

Full Length Research Paper

Adsorption of Arsenite onto Kemiron

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This study investigated the effect of pH and coexisting ions on As(III) adsorption using batch experiment and discovered that pH strongly influenced As(III) adsorption. However, differences in background ionic strengths of 0.001 N NaNO₃ and 0.1 N NaNO₃ had no effect on the sorption trend. The isotherms followed Freundlich model with K_f of 27.91, 35.67, and 43.76 (mg/g)(L/mg)ⁿ at pH 6, 7, and 9 respectively. The kinetic studies showed D_{app} values of $(6.52 \pm 0.024) \times 10^{-7}$ cm²/s and $(6.22 \pm 0.043) \times 10^{-7}$ cm²/s for the 38 μm and 500 to 600 μm particle sizes. The biot numbers of the sorption derived were 1.84×10^{-2} and 5.89×10^{-1} respectively. The presence of CO₃²⁻ had more impact than SO₄²⁻ ion but the presence of 300 mg/L NH₄⁺ - N had no significant impact on As(III) adsorption between pH 4 and 8 and so was the presence of 0.1 mg/L Ca²⁺ ion between pH 4 and 6.5. However, about 10% loss of the sorption capacity of Kemiron occurred between pH 6.5 and 9 in the presence of Ca²⁺ ion. The presence of 5 mg/L Ni(II) and Se(IV) also showed that Se(IV) was a stronger inhibitor of As(III) sorption than Ni(II).

Key words: Arsenite, ground water, Freundlich, diffusion coefficient, Ghana.

INTRODUCTION

There is a rise in the demand for ground water as an alternative source for water supply in many parts of the world. This is because fresh surface water resources are dwindling fast and are not meeting global demand. As a result there is heightened concern for aquifer contamination by such heavy metals as arsenic (As). Arsenite contaminates ground water either naturally or through anthropogenic activities. Activities like open cast mining, chemical/metal processing, and landfill operations increase the risk or directly contaminate neighboring ground water resources. For instance, in countries like Ghana and Guyana, cyanide spillage and tailings ponds collapses from gold processing plants have occurred. Cyanide, a very toxic chemical compound dissolves and forms complexes with heavy metals just as it does with gold, during gold processing. Thus the

spillage and seepage into aquifer from mine activities causes dissolution and mobilization of otherwise existing stable heavy metals in their environments. This change in aquifer chemistry could eventually release As from the solid phase into ground water. In Ghana, high levels of As concentrations above World Health Organization permissible level (10 μg/L) have been reported in ground and surface fresh water in and near mine sites. Research on the As contamination in the water has been identified to strongly correlate to the mining activities (Smedley, 1996). In the United States, As has been identified in surface and ground water in many States (Smedley and Kinniburgh, 2002) and some of the sources have been traced directly or indirectly to nearby landfill (Stollenwerk and Colman, 2004; Burns et al., 2006). At Polk County, Florida, a collapse of a landfill into an underlying sinkhole in 2011 created a great concern of seeping As and other contaminants into the underlying aquifer.

Arsenic ingestion is known to cause cancer, heart, black foot and other deadly diseases. And such incidents have been reported in West Bengal, Bangladesh and in

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many parts of the world including the United States (Buschmann et al., 2007; Dogan and Dogan, 2007; Robinson et al., 2007; Savarimuthu et al., 2006).

Inorganic component of As exists as arsenate As(V) and arsenite (As(III)). But most experiments on adsorption treatment of As has been focused on As(V) while in reality significant number of contaminated ground water boreholes are of As(III) dominance, rather than As(V) (Smedley and Kinniburgh, 2002). Articles by Baddruzzaman et al. (2004), Westerhoff et al. (2005), Sperlich et al. (2008) and others attested to that and the reason for the preference for As(V) is unclear. However, Zhang et al. (2007) stated that it was easier to effectively remove As(V) from aqueous solution by adsorption than it was for As(III). Other researchers who had worked on As(III) treatment had them converted to As(V) before the removal by the adsorption process. This pretreatment method adds cost to the removal process, making the adsorption method more expensive (Zhang et al., 2007) and more complex. Moreover, many of the researchers applied the adsorption method for the treatment of As(III) at pH 9.3 and above where As(III) ionizes. This process again requires skill and experience in order to achieve a significant removal. In designing for rural and for developing countries where expertise is lacking simplicity and cost effectiveness of operation are paramount parameters to consider. A removal process that does not require specific initial pH and oxidation of As(III) is of great essence in this case.

