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Comparative Sorption of Diatomic Oxyanions onto HDTMA-Br Modified Kaolinite Clay

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Abstract: *The adsorption isotherms and kinetic models were tested on the comparative sorption of oxyanions onto hexadecyltrimethylammonium bromide (HDTMA-Br) surfactant modified kaolinite clay also known as organo-kaolinite clay. The percentage removal of sulphate ion sorption was 40.42% and 78.13% onto MMC and BMC respectively, while chromate ion sorption was 26.72% and 58.62% onto MMC and BMC respectively. Thus, sulphate ion sorption shows better removal compared to chromate ion sorption of 33.60% and 24.97% onto MMC and BMC respectively. Langmuir and Frumkin isotherm models best described the adsorptive mechanism, hence the validity of the Langmuir-type separation factor R_L ($0<R_L<1$) was highly favourable and acceptable while the Frumkin isotherm gave the best regression correlation R^2 although sulphate ion sorption responded better than the chromate ion sorption. The initial adsorption rate 'α' and the extent of surface coverage 'β' was higher on sulphate ion sorption compared to chromate ion sorption. In general the models tested predicts exothermic and chemisorption processes.*

Keywords*: Hdtma-Br, Isotherms, Kaolinite clay, Kinetics, Oxyanion, Sorption.*

I. Introduction

The quality and accessibility of drinking water are of paramount importance to human health. Drinking water may contain disease-causing agents and toxic chemicals and to control the risks to public health, systematic water quality monitoring and surveillance are required. Thousands of chemicals have been identified in drinking water supplies around the world and are considered potentially hazardous to human health at relatively high concentrations[1].

The industrialization and modification of manufacturing processes have resulted in an increase in the volume of wastewater discharge into the environment which causes water pollution[2;3]. Wastewater from industrial operations transport many chemicals that have adverse effects on the environment[4].

Ammonia and amine compounds from carcass-processing and sewage-treatment plants[5], phosphates and nitrates from paper mills, fertilizer plants and detergent industries[6], cyanide and its compounds from electroplating and mining (extraction of gold, silver, etc.) industries end up in lakes, creeks and rivers[7]. These chemicals may be toxic to humans, environment and animals[8]. Drinking water free of toxic chemicals or having below the maximum acceptable limit of concentration is crucial for healthy life[9].

Increased industrialization, use of chemicals for various concerns, agricultural and domestic activities both in developing and developed countries have led to ground and surface drinking water contamination with a number of toxic pollutants[10;11;12]. It has been reported that 60% of the population of developing countries have no access to safe drinking water[9;10]. Nigeria being a developing country falls under this category.

Sulphates occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$). These dissolved minerals contribute to the mineral content of many drinking-waters.Sulphate and sulphuric acid products are used in the production of fertilizers, chemicals, dyes, glass, paper, soaps, textiles, fungicides, insecticides, astringents and emetics. They are also used in the mining, wood pulp, metal and plating industries, in sewage treatment and in leather processing[13]. Aluminium sulphate (alum) is used as a sedimentation agent in the treatment of drinking-water. Copper sulphate has been used for the control of algae in raw and public water supplies[14;15].Sulphates are discharged into water from mines and smelters and from kraft pulp and paper mills, textile mills and tanneries. Sodium, potassium and magnesium sulphates are all highly soluble in water, whereas calcium and barium sulphates and many heavy metal sulphates are less soluble[16]. Atmospheric sulphur dioxide formed by the combustion of fossil fuels and in metallurgical roasting processes, may contribute to the sulphate content of surface waters. Sulphur trioxide produced by the photolytic or catalytic oxidation of sulphur dioxide combines with water vapour to form dilute sulphuric acid, which falls as "acid rain"[17].

Chromate is a metallic species widely used in industrial applications including metal plating, leather tanning and dye manufacture. Historically, it has also been added to process waters used for cooling towers because it was considered an inexpensive corrosion inhibitor. The two major forms found in the environment are hexavalent Cr(VI) and trivalent Cr(III) species. Large doses of Cr(VI) have been linked to cancer, skin ulcers, and other maladies. The high mobility and solubility of Cr(VI) frequently results in contamination of soils, surface waters and groundwater. In contrast, trivalent species are generally considered innocuous in the environment because of its lack of mobility as an insoluble species and its beneficial use as a trace nutrient in plant and animal nutrition[19;20;21].

