Parametric studies of sulphate ion sorption at different pH on HDTMA-Br modified kaolinite clay

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Abstract—The adsorption of sulphate ion contaminant onto cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br) modified kaolinite was studied at different pH values, both sorption isotherm and kinetic models were tested. The sulphate ion uptake increases with as the pH value decreases with maximum adsorptive capacity of 1.906 mg/g at pH=3 in the 6 hours duration of batch process. The adsorption isotherms tested include: Freundlich, Langmuir, Temkin, and Redlich-Peterson. Temkinadsorption isotherm proved to be the best fit based on highest correlation factor R^2 values ranging from 0.996 to 0.998 for the pH values investigated. The negative values of Temkin binding energy b_T and Dubinin-Radushkevichrate constant K_{ad} indicate that the process is exothermic. The high values of Dubinin-Radushkevichfree energy E suggested that chemisorption is the rate controlling step. The separation factor RL was within the range of $0 < R_L < 1$ (0.31-0.32) which entails favourability and acceptability of the adsorption process.The best kinetic fit is Pseudo-second order model with highest correlation factor R^2 values ranging from 0.990 to 0.998 compared to other kinetic models tested.

Keywords—HDTMA-Br,Isotherms, Kinetics, Organo-kaolinite clay, Sorption, Sulphate ion.

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].

Inorganic oxyanion and non-ionic organic contaminants are typically mobile in soils and ground water since most natural materials have net negative surface charges[2;3], they are toxic to humans, wildlife and environment even at trace concentrations[4]. The removal of these pollutants should result in extremely low levels to comply with environmental regulations.

The World Health Organization (WHO) determined the maximum level of sulphate in drinking water as 500 mg/L[5], while the maximum values of 250 mg/L by Brazil, China and USA and 200 mg/L by Turkey[6].

The removal of sulphate ion from wastewater is a complex problem due to high solubility and stability of sulphate anions in aqueous solutions, established methods for sulphate removal include the biological treatment with sulphate reducing bacteria, membrane, ion exchange and chemical precipitation[5;7].

Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of these compounds at trace quantities[8]. Carbon adsorption is expensive, nonselective, adsorptive interference in the presence of naturally occurring organic matter and competition effects are exacerbated with time which interacts with treatment chemicals[9].

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 quaternary ammonium compounds (QAC)[1;10;11]. 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[2;12].

Hexadecyltrimethylammonium bromide is a type of surfactant used to modify the hydrophilic nature of kaolin clay to organophilic. It is as a solution in water with concentration of 24-26% (wt./vol.), pH value for 10% concentration of 2.8-3.2 and density of 0.97-0.98 g/cm³ at 20°C[13].

The research work encompasses the determination of effect and/or trend of pH on sulphate ion sorption using HDTMA-Br modified clay, predictions ofsorption kinetic and isotherm models that fits the data.

A.   Occurrences and effects of sulphate contaminant

Sulphates occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite ($MgSO_4 \cdot 7H2O$) and gypsum ($CaSO4 \cdot 2H_2O$). These dissolved minerals contribute to the mineral content of many drinking-waters[14].Sulphate in aquatic environment mainly comes from volcanic eruption, industrial wastewater emission and human excrement. Domestic sewage typically contains between 20 and 500 mg/L sulphate[15] while certain industrial effluents may contain several thousands of mg/L[2].

The threshold taste concentrations in drinking water are 250–500 mg/L (median 350 mg/L) for sodium sulphate, 250–1000 mg/L (median 525 mg/L) for calcium sulphate and 400–600 mg/L (median 525 mg/L) for magnesium sulphate[15]. Concentration of sulphate in water which are considered to have an "offensive taste" were approximately 1000 and 850 mg/L for calcium and magnesium sulphate, respectively[5;16].

B.   Organically modified clay

Due to the isomorphous substitutions in the aluminosilicate layers, natural clay minerals usually have a net negative charge, which is balanced by alkali metal and alkaline earth metal cations such as Na^+ and Ca^{2+} [1;17;18]. The strong hydration of these inorganic cations creates a hydrophilic environment on the surface and in the interlayer region of natural kaolin clay. When these cations are replaced by organic cations, producing an organoclay structure, the clay becomes hydrophobic in character and can be used to remove hydrophobic contaminants from water[2].

The degree of HDTMA+ addition is limited to the CEC of the clay being modified, where HDTMA+ replaces the charge-balancing cations on the surfaces[1].

