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Removal of arsenic from water using smectite rich clay soil: insight from adsorption kinetics and adsorption isotherms

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Abstract: This study evaluates the applicability of smectite rich clay soils in arsenic removal. The mineralogical and chemical composition of the clay soils were examined using x-ray diffraction (XRD) and X-ray fluorescence (XRF) respectively. Batch experiments were used to evaluate the adsorption kinetics, isotherms and the effect of pH on As(III) and As(V) adsorption. The results showed that the As(III) data fitted well to pseudo second order of reaction kinetics while As(V) adsorption data fitted well to pseudo first order of reaction. Isotherm data was described by the Freundlich adsorption isotherm model. The adsorption of both As species was found to be affected by the solution pH. Maximum percentage of removal was found to be 53.8% at pH 6 for As(V) and 52.9% for As(III) at pH 8. It was concluded that smectite rich clay soils can be used for arsenic remediation from water. The study recommended further studies to enhance adsorptive properties of smectite rich clay soils in arsenic removal.

Keywords: *Smectite rich clay soils; Adsorption kinetics; adsorption isotherm; mineralogical and chemical composition.*

1. Introduction

The presence of arsenic in groundwater has attained worldwide attention due to its negative implications on human health. Prolonged exposure to arsenic is linked to arsenicosis (Abdul *et al*., 2015). The disease is manifested by different types of cancer, kidney diseases, diabetes, skin lesions, circulatory disorders and neurological complications (Mandal and Suzuki, 2002; Duker et al., 2005; Ayotte *et al*., 2015). These symptoms have been observed in more than 105 countries worldwide where groundwater contains arsenic concentration beyond World Health Organization permissible limit value of 0.01 mg/L (Smith *et al*., 1999). Epidemiological studies have established a direct link between prolonged exposure to arsenic and these diseases (Bulka *et al*., 2016). Furthermore, it is estimated that more than 200 million people worldwide are at health risk due to arsenic rich water (Smith *et al*., 2004; Sarkar and Paul, 2016). As such, there is a great demand for either finding alternative source of drinking water or developing a flexible and sustainable method for arsenic removal from groundwater.

In water arsenic is commonly found in organic and inorganic form known as arsenite (As(III)) and arsenate (As(V)) respectively depending on the conditions (Mandal and Suzuki, 2002). Arsenate is found under oxidizing conditions and it is less toxic as compared to arsenite which is found under reducing conditions

The use of clay soils in arsenic removal has been extensively studied in different parts of the world and they have proved to be promising adsorbents for arsenic from water (Mishra and Mahato, 2016; Bentahar *et al*., 2016). Their physicochemical properties such as larger specific surface area, higher cation exchange capacity and chemical and mechanical stability makes clay soils to be excellent adsorbent (Bhattacharyya *et al*., 2008). Furthermore, clay soils are naturally available in abundance at little or no cost. The objectives of this study are therefore: i) to evaluate mineralogical and chemical composition of clay soils as potential arsenic adsorbents, ii) to evaluate adsorption kenetics, isotherms and effect of pH on As(III) and As(V) removal.

Table 1. Chemical composition of smectite rich clay soils

Oxides	**SiO_2**	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**
Composition (%w/w)	60.92	0.63	15.83	5.96	0.094	3.85	1.63	1.67	1.3	0.02

2 Material and methods

2.1 Sampling

Smectite rich clay soils were collected from Mukondeni Village, Ha-Mashamba Limpopo Province, South Africa. All chemical reagents purchased from Rochelle Chemicals & Lab Equipment CC, South Africa Ltd and were of analytical grade were of analytical grated and they were used without further purification. Composite solution containing 1000 mg/L As(III) and As(V) was prepared by dissolving 0.416 g $HAsNa_2O_4.7H_2O$ and 0.1733 g $AsNaO_2$ in 100 mL flask using Milli Q water (18.2 MΩ/cm). The solution was preserved by adding few drops of 3 M HNO_3. Working solutions were prepared by appropriate dilutions.

