limiting step is the chemical reaction(Luís*et al*., 2014). Since the energy at different pH ranges between 1.8227×10^1-1.0000×10^3 kJ/molshows that chemisorption process play an important role in the adsorption. The maximum adsorptive capacity q_s=8.2318 mg/g at pH5 with corresponding R^2=0.093 which is the lowest among the isotherms tested, the experimental data does not fit the D-R isotherm model based on evaluated R^2. The constant K_{ad} is related to the adsorption energy per mole of the sorbate as it is transferred to the surface of the solid(Han *et al*., 2008).The values ranged from -7.00×10^{-7} to -1.03×$10^{-3}$$mol^2/kJ^2$.

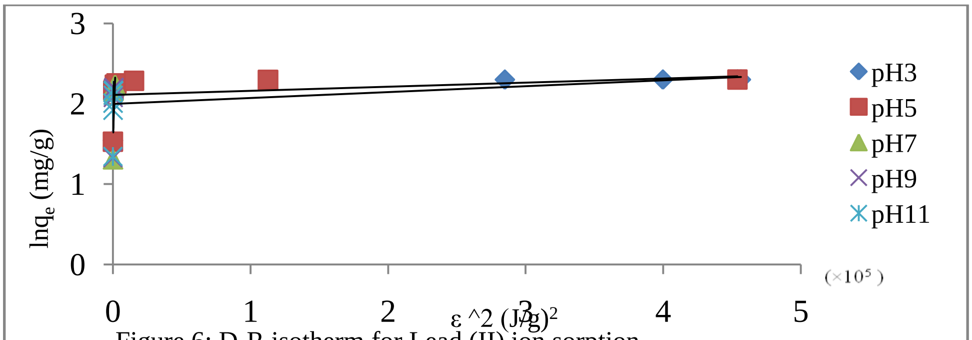

Figure 6: D-R isotherm for Lead (II) ion sorption

Brunauer–Emmett–Teller (BET) isotherm

The linearized plots of BET isotherm model (Eq. 16) at different pH values is shownin Fig. 7. The equilibrium sorption isotherm model parameters were evaluated and presented in Table 1. The maximum adsorptive capacity q_s=2.2124 mg/g at pH3 with correlation factor R^2=0.9710, meanwhile the adsorption capacity decreases as pH increases from pH3 to pH7 but irregular at pH9 and pH11. The BETconstant K_B,relating to the energy of surface interaction (L/mg)(Foo and Hameed, 2010), were negative which indicates that the energy of sorption may be exothermic. The correlation factors R^2 range from 0.9170-0.9900 which is the second best fit after Langmuir isotherm model.

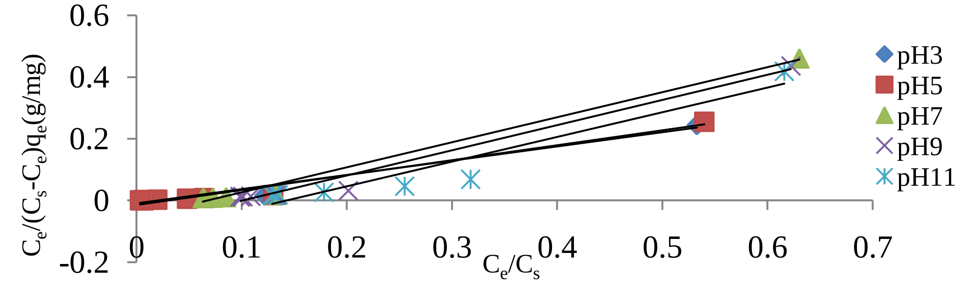

Figure 7: BET isotherm for Lead (II) ion sorption

Table 1revealed the parameters and constants for the five isotherms applied for this study, the best fitisotherms can be judge based on the correlation factor R^2 values in the following order:Langmuir > BET > Temkin >Freundlich> D-R.

