The feasibility of removing inorganic arsenic from landfill leachate via sorption to mineral oxide surfaces.

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1.5 ABBREVIATIONS, ACRONYMS & UNITS OF MEASUREMENT

As(V)	Arsenate
As(III)	Arsenite
BOD	Biological Oxygen Demand
CCA	Copper-chromate-arsenate
TCLP	Toxicity Characteristic Leaching Procedure
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EDS	Electron Dispersive Spectroscopy
FDEP	Florida Department of Environmental Protection
g	gram
GFAA	Graphite Furnace Atomic Absorption Spectrometry
g/L	grams per Liter
L	Liter
ppb	parts per billion
ppm	parts per million
M	Molar
MCL	Maximum Contaminant Level
mg/L	milligram per Liter
ml	milliliter
N	Normal
rtp	Room Temperature and Pressure
SEM	Scanning Electron Microscopy
Se(IV)	Selenite
µg/L	micro gram per Liter
XRD	X-ray diffractometry

1.6 ABSTRACT

Arsenic in landfill leachate poses a potential problem to landfills in Florida during final leachate disposal when concentrations are above allowable limits. From a list of 68 solid waste directors in Florida, 26 responded to our email or telephone queries and 7 identified arsenic as a problem during final leachate disposal. These sites included Alachua County, Lake County, Marion County, Martin County, Orange County, Polk County and Santa Rosa County. For all, leachate was treated offsite at either a waste water treatment plant or by deep well injection. These sites paid hauling and disposal fees and faced surcharges due to leachate characteristics like concentrations of arsenic and BOD. Mineral oxides sorbents that have been gaining wide use in arsenic removal during drinking water treatment were examined in this study for their potential to remove arsenic from landfill leachate, an onsite treatment option. Though physical characteristics of Bayoxide E33 (iron oxide), ADSORBSIA GTO (titanium oxide) and Kemiron (iron oxide) were done in this study, emphasis was placed on Kemiron which has a local distributor in Florida that was interested in this application. BET surface area of Kemiron is 39.8 m^2/g and Electron Dispersive Spectroscopy (EDS) studies found Kemiron to be 40.37% iron and 42.25 % oxygen by mass. Leachate (filtered) obtained from Polk County's North Central Landfill did not affect the sorption of 800 ppb arsenate (As(V)) onto 1 g/L Kemiron between pH 5 and 9. Batch systems for arsenate (As(V)), arsenite (As(III)) and selenite (Se(IV)) removal from aqueous solutions as a function of pH, ionic strength, and particle size (< 38 µm and between 250 and 425 µm) were investigated and showed typical anionic behavior whereas As(III) sorption showed a maximum around pH 8. Langmuir isotherms best described the As(V) and Se(IV) removal at pH 7 with maximum adsorption capacity of 82 mg/g and 52 mg/g respectively. As(V) and Se(IV) sorption decreased as pH increased and both anions were unaffected by sodium nitrate ($NaNO_3$) background electrolyte. As(V) sorption decreased in the presence of Se(IV), increased in the presence of Ca and remained unchanged in the presence of sulfate or carbonate. Though Bayoxide E33 had a higher surface area (95 m^2/g) than Kemiron, its sorption capacity for As(V) under similar conditions was significantly lower. GTO Adsorbsia on the other hand had a higher surface area than Kemiron and sorbed more As(V) under similar conditions. Rate of uptake experiments show that the capacity of 250-425 µm Kemiron particles to sorb As(V) to be significantly lower than the 38 µm particles.

Keywords: Arsenic, landfill, leachate, sorption

1.7 EXECUTIVE SUMMARY

CCA-treated wood or its combustion products in landfills in Florida are potential sources of arsenic which may become a part of the landfill leachate stream. Arsenic in landfill leachate solutions raises concerns over groundwater contamination for unlined landfills and proper disposal or management for lined landfills. Arsenic is toxic with a drinking water Maximum Contaminant Level of 10 ppb. There are options for treating landfill leachate to remove arsenic. For example, some landfills use membrane processes to remove arsenic whilst some ship the leachate offsite to a wastewater treatment facility. Costs associated with leachate disposal/treatment could potentially be high and in some cases is directly linked to the arsenic concentration in the leachate. This study examined the conditions under which arsenic can be removed from leachate on site through sorption processes using mineral oxide surfaces. This could potentially be a cost effective and efficient treatment alternative for arsenic in landfill leachate.

OBJECTIVES: 1) To identify Class 1 landfills in Florida with potential leachate disposal problems due to arsenic and select experimental conditions based on leachate characterization information, 2) To determine the influence of geochemical conditions pH, ionic strength, and the presence of competing ions on the removal of arsenic from landfill leachate solutions using commercially available mineral oxides, and 3) To model arsenic sorption to commercially available mineral oxides.

METHODOLOGY: Attempts were made to contact 68 solid waste directors on a master list provided by the Florida Department of Environmental Protection (FDEP). They were asked about arsenic concentrations in leachate and whether it posed a disposal problem to determine the scope of the problem due to arsenic in landfill leachate in Florida. Available leachate records from the landfills with problems were examined to identify contaminants and conditions for conducting further laboratory studies on arsenic removal from landfill leachate. Three different commercially available mineral oxide sorbents (Bayoxide E33, ADSORBSIA GTO and Kemiron) were characterized for surface area, porosity, mineralogy, and elemental make up. Kemiron, an iron oxide based sorbent, has a local distributor in Florida and was used for the majority of the studies done in this report. These experiments included batch equilibrium sorption and rate of uptake laboratory studies of As(V), As(III) and Se(IV). Se(IV) was chosen not only to serve as a co-contaminant, but also because its concentrations in leachate also approach regulatory limits though not as close as arsenic. The influence of geochemical conditions like pH (4-10), contaminant concentration, ionic strength (0.001 N and 0.1 N $NaNO_3$), and the presence of selenite, calcium, carbonate and sulfate on arsenic (As(V)) removal were examined in the laboratory. Arsenic removal in the presence of actual landfill leachate was characterized for Kemiron and ALCOA DD660, an aluminum based mineral oxide for which much As(V) and As(III) sorption has already been done.

RATIONALE: CCA-treated wood or its combustion products in landfills in Florida are potential sources of arsenic. Arsenic in landfill leachate solutions raises concerns over groundwater contamination for unlined landfills and proper disposal or management for lined landfills. Figure 1 depicts a typical lined landfill in which leachate in which some leachate is recycled through the landfill to assist with biodegradation processes. Waste distributed throughout a landfill releases heavy metals like arsenic which collect in leachate solution. That leachate solution is either hauled to an offsite treatment plant or recycled back into the landfill. If recycled into the landfill, the leachate containing the heavy metal of concern is sprayed throughout the landfill, thereby possibly contaminating a larger area of the landfill. Unlike organic compounds, heavy metals like arsenic do not degrade. An opportunity exists to capture the heavy metals released to leachate in an onsite treatment step that minimizes the volume occupied by the heavy metal, making it easier to recycle it or easier to dispose of it in a controlled environment. It should be noted that if leachate is sent to a waste water treatment plant, the heavy metals will more than likely return to the landfill in the biosolids waste from the treatment facility.

Figure 1 Schematic of rational for on-site treatment of landfill leachate.

One option for collecting the heavy metals in the leachate involves passing the leachate through fixed beds of adsorbent particles consisting of mineral oxides. Under the right conditions these particles can accumulate the heavy metals through sorption processes.

For example, the approximate surface area of Phase I and Phase II at Polk County North Central Landfill is 4 x 106 ft^2. In 2004, 7.9 x 10^6 gallons of leachate was produced. If we assume an average arsenic concentration in leachate of 100 µg/L, then the landfill would produce ~ 3023 g As/yr. If we assume that a sorbent has a capacity of 40 mg As/g sorbent, then, the amount of sorbent required to treat the arsenic would be (3023 g As/yr x 1000 mg/g)/40 mg As/g sorbent = 76,000 g sorbent/yr or 167 lbs/yr. Hence, the arsenic that was leached in a year from a landfill surface area of 424 ft^2, can be collected in a small footprint fixed bed reactor on mineral oxide sorbents weighing no more than an average man. The arsenic collected on the sorbents can either be recycled, fixed via some addition process, or stored in a smaller landfill site where it can be better managed to prevent leaching and contamination of a larger landfill area once again.

RESULTS: We attempted to contact 68 Florida landfills (not only active Class 1 landfills) via email and phone to learn about their leachate disposal practices and total arsenic concentrations. Of the 68 landfills on the list, we got 26 responses and of those 26 responses we identified 7 landfills in Florida that would benefit from this study. Landfills with leachate that had arsenic concentrations greater than 10 ppb combined with a disposal issue related to arsenic were identified. The seven landfills identified were:

- Alachua County
- Lake County
- Marion County
- Martin County
- Orange County
- Polk County
- Santa Rosa County.

These seven landfills paid for offsite leachate disposal and sometimes had an additional surcharge fee because arsenic concentrations were above permissible limits. Though leachate contained a list of other heavy metals, arsenic concentrations were closer to or above permissible limits. Arsenic speciation was not provided by the various landfills and this study examined both As(III) and As(V) sorption.

Mineral oxides sorbents that have been gaining wide use in arsenic removal during drinking water treatment were examined in this study for their potential to remove arsenic from landfill leachate, an onsite treatment option. Though physical characteristics of Bayoxide E33 (iron oxide), ADSORBSIA GTO (titanium oxide) and Kemiron (iron oxide) were done in this study, emphasis was placed on Kemiron which has a local distributor in Florida that was interested in this application. BET surface area of Kemiron is 39.8 m^2/g and Electron dispersive spectroscopy (EDS) studies found Kemiron to be 40.37% iron and 42.25 % oxygen by mass. Leachate (filtered) obtained from Polk County's North Central Landfill did not affect the sorption of 800 ppb arsenate (As(V)) onto 1 g/L Kemiron between pH 5 and 9 though it did reduce the sorption of 800 ppb As(V) on ALCOA DD660. Batch systems for arsenate (As(V)), arsenite (As(III)) and selenite (Se(IV)) removal from aqueous solutions as a function of pH, ionic strength, and particle size (< 38 µm and between 250 and 425 µm) were investigated using Kemiron. Langmuir isotherms best described the As(V), and Se(IV) removal at pH 7 with maximum adsorption capacity on Kemiron of 82 mg/g and 52 mg/g respectively. As(V) and Se(IV) sorption decreased as pH increased and both anions were unaffected by sodium nitrate ($NaNO_3$) background electrolyte. As(V) sorption decreased in the presence of Se(IV), increased in the presence of Ca and remained unchanged in the presence of sulfate or carbonate. The presence of calcium in a molar ratio of approximately 2:1 compared with As(V) enhanced As(V) removal from Kemiron. As(III) sorption onto Kemiron showed a maximum around pH 8 and was also not affected by ionic strength. Freundlich isotherms better described As(III) sorption to Kemiron and for the conditions studied in the lab, loadings of ~ 90 mg As(III)/g Kemiron were seen at pH 7.

The results of this research show that arsenic can be removed from landfill leachate via sorption to mineral oxide surfaces, however, more studies have to be completed to fully assess the feasibility of using this system in the field. Based on laboratory experiments, a pre-treatment step is necessary to filter leachate prior to interaction with mineral oxide surfaces. Membrane bioreactors are an example of a pretreatment step that not only reduces the solids loading, but also removes COD. Whilst such a system would change the overall make up of the leachate solution owing to the removal of organic compounds, it would not affect the total metal concentrations. Hence, the work initiated in this project would still be applicable in terms of assessing arsenic removal from complex matrices. Once developed fully this project will benefit landfill operators whose costs associated with disposal of their arsenic containing leachate are high.

This project directly supported Douglas Oti, a PhD student and provided research opportunities for undergraduate students Ryan Locicero and Austin Roe and high school teacher Ann McNicol. The following papers/presentations were made as a part of this project:

1. Oti, D. and M.A. Trotz. (2008) Characterization and Adsorption of Arsenate and Selenite onto Kemiron. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substance and Environmental Engineering,* 43 (10).
2. Oti, D.; Roe, A.; Trotz, M. A. Arsenic removal using Kemoxide, a commercially available iron oxide sorbent. Poster presentation to be made by Douglas Oti at the 2006 Florida AWMA conference on 9/22/2006.
3. Trotz, M. A. Arsenic removal from drinking water and landfill leachate via sorption to commercially available mineral oxides. Presented at the Florida Section of the American Chemical Society, FAME Environmental Chemistry symposium, Orlando, FL. Invited Presentation on 5/11/2006.
4. Locicero, R. Oti, D., Roe, M., and M. Trotz. Removing arsenic from Class 1 Florida landfill leachate using commercially available mineral oxides. Undergraduate posters were also presented at the USF REU poster symposium 4/2006. **http://reu.eng.usf.edu/Symposium/Symp2006/symposiumS2006.asp**
5. Oti, D., Thomas, K., and M.A. Trotz. Understanding the solid/liquid interface and its importance to arsenic mobility. Poster presented at the USF interdisciplinary graduate poster symposium (3/2007).

The original project website, landfillinfo.net, was replaced by landfillinfosite.com because of high fees associated with the expiration of the original domain name and hosting shifted to the USF server under the PI's account.

CONCLUSIONS: Onsite treatment of landfill leachate can potentially be economically more feasible than hauling to a treatment facility which incurs surcharges depending on concentrations of contaminants like arsenic and BOD. In Florida, seven landfill sites identified arsenic as a problem in leachate because concentrations were above limits acceptable to treatment facilities resulting in disposal surcharges. There may be more landfills in Florida facing this problem, however, of a list of 68 solid waste directors, project personnel were only able to reach 26 as a part of this project. This study showed that arsenic could be removed from leachate using commercially available mineral oxides, however, a pretreatment step was used to filter leachate through a 0.45 μm filter. In the field, this pretreatment step could take the form of a membrane bioreactor that not only reduces turbidity, but also removes BOD and COD.

KEY WORDS

Arsenic, arsenate, arsenite, mineral oxide, landfill, leachate, sorption, selenite.

1.8 INTRODUCTION

The use of copper-chromate-arsenate (CCA) as a wood preservative and the potential leaching of arsenic from that wood have raised major concerns in Florida, especially with respect to the disposal of the wood and its combustion products at landfills where geochemical conditions could mobilize the more toxic inorganic arsenic species. Leachates from new and weathered CCA-treated wood in Florida exposed to Toxicity Characteristic Leaching Procedure (TCLP) tests indicate that the most dominant species were the inorganic arsenic forms, especially As(V) though weathered samples did show higher As(III) concentrations than new samples; and that these woods would be classified as hazardous waste based on regulatory limits for arsenic [1]. Unlike discarded CCA-treated wood which is not treated as a hazardous waste and ends up in unlined non hazardous landfills, ash from incinerated CCA-treated wood that exceeds the regulatory limit is disposed of in hazardous landfills. The total TCLP leached arsenic concentrations in the ash of incinerated CCA-treated wood was as much as 100 times greater than unburned samples [1]. Ghosh et al. [2] found that the TCLP is conservative at estimating the arsenic leached from artificially contaminated activated alumina and granular ferric hydroxide (sorbents used in water treatment to remove arsenic) that would be placed in a landfill and it is highly likely that the studies done on the leaching of arsenic from CCA-treated wood in Florida underestimate the potential arsenic that will leach under landfill conditions. Hence, the disposal of unburned CCA-treated wood and the ash from incineration at landfills could provide significant sources of inorganic arsenic species in the leachate depending on the geochemical conditions in the landfill.