2.2 Mineralogical and chemical composition evaluation

Bulk mineralogy was evaluated using PANalytical X'Pert Pro powder diffractometer and mineral phase amounts were estimated using Rietveld method (Autoquan Program). The chemical composition were evaluated using S2 ranger X-ray fluorescence.

2.3 Batch experiment

Batch adsorption experiments were conducted to evaluate the optimum conditions for removing As(III) and As(V) using smectite rich clay soils. To evaluate the effect of adsorption kinetics, 100 mL solution containing 5 mg/L of As(III) and As(V) was pipetted into 250 mL polyethylene bottles and mass of 0.15 g smectite rich clay soils was added respectively to make up 0.15g/100 mL adsorbent dosage. Mixtures were then agitated for 10, 20, 30, 40, 50, 60, 90 and 120 mins. After agitation, mixtures were filtered through 0.45 µm filter membranes. Samples were then refrigerated at 4 ^{o}C until analyzed using 850 professional Metrohm ion chromatography. To evaluate the adsorption isotherms, initial concentration was varied from 1 to 15 mg/L and the adsorbent dosage of 0.15g /100 mL adsorbent dosage of both clay soils was added. Mixtures were added and agitated for 60 mins. To evaluate the effect of pH, the pH of the mixture was adjusted from 2-12 using 0.1 M NaOH and 0.1 M HCl. Adsorbent dosage of 0.15 g/100 mL of both clay soils was used. Initial concentration of 5 mg/L was used. Mixtures were agitated for 60 mins. All experiments were conducted in triplicate and the mean values were reported.

2.4 Arsenic analysis

Metrohm 850 professional ion chromatography (Switzerland) was used to analyze As(III) and As(V). Metrosep A Supp 5-150 column was used for separation and the guard column Metrosep A 4/5 was used. The eluent containing 15 mmol/L NaOH and 2.0 mmol/L Na_2CO_3 was used as the mobile phase. The conductivity detector was used to estimate the concentration of different chemical species.

3 Results and Discussion

3.1 Mineralogical and Chemical composition

The quantitative X-ray diffraction has revealed smectite, quartz and plagioclase are the main minerals of the clay soils amounting to 60.36%, 20.21% and 20.4% respectively. Hence the clay was then referred to as smectite rich clay soils. Albite and anthophyllite were detected as minor minerals of the clay soils. Table 1 summarizes the major chemical oxides of the clay soils. It is observed silica (SiO_2) is the main component at 60.92%, followed by Al_2O_3 at 15.83%. High concentrations of SiO_2 and Al_2O_3 reveal that the clay soil is an aluminosilicate material. Other oxides such as Fe_2O_3, MnO, MgO, CaO, Na_2O and K_2O were detected at trace concentration.

3.2 Evaluation of Adsorption kinetics

To evaluate the adsorption kinetics of As(III) and As(V) onto smectite rich clay soils, contact time was varied from 10 to 120 min. The initial concentration for both As(III) and As(V) was kept at 5 mg/L and adsorbent dosage used was 0.15 g/100 mL. The results are presented in Figure 1. It is observed that the percentage removal for both As(III) and As(V) increased with increasing contact time. For As(III) the optimum percentage of removal of 51.53% was achieved at 40 min while for As(V) the optimum percentage of removal of 60.49% was achieved at 60 min of contact. The lower percentage of removal for As(III) could be attributed to the fact that As(III) is neutrally charged at the pH between 0-9 making it difficult to remove from water. Pseudo first and second order depicted by Equation 1 and 2 respectively, were used to describe the adsorption kinetics.

$$\log_{(qe-qt)} = \log q_e - \frac{K_{ad}t}{2.303} \qquad (1)$$

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

Where q_e and q_t (both in mg/g) are the amount adsorbed per unit mass at a time, t (in min). K_{ad} (min^{-1}) and K_{2ads} (g.mg^{-1}/min) are first and second order rate constant. The value of K_{ad} is determined from the slope and intercepts of log (q_e–qt) vs t (min) and the value of K_{2ads} is determined from the slope and intercepts of t/q_t vs t. The constant values are presented in Table 2. The correlation coefficient values indicates that the adsorption data for As(III) fitted better to pseudo second order while adsorption data for As(V) fitted better to pseudo first order of reaction kinetics. This means As(III) was adsorbed via chemisorption while As(V) adsorbed via physiosorption.