Kinetics and Rate Parameters

Adsorption kinetics provides valuable information about the controlling mechanism of the adsorption process rate of adsorbate uptake and optimum operating conditions for the full-scale batch process(Saravanan and Ravikumar, 2015).Adsorption kinetic models namely: Pseudo-first order, Pseudo-second order and Elovich kinetic models were applied to the equilibriumdata (Fig. 1) as presented:

Pseudo-first order kinetic

The linearized plot for pseudo-first order kinetic model (Eq. 18) at different pH valuesis shown in Fig. 8. The kinetic parameters and constants evaluated is presented in Table 2.The highest rate constant value K_1=0.0760 min^{-1} with corresponding R^2=0.9770 and equilibrium sorption capacity q_e=15.6675 mg/g at pH3, signifies that the reaction is fast at this pH but shows irregularity from pH5 to pH11, while the lowest K_1=0.0322 min^{-1} with corresponding R^2=0.9530 and q_e=6.8865 mg/g at pH5 which also signifies that the reaction is low. The correlation factors R^2 ranges from 0.9610-0.9770.

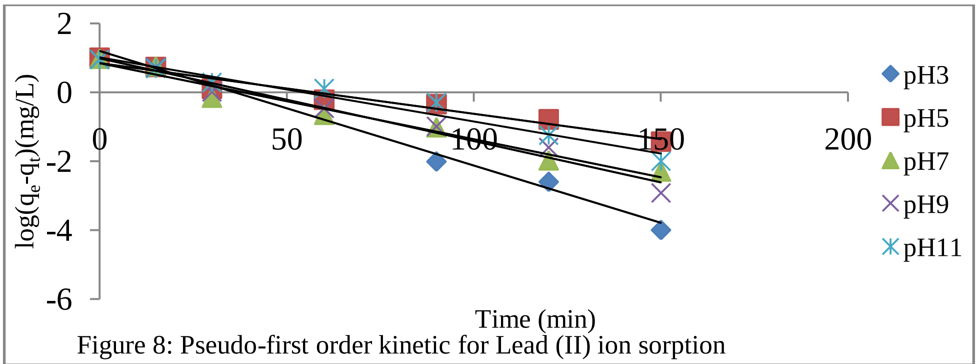

Figure 8: Pseudo-first order kinetic for Lead (II) ion sorption

Table 2: Kinetic parameters and constants for Lead (II) ion sorption onto BMC

Kinetic models	Parameters	pH				
		3	5	7	9	11
Pseudo-first order	$q_e(mg/g)_{exp}$	9.9681	9.9680	9.3700	9.0127	8.7100
	$q_e(mg/g)_{cal}$	15.6675	6.8865	6.9024	9.4842	10.2802
	$K_1(min^{-1})$	0.0760	0.0322	0.0507	0.0553	0.0415
	R^2	0.9770	0.9530	0.9690	0.9740	0.9610
Pseudo-second order	$q_e(mg/g)_{exp}$	9.9681	9.9680	9.3700	9.0127	8.7100
	$q_e(mg/g)_{cal}$	10.8696	10.8696	10.3092	9.9019	9.7087
	K_2(g/mg-min)	8.1699×10^{-3}	7.3921×10^{-3}	7.3681×10^{-3}	7.7811×10^{-3}	5.9467×10^{-3}

	R^2	0.9940	0.9950	0.9860	0.9900	0.9960
Elovich	B(g/mg)	0.5373	0.5400	0.5325	0.5549	0.5447
	A(mg/g-min)	3.2965	3.1472	2.3776	2.2574	2.1690
	R^2	0.7550	0.7670	0.6630	0.7250	0.8960

Pseudo-second order kinetic

The linearized plot for pseudo-second order kinetic model (Eq.18) at different pH is shown in Fig. 9 and kinetic parameters and constants evaluated is presented in Table 2.The highest rate constantvalue K_2=8.1699×10^{-3}g/mg-min with corresponding equilibrium sorption capacity q_e=10.8696 mg/g and R^2=0.9940 at pH3 which signifies that the reaction is fast and decreases as pH increased, while the lowest $K_{2=}$5.9467×10^{-3}g/mg-min with corresponding q_e=9.7087 mg/g and R^2=0.9960 at pH11. The maximum $q_e(mg/g)_{exp}$and$q_e(mg/g)_{cal}$occurred at pH3 and the variation between them is not much which shows the favourability of the process by pseudo-second kinetic. The correlation factors R^2 varied between 0.9860 and 0.9960 which are very high across the pH investigated. Furthermore, this model is based on the assumption that the rate-limiting step may be chemical sorption involving valence forces, through exchange or sharing of electrons between sorbate and sorbent(Ho and Mckay, 1999).

