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Cactus Mucilage-Assisted Heavy Metal Separation: Design and Implementation

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Cactus Mucilage-Assisted Heavy Metal Separation: Design and Implementation

by

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A dissertation submitted in partial fulfillment
of the requirements for the degree of
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DEDICATION

I dedicate this work to my mother, Mrs. Albertha King, for encouraging and teaching me to never put limits on my dreams, and to my husband, Mr. Terrence Fox, for his sacrifice which allowed me the opportunity to pursue this dream.

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TABLE OF CONTENTS

LIST OF TABLES iv

LIST OF FIGURES v

ABSTRACT ix

CHAPTER 1
INTRODUCTION 1
    1.1 Motivation 1
    1.2 Research objectives 5

CHAPTER 2
ARSENIC CONTAMINATION OF GROUNDWATER 6
    2.1 Introduction 6
    2.2 Arsenic occurrence 6
    2.3 Aqueous chemistry of arsenic 7
    2.4 Groundwater contamination with arsenic 9

CHAPTER 3
ARSENIC REMOVAL TECHNOLOGIES 10
    3.1 Introduction 10
    3.2 Centralized (conventional) technologies 11
        3.2.1 Precipitation-Coagulation-Flocculation (PCF) 11
        3.2.2 Adsorption 13
        3.2.3 Ion exchange 16
        3.2.4 Membrane filtration 16
        3.2.5 Electrochemical treatment 18
    3.3 Point-of-use (POU) treatment 18
    3.4 Emerging technologies 23
        3.4.1 Bioremediation 23
        3.4.2 Nanotechnology 24

CHAPTER 4
LITERATURE REVIEW 25
    4.1 Cactus mucilage 25
        4.1.1 Mucilage composition 25
    4.2 Mucilage properties 30
        4.2.1 Rheological properties 30

4.2.2 Flocculation by cactus extracts 34
4.2.3 Metal-complexation by cactus extracts..35
4.3 The arsenic system 37

CHAPTER 5

MUCILAGE CHARACTERIZATION: COMPOSITION AND MORPHOLOGY.........40
5.1 Introduction..40
5.2 Experimental 42
  5.2.1 Composition...42
    5.2.1.1 Sugars...42
    5.2.1.2 Inorganic elements 42
  5.2.2 Morphology..43
    5.2.2.1 Transmission Electron Microscopy (TEM) 43
  5.2.3 Surfactant properties 43
    5.2.3.1 Surface tensiometry 43
5.3 Results and discussion 44
  5.3.1 Composition...44
    5.3.1.1 Sugars...44
    5.3.1.2 Inorganic elements 45
  5.3.2 Morphology..46
  5.3.3 Surfactant properties 48
5.4 Summary and conclusions 49

CHAPTER 6

MUCILAGE EXTRACTION METHODS...51
6.1 Introduction..51
6.2 Experimental 52
  6.2.1 Materials 52
  6.2.2 Mucilage extraction (Original method) 52
    6.2.2.1 Cactus pad preparation..52
    6.2.2.2 NE extraction 53
    6.2.2.3 GE extraction 54
  6.2.3 Alternative extraction methods 55
    6.2.3.1 Cut-Scoop-Press (CSP) method.....................................55
    6.2.3.2 Dice-Boil-Press (DBP) method 56
    6.2.3.3 Grate-Boil-Press (GBP) method 56
  6.2.4 FTIR characterization of extracts..56
6.3 Results and discussion 58
  6.3.1 Extraction time and ease of methods 58
  6.3.2 Comparison of ATR-FTIR spectra 59
6.4 Summary and conclusions 63

CHAPTER 7

BATCH/KINETIC STUDIES: MUCILAGE ONLY AND HYBRID MUCILAGE AND IRON SYSTEMS 64
7.1 Introduction..64

7.2 Experimental 65
    7.2.1 Batch experiments...65
    7.2.2 Total Organic Carbon (TOC) analysis 67
    7.2.3 Hybrid iron-mucilage system..67
7.3 Results and discussion 68
    7.3.1 Effect of mucilage type and concentration 68
    7.3.2 Effect of pH...72
    7.3.3 TOC analysis..74
    7.3.4 Mucilage performance in groundwater 75
    7.3.5 Hybrid mucilage and iron system 76
        7.3.5.1 Effect of mucilage concentration 79
        7.3.5.2 Effect of Fe concentration...82
        7.3.5.3 Kinetic experiments 83
7.4 Summary and conclusions 86

CHAPTER 8

MECHANISM OF INTERACTION BETWEEN MUCILAGE AND ARSENATE 90
8.1 Introduction...90
8.2 Experimental 90
    8.2.1 ATR-FTIR film method 90
    8.2.2 ATR-FTIR layer method..91
    8.2.3 UV-VIS spectroscopy 92
8.3 Results and discussion 92
    8.3.1 ATR-FTIR spectroscopy...92
    8.3.2 Mechanisms of interaction...104
    8.3.3 UV-VIS spectroscopy 109
8.4 Summary and conclusions 111

CHAPTER 9

SUMMARY AND CONCLUSIONS 114

REFERENCES 120

ABOUT THE AUTHOR ....End page

LIST OF TABLES

Table 1.1 Arsenic levels in groundwater around the world…………………………….3

Table 3.1 Three best arsenic adsorbents……………………………………………15

Table 4.1 Reported composition of mucilage………………………………………27

Table 5.1 Sugars composition by mass (%) of GE and NE………………………...45

Table 7.1 Arsenic sorption capacity of selected sorbents…………………………..89

Table 8.1 Functional groups assigned to major bands in spectra of gelling (GE) and non-gelling (NE) extracts…...………..……..………93

Table 8.2 Functional groups assigned to major bands in spectra of gelling extract (GE), before and after reaction with arsenic, using the layer method…..……………………………………………...101

LIST OF FIGURES

Figure 2.1 Eh-pH diagram for aqueous As species in the system As-O_2-H_2O at 25 ºC and 1 bar total pressure…………………………………………......8

Figure 4.1 Schematic representations of (a) arabinose (b) galacturonic acid (c) galactose (d) rhamnose and (e) xylose..……………………………...28

Figure 4.2 Proposed chemical structure for cactus mucilage showing a linear "backbone" of galacturonic acid and rhamnose with a branch of either arabinose or xylose……………………………………………..29

Figure 4.3 Arsenic concentrations in samples taken from the air-water interface of solutions treated with GE at different concentrations………………...39

Figure 5.1 Major inorganic elements in extracts of cactus mucilage………………..46

Figure 5.2 TEM images of GE at magnifications of 11kx (l) and 28kx (r), showing a lace-like network with noticeable space between strands……47

Figure 5.3 TEM images of NE at magnifications of 11kx (l) and 28kx (r), showing a smoother, denser polymer network than GE…………………48

Figure 5.4 Surface tension as a function of mucilage concentration……….……….49

Figure 6.1 Photographs of cactus pad preparation showing diced pads (top left), boiling diced pads (right) and neutralizing the blended pads (bottom left)…………………………………………………………………...53

Figure 6.2 Cactus pad preparation showing vacuum filtration apparatus…………...54

Figure 6.3 Schematic representation of deposition of mucilage film on ZnSe crystal……………………………………………………………………57

Figure 6.4 Comparison of the extraction methods by extraction time and ease of operation………………………...…………………….………………59

Figure 6.5 FTIR spectrum of mucilage extracted by CSP method showing the main absorbance bands..……………………………………………...60

Figure 6.6 FTIR spectrum of mucilage extracted by DBP method showing the main absorbance bands……………………………………………….61

Figure 6.7 FTIR spectrum of mucilage extracted by GBP method showing the main absorbance bands ……………………………..………………..62

Figure 6.8 FTIR spectrum of NE mucilage extracted by original method showing the main absorbance bands …..……………………….…….…63

Figure 7.1 As concentrations at the air-water interface of mucilage-treated solutions relative to untreated solutions as a function of mucilage extract and concentration……………………………………………...69

Figure 7.2 Variation in mucilage performance by extract showing mean values (☐), mode (bar inside box), upper and lower quartiles (ends of box) and maximum and minimum values (stems)……………………………70

Figure 7.3 As concentrations at the air-water interface of mucilage treated solutions (GE) relative to untreated control solutions as a function of initial solution pH...…………………………...…………..…………73

Figure 7.4 Mass distribution of mucilage (reported as Total Organic Carbon) in solution………………………...…………….…………………75

Figure 7.5 Mucilage performance in groundwater as a function of concentration….76

Figure 7.6 Mucilage enhanced settling of iron arsenate……………………………..78

Figure 7.7 Removal of As and Fe as a function of mucilage concentration..……….80

Figure 7.8 Comparison of mucilage-treated solutions with solutions treated with Fe only..……………………..……………………………………81