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

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[19].

C.   Sorption of sulphate contaminant

Sorption of oxyanion contaminants by HDTMA-modified clays was attributed to anion exchange in which the sulphate ion replace bromide ion associated with the surfactant head group at the outer layer[1]. The exchange reaction on organoclay can be written as:

$$2(clayHDTMA.Br) + SO_4^{2-} \rightarrow (clayHDTMA)_2SO_4 + 2Br^- \qquad (2)$$

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions)[9]. Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution[17]. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases[20].

II.   SORPTION ISOTHERM

A sorption isotherm represents the amount of material bound at the surface (the sorbate) as a function of the material present in the gas phase and/or in the solution. Sorption isotherms are often used as empirical models, which do not make statements about the underlying mechanisms and measured variables[14]. They are obtained from measured data by means of regression analysis[11]. The most frequently used isotherms are the linear isotherm, Freundlich isotherm, the Langmuir isotherm, Frumkin isotherm Temkin isotherm and the BET model[21].

A.   Freundlich Isotherm model

The Freundlich isotherm model is an empirical equation employed to describe the isotherm data the linear form of the equation or the log form is [1]:

$$log\ q_e = \log K_F + \frac{1}{n}\log C_e \qquad (3)$$

Where K_F and n are Freundlich constants; n gives an indication of the favorability and K_F the capacity of the adsorbent. The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice versa[22]. Higher K_F value gives greater adsorption intensity[23].

B.   Langmuir Isotherm model

This model is based on two assumptions that the forces of interaction between adsorbed molecules are negligible, once a molecule occupies a site, and no further sorption takes place. The saturation value reached beyond which no further sorption takes place[24]. The saturation monolayer represented by the expression:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \qquad (4)$$

WhereC_e is equilibrium concentration (mg/L), q_e is the amount at equilibrium time per unit adsorbent (mg/g) and q_o and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively[25].

The essential characteristics of a Langmuir isotherm expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, defined by:

$$R_L = \frac{1}{(1 + bC_0)} \qquad (5)$$

Where Co is the initial adsorbate concentration (mg/L) and b is the Langmuir constant (L/mg)[22]. The R_L value indicates the adsorption nature to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$)[26].

C.   Temkin Isotherm model

Temkin equation is excellent for predicting the gas phase equilibrium (when organization in a tightly packed structure with identical orientation is not necessary), conversely complex adsorption systems including the liquid-phase adsorption isotherms are usually not appropriate to be represented[22].

The linear form of the equation is written as:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \qquad (6)$$

The curve is obtained by plotting q_e against$\ln C_e$, with A_T as Temkin isotherm equilibrium binding constant (L/g),b_TTemkin isotherm constant, R is universal gas constant (8.314 J/mol K) and T is temperature.

By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage[22;26].

D.   Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is an empirical model initially conceived for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism.It is generally applied to express the adsorption mechanism[27] with a Gaussian energy distribution onto a heterogeneous surface[21]. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions[22], with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship[27]:

$$E = (-2B_{DR})^{-0.5} \qquad (7)$$

Where B_{DR} is denoted as the isotherm constant, meanwhile, the parameter ε can be correlated as:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

The linear form is given as:

$$\ln(q_e) = \ln(q_s) - (K_{ad})\varepsilon^2 \qquad (9)$$

R, T and C_e are the gas constant (8.314 J/mol.K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively[21]. One of the unique features of the Dubinin–Radushkevich isotherm model lies on the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed against the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve[21;22].

E.   Redlich–Peterson isotherm model

Redlich–Peterson isotherm is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation[9;24]. The model has a linear dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria over a wide concentration range, that can be applied either in homogeneous or heterogeneous systems due to its versatility[28;29].

The general linear form of Redlich–Peterson isotherm is given by:

$$ln\left(K_R\frac{q_e}{C_e} - 1\right) = g ln(C_e) - ln(a_R) \qquad (10)$$

The curve is obtained by plotting $ln\left(K_R\frac{q_e}{C_e} - 1\right)$ (mg/g) against $ln\, C_e$ (mg/L), where g (mg/g) and a_R(mg^{-1}) are Redlich–Peterson isotherm constant[24].

Typically, a minimization procedure is adopted in solving the equations by maximizing the correlation coefficient between the experimental data points and theoretical model predictions with solver add-in function of the Microsoft excel[24]. In the limit, it approaches Freundlich isotherm model at high concentration (as the exponent tends to zero) and is in accordance with the low concentration limit of the ideal Langmuir condition (as the values are all close to one)[24].