In this experiment, Kemiron was used as the adsorbent to remove As(III) from DI water in a batch system. Kemiron is a newly developed and commercially available adsorbent, with no background literature on As(III) removal performance, to the best of our knowledge. The effectiveness in removing As(V) and Se(IV) in surface water (Oti and Trotz, 2008) was our motivation to investigate the treatment performance of As(III). The goal for the experiments was therefore to evaluate mass loadings of As(III) onto the Kemiron under various environmental conditions. And to achieve this, we The following were evaluated: 1) impact of pH on As(III) removal 2) effect of initial concentration of As(III) on the removal process 3) impact of the presence of CO_3^{2-} , SO_4^{2-} , and Ca^{2+} , Ni^{2+} , and NH_4^+ - N on the As(III) removal 4) effect of grain size on the removal performance. The rationale for this work was to gain an insight on Kemiron adsorption capacities under various environmental conditions that would enable us compare the capabilities with other well established adsorbents such as granular ferric hydroxide and clinoptilolite. And also to compare their cost effectiveness per the mass loadings of As(III).

MATERIALS AND METHODS

The Kemiron adsorbent was obtained from the Kemiron Company in Florida, USA. Kemiron is an iron based adsorbent with a total internal surface area of $\sim 39 \text{ m}^2/\text{g}$ and with an apparent (skeletal) density of 2.94 kg/L . Detailed physical characterization of the

adsorbent can be found elsewhere (Oti and Trotz, 2008). To obtain the grain sizes into the fractions required for this experiment, Kemiron was sieved with US standard testing sieves which conformed to ASTM E-11 specifications. Two different grain sizes were studied: ≤ 38 , and 500 to $600 \mu\text{m}$ and then stored the adsorbents dried in ziploc bags. The use of the $\leq 38 \mu\text{m}$ grain size was for the purpose of achieving quicker equilibration results while the bigger grains of Kemiron were studied to understand the effect of length path on adsorption.

Reagents

All the reagents used were of analytical grade from Fisher Scientific. Stock solutions were prepared by dissolving the solid reagents in ultrapure water (Barnstead) with resistivity of $18.2 \text{ M}\Omega\text{-cm}$. The rest of the reagents used included $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, NaNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HNO_3 , Na_2CO_3 , Na_2SO_4 , NH_4NO_3 , $\text{Ca}(\text{OH})_2$, Na_2SeO_3 . Also used were pH buffers of 4.0, 7.0, and 10.0 from Fisher Scientific as the standard calibration solutions for the pH measurement.

A stock solution of 150 mg/L Ni ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Fisher Scientific) as a modifier solution in the analysis of the arsenite, and a $0.001 \text{ N}/0.1 \text{ N NaNO}_3$ (Fisher Scientific) ionic strength and with $2\% \text{ HNO}_3$ was used as the background electrolyte. Prior to use, the NaNO_3 was dried at 80°C for 4 hours and stored in a desiccators and also adjusted pH with the HNO_3 and with CO_2 free NaOH (Fisher Scientific) of varying concentrations.

Instruments and apparatus

A graphite furnace Varian Spectra AA 240Z system equipped with automated sample injection (GTA 120) was used to analyze the As(III) as total As. A nitrogen sparging setup used was comprised of ultra high pure nitrogen gas cylinder coupled to 250 mL pyrex cylinder containing 40% potassium hydroxide solution, which in turn was connected to another 250 mL pyrex cylinder containing ultrapure water (Barnstead) and then to a polycarbonate batch reactor on a magnetic stirrer (CORNING). A Ross semi micro gel filled electrode with Orion 940 pH meter was used for the pH measurements and Mettler Toledo AB265-S and Denver Instrument APX-3202 scales for the weighing as well as Barnstead Thermolyne LABQUAKE for shaking the batch systems.

The methodology of the experiment used was a batch test and is one of the most frequently adopted experimental methods used to evaluate fundamental characteristics of chemical reactions. This method investigated the equilibration and average rate of As(III) adsorption, determined adsorption isotherms and also analyzed the impact of Ca^{2+} , Ni^{2+} , NH_4^+ - N, CO_3^{2-} , and SO_4^{2-} on the As(III) removal. CO_2 free DI water was used for making the solutions and this was prepared by sparging the ultrapure (Barnstead) water with ultra high pure nitrogen gas (Airgas Incorp.) for 24 h. All slurries were also purged with N_2 gas for 24 h prior to spiking. Prior to the start of the experiments all glassware was soaked in 1 N sodium hydroxide, NaOH for more than 1 h, rinsed with milliQ water and soaked again in $10\% \text{ HNO}_3$ overnight before finally rinsed with and left soaking in milliQ water overnight. Cleaning of polycarbonate (PC) containers was similar to that of glassware except that the concentrations of HNO_3 and NaOH were both 0.1 N . Two drops of Liquinox detergent dissolved in 500 ml ultra pure water was used to wash all containers prior to the base and acid wash.

