

## Removal of Lead (II) Ion onto Unmodified and HDTMA-Br Modified Kaolinite Clay: Equilibrium, Isotherm and Kinetic Studies

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### ABSTRACT

The removal of harmful substances such as Lead (Pb) from wastewaters using locally available resources is essential to the environment and in promoting indigenous technology. This study investigated the development of organically modified clay from Alkalari in North Eastern Nigeria for wastewater treatment containing Lead (II) ion. The batch adsorption of  $Pb^{2+}$  in aqueous solutions onto hexadecyltrimethylammonium bromide (HDTMA-Br) bilayer modified clay (BMC), monolayer modified clay (MMC) and unmodified kaolinite clay (UKC) was studied at constant pH of 3 and stirring speed of 400 rpm. The results obtained showed the removal efficiencies of  $Pb^{2+}$  by BMC, MMC and UKC from the contaminated wastewater as 99.68%, 69.22%, and 34.70% respectively. The maximum adsorption capacity of  $Pb^{2+}$  contaminant onto BMC, MMC and UKC were 9.9681 mg/g, 6.9217 mg/g and 3.4700 mg/g at 180 minutes respectively. Five adsorption isotherms namely: Langmuir, Freundlich, Frumkin, Temkin, Jovanovic and Harkins-Jura were tested for the best fit to the experimental data, and Temkin isotherm binding energy was negative, which indicated an exothermic process with  $R^2$  values of 0.7066, 0.9917, and 0.9988 for BMC, MMC and UKC respectively. Three kinetic models namely: Pseudo-first order, Pseudo-second order and Elovich were tested, and Pseudo-second order model described the adsorption data best indicating that the possible mechanism is chemisorption. The high performance of this clay in this study revealed that it can be a good substitute to the conventional material used and therefore becoming a source of revenue.

**Keywords:** Contaminant, HDTMA-Br, Isotherms, Kaolinite clay, Kinetics.

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### I. INTRODUCTION

The increasing contamination of groundwater, urban and industrial wastewater by toxic inorganic and organic chemicals is a worrying environment problem that has been recognized as an issue of growing importance in recent years [1]. Exposure to Lead and its compounds causes a variety of health effects and affects children in particular [2]. Currently there is a growing awareness of the impact of these contaminants on groundwater, rivers and lakes. Therefore, the removal of emerging contaminants of concern is now as ever important in the production of safe drinking water and the environmentally responsible release of wastewater [3]. The World Health Organization (WHO) stated a legal limit of 50 ppb for Lead in 1995 [4], which was decreased to 10 ppb in 2010 [5].

Lead compounds are generally soluble in soft, slightly acidic water. Lead has many different uses in pipes, solder and plumbing fittings, in batteries, ammunition, as roofing sheets or as a shield from X-rays. It was used extensively as an anti-knock and lubricating agent in fuel, such as petrol and in paints, as a pigment in dyes and ceramic glazes and in food cans which has been phased out [6]. This has resulted in a pronounced reduction in human Lead exposure. However, evidence from Scientific opinion on Lead in food, has shown that continuing to minimize exposure to Lead should remain a key public health concern, particularly because of its effects on infants and young children [7].

Treatment options which are typically considered for the removal of emerging contaminants from drinking water as well as wastewater include adsorption, advanced oxidation processes, nanofiltration and reverse osmosis membranes [8, 9]. Conversely adsorption processes do not add undesirable by-products and have been found to be superior to other techniques for wastewater treatment in terms of simplicity of design, operation and insensitivity of toxic substances [10, 11, 12].

Clays and clay minerals such as kaolinite have negatively charged surfaces which occupied by exchangeable cations of alkali and alkaline earth metals, which gives them strong affinity for surfactants [13]. Modification of clays using substances such as surfactants is termed as organoclay, thus clay is being widely used in various

industries[14]. Because of the hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature which makes natural clays effective sorbents for adsorbing organic compounds. The hydrophilicity of clays can be transformed into hydrophobicity when the exchange inorganic cations are replaced by surfactants like quaternary ammonium cations (QACs) in the form of  $[(CH_3)_3NR]^+$  or  $[(CH_3)_2NRR']^+$ . This replacement result in organophilic clays [15, 16].