The leachate from lined landfills is either sent to an external waste water treatment facility, recycled back through the landfill, or treated on site (e.g. reverse osmosis at the Martin County landfill). Wastewater treatment facilities have limits on the volume of leachate they can process based on the leachate quality which leads to expensive disposal costs for some Florida landfill facilities. For example, the Polk County Landfill in Lakeland transports approximately half of its leachate to a treatment facility in Jacksonville at a significant cost to the landfill facility because the local waste water treatment plants do not have the capacity to accept the high total dissolved solids concentration coupled with the concentrations of toxic metals like arsenic. Heavy metal concentrations in leachate from a municipal solid waste landfill cell in Florida showed decreasing trends over a twelve year period [3] suggesting that the more mobile forms of these metals had been removed from the landfill cell. Recycling of the leachate through the landfill is a low cost option for disposal, but the non-degradable nature of heavy metals like arsenic means that the landfill will be a continual source of arsenic susceptible to changing geochemical environments and will always have to be monitored, even after the degradation of toxic organic compounds. Recycling of heavy metals through the landfills may also increase their concentration to levels where microbial activity is significantly reduced. On site treatment of leachate to remove heavy metals could employ a suite of technologies based on precipitation, sorption, electroplating, reverse osmosis or ion exchange. On site removal would reduce the volume of the heavy metal contaminant which can then be recycled or disposed of in a controlled space at the landfill where the leachate is prevented from contaminating other leachate streams or landfill cells.

The recent reduction in the U.S. Maximum Contaminant Level (MCL) for arsenic in drinking water to 10 ppb (0.13 μM) coupled by the urgent need for remediation technologies for small drinking water distribution systems in Asia has led to a surge in research on the most efficient technologies for removing arsenic from aqueous systems, sorption being one of the most promising. By careful examination of the conditions influencing sorption it may be possible to adapt these technologies from drinking water treatment applications to remediate arsenic from more complex landfill leachate solutions. Table 1 shows some geochemical characteristics of leachate from the Polk County Landfill in Florida (as stated in the Report of Analysis by the Polk County Natural Resources Lab) which does not include speciation information.

Researchers have studied the sorption of arsenic to mineral oxide surfaces under various geochemical conditions like pH, ionic strength, and surface and arsenic concentration, either in an attempt to develop a treatment technology for arsenic (As) contaminated waters [4-17], or to understand the fate of arsenic in the natural environment [18-26]. Sorption capacities of over 50 mg As/ g sorbent have been observed and granular ferric hydroxide and activated alumina are two of the most promising sorbents to date. When these materials are packed into fixed beds the number of bed volumes that can be treated make it an attractive treatment technology [4, 27]. Figure 1 shows typical sorption edges for binary systems containing either the anions arsenate or arsenite or the cation cadmium on an activated alumina ALCOA by-product, DD660. Arsenate and arsenite sorption increases as pH decreases whereas cadmium sorption increases as pH increases. In some pH regions the sorption of each of those ions overlaps and experimental data would tell the influence of one on the other. The data in Table 1 shows that there are other parameters in the leachate which could influence the sorption of arsenic. The data reported in Table 1 are for samples that were acid digested without any prior treatment for the removal of particles or bacteria.

Table 1 Select geochemical parameters of the leachate from the Polk County North Central leachate tank (Data obtained from Polk County Environmental Services Department, Solid Waste Division).

Date	**As (mg/L)**	**Ni (mg/L)**	**Fe (mg/L)**	**TDS (mg/L)**	**Bicarbonate (mg/L as $CaCO_3$)**	**pH**	**DO (mg/L)**
3/6/03	0.043	0.072	27.16	3820	1873	7.21	6.21
3/8/04	0.071	0.148	6.30	4300	2913	7.51	4.82

Various researchers have studied the effect of phosphate, sulfate, carbonate and silicate on inorganic arsenic sorption to aluminum and iron oxide surfaces and found that these anions could decrease arsenic sorption depending on the pH and their concentrations relative to that of arsenic [22, 27-29]. Figure 2 plots the effect of phosphate and carbonate on As(V) and As(III) sorption to ALCOA DD660; the effect of sulfate is less than these two anions. Anions can potentially affect the sorption behavior of arsenic onto the mineral oxide surface by competing for surface sites, forming mobile complexes, modifying the surface electrostatics, and through other mechanisms like surface dissolution.

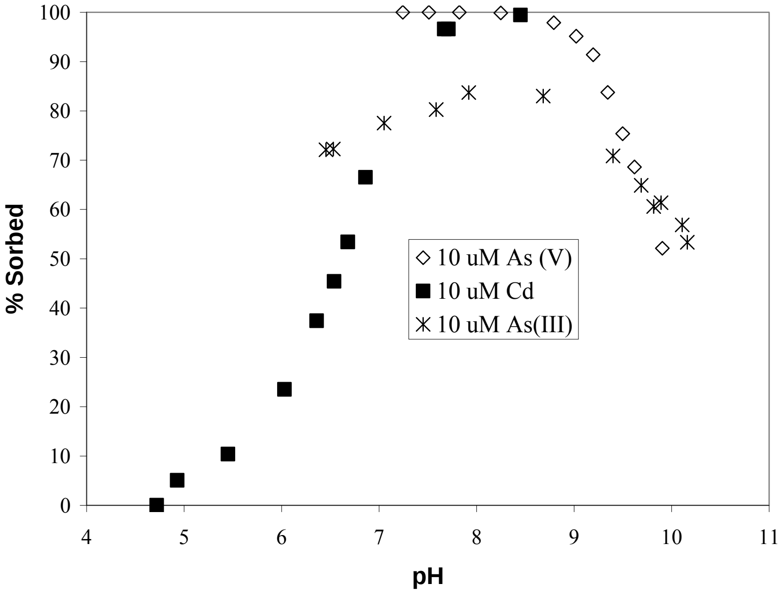

Figure 2 10 µM As(V), As(III) and Cd(II) sorption to 0.5 g/L ALCOA DD660 alumina in 0.01 M $NaNO_3$. CO_2 excluded. Total alumina surface area in solution = 200 m^2/L. As(V) and As(III) data taken from Trotz, 2002 [27] and Cd(II) data taken from Prasad, 2000 [30].

Actual landfill leachate has complex geochemical matrices that include microbial communities and potential competing anions and cations that can affect the removal of arsenic [3, 31, 32], however, experimental studies are needed to assess whether removal via sorption would be a viable remediation technique for the arsenic contaminated leachate at landfills. Once the right sorptive media and conditions under which removal of arsenic is favored given the leachate composition are identified, a treatment system that packs that media into fixed bed reactors can be installed on site to remove the arsenic species from the leachate solutions.

A review of the literature on leachate treatment techniques used for various contaminants is summarized in Table 2. Not much research has been done on heavy metal removal and more specifically arsenic removal from leachate. For those studies looking at heavy metal removal nanofiltration, sorption to limestone, phytoremediation, and electrochemical deposition have been used. Sorptive processes have also been applied to ammonia, COD, and some organics although the medium used, activated carbon, would not be one applicable to arsenic removal unless the surface is modified as was done for the removal of humic and fulvic acids.

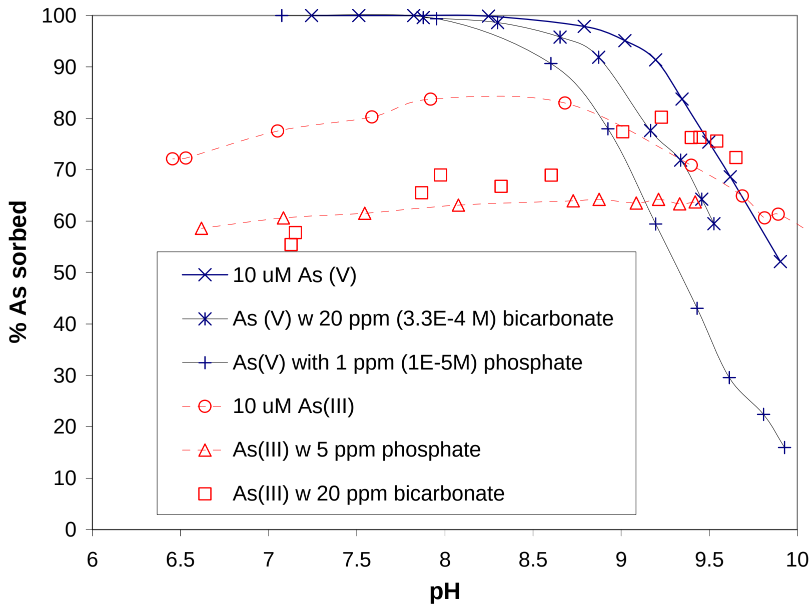

Figure 3 The effect of phosphate or carbonate on As(V) and As(III) sorption to 0.5 g/L ALCOA DD660 alumina in 0.01 M $NaNO_3$. Total alumina surface area in solution = 200 m^2/L. As(V) and As(III) data taken from Trotz, 2002 [27].

Objectives

The overall goal of this project was to determine the applicability of removing arsenic from landfill leachate via sorption to mineral oxide surfaces as a cost reduction option for landfill facility operations in Florida. The main objectives were:

1) To identify Class 1 landfills in Florida with potential leachate disposal problems due to arsenic and select experimental conditions based on leachate characterization information.
2) To determine the influence of geochemical conditions pH, ionic strength, and the presence of competing ions on the removal of arsenic from landfill leachate solutions using commercially available mineral oxides.
3) To model arsenic sorption to commercially available mineral oxides.

Table 2 Landfill leachate treatment techniques used for various contaminants.

Pollutant / Problem	**Treatment(s)**
Endocrine Disrupters	• Adsorption to activated carbon, aerobic digestion, membrane filtration [33] • Reverse Osmosis [33]
Chemical Oxygen Demand (COD) / non- biodegradable matter/	• WET promoted Oxidation • Chemical Oxidation with Ozone, with Fenton's reagent [34] • coagulation-flocculation with Fe(III) [35, 36] • Combined treatments [37] • Moving bed biofilm process [38] • Membrane sequencing batch reactor [39] • Aerobic reactor/membrane, RO [40] • Anaerobic sludge reactor [41, 42] • High frequency ultrasound [43] • Electrochemical oxidation [44] • Nanofiltration [45]
Fe and Ni	• Nanofiltration [45] • Sorbed on limestone [46]
Nitrification and denitrification inhibition	• Powdered Activated Carbon additive to traditional activated sludge process [47, 48] • *In situ* nitrogen management/ specific leachate recycle [49]
BOD/biodegradable matter	• Membrane Bioreactor (MBR) [38]
Carbon content	• Enzymatic (bioaugmentation) [50]
Nitrogen content	• Enzymatic (bioaugmentation) [50]
Ammonia and COD	• Zeolite and activated carbon sorption [51] • Hydrogen peroxide enhanced iron mediated aeration [52] • Aerobic/anaerobic process [53]
Metal content	• Adsorption by *Phragmites australis* roots in constructed landfill[54] or pine bark [55] • Short rotation coppice/ use of willow plants [56] • Electrochemical [57]
Humic and Fulvic Acid	• Iron coated activated carbon with hydrogen peroxide [58, 59] • Ozonation and coagulation [60]

1.9 BACKGROUND

1.9.1 Arsenic and Selenite Chemistry

The new maximum contaminant level, MCL for As in water of 10 ppb promulgated by USEPA in 2000 was a driving force for researchers to look into innovative ways for cheaper and more efficient adsorption technology. Understanding characteristic behavior of adsorbents surfaces and their interaction with contaminants of interest, namely, As in aqueous solution are crucial for improving adsorption methods. The inorganic forms of As(III), As(V) are the primary focus of this research. Se(IV) was also studied as a co-contaminant of interest in landfills.

The log Ks of the As(III), As(V) and Se (IV) species are shown in Table 3. Figures 4-6 show the distribution of major aqueous As and Se(IV) species as a function of pH. Figure 1 shows that only two As(V) species predominate over environmentally relevant pHs. In the acidic and alkaline regions, the dominant As(V) species is $H_2AsO_4^-$ and $HAsO_4^{2-}$, respectively. Similarly H_3AsO_3 and $H_2AsO_3^-$ predominate for As(III) in acidic and alkaline regions. For Se(IV), $HSeO_3^-$ and SeO_3^{2-} in acidic and alkaline regions respectively. It is often assumed that the dominant solution species is the dominant adsorbing species, and consequently, several authors have proposed mechanisms involving one or both of these species for the adsorption of arsenic onto various minerals [61, 62]. Whilst As(V) and Se(IV) exist as charged species above pH 2.22 and 2.63 respectively, As(III) remains a fully protonated anion until pH 9.32. In a reducing environment, As exists as As(III), while in an oxygen rich environment as As(V).

Table 3 Thermodynamic constants for As(III), As(V) and Se(IV). I = 0, T = 25°C.

Formation Reaction	Log K
$H_2AsO_3^- + H^+ = H_3AsO_3$	9.32
$HAsO_3^{2-} + H^+ = H_2AsO_3^-$	12.13
$AsO_3^{3-} + H^+ = HAsO_3^{2-}$	13.41
$H_2AsO_4^- + H^+ = H_3AsO_4$	2.22
$HAsO_4^{2-} + H^+ = H_2AsO_4^-$	7.00
$AsO_4^{3-} + H^+ = HAsO_4^{2-}$	11.54
$SeO_3^{2-} + H^+ = HSeO_3^-$	8.40
$HSeO_3^- + H^+ = H_2SeO_3$	2.63

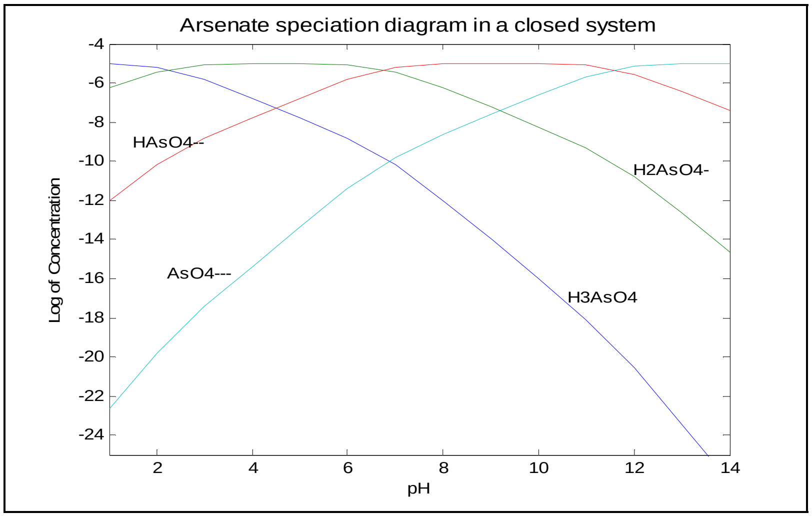

Figure 4 Arsenate (As(V)) speciation diagram in closed system with total As of 10^{-5} M (0.8 ppm).

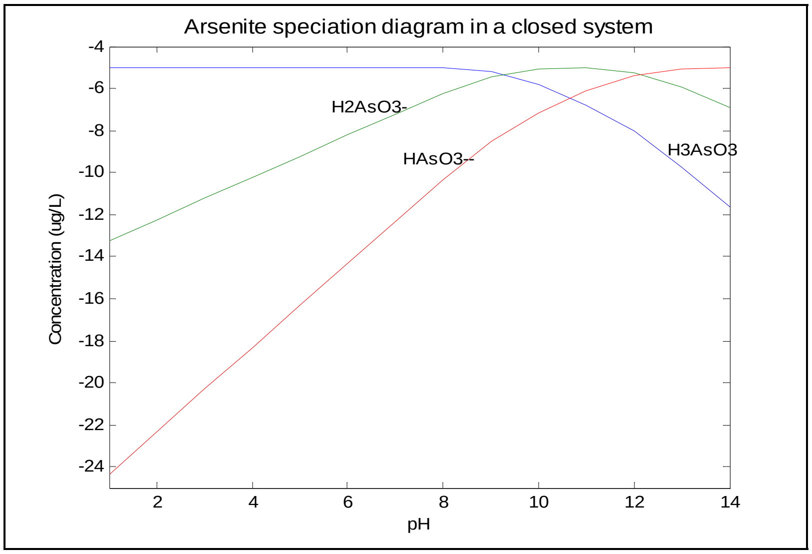

Figure 5 Arsenite (As(III)) speciation diagram in closed system with total As of 10^{-5} M (0.8 ppm).