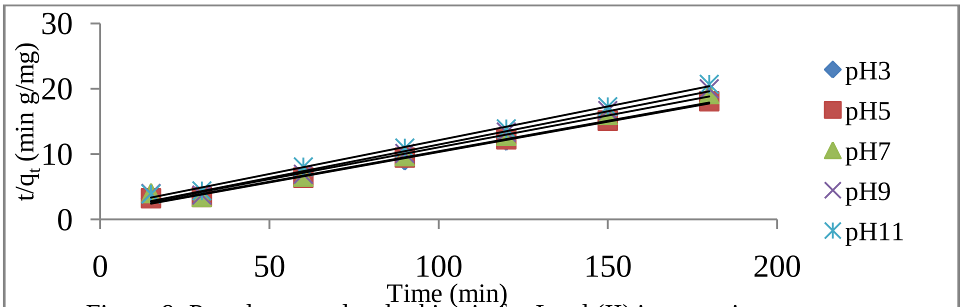

Figure 9: Pseudo-second order kinetic for Lead (II) ion sorption

Elovich kinetic

The linearized plots of Elovich kinetic model (Eq.21) at different pH values is shown in Fig. 10 and evaluated kinetic parameters and constantsis presented in Table 2.The initial adsorption rate 'A' decreases as pH increases which signifies that the reaction is fast at low pH and greater than unity while the desorption constant 'B' shows that the desorption rate increases as pH increases which implies that the reaction is fast at high pH but irregular between pH 7 and 11. The correlation factors R^2 ranges between 0.663 and 0.896 which is very low across pH investigated.

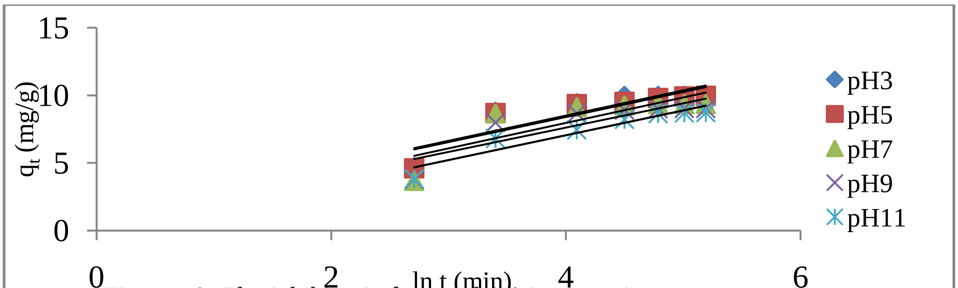

Figure 10: Elovich kinetic for Lead (II) ion sorption

Table 2 revealedthe parameters and constants for the three kinetic models applied for this study, the best fit kinetic can be judged based on the R^2 evaluated in the following order:Pseudo-second order> Pseudo-first order > Elovich.

IV. Conclusions

The following conclusions could be drawn from the batch adsorption of Pb^{2+} contaminant onto BMC at varied pH, constant stirring speed and temperature:

i. The equilibrium adsorption capacity for Pb^{2+} sorption onto BMC was found to be decreasing with increasing contaminant pH from acidic to alkaline medium (pH value 3-11). Maximum adsorptive capacity occurred at 150minutes with no significant adsorption thereafter.

ii. The mechanism of the adsorption is irreversible and chemisorption controlling step and exothermic process.

iii. Although the R_L values is undefined, the Langmuir isotherm model best fit the data with R^2 value ranges from 0.9630 to 0.9950 the highest among the isotherms investigated.
iv. The Pseudo-second order kinetic model best fit the sorption of Pb^{2+} onto BMC across the pH investigated with R^2 value ranges from 0.9860 to 0.9960.
v. The maximum removal of contaminant occurred at pH3 and pH5 with removal efficiency of 99.68% at time 150 minutes.

