ADSORPTIVE BEHAVIOR OF LOW-COST MODIFIED NATURAL CLAY ADSORBENTS FOR ARSENATE REMOVAL FROM WATER

Borano Te1,2, *Boonchai Wichitsathian1 and Chatpet Yossapol1

1School of Environmental Engineering, Suranaree University of Technology, Thailand; 2Department of Civil Engineering, Preah Kossomak Polytechnic Institute, Cambodia

*Corresponding Author, Received: 02 May 2016, Revised: 10 July 2016, Accepted: 11 Nov. 2016

ABSTRACT: Millions of people in more than 70 countries are at risk of developing arsenicosis and other health issues due to consuming elevated arsenic contaminated water. The present study aimed to use natural clays heated at high temperature and treated with ferrous and ferric solutions through a simple coating technique enhanced by moderate temperature for arsenate uptake from water. BET, XRF, XRD and SEM methods were applied for the adsorbent characterization. Adsorption experiments were conducted in a series of batch systems in terms of contact time, solution pH, initial concentration and the presence of coexisting anions. The results indicated that the adsorption kinetics was better described by the pseudo-second order rate model for all adsorbents. All adsorbents exhibited higher arsenate uptake efficiency in the acidic condition. Langmuir model provided the maximum arsenate adsorption capacity of 250µg/g, 429.74µg/g and 747.38µg/g for calcined clay (MC), ferric calcined clay (MC-FeII) and ferrous calcined clay (MC-FeII), respectively. Among added coexisting anions, phosphate (PO₄³⁻) significantly decreased the arsenate adsorption capacity of all adsorbents. Overall, regarded to a wide availability of raw materials, simplicity of the modification and improvement of arsenate adsorption capacity, modified natural clay adsorbents, especially MC-FeII, could be considered to be effective and low-cost to remove arsenate from water.

Keywords: Adsorption, Calcined clay, Ferrous Calcined Clay, Ferric Calcined Clay, Isotherm, Kinetics

1. INTRODUCTION

Arsenic is a toxic and carcinogenic element polluting water sources. This element enters into the environment through natural factors such as weathering reactions, biological activities, geochemical reactions and volcanic emissions, as well as anthropogenic activities such as mining activities, combustion of fossil fuels, use of arsenic pesticides and arsenic additives to livestock [1]. Health issues related to a long term exposure to arsenic include conjunctivitis, hyperkeratosis, hyper pigmentation, cardiovascular diseases, disorder of central nervous systems, skin cancer and gangrene of the limbs [2]. More than 100 million people in over 70 countries are at risk of having the diseases [3]. The World Health Organization (WHO) has lowered the maximum contaminant level of arsenic in drinking water from 50µg/L to 10µg/L [4].

Elevated arsenic concentration found in natural water is ranged from <100µg/L to 5000µg/L, i.e., an average of 552µg/L in groundwater in Cambodia [5], [6]. The major arsenic forms in natural water are arsenate and arsenite. Arsenite favors and predominates in reducing environments like groundwater, whereas arsenate predominates in oxygen-rich environments like surface water [7]. Practically, arsenite has been oxidized to arsenate before the treatment. Among arsenic remediation method such as coagulation, membrane separation, and ion exchange, adsorption has gained a considerable attention due to its simple operation and maintenance, high removal efficiency and low-cost [8]. Adsorption is based on either natural or synthetic materials possibly providing high affinity for dissolved arsenic. Several low cost materials such as natural materials, agricultural wastes, and industrial wastes have increasingly gained interest to be used as adsorbents for arsenic removal from water [9].