The carcinogenic effects of chromate exposure have been attributed to the accumulation of chromium within the cell. Primary accumulation in the cell generally manifests itself as Cr(III) precipitation due to uptake of Cr(VI) from the environment followed by intracellular reduction of the species[22]. Given widespread uncertainties concerning exposure and uptake, chromium remediation by reductive precipitation alone is not a foolproof strategy for mitigating exposure. In fact, the more prudent strategy is likely to incorporate complete removal from contaminated sites, eliminating any risks of exposure and oxidative remobilization[21].

II. Kaolin And Organo-Kaolinite Clay

Clay materials can be modified using a variety of chemical/physical treatments to achieve the desired surface properties for best immobilization of contaminants. For example, when surfaces of these clays are modified with organic molecules, the resulting products are called organoclay[23].

The various industrial uses of clays and clay minerals are due to their physical and chemical properties, being applied in oily well drilling muds, catalysts, adsorbents, emulsion stabilizers, loading agents, pharmaceutical industry, cosmetics, adhesives and so on, in the midst of other applications[24]. The importance of these clays is due to the fact that they are abundant in soils and sediments, besides having high specific area, properties of ionic exchange and thermal and chemical stability[25;26]. On the other hand, natural clays have intrinsic disadvantages; therefore, they may contain exchanged inorganic cations, which are highly hydrated in aqueous medium, rendering a hydrophilic character to the surfaces. Thus, they are good adsorbents for ionic and polar compounds, but not for nonionic and hydrophobic compounds[27].

Theintercalation of organic surfactants between the layers of the clays modifies some surface properties, causing the clays to swell and forming a thixotropic gel in organic environment, thus increasing the basal distance between the layers[28]. The d-spacing of the organoclays depend on the length of the alkyl chains and the packing density of the surfactants within the galleries of the clay minerals[27]. When large organic cations (derived from organic surfactants) of the form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$, where R is a long alkyl group (with 12 or more carbon atoms), accommodate on the exchanging sites of the clay, the surface properties change from hydrophilic to hydrophobic character. The combination of the hydrophobic character andthe layer-like structure of the silicates lead to these singular physico-chemical properties; the behavior and properties of the organoclays depend on their structure and which organic molecules can be found inside their galleries[29].

The organo-kaolinite clay is formed when cationic surfactant is retained by the kaolin clay in aqueous system. The quaternary ammonium compounds 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[27].

Once the organic cations are adsorbed on the surface of the clay, an organic phase is formed which is derived from the alkyl hydrocarbons chains. The presence of adsorbed organic cations on clay surface affects the interactions between the clay particles. As a result, rheological and colloidal properties of the clay dispersions may be greatly influenced, and the aggregates size may be increased via cluster-cluster aggregation, or decreased due to the deflocculating effect of the surfactants[29;30].

The organoclays swell in specific organic solvents and the cationic molecule portion of ammonium quaternary salts occupies the sites previously occupied by sodium cations, while the long organic chain remains intercalated in the clay lamellae[31]. The organically-modified clays turn into organoclays, whereby their surface energy is decreased and they become more compatible with organic liquids. Several organophilic clays have proved to be highly efficient in removing neutral organic contaminants from water and can be used, for instance, to adsorb oil and fuel spills and to treat contaminated water, line-waste reservoirs, industrial wastes, and so on[27;31].

2.1 Adsorption Isotherms

Among several existing models:Langmuir, Freundlich, Dubinin-Radushkevich and Frumkinadsorption isothermmodels were utilized to describe the optimum experimental data.