Kaolinite shows retention of surfactant up to 100% cation exchange capacity (CEC) of the clay and above[13, 16, 17].The nature of the QAC, the clay and the composition of the aqueous solution may all affect the stability of the QAC-clay complexes by influencing the degree of QAC retention via hydrophobic bonding. QACs with chain length greater than a critical value (i.e. eight carbons and above) are retained in clay via both cation exchange and hydrophobic bonding, the need arises to vary the concentration of the cationic surfactants (in this case hexadecyltrimethylammonium bromide (HDTMA-Br))base on the CEC of the clay to get the most stable organoclay and complete exchange of inorganic cations and the bond nature of both the QACs and clay[1, 18, 19].

The degree of HDTMA<sup>+</sup> addition is limited to the CEC of the clay being modified, where HDTMA<sup>+</sup> replaces the charge-balancing cations on the surfaces.



Where M<sup>+</sup> is the metal cation. The substitution of Na<sup>+</sup> or Ca<sup>2+</sup> 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[20, 21].

In the present study, 'Alkaleri' kaolinite clay in its unmodified and HDTMA-Br modified forms was used for batch sorption of Pb<sup>2+</sup> contaminant at constant pH, particle size and operating temperature. The work further involved determination of optimum performance of adsorbents for the adsorption of Pb<sup>2+</sup> in aqueous solution, prediction of the adsorption isotherm and kinetic models that fitted the experimental data.

## II. EXPERIMENTAL SECTION

### 2.1 Materials and chemicals

Kaolinite clay was obtained directly from mines site in Alkaleri LGA of Bauchi State, Northeast-Nigeria, which was subjected to preliminary treatment and physical beneficiation, well characterized and reported in a separate publication[16].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.

### 2.2 Preparation of Monolayer Modified Clay (MMC) and Bilayer Modified Clay (BMC)

Appropriate concentration of 0.095 and 0.190 mol of cationic surfactant HDTMA-Br was prepared in 1-litre beakers for MMC and BMC respectively based on 9.5 meq/100g CEC of the kaolinite clay. 100 g of kaolinite clay was accurately weighed into two separate petri dishes and each content vigorously stirred to dissolve in the cationic surfactant HDTMA-Br solutions. The aqueous mixture was transferred and charged into a batch reactor and stirred continuously for 24 hours at 740 rpm and 298 K, time enough to achieve equilibrium[1]. The content was discharged and further centrifuged at 3000 rpm for 30 minutes and the supernatant was decanted. The solid part (organoclay) was washed four times with deionized water and dried in an oven at 60 °C for 20 hours. The final organoclay was ground, sieved with 75 µm mesh size and stored in a desiccator for further use.

### 2.3 Preparation of Pb<sup>2+</sup> Contaminant

A stock solution containing 4.8266 mM Pb<sup>2+</sup> prepared by dissolving 1.0771 g of PbO into volumetric flask containing 1000mL of deionized water and the mixture was vigorously stirred until complete dissolution. The concentration was verified by using atomic absorption spectrophotometer (AAS) (Buck scientific, model: VGB 210)and the pH value adjusted to 3 using dilute HCl and verified by using pH meter (Hanna Italia, model: 800-276868).

### 2.4 Batch Adsorption Process

Each adsorbent (UKC, MMC and BMC) dosage of 100 g/L were contacted with appropriate contaminant (Pb<sup>2+</sup>) in three different beakers, the mixture was transferred into an orbital shaker and operated at stirring speed of 400 rpm while samples collected at 30 minutes' interval over a period of 180 minutes at constant temperature of 298 K for centrifugation (Gallenkamp Angle Head) separation. The two phases were separated and supernatants analyzed using AAS to determine the amount of Pb<sup>2+</sup> unadsorbed in each of the mixture where the equilibrium relationship curve was established to determine the trend of sorption at pH value of 3 (acidic medium).

