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REMOVAL OF AS (III) AND AS (V) FROM POTABLE WATER
USING ZNO NANOPARTICLES

A Thesis

by

GRECIA TORREBLANCA BAEZ

Submitted to the Graduate College of
The University of Texas Rio Grande Valley
In partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2019

Major Subject: Chemistry

REMOVAL OF AS (III) AND AS (V) FROM POTABLE WATER
USING ZNO NANOPARTICLES

A Thesis
by
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August 2019

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ABSTRACT

Torreblanca Baez, Grecia, Removal of As (III) and As (V) from Potable Water Using ZnO Nanoparticles. Master of Science (MS), August 2019, 33 pp., 5 tables, 10 figures, references, 23 titles.

Heavy metal contamination of the environment has been increasing since industrialization of the world had begun. Of the toxic elements released through anthropogenic processes arsenic has become a great concern due its toxicity. As toxicity is dependent on the oxidation state present. As(III) is observed to be much more toxic than As(V), as well the removal is much more difficult than As(V) using traditional water treatment technology. In the present study, the removal of As (III) and As(V) was investigated using a zinc oxide nanomaterial. The ZnO nanomaterial was synthesized using a titration/precipitation technique, and characterized using powder x-ray diffraction. In the present study, kinetics of adsorption, adsorption isotherms, influence of contact time, concentration, pH, and temperature on the adsorption of As (III) and As (V) by zinc oxide were studied. In addition, the effect of common anions and cations on the adsorption of As(III) and As(V) were also investigated.

DEDICATION

I would like to dedicate this to my family. My parents Alberto Torreblanca and Carmen Baez. And Hugo, Luis, Layla, Andre.

Thank you for always believe in me, and supported me when I decided to start with this dream and encouraged me to keep going when I thought I could not do it. Thank you for all your support and love that you gave me during this process, everything would have been more difficult without you.

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I am really grateful with all of you because you really gave me all your support and knowledge so that I could be at this point, definitely it was a very hard process for me, but all of you made me achieve it, this would not have been possible without all of you.

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CHAPTER I

INTRODUCTION

The contamination of the environment with heavy metals and toxic elements is an emerging problem all over the world and has been increasing as industrialization has been increasing.

Arsenic is the 53rd most abundant element on the planet and is a natural component of the earth's crust and has been widely distributed throughout the environment. For example, arsenic can be found in the air, water, and soil. Furthermore, As is one of the most toxic ions which poses a serious health risk including increasing the risk of cancer ^[1].

The maximum contaminant level (MCL) of arsenic in drinking water before 2006 was 50 ppb which was established by the United States Public Health Service. However, in January of 2006, the MCL of arsenic was decreased from 50 ppb to 10 ppb by the United States Environmental Protection Agency (US EPA) ^[2] and the World Health Organization (WHO).

Magnitude of the problem

Arsenic is an odorless and tasteless element which can pose a problem for rural communities with a perception that water is clean when it does not have any visible contaminants. Arsenic contamination of ground water is found in many countries throughout the world, including the US ^[3]. It is now recognized that at least 140 million people in 50 countries

have been drinking water containing arsenic at levels above the recently set drinking water standard of 10 ppb ^[4].

The serious health concern that is arsenic can be seen through the mass poisoning of water in Bangladesh ^[5]. It was estimated that in 2012 about 19 and 39 million people were exposed to arsenic concentrations above the maximum contaminant level ^[6]. According to the Bangladesh Atomic Energy Commission, the level of arsenic was between 150 and 200 ppb in well water. In a highly affected area, 21.4% of all deaths were attributed to arsenic levels above 10 ppb ^[7].

However, on the other-hand there are areas in the world where arsenic concentration in aquifers are extremely low. Based on studies performed in 2018 by the Brownsville Public Utilities Board on water samples from natural deposits in the area of Brownsville, Texas, the highest arsenic concentration that was detected was 2.1 ppb ^[8].

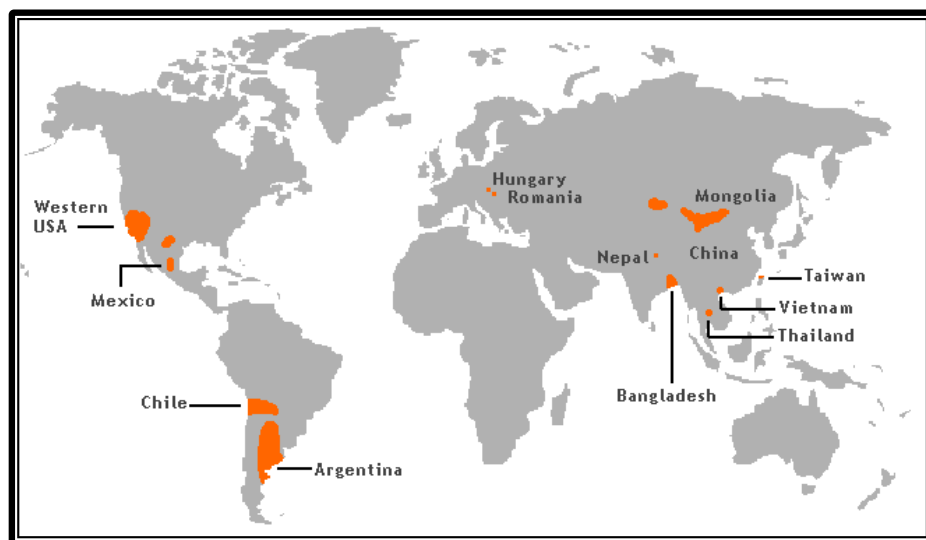


Figure 1. Arsenic contaminated areas.

Arsenic contamination of ground water

Arsenic is a naturally occurring element in the environment and occurs in two common forms arsenite (As(III)), and arsenate (As(V)). However, these compounds do not exceed several parts per billion, in general. Typical background concentrations of arsenic in the atmosphere do not exceed 3 ng/m³, in soils 100 mg/kg, and in fresh water 10 ppb. The low levels of arsenic observed in background concentrations means arsenic is introduced in water sources through a combination of processes which include geochemical reactions, industrial waste discharges, or agricultural use of arsenical pesticides.