Local available clay has been interestingly used as adsorbents to uptake various pollutants due to its widely availability and low cost [10]. However, clays or clay minerals appeared as adsorbents in the form of powder occur to be difficult to separate after adsorption and limit further potential applications like in a dynamic flow system. From a preliminary observation, natural clays with bigger size tends to break down when mixing with water, while clays heated at high temperature appear to be stable in the particle size. Furthermore, the arsenic adsorption capacity of natural adsorbents seems to be lower than that of synthetic or modified adsorbents with metal oxides known for having high affinity toward arsenic. Thus, modification of natural clay to produce a more effective adsorbent is needed. Among many modification methods, iron coating or impregnation seems to be simple, cost-effective, pollutant removal efficiency-
improved and gaining more popularity to be applied for developing an efficient adsorbent for pollutant removal.

The objective of this study was to treat natural clays calcined at high temperature with ferrous and ferric solutions through a simple coating technique enhanced by heating at moderate temperature. The developed adsorbents were applied to adsorb arsenate from water. The experimental parameters such as contact time, initial concentration, solution pH and coexisting anions were investigated.

2. MATERIALS AND METHODS

2.1 Chemical Reagents

All experiments were conducted with chemicals of analytical grade without further purification. Arsenate stock solution (100 mg/L) was prepared by dissolving Na$_2$H$_3$AsO$_4$·7H$_2$O (Sigma Aldrich, USA) in deionized (DI) water. FeSO$_4$·7H$_2$O and FeCl$_3$·6H$_2$O were used for developing ferrous and ferric solutions, respectively. NaOH and HCl were used to create alkaline and acidic solutions, respectively, for pH adjustment. NaCl, NaNO$_3$, NaHCO$_3$, Na$_2$CO$_3$, Na$_2$SO$_4$, and Na$_2$PO$_4$ were used for obtaining anions Cl$^-$, NO$_3^-$, HCO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$, and PO$_4^{3-}$, respectively. To prevent chemical interferences, all needed glassware and apparatus were washed with DI water and exposed to a 5% nitric acid solution overnight prior to being used in the experiments.

2.2 Preparation and Characterization of Adsorbents

Natural clay, collected from Dan Kwian District, Nakhonratchasima 30000, Thailand, was manually cleaned and ground for the particle size of 0.45-0.85mm. The natural clay was then calcined at 550˚C for 4 to 5h in a muffle furnace. The calcined clay was labeled as MC. The modification process was conducted with ferrous or ferric solutions as follow: twenty gram (20g) of MC was added to 100 mL of 0.25M FeCl$_3$·6H$_2$O or 0.25M FeSO$_4$·7H$_2$O. The mixture was magnetically stirred on a hot plate with temperature of 60˚C under agitation speed of 250 rpm for 24h. The suspension was dried at 105˚C for 24h and then further heated at 350˚C for 3h to ensure higher effective affinity of iron. After being cooled to room temperature, the products were washed with DI water until no reddish color or precipitate formed upon addition of a few drops of 1:10-phenanthroline. The ferrous and ferric coated calcined clays were labeled as MC-FeII and MC-FeIII, respectively. The adsorbents were kept in dry and clean plastic containers for further uses.

The chemical composition was determined by the Energy Dispersive X-ray Fluorescence (EDS-XRF, HORIBA Ltd., Japan). The mineralogical phases were analyzed by the X-ray diffraction method with the Bruker XRD (D2-PHASER). The surface morphology were examined by a scanning electron microscope (SEM, JSM-6010LV, JEOL, Japan). The surface area, pore volume, and average pore diameter were obtained from the nitrogen adsorption-desorption isotherm data at 77K with the Brunauer-Emmett-Teller ( BET) methods using the BET analyzer (BELSORP Mini II, BEL Inc., Japan). The samples were outgassed by heating at 60˚C for 24 h under N$_2$ flow using the pretreatment instrument, BELSORP Mini II (BEL Inc. Japan). The point of zero charge (pH$_{pc}$) was evaluated by plotting the initial pH versus the equilibrium pH (using 0.01M NaCl as background electrolyte with the equilibrium time of 72h) [11].