2.1.1 Langmuir isotherm

The Langmuir isotherm model is based on the hypothesis that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The linearized Langmuir model is[32;33]:

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

Where q_o indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant b (L/mg) is relatedto the energy of adsorption. For fitting the experimental data, a plot of $\frac{C_e}{q_e}\ (g/L)$ against $C_e\ (mg/L)$ was done to determine the constants and correlation factor (R^2) values. A dimensionless constant separation factor, R_L, to test suitability of the Langmuir-type adsorption process can beexpressed as:

$$R_L = \frac{1}{1 + bC_0} \qquad (2)$$

Where b is the Langmuir constant (L/mg) and C_0 is the initial concentration (mg/L). The value of R_L indicates whether the isotherm is irreversible (R_L=0), favourable (0<R_L<1), linear (R_L=1) or unfavourable (R_L>1).

2.1.2 Freundlich isotherm

The Freundlich isotherm model which is an empirical equation used to describe heterogeneous adsorption systems, thus the linearized Freundlich model can be expressed as:

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

Where K_F (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent, n is the Freundlich exponent related to adsorption intensity and values of n>1 represent favorable adsorption condition. For fitting the experimental data, a plot oflogq_e(mg/g) againstlogC_e(mg/L)yield the constants and correlation factor (R^2) values[24;34].

2.1.3 Dubinin-Radushkevich (D-R) isotherm

D–R 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 with a Gaussian energy distribution onto a heterogeneous surface. Its linearized form can be express as[24]

$$\ln(q_e) = \ln(q_s) - K_{ad}\,\varepsilon^2 \qquad (4)$$

With parameter ε which can be correlated as

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \qquad (5)$$

where R, T, q_e and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K), adsorptive capacity (mg/g) and adsorbate equilibrium concentration (mg/L) respectively, while q_s (mg/g) and K_{ad} are D-R constants respectively.A plot of $\ln q_e\ (mg/g)$ against $\varepsilon^2 (J/g)^2$ was carried out to evaluate the constants and R^2 values.The 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[35;36]:

$$E = \frac{1}{\sqrt{2B_{DR}}} \qquad (6)$$

Where B_{DR} is denoted as the isotherm constant. One of the unique features of the D–R 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 curve, named as the characteristic curve[24;37].

2.1.4Frumkin isotherm

The linearized form of Frumkin isotherm model is given as[22]:

$$q_e = n_T \ln K_T + n_T \ln C_e \qquad (7)$$

Where q_e is the sorbed amount (mg/g); C_e is the equilibrium concentration of the sorbate (mg/L) and K_T (L/g) and n_T(J/mol) are the Frumkin constants. This is a hybrid of Langmuir and Freundlich isotherm models, it uses the same plot as the Tempkin isotherm but differs in equation expression and constants determination[22;38].A plot of $q_e (mg/g)$ against $\ln C_e (mg/L)$ was carried out to evaluate the constants and R^2 values.

2.2 Adsorptionkinetics

Adsorption kinetics is investigated to develop an understanding of the chemisorption, physisorption and the possible mechanism of sorption reactions[39;40]. Kinetic data can be used to predict the rate at which the targeted contaminant is removed from aqueous solutions.It is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants[41].

2.2.1 Pseudo-first order kinetic model

In order to investigate the optimum sorption kinetics, the Lagergren pseudo-first ordermodel proposed in which the linearized form can be express as

$$\log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \qquad (8)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), q_t is the amount adsorbed at time t (mg/g), k_1 is the first order rate constant (hr^{-1}) and t is the time (hr). A linear trace is expected between the two parameters $\log(q_e$-$q_t)$(mg/g) and t(hr)with the slope of $\frac{k_1}{2.303}$(mg/g.hr) and intercept of $\log q_e$ (mg/g). One of the primary goals of chemical kinetics experiments is to measure the rate law for a chemical reaction. This method is sometimes also referred to as the method of isolation or the method of flooding[42].

2.2.2 Pseudo-second order kinetic model

In this model, the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases[40]. The model is usually represented by its linear form as[41]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (9)$$

Where k_2 is the equilibrium rate constant of pseudo-second order sorption (g/mg-hr), q_e is the amount of oxyanion sorbed at equilibrium (mg/g) and q_t is amount of oxyanion on the surface of the sorbent at any time t, (mg/g) and t is the time (hr)[43;44].