III. KINETIC MODELS

Kinetic models are rate equations or rate laws use to describe the relationship that links a reaction rate with concentration or pressure of the reactants and constant parameters (normally rate coefficients and partial reaction orders)[30]. To determine the rate equation for a particular system one combines the reaction rate with a mass balance for the system[31].

A.   Pseudo First-Order Kinetic Model

One of the primary goals of chemical kinetics experiments is to measure the rate law for a chemical reaction[22]. There are many ways to do this, but one of the most often used is the method of pseudo-first order conditions. This method is sometimes also referred to as the method of isolation or the method of flooding[30]. The linearized form can be represented by:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (11)$$

A plot of $\log(q_e - q_t)$ (mg/g) against time t(s) gives a straight line with the slope of $\frac{K_1}{2.303}$(mg/g.s) and intercept of $\log q_e$ (mg/g)[1;30].

B.   Pseudo Second-Order Kinetic Model

For adsorption system following the pseudo second kinetics, the adsorbate was assumed to get adsorbed onto two surface sites[32]. Thus the sorption kinetics following pseudo second-order kinetics can be represented in the linearized form by:

$$\frac{1}{q_t} = \left(\frac{1}{K_2 q_e^2}\right)\frac{1}{t} + \frac{1}{q_e} \qquad (12)$$

Where K_2 is the rate of sorption (g/mg min), q_e the amount of substance adsorbed onto organoclay at equilibrium (mg/g) and q_t is the amount of substance adsorbed at any time (mg/g)[33].

C.   Elovich kinetic model

Elovich equation is one of the useful kinetic models for describing chemisorption. The simplified Elovich model is presented by[34].

$$q_t = \frac{1}{B}\ln(AB) + \frac{1}{B}\ln(t) \qquad (13)$$

Where A is the initial adsorption rate (mg/g·min) and B is desorption constant (g/mg) for a particular experiment. Because adsorption is a time dependent process, prediction of the rate determining step is important for evaluation of adsorbent and design of a system for removal of sulphate from aqueous solutions[34].

Generally, for a solid-liquid adsorption process, the solute transfer typically is characterized by either external mass transfer, intraparticle diffusion, or both[35]. This step might be controlled by both intraparticle and external transport mechanisms.

III.   EXPERIMENTAL SECTION

A.   Preparation of bilayer modified clay and sulphate contaminant

Bilayer modified clay was prepared according to Aroke *et al.*,[36]. A stock solution containing 5mM concentration of sulphate ion (SO_4^{2-}) from sodium sulphate (Na_2SO_4) was prepared and confirmed by DR 2000 spectrophotometer.

B.   Batch adsorption process

Studying the effect of pH on sorption for optimum BMC dosage of 200 mg in 10mL of sulphate ion contaminant was shaken laterally at 1200rpm and readings taken at interval for 6 hours at 298K. The two phases are then

separated by means of centrifugation and supernatant was analysed using DR 2000 spectrophotometer to determine the amount of sulphate ion contaminant unadsorbed in the supernatant. Thus, the equilibrium relationship curve was established to know the trend of sorption at different pH values.

<center>IV.   RESULTS AND DISCUSSION</center>

A.   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 bilayer modified BMC were calculated using equilibrium studies at different pH values with respect to time. The mass balance equation for this process at equilibrium is given by[37].

$$q_e = (C_o - C_e)\frac{v}{m} \qquad (14)$$

Where q_e (mg/g) is the adsorbent capacity, 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).

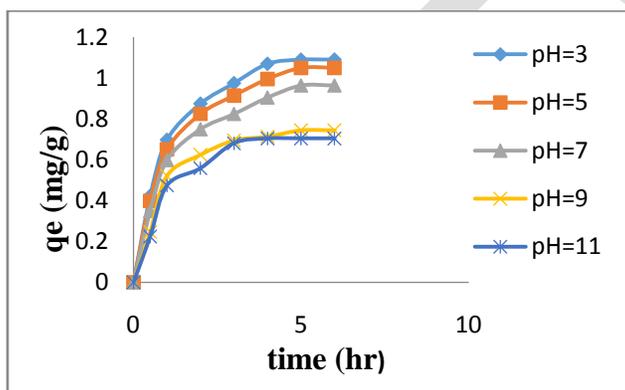

Fig. 1: Sulphate ionadsorptive capacities onto BMC at different pH values

From Figure 1, the data shows adsorptive capacities for contact time ranging from 0 to 6 hours. It is observed that after 6hours no significant adsorption of sulphate ion onto BMC was recorded. At this point and thereafter, the adsorption and desorption of sulphate contaminant reach a dynamic equilibrium.

