Removal of Oxyanion Contaminants from Wastewater by Sorption onto HDTMA-Br Surface Modified Organo-Kaolinite Clay

Aroke U. O¹, El-Nafaty U. A², Osha O. A³

Chemical Engineering Programme Abubakar Tafawa Balewa University, Bauchi-Nigeria

Abstract — In the present study, kaolin clay from Alkaleri, Bauchi State, Northeastern Nigeria was modified with cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br) and used for sorption of inorganic oxyanion contaminants (NO₃⁻ and CrO₂⁴⁻) from simulated wastewater. Batch adsorption test method was employed to optimize the performance, sorption isotherms and kinetic parameters of the organoclay. The result showed that the optimum adsorbent dosage was 200g/L⁻¹. The theoretical correlation of the experimental equilibrium adsorption data for the oxyanion contaminants-organoclay system fitted well with the Frumkin isotherm model for nitrate (correlation coefficient R², 0.984) and Langmuir isotherm model for chromate (R², 0.979). The correlation coefficients were closer to unity for pseudo-second-order kinetic model than that for the pseudo-first-order kinetic model.

Keywords — HDTMA-Br, Isotherm, Kinetics, Organoclay, Oxyanions, Sorption, Surfactant.

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 [1,2]. Many researchers began to use cationic surfactant [3,4] to modify natural soil to enhance the sorption capacity of inorganic oxyanion contaminants (IOCs) such as nitrate, sulphate, arsenate, selenate and chromate [5] and nonionic organic contaminants (NOCs) such as benzene, toluene, ethylbenzene and xylene [6,7].

These IOCs and NOCs are typically mobile in soils and ground water since most natural materials have net negative surface charges [5,8]. They are toxic to humans, wildlife and environment even at trace concentrations [9]. The removal of these pollutants should result in extremely low levels to comply with environmental regulations.

Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of these compounds at trace quantities [10]. Carbon adsorption is expensive, nonselective, adsorptive interference in the presence of naturally occurring organic matter (NOM), competition effects of NOM are exacerbated with time, and it interacts with treatment chemicals [11].

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) [12,13]. 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 [3,14].

The aim of this study was to remove oxyanion contaminants from wastewater using kaolin clay [15]. Further objectives of the work were to determine the optimum adsorbent dosage required for sorption process, obtain experimental equilibrium data and estimate transport parameters.

II. ORGANICALLY MODIFIED CLAYS

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 Ca²⁺. The strong hydration of these inorganic cations creates a hydrophilic environment on the surface and in the interlayer region of natural kaolin clay [16].

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 [5]. The substitution of Na⁺ or Ca²⁺ 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 [6,17,18].
The use of organoclays in conjunction with conventional kaolin clay provides a barrier with the combined ability to act as a sealant and to effectively adsorb and retain dissolved organic contaminants. This type of composite liner provides an additional barrier to the escape of chemicals from storage tanks and landfills and represents a fundamental improvement in liner technology.

The successful utilization of remediation technology based on organoclay depends in part on the chemical stability of cationic surfactants-clay complexes. 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 lengths 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 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.

A. Occurrences and effects of oxyanion contaminants

Anions such as nitrate and chromate are mobile species in soils and ground water as most of the natural materials have net negative surface charges.

The primary source of nitrate is surface run off from agricultural or landscaped areas that have received excess nitrate fertilizer. These levels of nitrate can also lead to algae blooms, and when nutrients become limiting (such as potassium, phosphate or nitrate) then eutrophication can occur. As well as leading to water anoxia and dead zones, these blooms may cause other changes to ecosystem function, favouring some groups of organisms over others. As a consequence, as nitrate forms a component of total dissolved solids, they are widely used as an indicator of water quality.

Nitrate also is a by-product of septic systems. It is a naturally occurring chemical that is left after the breakdown or decomposition of animal or human waste. Water quality may also be affected through ground water resources that have a high number of septic systems in a watershed. Septics leach down into ground water resources or aquifers and supply nearby bodies of water. Lakes that rely on ground water are often affected by nitrification through this process.

In humans nitrate toxicity (harmful effects) occurs through enterohemepatic metabolism of nitrate to ammonia, having nitrite as the intermediate. Nitrites oxidize the iron atoms in hemoglobin from ferrous iron (Fe²⁺) to ferric iron (Fe³⁺), rendering it unable to carry oxygen.