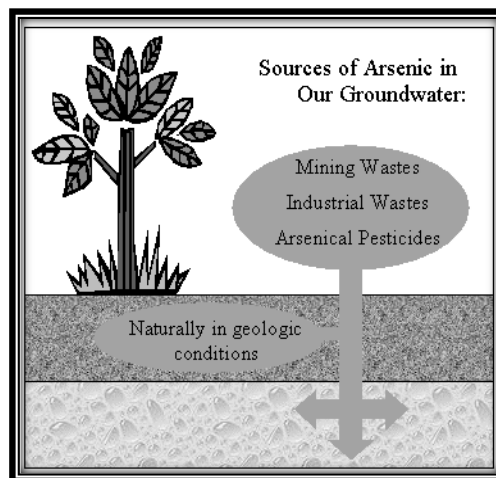


Figure 2. Sources of arsenic in groundwater.

Health effects

The US EPA states that all forms of arsenic are a serious risk to human health, but the toxicity of arsenic varies greatly according to its oxidation state; for example, As (III) is far more toxic than As (V) ^[9]. The International Agency for Research on Cancer (IARC) recognizes arsenic trioxide and arsenic pentoxide, as category 1 carcinogens.

Acute effects

The immediate symptoms of acute arsenic poisoning include vomiting, abdominal pain and diarrhoea.

Long-term effects

The first symptoms of long-term exposure to high levels of arsenic are usually observed in the skin, and include pigmentation changes, skin lesions on hands and feet. These occur after a minimum exposure of approximately five years and may be a precursor to skin cancer. In addition to skin cancer, long-term exposure to arsenic may also cause cancers of the bladder and lungs.



Figure 3. Skin lesions due to arsenic poisoning.

What is the amount of arsenic that can lethally affect our health?

According to the World Health Organization, the estimated dose of arsenic that can cause poisoning is 70 to 200 mg or 1 mg/kg/day. The dosage also depends on who consumes it, if consumed by children; a dose of 70 mg is already toxic to their health. Since adults are already exposed to certain pollutants and chemicals that are present in the environment nowadays, the amount of arsenic poisoning can sometimes exceed to more 200 mg, which is considered lethal.

Arsenic removal technologies

Since As(III) is much more toxic than As(V) the removal of As(III) is more important than As(V) in water treatment technology. It should also be noted that the removal As(III) from aqueous solution is much more difficult than As(V).

Many various physicochemical techniques have been developed to remove arsenic from water. The conventional methods used to remove arsenic include but are not limited to membrane techniques (reverse osmosis, nanofiltration, etc.), oxidation/ precipitation, coagulation and flocculation, ion-exchange, and adsorption. However, these methods have several disadvantages, which include incomplete removal, high capital and operational cost or and the disposal of the residual sludge.

Adsorption processes are effective techniques and they have long been used in water and wastewater industries to remove both inorganic and organic pollution for easy handling, minimal sludge production and in general has a good regeneration capability^[10]. In the present study, As(III) and As(V) removal by adsorption was investigated using a zinc oxide nanomaterial.

Adsorption

Adsorption is defined as the adhesion of a chemical species onto a surface. In adsorption, particles bind to a surface, which is termed the adsorbent. Adsorbents typically have high surface areas which to facilitate higher adsorption densities.

Adsorption depends on surface energy, which can be related to surface atoms of the adsorbent that are exposed so they can attract the adsorbate molecules. Adsorption can result from electrostatic attraction, chemisorption, or physisorption. Chemisorption is a chemical base adsorption in which the adsorption is caused by the formation of chemical bonds between the surface of solids (adsorbent) and the adsorbate. Therefore, the energy of chemisorption is considered like chemical reactions. It may be exothermic or endothermic processes ranging from very small to very large energies. The elementary step in chemisorption often involves large activation energy. This means that the true equilibrium may be achieved slowly. In addition, high temperatures is favored for this type of adsorption, it increases with the increase of temperature. Physisorption on the other hand is a physical adsorption involving intermolecular forces, which do not involve a significant change in the electronic orbital patterns of the species or energy ^[11]. Low activation energies are associated with this type of adsorption. In addition, physisorption low temperature is favorable for the adsorption. Therefore, the physisorption generally decreases with increase temperatures.

Adsorption by nanoparticles

Nanomaterials have been extensively studied for heavy metal ions as well as organic molecules such as the removal of dyes from water. In recent years, numerous nanomaterial adsorbents have been developed for enhancing the efficiency and adsorption of contaminants from water. Nanomaterials have many unique properties that qualify them to be used as effective adsorbents to solve several environmental problems ^[12]. A consistent body of evidence has shown that nano-sized sorbents are more effective compared to their macro-sized counterparts largely due to: (1) the high surface area to mass ratio; (2) high surface reactivity; and (3) unique catalytic activity.

Zinc oxide

Zinc oxide is an inorganic compound with the formula ZnO. It is a white powder that is insoluble in water. In nature it occurs as the mineral zincite, but most of the ZnO used commercially is synthetic^[13]. It is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, etc. Zinc oxide crystallizes in two main forms, hexagonal wurtzite (most common) and cubic.

Chemical formula	ZnO
Molar mass	81.406 g/mol
Appearance	White solid
Odor	Odorless
Density	5.1 g/cm ³
Melting point	1,974 °C
Boiling point	1,974 °C
Solubility in water	0.0004%
Band gap	3.3 eV

Table 1. Zinc oxide properties.

CHAPTER II

MATERIALS AND METHODS

The present study was performed in Department of Chemistry of The University of Texas Rio Grande Valley. The detail of materials used, methodologies employed, experiments and techniques have been elaborated below.

Solutions preparation

All chemicals used were of analytical grade. All solutions were prepared in millipore water (resistivity 18M Ω) obtained with a Milli-Q water purification system and stored at room temperature. All solutions were diluted to the required concentrations in each of the studies.

Zinc nitrate solution

A 60 mmol solution of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Fisher chemical) was prepared by dissolving 17.847 g in 1000 ml of millipore water.