2.3 Adsorption Experiments

Adsorption experiments were conducted in a series of batch modes at room temperature (25±1˚C). The mixtures between adsorbents and adsorbate were agitated at 200 rpm on a horizontal mechanical shaker. The supernatant was filtered through 0.22 µm syringe filters and the filtrates were acidified with concentrated nitric acid (65%) and stored at 4˚C until the time for arsenate measurement. The measurements were carried out within 24h. Arsenate concentration was measured by ICP-OES (Optima 8000, PerkinElmer, USA) using a wavelength of 193.7nm. The contact time was conducted by mixing 10g/L of the adsorbents with 25mL of the 500µg/L arsenate solution (pH=7 ± 0.1) from 0 to 72h. The effect of solution pH was investigated in the pH range of 3 to 11. Isotherm study was carried out by varying arsenate concentrations from 100 to 10000µg/L. The effect of coexisting anions was investigated by adding a certain amount of anions to 500µg/L arsenate solution. Each experiment was conducted in duplicate and the average was reported. The arsenate adsorption efficiency and capacity were calculated with the following equations:

\[
P = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)
\]

\[
q_e = \frac{(C_0 - C_e) \times V}{M} \quad (2)
\]

where P is the adsorption efficiency (%); $q_e$ is the adsorption capacity at equilibrium (µg/g); $C_0$, $C_e$ and $C_n$ are the arsenate concentration at initial, particular and equilibrium time (µg/L), respectively; V is the adsorbate volume (L); and M is the mass of adsorbents (g).
3. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

The characteristic analysis of the physico-chemical properties of the adsorbents is illustrated in Table 1. The results indicated that the main chemical constituents of all the adsorbents were silicate (SiO$_2$), alumina (Al$_2$O$_3$) and iron oxide (Fe$_2$O$_3$). After a long time exposure to ferrous solution (pH=3.08) and ferric solution (pH=1.28), the percentage of silica and alumina of MC-FeII and MC-FeIII were observed to be lower than those of MC. This could be explained by the occurrence of corrosion due to the acidic behavior of iron solutions. However, an increase of iron oxide was observed for modified adsorbents compared to that of MC (roughly 1.5 and 2 times for MC-FeII and MC-FeIII, respectively). This indicated that applied iron coating technique in this study successfully improved iron content.

The surface area of MC, MC-FeII and MC-FeIII were 41.69m$^2$/g, 55.41m$^2$/g and 55.99m$^2$/g, respectively. The improvement of surface area after the treatment was due to the open space by acidic corrosion. It was consistent with the increase of total pore volume. All adsorbents exhibited the mean pore size within 2 to 50 nm, indicating that the materials are relatively mesoporous according to the pore classification recommendation of the International Union of Pure and Applied Chemistry [12].

XRD pattern analysis of the adsorbents is presented in Fig. 1. The pattern of all adsorbents was almost identical. However, the intensity to develop peaks for the modified adsorbents increased and the development of new peaks was observed for MC-FeIII. This may be contributed to the increase in the amount of iron oxide on the surface. The main composting minerals for the adsorbents include quartz, illite-montmorillonite, kaolinite and hematite.

Table 1 The physico-chemical properties of MC, MC-FeII, and MC-FeIII

<table>
<thead>
<tr>
<th>Properties</th>
<th>MC</th>
<th>MC-FeII</th>
<th>MC-FeIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>71.25</td>
<td>68.34</td>
<td>68.63</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>20.51</td>
<td>20.07</td>
<td>16.55</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>5.585</td>
<td>8.361</td>
<td>11.77</td>
</tr>
<tr>
<td>$S_{BET}$ (m$^2$/g)</td>
<td>41.69</td>
<td>55.41</td>
<td>55.99</td>
</tr>
<tr>
<td>$a_T$ (cm$^3$/g)</td>
<td>0.059</td>
<td>0.067</td>
<td>0.068</td>
</tr>
<tr>
<td>$a_0$ (nm)</td>
<td>5.712</td>
<td>4.807</td>
<td>4.799</td>
</tr>
<tr>
<td>$p_{H}_{pzc}$</td>
<td>6.3</td>
<td>5.9</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Note: $S_{BET}$ = Surface area; $a_T$ = Total pore volume; $a_0$ = Mean pore diameter

Figure 2 shows the surface morphological feature of MC, MC-FeII and MC-FeIII analyzed by SEM.
A pretty smooth with few rough particle attachments was observed on the surface of MC, that could be a result of exposure of silica to high temperature. Surface features of MC-FeII and MC-FeIII were similar with the occurrence of several concave shapes and many small pores. This was strongly supportive to the corrosion effect of iron solutions.