Batch adsorption tests

200 ml equilibration tests were conducted in a 250 ml PC batch reactor on 5 mg/L As(III) at ionic strength of 0.1 N and 0.001 N of

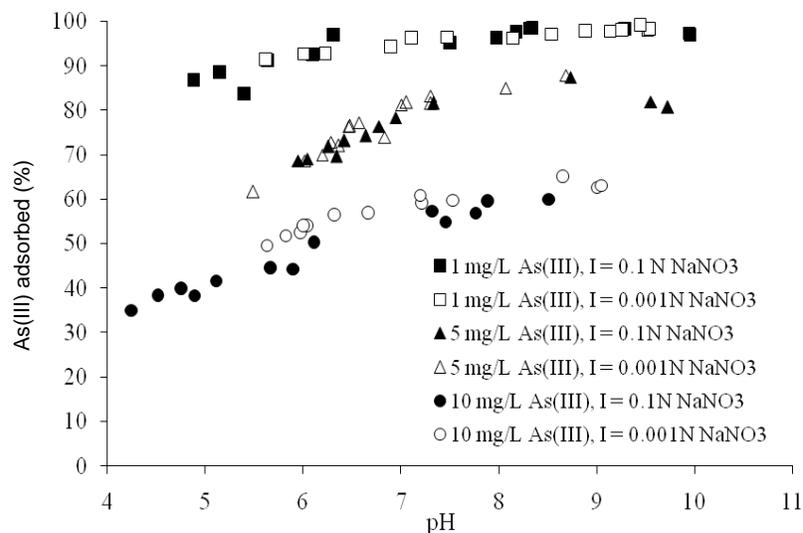


Figure 1. As(III) adsorption onto 0.1g/L Kemiron (grain size $\leq 38 \mu\text{m}$) at $I = 0.1$ and 0.001 N NaNO_3 and at room temperature.

NaNO_3 . 0.1 g/L of Kemiron (grain size $\leq 38 \mu\text{m}$) prepared in a polycarbonate (PC) batch reactor with CO_2 free ultrapure water (Barnstead), was used as the adsorbent slurry. Dissolved CO_2 in the slurry was removed by sparging the slurry with ultra high pure nitrogen gas for 24 h and at pH ~ 5.5 . The pH was then raised to ~ 10 with $30 \mu\text{L}$ of 0.1 N NaOH and the slurry was spiked to the 5 mg/L As(III) solution from sodium arsenite, NaAsO_2 . Fifteen samples of 8 mL were then taken into 10 mL PC tubes at various lower pH levels. The lowering of pH in the 250 mL PC was done with $10 \mu\text{L}$ of HNO_3 drops before the samples were taken. The head spaces in the 10 mL PC tubes were then filled with ultrapure nitrogen gas. The samples were filtered with $0.20 \mu\text{m}$ MILLIPORE filters after 72 h of equilibration in an agitator. The filtrates were acidified with concentrated HNO_3 to 0.7% and analyzed for As(III). The binary batch experiments were carried out on initial As(III) concentrations of 1 mg/L , 5 mg/L and 10 mg/L with 0.001 N and 0.1 N NaNO_3 ionic strength. Tests were conducted that evaluated the impact of $\text{NH}_4^+ - \text{N}$, Ca^{2+} , SO_4^{2-} , CO_3^{2-} , Se(IV), and Ni(II). For the $\text{NH}_4^+ - \text{N}$ impact assessment, the equilibration experiment was repeated as detailed above but spiked into the system 300 mg/L of $\text{NH}_4^+ - \text{N}$ prior to the addition of the 5 mg/L As(III) followed by taking of the samples into the 8 mL PC tubes for the equilibration reaction. The experiments were performed another five separate times and for each time a different adsorption competitor was added to the batch system. The following were used for the five tests: 0.1 mg/L Ca^{2+} ion spike for one test, a $1000 \text{ mg/L SO}_4^{2-}$ for another, a $1000 \text{ mg/L CO}_3^{2-}$ for another, a 5 mg/L Se(IV) for one and finally 5 mg/L Ni(II) .

Batch isotherm was also done at room temperature on As(III) with initial concentrations of $1, 3, 5, 6.5, 7.2, 8, 9$ and 10 mg/L at a pH $6, 7,$ and 9 for 72 h and with ionic strength of 0.001 N NaNO_3 . The As(III) stock solutions were freshly prepared for each experiment. 5 samples each having a volume of 8 mL were taken from the slurry into 10 mL PC tubes for each initial concentration. The preparations and the filtrations of the samples for analysis for isotherm were done in the same way as they were for the batch equilibrations. The mean of the analysis results of the samples taken at each pH was plotted as the isotherm graph.