The adsorptive capacities of UKC, MMC and BMC equilibrium studies with respect to time at constant pH, adsorbent dosage and temperature were calculated from mass balance relationship Eq. (2) [22, 23].

$$Q_e = (C_o - C_e) \frac{v}{m} \quad (2)$$

and removal efficiency of  $Pb^{2+}$  by UKC, MMC and BMC were evaluated using the relationship Eq. (3):

$$removal\ efficiency\ Pb^{2+}(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (3)$$

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,  $v$  is the experimental solution volume (L), and  $m$  is the adsorbent dosage (g) [1, 17].

Adsorption isotherms are important to describe how adsorbate will interact with the adsorbent and so are critical for design purposes; therefore, the correlation of equilibrium data using such equations are essential for practical adsorption operation [22]. Five adsorption isotherm models were tested by applying their linearized form for the best fit of experimental equilibrium data, such as:

The Freundlich isotherm model used to describe the adsorption characteristics for the heterogeneous surface [24, 25, 26] expressed in linearized form as:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

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

The Langmuir isotherm model is based on uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [27], which can be represented in linearized form as [25, 28, 29]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad (5)$$

Where  $Q_o$  is the maximum monolayer coverage capacity (mg/g) and  $K_L$  is the Langmuir isotherm constant energy of adsorption (L/mg). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter  $R_L$ , which is a dimensionless constant referred to as separation factor or equilibrium parameter [30].

$$R_L = \frac{1}{1 + K_L C_o} \quad (6)$$

The separation factor  $R_L$  value indicates the adsorption nature to be either unfavourable if  $R_L > 1$ , linear if  $R_L = 1$ , favourable if  $0 < R_L < 1$  and irreversible if  $R_L = 0$  [1, 31].

The Temkin isotherm model is given by the following linearized equation as [32, 33]:

$$Q_e = \left(\frac{RT}{b_T}\right) \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e \quad (7)$$

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

The Jovanovic isotherm model is given by the following linearized relationship [33, 34, 35]:

$$\ln Q_e = \ln Q_{max} - K_J C_e \quad (8)$$

Where  $K_J$  (L/g) is the Jovanovic isotherm parameter and  $Q_{max}$  (mg/g) is the maximum uptake of solute.

The Harkins-Jura adsorption isotherm model can be expressed in linearized form as [33, 36, 37]:

$$\frac{1}{Q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e \quad (9)$$

Where  $A_H$  (g<sup>2</sup>/L) and  $B_H$  (mg<sup>2</sup>/L) are two parameters characterizing the sorption equilibrium.

The overall adsorption process can be controlled either by one or more steps such as pore diffusion, surface diffusion or a combination of more than one step. Kinetics of adsorption is an important characteristic in evaluating the performance of a given adsorbent and gain insight into the underlying mechanisms [38, 39]. In view of these, three adsorption kinetic models were applied in its linearized forms to determine the rate equation that will best fit the experimental data, such as:

The pseudo-first order kinetic equation of Lagergren model is given in linearized form as [1, 40]:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t \quad (10)$$

Where  $Q_t$  is the amount of adsorbed solute (mg/g) at any instant of time  $t$  (min) and  $K_1$  is the rate constant of pseudo-first order adsorption operation (min<sup>-1</sup>).

The pseudo-second order equation based on equilibrium adsorption [41, 42] is expressed in linearized form as:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \left(\frac{1}{Q_e}\right) t \quad (11)$$

Where  $K_2$  (g/mg-min) is the equilibrium rate constant of pseudo-second order adsorption.