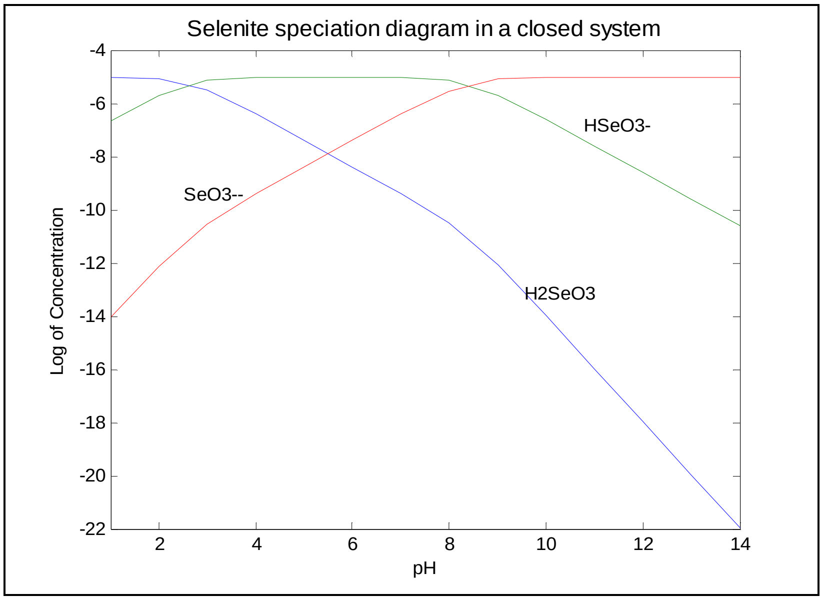

Figure 6 Selenite (Se(IV)) speciation diagram in closed system with total Se(IV) of 10^{-5} M (0.79 ppm).

1.9.2 Mineral Oxide/Hydroxide Surface Chemistry

When the surfaces of mineral oxide particles like an iron oxide are exposed to solution, the surfaces are usually treated as amphoteric and assigned charges that vary between +1 and -1. For example, a neutral ≡FeOH group in solution may become protonated to form $\equiv FeOH_2^+$ or deprotonated to form $\equiv FeO^-$ species. The surface acidity reaction can be written as:

Table 3 Speciation reaction of Iron Hydroxide. Constants taken from

Formation Reaction	**Log K**
$\equiv FeOH + H^+ = \equiv FeOH_2^+$	7
$\equiv FeO^- + H^+ = \equiv FeOH$	9.2

From Table 3, $\equiv FeOH_2^+$ dominates below the point of zero charge (pH_{pzc}) while $\equiv FeO^-$ dominates above the pH_{pzc}. This is illustrated in Figure 5.

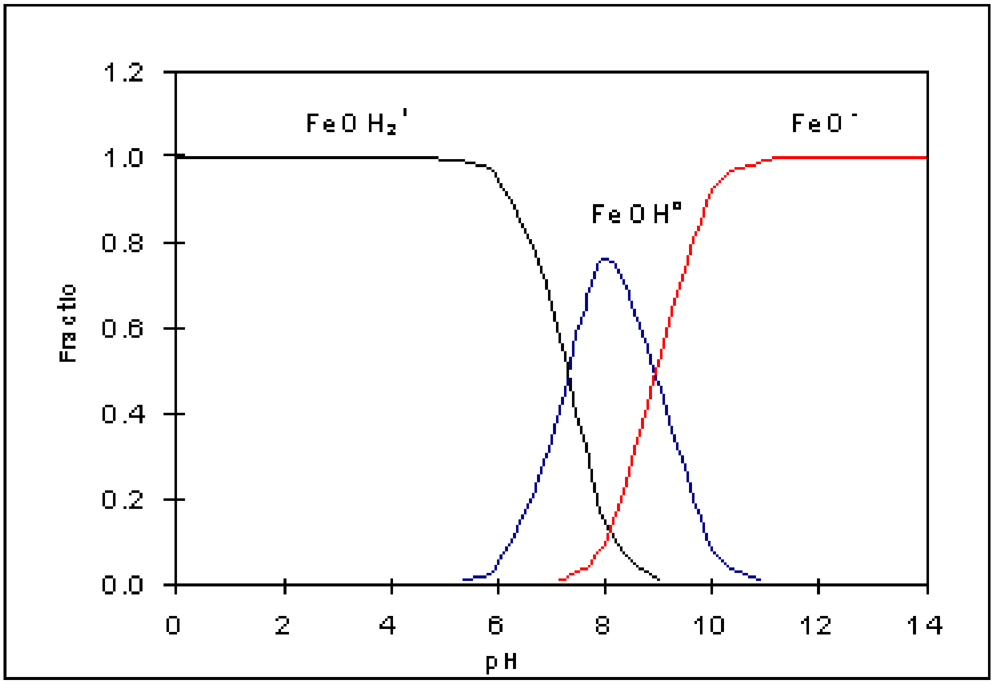

Figure 7 Distribution of the charge of surface sites for $Fe(OH)_3$.

Many iron based adsorbents have their pH_{pzc} between 8 and 9.5 [63-65]. Villalobos et al. [6] found that surface area, particle size and method of preparation affected the pH_{pzc} of goethite and universal pH_{pzc} values for sorbents may introduce errors in surface modeling attempts. For the most part, however, the neutral FeOH dominates iron species in water at pH 8. In adsorption studies, the amount of anions sorbed decreased as a function of pH. This has been explained with electrostatic influence. The charges on iron hydroxide surfaces are neutral at pH_{pzc}. An increase in pH induces negative charges on the adsorbent surface and this repels the negatively charged adsorbate species.

1.9.3 Modeling Sorption Behavior

For dependency of the equilibrium adsorbed amount on the concentration of the contaminant, many equations, based on different concepts have been proposed. Langmuir, Freundlich, and Linear equations are the commonest used by many authors. The Langmuir equation assumes a uniform surface, a single layer of adsorbed material, and constant temperature. The Langmuir equation is:

$$q = \frac{q_m K_a C}{1 + K_a C} \tag{1}$$

where $q_m = q$ for a complete monolayer
K_a = adsorption coefficient ,
C = concentration of solute in the solution at equilibrium

The Freudlich isotherm is:

$$q = K_f C^n \qquad (2)$$

where K_f = adsorption coefficient,
C = concentration of solute in the solution at equilibrium
$0 <= n >= 1$

The Linear isotherm is:

$$q = K_d C \qquad (3)$$

where K_d = distribution coefficient,
C = concentration of solute in the solution at equilibrium

Experimental data is usually modeled under specific conditions (e.g. pH, ionic strength, concentration of competing ion). Hence, constants obtained for As(V) sorption at pH 6 for example will most likely be different from those at pH 7 given the dependency of As(V) sorption on pH. For systems where conditions are constrained within a limited range or for which conditions remain the same, constants derived from these model fits are helpful in comparing sorption behavior of different systems. More complex surface complexation models are also used to describe sorption of species onto hydrated oxide surfaces. These surface complexation models include Diffuse Layer Model (DLM) [66,67], Constant Capacitance Model (CC), Triple Layer Model (TLM) [61], Ligand and Charge Distribution (LCD) model, and CD-MUSIC model [68] for ion adsorption. These models require inputs like available sites and various surface acidity constants and in some cases electrolyte binding constants. Surface complexation modeling using the Triple Layer Model was initially proposed as a part of this project, however, simpler fits to experimental data was done using isotherms.

1.9.4 Batch kinetics

In adsorption processes, contaminant species generally diffuse to adsorptive sites. During the migration of the species to the sites, resistances are encountered. The migration process is explained by two resistance theory and the resistance termed the rate limiting step is caused by either a hypothetical external thin film surrounding the assumed spherical adsorbent particles or the internal pores that are also assumed to be uniformly distributed in the solid particles.

Studies and models of the rate of adsorption of arsenate As(V) and selenite Se(IV) onto solid surfaces have been done. Many authors have used one of the two diffusion models to describe non-equilibrium adsorption process. Some authors have used homogeneous surface diffusion model (HSDM) [65, 69, 70] while others have used pore diffusion models (PDM) [71]. Some authors have used first order models. A first order model considers the rate of solute mass transfer as proportional to the concentration difference between the bulk solution and that in the sorbent particles.

1.9.5 External Film Diffusion

As the bulk of the species approach the solid particle, they diffuse through a hypothetical thin film which separates the bulk of the solution and the adsorbent particle. Fick's law is usually used to explain the mass flux of the species across the film onto the surface of the solid. In a batch system, the mass change of the number of surface sites per time in the spherical solid is given in a linear model as:

$$\frac{dC_b(t)}{dt} = -k_F[C_b(t) - C_{eq}] \tag{4}$$

Where:

C_b is solute concentration in the bulk solution
t is time
k_F is coeffiecient of solute removal
C_{eq} is solute concentration in the bulk solution at equilibrium

k_F describes the solute transport through an external diffusive boundary layer. Equation (4) is a rate limiting step in cases of quiescent and very small or nonporous adsorbents. After going through the film surrounding the solid, adsorbate species would either be sorbed directly onto the external surface of the solid or diffuse further into the pores of the solid.

1.10 SCOPE AND LIMITATIONS OF STUDY

This project aimed to identify Class 1 landfills in Florida that face leachate disposal problems due to arsenic concentrations and assess the feasibility of using commercially available mineral oxide particles to remove the arsenic on site through sorption mechanisms. We got a 38% response rate from solid waste directors, not all of whom were in charge of Class 1 landfills. Data of leachate quality from the landfills identified as having an arsenic problem was not readily available and only a few landfill leachates were used to identify conditions appropriate for experimental studies. More information on landfill age and geochemical conditions is something that can be compiled in the future. Arsenic speciation studies in leachate was not available and leachate concentrations reflected total concentrations versus dissolved or particulate concentrations. Laboratory studies used filtered landfill leachate which may have concentrations that are different than the totals that were supplied by the landfills. Arsenic speciation of the actual leachate used in this study was not available due to limited resources for instrument maintenance. During the method development phase for arsenic speciation on a HPLC that was purchased with funds from the project, column clogging and instrument failure resulted. Lack of funds for resolving these problems (these were not covered by the project) resulted in the speciation analysis not being done. Total metal analysis by ICP-MS was also not done on the leachate used in this study. Original plans were to run these in a USF laboratory, however, access was denied due to the complex nature of the matrix once the samples were obtained and funding was not allocated for analyzing these samples using an external laboratory. Quarterly leachate analysis was available from the landfill, however, for the leachate used in this study.

In real landfill leachate, redox chemistry could play an important role in the sorptive behavior of arsenic and this was not assessed in this study. A clearer picture of the pre-treatment step needed to remove particulate matter is needed to further identify conditions that would prevail during the arsenic removal process. This project started to look at four different adsorbents (Bayoxide E33, ADSORBSIA GTO, Kemiron, and a limited number of studies with ALCOA DD660), however, the majority of the equilibrium and rate of uptake studies focused on Kemiron. Initial comparisons of Kemiron with Bayoxide E33 showed higher sorption capacity on Kemiron and the presence of leachate did not affect As(V) removal by Kemiron compared with ALCOA DD660. These experiments coupled with the fact that the US distributor for Kemiron is based in Florida and a company representative showed a keen interest in this work, encouraged us to adjust the study to include more experiments using Kemiron as opposed to the other sorbents. Kemiron studies were extended to include co-contaminant studies with calcium, carbonate, sulfate and rate of uptake studies were done for As(V), As(III) and Se(III) at various pH values. Adsorbsia GTO studies were not completed during the time frame of this study.

1.11 BODY

1.11.1 Scope of Problem in Florida

One of the first tasks included identifying the scope of the problem in Florida, i.e., the number of landfills that have leachate with arsenic concentrations greater than 10 ppb and for which this poses a disposal problem. The Florida Department of Environmental Protection (FDEP) Water Assurance Compliance System (WACS) - Solid Waste Facility inventory was searched online for all Class 100 landfills (http://appprod.dep.state.fl.us/www_wacs/Reports/SW_Facilities_P1.asp). The list produced the following results: 230 Class 1 Landfills of which 52 are ACTIVE, 1 ACT NOT PERMITED, 1 CLEANUP, WASTE REMOVED, 19 CLOSED NO MONITORING, 127 CLOSED, MONITORING, 21 INACTIVE, 4 NEV.OPER., PERMIT NEVER USED, and 5 NFA,NO FURTHER ACTION/INACTIVE. The list of active Class 100 landfills from this site is given in ider when dealing with leachate.

Table 4 and we found that many of the contact numbers listed there were incorrect. Mr. Lee Martin of the FDEP provided another list of solid waste directors in the state (

Table 5). This updated list of contacts was for 68 Florida landfills (not only active Class 1 landfills) and we attempted to contact via email and phone all of the landfills to learn about their leachate disposal practices and total arsenic concentrations. Landfills with leachate that had arsenic concentrations greater than 10 ppb combined with a disposal issue related to arsenic were identified. Of the 68 landfills on the list, we got 26 responses and of those 26 responses we identified 7 landfills in Florida that would benefit from this study. Leachate query data was also obtained from the FDEP website and was used to identify landfills with As > 10 ppb.

The seven landfills identified were:

- Alachua County Public Works. phone: (352) 374-5213, contact: David Wood; Average Arsenic concentration 130 ppb, cost of transporting to facility $70-73/1000 gallons.
- Lake County, Solid Waste Mgmt Services. phone:(352) 343-6030, contact Gary Debo. Leachate disposal is accomplished by trucking to Jacksonville (approx. 130 miles one way) at a cost of $0.13/gallon for transportation & disposal. $130.00/1,000 gallons. Arsenic Levels 10/2/04 - 11ug/L, 10/26/04 - 18ug/L, 05/10/05 - 19ug/L.
- Marion County Solid Waste Dept, Ocala, FL. phone: (352) 245-4584, contact: Mike Sims. current Arsenic concentrations 78 ppb, method of disposal is a Pipeline to the City of Ocala Waste Water Treatment Plant #2. Cost of disposal $9.00 / 1000 gallons. Arsenic surcharge in effect.
- Martin County Solid Waste Management Department. phone (772) 221-1386, Stuart, FL, contact: Patrick N. Yancey. Arsenic concentration level 280 ppb. Martin County hauls all leachate and it is deep well injected at a local Utility (a permitted disposal site). Hauling and disposal costs are $23.23/1000 gallons.
- Orange County Resource Rec Dept. phone (407) 836-7251, contact: Ryan. Arsenic concentration is 280 ppb. The leachate is disposed of through a pipe network to the nearby Orange County wastewater treatment plant. Cost of treatment is $3.17/1,000 gallons. Though they are surcharge for high concentration of heavy metals and for BOD that is over 300 mg/l and TSS that is over 300 mg/l. For July the flow was 3,584,000 gallons ($11,361.28) and the surcharge bill was $43,737.53.
- Polk County Solid Waste Division. (863) 284-4319, Interim solid waste director, Brooks Stayer. Maintain North Central Polk county, NE Landfill (Hanes City), SE Landfill (whales); also contact Allan Choate Sample date 4/14/05, 0.131 mg/l at Phase I Leachate Pumping Station; 0.072 mg/l at Phase II Leachate Pumping Station. Haul by truck to an industrial wastewater treatment facility. The County has an annual contract for the service. The contractor is Aqua Clean Environmental Co., Inc. in Lakeland. Hauling at $10.00 +Treatment/Disposal at $100.00 = $110.00/1,000 gallons.
- Santa Rosa County. (850) 626-0191, contact Julian Cooey. Central Landfill leachate has arsenic: 11/11/03: 480.0 ppb, 06/01/04: 24.0 ppb, 12/06/04: <5.0 ppb, 05/10/05: <5.0 ppb; Holley Landfill leachate has arsenic: 11/04/03: 28.0 ppb, 05/24/04: 23.0 ppb, 11/15/04: 17.0 ppb, 05/17/05: 30.0 ppb. Current method

of leachate disposal: Leachate from Central and Holley landfills are presently trucked to a waste water treatment facility in Milton, Florida. Disposal cost $7/1000 gallons.