The batch kinetics studies of two grain sizes of Kemiron (≤ 38 and $500 - 600 \mu\text{m}$) were done in a 1000 mL Nalgene batch bottle. A solid concentration of 0.1 g/L Kemiron in 1000 mL solution was

made. The pH of the solution was then lowered to 5 with $10 \mu\text{L}$ of 0.1 N HNO_3 before it was sparged with the ultra high pure nitrogen gas for 24 h. The pH was then raised to 7 with 0.1 N NaOH and then 5 mg/L As(III) was spiked into it. The pH was maintained at 7 with the 0.1 N NaOH and within predetermined period, 0.2 mL of samples was taken. Ten samples were taken in both cases of the $< 38 \mu\text{m}$ and $500 - 600 \mu\text{m}$. The results from the analyses were modeled with mass transfer and diffusion equations.

Analytical methods

All samples and calibration standards were analyzed in triplicates and recalibrations were done after every 8 samples. The lower detection limit for As(III) was $5 \mu\text{g/L}$ and the calibration range used was between 10 and $60 \mu\text{g/L}$. Volumes of $10 \mu\text{L}$ of As and $5 \mu\text{L}$ of modifier ($200 \mu\text{g Ni}$ from NiNO_3 stock solution) were injected by the auto sampler into a graphite coated partition tube. The injected samples were fired to 2600 degrees with As lamp at wavelength of 193.7 nm .

RESULTS AND DISCUSSION

Equilibration experiment

In this work, the experiment was conducted with initial As(III) concentrations of $1, 5$ and 10 mg/L . And as illustrated in Figure 1, the pH-percentage adsorbed curve shows typical dome shape as it was indicated by Chakraborty et al. (2007) and Gu et al. (2007). The pH changes affected the percentages of As(III) adsorbed. The amount of As(III) adsorbed rose from pH 4 to 7.5 and then peaked between pH 7.5 and 9.5 with initial concentration of 5 to 10 mg/L . For As(III) with the initial concentration of 1 mg/L , the sorption curve rose from pH 4.5 to about 7.5 and then leveled off up to about 10.5.

For the initial concentration of 1 mg/L , 87% of As(III)

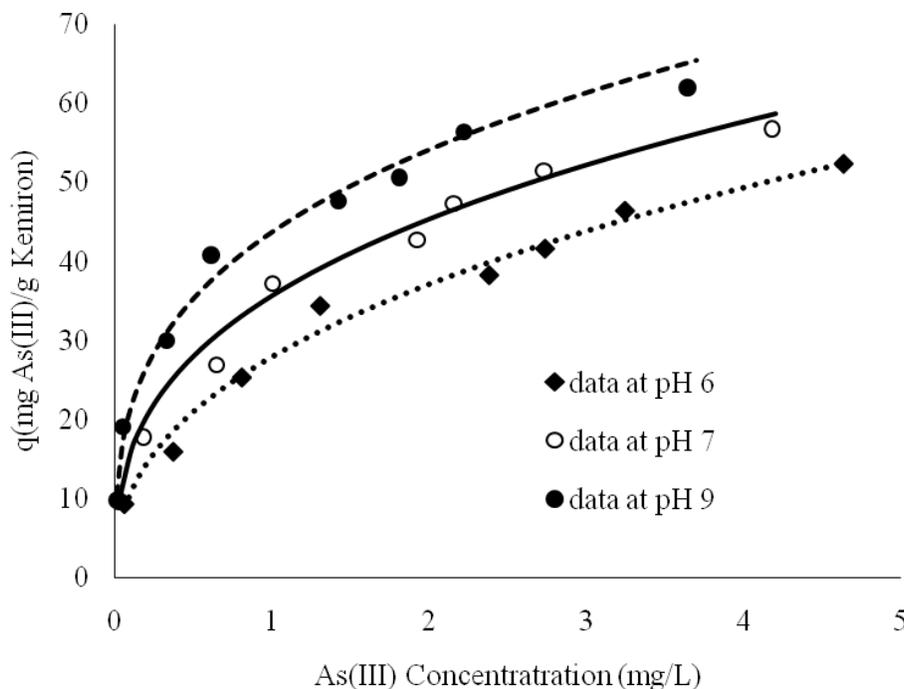


Figure 2. Freundlich adsorption isotherm models of As(III) with 0.1 g/L Kemiron ($\leq 38 \mu\text{m}$), $I = 0.001 \text{ N NaNO}_3$ at pH 6, 7, and 9 for 72 h.

concentration was adsorbed at pH 5 and 100% adsorbed at pH 8.5 to 10, while for the initial concentration of 5 mg/L As(III) 62% of the concentration was adsorbed at pH 5.2 and 87% at the maximum adsorbed occurred around the pH of 8.7. Similarly, 35% of 10 mg/L initial concentration was adsorbed at pH 4.2 but 65% was adsorbed at pH 8.7.

The adsorption behavior was unaffected by the background ionic strength which was between 0.001 N NaNO_3 and 0.1 N NaNO_3 , a characteristic that is indicative of innersphere adsorption mechanism (McBride, 1997). The percentages of As(III) adsorbed at the two various ionic strengths were about the same in all the various initial As(III) concentrations.