B.   Adsorption Isotherms

The fit of sorption experimental data by means of different isotherm models is an important step in finding the suitable model for the design process and hence to improve knowledge concerning the adsorption mechanism[38].

Freundlich isotherm

The equilibrium sorption parameters were evaluated using linearized form of Freundlich isotherm (Eq.3) for the values of n (indication of favorability) and K_F (capacity of adsorbent) (only pH=3 shown as Fig. 2). The evaluated parameters presented in Table I.
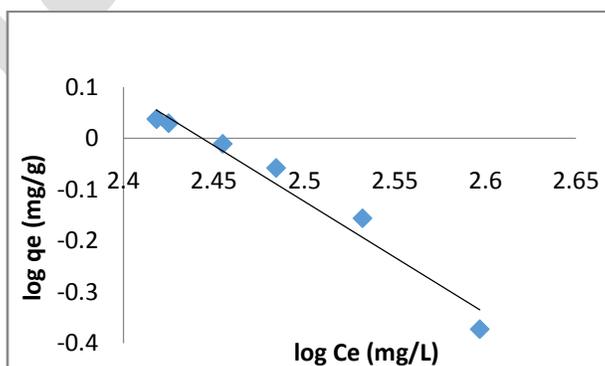

Fig. 2: Freundlich adsorption isotherm plot at pH=3.

Table I: Freundlich constants and correlation factors

pH value	n	K_f (mg/g)	R^2
3	-0.4587	2.13×10^5	0.965
5	-0.4259	5.19×10^5	0.971
7	-0.3672	5.10×10^6	0.962
9	-0.2434	1.74×10^{10}	0.971
11	-0.2294	7.76×10^{10}	0.965

The values of (n and 1/n) are negative which are below unity implies chemisorption[39]. K_f are very high and increases with pH, with the lowest value at pH=3 showing that adsorption of sulphate ion contaminant onto modified clay is higher and more favourable at lower pH values.

Langmuir isotherm
Langmuir isotherm model (Eq. 4) was used to evaluate the equilibrium processes for sulphate ion sorption parameterssuch as; maximum sorption capacity (q_0), sorption energy (b) and correlation factors (R^2) while separation factor (R_L) was evaluated using Eq. 5. The linear plot of Langmuir isotherm model for different pH values was evaluated (only pH=3 shown as Fig. 3) and evaluated parameters presented in Table II.
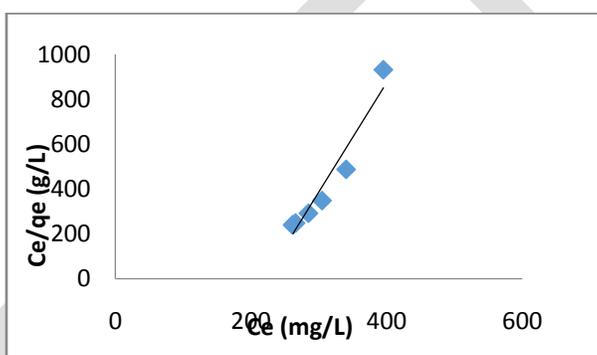

Fig. 3: Langmuir adsorption isotherm plot at pH=3

Table II. Langmuir constants, correlation and separation factors

pH value	q_o (mg/g)	b (L/mg)	R^2	R_L
3	0.2053	0.00454	0.936	0.31
5	0.1685	0.00476	0.932	0.31
7	0.1490	0.00397	0.924	0.31
9	0.0789	0.00330	0.938	0.32
11	0.0707	0.00322	0.921	0.32

The dimensionless constant R_L referred to as separation factorwas used to evaluate the whether or not the sorption is favorable and acceptable (Eq. 5). Since the values of R_L are less than unityat all the pH values evaluated, it can be inferred that the adsorption of sulphate ion contaminant onto HDTMA-Br modified clay is highly favorable and acceptable [17].