This process can lead to methemoglobinemia which is a dangerous condition resulting from a generalized lack of oxygen in organ tissue.

Infants in particular are especially vulnerable to methemoglobinemia due to nitrate metabolizing triglycerides present at higher concentrations than at other stages of development. Methemoglobinemia in infants is known as blue baby syndrome.

The Spanish legislation established a maximum allowed concentration of 50mg-NO₃⁻L⁻¹ in drinking-water and European Community and World Health Organization established a recommended level of 25mg-NO₃⁻L⁻¹.

Chromium and chromates are also commonly found in products made of chrome and stainless steel, cement and leather. At work and home, you may find chromium or chromate in Construction materials such as cement, mortar concrete, bricks, plaster and drywall; Leather tanning and product manufacturing including shoes, boots, gloves; Primers and chrome-based pigments in paints; Cutting oils, corrosion inhibitors, oils, fuels and drilling muds; Liners in high temperature industrial furnaces; Pigments inks and paints; Manufacturing, plating and metal working with chrome alloys and stainless steel; Orthopedic and dental implants, dental prosthesis; Wood preservative manufacturing; Chromic surgical gut sutures.

Chromate often associated with industrial and power generation (coal fuel) wastes that are disposed to the land surface. For the purpose of chromate remediation in groundwater and soil, efforts have been made to reduce Cr⁶⁺ to Cr⁴⁺ via in situ chemical reduction. This process produces less soluble and less mobile species, and enhances the sorption possibility to solid surfaces via complexation or ion exchange processes.

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in products) is of low toxicity, the hexavalent form is toxic. Also, inhalation of hexavalent chromium compounds can result in perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Maximum contaminant level for chromium set by Environmental Protection Agency drinking water standard is 0.1mgL⁻¹. World Health Organization recommended the maximum allowable concentration of 0.05mgCr⁶⁺L⁻¹ in drinking water. For Indian Standard Institution, the tolerance limit for discharge of chromium containing wastewater in inland surface water, public sewers and marine/coastal areas is 2.0mgL⁻¹.

476
B. Sorption of oxyanion contaminants

Sorption of oxyanion contaminants by HDTMA-modified clays was attributed to anion exchange in which the nitrate or chromate ions replace bromide ion associated with the surfactant head group at the outer layer \([5,9]\). The exchange reaction on organoclay can be written as (Eq. 1):

\[
x(HDTMA-\text{Clay}-\text{Br}) + \text{NO}_3^- \rightarrow (HDTMA-\text{Clay})_x - \text{NO}_3^- + x\text{Br}^-
\]

Where A is N or Cr; this sorption phenomenon on organoclay surface is schematically shown in Figures 1 and 2 for nitrate and chromate ions sorption respectively.

Figure 1: Sorption of nitrate on bilayer HDTMA modified clay surface \([29]\)

Figure 2: Sorption of chromate on bilayer HDTMA modified clay surface \([29]\)

The sorption of nitrate by organoclay due to anion exchange in which the nitrate ions replace bromide ions, the ratio of the bromide ion released to nitrate ion sorbed is 1:1. Also, the sorption of chromate by organoclay due to anion exchange in which the chromate ions replace bromide ions, the ratio of bromide ion released to chromate ion sorbed is 2:1.

C. Adsorption isotherms

The fit of experimental adsorption data by means of different isotherm models is an important step in finding the suitable model for the design process and hence to improve the knowledge concerning the adsorption mechanism. When the solute is retained in only one molecular layer, namely in the case of mono-component systems, the Langmuir (Eq. 2), Freundlich (Eq. 3) and Frumkin (Eq. 4) isotherms are the most commonly used models to describe experimental equilibrium data \([10,28,30]\).

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

Where \(q_e\) is the sorbed amount (mg/g); \(C_e\) is the equilibrium concentration of the sorbate (mg/L) and \(q_0\) (mg/g) and \(b\) (L/mg) are the Langmuir constants related to maximum sorption capacity and energy of sorption respectively. Thus, when \(q_e\) is plotted against \(q_e/C_e\) a linear relationship should indicate the existence of a Langmuir type of sorption. In this case the slope of the line will be equal to \(1/q_0\) and the intercept will be \(b\).

