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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 pH 3 and least at pH 11 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 $E (1.8227\times10^3-1.0000\times10^4 \text{ kJ/mol})$ 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$^4+$ 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.

$$M.\text{clay} + \text{HDTMA}^+ \rightarrow \text{clayHDTMA} + \text{M}^+ \tag{1}$$
Removal of Pb\(^{2+}\) onto HDTMA-Br Modified Kaolinite Clay as function of pH: Batch Sorption, ...

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 and kinetic 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°C 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&NaOH and 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).

\[
q_e = \left( C_o - C_e \right) \frac{\nu}{m}
\]  

(2)

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

\[
\text{removal efficiency Pb}^{2+} (\%) = \frac{C_o - C_e}{C_o} \times 100
\]  

(3)

Where \( q_e \) (mg/g) is the amount of solute adsorbed at equilibrium per unit mass of adsorbent, \( C_o \) (mg/L) is the initial concentration, \( C_e \) (mg/L) is the final or equilibrium concentration, \( \nu \) 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):

\[ q_e = K_F C_e^{1/n} \]

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

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]

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).

\[ \frac{q_e}{b C_e} = \frac{1}{(1 + (b C_e))} \]

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

\[ C_e = \frac{1}{q_e} + \frac{1}{q_0} \]

Where \( q_e \) (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:

\[ R_L = \frac{1}{(1 + b C_0)} \]

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., 2015; Zheng et al., 2009).

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

\[ q_e = \frac{R T}{b_T} \ln(A_T C_e) \]

The linear form of the equation is written as:

\[ q_e = \frac{R T}{b_T} \ln A_T + \frac{R T}{b_T} \ln C_e \]

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; Dahrowski, 2001; Chen, 2015):

\[ q_e = q_e \exp(-K_{ad} \varepsilon^2) \]

The linear form is given as:

\[ \ln q_e = \ln(q_e) - (K_{ad}) \varepsilon^2 \]

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

\[ E = \frac{1}{\sqrt{2 B_{DR}}} \]

Meanwhile, the parameter \( \varepsilon \) can be correlated as:

\[ \varepsilon = RT \ln(1 + \frac{1}{C^*_e}) \]

Where \( B_{DR} \) is D-R isotherm constant, \( q_e \) is theoretical isotherm saturation capacity (mg/g) and \( K_{ad} \) is D-R isotherm constant (mol²/kJ) (Foo and Hameed, 2010).

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

\[ q_e = \frac{K_B C_e}{(C_e - C_s)[1 + (K_B - 1) \left( \frac{C_e}{C_s} \right) \}} \]

The BET isotherm in linearized form for solid-solution system is given as \([28]\):

\[ \frac{C_e}{(C_e - C_s)q_e} = \frac{1}{K_B q_e} + \left( \frac{K_B - 1}{K_B q_e} \right) \left( \frac{C_e}{C_s} \right) \]

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
Removal of Pb\(^{2+}\) onto HDTMA-Br Modified Kaolinite Clay as function of pH: Batch Sorption, ...

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):

\[
\frac{dq_t}{dt} = K_1(q_e - q_t)
\]

By using the boundary conditions \(t = 0\) to \(t = t\) and \(q_t = 0\) to \(q_t = q_e\) the linearized form becomes (Bilgin and Tulun, 2015).

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t
\]

Where \(q_e\) 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 \((\text{min}^{-1})\).

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

\[
q_e = \frac{q_e^2 K_2 t}{1 + q_e K_2 t}
\]

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

\[
\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \frac{1}{q_e} t
\]

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

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

\[
q_t = \frac{1}{B} \ln(AB) + \frac{1}{B} \ln t
\]

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

III. Results And Discussion

**Equilibrium adsorptive capacity**

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 represents the 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 150 min 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 relationship Eq. (3).
Sorption isotherm and parameters

Freundlich isotherm

The linearized plot of Freundlich isotherm model (Eq.5) at different pH values is 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. Kf are very high and increases with pH, showing that adsorption of Pb²⁺ contaminant onto modified clay is higher and more favourable at lower pH with corresponding value of R²=0.6520 but the highest R²=0.9420 at pH7. The evaluated parameters is presented in Table 1.