Sodium hydroxide solution

A 120 mmol solution of sodium hydroxide (NaOH) (Fisher chemical) was prepared by dissolving 4.8 g in 1000 ml of millipore water.

As(III) solution

A 1000 ppm solution of As(III) was prepared using 2.64 g of arsenic oxide (As_2O_3) (Alfa Aesar, purity 99.5%) dissolved in 1000 ml of millipore water.

As(V) solution

A 1000 ppm solution of As(V) was prepared using 4.16 g of sodium hydrogen arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) (Alfa Aesar, purity 98%) dissolved in 1000 ml of millipore water.

As (III) cation solutions

Na⁺ solution. A 1000 ppm solution of Na⁺ cation was prepared using 2.54 g of sodium chloride (NaCl) (Fisher chemical, purity 100%) dissolved in 1000 ml of millipore water.

K⁺ solution. A 1000 ppm solution of K⁺ cation was prepared using 1.9 g of potassium chloride (KCl) (EM science, purity >99%) dissolved in 1000 ml of millipore water.

Mg²⁺ solution. A 1000 ppm solution of Mg²⁺ cation was prepared using 8.36 g of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) (ACROS organics, purity 99%) dissolved in 1000 ml of millipore water.

Ca²⁺ solution. A 1000 ppm solution of Ca²⁺ cation was prepared using 3.66 g of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (Fisher chemical, purity 100%) dissolved in 1000 ml of millipore water.

Cations combination. A solution with the combination of all the cations used was made by adding the corresponding grams of each of the cations in 1000 ml of millipore water.

As (V) anion solutions

NO₃⁻ solution. A 1000 ppm solution of NO₃⁻ anion was prepared using 1.37 g of sodium nitrate (NaNO₃) (Fisher chemical) dissolved in 1000 ml of millipore water.

SO₄²⁻ solution. A 1000 ppm solution of SO₄²⁻ anion was prepared using 1.47 g of sodium sulfate (Na₂SO₄) (Fisher chemical, purity 99.6%) dissolved in 1000 ml of millipore water.

PO₄³⁻ solution. A 1000 ppm solution of PO₄³⁻ anion was prepared using 1.49 g of sodium phosphate (Na₂HPO₄) (JT Baker, purity 98.2%) dissolved in 1000 ml of millipore water.

Cl⁻ solution. A 1000 ppm solution of Cl⁻ cation was prepared using 1.64 g of sodium chloride (Fisher chemical, purity 100%) dissolved in 1000 ml of millipore water.

Cations combination. A solution with the combination of all the anions used was made by adding the corresponding grams of each of the anions in 1000 ml of millipore water.

Synthesis of ZnO nanoparticles

The zinc oxide was synthesized using a titration/precipitation technique. Under high-speed stirring, using a Fisher Scientific mini-pump variable flow, 120 ml of the sodium hydroxide solution was added drop wise into a beaker containing 500 ml of the zinc nitrate solution. After adding all the NaOH, the solution was heated to about 50 °C for 2 hours. ZnO nanoparticles were collected using centrifugation with a Fisher Scientific Marathon 8K centrifuge at a speed of 3000 rpm for 5 minutes. The collected nanoparticles were washed 3 times with millipore water, and then dried overnight at about 75 °C.

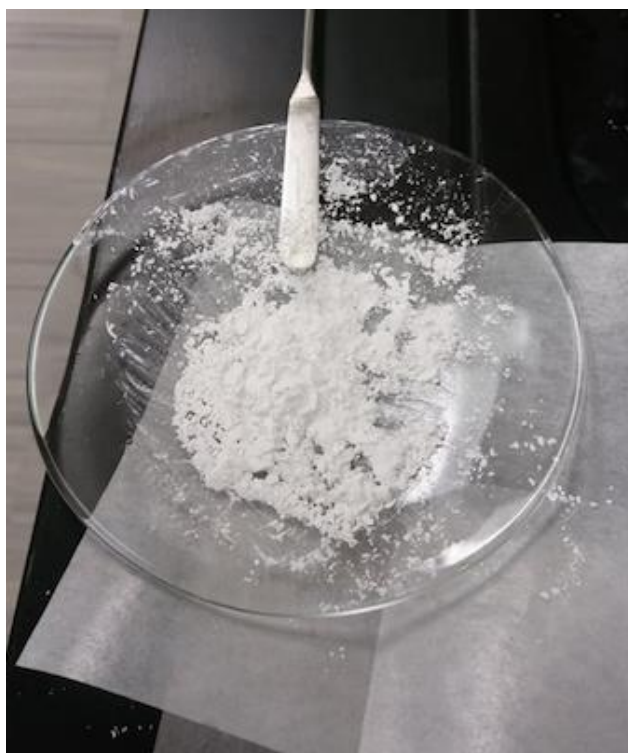


Figure 4. Synthesized zinc oxide nanoparticles.

Characterization

The synthesized ZnO was characterized using powder X-Ray Diffraction (XRD) and all reactions concentrations were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Powder X-Ray Diffraction analysis

To determine the phase of the ZnO nanoparticles, XRD was collected using a Bruker D2 phaser diffractometer fitted with a cobalt filament and a iron filter from 10 to 80 2θ with a 0.05° step size.

Adsorption studies

pH studies

1000 ppm As(III) and As(V) solutions were diluted to a concentration of 0.3 ppm and were pH adjusted. The pH range of 2 through 6 was utilized in the study, which was performed at room temperature. The initial pH values of the solutions were adjusted with either a strong acid (HCl) or a strong base (NaOH). Samples were prepared adding 4 ml of the pH adjusted solutions of either As(III) and As(V) to 10 mg of ZnO into a 5 ml test tube and were shaken continuously for an hour in a Fisher Scientific nutating mixer at a speed of 24 rpm. Subsequent to rocking the samples were centrifuged at 3000 rpm for 5 minutes and decanted. Controls were prepared that contained the arsenic solution in the absence of ZnO. Initial and final arsenic concentrations were compared. In addition, all reaction and control samples were repeated in triplicate for statistical purposes.