Temkin isotherm
Using linearized form of Temkin isotherm (Eq. 6), the equilibrium sorption parameters were evaluated at different pH values (only pH=3 shown as Fig. 4) and results presented in Table III.
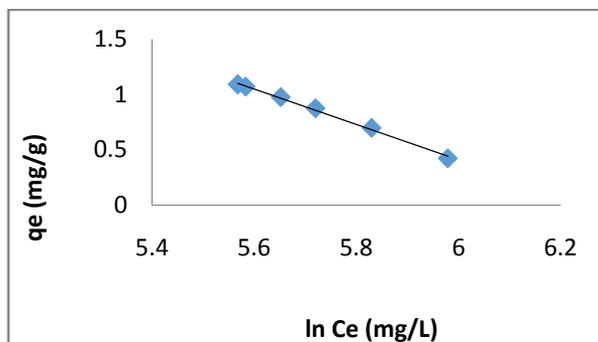
Fig. 4: Temkin adsorption isotherm plot at PH=3.

Table III: Temkin constants and correlation factors

pH value	b_T (kJ/mol)	A_T (L/g)	R^2
3	-1.56	0.00191	0.996
5	-1.51	0.00197	0.996
7	-1.45	0.00197	0.997
9	-1.31	0.00203	0.998
11	-1.30	0.00203	0.998

Temkin isotherm equilibrium binding constant A_T(L/g) was found to be irregular as the pH increases while Temkin isotherm constant b_T relating to energy of adsorption shows that the adsorption process is exothermic. Temkin recorded the highest R^2 values of 0.996-0.998 compared to other isotherm model.

Dubinin-Radushkevich isotherm
The linearized form of Dubinin-Radushkevich isotherm (Eq. 9) was used to evaluate equilibrium sorption parameters at different pH values (only pH=3 shown as Fig. 5) and the free energy (E) calculated using (Eq. 9). The evaluated parameters presented in Table IV.
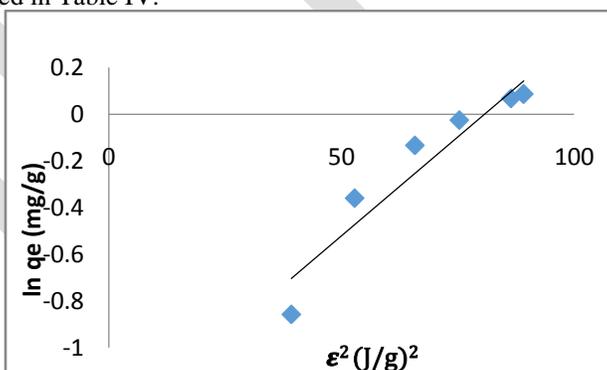

Fig. 5: Dubinin-Radushkevich adsorption isotherm plot at pH=3.

Table IV: Dubinin-Radushkevich constants, correlation factor and free energy

pH value	q_s (mg/g)	K_{ad}(mol^2/kJ^2)	R^2	E (kJ/mol)
3	0.2546	-0.017	0.913	9.4233
5	0.2240	-0.019	0.912	19.4233
7	0.1685	-0.024	0.913	27.4233
9	0.0602	-0.046	0.941	41.2705
11	0.0509	-0.050	0.935	50.1299

Since the energy at pH = 3 falls between 8-16 kJ/mol the process can be termed ion-exchange mechanisms while for pH value between 5 and 11 ranges between 19.4233-50.1299kJ/mol shows that chemisorption process play an

important role in the adsorption[32]. The maximum adsorptive capacity (q_s) decreases as pH value increases (0.0509-0.2546 mg/g) while the adsorption equilibrium rate constants also decreases as pH value increases (-0.017 to -0.050 mol^2/kJ^2) showing exothermic process[40].

Redlich-Peterson isotherm
Using linearized form of Redlich-Peterson isotherm model (Eq. 10). The equilibrium sorption parameters were evaluated at different pH values (only pH=3 shown as Fig. 6) and evaluated parameter such as equilibrium adsorption capacity (g), adsorption constant (mg-1) and correlation factors presented in Table V.
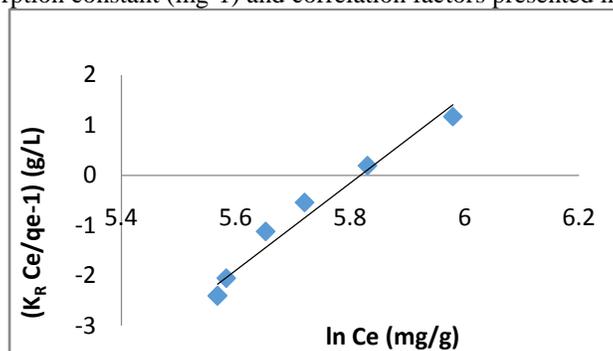

Fig. 6: Redlich-Peterson adsorption isotherm plot at pH=3.