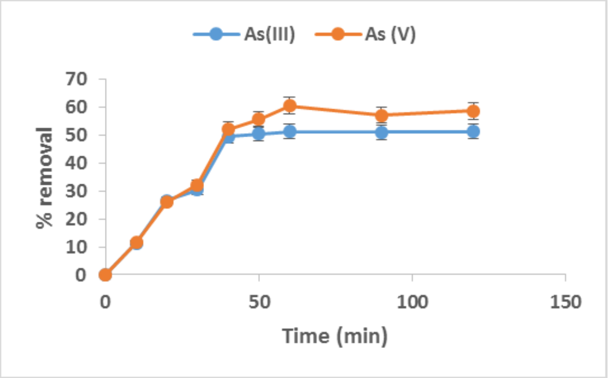

Figure 1: Adsorption of As(III) and As(V) onto smectite rich clay soils as function of time (5 mg/L initial concentration, 0.15 g/100 mL adsorbent dosage, pH 8.53 and shaking speed of 250 rpm).

Table 2: constant values for pseudo first and second order of reaction kinetics

	Pseudo first order		**Pseudo second order**	
	K_{ad} (min^{-1})	R^2	K_{2ad} (g.mg^{-1}/min)	R^2
As(III)	0.047	0.65	0.0115	0.89
As(V)	0.030	0.97	0.0043	0.84

3.3 Adsorption isotherms

To study the adsorption isotherms, the initial As(III) and As(V) concentrations were varied from 1 to 15 mg/L. The adsorbent dosage of 0.15 g/100 mL was used. Mixtures were agitated for 60 min. The results are presented in Figure 2. It is observed that the percentage removal decreased with increasing initial concentration. This was observed for both arsenic species. The decrease in percentage removal could be attributed to more availability of As(III) and As(V) ions in the solution as the initial concentration increases. At lower initial concentration, the ratio of adsorbent’s active sites to adsorbate concentration was high and as a results the interaction between the As(III) and As(V) with the adsorbent was efficient to for their removal. The two commonly used adsorption isotherms i.e., Langmuir and Freundlich adsorption isotherms were used to describe the adsorption isotherm. Linearized form of Langmuir and Freundlich (Eq. 3 and 4) were used.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \qquad (3)$$

$$\log Q_e = \log K_f + \frac{1}{n}\log Ce \qquad (4)$$

Where, C_e is the equilibrium concentration (mg/L), Q_e is the adsorption capacity (mg/g), Q_m is theoretical maximum adsorption capacity (mg/g) and *b* is the Langmuir constant related to enthalpy of adsorption (L/mg). Q_m and *b* are determined from the slope and intercept of the plot of $\frac{C_e}{Q_e} Vs\ C_e$. K_f is the Freundlich constant related to adsorption capacity and represents the strength of adsorptive bonds and *1/n* is the adsorption intensity. When 0<*1/n*<1, the adsorption is favorable; when *1/n*=1, the adsorption is irreversible; and when *1/n*>1, the adsorption is unfavorable. The constant values are presented in Table 3. Based on the correlation coefficient value, adsorption data of both As(III) and As(V) fitted better to Freundlich isotherm model. This indicates that the adsorption occurred on a heterogeneous surface. Furthermore, the value of 1/n lies below 1 which means adsorption of both As species onto smectite rich clay soils was favourable.

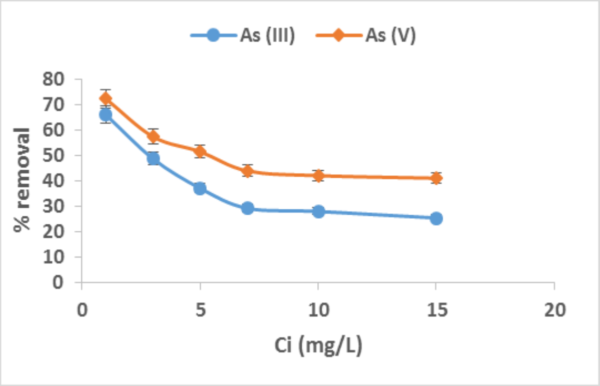

Figure 2: Adsorption of As(III) and As(V) onto smectite rich clay soils as a function of adsorbate concentration (60 min contact time, 0.15 g/100 mL adsorbent dosage, pH 8.53 and shaking speed of 250 rpm).