Adsorption isotherm

Studies were performed at 4°C, 22°C and 45°C. Arsenic (III) and (V) solutions with concentrations of 3, 30, 100, 300 and 1000 ppm at their respective optimal pH were used. Samples were prepared by adding 4 ml of the solutions of either As(III) and As(V) to 10 mg of ZnO into a 5 ml test tube and were shaken continuously for an hour in a Fisher Scientific nutating mixer at a speed of 24 rpm. After equilibration the samples were centrifuged at 3000 rpm for 5 minutes and decanted. Controls were prepared that contained the arsenic solution in the absence of ZnO. Initial and final arsenic concentrations were compared. In addition, all reaction and control samples were repeated in triplicate for statistical purposes.

Adsorption kinetics

Studies were performed at 10°C, 22°C and 45°C. Arsenic (III) and (V) solutions, at their respective optimal pH, were conducted using an As concentration of 30 ppm. Samples were prepared adding 4 ml of the solutions of either As(III) and As(V) to 10 mg of ZnO into a 5 ml test tube and were shaken continuously for timed intervals of 5, 15, 30, 45, 60, 75, 90, 105 and 120 minutes in a Fisher Scientific nutating mixer at a speed of 24 rpm. Subsequent to equilibration samples were centrifuged at 3000 rpm for 5 minutes and decanted. Controls were prepared that contained the arsenic solution in the absence of ZnO. Initial and final arsenic concentrations were compared. In addition, all reaction and control samples were repeated in triplicate for statistical purposes.

Interference studies

Solutions were prepared at room temperature and adjusted to their optimal pH. Concentrations of 3, 30, 100, 300 and 1000 ppm were used to make the cations and anion solutions while As(III) and As(V) remained at 300 ppb. Cation solutions of Na^+ , K^+ , Mg^{2+} , Ca^{2+} and a combination of all were used for As(III) at according concentrations. Anion solutions of NO_3^- , SO_4^{2-} , PO_4^{3-} , Cl^- and a combination of all were used for As(V) at according concentrations. Samples were prepared adding 4 ml of the solutions of either As(III) and As(V) to 10 mg of ZnO into a 5 ml test tube and were shaken continuously for an hour in a Fisher Scientific nutating mixer at a speed of 24 rpm. Samples were centrifuged at 3000 rpm for 5 minutes and decanted. Controls were prepared that contained the arsenic solution in the absence of ZnO. Initial and final arsenic concentrations were compared. In addition, all reaction and control samples were repeated in triplicate for statistical purposes.

Arsenic analysis

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis

ICP-OES is an analytical technique used for the detection of trace metals in environmental samples. In addition all calibration curves had correlation coefficients of 0.99 or better. Furthermore, any samples that were beyond the calibration curves were diluted to fit within the calibration curves. All reactions concentrations were determined using a Perkin Elmer Optima 8300 ICP-OES with these parameters:

Parameter	Setting
λ	193.696 nm
RF power	1500 W
Nebulizer	Gemcone (low flow)
Plasma Flow	15 L/min
Auxiliary Flow	0.2 L/min
Nebulizer Flow	0.55 L/min
Sample Flow	1.50 mL/min
Injector	2.0 mm Alumina
Spray Chamber	Cyclonic
Integration Time	20 seconds
Replicates	3

Table 2. Parameters used in ICP-OES.

CHAPTER III

RESULTS AND DISCUSSION

In the present study, the kinetics of adsorption, the adsorption isotherms as well as the influence of contact time, concentration, pH, and temperature on the adsorption of As (III) and As (V) by zinc oxide nanomaterial was investigated. From the isotherm studies, performed at three temperatures, the binding capacity of As(III) and As(V) to the ZnO nanoparticles was determined, from the kinetics studies the activation energy of the reaction was determined. The effect of common anions and cations on the adsorption of arsenic was also investigated.

XRD Results

The X-Ray diffraction pattern of the ZnO nanoparticles prepared by the titration/precipitation technique is shown in figure 5. A definite line broadening of the XRD peaks indicates that the prepared material consist of particles in nanoscale range. The diffraction peaks located at 37° , 40.05° , 42° , 51° , 67.05° , 74.97° and 79° can be indexed to ZnO in the hexagonal wurtzite structure ^{[14] [15]}. All the diffraction peaks are in agreement with the reported crystal structure in the JCPDS data ^[16]. The diffraction data confirms the synthesized nanomaterial was free of impurities as ZnO in the hexagonal wurtzite structure.