Figure 7.9 Removal of As and Fe as a function of Fe concentration………..………83

Figure 7.10 Kinetics of iron-mucilage system at (a) one hour, (b) 6 hours (c) 24 h and (d) one week……………………………………….....….85

Figure 7.11 Removal of As as a function of Fe hydrolysis...…………………………86

Figure 8.1 ATR-FTIR Spectrum of native Gelling Extract (GE) showing the major absorption bands…………………….……...……………………..94

Figure 8.2 ATR-FTIR Spectrum of native Non-gelling Extract (NE) showing the major absorption bands……………………......…..…………..95

Figure 8.3 ATR-FTIR spectra of GE before (dotted line) and after (bold line) reaction with arsenic……………………………………………………..97

Figure 8.4 ATR-FTIR spectra of NE before (dotted line) and after (bold line) reaction with arsenic………………………………….….……..……....98

Figure 8.5 Expanded sections of GE spectra (top) and NE spectra (bottom) showing the bands undergoing significant change on account of interaction with As…..……………………………………………………99

Figure 8.6 ATR-FTIR spectrum of native gelling extract (GE) in aqueous environment (using layer method)……………………………………...103

Figure 8.7 ATR-FTIR spectrum of gelling extract (GE) in aqueous environment with arsenic (using layer method)…………………………...104

Figure 8.8 Schematic representation of hydrogen bonding/bridging interaction…..105

Figure 8.9 Schematic representation of cation-mediated interaction………………107

Figure 8.10 Schematic representation of donor-acceptor interaction…………..……108

Figure 8.11 UV-VIS spectra of NE with arsenic…………………………………….110

Figure 8.12 UV-VIS absorption spectra of GE with arsenic showing hyperchromic shift at 225 nm and 280 nm……………….……………111

ABSTRACT

Natural contamination of groundwater by arsenic (As) has become a critical public health threat in many parts of the world. The well-known regions associated with As contamination of groundwater are Bangladesh and West Bengal, India where approximately 100 million people are exposed to high levels of arsenic by drinking arsenic-contaminated groundwater and about 35 million are already affected. Long-term drinking of arsenic-contaminated water leads to arsenicosis, which is characterized by cancers of the skin, organ disease and certain other types of cancer. Affected developing communities are at higher risk because they may not have access to conventional water treatment facilities. This problem has focused research efforts on providing accessible arsenic removal technologies. In this study, cactus mucilage, an extract from the *Opuntia ficus-indica* (also known as Nopal and Prickly Pear cactus), is investigated as a natural agent for As removal from water. Cactus mucilage is a natural hydrocolloid with known flocculant abilities and a demonstrated interaction with As. Two mucilage fractions were extracted – a gelling extract (GE) and a non-gelling extract (NE). Two As removal systems were studied: the cactus mucilage acting alone and a hybrid mucilage and iron treatment system. The mechanism of action of the mucilage's interaction with arsenic was also studied. Batch experiments were used to study the arsenic removal systems. Total As was determined with Hydride Generation – Atomic Fluorescence Spectroscopy (HGAFS) and Inductively Coupled Plasma – Mass Spectroscopy (ICPMS). In the hybrid system, iron (Fe) was also determined by ICP-MS. Total Organic Carbon (TOC) analysis

was used to determine mucilage concentration. Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Ultraviolet-Visible Spectroscopy (UVVIS) were used to study the molecular composition. Additionally, the mucilage was characterized by Transmission Electron Microscopy (TEM) for physical morphology and by Laser-induced Breakdown Spectroscopy (LIBS) and High Performance Liquid Chromatography (HPLC) for inorganics and sugars composition.

Both cactus extracts showed an interaction with As by binding and transporting As to the air-water interface of the treatment container, with GE and NE causing a 14% and 9% respective increase in As concentration at the air-water interface. TOC analysis showed that the mucilage migrated to the top of the treatment container but also settled on the bottom. This interaction with As was shown to be pH dependent – optimal performance was at pH 5.5 and 9. The mucilage interaction with As was also dependent on the ionic strength of the solution. ATR-FTIR showed the role of the carboxyl functional group as the binding site for the As(V). The hybrid iron-mucilage treatment system was studied in order to capitalize on the strong affinity of iron for As, as well as to exploit the flocculant properties of the mucilage. Mucilage was successfully applied as a coagulant aid in the removal of As by Fe(III) salt, achieving between 75% to 96% As removal. The process depended on the hydrolysis of the Fe(III) salt to form iron hydroxides and oxyhydroxides, which reacted with and adsorbed the dissolved As(V). The iron arsenate colloidal precipitate which formed was then adsorbed onto the mucilage surface forming larger, heavier, denser flocs. The As removal increased with increasing mucilage concentration reaching a maximum at 100 mg/L GE. Increasing Fe(III) concentration increased the As removal reaching an optimum concentration at 40 mg/L Fe. The As removal had rapid kinetics, achieving visual separation within 10 minutes and completing the majority of the removal within 30 minutes. These results are important because they demonstrate that the mucilage is the versatile basis for an As removal treatment, being able to interact as a complexant for the arsenic as well as an effective coagulant aid for iron arsenate precipitation.

CHAPTER 1

INTRODUCTION

1.1 Motivation

This work explores the use of natural materials from the *Opuntia ficus-indica* (OFI), also known as Nopal, Prickly Pear cactus and Cochineal, to remove arsenic from drinking water coming from groundwater sources. To gain a contextual understanding for the motivation for this work, the incidence of arsenic contamination of groundwater along with the need for accessible technologies will be presented. Cultural sensitivity and indigenous knowledge were critical in choosing OFI and this will be presented along with the vision for cactus-based water remediation technology.

The most well-known regions associated with arsenic contamination of groundwater are Bangladesh and West Bengal, India where approximately 100 million people are exposed to high levels of arsenic by drinking arsenic-contaminated groundwater and about 35 million are already affected (Nordstrom 2002; Kinniburgh, Smedley et al. 2003; Ng, Wang et al. 2003; Ahmed, Ahuja et al. 2006; Chen, Graziano et al. 2011). In 1993, the World Health Organization (WHO) set a provisional guideline value for As at 10 µg/L based on health concerns (WHO 2008). However, in affected areas, levels as high as 48,000 µg/L have been reported (refer to Table 1.1). The WHO found that drinking contaminated groundwater was the major route for groundwater was the major route for arsenic poisoning (WHO 2001). Long-term consumption of arsenic contaminated water leads to chronic arsenic poisoning, and is called arsenicosis. Unfortunately, the symptoms of arsenicosis usually only show up after 5 to 15 years of exposure.

Arsenicosis is characterized by diseases and cancer of the skin, organ disease and certain other types of cancer. The most readily recognized symptom being skin lesions, typically hyperpigmentation and keratosis of the hands and feet and skin cancers. However, the effects are widespread throughout the human body. Rahman et al (2009) reviewed the literature on various effects of chronic arsenic poisoning by drinking water exposure. Arsenicosis affects the respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, and hepatic systems, shows dermatological, neurological and immunological symptoms, is linked to diabetes and also affects pregnancy outcomes. Apart from skin cancer, arsenicosis also leads to cancers of the lung, bladder, liver and kidneys.

Arsenic levels higher than the recommended 10 μg/L have been found in groundwater around the world (refer to Table 1.1). However, the populations most at risk are those in countries with communities that do not have access to centralized conventional water treatment. As such, arsenicosis has become a widespread health issue problem in Bangladesh, West Bengal region of India, Vietnam, Xinjiang Province China and Nepal among others (Mondal, Majumder et al. 2006; Chen, Graziano et al. 2011). However, with the exception of drinking water consumers from private and public wells in the Western US (Kumar, Adak et al. 2010), arsenicosis is not a major public health concern in the United States. This is because the arsenic removal technologies employed in developed countries, namely precipitation (coagulation-flocculation-sedimentation), lime softening, adsorption, ion exchange, membrane filtration, electrodialysis reversal and electrocoagulation, are not accessible to developing communities. Consequently, there is a need in developing communities for accessible technologies for arsenic removal.

Table 1.1 Arsenic levels in groundwater around the world

Adapted from (Mandal and Suzuki 2002; Nordstrom 2002; Garelick, Dybowska et al. 2005; Mondal, Majumder et al. 2006)[#]

Country	**Arsenic concentration (μg/L)**	**Estimated population exposed**
Argentina	1 – 9,900	200,000 – 2,000,000
Bangladesh	<1 – 2500	57,000,000 at > 10 μg/L
Chile	100 – 1000	400,000
China (Mongolia)	40 – 4440	5,600,000
(Xinjiang)	0.05 – 850	>500
Hungary	<2 – 176	400,000
India (West Bengal)	<1 – 3700	6,000,000
Mexico (Region Lagunera)	8 – 624	400,000
Nepal	<10 – 340	3,190,000 at > 10 μg/L
Taiwan	10 – 1820	100,000-200,000
USA (Western USA)	48,000	---
(Southern Iowa and western Missouri)	34 - 490	---
UK	<1 – 80	---
Vietnam (Hanoi)	1 – 3100	> 1,000,000

[#] The most inclusive data from these sources have been presented.