Figure 1 As(III) adsorption onto 0.1g/L Kemiron (grain size $\leq 38 \mu\text{m}$) at $I = 0.1$ and 0.001 N NaNO_3 and at room temperature.

Batch isotherm experiment

The mass loadings of As(III) onto the $\leq 38 \mu\text{m}$ Kemiron grain size in the batch system followed Freundlich model which can be written as:

$$q = K_f C^{1/n} \quad (1)$$

where q is the mass of As(III) (mg) adsorbed per mass of Kemiron (g) in the bulk solution.

K_f is an adjustable parameter and is called Freundlich coefficient of adsorption.

C is the aqueous concentration of As(III) at equilibrium.

n is an adjustable parameter and is an indicator of adsorption intensity.

The mass loadings of As(III) as shown in Figure 2 depicted a trend of higher loadings onto the adsorbent occurred as the pH values increased. This indicated that the mass loadings were lowest at pH 6 and it conformed to the data points exhibited in Figure 1 for the pH values between 4 and 11 and for initial As(III) concentrations up to 10 mg/L. The resulting K_f values also increased with increasing pH of 6, 7 and 9 and were 27.91, 35.67, and 40.76 (mg/g) $(\text{L/mg As(III)})^n$ respectively. The $1/n$ values also showed a decreasing trend with increasing pH values and with the $1/n$ values being 0.36, 0.35, and 0.29. The coefficients of determinations (R^2) between Freundlich model and the experimental data of the isotherms were within a range of 0.99 ± 0.003 . Ideally,

Kemiron (iron based adsorbent) was expected to possess positively charged surface at lower pH values and then transition through point of zero charge (PZC) and then into negatively charged surface as the pH increases. Electrostatic effect is considered as a paramount force in sorption capacity enhancement and the absence of the force greatly diminish the capacity. As(III) known to be neutral until at pH 9.2 and above and thus lacked electrostatic effect in the sorption process at

the low pH values. That accounted for the nature of the curve of As(III) sorption and such trend have been reported to be typical for As(III) sorption with varying pH. Figure 2 Freundlich adsorption isotherm models of As(III) with 0.1 g/L Kemiron ($\leq 38 \mu\text{m}$), $I = 0.001 \text{ N NaNO}_3$ at pH 6, 7, and 9, for 72 h.

Batch kinetics

To experimentally determine the rate of uptake of As(III) onto Kemiron in the batch system, the fractional method was adopted and can be written as:

$$\frac{C_0 - C_{bt}}{C_0 - C_{be}} = \frac{M_t}{M_\infty} \tag{2}$$

where C_0 is the initial As(III) concentration in the bulk solution.

C_{bt} is the As(III) concentration in the bulk solution at any given time.

C_{be} is the As(III) concentration in the bulk solution at equilibrium.

M_t is the mass of As(III) adsorbed at any given time t .

M_∞ is the mass of As(III) adsorbed at equilibrium.

Then fitted the fractional rates of As(III) removal onto Kemiron at pH 7 were fitted with Crank’s (1975) solution to Fick’s law of diffusion. Equation (3) is the Fick’s law of diffusion and many authors including Ball and Roberts (1991) adopted Crank’s solution to Fick’s law of diffusion shown in Equation (4) below to determine diffusivities in batch experiments.

$$\frac{\partial q}{\partial t} = D_{app} \left(\frac{\partial^2 q_p}{\partial r^2} + \frac{2}{r} \frac{\partial q_p}{\partial r} \right) \tag{3}$$

where t is the time length of As(III) loadings.

D_{app} is the apparent diffusivity of As(III) into Kemiron.

q_p is the mass loadings per mass of Kemiron in the pores of Kemiron particle.

r is the path length from the periphery to the core of Kemiron particle.

The Crank’s solution to Equation (3) with fixed diffusivity is also given as:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6 \alpha (1+\alpha)}{9 + 9 \alpha + q_n^2 \alpha^2} e^{-\left(\frac{D_{app} q_n^2 t}{r^2}\right)} \tag{4}$$

where q_n is a non-zero root of the equation below:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \tag{5}$$

α can be determined from:

$$\frac{M_\infty}{VC_0} = \frac{1}{1 + \alpha} \tag{6}$$

where V is the volume of the batch system.

Equations (2) and (4) were equated and to achieve the best fit, which then allowed for the adoption of least squared method with an objective function that minimized the sum of squared of error between the experimental data and the fitting Crank’s solution. Then applied the Levenberg – Marquardt search method to arrive at the value of the apparent diffusion coefficient, D_{app} at which the objective function was the least. The results were $(6.52 \pm 0.024) \times 10^{-7} \text{ cm}^2/\text{s}$ and $(6.22 \pm 0.043) \times 10^{-7} \text{ cm}^2/\text{s}$ for the $38 \mu\text{m}$ and $500 - 600 \mu\text{m}$ particle sizes respectively.