The Elovich kinetic models for describing chemisorption is presented in linearized form as [43, 44].

$$Q_t = \frac{1}{B} \ln(AB) + \frac{1}{B} \ln t \quad (12)$$

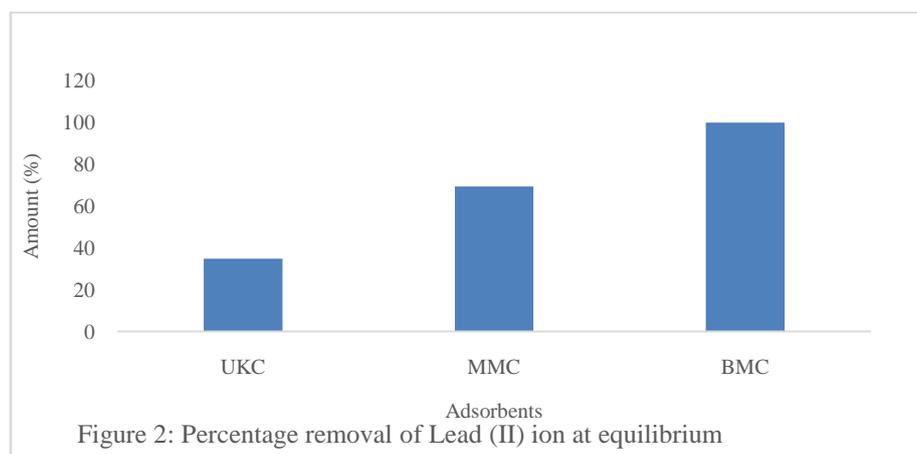
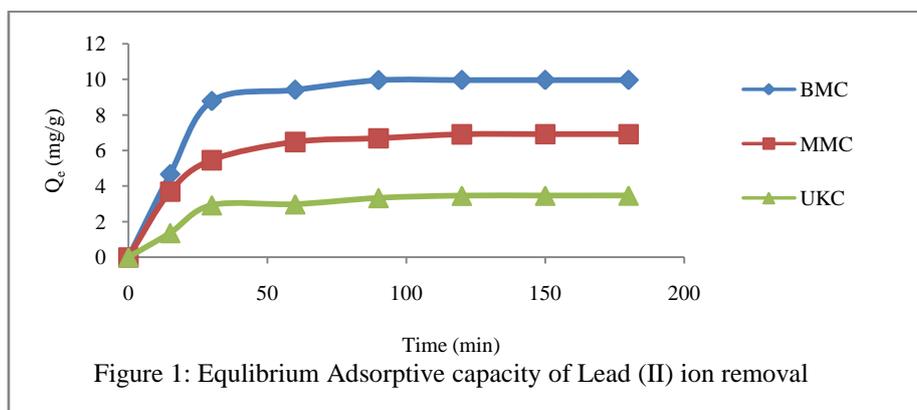
Where  $A$  is the initial adsorption rate (mg/g-min) and  $B$  is desorption constant (g/mg) for a particular experiment.

### III. RESULTS AND DISCUSSION

#### 3.1 Equilibrium Adsorptive Capacity

In the present investigation UKC, MMC and BMC has been used as adsorbents for the removal of  $Pb^{2+}$  contaminant at time 150 minutes the adsorbents begins to show insignificant removal until equilibrium was attained 180 min. After the sorption equilibrium was attained, the  $Pb^{2+}$  uptake by each adsorbent was evaluated based on mass balance (Eq. 2) as presented in Fig. 1.

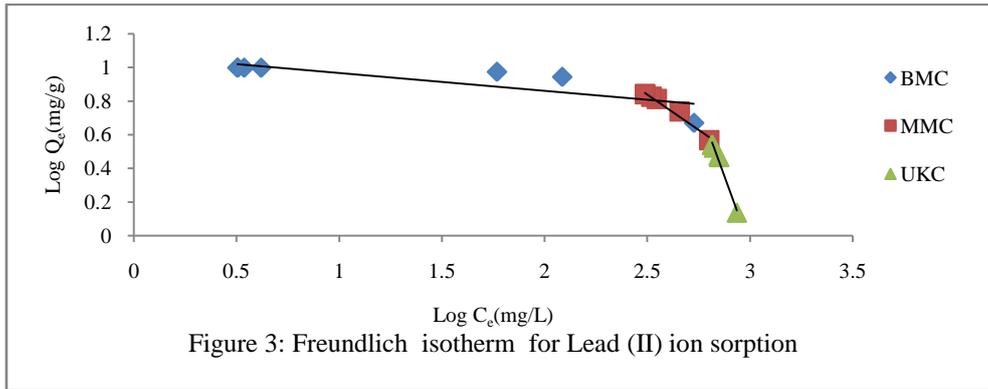
The removal efficiency of  $Pb^{2+}$  by adsorbents UKC, MMC and BMC as evaluated from Eq. 3 and presented in Fig. 2. At equilibrium the removal efficiencies of UKC, MMC and BMC are 34.70, 69.21 and 99.68% respectively.