The allowable limits of heavy metals in leachate depends on the county and disposal options. For example, the Marion county allowable limits for As, Cr, Ni and Se are 60, 14,440, 4,380 and 540 ppb respectively. For the data given in Table 6, Arsenic is the heavy metal that is either close to or above the limits in the landfill leachate. Concentrations of other ions were at least 15 times lower than allowable limits (using limits from Marion county), except for selenium concentrations at Alachua which closer to the limits. Though the other ions present are not above the allowable limits for disposal, they could potentially affect the sorption of arsenic to mineral oxide surfaces, either decreasing sorption through competition for surface sites or increasing sorption through changes in surface charge to better attract arsenic. Table 1 and Table 6 provide only a glimpse of the various chemicals present in leachate as other heavy metals and organics are also present. Table 7 summarizes ranges of values of BOD, COD, DO and pH obtained from young and aged landfills and provides some guidance on other conditions that one must consider when dealing with leachate.

Table 4 List of Active Class 1 Landfills in Florida

Facility ID	Facility Name	County	Phone Number
00000016	STEELFIELD	BAY	(850) 784-4056
00016256	CENTRAL LANDFILL	BREVARD	(321) 633-7112
00055093	CENTRAL SANITARY LANDFILL & RECYL.	BROWARD	(954) 984-2000
00053209	BROWARD CO.SOUTH RESOURCE	BROWARD	(954) 581-6606
00053328	BROWARD CNTY INTERIM CONTINGENCY	BROWARD	(954) 971-6220
00071714	CHARLOTTE COUNTY SLF (ZEMEL RD LF)	CHARLOTTE	(941) 639-1802
00039859	CITRUS CENTRAL SLF	CITRUS	(352) 726-8500
00073046	NAPLES SLF CELL #6 (COLLIER COUNTY)	COLLIER	(954) 984-2000
00073114	IMMOKALEE LF (#2 - STOCKADE)	COLLIER	(954) 984-2000
00031495	WINFIELD SW FACILITY LF1	COLUMBIA	(386) 752-6050
00040512	SECTION 16 LF EXPANSION	DESOTO	(863) 993-4826
00033628	TRAIL RIDGE LANDFILL LF1	DUVAL	(904) 289-9100
00001688	PERDIDO LANDFILL	ESCAMBIA	(850) 968-6628
00074648	GLADES CO. SAN. LANDFILL #2	GLADES	(941) 946-0771
00040612	HARDEE COUNTY REGIONAL LANDFILL	HARDEE	(863) 773-5089
00074773	HENDRY COUNTY SLF	HENDRY	(863) 675-5222
00074766	LEE/HENDRY CO REGIONAL SW DISP FAC	HENDRY	
00040722	HERNANDO COUNTY NORTHWEST LF	HERNANDO	(352) 754-4112
00074956	HIGHLANDS COUNTY SW MGMT.CENTER	HIGHLANDS	(941) 655-4055
00041193	SOUTHEAST COUNTY SLF (PICNIC LF)	HILLSBOROUGH	(813) 276-2908
00043384	KINGSWAY RD LF (DAVID J JOSEPH)	HILLSBOROUGH	(513) 621-8770
00019134	INDIAN RIVER COUNTY LF - CLASS I	INDIAN RIVER	(561) 770-5113
00006319	SPRINGHILL REGIONAL LANDFILL	JACKSON	(954) 984-2000
00019823	LAKE CNTY SOLID WASTE MGT	LAKE	(352) 343-3776
00076728	GULF COAST SLF	LEE	(954) 984-2000
00006660	US 27 SOUTH LANDFILL	LEON	(850) 488-4710
00036895	BRONSON LANDFILL LEVY CO LF1	LEVY	(352) 486-4311
00037059	AUCILLA AREA SW FACILITY LF1	MADISON	(850) 948-4875

00044795	LENA RD COUNTY LF	MANATEE	(941) 748-5543
00020906	BASELINE LANDFILL CLASS I	MARION	(352) 671-8465
00068803	MARTIN COUNTY (PALM CITY II) SLF	MARTIN	(772) 221-1442
00060080	MEDLEY LANDFILL AND RECYCLING	MIAMI-DADE	(954) 977-9551
00056824	SOUTH DADE SHREDDED WASTE LF	MIAMI-DADE	(305) 579-3997
00037140	WEST NASSAU LANDFILL LF1	NASSAU	(904) 261-6127
00070436	OKEECHOBEE LANDFILL, INC. AKA BERMAN	OKEECHOBEE	(863) 763-4818
00021847	ORANGE COUNTY LF	ORANGE	(407) 836-6600
00025473	SOUTHPORT RD SLF, PHASE I & II	OSCEOLA	(407) 847-4481
00089544	OAK HAMMOCK DISPOSAL	OSCEOLA	
00065551	PBCSWA RRF SITE #7	PALM BEACH	(561) 640-4000
Facility ID	**Facility Name**	**County**	**Phone Number**
00045799	PASCO COUNTY RESOURCE RECOVERY	PASCO	(727) 856-0119
00045797	EAST PASCO LF (DADE CITY LF)	PASCO	(727) 856-0119
00046742	BRIDGEWAY ACRES CLASS I LF	PINELLAS	(727) 464-7565
00049723	SOUTHEAST POLK LF (SITE 203)	POLK	(863) 284-4319
00049722	NORTH POLK CENTRAL LF (SITE 201)	POLK	(863) 284-4319
00037570	PUTNAM CO CENTRAL LANDFILL LF1	PUTNAM	(904) 329-0395
00012300	SANTA ROSA CENTRAL LF	SANTA ROSA	(850) 994-5387
00051614	SARASOTA CENTRAL LANDFILL	SARASOTA	(941) 486-2600
00026122	OSCEOLA RD LF (SEMINOLE COUNTY)	SEMINOLE	(407) 665-2022
00070652	ST LUCIE CO SLF	ST. LUCIE	(561) 462-1100
00039815	NEW RIVER REGIONAL LANDFILL LF1	UNION	(904) 259-4911
00027540	TOMOKA FARMS ROAD LANDFILL	VOLUSIA	(904) 943-7889
00014494	LOWER BRIDGE LANDFILL	WAKULLA	(850) 926-3341

Table 5 FDEP master list of solid waste directors in Florida.

County	Office Phone
ALACHUA	(352) 374-5213
BAKER	(904) 275-2373
BAY	(850) 784-4028
BRADFORD	(904) 966-6212
BREVARD	(407) 633-2043
BROWARD	(954) 765-4202
CALHOUN	(850) 674-8075
CHARLOTTE	(941) 639-1349
CITRUS	(352) 746-5000
CLAY	(904) 284-6374
COLLIER	(941) 732-2508
COLUMBIA	(904) 758-1328
DADE	(305) 594-1520
DE SOTO	(863) 993-2068
DIXIE	(352) 498-1432
DUVAL	(904) 665-4493
ESCAMBIA	(850) 937-2160
FLAGLER	(904) 517-2075
FRANKLIN	(850) 670-8167
GADSDEN	(850) 875-8658
GILCHRIST	(352) 463-3185
GLADES	(941) 675-0124
GULF	(850) 227-3696
HAMILTON	(904) 792-1020
HARDEE	(863) 773-5089
HENDRY	863 675 5252
HERNANDO	(352) 754-4112
HIGHLANDS	(863) 655-6477
HILLSBOROUGH	(813) 272-5680
HOLMES	(850) 547-0922
INDIAN RIVER	(561) 770-5112
JACKSON	(850) 482-9083
JEFFERSON	(850) 342-0184
LAFAYETTE	386 208 2795
LAKE	(352) 343-6030
LEE	239 338 3303
LEON	(850) 427-2890
LEVY	(352) 486-5127
LIBERTY	(850) 643-3777
MADISON	(850) 973-2611
MANATEE	(941) 792-8811
MARION	(352) 245-4584
MARTIN	(772) 221 1386
MONROE	(305) 292-4432
NASSAU	(904) 879-5722
OKALOOSA	(850) 651-7394
OKEECHOBEE	(941) 651-7395
ORANGE	(407) 836-7251
OSCEOLA	(407) 926 1100
PALM BEACH	(561) 640-4000
PASCO	(813) 847-8041
PINELLAS	(813) 464-7565
POLK	(863) 284-4319
PUTNAM	(904) 329-0395
ST. LUCIE	(407) 462-1634
SANTA ROSA	(850) 626-0191
SARASOTA	(941) 378-6100
SEMINOLE	(407) 322-7605
ST. JOHNS	(904) 824-9720
SUMTER	352 793 3368
SUWANNEE	(904) 362-3992
TAYLOR	(850) 838-3533
UNION	(904) 496-2180
VOLUSIA	(904) 947-2952
WAKULLA	850 926 7010
WALTON	(850) 892-8108
WASHINGTON	850 638 6200

Grey areas are landfills that could not be contacted, or that did not have a problem with arsenic in leachate. Yellow areas are landfills that had arsenic in leachate greater than 10 ppb and had a disposal issue wrt arsenic.

Table 6 Concentrations in ppb of select heavy metals at some landfills in Florida.

County	Date Sampled	As	Cd	Cr	Cu	Pb	Ni	Se	Zn
Marion	10/2/2002	40	5	38	50	10	110	10	100
	3/26/2003	33	-	13	13	-	-	-	22
	3/4/2004	66	-	39	5	-	150	-	50
	3/8/2005	100	-	100	15	97	170	2	190
	3/10/2006	100	-	72	11	6	110	7	66
Polk*	3/26/03-7/16/03	43	5	11	-	34	-	-	13
Leachate 1	9/10/03-1/15/04	83	5	18	-	28	219	-	35
Leachate 2	9/10/03-1/14/04	70	5	8	-	26	161	-	121
Tank	3/8/04-7/15/04	71	6	2	5	33	148	-	34
	4/14/2005	131	5	20	1	1	199	186	10
Alachua**	Average	130	7	50	21	30	210	100	50
	Minimum	30	6	10	14	1	40	60	30
	Maximum	250	13	190	47	264	300	180	110

* 3/26 and 3/8 samples are from the leachate tank; 4/14 results obtained from Flowers Chemical Laboratories Inc. (no specific location identified).
** Data obtained from Alachua County Public Works Department on 4/26/06 and represents results collected from the University of Florida since 1998.

Table 7 Mean leachate quality values from various landfill sites worldwide. Taken from Alvarez-Vazquez et al., 2004.[72]

Parameters (mg dm^{-3})	Young leachate (<2 years)	Old leachate (>6.5 years)	Young Leachate (<2 years)	Old leachate (>10 years)
BOD	24,000	150	2500-3000	10-20
COD	62,000	3000	3000-60,000	100-500
TOC	Not Given	Not Given	1500-20,000	80-160
BOD/COD	0.39	0.05	0.05-0.67	0.04-0.1
N-NH4	1400	350	10-800	20-40
pH	5.8	8	4.5-7.5	6.6-7.5

1.11.2 Experimental Methods

Materials

The following three commercially available mineral oxides were characterized for this study:

1. Kemiron from Kemiron, U.S.A
2. Lanxess Bayoxide E33 from Severn Trent Services, USA
3. ADSORBSIA GTO (Titanium oxide) from DOW Chemical Company, USA.

The solids were ground in a ceramic mortar and sieved through American Society for Testing and Materials (ASTM) stainless steel sieves to obtain particles less than 38 μm (fines) in diameter and particles between 250 and 425 µm. The fine particles were examined under a Hitachi H-7010 Scanning Electronic Microscope (SEM) with a Joel JSM-840 Energy Dispersive Spectroscopy (EDS) for particle morphology and percentage by mass of elemental constituent. A Philips X-ray diffractometer (XRD) was used to identify mineral makeup of using a copper target for the x-ray source with a strongest characteristic radiation ($K\alpha_1$) at a wavelength of 1.54 angstroms. Samples were sent to Micromeritics laboratory in Atlanta, GA for 5 point BET surface area of the fines and effective pore size, total pore volume and total pore surface area of the 250 and 425 µm fraction using mercury intrusion porosimetry. Prior to the multipoint surface area and pore analyses, samples were dried at 80°C for 18 h and degassed at 80°C for 3 h. ADSORBSIA was dried at 250°C. ALCOA DD660, an alumina based sorbent, was also used in preliminary experiments with landfill leachate and this was previously characterized. [30]

Reagents and Stock Solutions

All solutions were prepared from American Chemical Society (ACS) reagent grade chemicals and ultrapure water (Barnstead) with resistivity of 18.2 MΩ-cm. The reagents included Na_2SeO_3 (Sigma Aldrich) and Fisher Scientific's $Na_2HAsO_4.7H_2O$, Na_2SO_4, $NaHCO_3$, $Ca(NO_3)_2$, $NaNO_3$, $NaAsO_2$, HNO_3, NaOH, and $(Ni(NO_3)_2.6H_2O)$30% Hydrogen peroxide. Arsenic and selenium in 2% HNO_3 solution (Spex CertiPrep) were used to make standard solutions for atomic absorption measurements. A stock solution of nickel (150 mg/L) was used as modifier solution in the determination of arsenic and selenium by graphite furnace atomic absorption spectrometry (GFAA) on a Varian DUO AA240Z equipped with automated sample injection. 0.001 N and 0.1 N $NaNO_3$ with 2% HNO_3 was used as the blank and make up solutions for GFAA analysis. A Ross semi micro gel filled electrode coupled to an Orion 940 pH meter was used for pH measurements after being calibrated with Fisher Scientific pH buffers, 4.0, 7.0, and 10.0. Prior to use, all glassware was washed with Liquinox detergent, soaked in 1 N NaOH for more than 1 hour and then soaked in 10% HNO_3 overnight and finally rinsed with, and left soaking in ultrapure water overnight. Cleaning of polycarbonate containers used during experiments was similar to that of glassware except 0.1 N concentrations of acid and base were used.

Experimental Techniques

The experiments performed included batch adsorption equilibration as a function of pH (4.0 - 10.0), ionic strength (0.001 and 0.1 N), and presence of other ions, adsorption isotherms at pH 7.0 and rate of uptake experiments at pH 7.0. Figure 8 shows the experimental set up.

Figure 8 Experimental set up of batch sorption experiments.

Batch kinetic studies were done on two different grain sizes (250 – 425 µm and < 38 µm) of Kemiron in a 1000 mL Nalgene batch bottle. A solid concentration of 0.1 g/L Kemiron in a 1000 mL solution was made for each grain size. The pH of the solutions was then lowered to 5.5 with 0.1 N HNO_3 before the solutions were sparged with the ultra high pure nitrogen gas overnight. The pH of the solution was then raised to 7.0 with 0.1 N NaOH and then spiked with the appropriate volume of adsorbate. NaOH and HNO_3 were used to maintain the pH at 7.0 and samples were removed as a function of time. The samples were immediately filtered (0.2 µm MILLIPORE) and acidified (to 0.7% HNO_3) and stored for analysis of As and Se. Results from the rate of uptake experiments using the fines at pH 7 of As(V), As(III) and Se(IV) at concentrations of 5 m/L were used to determine the equilibration time for the sorption experiments.