References

[1]. Ahmed M. E. I. (2016) Selective Adsorption of Cadmium Species onto Organic Clay Using Experimental and Geochemical Speciation Modeling Data, IACSIT International Journal of Engineering and Technology, 8(2)128-131

[2]. Ahmed S. A. S. (2009) Removal of Toxic Pollutants from Aqueous Solutions by Adsorption onto Organo-kaolin, Carbon Letters. 10(4)305-313

[3]. Anguile J. J., Mbadcam J. K., Ndaghu D. D. and Dongmo S. (2013) Effect of Solution parameters on the Adsorption of Cobalt (II) ions on Smectite from Cameroon: Equilibrium studies, Journal of Academia and Industrial Research, 2(4)210-215

[4]. Aroke U. O. and El-Nafaty U. A. (2014) XRF, XRD and FTIR Properties and Characterization of HDTMA-Br Surface Modified Organo-Kaolinite Clay, International Journal of Emerging Technology and Advanced Engineering, 4(4)817-825

[5]. Aroke U. O., El-Nafaty U. A. and Osha O. A. (2014) Removal of Oxyanion Contaminants from Wastewater by Sorption onto HDTMA-Br Surface Modified Organo-Kaolinite Clay, International Journal of Emerging Technology and Advanced Engineering. 4(1)475-484

[6]. Aroke U. O., El-Nafaty U. A. and Osha O. A. (2016) Characterization, Synthesis and Applicationof Organo-kaolinite Clay, Lambert Academy Publishing, Germany

[7]. Aroke U. O., Ibrahim M. and Okoroma L. A. (2015b) Parametric Studies of Nitrate Ion Sorption on varied Mass of HDTMA-Br Modified Kaolinite Clay. International Journal of Emerging Technology and Advanced Engineering 5(3)14-23

[8]. Aroke U. O., Ibrahim M., Osha O. A. and Yunus M. H. (2015a) Parametric studies of sulphate ion sorption at different pH on HDTMA-Br modified kaolinite clay, International Journal of Emerging Trends in Engineering and Development, 3(5)250-260

[9]. Badmus M. A. O., Audu T. O. K. and Anyata B. U. (2007) Removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells (Typanotonusfuscatus), Turkish Journal of Engineering and Environmental Science, (31)251-263

[10]. Bilgin M. and Tulun S. (2015) Use of diatomite for the removal of lead ions from water: thermodynamics and kinetics, Biotechnology & Biotechnological Equipment, 29(4)696-704

[11]. Chen X. (2015) Modeling of Experimental Adsorption Isotherm Data, Information, (6)14-22

[12]. Dabrowski A. (2001) Adsorption from theory to practice, Adv. Colloid Interface Sci., (93)135–224

[13]. Dada A. O., Olalekan A. P., Olatunya A. M. and Dada O. (2012) Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk, IOSR Journal of Applied Chemistry, 3(1)38-45

[14]. Dawodu F. A., Akpomie G. K. and Ejikeme P. C. N. (2012) Equilibrium, Thermodynamic and Kinetic Studies on the Adsorption of lead (II) from Solution by "Agbani Clay", Research Journal of Engineering Sciences, 1(6)9-17

[15]. Emmanuel C. C. and Odigie O. I. (2014) Adsorption of Acetaminophen from aqueous solutions onto hexadecyltrimethylammonium modified kaolinite, Nature and Science, 12(11)147-154

[16]. Farouq R. and Yousef N. S. (2015) Equilibrium and Kinetics Studies of adsorption of Copper (II) Ions on Natural Biosorbent, International Journal of Chemical Engineering and Applications, 6(5)319-324