Table V: Redlich-Peterson constants and correlation factors

pH value	g (mg/g)	a_R (mg^{-1})	R^2
3	8.690	1.10×10^{-22}	0.968
5	7.639	5.54×10^{-20}	0.986
7	6.938	3.28×10^{-18}	0.998
9	7.231	5.87×10^{-19}	0.995
11	7.442	1.65×10^{-19}	0.992

The equilibrium adsorption capacity was found to be above the initial adsorbent dosage of 2mg/g, this show the model does not fit the given date. Also, the adsorption constant a_R varied between 1.10×10^{-22} to 3.28×10^{-18} mg^{-1} which is rather too low and insignificant, that is, very low rate.

C.   Kinetics and Rate Parameters
Adsorption kinetics is another important characteristic for evaluating the efficiency of adsorption. The sorption of oxyanion contaminants from liquid phase to solid phase is normally assumed to be controlled by physicochemical processes[41]. For this research work pseudo-first order, pseudo-second order and Elovich kinetic models were used.

Pseudo-first order kinetics
From Eq. 11 the linearized plot for Pseudo-first order kinetic model for sulphate ion sorption at different pH values was plotted as shown in Fig. 8. The kinetic parameters such as rate constant (K_1), equilibrium sorption capacity (q_e) and the correlation factor (R^2)value were evaluated as presented in Table VI.
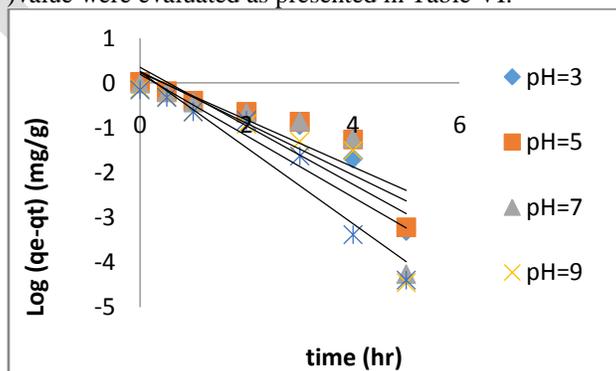

Fig. 7: Pseudo-first order kinetic model at different pH values.

Table VI: Pseudo-first order kinetic constants and correlation factors

pH value	K_1 (hr^{-1})	R^2	q_e (mg/g)
3	1.3288	0.874	1.8155
5	1.2091	0.807	1.6827
7	1.5016	0.704	2.2284
9	1.5776	0.760	1.5560
11	1.9506	0.924	1.7947

The highest value of rate constant K_1 is 1.9506 hr^{-1} with corresponding correlation factor R^2 of 0.924 and equilibrium sorption capacity q_e of 1.7947 mg/g at pH=11. Also the lowest value of rate constant K_1 is 1.2091 hr-1 with corresponding correlation factor R^2 of 0.807 and equilibrium sorption capacity q_e of 1.6827 mg/g at pH=5. The correlation factors R^2 varied between 0.704 and 0.924 which are generally low across the pH values investigated.

Pseudo-second order kinetics
From Eq. 12 the linearized plot for pseudo-second order kinetic model for sulphate ion sorption at different pH values plotted as shown in Fig. 9 and evaluated kinetic parameters as presented in Table VII.
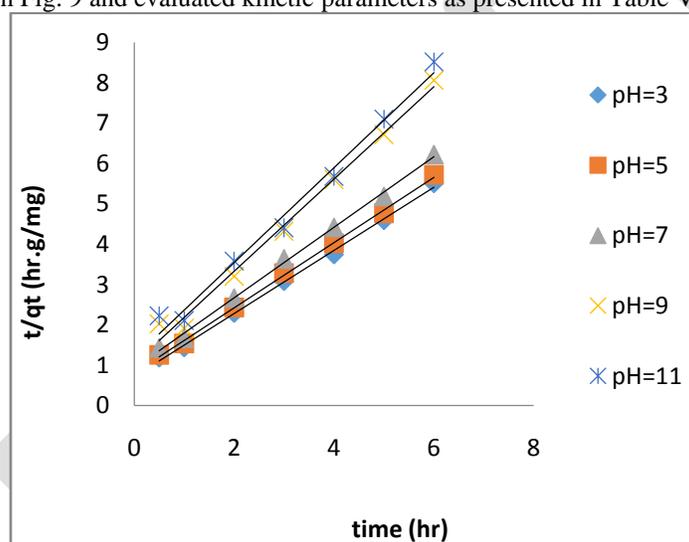

Fig. 8: Pseudo-second order kinetic model at different pH values.