For the batch adsorption equilibrium experiments, 200 mL of 0.1 g/L of Kemiron slurry (grain size ≤ 38 µm) at a given ionic strength was stirred in a 250 mL polycarbonate (PC) batch reactor. The pH was adjusted to ~ 5.5 the slurry sparged with nitrogen gas for 24 h to remove dissolved carbon dioxide. The pH was then raised to 10 and spiked with As(V), As(III) or Se(IV) solutions to obtain specific total concentrations: 5 and 10 mg/L for As(V) and As(III) and 5,10 and 15 mg/L for Se(IV). An 8 mL sample was removed and placed into a 10 mL PC tube where the headspace was filled with nitrogen gas and then the tube capped tightly. The pH of the slurry was then lowered using nitric acid to various pH values; 8 ml samples being removed each time. The 8 mL samples were placed on end over end shakers for as long as 72 h for As(V) and 48 h for Se(IV) and As(III). After the given equilibration time the pH of the sample was measured and the sample filtered, acidified and analyzed for As or Se. The adsorption isotherm experiments at pH 7 were similar to those discussed above, except that for a given run a set of samples were taken at pH 7, placed on the end over end shaker, checked periodically for pH and readjusted to pH 7.0 with 0.1 N HNO_3 and 0.1 N NaOH. After the set time the sample was filtered, acidified and analyzed for As or Se.

Batch equilibrium sorption experiments were also done for As(V) in the presence of other ions (Se(IV), Ca, Ni, SO_4^{2-} and CO_3^{2-}) and using a real leachate solution. Arsenic in experiments using leachate was determined using standard additions methods. Leachate was digested on an Environmental Express Hotblock set at 105°C (sample temperatures were 95°C). 100 ml of leachate sample was placed in a 250 ml beaker to which 3 ml concentrated HNO_3 was added and the mixture boiled down to ~ 5 ml. 3 ml more of concentrated nitric acid were added and the mixture boiled until constant color. 10 ml of concentrated HCl was then added along with ultrapure water and the mixture boiled for 15 minutes after which the cooled mixture was made to mark in a 100 ml volumetric flask. This procedure was repeated using a 100 ml Environmental Express polyprophene container, and then 1 mL of 30% H_2O_2 plus 2.5 mL of concentrated HNO_3 was added and the samples allowed to heat for 2 hours after which they were cooled, diluted and analyzed on the GFAA.

1.11.3 Results and Discussion

Solids Characterization

The results of the solids characterization are summarized in the table and figures below.

Table 8 Surface Characterization results from Mercury Porisimetry and 5 point BET analysis.

	Bayoxide		**Adsorbsia**		**Kemiron**	
Property	**Mercury Intrusion Porosimetry**	**N2 BET Analysis**	**Mercury Intrusion Porosimetry**	**N2 BET Analysis**	**Mercury Intrusion Porosimetry**	**N2 BET Analysis**
Total Pore Volume (ml/g)	1.5	0.46	0.90	0.26	0.25	0.42
Bulk Density @ 55 psia (g/ml)	0.57	-	0.74	-	1.32	-
Porosity (%)	85.36	-	67.35	-	55.19	-
Max Pore Diameter (micron)	328.46	0.18	327.69	1.52	327.69	0.076
Min Pore Diameter (micron)	0.003	0.002	0.003	0.002	0.003	0.002
Median Pore Diameter (micron)	0.002	0.004	0.006	0.004	0.007	0.004
Mean Pore Diameter (microns)	0.04	0.02	0.04	0.01	0.08	0.01
Total Pore Surface Area (m2/g)	151.31	94.98	105.00	207.45	22.1	40
Skeletal Density (g/ml)	3.9	-			2.94	-

Table 9 SEM and EDS of Bayoxide.

Bayoxide		SEM of Bayoxide

Table 10 SEM and EDS of Adsorbsia GTO.

Adsorbsia		SEM of Kemiron

Table 11 SEM and EDS of Kemiron.

Kemiron		SEM of Kemiron

Sorption Studies

Landfill leachate was obtained from the Polk County North Central Landfill facility. Leachate was collected from three sample points referred to as Phase 1, Phase 2 and the leachate tank. Preliminary studies looking at the effect of filtration on arsenic concentrations were done on samples taken on 4/12/05 from the Phase 1 sample point and the leachate tank. These samples were first filtered through a 0.25 μm PES filter and then a 0.02 μm Anatop filter (Table 12). There was no significant difference in arsenic concentrations using the smaller filter.

Table 13 shows the effect of filtration and acid digestion on leachate samples taken on 4/27/06. Acid digestion increased total arsenic concentrations though this was not evident with the Phase 2 data. Comparing the total arsenic concentration of acid digested samples in the presence and absence of filtration shows no significant difference in arsenic concentrations. This suggests that the arsenic concentrations in landfill leachate are due to dissolved species. Pretreatment steps needed to reduce turbidity of samples may not affect this total arsenic concentration. This also suggests that total arsenic concentrations reported in landfill leachate reports adequately reflects the concentration of arsenic that would be needing treatment via sorption processes addressed in this project.

Table 12 Effect of filter size on arsenic concentration in leachate from Polk County North Central landfill sampled on 4/12/05.

Sample	As in acid digested filtrate through 0.25 μm (ppb)	As in acid digested filtrate through 0.02 μm (ppb)
Phase 1	157 ± 10	177 ± 11
Leachate Tank	89 ± 5	96 ± 5

Table 13 Effect of acid digestion and filtering on As concentrations in leachate sampled from the Polk county North Central landfill on 4/27/06

Sample	As in filtrate through 0.45 μm Millipore filter (ppb)	As in acid digested filtrate through 0.45 μm Millipore filter (ppb)	As in unfiltered, digested leachate (ppb)
Phase 1	29 ± 2	92 ± 14	90 ± 7
Phase 2	76 ± 4	61 ± 3	64 ± 3
Leachate Tank	98 ± 5	126 ± 6	114 ± 6

Filtered leachate from Phase 1 was used to conduct sorption experiments of 800 ppb As(V) using both Kemiron and ALCOA DD600 and the results are displayed in Figure 9 and Figure 10. The presence of leachate reduced As(V) sorption to ALCOA DD660 by almost 50% at pH 7. As(V) sorption on Kemiron was not affected by the presence of leachate for the concentration studied. It should be noted that 800 ppb As(V) sorption on Kemiron gave aqueous concentrations, for the most part, that were below detection limits of the instrument and 800 ppb As(V) sorption in the absence of leachate was close to 100% across the pH range studied.

Figure 9 μg As(V)/m^2 solid using Kemiron (1 g/L, 40 m^2/g) and ALCOA DD660 (0.5 g/L, 400 m^2/g) and in the presence of filtered Phase 1 leachate. Particle size used was < 38 μm, T = 25^{o}C

Figure 10 % As(V) removed using Kemiron (1 g/L, 40 m^2/g) and ALCOA DD660 (0.5 g/L, 400 m^2/g) and in the presence of filtered Phase 1 leachate. Particle size used was < 38 μm, T = 25^{o}C.

Figure 11, Figure 12, and Figure 13 show the influence of pH and ionic strength on As(V), As(III) and Se(IV) adsorption onto Kemiron respectively. As(V) and Se(IV) show typical oxyanionic adsorption behavior with the percentages of As(V) and Se(IV) adsorbed decreasing with increasing pH values. The dominating species of As(V) below pH 2.2 is H_3AsO_4, between pH 2.2 and 7.0 it is $H_2AsO_4^-$, while $HAsO_4^{2-}$ dominates between pH of 7.0 and 12.1. Similarly, the dominating species of Se(IV) up to pH 2.6 is H_2SeO_3 and between pH 2.6 and 8.4 is $HSeO_3^-$ while SeO_3^{2-} dominates above pH 8.4. For similar total concentrations of 6.7 E-5 M (~5 m/L Se or As), Se(IV) sorption was higher than that of As(V) at all pH values. When that concentration increased two fold, the amount of Se(IV) sorbed was similar to that of As(V). As(III) sorption reached a maximum in the pH 8 region and also did not show any ionic strength effects. As(III) remains an uncharged species up until pH 9.32 which likely explains its sorption curve compared with As(V), especially below pH 8.

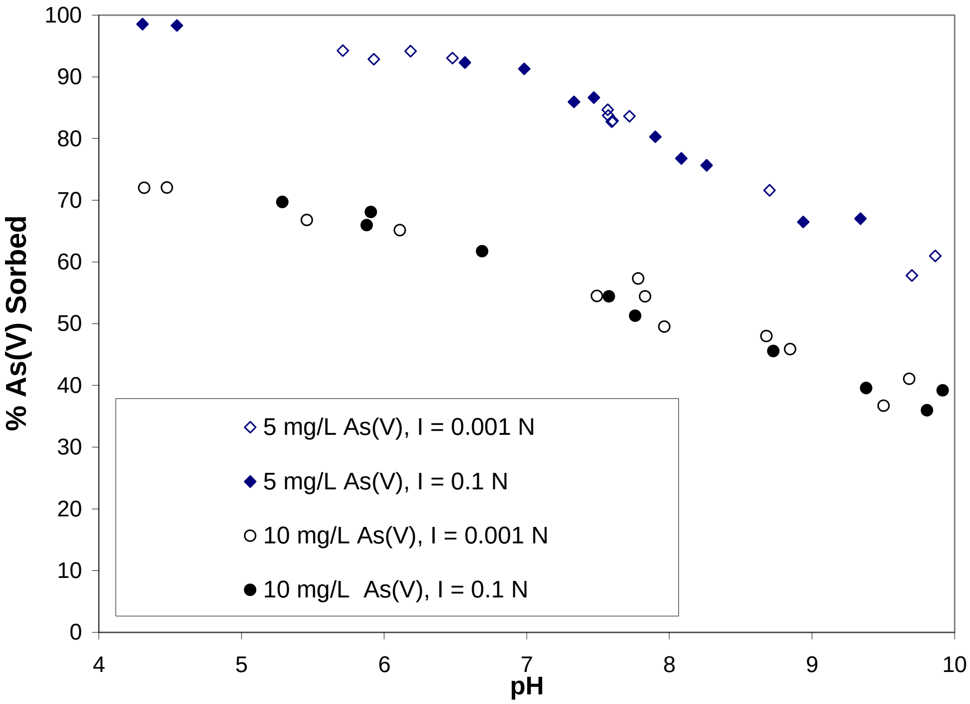

Figure 11 Percentages of various initial concentrations of As(V) adsorbed onto 0.1 g/L Kemiron (≤ 38 μm) as a function of pH at I = 0.001N and 0.1 N $NaNO_3$, at room temperature (rtp).

Many iron based adsorbents have their pH point of zero charge (pH_{PZC}) between pH 8.0 and 9.3 [10-16] and this is affected by the presence of carbonate and the way in which the particles are made. [61, 73] The percentage adsorption of negatively charged ions onto iron based adsorbent drops appreciably above the pH_{PZC} and one would expect this behavior of Kemiron given its high iron based content and XRD. In Figure 11 and Figure 13 show that the the adsorption edges of both As(V) and Se(IV) drop above pH 7.5 (for Se(IV) the edge is shifted to a higher pH and may be due to the second pK_a being higher when compared with arsenate). Above the pH_{PZC}, the charges on the adsorbent surface go from neutral to negative and this reduces the attraction between the negatively charged As(V) and Se(IV).

Differences in ionic strength did not affect As(V) with initial concentrations of 5 and 10 mg/L or Se(IV) with initial concentrations of 5, 10, and 15 mg/L within a pH value range of 4.0 and 10.0. As(III) was also unaffected by changes in ionic strength. This lack of ionic strength effect suggests inner-sphere surface complexation formation [17] between the ion and the Kemiron surface. This can be beneficial during treatment of a contaminated water where competition for sorption sites by other ions is expected.

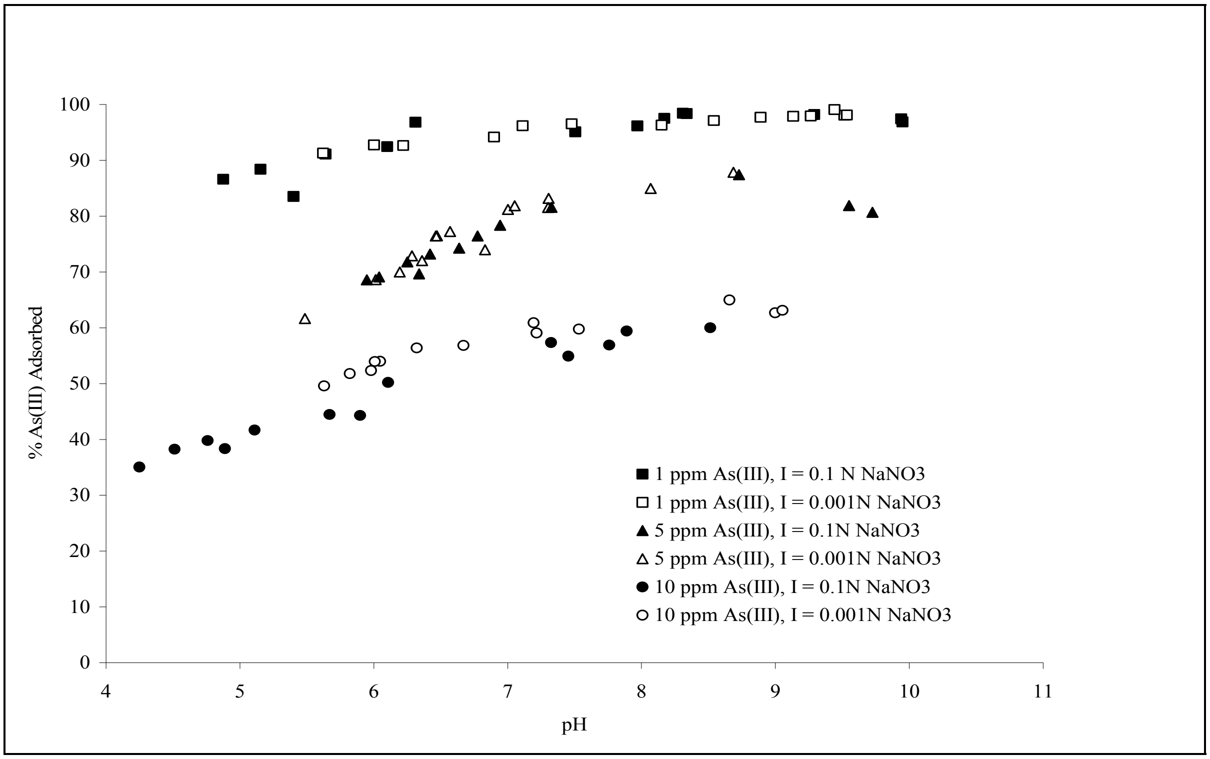

Figure 12 Percentages of various initial concentrations of As(III) adsorbed onto 0.1 g/L Kemiron (≤ 38 μm) as a function of pH at I = 0.001N and 0.1 N $NaNO_3$, at rtp