In order to be widely accessible to developing communities, arsenic removal technologies must be readily available, robust, reliable, easy to operate, require little or no fossil fuel energy or maintenance, in addition to being renewable and sustainable. Moreover, social acceptance of the technology is critical for its use.

Plant based materials are very attractive for many of the accessibility criteria. This is because they usually are renewable, abundant, environmentally friendly or benign, adaptable and biodegradable. In many instances, plant based materials used for water remediation are waste products from other primary industries which makes them cost effective as well.

OFI is native to Mexico (Cruz-Hernandez and Paredes-Lopez 2010; Padron, Nogales et al. 2011) and in this study, plant based materials from the cactus were used to remediate arsenic contaminated groundwater in developing Mexican communities because the materials would be accessible to these communities. OFI is highly adaptable and, while suited to arid and semiarid climes, can thrive in almost any climate except for freezing temperature.

In Mexico, the pads of OFI are mainly eaten fresh or cooked in various dishes. They are also used to make several food and cosmetic products and for the production of carminic acid, the main component of a red dye that the plant is known for (Saenz-Hernandez, Corrales-Garcia et al. 2002; Guevara-Arauza, Paz et al. 2011). As such, the water remediation materials made from this plant are also expected to be socially acceptable.

The plants are abundant and renewable, being also grown as forage and fodder, and are under cultivation in 20 countries (Nobel 2002). Inherently, the cactus-based materials are biodegradable which enhances their environmental attractiveness.

1.2 Research objectives

The purpose of this research was to design an arsenic removal treatment which uses cactus mucilage as the active agent. The parameters for the design were that the treatment should be simple, reliable, low cost, easy to operate and maintain, and require little or no fossil fuel energy to work. Additionally, the research was aimed at understanding how the mucilage works to remove arsenic. The specific research objectives were:

(i) To characterize the mucilage extracts in terms of composition and morphology;

(ii) To give a mechanistic description of the interaction of cactus mucilage with dissolved As, and to identify the factors affecting the interaction and

(iii) To design a filter that uses the interaction of the mucilage with arsenic, as well as the flocculant properties of the mucilage, to remove arsenic and particulates from water.

CHAPTER 2

ARSENIC CONTAMINATION OF GROUNDWATER

2.1 Introduction

In this chapter general background information on arsenic will be presented in order to familiarize the reader with its aqueous chemistry and the modes of entry into groundwater. This will provide the basis for understanding the removal technologies.

2.2 Arsenic occurrence

Arsenic is a metalloid in the chemical family of nitrogen; it is solid at room temperature and has a gray color, characteristic to metals. However, elemental occurrence is rare. The concentration of arsenic on earth has been estimated as being between 1.5 mg kg $^{-1}$ to 3.0 mg kg $^{-1}$ (Mandal and Suzuki 2002). It is ranked 20th in abundance among the elements in the earth's crust, occurring in 245 mineral species which include arsenates (60%), sulfides and sulfosalts (20%), and the minor amounts of arsenides, arsenites, oxides, silicates, and As in its native form (Onishi 1969). Major As-containing primary minerals are arsenopyrite (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3). Realgar and orpiment are two commom reduced forms of arsenic. Arsenic occurs in oxidized form in the mineral arsenolite (As_2O_3). Other naturally occurring As-bearing minerals include loellingite ($FeAs_2$), safforlite (CoAs), niccolite (NiAs), rammelsbergite ($NiAs_2$), cobaltite

(CoAsS), enargite (Cu_3AsS_4), gerdsorffite (NiAsS), glaucodot ((Co,Fe)AsS), and elemental As (Greenwood and Earnshaw 1989; Nriagu, Bhattacharya et al. 2007) However, As is also present in water, air and living organisms. The actual concentrations of arsenic in water vary according to the type of water body, whether fresh or saline, surface or groundwater, and also according to the proximity to geothermal and anthropogenic sources. Fresh water usually contains less than 10 µg/L As; however, much higher concentrations are observed close to industrial sources. Oceanic arsenic is estimated at an average 2 µg/L average concentration (Ferguson and Gavis 1972). Groundwater shows the largest variations in arsenic concentrations with geographic locations, mainly due to the geochemistry of the aquifers, but also due to anthropogenic interventions. For example, bore-hole drilling causes oxidative release of As since this provides a source of oxygenation for the water in the aquifer. Also, aquifer storage and recovery (ASR) has been linked to leaching of As from As-bearing rocks by high purity water. In this method of water conservation, treated water is pumped into aquifers during the wet season to be stored for times of need during the dry season. However, the high purity (low ionic strength) of the water is a strong solvent for the aquifer minerals and cases have been reported of high As content in the recovered water due to dissolution of As-bearing minerals.

2.3 Aqueous chemistry of arsenic

Smedley and Kinniburgh (2002) is the accepted source for the aqueous chemistry of arsenic in natural waters. Under conditions expected in natural waters, only arsenic species in the +5 (arsenate) and +3 (arsenite) oxidation states can be expected to prevail.

In oxygenated waters (like surface waters), the (+5) oxidation state is more stable and arsenate predominates; this is shown in Figure 2.1. Moving from low to high pH the following species predominate: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. Conversely, under mildly reducing conditions (as is the case with groundwater and other subsurface waters), the (+3) state is more stable and the arsenite predominates; H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} from low to high pH. Under anoxic conditions and in the presence of sulfur, arsenic forms stable solid sulfides.

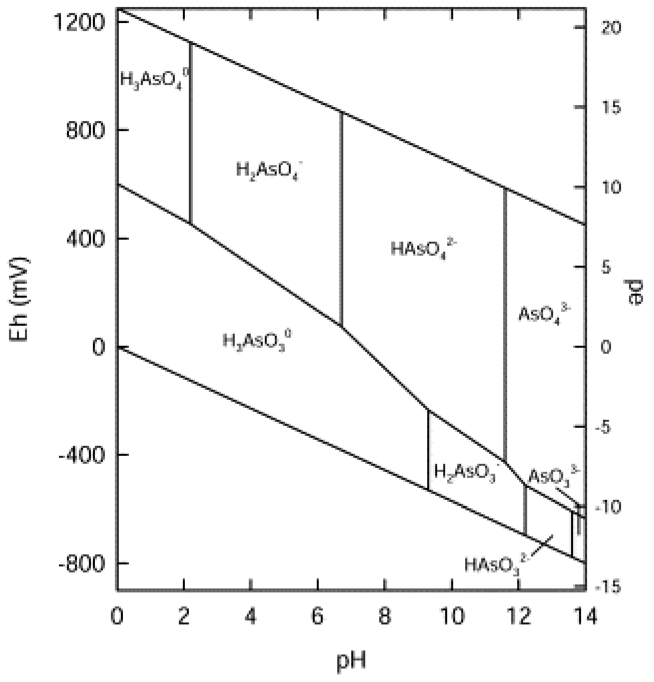


Figure 2.1 Eh-pH diagram for aqueous As species in the system As-O_2-H_2O at 25 ºC and 1 bar total pressure.

2.4 Ground water contamination with arsenic

Welch et al. (2000) described the main mechanisms of ground water contamination with arsenic as oxidation of arsenic-bearing sulfides, desorption of arsenic from oxides and hydroxides, reduction and dissolution of arsenic-bearing ores, influx of arsenic from geothermal waters, and evaporative concentration. Kim et al. (2000) included the leaching of arsenic from sulfides by carbonates. Schreiber et al. (2003) gave an insight into the complexity of the investigative approaches necessary to determine which of the mechanisms may be occurring in any particular instance. These include studying the geologic setting, site mineralogy, hydrogeologic setting, water chemistry, isotopes (as a confirmation of methods of release) and subsurface microbiology (to evaluate the role of bacteria in arsenic release).

CHAPTER 3

ARSENIC REMOVAL TECHNOLOGIES

3.1 Introduction

The reviewed technologies for removing arsenic from drinking water have been classified according to scale of use. Centralized treatments refer to modern, conventional technologies used in developed countries at centralized water treatment plants before the water is distributed via a pipeline network. These are primary treatments, i.e., the water is pumped directly from the source to the treatment plants. Centralized treatments are relatively expensive and rely on economies of scale to be feasible; as such they are only industrially applicable. Point-of-use (POU) treatments refer to home-based technologies used by individuals to treat water before use or consumption. This may be a primary or secondary treatment, and the technologies range from commercially available highly engineered adsorptive filters to home –made cloth or sand filters. In many instances, POU treatments are small scale versions of conventional technologies adapted for home use. Emerging technologies refer to those still under investigation and, while not yet available for commercial or industrial use, show promise in laboratory or pilot-scale trials.