2.2.3 Elovich kinetic model

The Elovich equation is mainly applicable for chemisorption process. The equation is often valid for systems in which the adsorbing surface is heterogeneous. TheElovich model is generally expressed as[45]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (10)$$

The plot of $q_t$against $\ln t$is expected to give a straight line with a slope of $\frac{1}{\beta}$ and an intercept of $\frac{1}{\beta}ln(\alpha\beta)$. Where $\alpha$is the initial adsorption rate (mg/(g·hr)) and βis desorption constant (g/mg) for a particular experiment.Because adsorption is a time dependentprocess,prediction of the rate determiningstep is important forevaluation of adsorbent and design of a system for removal of contaminants from aqueous solutions[46]. Generally, for a solid-liquid adsorption process, the solute transfer typically is characterized by either external mass transfer, intraparticle diffusion, or both. This step might be controlled by both intraparticle and external transport mechanisms[47].

III. Experimental Section

3.1 Organo-kaolinite clay and contaminant preparation

Clay was obtaineddirectly from mines site in Alkaleri LGA of Bauchi State, Northeast-Nigeria,which was subjected to preliminary treatment and physicalbeneficiation according to Aroke, *et al.*[48]. 100.00g of pre-treated raw kaolin clay was accurately measured and dissolved into 0.095 and 0.190mol of cationic surfactant HDTMA-Br based on cation exchange capacity of the clayfor monolayer modified (MMC) and bilayer modified (BMC) organo-kaolinite clay respectively. The aqueous mixture was charged into a batch mixer and stirred continuously 24 hours (time required to reach equilibrium) at stirring speed of 740rpm at 298K[27]. The contents was centrifuge at 3000rpm for 30 minutes and supernatant decanted. The solid part was washed with distilled water for four times and finally dried in oven at 60°C for 20 hours.

Solutions containing 1mM concentration of sulphate ion and chromate ion respectively was prepared using de-ionized water and confirmed by Atomic Absorption Spectrophotometer (AAS). The solution pH was adjusted to 3 (acidic medium) using dilute hydrochloric acid and verified with pH meter.

3.2 Batch adsorption

Organo-kaolinite clay optimum dosage of 200g/L wasshaken laterally at 1200rpm at 298K and sample collected for analyses of supernatant at intervals between 0 and 6hours after centrifuging. The AAS was used to analyse the supernatant and the amount of oxyanions contaminant unadsorbed was determined.

The equilibrium relationship curve was used to know the trend of contaminant sorption as a function of time. The equilibrium relationship curve was established for organo-kaolinite clay in the sorption of sulphate and chromate ions. Equilibrium isotherm and kinetic modelsparameters and constants were determined.

IV. Results And Discussion

4.1Adsorption equilibrium studies

The adsorptive capacity of oxyanions sorption by organo-kaolinite clay was obtained from equation (11)[23;49] and the equilibrium plot shown in Figure 1

$$q_e = (C_0 - C_f)\frac{V}{m} \qquad (11)$$

Where q_e (mg/g) is the adsorbent capacity, C_0 (mg/L) is the initial concentration, C_f (mg/L) is the final or equilibrium concentration, V is the experimental solution volume (L) and m is the adsorbent dosage (g).

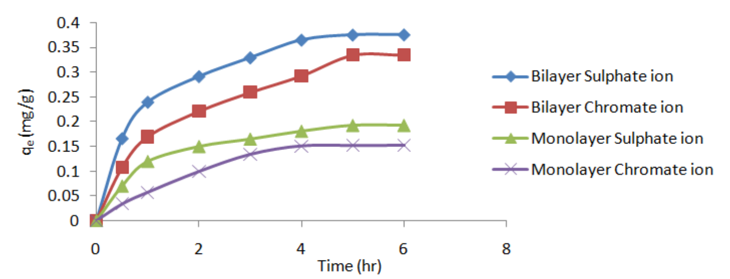

Figure 1: Equilibrium adsorptive capacity of chromate and sulphate ions sorption

The amount of oxyanions adsorbed from initial solution concentration was obtained from equation (12)[23;49;50]:

$$\%\, oxyanion\ removal = \left(\frac{C_0 - C_e}{C_0}\right)100 \qquad (12)$$

The percentage removal of sulphate ionby MMC and BMC was 40.24%and 78.13% respectively,while for chromate ion was 26.72% and 58.62% respectively.Hence sulphate ion shows greater sorption ability than chromate ion for both modified kaolinite clays,which is equally obvious from the adsorptive capacity versus time curve of Figure 1.