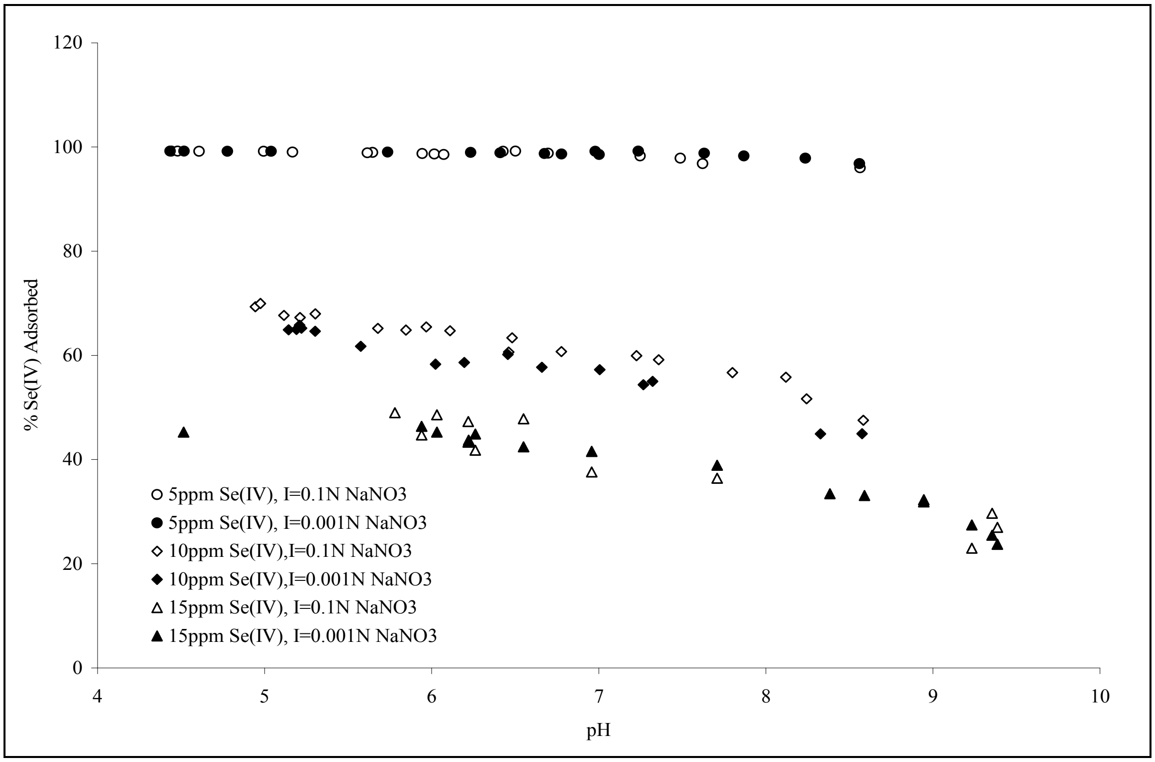

Figure 13 Percentages of various initial concentrations of Se(IV) adsorbed onto 0.1 g/L Kemiron (≤ 38 µm) as a function of pH at I = 0.001N and 0.1 N $NaNO_3$, at rtp.

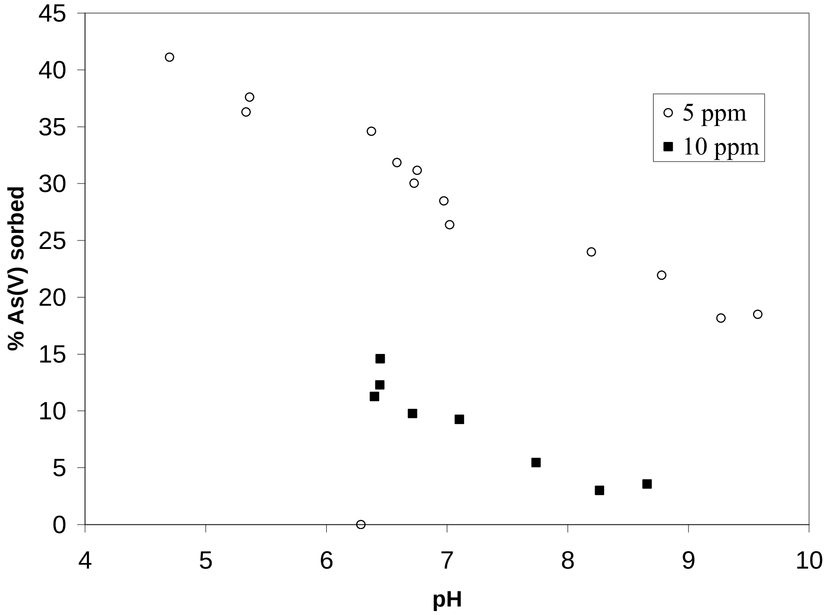

Figure 14 Percentages of various initial concentrations of As(V) adsorbed onto 0.1 g/L Bayoxide (≤ 38 µm) as a function of pH at I = 0.001N $NaNO_3$, at room temperature.

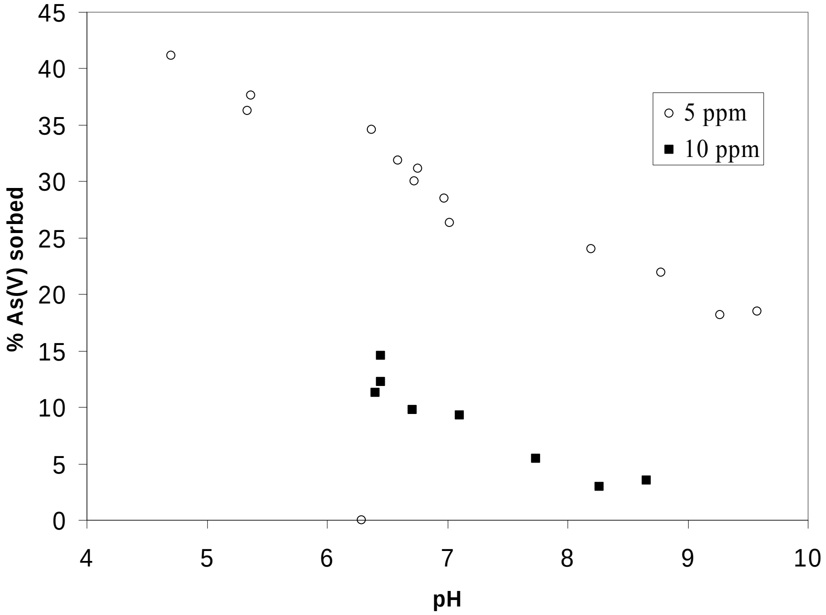

Figure 14 shows the sorption behavior of As(V) on Bayoxide E33 as a function of arsenic concentration. Even though the surface area of Bayoxide E33 is twice that of Kemiron, Kemiron is more efficient at removing the amount of As(V) sorbed. At pH 7, the amount of As(V) removed by a similar weight of Bayoxide E33 is only 30% that removed by Kemiron. 5 ppm As(V) sorption to 0.1 g/L GTO Adsorbsia resulted in greater than 99% sorption between pH 5 to 10.

Results of studies done on As(V) sorption in the presence of other ions are presented in Figures 15 through 19. A study done with 5 ppm As(V) in the presence of 100 ppm SO_4^{2-} showed no significant difference in As(V) sorption. Carbonate also showed little effect. As(V) sorption decreases in the presence of an equimolar concentration of Se(IV) probably owing to competition for sorption sites since both are negatively charged species in the pH range considered. From landfill leachate data, though selenium is a potential concern in terms of its own allowable limits and health effects, its concentration may be lower than that of arsenic and hence, competitive effects reduced. Other ions like Cr may pose a greater risk to As(V) sorption in terms of competitive effects. Ca^{2+} increased As(V) sorption to Kemiron when the molar ratio of As:Ca was approximately 1:2. This increase could be due to a change in surface charge owing to calcium sorption that causes more of the As(V) anion to sorb to the surface. The calcium concentrations used are too low to expect any calcium hydroxide or calcium carbonate (the systems were purged with nitrogen and headspace maintained with N_2 to eliminate CO_2 effects) precipitates. Depending on calcium concentrations in a given leachate, the addition of calcium during the sorption step may enhance arsenic removal and this should be further explored. Ni did not affect the sorption of As(V) or As(III) to Kemiron.

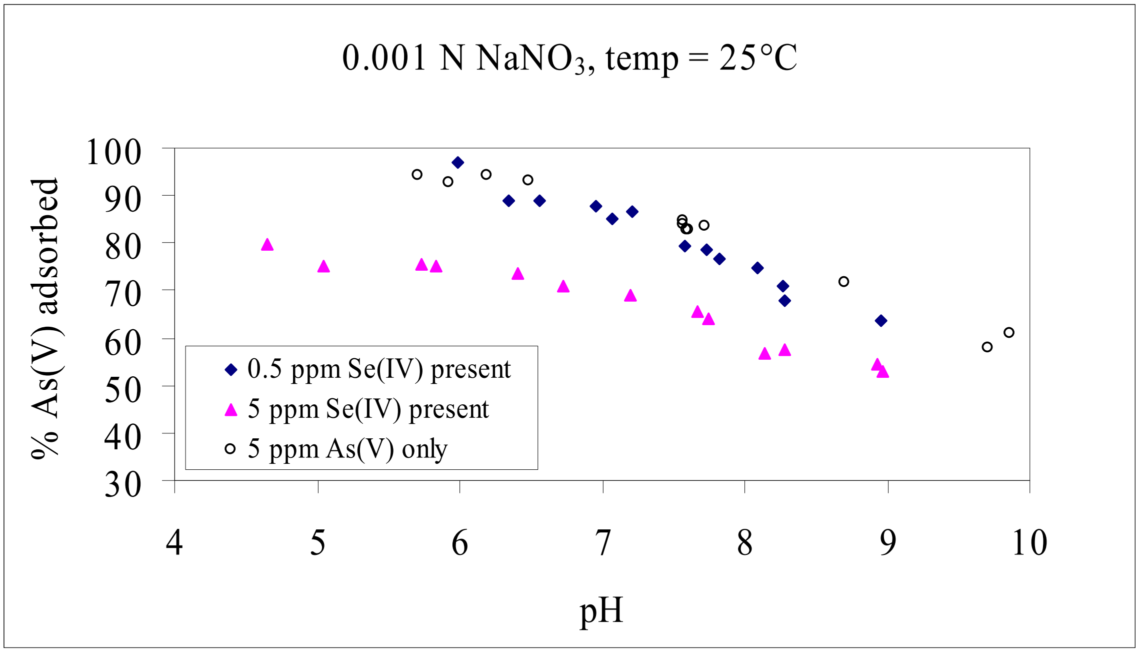

Figure 15 Percentage of 5 ppm As(V) adsorbed onto 0.1 g/L Kemiron (≤ 38 μm) as a function of pH and Se(IV) concentration.

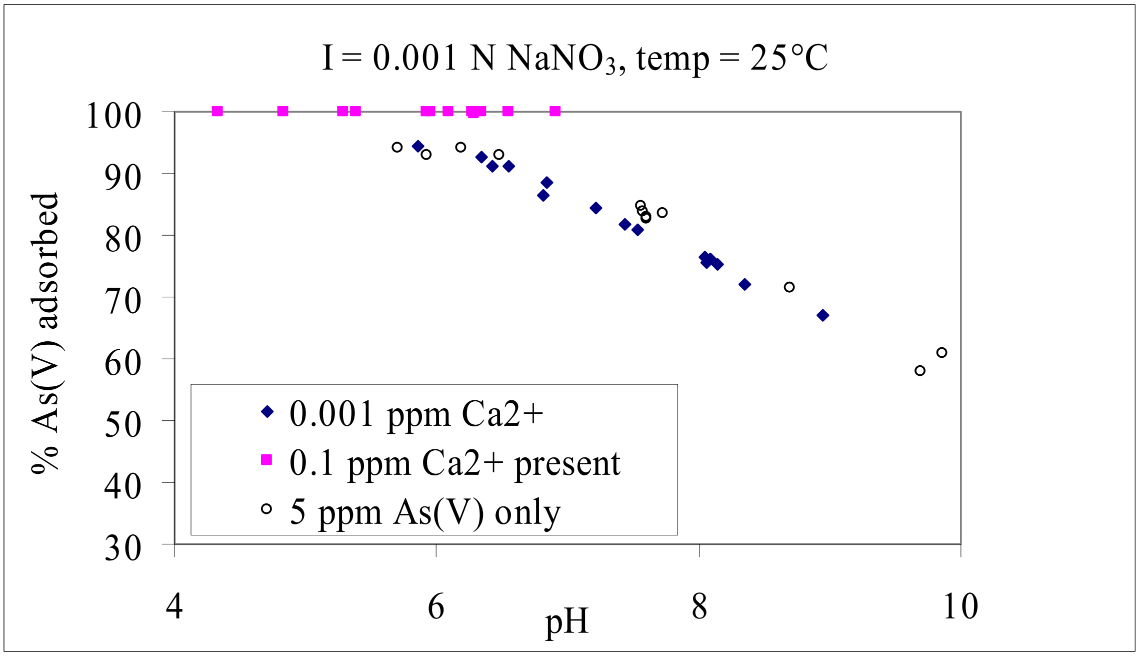

Figure 16 Percentage of 5 ppm As(V) adsorbed onto 0.1 g/L Kemiron (≤ 38 μm) as a function of pH and Ca^{2+} concentration.

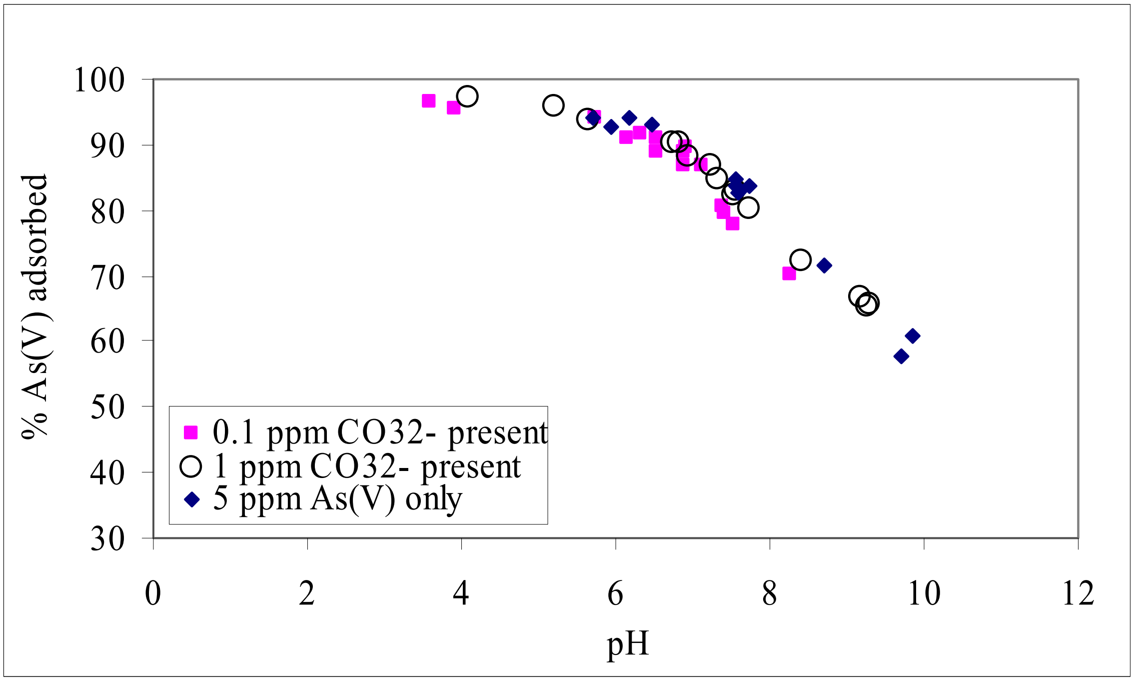

Figure 17 Percentage of 5 ppm As(V) adsorbed onto 0.1 g/L Kemiron (≤ 38 µm) as a function of pH and CO_3^{2-} concentration.