3.2 Centralized (conventional) technologies

3.2.1 Precipitation-Coagulation-Flocculation (PCF)

Coagulation is often used as an umbrella term to describe the three distinct mechanisms involved in this process. The first step is precipitation, which is the conversion of dissolved arsenic species into insoluble salts by a chemical reaction. The precipitate formed is usually colloidal and hence a suspension forms. Coagulation refers to the destabilization of the colloidal suspension by neutralization of charge spheres which prevent individual colloidal particles from approaching closely enough to form larger particles. Flocculation refers to the aggregation of colloidal particles into larger particles or "flocs". The flocs are then heavy enough to settle out of solution due to gravity. Usually the same chemical is used for precipitation and coagulation and is commonly referred to as a coagulant. Commonly used coagulants for arsenic removal include ferric salts, alum, manganese sulfate, ammonium sulfate, and copper sulfate (Mondal et al., 2006).

Although generally referred to as simply coagulation, several mechanisms are responsible for arsenic removed by this method: direct precipitation of an insoluble arsenic salt, adsorption of arsenic species onto forming precipitates and occlusion/entrapment of arsenic species in forming precipitates (Edwards, 1994). Due to its simplicity and familiarity of use in water treatment systems, PCF is one of the most common conventional arsenic removal treatments.

This technology is typically used in conjugation with:

(i) pre-oxidation systems such as chlorination; this is because it has been established that As (V) is easier to precipitate and adsorb than As (III) (Clifford 1990);

(ii) and filtration systems, like sand filters, to effectively remove the precipitate (Choong, Chuah et al. 2007).

The main concern is that the efficiency of this method varies considerably with the chemical (and biological) characteristics of the feed water. Currently, ferric salts ($FeCl_3$ in particular) are documented as the most effective coagulants since arsenic removal is achieved by the two-fold mechanism of reaction with and adsorption/sorption (including occlusion and entrapment) onto the oxides and hydroxides formed in situ (Wickramasinghe, Han et al. 2004; Lakshmanan, Clifford et al. 2008). In recent comparisons with relatively novel coagulants titanium and zirconium, ferric salts emerged the best coagulant in performance and price, while the well-documented phenomena of pH dependent removal and preferential removal of As(V) over As(III) remained (Lakshmanan, Clifford et al. 2008). Interestingly, these researchers found that titanium chloride ($TiCl_3$) was the best coagulant for As(III) removal but suspected that it was due to pre-oxidation to As(V) by hydrolysis of the titanium salt.

Advances in this technology are focused on improving the efficiency. One method is by using more efficient pre-oxidation methods such as ozonation, dissolved air flotation and sonnication in the presence of Fe^{2+} (Kordmostafapour, Pourmoghadas et al. 2006; Tubic, Agbaba et al. 2010; Cui, Jang et al. 2011). Also, oxidation and coagulation can be simultaneously achieved by using combination oxidant-coagulant reagents such as Fe-Mn binary oxides (Wu, Wang et al. 2011). Another area of development is in overcoming the challenges of sedimentation. Several methods are used including providing a surface for the coagulates and using polymeric coagulants and coagulant aids (Song, Lopez-Valdivieso et al. 2006; Ingallinella, Pacini et al. 2011). Also an option is to bypass sedimentation altogether in favor of direct filtration, either with regular coarse filtration systems (like sand) or with membrane filtration which can trap the small coagulates (Zouboulis and Katsoyiannis 2002; Ghurye, Clifford et al. 2004).

3.2.2 Adsorption

This is a heterogeneous process in which the dissolved arsenic ions form physical and chemical bonds with the solid surface of an adsorbent. For maximum efficiencies, adsorbents are usually highly porous materials to present a large internal surface area to the adsorbate (the arsenic ions in this case). Many factors affect the efficiencies of adsorption particularly solution pH and the strength of the interaction between the surface and the adsorbate. Typical adsorbents include activated carbon, activated alumina, greensand (gluconite coated with $KMnO_4$), granular ferric hydroxide, iron oxide coated sand, titanium oxides and copper-zinc granules (Mondal, Majumder et al. 2006).

Mohan and Pittman (2007) have compiled the most recent, comprehensive review (approximately 600 references) of the plethora of adsorbents used for arsenic removal. They compared the arsenic-adsorbing capacity of commercial and experimental activated carbon as well as low-cost sorbents based on the type of water treated, the operational pH and temperature, the arsenic concentration range treated, and the adsorption capacity for As(III) and As(V). Of the adsorbents reviewed, 106 materials dealt with drinking water or its sources (such as ground water and surface water) and experimental synthetic aqueous solutions. Apart from activated carbons, the adsorbents reviewed included:

(i) Agricultural by-products, such as rice husks;

(ii) Industrial by-products, including chars/coals, red mud and slag;

(iii) Soils and sands, including iron-coated sand particles, clay minerals, and zeolites;

(iv) Oxides and hydroxides, including iron oxides and hydroxides, manganese dioxide, activated alumina, zirconium oxides, mixed metal oxides and Portland cement;

(v) Metal-based methods, including zero valent iron (Fe(0)) and metal-chelated ligands; and

(vi) Biosorbents, including chitin, chitosan, cellulose and biomass.

Cognizant of difficulties inherent in comparing data from various sources, the authors nevertheless performed a comparative evaluation to show the 33 best performing adsorbents for arsenic based on arsenic loading capacity. The top three are given in Table 3.1. It is interesting to note that commercial activated carbons did not rank among the top 33. The majority of the materials reviewed were experimental; no pilot or large scale performance data are available to date. The major concerns with adsorbents are regeneration and end-of-life disposal.

Table 3.1 Three best arsenic adsorbents

(adapted from Mohan and Pittman, 2007)

As speciation	Best adsorbents	Approx. loading capacity (mg/g)
As (III)	Goethite	425
	Basic yttrium carbonate	325
	Gibbsite	325
As (V)	Immobilized biomass	700
	Basic yttrium carbonate	425
	Ferrihydrite	260

Research into new sorbents is ongoing. Nanoparticles of iron oxides show promise (Nabi, Aslam et al. 2009; Tang, Li et al. 2011), as well as composite or hybrid sorbents. The composites usually comprise an active material combined with a high surface area material; these include titania on activated carbon and titania-silica on polyacrylonitrile polymer (Yao, Jia et al. 2010; Nilchi, Garmarodi et al. 2011). Additionally, chemically modified biosorbents have received attention, most likely because of the low cost and abundance of the biomaterials. Among these are chemically modified maize cobs (Elizalde-Gonzalez, Mattusch et al. 2008), zirconium-loaded biosorbents (Biswas, Inoue et al. 2008; Huang, Jiao et al. 2008), and iron oxide-coated fungal biomass (Pokhrel and Viraraghavan 2008).

3.2.3 Ion exchange

An ion exchange resin is an organic polymer substrate which has been functionalized to attract anions or cations from solution while releasing a substitute cation or anion from its matrix. Arsenic ions are removed by electrostatic attraction to a strong base anion exchange resin and are exchanged for a (harmless) anion of similar charge (Mondal et al., 2006).

Mohan and Pittman (2007) summarized the results of several trials with metal-impregnated/metal-chelated resins used as cation exchangers. The experimental metals include cerium (IV), copper (II), iron (III), lanthanum (III), yttrium (III) and zirconium (IV). Typically greater than 95% removal was achieved and low pH was generally more favorable. These reviewers reported the use of titanium dioxide and coconut coir pith as novel active agents in anion exchange resins, giving better than 95% removal. The main limitation for ion exchange resins is that waters with high ionic strengths and high levels of total dissolved solids provide competing ions which may be selectively exchanged and significantly compromise the method's performance.

3.2.4 Membrane filtration

Membranes are semipermeable organic sieves with very small pore sizes which selectively allow solution components through. A high pressure is used to push the solution through the membranes; contaminants are rejected based on their size and the pore size of the membrane; they accumulate on one side of the membrane forming the concentrate (waste stream).

There are four types of membranes categorized by their pore size:

(i) microfiltration (MF) with pore sizes greater than 50 nm;

(ii) ultrafiltration (UF) with pore sizes in the range 2-50 nm;

(iii) nanofiltration (NF) with pore sizes less than 2 nm; and

(iv) reverse osmosis (RO) with pore sizes less than 1 nm.

Choong et al. (2007) reviewed the membrane based research for arsenic removal between the periods of 1992 to 2005; the key points emerging were that NF and RO are the best of these technologies and can remove As (III) and As (V) to produce water with the desired 10 ppb As level. NF appears to be the more robust, achieving 99% total As rejection without preferential rejection of As (V) over As (III). Further it was reported that there was evidence for size exclusion being the dominant separation mechanism and that co-occurrence of dissolved inorganics was not a threat to As rejection. The main concerns were the cost of a high pressure system, and the preservation of membrane life (threatened by fouling and chemical attack).