[17]. Foo K. Y. and Hameed B. H. (2010) Insights into the modeling of adsorption isotherm systems, Chemical Engineering Journal, (156)2-10

[18]. Georgaka A. and Spanos N. (2010) Study of the Cu (ii) removal from aqueous solutions by adsorption on titania, Global NEST Journal, 12(3)239-247

[19]. Han R., Han P., Cai, Z., Zhao Z. and Tang M. (2008) Kinetics and isotherms of Neutral Red adsorption on peanut husk, Journal of Environmental Sciences, (20)1035-1041

[20]. Hassan M. M., Nuhu A. A., Sallau M. S., Majiya H. M. and Mohammed A. K. (2015) Zamfara lead poisoning saga: Comparison of lead contamination level of water samples and lead poisoning in Bagega Artisanal gold mining district, Nigeria, Journal of Chemical and Pharmaceutical Research, 7(3)7-12

[21]. Heimberg J. A., Wahl K. J., Singer I. L. and Erdemir A. (2001) Superlow friction behavior of diamond-like carbon coatings: time and speed effects, Applied Physics Letters, 78(17)2449-2451

[22]. Ho Y. S. and Mckay G. (1999) Pseudo-second order model for sorption process, Process Biochem, 34(5)451-465

[23]. Khan M. A., Alemayehu A., Duraisamy R. and Berekete A. K. (2015) Removal of Lead ion from aqueous solution by Bamboo activated Carbon, International Journal of Water Research, 5(2)33-46

[24]. Khan M. A. and Ho Y. S. (2015) Impact of Brunauer Emmett Teller isotherm on research in science citation index expanded, Environmental Engineering and Management Journal, 14(9)2163-2168

[25]. Luís P. M. S. S., Cheng C. Y. and Boaventura R. A. R. (2014) Adsorption of a basic dye onto esmegel clay, Environmental Engineering and Management Journal, 13(2)395-405

[26]. Mbadcam J. K., Anagho S. G., Nsami J. N. and Kammegne A. M. (2011) Kinetic and equilibrium studies of the adsorption of lead (II) ions from aqueous solution onto two Cameroon clays: Kaolinite and smectite, Journal of Environmental Chemistry and Ecotoxicology, 3(11)290-297

[27]. Rudzinski W. and Panczyk T. (2000) Kinetics of isothermal adsorption on energetically heterogeneous solid surfaces: a new theoretical description based on the statistical rate theory of interfacial transport, Journal of Physical Chemistry, 104(39)9149-9162

[28]. Samiey B. and Abdollahi J. S. (2015) A New Approach for Analysis of Adsorption from Liquid Phase: A Critical Review, Journal of Pollution Effects and Control, 3(2)1-9

[29]. Sampranpiboon P., Charnkeitkong P. and Feng X. (2014) Equilibrium Isotherm Models for Adsorption of Zinc (II) ion from Aqueous Solution on Pulp Waste, WSEAS Transactions on Environment and Development, (10)35-47

[30]. Saravanan R. and Ravikumar L. (2015) The Use of New Chemically Modified Cellulose for Heavy Metal Ion Adsorption and Antimicrobial Activities, Journal of Water Resource and Protection, (7)530-545

[31]. Shahbeig H., Bagheri N., Ghorbanian S. A., Hallajisani A. and Poorkarimi S. (2013) A new adsorption isotherm model of aqueous solutions on granular activated carbon, World Journal of Modelling and Simulation, 9(4)243-254

[32]. WHO (2011) World Health Organization, Lead in Drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality (WHO/SDE/WSH/03.04/09/Rev/1), Geneva 27, Switzerland

[33]. Yakout S. M. and Elsherif E. (2010) Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons, Carbon – Sci. Tech, (1)144-153

[34]. Zheng H., LiuaD., Zheng Y., Liang S. and LiuZ. (2009) Sorption isotherm and kinetic modeling of aniline on Cr-bentonite, Journal of Hazardous Materials, (167)141–147