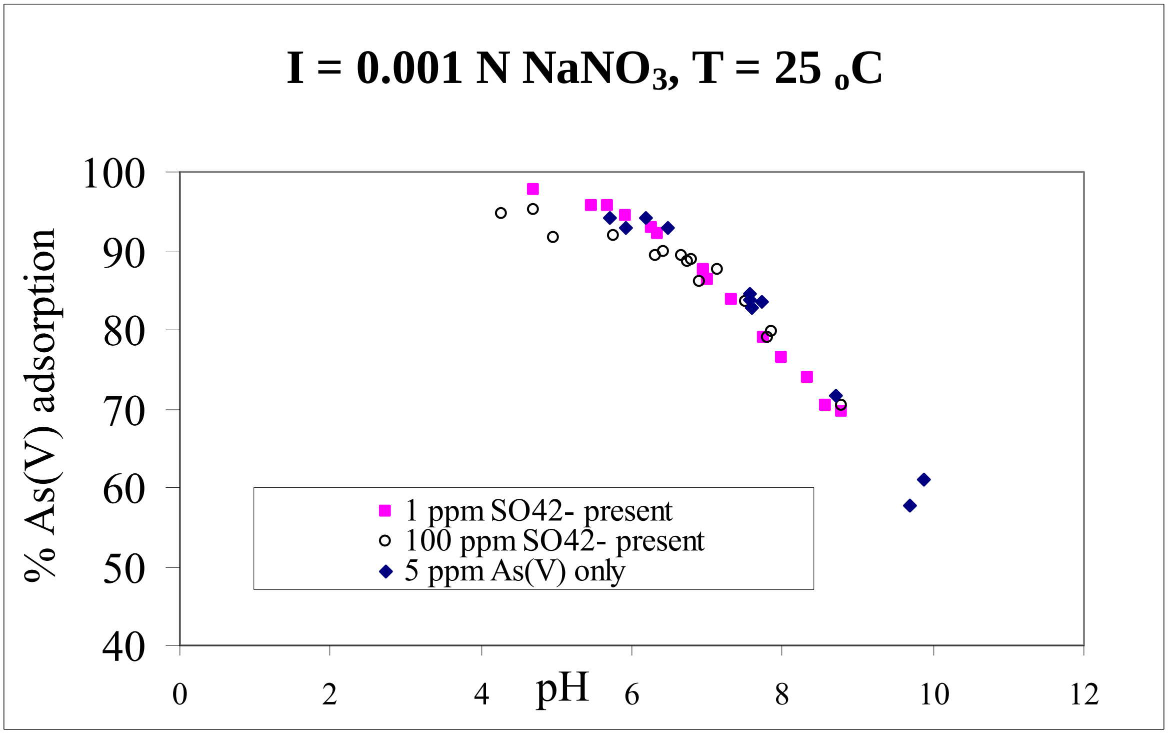

Figure 18 Percentage of 5 ppm As(V) adsorbed onto 0.1 g/L Kemiron (≤ 38 µm) as a function of pH and SO_4^{2-} concentration.

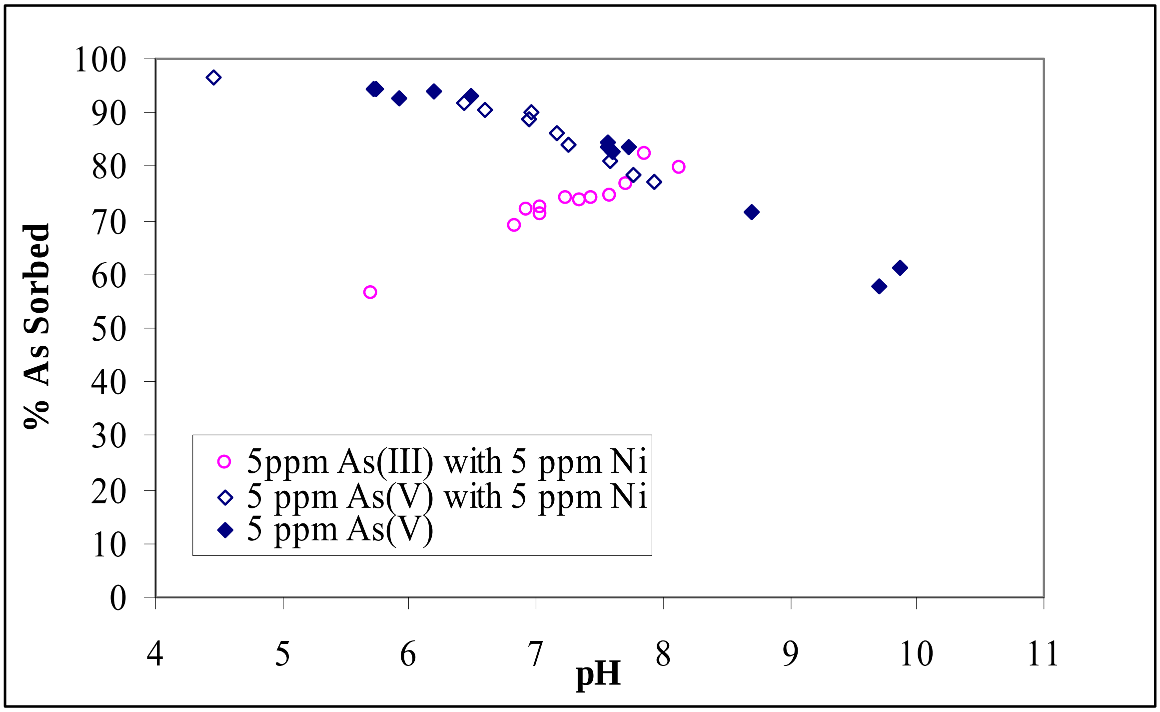

Figure 19 Effect of 5 ppm Ni2+ on adsorption of As(V) and As(III) onto 0.1 g/L Kemiron (≤ 38 μm) as a function of pH. I = 0.001 N, T = 25°C.

In this work, Langmuir and Freundlich isotherms were used to describe the relationship between the amount of As(V) and Se(IV) adsorbed and the concentration in solution at pH 7.0. As shown in Figure 20, Langmiur model fits As(V) and Se(IV) adsorption onto Kemiron better than the Freundlich model with maximum adsorption density of 82 mg/g and 52 mg/g respectively. The coefficients of correlation between the experimental data and the Langmuir models are 0.93 and 0.95 for As(V) and Se(IV) respectively, while those for the Freundlich models were 0.88 and 0.89 respectively. Freundlich fits to As(III) data are provided in Table 15.

Table 14 lists adsorption densities of As(V) and Se(IV) on other metal oxides and hydroxides. Comparing these published results with the results obtained in this work, the adsorption capacity of Kemiron towards As(V) and Se(IV) would be on the higher end of the spectrum.

Table 14 Adsorption capacities of some adsorbents at pH 7 and at room temperature

Source	**Adsorbate**	**Adsorbent**	**Model**	**Max q (mg/g)**
[74]	As(V)	Laterite	Langmuir	0.04
[75]	Se(IV)	Mn nodules	Langmuir	55 (pH 5)
[76]	Se(IV)	Coal soils	Langmuir	(2.3-24) x 10^{-3}
[77]	As(V)	Calcined bauxite	Langmuir	1.56
[13]	As(V)	GFH	Freundlich	3.60 and 4.45 *

* The unit is (L/μg)$^{1/n}$

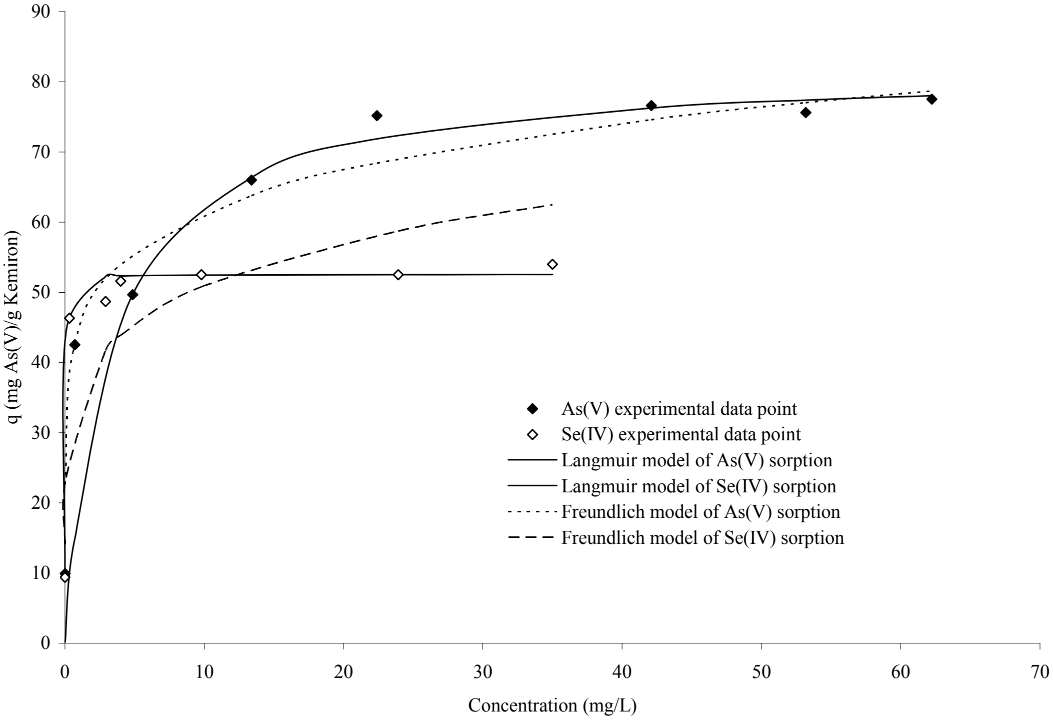

Figure 20 Isotherm models of As(V) and Se(IV) with 0.1 g/L Kemiron (≤ 38 μm), I = 0.1 N $NaNO_3$ at pH 7, CO_2 excluded, 25°C.

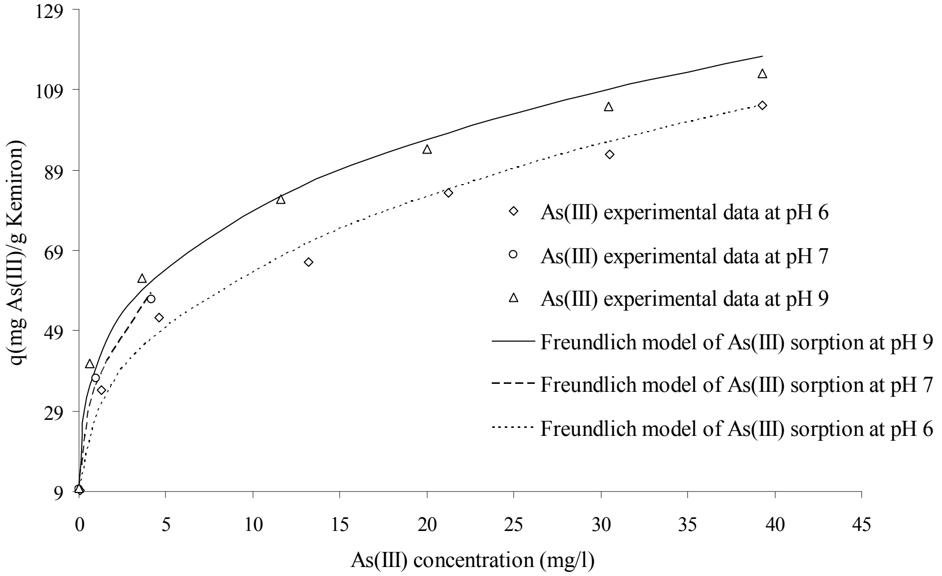

Figure 21 Freundlich adsorption isotherm models of As(III) onto 0.1 g/l Kemiron (<38 μm), I = 0.001 N $NaNO_3$ at pH 6, pH 7, and pH 9 at 25°C for 72 h.

Table 15 Constants obtained by fitting the Freundlich isotherm for As(III)($q = KC^{1/n}$)

pH	K	1/n
pH 6	27.911	0.3615
pH 7	35.67	0.346
pH 9	40.761	0.2878

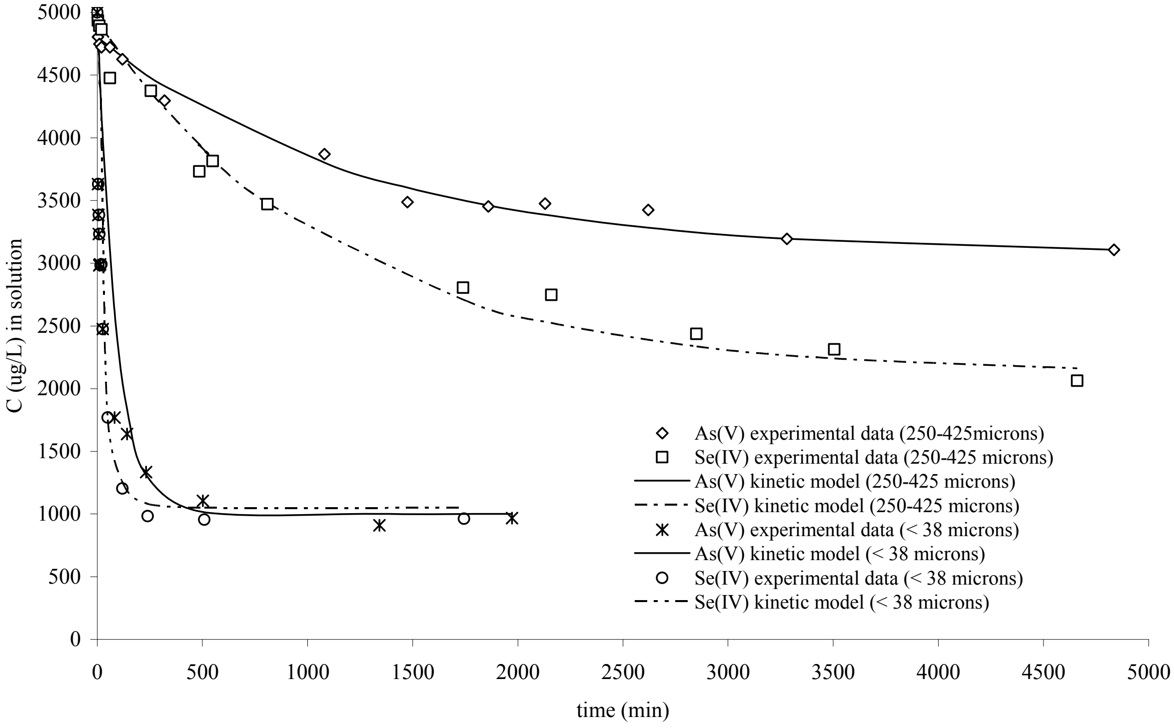

Figure 22 Rate of uptake of 5 ppm As(V) and Se(IV) onto 0.1 g/L Kemiron (< 38 μm and 250-425 μm), I = 0.001 N $NaNO_3$ at pH = 7, CO_2 excluded, rtp.

Both the experimental and model plots of $C_b(t)$ against time t, for As(V) and Se(IV) are shown in Figure 22. The mass transfer coefficients for As(V) and Se(IV) from the models are 0.0008 min^{-1} and 0.0009 min^{-1} respectively and the external mass transfer coefficients for As(V) and Se(IV) are 3.34×10^{-7} cm/s and 3.76×10^{-7} cm/s respectively. Table 16 summarizes external mass transfer k_f coefficients obtained by other researchers for similar systems. The values obtained in this work are lower and suggest diffusion controlled adsorption behavior into the particles. Figure 23 shows the rate of uptake data for As(III) and the mass transfer coefficient is 0.00089 min^{-1}.