3.2.5 Electrochemical treatment

Electrochemical treatments may have different objectives including:

(i) electrochemical reduction of dissolved As (III) and As(V) to the metallic arsenic;

(ii) electrodialysis, in which an electric current is applied across a semipermeable membrane to prevent the arsenic ions from passing through;

(iii) electroprecipitation of dissolved arsenic species;

(iv) electroprecipitation of iron oxides to entrap/adsorb arsenic species.

This method has not received much current study and this may be due to projected constraints in making it energy feasible as a drinking water treatment option. Further, the operational conditions studied are not reflective of natural source waters but rather more likely found in industrial aqueous waste streams.

3.3 Point-of-use (POU) treatment

Small scale and household arsenic removal units are feasible when, due to size or cost, conventional, centralized water treatment systems are not accessible. In many instances, these smaller point-of-use (POU) systems, whether house hold or community based, are simply downsized versions of the conventional technologies. Much research is ongoing into appropriate technologies for small scale and household use in rural, developing communities. The objective is to have effective, low cost technologies which are easy to operate and maintain, and require little or no fossil fuel energy or added chemicals to work. In reviewing the literature, iron or iron oxides are used in almost all these technologies to capitalize on the strong affinity of iron and iron oxides for arsenic. Further, sorptive filtration technologies appear to be preferred over others, presumably due to ease of operation. The following discussion reviews the technologies categorized by mode of action that have a specific focus on household (or small scale) application.

Iron-based adsorption is popular in three formulations: zerovalent iron (Fe^0), iron oxides/composite iron matrix (CIM) and iron oxide coated sand (IOCS). Zerovalent iron, commonly used as iron filings, was reported to remove greater than 93% of 2000 µg/L As (Ramaswami, Tawachsupa et al. 2001) and between 68 to 100% of 34 to 105 µg/L As (Awuah, Morris et al. 2009). This formulation is attractive because of its simplicity allowing the contaminated water to be poured through a bed of the filings or decanted after being mixed with the filings.

Iron Oxide Coated Sand (IOCS) is made by heating the sand and an iron salt to high temperatures. The product is the porous sand being coated with iron oxides formed from the heat treatment. IOCS is able to produce treated water that meets the 50 µg/L As level mandated in some developing countries (Yuan, Hu et al. 2002) and even the 10 µg/L As level recommended by the WHO (Van Den Bergh, Du Laing et al. 2010). Additionally, because it is a sand filter, the IOCS media can remove sediments and lower turbidity and also remove some microbial load. The media does become clogged and requires washing, and it requires regeneration with NaOH. IOCS has been tested in Shanyin county, Shanxi province (China) and was able to reduce As concentration from 202 µg/L to 1733 µg/L down to 50 µg/L (Yuan, Hu et al. 2002).

Iron oxide sorptive treatment is exemplified by the Kanchan™ filter. This is a modified biosand filter developed by the Massachusetts Institute of Technology (MIT) and the Environment and Public Health Organization (ENPHO) of Nepal (Ngai, Shrestha et al. 2007). Simply, it consists of a plastic or concrete container filled with gravel, sand, brick chips and iron nails. The nails rust and As is adsorbed unto the iron oxide layer on the rusty nails. The filter achieves 88% to 95% As removal. The nails need to be replaced every three years at a production of 25 L/h. It was deployed and evaluated in Nepal meeting the 50 µg/L As Nepali effluent criteria.

A combination of different iron forms is referred to as a composite iron matrix or CIM. The SONO filter, developed by Dr. Abdul Hussam's team at George Mason University is the most successful example of a CIM filter, winning the Grainger Challenge Prize for "sustainability with the highest award for its affordability, reliability, ease of maintenance, social acceptability, and environmental friendliness, which met or exceeded the local government's guidelines for arsenic removal" (Hussam and Munir 2007). The filter consists of a two bucket system. In the first bucket the water is purified by passing through coarse sand, brick chips and the active CIM material, which is a proprietary blend of cast iron turnings. Mn in the CIM catalyzes the oxidation of As(III) to As(V), reducing the concentrations of both species in solution. The filter was able to treat influent As concentrations ranging from 32 µg/L to 2423 µg/L down to less than the recommended 10 µg/L. The conservative lifetime estimate of 14 years means that there is less waste media to dispose of. With the exception of the SONO filter, the common challenges to these technologies include disposal of spent filter media, clogging of filter media and hazards of chemically regenerating the filter media. Other sorbents include laterite (Viet, Con et al. 2003; Kumar, Anjali et al. 2008), plain sand filters (Berg, Luzi et al. 2006), wood and charcoal filters (Singh 2007) and activated alumina (Sarkar, Gupta et al. 2005).

Arsenic removal by coagulation has been successfully scaled down to household treatment level. Ferric salts (mainly sulfate) and an oxidant, such as hypochlorite, are mixed into the contaminated water forming coagulates. The water is then passed through a sand filter which traps the coagulates (Meng, Korfiatis et al. 2001; Yuan, Luo et al. 2003; Cheng, Van Geen et al. 2004). Additional technologies for arsenic removal include aeration (oxidation), subsurface aeration (van Halem, Heijman et al. 2010), ion exchange (Sarkar, Blaney et al. 2007), and membrane filtration (Manna, Sen et al. 2010).

Ahmed et al. (2005) compiled a technical report on the major household and community level POU (and point of extraction) technologies currently employed in South and East Asian countries, where the majority of households received their water supply from tubewells. This provides insight to the typical POU formulations available in developing countries. These technologies are all adaptations of conventional technology in terms of scale and ease of use and maintenance, and were organized according to method of operation as oxidation-sedimentation, coagulation-sedimentation-filtration, sorptive media and membrane technology.

The basis of the oxidation-sedimentation method is to promote oxidation As(III) to As(V) and iron naturally present in the ground water to iron oxides which will adsorb As(V) species as they precipitate. The common oxidants used are those cheaply and readily available in developing countries – air (atmospheric oxygen), bleach (hypochlorite) and permanganate. In one method, water extracted from a tube well was aerated and returned to the well to promote the oxidation mechanisms. Sedimentation of the precipitates is usually achieved by passive sedimentation, i.e. letting the water sit in a vessel. Solar oxidation was also done by putting water in translucent plastic bottles out in the sun, but this was not time efficient.

Several formulations for the coagulation-sedimentation-filtration technology adaption were reported. Each one consisted of a means of mixing the coagulant into the extracted water, a means to allow the arsenic-containing precipitate to settle and a means of filtering the clean water to reject the precipitate. Conventional coagulants (alum and ferric salts) and sand filters were usually employed.

A variety of sorbents (some indigenous to the region) were used to provide community level treatment (15 to 100 households) including activated alumina, granular ferric hydroxide (GFH), iron-coated sand and other iron-adsorption based materials.

3.4 Emerging technologies

3.4.1 Bioremediation

Bioremediation is an umbrella term for technologies based on living (or once-living) organisms. This field is receiving significant research attention because of the advantages of low material and energy costs. Bioremediation can be differentiated (although not exhaustively) into:

(i) bioaccumulation – active uptake and storage of pollutants by organisms;

(ii) biosorption – passive sorption by immobilized biomass; and

(iii) biodegradation – the direct or indirect conversion of contaminants to less harmful or less available species by metabolic processes of organisms.

The kinetics of bioaccumulation, particularly in the case of plants, usually precludes the incorporation into real-time treatment processes. Mohan and Pittman (2007) provide a useful compilation of the range and performance of biosorbents currently under investigation. These include: chitin and cellulose and their derivatives, various fungi (notably *Garcinia cambogia* and *Penicillium purpurogenum*) and plant and plant extracts. Water hyacinth (*Eichornia crassipes*) has received attention due to arsenic removal abilities of the live plants and its dried roots. Young et al. (2006) presented evidence that mucilage from the Prickly pear cactus (*Opuntia ficus-indica*) is a promising natural material for arsenic removal. Zouboulis and Katsoyiannis (2005), in an example of indirect biodegradation demonstrated that biological iron oxidation was effective in removing As(III) and As(V) from water mainly by adsorption onto the iron oxides produced.

3.4.2 Nanotechnology

In recent time, researchers have been seeking to focus nanotechnology on the arsenic removal problem. Generally the means was to replace the active materials in conventional treatment setups with nanoparticles. Two recent studies illustrate this concept:

(i) Peng et al. (2005) prepared ceria nanoparticles supported on carbon nanotubes (CNTs) as a novel adsorbent for As(V) removal from water. The maximum loadings were around 80 mg/g and sorption depended on pH and the concentration of Mg^{2+} and Ca^{2+} ions.

(ii) Sylvester et al. (2007) created an anion exchanger resin by impregnating nanoparticles of hydrous iron oxide into porous polymeric beads. The noted advantages of this material were durability and length of continuous performance (between 91 to 122 days) before recharging was needed.