3.2 Kinetic Studies

Figure 3 shows the effect of time dependent for arsenate adsorption onto the adsorbents. Within the first 18h, all adsorbents expressed fast adsorption toward arsenate in the aqueous solution. Later, the uptake rate was insignificantly improved and reached the equilibrium with 72h. This was due to having more active sites initially and later filled up.

Pseudo-first order and pseudo-second order models were applied to predict the kinetic data. Their non-linearized equations can be expressed as follow:

Pseudo-1st order: \( q_t = q_e \left(1 - e^{-kt}\right) \) (3)

Pseudo-2nd order: \( q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \) (4)

where \( q_t \) (µg/g) is the adsorption capacity at time \( t \) (h), and \( k_1 \) (h\(^{-1}\)) and \( k_2 \) (g·µg\(^{-1}\)·h\(^{-1}\)) are pseudo-first order and pseudo-second order rate constant, respectively. Kinetic parameters obtained from the kinetic models are presented in Table 2. For all adsorbents, the correlation coefficients (\( R^2 \)) of pseudo-second order model were higher than those of pseudo-first order model. Plus, the arsenate adsorption capacity obtained from pseudo-second order model (\( q_{e,cal.} \)) was comparable to the arsenate adsorption capacity from the experiment (\( q_{e,exp.} \)).

Thus, kinetic data were well described by pseudo-second order model. This suggests that the adsorbate and adsorbents exchange or share electron and the surface properties of adsorbents and adsorbate concentration play significant roles in controlling the uptake rate [13].

3.3 Isotherm Studies

Langmuir and Freundlich models were applied to fit the isotherm data. Their non-linearized equations are represented as follow:

Langmuir: \( q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \) (5)

Freundlich: \( q_e = K_F C_e^{1/n} \) (6)

where \( q_m \) (µg/g) is the maximum adsorption capacity based on Langmuir equation; \( K_L \) (L/µg) is Langmuir constant; \( K_F \) and \( n \) are the adsorption coefficient from Freundlich equation. Figure 4 shows the plots of the models for obtaining the isotherm parameters.

The calculated isotherm parameters including the maximum arsenate adsorption capacity are summarized in Table 3.

![Fig. 3 Effect of contact time and its fitting model for arsenate adsorption efficiency by the adsorbents](image)

![Fig. 4 Isotherm models for arsenate adsorption by the adsorbent](image)
Table 3 Isotherm parameters for arsenate adsorption by the adsorbents

<table>
<thead>
<tr>
<th>Models</th>
<th>MC</th>
<th>MC-FeII</th>
<th>MC-FeIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>q_m</td>
<td>250.00</td>
<td>747.38</td>
<td>429.74</td>
</tr>
<tr>
<td>K_L</td>
<td>0.0012</td>
<td>0.0043</td>
<td>0.0025</td>
</tr>
<tr>
<td>R^2</td>
<td>0.9556</td>
<td>0.9801</td>
<td>0.9883</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/n</td>
<td>0.4427</td>
<td>0.5584</td>
<td>0.4765</td>
</tr>
<tr>
<td>K_F</td>
<td>4.9413</td>
<td>11.989</td>
<td>8.7845</td>
</tr>
<tr>
<td>R^2</td>
<td>0.9887</td>
<td>0.9619</td>
<td>0.9438</td>
</tr>
</tbody>
</table>