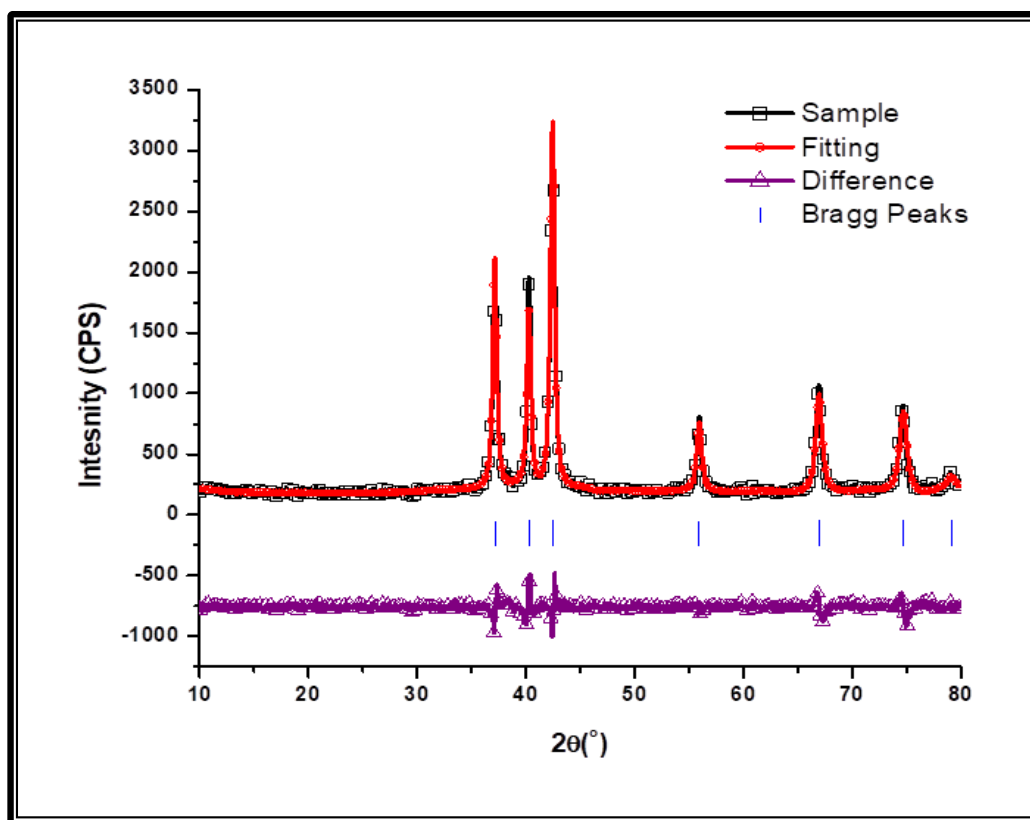


Figure 5. X-Ray diffraction pattern of the synthesized ZnO nanoparticles.

pH studies

The degree of ionization of a species is affected by the pH, and this affects adsorption ^[17]. One of the most critical parameters in the adsorption process of arsenic ions from aqueous solutions is the pH of the medium ^[18]. The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbents ^[19]. The purpose of this study is to investigate the impact of pH on the adsorption capacity of ZnO nanoparticles for the removal of arsenic from water.

The effect of pH on As(III) and As(V) adsorption by ZnO nanoparticles was studied in the pH range between 2 and 6. The results are shown in figure 6. It was observed that the binding of As(III) and As(V) to ZnO nanoparticles was pH dependant and that As(V) was better removed than As(III). Also was observed that the adsorption of As(III) and As(V) was high in the pH range between 2 and 6, with the exception of the adsorption of As(III) with a pH of 5, where the adsorption was the lowest with 81.91%.

It was also observed that at the pH 3 the As(III) and As(V) removal was the greatest, with a 94.12% and 95.19%, respectively. But because that pH is very acidic, it was decided that at a pH of 4 was the optimal pH. At pH 4 the adsorption of As(III) and As(V) was similar to the pH of 3, with a 93% and 95.01%, respectively. Thus pH of 4 was selected for all the following reactions.

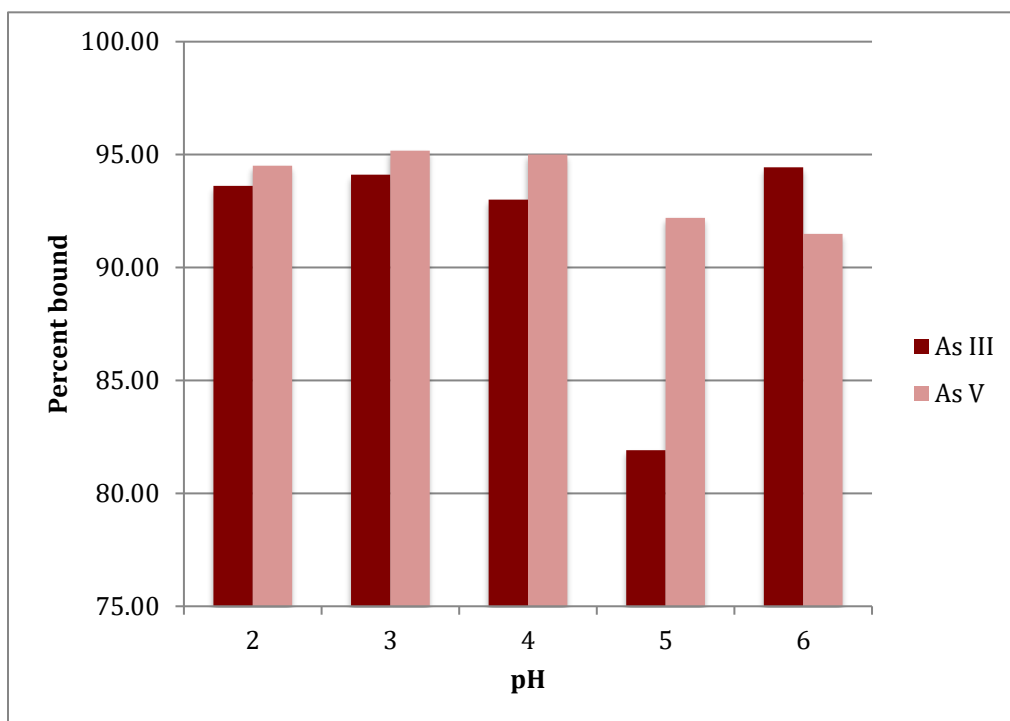


Figure 6. Effect of the pH on the binding of As (III) and As (V) to ZnO nanoparticles.

Adsorption isotherm

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among the solid and liquid phases, and are important data to understand the mechanism of adsorption ^[10]. Isotherms are used to describe adsorption because the temperature has a significant effect on the process. Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir, Freundlich and Temkin models are the most frequently employed models. In this study, the Langmuir model was used to describe the relationship of the adsorbed amount of As(III) and As(V) by the ZnO nanoparticles.

The thermodynamic parameters such as standard Gibbs free energy (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were estimated to evaluate the feasibility and nature of the adsorption process. The values of standard Gibbs free energy change for the adsorption process were evaluated by using values obtained from the Langmuir model at different temperatures and thermodynamic parameters are presented in table 3. The Gibbs free energy change, of the process is related to equilibrium constant by following the equation ^[20]:

$$\Delta G^0 = -RT \ln k_L \quad (1)$$

where T is temperature in Kelvin, R is the gas constant, and k_L is the equilibrium constant obtained from the Langmuir model.