Several other functions of nanocatalysts can be harnessed for this application but the main limitation will be the feasibility of using a highly-engineered (and hence costly) material for widespread water treatment applications.

CHAPTER 4

LITERATURE REVIEW

4.1 Cactus mucilage

4.1.1 Mucilage composition

Cactus mucilage is the clear, colorless slimy fluid secreted by cactus pads when they are cut or pressed. Mucilage production is characteristic of the Cactaceae family and was shown to play a key role in water retention and release (Nobel, Cavelier et al. 1992).

The terms “cactus mucilage”, “cactus pectin” and “mucilage gum” have been used interchangeably in the literature to refer to two distinct carbohydrate polymer fractions; an extract which gels in the presence of Ca^{2+} ions, and a non-gelling extract (Cardenas, Goycoolea et al. 2008). The main distinction between the two is that the gelling extract is a pectin. Within this document, the term mucilage (abbreviated Mu) will be used generically while the two specific extracts will be differentiated as GE for the pectic gelling extract, and NE for the non-gelling extract.

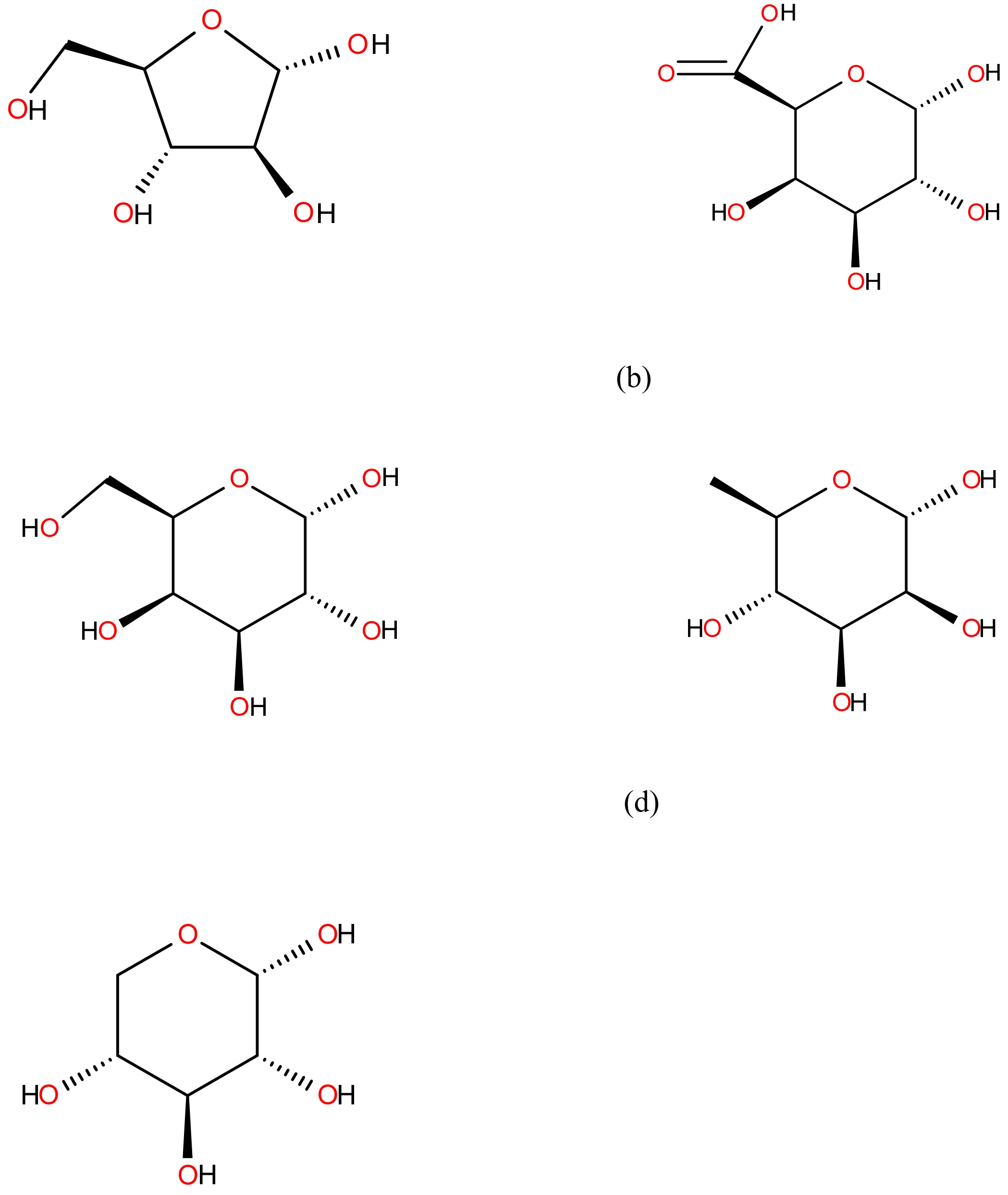
With specific reference to *Opuntia ficus-indica*, commonly known as Prickly Pear cactus (USA) or Nopal (Mexico), the NE is a heteropolysaccharide blend comprising mainly L-arabinose, D-galactose, L-rhamnose and D-xylose as well as galacturonic acid

(Amin, Awad et al. 1970; Saag, Sanderson et al. 1975; McGarvie and Parolis 1979; Paulsen and Lund 1979; Trachtenberg and Mayer 1981; Forni, Penci et al. 1994). The NE is produced in the mucilaginous cells found mainly in the parenchyma (inner whitish tissue) but also in the chlorenchyma (green outer skin) of cactus cladodes (Terrazas and Mauseth 2002). The GE is also known as cactus pectin. Pectins are found mainly between the cells and in the primary cell walls in most plants (Stephen 1983; O'Neill, Albersheim et al. 1990). Pectins are polyuronides composed of a linear or "smooth" α-D-galacturonic acid backbone supporting neutral sugar residues branches referred to as "hairy" regions (Schols and Voragen 2002). GE was shown to have considerable chemical group similarity to the more widely studied citrus pectin (Cardenas et al. 2008). The neutral sugars found in GE strongly resemble the sugars in NE, namely L-arabinose, D-galactose, L-rhamnose and D-xylose and galacturonic acid. However, the main difference is that the GE has a much higher proportion of galacturonic acid (Goycoolea and Cardenas 2003). Table 4.1 below shows some reported compositions of mucilage extracted as the non-gelling extract, NE. Schematic representations of the sugar residues in mucilage are shown in Figure 4.1.

Table 4.1 Reported composition of mucilage

Source	**Composition (%)**	**Comments**
McGarvie and Parolis (1981a)**	Galactose 18.4 Arabinose 42.4 Xylose 24.5 Rhamnose 6.4 Galacturonic acid 8.4	This was a purified aqueous extract precipitated with acetone (mostly NE). Rhamnose and galacturonic acid in core, other sugars in periphery. Beta linkages for rhamnose, galactose and xylose; arabinose link uncertain.
Paulsen and Lund (1979)	Similar sugars but with different proportions in different fractions of extract.	Separated an aqueous extract following ethanol treatment of pad by chromatography. Yielded one neutral and two acidic fractions.
Saag et al. (1975)	Similar sugars found in other *Opuntia* species.	
Amin et al. (1970)*	Arabinose 37.5 Galactose 35.7 Xylose 15.5 Rhamnose 11.5 Uronic acids ---	Arabinose shown to be a terminal group giving agreement with McGarvie and Parolis (1981a). Fifty-five (55) sugar residues comprise the mucilage polymer.

Legend: **Mole% *Mass%



(a)

(b)

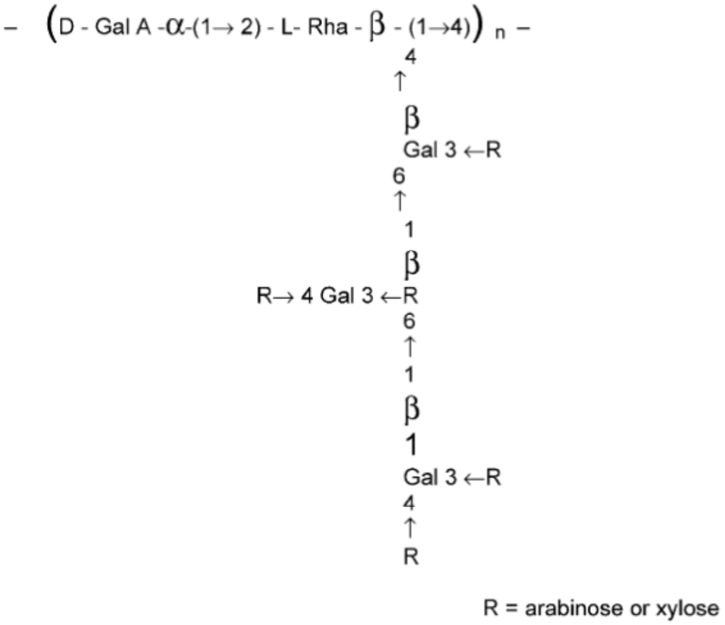
(c)

(d)

(e)

Figure 4.1 Schematic representations of (a) arabinose (b) galacturonic acid (c) galactose (d) rhamnose and (e) xylose

McGarvie & Parolis (1981b) first proposed a structure for cactus mucilage, most likely referring to a co-extract of NE and GE. The abbreviated structure is shown in Figure 4.2 below and proposes a linear backbone of galacturonic acid and rhamnose with branches of arabinose and xylose.