In this model, mass transfer coefficients were obtained as fitting parameters to the experimental data. The coefficients of correlation of Figure 22 are 0.99 for As(V) and 0.98 for Se(IV). The adsorption capacity decreased by 53 % when the 250-425 µm particle grain size was used in the rate of uptake studies compared to the fine grain size (≤ 38 µm). When the fine grains were used 4.07 mg/L As(V) was sorbed at equilibrium but 1.93 mg/L As(V) was sorbed at equilibrium in the case of the coarser grains. Similarly, for the Se(IV), the capacity dropped by 28 % from 4.01 mg/L to 2.9 mg/L. This may be due to inaccessibility of some sorption sites in the coarser grains [78].

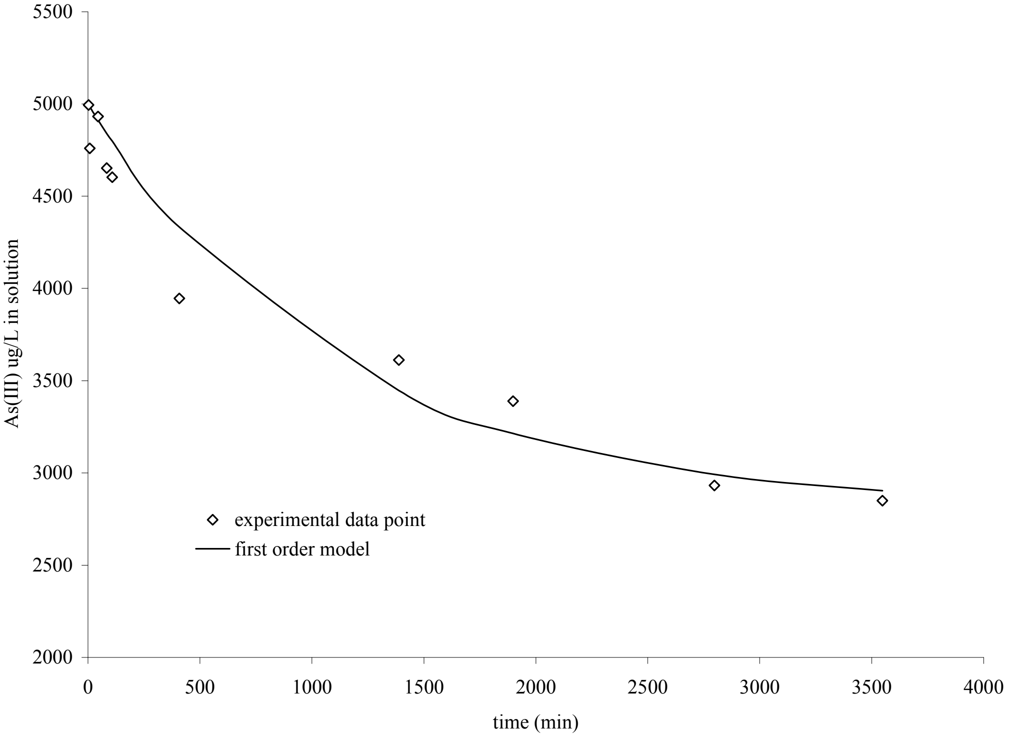

Figure 23 Rate of uptake of 5 ppm As(III) onto 0.1 g/L Kemiron (250-425 µm), I = 0.001 N $NaNO_3$ at pH = 7, CO_2 excluded, rtp.

Table 16 External mass transfer coefficients observed by other researchers.

Source	**Adsorbate**	**Adsorbent**	k_f (cm/s) x10^{-3}
[65]	As(V)	GFH	0.89-1.33
[13]	As(V)	GFH	2 -4.7
[64]	Pb^{2+}	Iron	1.5 -5

1.11.4 CONCLUSIONS

The overall goal of this project was to determine the applicability of removing arsenic from landfill leachate via sorption to mineral oxide surfaces as a cost reduction option for landfill facility operations in Florida. We attempted to contact 68 Florida landfills (not only active Class 1 landfills) via email and phone to learn about their leachate disposal practices and total arsenic concentrations. Of the 68 landfills on the list, we got 26 responses and of those 26 responses we identified 7 landfills in Florida that would benefit from this study. Landfills with leachate that had arsenic concentrations greater than 10 ppb combined with a disposal issue related to arsenic were identified. The seven landfills identified were:

- Alachua County
- Lake County
- Marion County
- Martin County
- Orange County
- Polk County
- Santa Rosa County.

These seven landfills paid for offsite leachate disposal and sometimes had an additional surcharge fee because arsenic concentrations were above permissible limits. Though leachate contained a list of other heavy metals, arsenic concentrations were closer to or above permissible limits. Arsenic speciation was not provided by the various landfills and this study examined both As(III) and As(V) sorption.

Mineral oxides sorbents that have been gaining wide use in arsenic removal during drinking water treatment were examined in this study for their potential to remove arsenic from landfill leachate, an onsite treatment option. Though physical characteristics of Bayoxide E33 (iron oxide), ADSORBSIA GTO (titanium oxide) and Kemiron (iron oxide) were done in this study, emphasis was placed on Kemiron which has a local distributor in Florida that was interested in this application. BET surface area of Kemiron is 39.8 m^2/g and Electron dispersive spectroscopy (EDS) studies found Kemiron to be 40.37% iron and 42.25 % oxygen by mass. Leachate (filtered) obtained from Polk County's North Central Landfill did not affect the sorption of 800 ppb arsenate (As(V)) onto 1 g/L Kemiron between pH 5 and 9. Batch systems for arsenate (As(V)), arsenite (As(III)) and selenite (Se(IV)) removal from aqueous solutions as a function of pH, ionic strength, and particle size (< 38 μm and between 250 and 425 μm) were investigated. Langmuir isotherms best described the As(V) and Se(IV) removal at pH 7 with maximum adsorption capacity of 82 mg/g and 52 mg/g respectively. As(V) and Se(IV) sorption decreased as pH increased and both anions were unaffected by sodium nitrate ($NaNO_3$) background electrolyte. As(V) sorption decreased in the presence of Se(IV), increased in the presence of Ca and remained unchanged in the presence of sulfate or carbonate. As(III) sorption sowed a maximum around pH 8 and was unaffected by changes in ionic strength. Rate of uptake experiments using larger grained particles which would more than likely be used in the actual treatment application showed reduced sorption capacity for As(V) and Se(IV) in the time frame of the experiments when compared with the fines. The rate of uptake by these particles will be an important step in determining the most suitable conditions for sorption and more work needs to be done in this area.

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1.13 APPENDIX: Raw Experimental Data

As(V) sorption data on 0.1 g/L Kemiron.

5 ppm As(V), 0.001 N	
Final pH	**% sorbed**
9.70	57.83
9.86	60.99
8.70	71.60
7.60	82.86
7.57	84.68
7.60	82.74
7.57	83.75
7.72	83.62
7.42	
5.71	94.25
6.19	94.16
6.48	93.03
5.93	92.85

5 ppm As(V), 0.1 N	
Final pH	**% sorbed**
9.34	67.01
8.94	66.51
8.26	75.66
7.90	80.28
8.08	76.77
7.33	85.95
7.47	86.64
6.57	92.31
6.98	91.29
4.55	98.33
4.31	98.55

5 ppm2 As(V), 0.1 N	
Final pH	**% sorbed**
8.78	64.58
7.90	73.51
7.87	71.36
7.73	74.80
7.41	78.53
7.26	78.25
7.00	81.10
6.90	83.03
6.70	84.07
6.68	84.39
6.25	86.61
5.74	89.41
5.59	87.92

10 ppm As(V), 0.001 N	
Final pH	**% sorbed**
9.50	36.70
9.68	41.07
8.68	48.01
8.46	
7.96	49.53
8.85	45.89
7.49	54.49
7.78	57.33
7.83	54.44
5.46	66.80
4.32	72.02
6.11	65.16
4.48	72.07

10 ppm As(V), 0.1 N	
Final pH	**% sorbed**
8.71	37.27
7.11	47.19
6.89	46.17
6.65	47.50
6.63	47.21
6.02	46.92
6.01	44.68
6.00	47.04
5.27	58.82
5.22	58.18
5.20	59.44
5.00	61.38

10 ppm As(V), 0.1 N	
Final pH	**% sorbed**
9.81	35.97
9.92	39.20
9.38	39.58
8.73	45.57
7.58	54.42
7.76	51.28
6.69	61.73
5.29	69.71
5.88	65.96
5.91	68.10

5 ppm As(III) sorption data on 0.1 g/L Kemiron.

10 ppm As(III), 0.001 N sodium nitrate

Final pH	% As(V) removed
9.7	61.5
9.2	65.2
6.6	55.6
7.0	61.8
7.0	58.9
7.3	63.1
7.4	62.6
8.0	69.0
7.1	59.5
6.6	56.7
6.2	53.4
5.7	41.0
4.7	36.7
4.6	31.1
4.6	30.3
4.2	27.3
4.1	26.9
1 ppm As(III), 0.1 N sodium nitrate	
8.9	98.4
8.7	98.9
7.7	98.2
5.9	98.4
5.8	96.1
5.8	98.3
5.8	97.5
5.6	95.1
5.1	92.4
5.1	96.8
4.7	91.1
4.5	88.4
4.3	83.5
4.1	86.6
5 ppm As(III), 0.1 N sodium nitrate	
9.6	78.1
9.6	81.9
9.7	80.7
8.7	87.4
7.3	81.6
6.9	78.4
6.0	69.1
6.3	71.8
6.6	74.3
6.8	76.4
4.0	38.2
4.2	43.8

10 ppm As(III), 0.1 N sodium nitrate

pH	% As(V) removed
8.5	55.0
7.9	59.4
7.8	56.9
7.5	54.9
7.3	57.4
6.1	50.2
5.9	44.3
5.9	44.6
5.1	41.7
4.8	39.8
4.5	38.3
4.3	35.0

5 ppm As(III) Isotherm data on 0.1 g/L Kemiron, I = 0.01 N $NaNO_3$.

pH	Ceq(mg/l)	q(mg/g)
6	0.06	9.28
6	1.30	34.34
6	4.63	52.32
6	13.20	66.13
6	21.23	83.26
6	30.49	92.84
6	39.29	105.03

pH	Ceq(mg/l)	q(mg/g)
7	0.02	9.61
7	1.00	37.18
7	4.18	56.74
7	40.22	95.97

pH	Ceq(mg/l)	q(mg/g)
8	0.01	9.75
8	0.75	39.46
8	11.49	82.79
8	29.95	98.12
8	38.15	116.19

pH	Ceq(mg/l)	q(mg/g)
9	0.01	9.75
9	0.61	40.80
9	3.64	61.98
9	11.59	81.80
9	19.99	94.12
9	30.46	104.76
9	39.27	113.00

5 ppm As(V) Sorption on 0.1 g/L Bayoxide; 0.01 N $NaNO_3$.

0.1g/L BayOxide

5 ppm initial As(V) concentration

Final pH	**% As(V)** 5 ppm
9.3	18.2
9.6	18.5
8.9	
8.8	21.9
8.2	24.0
7.0	26.4
7.0	28.5
6.7	30.0
6.8	31.2
6.3	29.1
6.6	31.8
6.4	34.6
5.4	37.6
5.3	36.3
4.7	41.1

10 ppm initial As(V) concentration

Final pH	**% As(V)** 10 ppm
8.7	3.6
8.3	3.0
7.7	5.4
7.1	9.3
6.7	9.8
6.5	
6.4	12.3
6.4	11.3
6.4	14.6

5 ppm As(V) sorption to 0.1 g/L Kemiron in the presence of Se(IV), I = 0.001N $NaNO_3$.

w 5 ppm Se(IV)

Final pH	**% As(V) removed**
8.97	53.12
8.93	54.51
8.14	56.90
8.28	57.56
7.74	64.11
7.67	65.76
7.19	68.86
6.72	71.11
6.41	73.55
5.05	75.32
5.73	75.57
5.84	75.08
5.05	
4.65	79.73

w 0.5 ppm Se(IV)

Final pH	**% As(V) removed**
8.27	70.88
8.28	67.82
8.96	63.50
8.09	74.92
7.82	76.61
7.73	78.57
7.58	79.16
7.21	86.64
7.07	85.18
6.96	87.60
6.57	89.04
6.35	88.79
5.99	97.07

5ppm As(V) sorption to 0.1 g/L Kemiron in the presence of Ca^{2+}, I = 0.001N $NaNO_3$.

W 0.1 ppm Ca^{2+}

Final pH	**% As(V) removed**
3.81	99.99
5.38	99.95
6.09	99.98
6.55	99.99
5.29	99.96
5.92	100.00
6.34	100.00
6.28	100.00
6.91	100.00
5.96	100.00
6.28	99.65
4.83	100.00
4.33	100.00

w 0.001 ppm Ca^{2+}

Final pH	**% As(V) removed**
8.95	66.98
8.05	76.42
8.35	71.93
8.06	75.49
8.08	76.15
8.14	75.15
7.54	80.95
6.81	86.49
7.43	81.90
7.21	84.43
6.84	88.42
6.43	91.06
6.55	91.19
6.34	92.66
5.85	94.45

5 ppm As(V) sorption to 0.1 g/L Kemiron in the presence of CO_3^{2-} I = 0.001N $NaNO_3$.

0.1 ppm CO32-	
Final pH	% As(V) sorbed
8.27	70.1
7.52	77.9
7.42	79.7
7.37	80.6
3.59	96.6
3.91	95.6
6.14	91.2
6.52	88.8
6.54	90.8
6.88	89.0
6.89	86.8
6.91	89.6
7.13	86.7
6.32	91.5
5.75	94.0
1 ppm CO32-	
9.27	65.3
9.28	65.8
9.16	66.8
8.42	72.1
7.73	80.3
7.53	82.3
7.55	83.0
7.23	86.8
7.33	84.6
6.83	90.1
6.93	88.1
6.73	90.4
4.09	97.3
5.65	93.7
5.21	95.9
100 ppm CO32-	
9.99	58.0
9.91	61.0
9.42	66.8
7.99	82.1
8.14	82.6
8.11	83.1
7.88	86.0
7.49	86.6
7.31	90.2
6.96	90.2
6.73	91.4
6.33	93.5
5.96	94.8
3.82	97.7

5 ppm As(V) sorption to 0.1 g/L Kemiron in the presence of SO_4^{2-} I = 0.001N $NaNO_3$.

1 ppm SO42-	
Final pH	% As(V) sorbed
8.57	70.3
8.79	69.7
8.33	73.9
8.00	76.4
7.75	79.0
7.01	86.3
7.32	83.9
6.97	87.7
6.95	87.4
6.34	92.2
6.26	92.9
5.91	94.5
5.69	95.7
5.48	95.8
4.69	97.7
100 ppm SO42-	
7.80	78.9
8.79	70.3
7.85	79.8
7.50	83.5
7.14	87.6
6.65	89.4
6.32	89.4
5.76	92.0
4.96	91.7
6.90	86.2
6.79	89.0
4.71	95.1
6.73	88.6
4.28	94.6
6.42	89.9

5 ppm As(V) or As(III) sorption to 0.1 g/L Kemiron in the presence of 5 ppm Ni. I = 0.001N $NaNO_3$.

As(V) pH	%As(V) Sorbed
7.93	76.9
7.76	78.3
7.57	81.0
7.25	84.0
7.15	86.0
6.94	88.9
6.59	90.3
6.43	91.9
5.74	94.4
6.97	90.2
4.46	96.7

As(III) pH	% As(II) Sorbed
8.13	79.8
7.72	76.5
7.59	74.8
7.43	74.2
7.35	73.5
6.93	71.8
6.84	68.8
5.70	56.3
7.03	71.1
7.03	72.6
7.24	74.2
7.86	82.2