Table 3: Constant values for Langmuir and Freundlich adsorption isotherms

		Langmuir isotherm			**Freundlich isotherm**		
	Q_{exp} (mg/g)	Q_m (mg/g)	b(L/mg)	R^2	K_f (mg/g)	1/n	R2
As(III)	0.76	0.9	0.26	0.86	4.53	0.47	0.98
As(V)	1.23	1.69	0.2	0.81	3.32	0.59	0.99

3.4 Effect of pH

To evaluate the effect of pH, initial pH was adjusted from 2 to 12 using 0.1 M NaOH and 0.1 M HCl. Mixtures were agitated for 60 min at 250 rpm on Table Shaker. Adsorbent dosage of 0.15 g/100 g was used. The results are presented in Figure 3. From figure, it is observed that the % removal was optimum at pH 6 and 8. Percentage removal decreased as the solution becomes acidic and also as it becomes alkaline. The same trend was observed for both arsenic species. The pHpzc of the smectite rich clay as reported by Mudzielwana *et al.*, (2016) is 6.2±0.2. Therefore, at pH below 6.2 the surface of the clay is positively charged while at pH beyond 6.2 the surface is negatively charged. Low percentage of removal of As(III) at extreme acidic pH could be explained by the fact that at this pH it exist as H_3AsO_3 which is neutrally charged and as a results there is weaker attraction force with the surface of the adsorbent. As the solution pH increases the surface of the clay becomes neutrally charged and as a results the Van der Waal attraction force dominate resulting in increasing percentage of removal. As the pH increases to beyond pHpzc the surface becomes negatively charged and also As(III) exist as $H_2As_3^-$ therefore, reduction in percentage removal could be attributed to electrostatic repulsion. The decrease in As(V) as the pH increases could also be explained by fact that at alkaline pH, As(V) exist as $H_2AsO_4^-$ and $HAsO_4^{2-}$ as a results it repels with the surface charges. At extreme acidic pH, As(V) exist as H_3AsO_4 which dissociate to form $H_2AsO_4^-$ which is then attracted to the positive surface electrostatically.

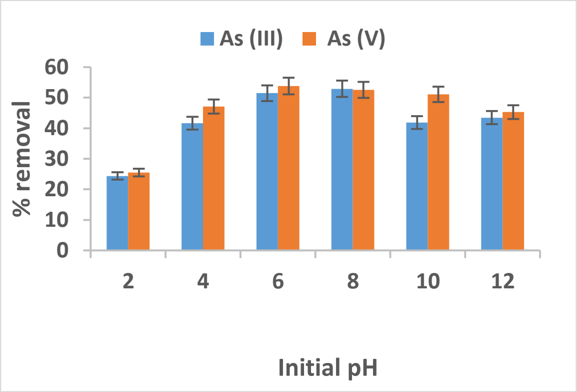

Figure 3: Adsorption of As(III) and As(V) onto smectite rich clay soils as a function of pH (5 mg/L initial concentration, contact time 60 min, 0.15 g/100 mL adsorbent dosage, and shaking speed of 250 rpm).

4 Conclusions

The applicability of smectite rich clay soils in arsenic removal was successfully evaluated. The kinetic data showed that the As(III) sorption onto the clay soils occurred via chemisorption while the As(V) sorption occurred via physiosorption. Furthermore, the isotherm data showed that the surface of the clay soils is heterogeneous in nature. The evaluation of pH showed that the maximum percentage of both As(III) and As(V) removal occurred between the pH 6 and 8. The study recommends that smectite clay soils can be used for arsenic removal. However, further studies should be conducted to improve its sorption capacity.

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