R = arabinose or xylose

Figure 4.2 Proposed chemical structure for cactus mucilage showing a linear “backbone” of galacturonic acid and rhamnose with a branch of either arabinose or xylose (McGarvie and Parolis 1981)

There have been differences reported in the literature regarding the components and proportions of components in the cactus extracts. Several factors are responsible including differences in extraction methods, co-extraction of GE and NE, which occurs when the parenchyma and skin cells are not separated, and differences in fraction determination. GE and NE contents vary among varieties of *Opuntia ficus-indica* (Nobel, Cavelier et al. 1992; Valdivia and Urdaneta 2004), and also with time or season of harvest (McGarvie and Parolis 1979). Irrigation and temperature also influenced mucilage production (Nobel, Cavelier et al. 1992). As with any plant, soil composition, climate, and environmental factors, are expected to impact the exact composition of secondary metabolites.

4.2 Mucilage properties

GE and NE have been studied with the intent to find industrial applications for this naturally abundant and highly adaptable plant. Most of the applications are centered on the food industry, but include dietary and medical applications (Saenz, Sepulveda et al. 2004). Since the current study deals with an aqueous application of the mucilage, it is important to understand the documented properties which most significantly impact how the mucilage behaves in water, namely the rheological properties, and the gelling and aggregation behavior.

4.2.1 Rheological properties

In this section, the inferences about conformational changes to the mucilage polymers brought about by the ions present in solution will be illustrated by reviewing their rheological properties. This is important for the current study because conformational changes involve and dictate availability of "active sites" on the polysaccharide polymers to interact with the ionic species and also the types of separation methods needed to effect removal.

The slimy texture of cactus mucilage has fuelled several investigations into its rheological properties. It should be noted that researchers often did not distinguish between GE and NE, and with notable exceptions, did not use rigorous enough methods to preclude co-extraction. This is because most methods prescribe maceration of the cladode, in which case it is very difficult to exclude cell wall components (such as pectins) to co-extract with the mucilage.

Cardenas et al. (1997) studied the NE rheology and reported shear thinning behavior; that is, as more stress is applied to the NE, the viscosity decreases and flow rate increases. Since this rheological response is typical of polymers which adopt a random, disordered coil conformation (Morris 1990), it gave the researchers first insight into the NE configuration in solution. They reported that the shear thinning was dependent on NE concentration and drew a comparison to the similar behavior of okra mucilage (Meister, Anderle et al. 1983; Ndjouenkeu, Goycoolea et al. 1996). Based on this similarity they extrapolated that, since the constituents of okra mucilage were known to aggregate, it was possible that the NE polysaccharide polymers were undergoing a similar aggregation. These findings are important to the current study because, depending on the mechanism of aggregation, these conformational changes may either be harnessed to benefit the intended use or heavy metal removal or be prevented if it presents a competing scenario. Medina-Torres et al. (2000) did a more comprehensive study of the rheological properties of NE with the potential application of using the material as a food additive. They found that NE showed similar shear thinning properties as reported earlier by Cardenas et al.

(1997); their findings also pointed to the NE assuming a random coil formation, typical of non-gelling carbohydrate polymers.

Changes in NE behavior with pH and salt (cation) concentration were of interest to the current study. Viscosity decreased with increasing salt concentration and increased with increasing pH. From these observations, the researchers deduced that the NE was negatively charged. Further, they explained their observation of increasing NE viscosity with increasing pH as being the result of a more expanded configuration for the mucilage due to intermolecular repulsions by the negative charges. These conclusions are of interest to the current study because pH and ionic strength are parameters which may vary in water bodies. Further, it is expected that conformational changes may influence the way the NE interacts with dissolved species.

Madjoub et al. (2001) also investigated rheological properties of cactus extracts; however, their extraction methodology was significantly different from those in preceding research, involving significant ultrafiltration of the product. They extracted two fractions; a high molecular weight extract with polysaccharides and galacturonic acid (which they thought to be pectin) and a low molecular weight extract thought to be a protein. Rheological trials on their high weight sample showed shear thinning which was significant in the presence of Ca^{2+} ions. This behavior was notably similar to the findings of Medina-Torres et al. (2000) working with NE. The consensus was that shear thinning was due to a random coil formation of the polysaccharide polymer components

(Cardenas, Higuera-Ciapara et al. 1997; Medina-Torres, Brito-De La Fuente et al. 2000; Majdoub, Roudesli et al. 2001).

Cardenas et al. (2008) extracted GE (cactus pectin) to study the mechanism of gel formation. They were sure that they extracted pectin by significant FTIR coincidence with citrus pectin; their extract was predominantly galacturonic acid. They observed that at high temperature (85 ºC), the material forms a loose gel network where Ca^{2+} acts as a cross-linker and the degree of cross-linking was related to the Ca^{2+} concentration. At low temperature, a denser polymer network formed with T_{gel} (critical temperature of gelation) increasing with increasing stoichiometric amounts of Ca^{2+}. The researchers proposed that at higher temperatures, the GE assumed the "egg-box" conformation first proposed by Grant et al. (1973). The egg-box model refers to a two-fold (2_1) zig-zag type conformation of the polysaccharide polymer strands where the ion is bound to the inner faces of both strands to form a larger, even three dimensional ensembles. Cardenas et al. (2008) essentially proposed that at high temperatures, the cactus pectin forms short range egg-box type associations which give it the loose gel network. However, at low temperatures extended egg-box type associations form as well as aggregation, due to lower chain mobility and Ca^{2+} mediated charge neutralization. This mechanism is described to underscore the sensitivity of the mucilage to the chemistry of its aqueous environment.

4.2.2 Flocculation by cactus extracts

The practice of using cactus mucilage to clarify dirty water is indigenous to Mexico and dates back to remote times. The author was informed by personal communication (Alcantar 2007) that the waster used to boil the cactus pads (in preparation of nopalito salad) was added to cloudy, dirty water, which would become clear. However, there was no scientific understanding of the mechanism by which the cactus mucilage clarified the dirty water. This motivated the Alcantar[1] group to undertake the pioneering effort.

Young (2006) modeled turbid water with kaolin slurries and compared the extracts' abilities to clarify the turbid water against aluminum sulfate (aka alum), a commercial flocculant by comparing the rate of kaolin settling in a column of turbid water. They reported that all the cactus extracts outperformed the alum and that the gelling extract was the best flocculant overall, settling kaolin at a rate 300 times the settling rate of the alum test (Young 2006; Young, Pichler et al. 2008).

This work was extended by Buttice (2009) who examined the role of water characteristics in turbidity removal. Buttice observed that for both extracts studied (GE and NE), kaolin setting rates increased with increasing ionic strength of the model water. This settling rate also increased with increasing concentration of GE and NE but up to an optimal point. High magnification images of the model water samples showed aggregated flocs of kaolin in extract-treated water as against free-floating kaolin particles in untreated controls. From these observations, the turbidity removal was shown to be due to extract-induced clumping (flocculation) of kaolin particles. In a novel application of cactus

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extracts, Buttice (2009) also investigated bacteria removal from water. Gram-positive *Bacillus cereus* was flocculated from water using GE and NE in the presence of Ca^{2+} ions; optimal removal rates were between 95-99%. Buttice reported an interesting reversal in bacteria flocculation; both GE and NE were more effective at lower concentrations (0.5 to 4 ppm) but were not effective above 10 ppm. The flocculation performance improved with increasing Ca^{2+} concentration.

In a related endeavor, Miller et al. (2008) reported turbidity removal from model turbid by sorbents made from different parts of *Opuntia spp.* cladodes. Based on the method of preparation, the sorbents would have retained both mucilaginous and pectic polysaccharides. They proposed adsorption and bridging as the mechanistic model for turbidity removal by their sorbents.

The flocculation ability of the cactus mucilage is not expected to play a significant role in their interaction with dissolved species. However, these mechanisms are critical to understanding complex multi-contaminant systems and demonstrate the versatility of the mucilage as a water treatment material.