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

<table>
<thead>
<tr>
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<th>Parameters</th>
<th>pH</th>
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<tr>
<td>Freundlich</td>
<td>qₑ (mg/g)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Kₑ (mg/g)</td>
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</tr>
<tr>
<td></td>
<td>N</td>
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<td>R²</td>
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<td>Langmuir</td>
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<tr>
<td></td>
<td>qₑ (mg/g)</td>
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</tr>
<tr>
<td></td>
<td>b (L/mg)</td>
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</tr>
<tr>
<td></td>
<td>Rₑ</td>
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</tr>
<tr>
<td></td>
<td>R²</td>
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</tr>
<tr>
<td>Temkin</td>
<td>bₑ (kJ/mol)</td>
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<tr>
<td></td>
<td>Aₑ (L/g)</td>
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<td></td>
<td>R²</td>
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<td>D-R</td>
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<td>E (kJ/mol)</td>
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<td></td>
<td>R²</td>
<td>0.9710</td>
</tr>
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Langmuir isotherm

The linear plots of Langmuir isotherm model (Eq.7) is shown in Fig. 4 for different pH values. The maximum adsorption capacity, qₑ=4.6512 mg/g at pH3 with corresponding correlation factor R²=0.9870, also experimental maximum adsorption capacity qₑ=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 Rₑ 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 Rₑ values was out of range, it can be inferred that the adsorption of Pb²⁺ is undefined, but the correlation factor R² values (0.9630-0.9950) shows best fit compared with Freundlich isotherm model. The evaluated parameters from the model is presented in Table 1.
Removal of Pb$^{2+}$ onto HDTMA-Br Modified Kaolinite Clay as function of pH: Batch Sorption,

Temkin isotherm

The linear plots of Temkin isotherm model (Eq. 10) is shown in Fig. 5 for 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 $A_T=3.7000\times10^{-4}$ L/g and the lowest $R^2=0.6530$ at pH5 with corresponding $A_T=1.2540\times10^{-6}$ L/g. The ranges of correlation factors were higher than that of Freundlich but lower than that of Langmuir and BET isotherm respectively.

Dubinin–Radushkevich (D-R) isotherm

The linearized plots of D-R isotherm model (Eq. 12) at different pH is shown in Fig. 6. 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 is intra-particle diffusion; if $E$ is greater than 12kcal/mol (50.23kJ/mol), the limiting step is the chemical reaction (Luis et al., 2014). Since the energy at different pH ranges between $1.8227\times10^{-1}$-$1.0000\times10^{-3}$ kJ/mol shows 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 $-7.00\times10^{-7}$ to $-1.03\times10^{-3}$ mol$^2$/kJ.$^2$. 

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

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

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 shown in Fig. 7. The equilibrium sorption isotherm model parameters were evaluated and presented in Table 1. The maximum adsorptive capacity \( q_s = 2.2124 \text{ mg/g} \) 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 BET constant \( K_B \), 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](image)

Table 1 revealed the parameters and constants for the five isotherms applied for this study, the best fit isotherms 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 equilibrium data (Fig. 1) as presented:

Pseudo-first order kinetic

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

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
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<td>( K_B \text{ (mg/g)} )</td>
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<td>7.7811×10^{-3}</td>
<td>5.9467×10^{-3}</td>
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Removal of Pb²⁺ onto HDTMA-Br Modified Kaolinite Clay as function of pH: Batch Sorption,..

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 constant value $K_2=8.1699\times10^{-3}$ g/mg-min with corresponding equilibrium sorption capacity $q_{qe}=10.8696$ mg/g and $R^2=0.9940$ at pH3 which signifies that the reaction is fast and decreases as pH increased, while the lowest $K_2=5.9467\times10^{-3}$ g/mg-min with corresponding $q_{qe}=9.7087$ mg/g and $R^2=0.9960$ at pH11. The maximum $q_e$ 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).

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 constant is 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.

IV. Conclusions

The following conclusions could be drawn from the batch adsorption of Pb²⁺ contaminant onto BMC at varied pH, constant stirring speed and temperature:

i. The equilibrium adsorption capacity for Pb²⁺ 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 150 minutes with no significant adsorption thereafter.

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

Table 2 revealed the 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.

<table>
<thead>
<tr>
<th>$R^2$</th>
<th>0.9940</th>
<th>0.9950</th>
<th>0.9860</th>
<th>0.9900</th>
<th>0.9960</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elovich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$ (g/mg)</td>
<td>0.5373</td>
<td>0.5400</td>
<td>0.5325</td>
<td>0.5549</td>
<td>0.5447</td>
</tr>
<tr>
<td>$A$ (mg/g-min)</td>
<td>3.2965</td>
<td>3.1472</td>
<td>2.3776</td>
<td>2.2574</td>
<td>2.1690</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.7550</td>
<td>0.7670</td>
<td>0.6630</td>
<td>0.7250</td>
<td>0.8960</td>
</tr>
</tbody>
</table>

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ii. The mechanism of the adsorption is irreversible and chemisorption controlling step and exothermic process.
iii. Although the $R_e$ 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 $\text{Pb}^{2+}$ 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


DOI: 10.9790/2402-1010012534 www.irosjournals.org 33 | Page
Removal of Pb\textsuperscript{2+} onto HDTMA-Br Modified Kaolinite Clay as function of pH: Batch Sorption, ...