Figure 3 Fractional As(III) retained in solution in the presence of Kemiron ($\leq 38 \mu\text{m}$ and 500 to $600 \mu\text{m}$), $I = 0.001 \text{ N NaNO}_3$ at $\text{pH} = 7$.

Biot number (B) describes the relative importance of external mass transfer to intraparticle diffusion. The formula for Biot number according to Valsaraj 1995 is given as:

$$Bi = \frac{K_i r}{D_{app}} \tag{7}$$

Where K_i and r are the external mass transfer coefficient and radius of the adsorbent particles respectively. If the numerator of Equation (7) is higher than the denominator, then the As(III) uptake in the system is considered to be intra particle diffusion dependent. However, Traegner and Suidan (1989) declared that if Bi lied between 1 and 100, both external mass transfer and intra particle diffusion were important. Here, an external mass transfer coefficient value determined for As(V) by Oti and Trotz (2008) as adopted for use. And in order to do so it had to be assumed that the external mass transfer was the same for all species of the inorganic arsenic and also the grain size of the adsorbent, Kemiron, had no impact. The Bi of As(III) sorption onto $\leq 38 \mu\text{m}$ and $500 - 600 \mu\text{m}$ derived were 1.84×10^{-2} and 5.89×10^{-1} respectively. These fractional values indicated that the adsorption was intra particle diffusion controlled. And the internal diffusion controlled mechanism as an adsorption rate

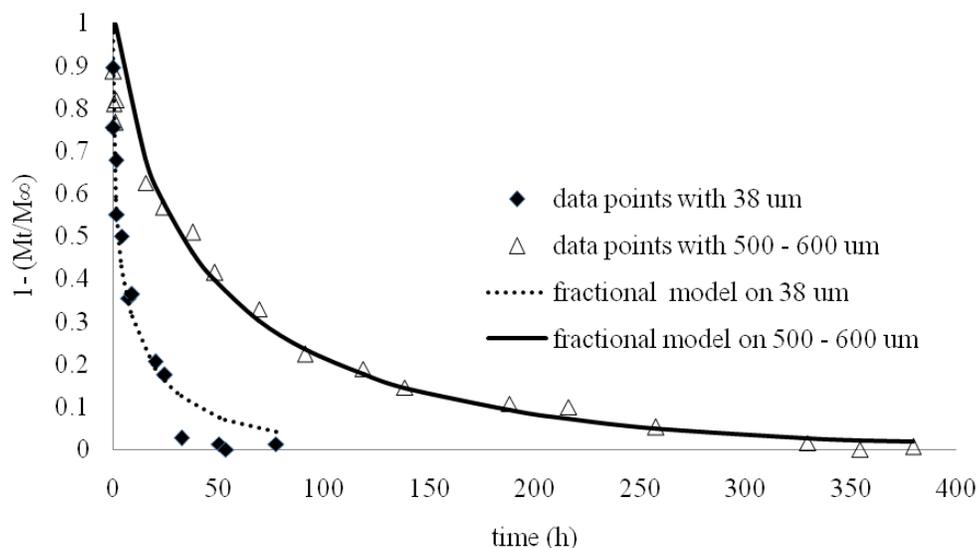


Figure 3. Fractional As(III) retained in solution in the presence of Kemiron ($\leq 38 \mu\text{m}$ and $500 - 600 \mu\text{m}$), $I = 0.001 \text{ N NaNO}_3$ at $\text{pH} = 7$.

limiting factor has been reported by many authors. Part of this study also compiled the sorption isotherm (Freundlich) characteristics of As(III) as reported by Payne and Abdel-Fattah (2005), Maji et al. (2007), and Tuzen et al. (2009) and this can be found on Table 1. The objective was to compare the sorption capacity of Kemiron with other established As adsorbents in terms of K_f . The K_f measures the mass loadings of As(III) per the concentration in the aqueous solution and high values of K_f implied high mass loading of As(III). Table 1, at $\text{pH} 6$ indicate an approximately 10 times K_f value for Kemiron in relation to that of *Ulothrix cylindricum* and 58 times when compared with K_f of laterite soil with pH of 0.3 less. At $\text{pH} \sim 7$, the sorption capacity of Kemiron was still stronger than that of Clinoptilolite with Fe modified and R_{Fe} modified by a factor of 2.5 and 3.0 respectively. Chabazite, R_{Fe} modified, however, was stronger than Kemiron by a factor of 1.58. Kemiron adsorption performance can therefore be inferred as a better adsorber of As(III) than Clinoptilolite and Algae *Ulothrix cylindricum* between $\text{pH} 6$ and ~ 7 .