Table VII: Pseudo-second order constants and correlation factors

pH value	K_2 (g/mg.hr)	R^2	q_e (mg/g)
3	0.8672	0.998	1.2772
5	0.8161	0.998	1.2392
7	0.8367	0.997	1.1429
9	1.2631	0.990	0.8749
11	1.1651	0.986	0.8503

The highest value of rate constant K_2 is 1.2631 g/mg.hr with corresponding equilibrium sorption capacity q_e of 0.8749 mg/g and correlation factor R^2 of 0.990at pH=9 while the lowest value of rate constant K_2=0.8162 g/mg.hrwith corresponding equilibrium sorption capacity q_e of 1.2392 mg/g and correlation factor R^2 of 0.998at pH=5. The correlation factors R^2 varied between 0.990 and 0.998 which are very high across the pH values investigated compared with both Pseudo-first order and Elovich kinetics. Since pseudo-second order best describe the process, then chemisorption is the rate controlling step[42].

Elovich kinetic model
From Eq. 13 the linearized plots of Elovich kinetic model for sulphate ion sorption at different pH values plotted as shown in Fig. 9 and evaluated kinetic parameters presented in Table VIII.
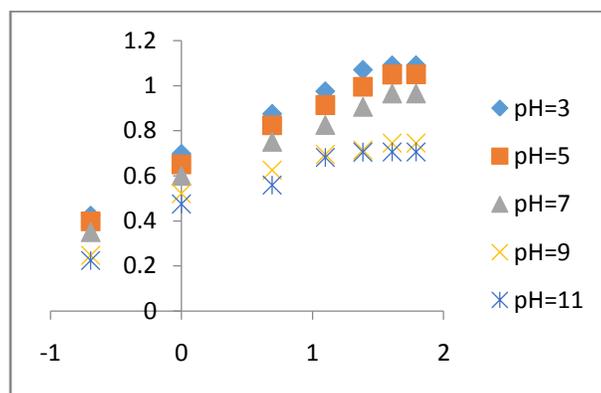
Fig. 9: Elovich kinetic modelat different pH values.

Table VIII: Elovich constants and correlation factors

pH value	A (mg/g.hr)	R^2	B (g/mg)
3	3.0950	0.975	3.6900
5	2.7572	0.968	3.8023
7	2.3890	0.973	4.0816
9	2.0617	0.920	5.2632
11	1.7040	0.929	5.2632

The initial adsorption rate (A) decreases as pH value increases and are greater than unity while the desorption constant (B) shows that the desorption rate increases as pH value increases but constant at pH value of 9 and 11. The correlation factors R^2 ranges between 0.920 and 0.975 which is higher than Pseudo-first order kinetic but lower than Pseudo-second order kinetic model.

V.   CONCLUSIONS

The batch adsorption process for sulphate ion contaminant onto BMC was conducted and the following conclusions could be drawn:

- The equilibrium adsorption capacity of BMC decreases with increasing contaminant pH value from acidic to basic medium (pH value 3 to 11).
- From the different adsorption isotherms employed, Temkin model shows the best fit based on correlation factor R^2 valuesthat ranges between 0.996and 0.998 for the pH values investigated.
- The separation factor R_L was found to be within $0<R_L<1$ (0.31-0.32) for all the pH values investigated, the indicating a highly favourable and acceptable adsorption process.
- From the kinetic models studied, the pseudo-second order kinetic model best fit sorption process having the highest R^2 (0.986-0.998) for the kinetic models tested and pH values.
- The rate controlling mechanism is chemisorption as evident from high R^2 value of Elovich kinetic model and high free energy (E) from Dubinin-Radushkevich isotherm model.
- The adsorption process is exothermic as shown by Temkin binding energy (b_T) and Dubinin-Radushkevich adsorption energy (K_{ad}) which are all negatives for all pH values investigated.

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