According to thermodynamics, the Gibbs free energy change is also related to the enthalpy change (ΔH^0), and entropy change (ΔS^0) at constant temperature by the following equation,

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (2)$$

Equations (1) and (2) can be equalized to each other and transformed into equation (3).

$$\ln k_L = (\Delta S^0/R) - (\Delta H^0/RT) \quad (3)$$

The values of enthalpy change and entropy change were calculated from the slope and intercept of the plot of $\ln k_L$ versus $1/T$ [21].

It can be seen in table 3 that ΔG^0 values were found to be negative for both systems at 4°C and 22°C indicating that the adsorption process was spontaneous and a positive value at 45°C in both systems indicate a non spontaneous nature. The results for ΔH^0 were found to be 68.18 and 38.45 kJ/mol and ΔS^0 were -215.08 and -130.65 J/mol for As(III) and As(V) respectively. Unlu and Ersoz stated that although there are no certain criteria that are related to the ΔH^0 values defining the adsorption, heats of adsorption between 20.9 and 418 kJ/mol, which are heats of chemical reactions, are frequently assumed to be comparable to those associated with the chemisorption processes [22]. Based on the result of ΔH^0 values, this study suggests that the adsorption of As(III) and As(V) onto ZnO nanoparticles proceeded via chemisorption and that the adsorption process was endothermic in nature. This result is also supported by the increase in the value of uptake capacity of the adsorbent with the rise in temperature. Han et al. (2006) stated that the increasing sorption capacity of the sorbent with temperature is attributable to the enlargement of pores and/or the activation of the sorbent surface [23]. So it was found that the reactions were temperature dependant. Results are shown in table 4.

Sample	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
As(III) 4°C	-8.246	68.18	-215.08
As(III) 22°C	-5.466		
As(III) 45°C	0.583		
As(V) 4°C	-1.995	38.45	-130.65
As(V) 22°C	-0.021		
As(V) 45°C	3.377		

Table 3. Thermodynamic parameters determined from the Langmuir isotherms of As(III) and As(V) binding to ZnO synthesized nanomaterial, at 4°C, 22°C and 45°C.

Sample	Capacity (mg/g)
As(III) 4°C	11.37
As(III) 22°C	7.69
As(III) 45°C	4.46
As(V) 4°C	11.90
As(V) 22°C	90.90
As(V) 45°C	16.69

Table 4. Capacities determined from the Langmuir isotherms of As(III) and As(V) binding to ZnO synthesized nanomaterial, at 4°C, 22°C and 45°C.

Adsorption kinetics

The kinetics of the adsorption process is the measure of the adsorption uptake with respect to time at a constant concentration. The longer residence time means the more complete the adsorption will be. Therefore, the required contact time for sorption to be completed gives important insight into the sorption process. Kinetics also provides information on the minimum time required for considerable adsorption to take place or the efficiency of the process ^[19]. In this study, the samples were shaken continuously for timed intervals of 5, 15, 30, 45, 60, 75, 90, 105 and 120 minutes. The results are shown in figures 7 and 8, for As(III) and As(V), respectively.

As(V) was found to be removed from solution at a much faster than As(III) and the adsorption was greater at a temperature of 45°C compared to the temperatures of 10°C and 22°C in both systems. As(III) and As(V) removal was found to increase with increasing the time. Within the first 5 minutes at 45°C the 48.84% of As(V) was already removed from the solution, compared with As(III) that only the 19.43% was removed at that time. At the end of the 120 minutes, 71.69% of As(V) was removed, compared to the 43.31% of As(III).

It should be noted that at that same temperature (45 °C) the As (V) removal varies slightly after 30 minutes and stayed between 68.89% and 71.69% until reaching the 120 minutes, the same way it can be appreciated that in the removal of As(III) varies slightly after 45 minutes and stayed between 39.32% and 43.31% until reaching the 120 minutes.

From the kinetics studies the activation energy of the reaction was determined. Results are shown in table 5.

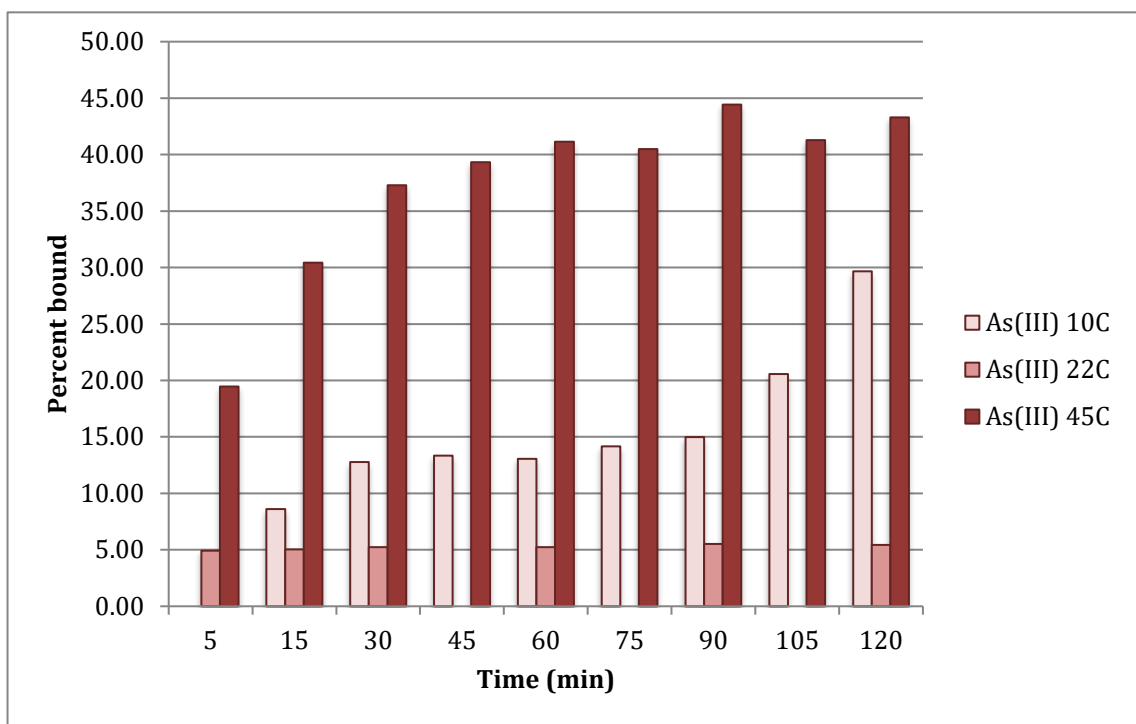


Figure 7. Effect of time on binding of As(III) to ZnO nanoparticles.