#### 3.2 Adsorption Isotherm and Parameters

##### 3.2.1 Freundlich Isotherm

The linear form of this isotherm (Eq. 4) was used to evaluate the values of  $n$  and  $K_F$  (Fig. 3), which indicates the parameter  $\frac{1}{n}$  is not equal 1 and also  $n$  does not lies between 1 and 10, this shows unfavorable sorption process [45, 46]. All values obtained for  $n$  and  $\frac{1}{n}$  are negative which implies chemisorption but very high in BMC compared to MMC and UKC. The  $K_F$  and  $R^2$  values are high with 0.9964 mg/g and 0.9834 respectively for UKC while the lowest values of  $K_F$  and  $R^2$  was obtained for BMC with 0.0302 mg/g and 0.6529 respectively as presented in Table 1.

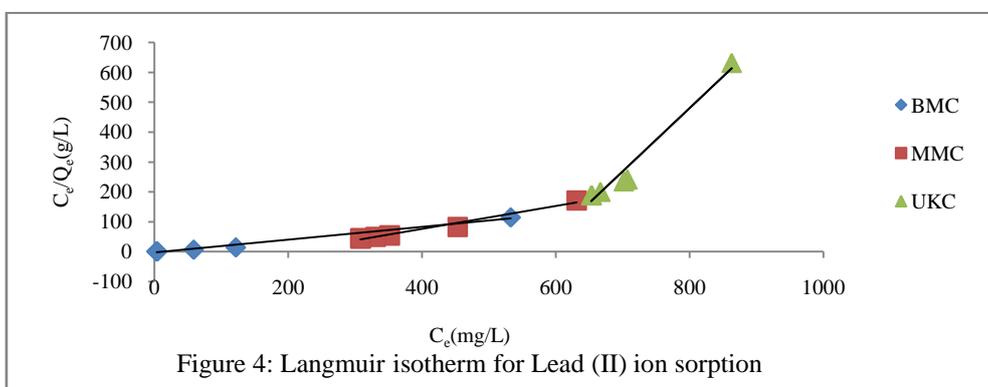


**Table 1:** Isotherm parameters and constants for Lead (II) ion sorption

Isotherm	Parameters	Adsorbents		
		BMC	MMC	UKC
Freundlich	$K_F$ (mg/g)	0.0302	0.4699	0.9964
	$n$	-9.4787	-1.1843	-0.3007
	$R^2$	0.6529	0.9728	0.9834
Langmuir	$Q_0$ (mg/g)	4.6512	2.6151	0.4738
	$K_L$ (L/mg)	-0.6394	-29.3821	-2552.5596
	$R_L$	$-1.57 \times 10^{-3}$	$-3.40 \times 10^{-5}$	$-3.90 \times 10^{-7}$
	$R^2$	0.9877	0.9786	0.9715
Temkin	$b_T$ (kJ/mol)	-7.5277	-4.4190	-7.5277
	$A_T$ (L/g)	$4.59 \times 10^{-7}$	$6.69 \times 10^{-4}$	$9.63 \times 10^{-4}$
	$R^2$	0.7066	0.9917	0.9988
Jovanovic	$Q_{max}$ (mg/g)	10.1097	12.6341	64.1805
	$K_J$ (L/g)	0.0014	0.0190	0.0044
	$R^2$	0.9963	0.9944	0.9912
Harkins-Jura	$A_H$ (g <sup>2</sup> /L)	-92.5926	-6.3816	-0.2702
	$B_H$ (mg <sup>2</sup> /L)	-0.2130	2.3733	2.8005
	$R^2$	0.5697	0.9120	0.9341