4.2 Modeling of sorption isotherms

The fit of experimental data was tested by four different adsorption isotherms namely:Langmuir, Freundlich,Dubinin-Radushkevich and Frumkin as presented in linearized form of Eqs. 1, 3, 4 and 7; while the plots of isotherms are shown in Figures 2-5, the evaluated parameters and constants are also presented in Tables 1 and 2. The test for best fit is an important step in finding the suitable isotherm for the design process and hence to improve knowledge concerning the adsorption mechanism[51].

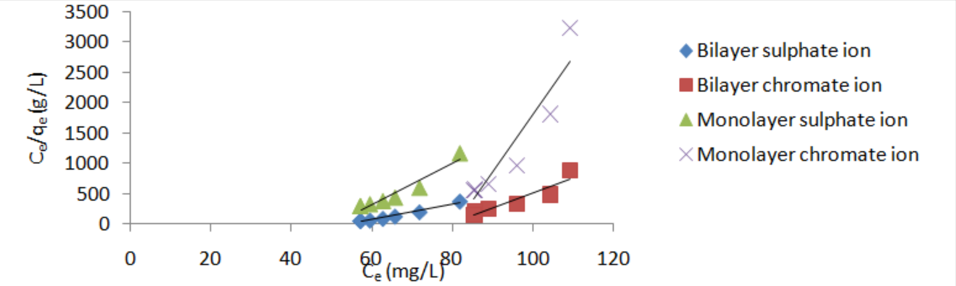

Figure 2: Langmuir isotherm of chromate and sulphate ions sorption

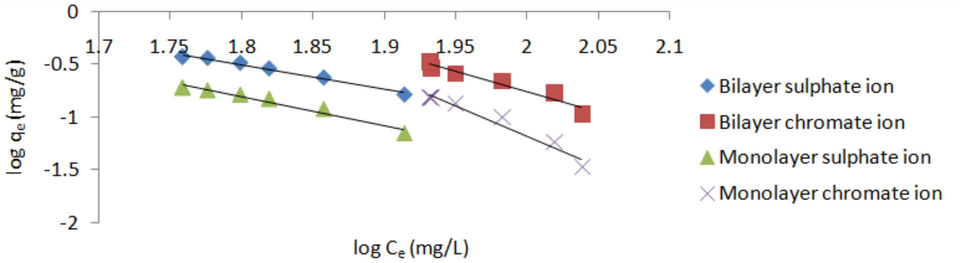

Figure 3: Freundlich isotherm of chromate and sulphate ions sorption

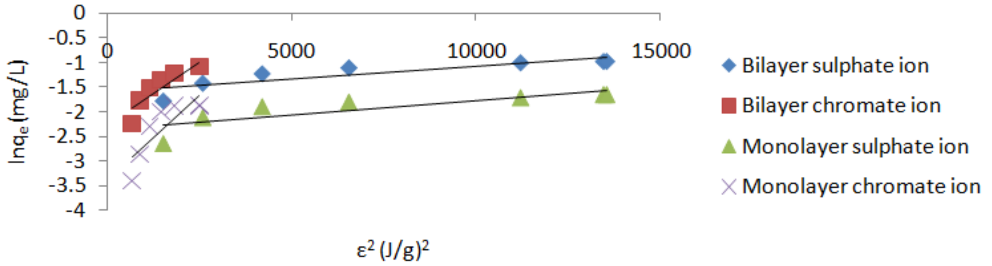

Figure 4: D-R Isotherm of chromate and sulphate ions sorption

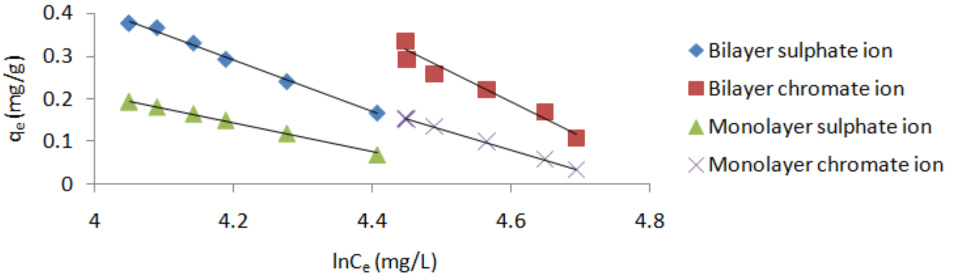

Figure 5: Frumkin isotherm of chromate and sulphate ions sorption

The validity of the Langmuir-type adsorption process referred to as separation factor R_L (Eq. 2) was found to be within the range $0<R_L<1$ (0.261-0.408) for sorption of oxyanions onto MMC and BMC, indicating a highly favourable and acceptability of the process. The Langmuir constant 'b' are negative (-0.012 to -0.020 L/mg) showing that the energy of sorption may be exothermic. This implies that the adsorption mechanism can be described by Langmuir isotherm.

The Freundlich constant K_F is an indicator of adsorption capacity occurred highest K_F=1.31E+10 mg/g for chromate ion sorption onto MMC and least K_F=4120.90 mg/g for sulphate ion sorption onto BMC. The adsorption intensity 'n' values falls below unity (-0.177 to -0.437) which implies chemisorption.The D-R adsorption equilibrium rate constant K_{ad} are negative (-0.00 