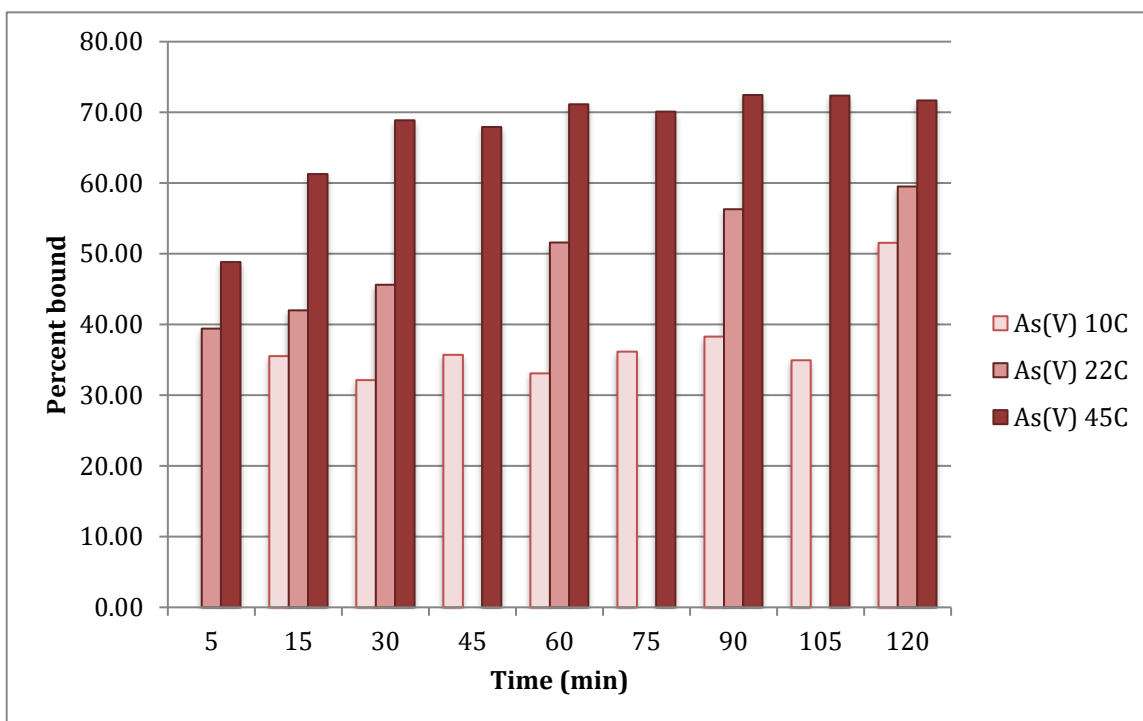


Figure 8. Effect of time on binding of As(V) to ZnO nanoparticles.

Sample	Ea (KJ)
As(III)	115.59
As(V)	34.61

Table 5. Activation energies of As(III) and As(V).

The activation energies are dramatically different between As(III) and As(V), indicating that two different processes are occurring. Arsenic(III) appears to bind through chemisorption. Whereas the As(V) binds through physisorption. The binding can be determined through size of the activation energies. Activation energies above 40 kJ/mol are indicative of chemisorption. Activation energies below 40 kJ/mole are associated with physisorption processes ^[17].

Interference studies

Up to now the adsorption results discussed were obtained by taking As(III) and As(V) as adsorbates in “clean solution”. However, in the real world, water contains several other ions (cations and anions) which can affect possibly the adsorption of As(III) and As(V). In a representative test, the effect of the presence of individual and combined anions and cations such as: sulfate, chloride, nitrate, phosphate, sodium, potassium, magnesium and calcium on the adsorption capacity of ZnO nanoparticles for As(III) and As(V) were investigated. The amount of As(III) and As(V) removal values in the presence of these cations and anions are given in figures 9 and 10.

The binding of As(III) was observed to be only slightly affected as the concentration of Na^+ ions increase causing the binding to decrease. But the binding of As(III) was greatly affected by the K^+ ions interference.

In Figure 10 it can be seen that the binding of As(V) appeared only to be effected to be in the presence of PO_4^{3-} ions and in the presence all the anions combined. As can be seen in Figure 10 as the concentration of the PO_4^{3-} and combined interference increased the binding of the As(V) decreased . It should also be noted that the binding of As(V) was not greatly affected by the NO_3^- , SO_4^{2-} , and Cl^- interferences.