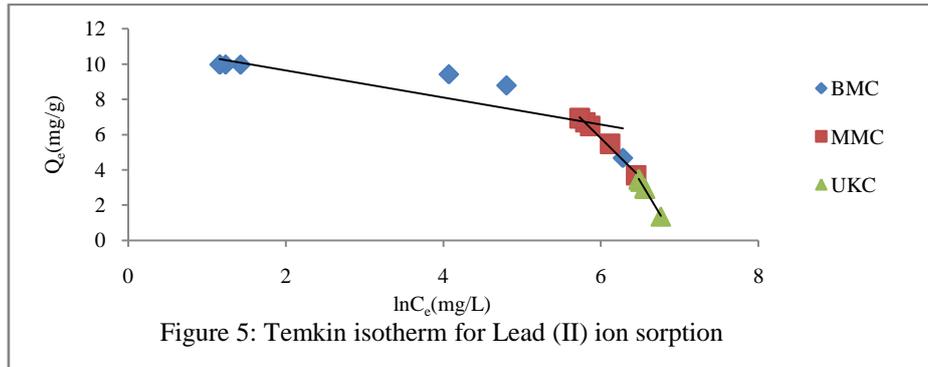
### 3.2.2 Langmuir Isotherm

The linear form of the isotherm (Eq. 5) was used to evaluate sorption parameters and constants as shown in Fig. 4, while Eq. 6 was used to evaluate the separation factor ( $R_L$ ) and values obtained are presented in Table 1. The  $R_L$  are negative (out of range which can be inferred that the sorption of  $Pb^{2+}$  is undefined) indicating unfavorable Langmuir isotherm. The negative values of  $K_L$  show that the energy of sorption may be exothermic. The maximum sorption capacity ( $Q_0$ ) and correlation factor ( $R^2$ ) follows a common trend in the following order  $BMC > MMC > UKC$ .



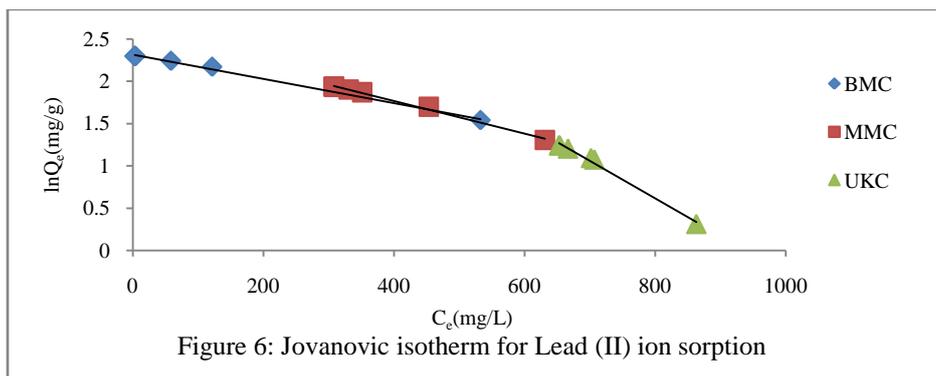
### 3.2.3 Temkin Isotherm

The linear plot of Temkin isotherm (Eq. 7) and evaluated parameters are presented in Fig. 5 and Table 1 respectively. The Temkin isotherm equilibrium binding constant  $A_T$  (L/g) and  $R^2$  follows a trend in the order:  $UKC > MMC > BMC$  while the negativity values of Temkin isotherm constant  $b_T$  (kJ/mol) relating to energy of adsorption indicating an exothermic process [37, 47].