to -6.0E-5 mol^2/kJ^2) showing exothermic process. The maximum adsorptive capacity $q_s$was strongest(0.200 mg/g) for sulphate ion sorption onto BMCand least (0.034 mg/g) for chromate ion sorption onto MMC. The Frumkin constant $n_T$relates to heat of sorption and vary within a range -0.341 to -0.812 J/mol, it predicts exothermic process as sorbate interacts with the sorbent. The equilibrium binding constant K_T were found to vary within the range of 100.00 to 125.00 L/g. The regression coefficient R^2 was strongest(0.999 and 0.994) for sulphate ion sorption onto MMC and BMC at Frumkin isotherm respectively and least (0.690 and 0.719) for sulphate ion sorption onto MMC and chromate ion sorption onto MMC at D-R isotherm respectively.

Table 1: Isotherm parameters and constants for oxyanions sorption onto MMC

Isotherm	Chromate ion	Sulphate ion
Langmuir	R_L=0.261; q_0=0.011(mg/g); b=-0.012(L/mg); R^2=0.875	R_L=0.345; q_0=0.030(mg/g); b=-0.020(L/mg); R^2=0.924
Freundlich	K_F=1.31E+10(mg/g); n=-0.177; R^2=0.960	K_F=12542.96(mg/g); n=-0.367; R^2=0.962
D-R	q_s=0.034(mg/g); K_{ad}=-0.000(mol^2/kJ^2); R^2=0.719	q_s=0.093(mg/g); K_{ad}=-6.0E-5(mol^2/kJ^2); R^2=0.690
Frumkin	K_T=111.11(L/g); n_T=-0.4809(J/mol); R^2=0.998	K_T=100.00(L/g); n_T=-0.341(J/mol); R^2=0.999

Table 2: Isotherm parameters and constants for oxyanions sorption onto BMC

Isotherm	Chromate ion	Sulphate ion
Langmuir	R_L=0.408; q_0=0.040(mg/g); b=-0.013(L/mg); R^2=0.885	R_L=0.363; q_0=0.078(mg/g); b=-0.018(L/mg); R^2=0.969
Freundlich	K_F=1.17E+7(mg/g); n=-0.256; R^2=0.941	K_F=4120.90(mg/g); n=-0.437; R^2=0.984
D-R	q_s=0.103(mg/g); K_{ad}=-0.000(mol^2/kJ^2); R^2=0.821	q_s=0.200(mg/g); K_{ad}=-5.0E-5(mol^2/kJ^2); R^2=0.757
Frumkin	K_T=125.00(L/g); n_T=-0.812(J/mol); R^2=0.953	K_T=111.11(L/g); n_T=-0.605(J/mol); R^2=0.994