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

Where \(q_e\) is the sorbed amount (mg/g); \(C_e\) is the equilibrium concentration of the sorbate (mg/L) and \(K_F\) (L/g) and \(n\) are Freundlich constants related to sorption capacity and sorption intensity, respectively. The constants \(n\) and \(K_F\) are calculated by plotting \(\ln C_e\) against \(\ln q_e\) which will give a slope \(1/n\) and an intercept \(\ln K_F\).

\[
q_e = n_T \ln K_T + n_T \ln C_e
\]

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 \(n_T\) are the Frumkin constants.

A dimensionless constant separation factor, \(R_L\), to assess the validity of the Langmuir-type adsorption process can be expressed as (Eq. 5) \([28,30]\):

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

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 (\(R_L>1\)).
D. Kinetics of the Adsorption Process

The rate of sorption is of particular importance for the practical application of suggested sorption material and has also great significance since it will facilitate the scale-up of the treatment process to smaller reactor volumes ensuring efficiency and economy [31]. The process efficiency is controlled by the kinetics of adsorption, and hence several kinetic models are available in order to predict the mechanism involved in the sorption process.

Among these models, Lagergren’s rate equation (Eq. 6) appears to be one of the most widely used for the sorption of a solute from a liquid solution for pseudo-first-order sorption [28,30,31,32]. The sorption of oxyanions from liquid phase to solid phase is normally assumed to be controlled by physicochemical processes [33].

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]  

(6)

The plot of \( \log(q_e - q_t) \) against \( t \) provides a linear relationship from which \( k_1 \), constant of pseudo-first-order sorption (hr\(^{-1}\)) and \( q_e \), sorption capacity at equilibrium (mg/g) are determined from the slope and intercept of the plot, respectively, given that \( q_t \) is the sorption capacity at time \( t \) (mg/g).

The sorption kinetics can also be described by pseudo-second-order rate equation (Eq. 7) [33].

\[
\frac{t}{q_t} = \frac{t}{q_e} k_2 + \frac{1}{q_e} t
\]  

(7)

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). Equation (7) can be rearranged and linearized to obtain Eq. 8 [31,32,33]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t
\]  

(8)

If the initial sorption rate, as \( h = q_t/t \) when \( t \) approaches 0, \( h \) (mg/g hr), is

\[
h = k_2 q_e^2
\]  

(9)

The values for \( k_2 \) and \( q_e \) can be determined experimentally by plotting \( t/q_t \) against \( t \).

There are many factors which influence the sorption capacity, including the initial sorbate concentration, the reaction temperature, the solution pH value, the sorbent particle size and dose, and the nature of the solute [12]; a kinetic model is concerned only with the effect of observable parameters on the overall rate [33]. In order to distinguish the kinetics equation based on the concentration of a solution from the sorption capacity of solids, the rate equation has been called a pseudo first and/or second-order [33].

III. EXPERIMENTAL SECTION

All reagents and chemicals are analytical grade from British Drug Houses (BDH) laboratory supplies. Distilled water was obtained from Gubi Water Treatment Plant, Bauchi State. A stock solution containing 50mM concentration of nitrate ion (NO\(_3\)) from sodium nitrate (NaNO\(_3\)) and chromate ion (CrO\(_4^{2-}\)) from sodium chromate (Na\(_2\)CrO\(_4\).4H\(_2\)O) was prepared and confirmed by DR 2000 spectrophotometer.

Studying the effect of adsorbent dosage on sorption for optimum adsorbent required, precisely weighed amount of bilayer surface modified clay (BMC) in the range of 50 to 250mg at 50mg interval was shaken laterally at 1200rpm in 10mL of oxyanion contaminants solution for 12 hours. The two phases are then separated by means of centrifugation and supernatant was analysed using DR 2000 spectrophotometer to determine the oxyanion contaminant left in the supernatant. Thus, the equilibrium relationship curve was established to know the trend of sorption with different adsorbent dosage.