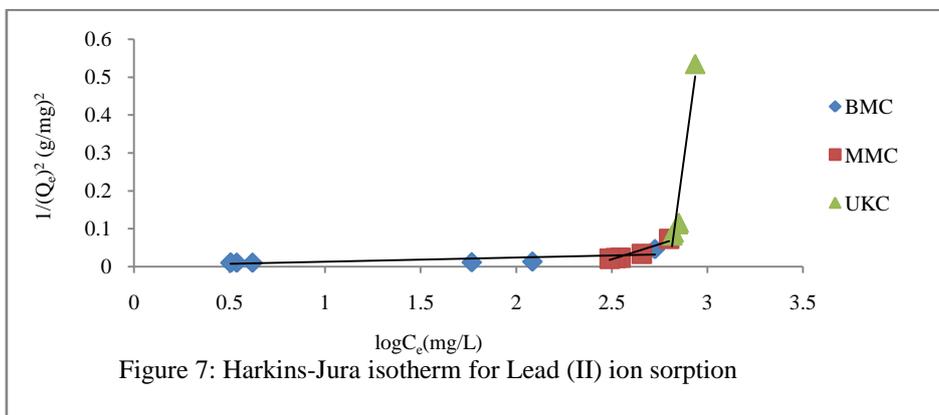
### 3.2.4 Jovanovic isotherm

This model of an adsorption surface (Eq. 8) is essentially the same as that considered by Langmuir [33, 34]. As presented in Fig. 6 and evaluated parameters presented in Table 1, the  $R^2$  follow this trend  $BMC > MMC > UKC$  while the  $Q_{max}$  follow this trend  $UKC > MMC > BMC$ .



### 3.2.5 Harkins-Jura isotherm

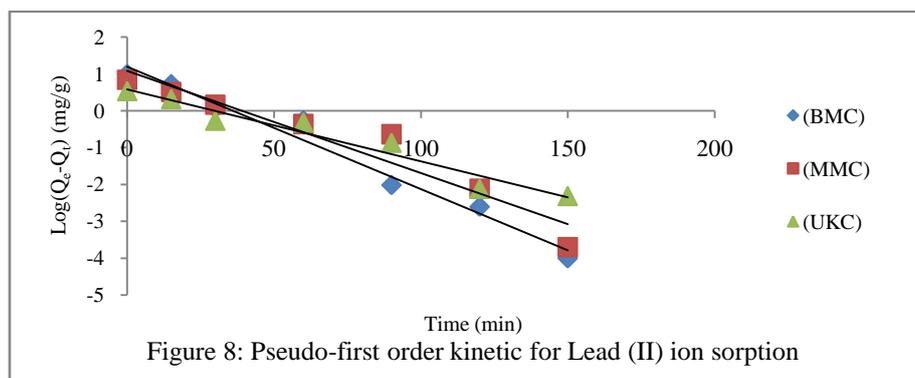
The isotherm (Eq. 9) accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution [48, 49]. As presented in Fig. 7 and evaluated parameters in Table 1, it was observed that the sorption equilibrium parameters are negative and  $R^2$  in this model is least which do not correspond with the experimental data.



## 3.3 Kinetics and Rate Parameters

### 3.3.1 Pseudo-first Order Kinetic

The model equation (Eq. 10) refers to the assumption of the rate of change of solute uptake with time which is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time [40]. Figure 8 shows the linear plot and its evaluated kinetic parameters presented in Table 2. There is no agreement between  $Q_{e(Exp)}$  &  $Q_{e(Cal)}$ , also  $K_1$  shows that the reaction is very slow calculated. Hence, the model does not fit the adsorption kinetics.