4.3Kinetics and rate parameters

The kinetic model is a very important characteristic for evaluating the efficiency and rate parameters of adsorption processes. The sorption of oxyanion contaminants from liquid phase to solid phase is always assumed to be controlled by physicochemical processes, thus different kinetic models will be tested which include: Pseudo-first order, Pseudo-second order and Elovich kinetic models as presented by their linearized form of Eqs. 8-10; while the plots of the kinetic models are as shown in Figures 6-8 and evaluated parameters and constants to ascertain the best fit also presented in Tables 3 and 4.

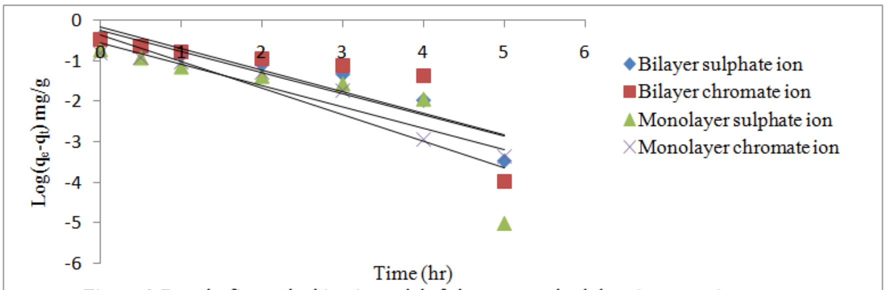

Figure 6: Pseudo-first order kinetic model of chromate and sulphate ions sorption

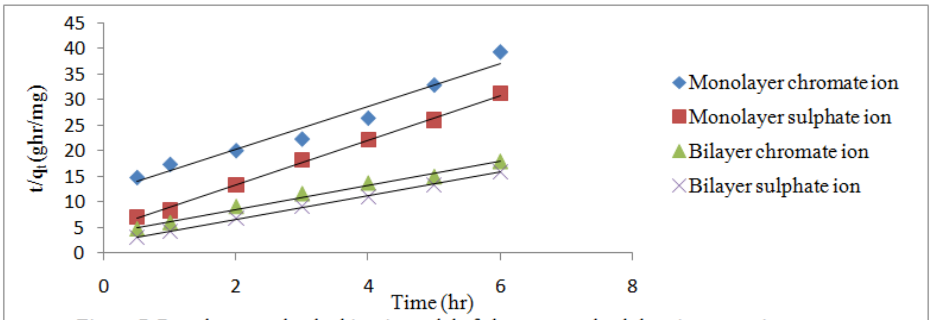

Figure 7: Pseudo-second order kinetic model of chromate and sulphate ions sorption