At optimum adsorbent dosage (200mg of BMC), 10mL of known concentration of oxyanion contaminants and clay minerals (modified and unmodified) was shaken laterally at 1200rpm 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 oxyanion contaminant left in the supernatant. The equilibrium relationship curve was established for BMC, monolayer surface modified clay (MMC) and unmodified kaolin clay (UKC) from which sorption capacities, removal efficiencies, suitable sorption isotherms and kinetic parameters were determined.
IV. RESULTS AND DISCUSSION

A. Effect of adsorbent dosage

The study for the removal of oxyanion contaminants with respect to sorbent dose was conducted over the range 50-250 g/L at pH 7.6 and 7.5 for nitrate and chromate respectively. Other conditions include: room temperature of 298K, contact time of 12 hours, shaken laterally at 1200rpm and 5mM initial concentration. Figures 3 and 4 shows the rate of sorption of nitrate and chromate ions increased as sorbent dosage increases and attained equilibrium at 200g/L. With further increment of sorbent to 250g/L the sorption rate decreases for both oxyanion contaminants. The amount of oxyanion adsorbed from initial solution concentration was calculated from the following equation (10) [34,35].

\[
\text{% Removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]  
(10)

Where \( C_0 \) and \( C_e \) are the initial and equilibrium concentration (mg/L) respectively.

For sorbent removal efficiencies of contaminants increased from 23.15% to 81.56% and 8.7% to 33% for nitrate and chromate ions respectively in the range 50-200g/L. Further increment of BMC to 250g/L rather showed decrease in removal efficiencies (Figure 5).

![Removal efficiencies of oxyanion contaminants by different adsorbent dosage](image)

The optimum BMC dosage was 200g/L for contaminant under study. It is apparent that the removal efficiency of contaminants increases rapidly with increase in the dose of modified clay due to availability of the sorption sites or surface area. For the same conditions of batch adsorption, adsorbent dosage efficiency is more prominent in nitrate ion removal than chromate ion; this could be largely attributed to planar nitrate and tetrahedral chromate structure [36].

B. Equilibrium Sorption Process and Performance of Adsorbents

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, MMC and UKC were calculated using equilibrium studies. The mass balance equation for this process at equilibrium is given by equation (11) [24,30,34,37].

\[
q = \left( C_0 - C_e \right) \frac{V}{m}
\]  
(11)

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

The effect of 5mM oxyanion contaminants sorption was investigated for BMC, MMC and UKC at pH 7.1 and 7.5 for nitrate and chromate ions respectively. Other experimental conditions include: room temperature 298K, contact time 6 hours, shaken laterally at 1200rpm and sorbent dosage of 200g/L (Figures 6 and 7).
In the batch system, removal efficiencies of nitrate ion by BMC is 82.50%, MMC is 40.33% and UKC is 11.98% while for chromate ion by BMC is 43.21%, MMC is 26.34% and UKC is 5.17%. It is obvious that modification of clay mineral with cationic surfactant improves its affinity towards oxyanion contaminants sorption.

C. Adsorbent Selectivity

To evaluate the sorbents selectivity toward oxyanion contaminants, distribution coefficient $K_d$, was calculated using the following equation (12) [2]:

$$K_d = \left( \frac{C_0 - C_f}{C_f} \right) \frac{V}{m} \tag{12}$$

Where $C_0$ and $C_f$ are the initial and the final concentration of oxyanion contaminants respectively, $m$ is the weight of sample in grams and $V$ is the volume of contaminant in milliliters. Since the contaminant concentration is one of the key parameters of the ion exchange investigations for environmental purposes and in order to consider the influence of nitrate and chromate ions concentration on behaviour of the sorbent, the effect of concentration of the oxyanion contaminants on its distribution coefficients ($K_d$, mL/g) on modified and unmodified clay was examined (Table 1). The $K_d$ for nitrate ion sorption by BMC is 23.576mL/g, MMC is 3.38mL/g and UKC is 0.681mL/g while for chromate ion sorption by BMC is 3.804mL/g, MMC is 1.788mL/g and UKC is 0.273mL/g.

Based on the data, sorbent selectivity toward the oxyanion contaminants was higher for BMC and least for UKC which implies that the surface modified sorbents show higher affinity to the oxyanion contaminants. This behaviour is promising for environmental application of sorbents, where removal of trace concentration is a difficult challenge due to stringent rule on liquid waste management.

D. Modeling of the Sorption Isotherms

The fit of experimental adsorption 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 [29]. To optimize the design of a sorption system for the sorption of sorbates, it is important to establish the most suitable correlation for the equilibrium curves to understand the sorption behaviour in solution of oxyanion by the modified and unmodified clay. When the solute is retained in only one molecular layer, namely in the case of mono-component systems; the Langmuir, Freundlich, and Frumkin isotherms are the most commonly used models to describe experimental equilibrium data [5,10,24,28,35].