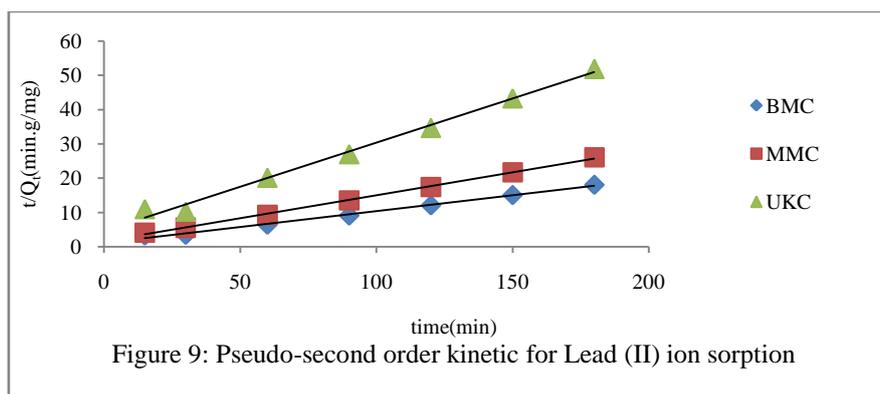


**Table 2:** Kinetic parameters and constants for Lead (II) ion sorption

Kinetic models	Parameter	Adsorbent		
		BMC	MMC	UKC
Pseudo-firstorder	$Q_{e(cal)}(mg/g)$	0.0777	0.0367	-0.2356
	$Q_{e(Exp)}(mg/g)$	9.9681	6.9270	3.4000
	$K_1(g/mg-min)$	0.0401	0.0343	0.0226
	$R^2$	0.9776	0.9268	0.9506
Pseudo-secondorder	$Q_{e(cal)}(mg/g)$	10.7643	7.4627	3.8865
	$Q_{e(Exp)}(mg/g)$	9.9681	6.9270	3.4000
	$K_2(g/mg-min)$	111.7998	35.8906	3.2856
	$R^2$	0.9945	0.9986	0.9916
Elovich	$A(mg/g-min)$	2.9005	2.3261	0.8316
	$B(g/mg)$	0.5372	0.7988	1.3317
	$R^2$	0.7555	0.8895	0.8114

### 3.3.2 Pseudo-second Order Kinetic

The model equation (Eq. 11) is based on the assumption that chemisorption is the rate determining step [50]. The linearized plot (Fig. 9) and its evaluated parameters (Table 2), shows closed trend of values between  $Q_{e(Exp)}$  &  $Q_{e(Cal)}$ , while  $K_2$  follow the trend  $BMC > MMC > UKC$  which shows that the reaction is faster and give a better fit adsorption kinetics.



### 3.3.3 Elovich Kinetic

The model equation (Eq. 12) was first developed to describe the kinetics of chemisorption of gas onto solids [50]. Linearized plot (Fig. 10) and corresponding evaluated parameters (Table 2), shows that the initial adsorption rate (A) follow the trend  $BMC > MMC > UKC$  while desorption constant (B) shows a reverse order of  $UKC > MMC > BMC$ . The  $R^2$  for BMC, MMC and UKC are was 0.7555, 0.8895 and 0.8114 respectively, which is not better fitted compared with both pseudo-first and pseudo-second order models.

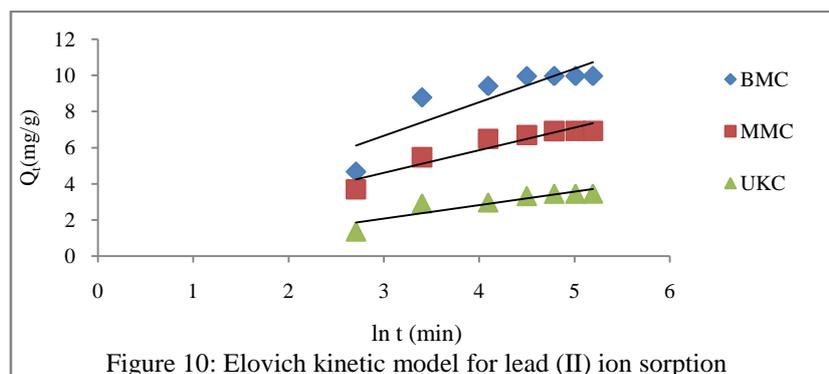


Figure 10: Elovich kinetic model for lead (II) ion sorption

#### IV. CONCLUSIONS

The modification of 'Alkali' Kaolinite clay by organic surfactant HDTMA-Br has greatly improved the removal of toxic  $Pb^{2+}$  from wastewater. The tested adsorption isotherms on equilibrium data shows the following trend of fitness Jovanovic>Langmuir>Temkin>Freundlich>Harkins-Jura. The kinetic models show the pseudo-second order to be the best fits of the equilibrium data, that is, chemisorption is the rate controlling mechanism.

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