The results indicated that MC-FeII and MC-FeIII were better fitted to Langmuir model due to the higher values of correlation coefficient (R^2). However, MC was well described by Freundlich model. This implied that MC possessed a heterogeneous surface with multi layers adsorption for arsenate. The improvement of iron contents of MC-FeII and MC-FeIII seems to overpass the uptake capacity of other parallel existing minerals and possibly provided a monolayer arsenate adsorption on the their homogeneous surface without having any interaction between adsorbed adsorbate [14]. The maximum arsenate adsorption capacity from Langmuir models were 250µg/g, 747.38µg/g and 429.74µg/g for MC, MC-FeII and MC-FeIII, respectively.

The type of isotherm can be evaluated using the value of a separation factor constant and Freundlich constant (1/n). A separation factor constant (R_L) is expressed as follow:

\[ R_L = \frac{1}{1 + K_L C_0} \]  \hspace{1cm} (7)

The adsorption process is irreversible if \( R_L = 0 \), favorable if \( 0 < R_L < 1 \), linear if \( R_L = 1 \) and unfavorable if \( R_L > 1 \) and the adsorption is favorable when \( 0 < 1/n < 1 \), irreversible when \( 1/n = 1 \) and unfavorable when \( 1/n > 1 \) [15]. For all adsorbents, 1/n values were within 0-1. With the studied arsenate range, \( K_L \) were 0.07-0.89, 0.02-0.67 and 0.04-0.79 for MC, MC-FeII and MC-FeIII, respectively. This implied adsorbents expressed favorably adsorption toward arsenate.

3.4 Effect of pH

The effect of solution pH on the arsenate adsorption onto MC, MC-FeII and MC-FeIII is presented in Fig. 5. All the adsorbents shared a similar pattern of the adsorption efficiency over the studied pH range. The arsenate adsorption efficiency gradually decreased for pH from 3 to 7. When pH was beyond 7, the decrease was significantly improved and the dramatically decline was observed for pH 11.

3.5 Effect of coexisting anions

The effect of coexisting anions on the arsenate adsorption by the adsorbents were conducted by separately adding 0.1mM of univalent anions (Cl^-, NO_3^-, HCO_3^-), bivalent anions (CO_3^{2-}, SO_4^{2-}) and trivalent anion (PO_4^{3-}) to 500µg/L of arsenate solution. The arsenate adsorption efficiency in the presence of each individual anion is shown in Fig. 6.
The results showed that a similar trend of influence on the arsenate efficiency was observed for all adsorbents. The presence of univalent anions showed less reduction in arsenate adsorption efficiency. The increasing reduction of adsorption efficiency was observed when bivalent anions were added. Trivalent anion (PO$_4^{3-}$) significantly influenced on decreasing the arsenate adsorption efficiency. The competition for active sites on the surface of the adsorbents could be a reason for remarkably reduction of arsenate adsorption efficiency in case of PO$_4^{3-}$. Phosphate shares similar chemical properties to arsenic and easily attaches to iron hydroxide to form an inner-sphere complex compared to arsenic [17], [18].

4. CONCLUSION

Natural clay could be stabilized the particle size by calcination. Iron impregnation on MC improved the iron oxide content for MC-FeII and MC-FeIII, as well as their adsorption efficiency. Pseudo-second order model was more suitable for fitting the kinetic data for all adsorbents. Both applied isotherm models were suitable to describe the isotherm data for MC adsorbent. Langmuir was better in case of iron modified adsorbents. All adsorbents exhibited high arsenate adsorption efficiency at lower initial solution pH and significant reduction occurred at high pH value. The introduced coexisting anions influenced on the arsenate adsorption efficiency of all adsorbents in the following order: trivalent> bivalent> univalent anions. Modified adsorbents, particularly MC-FeII and MC-FeIII, were easily and economically produced that could be effective and low-cost adsorbents to remove arsenate from water.

5. ACKNOWLEDGEMENTS

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6. REFERENCES


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