Langmuir isotherm model was used to evaluate the equilibrium processes for nitrate and chromate ions sorption parameters such as; maximum sorption capacity ($q_0$), sorption energy ($b$), correlation factors ($R^2$) and separation factor ($R_L$). The linear plot of Langmuir isotherm model are shown in Figures 8 and 9 for nitrate and chromate ions sorption respectively, using BMC (MMC and UKC not shown) and evaluated parameters presented in Table 1.
TABLE I

<table>
<thead>
<tr>
<th>Parameters</th>
<th>BMC</th>
<th>MMC</th>
<th>UKC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate (1mM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_0$ (mg/g)</td>
<td>0.123</td>
<td>0.207</td>
<td>0.001</td>
</tr>
<tr>
<td>b (L/mg)</td>
<td>0.168</td>
<td>0.0341</td>
<td>0.0188</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.935</td>
<td>0.993</td>
<td>0.999</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.103</td>
<td>0.321</td>
<td>0.462</td>
</tr>
<tr>
<td>$K_d$ (mL/g)</td>
<td>23.576</td>
<td>3.380</td>
<td>0.681</td>
</tr>
<tr>
<td>% removal</td>
<td>82.50</td>
<td>40.33</td>
<td>11.98</td>
</tr>
<tr>
<td>Chromate (1mM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_0$ (mg/g)</td>
<td>0.045</td>
<td>0.012</td>
<td>0</td>
</tr>
<tr>
<td>b (L/mg)</td>
<td>0.0182</td>
<td>0.0126</td>
<td>0.0093</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.979</td>
<td>0.996</td>
<td>0.999</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.321</td>
<td>0.406</td>
<td>0.481</td>
</tr>
<tr>
<td>$K_d$ (mL/g)</td>
<td>3.804</td>
<td>1.788</td>
<td>0.273</td>
</tr>
<tr>
<td>% removal</td>
<td>43.21</td>
<td>26.34</td>
<td>5.17</td>
</tr>
</tbody>
</table>

The influence of sorption isotherm shaped to know whether the sorption is favourable or not has been discussed in terms of a dimensionless constant $R_L$ referred to as separation factor (Eq. 5). The $R_L$ values (Tables 1) was found to be within the range $0 < R_L < 1$ (BMC=0.103, MMC=0.321, UKC=0.462 for nitrate ion sorption and BMC=0.321, MMC=0.406, UKC=0.481 for chromate ion sorption) indicating a highly favourable and acceptability of the process.

The equilibrium sorption parameters were also evaluated using linearized form of Freundlich, and Frumkin isotherm models (Figures not shown) the evaluated parameters are presented in Tables II and III for nitrate and chromate ions sorption respectively. The best fit of experimental data was recorded for the highest $R^2$ value for BMC sorption for both oxyanion is 0.966 while the least is 0.858.

TABLE II

<table>
<thead>
<tr>
<th>Parameters</th>
<th>BMC</th>
<th>MMC</th>
<th>UKC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate (1mM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$lnK_F$ (mg/g)</td>
<td>0.108</td>
<td>2.761</td>
<td>3.801</td>
</tr>
<tr>
<td>$1/n$</td>
<td>1.736</td>
<td>0.413</td>
<td>0.062</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.963</td>
<td>0.982</td>
<td>0.949</td>
</tr>
<tr>
<td>Chromate (1mM)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$lnK_F$ (mg/g)</td>
<td>3.727</td>
<td>4.141</td>
<td>4.587</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.357</td>
<td>0.169</td>
<td>0.032</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.879</td>
<td>0.959</td>
<td>0.890</td>
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TABLE III

<table>
<thead>
<tr>
<th>Parameters</th>
<th>BMC</th>
<th>MMC</th>
<th>UKC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate (1mM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$lnK_T$ (mg/g)</td>
<td>4.903</td>
<td>4.206</td>
<td>4.129</td>
</tr>
<tr>
<td>$n_T$</td>
<td>0.103</td>
<td>0.214</td>
<td>0.286</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.984</td>
<td>0.998</td>
<td>0.999</td>
</tr>
<tr>
<td>Chromate (1mM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$lnK_T$ (mg/g)</td>
<td>4.854</td>
<td>4.771</td>
<td>4.763</td>
</tr>
<tr>
<td>$n_T$</td>
<td>0.378</td>
<td>0.480</td>
<td>0.515</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.949</td>
<td>0.999</td>
<td>0.933</td>
</tr>
</tbody>
</table>

E. 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.

The linear plots of pseudo-first-order kinetic model (Eq. 6) for nitrate and chromate ions are shown in Figures 10 and 11 respectively and corresponding evaluated parameters are listed in Tables IV and V. The highest $R^2$ value for BMC sorption for both oxyanion is 0.966 while the least is 0.858.