Effect of CO_3^{2-} , SO_4^{2-} , $\text{NH}_4^+\text{-N}$, Ca^{2+} , Ni^{2+} , and Se(IV)

In the binary system involving only the As(III) with initial concentration of 5 mg/L and 0.1 g/L Kemiron adsorbent, the percentage of As(III) adsorbed at $\text{pH} 5.5$ was about 62. This rose steadily as the pH increased and peaked at $\text{pH} 8.8$ where the percentage sorption was about 90% and this is shown in Figure 4A. The presence of both SO_4^{2-} and CO_3^{2-} ions hindered the removal of As(III). This was expected since Kemiron sorption sites at $\text{pH} 7$ and below were estimated to be positively charged with

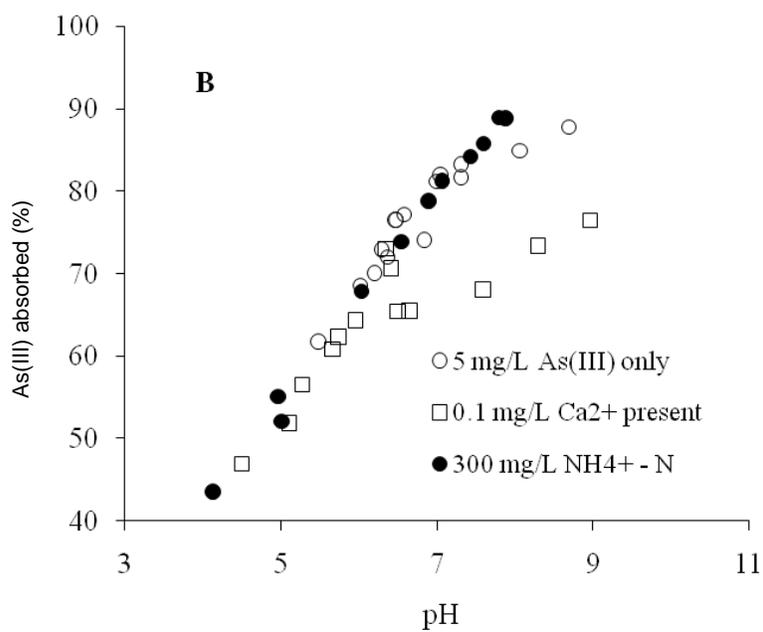
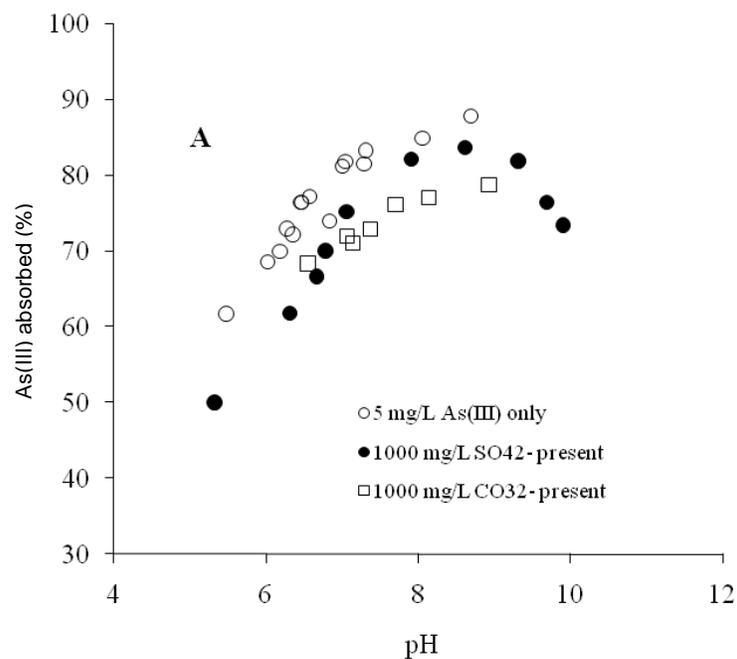
PZC between 7 and 8. Thus for a concentration of 1000 mg/L of CO_3^{2-} or SO_4^{2-} present in the batch system and at $\text{pH} 6.7$, the positively charged sites were expected to have preferential affinity for the negatively charged species of CO_3^{2-} and SO_4^{2-} . That accounted for the drop in the percentages of As(III) from 80% in binary system to 68% in the tertiary system where As(III) existed as neutral. Between $\text{pH} 6.7$ and 8.8 , the impact of the anions differed and widened from $\text{pH} 6.7$ to 8.8 . The presence of CO_3^{2-} had more impact than the presence of SO_4^{2-} ion. In the Figure 4A for instance, the percentage of As(III) sorbed at the $\text{pH} 8.8$ dropped from 90 to 85 in the presence of SO_4^{2-} and 75 in the presence of CO_3^{2-} . In Figure 4B, the presence of $300 \text{ mg/L NH}_4^+\text{-N}$ in the batch system had no significant impact on the percentages of As(III) adsorbed between $\text{pH} 4$ and 8 . This was also true for the presence of 0.1 mg/L Ca^{2+} ion in the batch system between $\text{pH} 4$ and 6.5 where the positively charged sites repelled the positively charged Ca^{2+} ion. However, the presence caused about 10% loss of the sorption capacity of Kemiron for As(III) between $\text{pH} 6.5$ and 9 where preferential choice for Ca^{2+} ion was expected.