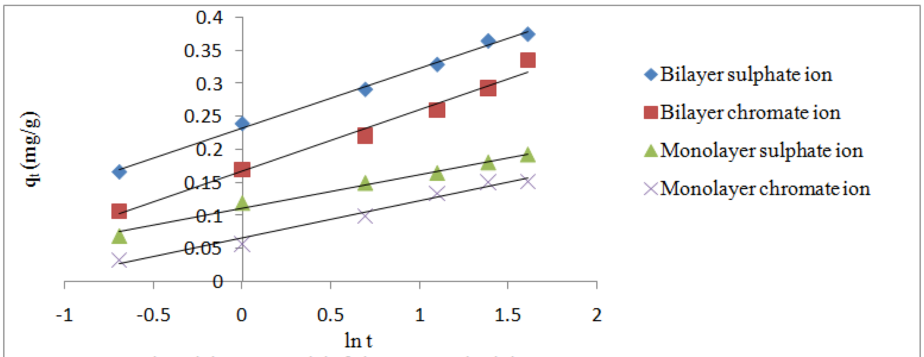

Figure 8: Elovich kinetic model of chromate and sulphate ions sorption

The best regression correlation R^2 kinetic model is the Pseudo-second order of 0.989 and 0.998 for chromate ion sorption and sulphate ions sorption onto BMC respectively. Elovich kinetic model gave the best R^2=0.972 for chromate ion sorption and Pseudo-second order model gave the bestR^2=0.997 for sulphate ion sorption onto MMC respectively.The initial adsorption rate ‘α’ represents chemisorption[45] and is strongest (1.252 mg/g-hr) for sulphate ion sorption onto BMC and least (0.184 mg/g-hr) for chromate ion sorption onto MMC. The parameter ‘β’ is related to the extent of surface coverage and varied from 10.753 g.hr/mg for chromate ion sorption onto BMC, to a maximum value of 20.408 g.hr/mg for sulphate ion sorption onto MMC. These are due to the exothermic nature of the present adsorption process[36].

Table 3: Kinetic parameters and constants for oxyanions sorption onto MMC

Kinetic model	Chromate ion	Sulphate ion
Pseudo-firstorder	k_1=1.216(hr^{-1}); q_e=0.279(mg/g); R^2=0.927	k_1=1.515(hr^{-1}); q_e=0.453(mg/g); R^2=0.702
Pseudo-second order	k_2=1.484(g/mg-hr); q_e=0.239(mg/g); R^2=0.962	k_2=4.185(g/mg-hr); q_e=0.229(mg/g); R^2=0.997
Elovich	α=0.184(mg/g-hr); β=18.868(g.hr/mg); R^2=0.972	α=0.472(mg/g-hr); β=20.408(g.hr/mg); R^2=0.983

Table 4: Kinetic parameters and constants for oxyanions sorption onto BMC

Kinetic model	Chromate ion	Sulphate ion
Pseudo-first order	k_1=1.223(hr^{-1}); q_e=0.7000(mg/g); R^2=0.677	k_1=1.159(hr^{-1}); q_e=0.559(mg/g); R^2=0.868
Pseudo-second order	k_2=1.425(g/mg-hr); q_e=0.426(mg/g); R^2=0.989	k_2=2.706(g/mg-hr); q_e=0.434(mg/g); R^2=0.998
Elovich	α=0.560(mg/g-hr); β=10.753(g.hr/mg); R^2=0.986	α=1.252(mg/g-hr); β=11.494(g.hr/mg); R^2=0.989

V. Conclusions

The following conclusions could be drawn from the results of this batch comparative sorption of oxyanions onto organo-kaolinite clay:

a) The performance of HDTMA-Br modified clay was 33.60% and 24.97% higher in sulphate ion sorption than chromate ion sorption onto MMC and BMCrespectively.

b) The isotherm models which described the adsorptive mechanism include the Langmuir and the Frumkin isotherms. Theseparation factor R_L was found to be within the range $0<R_L<1$ (0.261-0.408) for both oxyanions. The Frumkin isotherm give the best regression correlation R^2 among other isotherms tested although sulphate ion sorption responded better.

c) The Langmuir, D-R and Frumkin isotherms predict exothermic process from the negativity value of their respective constants. The adsorption intensity 'n' value of Freundlich isotherm which falls below unity (-0.177 to -0.437) implies chemisorption.

d) The best fit kinetic model that describe the sorption process is the pseudo-second order with R^2 values of 0.997 and 0.962 for sulphate ion sorption and chromate ion sorption onto MMC respectively while R^2 values of 0.998 and 0.989 for sulphate ion sorption and chromate ion sorption onto BMC respectively.

e) The initial adsorption rate 'α' represents chemisorption is strongest for sulphate ion sorption (0.472 mg/g-hr and 1.252 mg/g-hr onto MMC and BMC respectively) and least for chromate ion sorption (0.184 mg/g-hr and 0.560 mg/g-hr onto MMC and BMC respectively). The extent of surface coverage'β'shows better performance on sulphate ion sorption (11.494 g.hr/mg onto BMC and 20.408 g.hr/mgonto MMC) while for chromate ion sorption (10.753 g.hr/mgonto BMC and 18.868 g.hr/mgonto MMC).

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