TABLE IV

<table>
<thead>
<tr>
<th>Clay type</th>
<th>$q_e$ (mg/g)</th>
<th>$k_1$ (hr$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UKC</td>
<td>0.0284</td>
<td>1.0801</td>
<td>0.926</td>
</tr>
<tr>
<td>MMC</td>
<td>0.1042</td>
<td>0.9719</td>
<td>0.990</td>
</tr>
<tr>
<td>BMC</td>
<td>0.2858</td>
<td>1.2183</td>
<td>0.966</td>
</tr>
</tbody>
</table>

Figure 10: Pseudo first order kinetic model for nitrate ion contaminant adsorption

TABLE V

<table>
<thead>
<tr>
<th>Clay type</th>
<th>$q_e$ (mg/g)</th>
<th>$k_1$ (hr$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UKC</td>
<td>0.0284</td>
<td>1.0801</td>
<td>0.926</td>
</tr>
<tr>
<td>MMC</td>
<td>0.1042</td>
<td>0.9719</td>
<td>0.990</td>
</tr>
<tr>
<td>BMC</td>
<td>0.2858</td>
<td>1.2183</td>
<td>0.966</td>
</tr>
</tbody>
</table>
Also the linear plots of pseudo-second-order kinetic model (Eq. 8) for nitrate and chromate ions are shown in Figures 12 and 13 respectively and corresponding evaluated parameters are listed in Tables VI and VII. The highest $R^2$ value for BMC sorption for both oxyanion is 0.997 while the least is 0.985.

**TABLE VI**

**PSEUDO-SECOND-ORDER KINETIC PARAMETERS FOR NITRATE ION ADSORPTION**

<table>
<thead>
<tr>
<th>Clay type</th>
<th>$q_e$ (mg/g)</th>
<th>h (mg/g hr)</th>
<th>$k_2$ (g/mg hr)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UKC</td>
<td>0.0302</td>
<td>0.0285</td>
<td>31.2486</td>
<td>0.986</td>
</tr>
<tr>
<td>MMC</td>
<td>0.1378</td>
<td>0.2616</td>
<td>13.7765</td>
<td>0.998</td>
</tr>
<tr>
<td>BMC</td>
<td>0.2665</td>
<td>0.5131</td>
<td>7.2245</td>
<td>0.997</td>
</tr>
</tbody>
</table>

The correlation $R^2$, are closer to unity for pseudo-second-order kinetic model than that for the pseudo-first-order kinetic model. Therefore, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model for the sorption of the oxyanion contaminants under study.

**V. CONCLUSIONS**

From the study, the following conclusions could be made:

1. HDTMA-Br surface modified clay has a higher ability to sorb oxyanion contaminants under study from simulated contaminated water than unmodified kaolin clay.
2. The optimum adsorbent dosage for sorption of oxyanions under study was found to be 200gL$^{-1}$.
3. Based BMC adsorbent correlation coefficient $R^2$, the adsorption isotherms of oxyanion contaminants under study were better fitted by the Frumkin isotherm model (0.984) for nitrate ion and Langmuir isotherm model (0.979) for chromate ion under the considered conditions.
4. The separation factor $R_L$ was found to be within 0<RL<1, (0.103-0.462 for nitrate ion sorption and 0.321-0.481 for chromate ion sorption) indicating a highly favourable and acceptability of the process.
5. Sorbent selectivity towards oxyanion contaminants was higher for BMC compared to MMC and UKC. This behaviour is promising for environmental application of sorbent where removal of trace concentration is a difficult challenge due to stringent rule on liquid waste management.

6. The pseudo-second-order rate equation appears to be the most appropriate to describe the adsorption kinetic of oxyanions on organo-kaolinite clay.

REFERENCES


[29] Li, Z. 1999. Oxyanion sorption and surface anion exchange by surfactant modified clay minerals, J. Environ. Quality 28 (5) 1457-1463