Figure 4 Percentages of 5 mg/L As(III) adsorbed in the presence of SO_4^{2-} and CO_3^{2-} (A), Ca^{2+} and $\text{NH}_4^+\text{-N}$ (B), Se(IV) and Ni(II) (C) onto 0.1 mg/L Kemiron at room temperature and over a pH range of 4 and 10.

From Figure 4C, the presence of Ni(II) and Se(IV) of the same concentration of 5 mg/L , showed that Se(IV) was stronger in inhibiting As(III) sorption than Ni(II) . Between $\text{pH} 5.5$ and 8 , Se(IV) caused twice as sorption capacity loss as Ni(II) . At $\text{pH} 5.5$, the sorption capacity dropped from 62 to 48% due to the presence of the Ni(II) but to 25% due to Se(IV) , creating a difference of 23%.

Table 1. Freundlich isotherm characteristics of As(III).

Adsorbent	K_f	$1/n$	pH
Kemiron	27.91	0.41	6
Kemiron	35.67	0.35	7
Kemiron	43.76	0.31	9
Algae <i>Ulothrix cylindricum</i>	2.85	0.53	6
Chabazite, R_{Fe} modified	56.25	1.57	7
Clinoptilolite, Fe modified	14.19	1.43	7
Clinoptilolite, R_{Fe} modified	11.86	1.42	7.2
Laterite soil	0.48	1.00	5.7



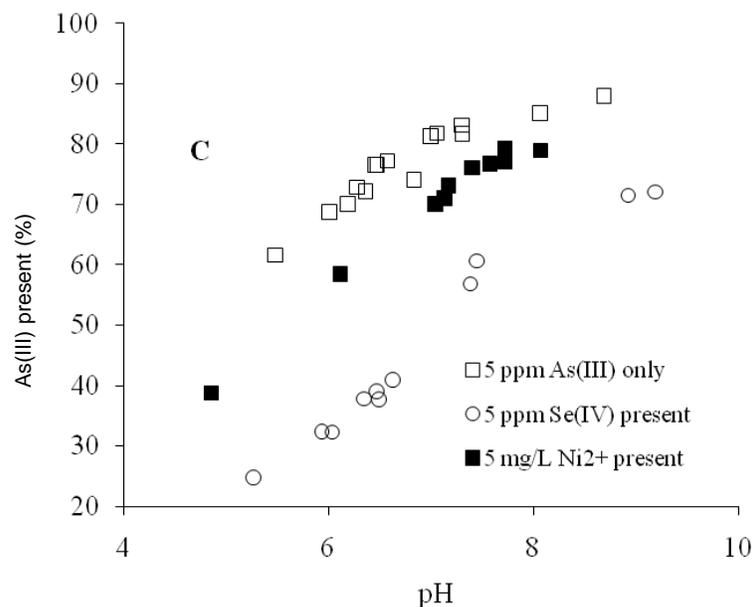


Figure 4. Percentages of 5 mg/L As(III) adsorbed in the presence of SO_4^{2-} and CO_3^{2-} (A), Ca^{2+} and $\text{NH}_4^+\text{-N}$ (B), Se(IV) and Ni(II) (C) onto 0.1 mg/L Kemiron at room temperature and over a pH range of 4 and 10.

The differences in the sorption loss due the presence of these co-contaminants narrowed up as the pH increased. At pH 8 for instance, the percentage of sorption in the binary system was 80, and that when Ni(II) and Se(IV) were present were about 75 and 63 respectively, a difference of 12%.

Conclusion

The pH-percentage adsorbed curve shows a typical As(III) sorption dome shape depicting pH having strong influence on percentages of As(III) adsorbed. The adsorption behavior, however, was unaffected by the background ionic strength which was between 0.001 N NaNO_3 and 0.1 N NaNO_3 , a characteristic that is indicative of innersphere adsorption mechanism (McBride, 1997). The batch isotherms followed Freundlich model and appeared stronger in sorption capacity than clinoptilonite between pH 6 and 7. The presence of both SO_4^{2-} and CO_3^{2-} ions hindered the removal of As(III) and CO_3^{2-} had more impact than the SO_4^{2-} ion. However, the presence of 300 mg/L $\text{NH}_4^+\text{-N}$ in the batch system had no significant impact on the percentages of As(III) adsorbed between pH 4 and 8. These findings indicated that Kemiron was a potential candidate for use in the treatment of As(III) via sorption in surface and ground water.

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