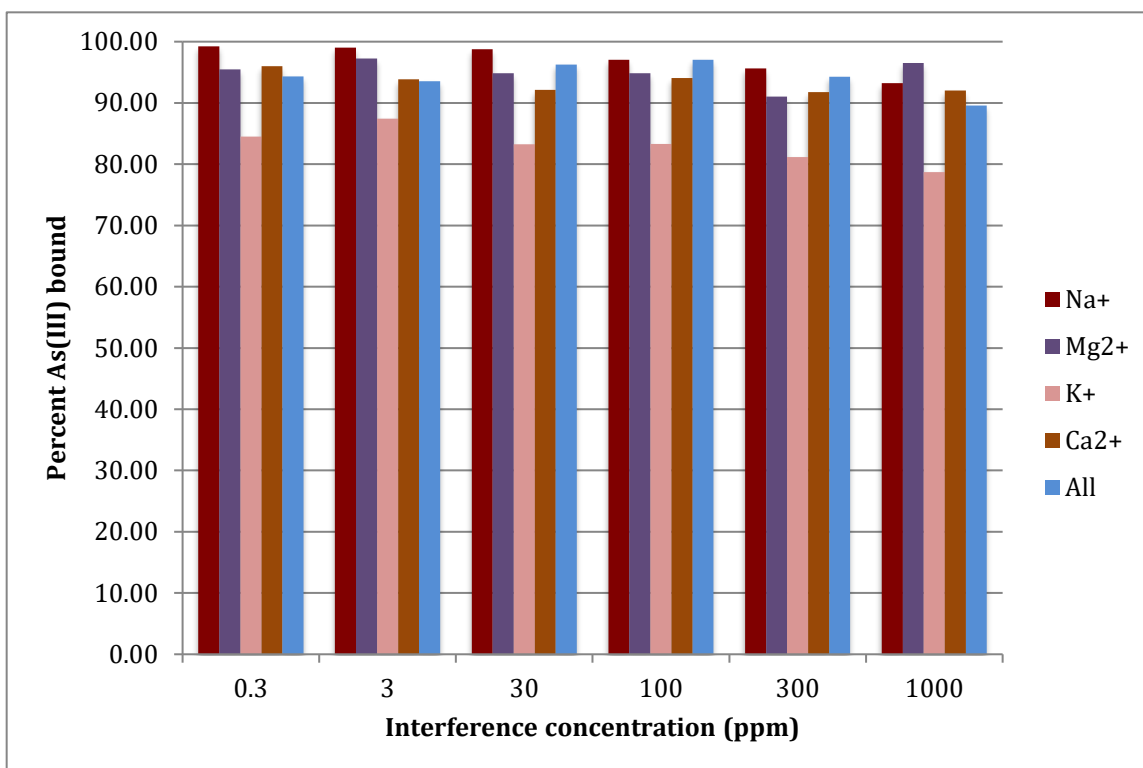


Figure 9. Interference study on As(III) at various concentrations.

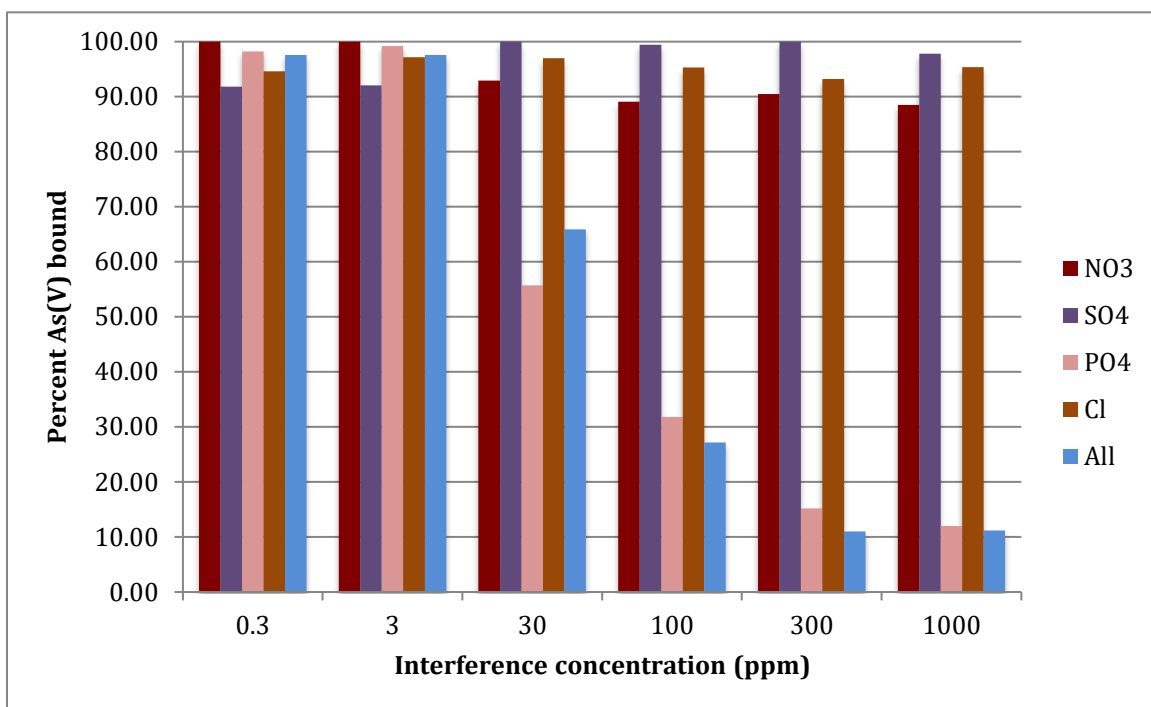


Figure 10. Interference study on As(V) at various concentrations.

CHAPTER IV

CONCLUSION

The present study indicates that ZnO nanoparticles can be used as adsorbent for the treatment of water contaminated with As(III) and As(V). The adsorption process has been shown to be affected from experimental conditions such as pH, initial arsenic concentration, temperature and contact time. Adsorption experiments indicated that arsenic removal was best accomplished in the As(V) state. Batch adsorption studies under varying experimental conditions showed the adsorption of As(III) and As(V) is fairly rapid within the first 30 minutes and increases slowly thereafter. The maximum As(III) and As(V) removal was observed at pH 4.0. The percentage removal of As(III) and As(V) at this pH was 93% and 95.01%, respectively. The isotherm data was observe to fit well to the Langmuir isotherm model, in the studied concentration range at all temperatures studied. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic parameters such as ΔG^0 , ΔH^0 , and ΔS^0 of adsorption. A positive value of the standard enthalpy change suggests that the interaction of As(III) and As(V) is of endothermic nature. The values of ΔG^0 were found to be negative for both systems at 4°C and 22°C indicating that the adsorption process was spontaneous and a positive value at 45°C in both systems indicate a non spontaneous nature. The results for ΔH^0 were found to be 68.18 and 38.45 kJ/mol indicating a chemisorption process. Although based on the activation energies studies As(III) is definitely binds through chemisorption. However, the As(V) activation energy is close but slightly below the limit in the literature for chemisorption,

indicating the As(V) may be binding through a combination of processes both chemisorption and physisorption. ZnO nanoparticles are a suitable candidate as adsorbent in As(III) and As(V) removal techniques.

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BIOGRAPHICAL SKETCH

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