4.2.3 Metal-complexation by cactus extracts

Cactus pectin bears a significant functional group resemblance to citrus pectin (Cardenas, Goycoolea et al. 2008). Pectins from various plant sources have been studied extensively as sorbents for heavy metal cations (Dronnet, Renard et al. 1996; Harel, Mignot et al. 1998; Melo and D'Souza 2004; Serguschenko, Kovalev et al. 2004; Nawirska 2005;

Arslanoglu, Altundogan et al. 2008; Balaria and Schiewer 2008; Schiewer and Patil 2008; Schiewer and Patil 2008; Mata, Blazquez et al. 2009; Schiewer and Balaria 2009; Mata, Blazquez et al. 2010; Elmachliy, Chefetz et al. 2011). The plant sources were predominantly citrus (lemon and orange) peels, but included sugar beet pulp, and alginates.

Industrially manufactured pectins have also been investigated (Kartel, Kupchik et al. 1999; Chauhan, Kumari et al. 2007; Khotimchenko, Kovalev et al. 2007). The adsorbates studied were mostly divalent heavy metal cations (Cu^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+} and Sr^{2+}) and optimal adsorption regimes were found by manipulating solution variables such as pH and ionic strength. In every case, pectins were reported to successful sorb, adsorb or bind metallic cations, thereby removing them from solution.

The research team of Balaria and Schiewer (2008, 2009) showed spectroscopic (FTIR) evidence for the involvement of carboxylic acid functional groups in Pb binding. Mata, Blasquez et al. (2009) proposed that divalent heavy metal cations in solution were being exchanged Ca^{2+} associated with carboxylic acid groups. The noticeable omission in this body of work is the application to anionic contaminants. This may have been due to concerns about electrostatic repulsions between negative ionizable functional groups and negative ions.

4.3 The arsenic system

The documented interaction of As(III) and As(V) with humic acid provides evidence of the feasibility of anion interaction with negatively charged organics such as pectic polysaccharides. Humic acids are formed by decay of organic matter. These acids typically have carboxyl and phenolate functional groups and thus are negatively charged and would not be expected to interact with negatively charged hydroxo anions of As(III) and As(V). However, a brief review of the literature shows that humic acids do bind arsenate and arsenite (Thanabalasingam and Pickering 1986; Redman, Macalady et al. 2002; Saada, Breeze et al. 2003; Lin, Wang et al. 2004; Buschmann, Kappeler et al. 2006). The possibilities for interaction are ligand interactions (electron donation from the negatively charged acids to the metal centre), H-bridging, cation bridging and van der Waal's interactions.

Thanabalasingam and Pickering (1986) correlated higher ash and Ca content of humic acids with higher sorption of arsenate and arsenite supporting the feasibility of a cation bridging mechanism. Redman et al (2002) and Lin et al. (2004) had similar conclusions showing the correlation of cation content with sorption ability of the humic acids. Lin et al (2004) showed the role of Ca, Mg, Fe, Al and Mn as bridging cations.

Conversely, Buschmann et al (2006) developed binding constants for humic acids and As oxyanions showing binding was higher at lower relative As concentrations. They proposed a direct binding mechanism between the humic acid and the As oxyanions based on lower binding in the presence of Al.

Alternatively, Saada et al. (2002) showed that amine groups played a role in As(V) adsorption by humic acids. By extrapolation, this body of knowledge shows that there is a variety of ways in which the pectic polysaccharides, sharing carboxyl functionality with humic acids, may be able to interact with As oxyanions.

Young et al. (2006; 2008) first reported evidence of an interaction of cactus extracts with arsenite and arsenate ions (As IIII and As V). Synthetic arsenic-contaminated water columns were treated with known concentrations of GE. After one hour, samples taken from the top of the water column showed concentrations higher and lower than the initial concentrations; the mucilage did not have an As source. These results are shown in Figure 4.2. The researchers deduced that these results were consistent with the GE binding the As ions and transporting them to the top of the column, i.e., to the air-water interface. Using this increase in As concentration at the top of the water column to calculate removal of As from the bulk solution, the researchers reported an optimal 35% As removal when the water column was dosed multiple times with mucilage, in the approximation of a continuous process. Mucilage pH and arsenic speciation were both shown to influence the As removal performance.

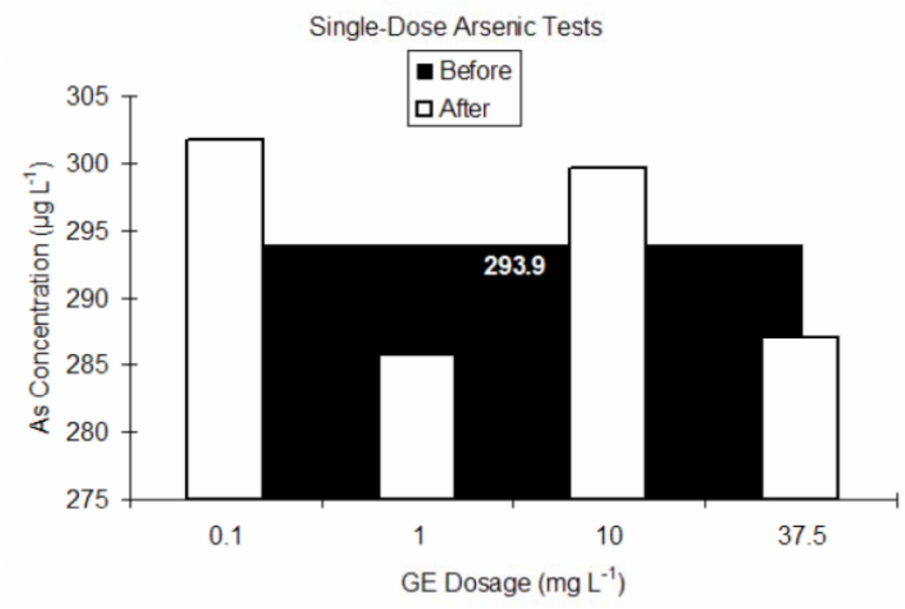


Figure 4.3 Arsenic concentrations in samples taken from the air-water interface of solutions treated with GE at different concentrations (Young 2006).

This work was groundbreaking as it represented a new alternative technology for arsenic removal. This is a field where the predominant technologies rely on the interaction between iron oxide and arsenic and very few effective alternatives exist. Further, it represents a new area in interactions of pectins, i.e., the interaction of cactus pectin with anions, when pectins have been studied extensively and exclusively for cation binding. As such the interaction of pectic cactus mucilage, such as GE, is counterintuitive. These very preliminary results demonstrating the interaction of cactus mucilage with As laid the foundation for the objectives of the current work.

CHAPTER 5

MUCILAGE CHARACTERIZATION: COMPOSITION AND MORPHOLOGY

5 1 Introduction

The aim of this chapter is to present the composition and properties of the mucilage in order to relate these to its ability to interact with the arsenate species being studied. Further, it seeks to differentiate between the GE and the NE in order to propose compositional differences for observed differences in performance. In so doing, it may be possible to pinpoint the active component(s) of these two extracts.

Chapter 4 section 4.1 deals with the work done by previous researchers on the mucilage composition. As previously reported, the mucilage consists of two carbohydrate polymer fractions; a gelling extract (GE) and a non-gelling extract (NE) (Cardenas, Goycoolea et al. 2008). The GE has a polygalacturonic acid backbone with neutral sugar branches, while the NE is a heteropolysaccharide blend comprising mainly L-arabinose, D-galactose, L-rhamnose and D-xylose as well as galacturonic acid but a much smaller amount than the GE.

There was some variation in the literature concerning the relative amounts of the various components of GE and NE. This may have been primarily due to differences in extraction method but could also have been influenced by the cactus pads themselves such as the plant species, age at harvest, time of harvest, and growth conditions such as climate and soil. For this reason, it is important to know the composition of the mucilage fractions extracted for this study.

The strategy is to determine the sugars and minerals as well as the morphology in both fractions of mucilage for comparison with the literature and for comparison with each other. These measures will give an immediate distinction between the mucilage fractions and shed light into reasons for differences in behavior. In each case, the major component will be identified as the active ingredient to inform future testing of single components.

This chapter and all others, with the exception of the concluding chapter, will be organized in the style of a conventional research paper. Following the introduction is an experimental section giving laboratory details of the methods used. Next, in the combined results and discussion section, the main findings and their contextual significance will be presented. For this chapter, the main finding was that there were distinguishing differences between the two fractions both in sugar as well as in mineral composition. The broader implications will be presented in the conclusions.

5.2 Experimental

5.2.1 Composition

5.2.1.1 Sugars

The carbohydrate composition of the GE and NE was done in the laboratory of Dr. Julie Carrier, Associate Professor at the University of Arkansas Department of Biological and Agricultural Engineering. The method used was a modified version of the NREL LAP "Determination of Structural Carbohydrates and Lignin in Biomass" (NREL 2008). The modifications were that the experiment was scaled to 1/5 of the suggested masses and volumes, and the 4% acid hydrolysis took place in the reactor tubes in the sand bath instead of the autoclave.

5.2.1.2 Inorganic elements

The inorganic element composition of the mucilage extracts was determined by Laser-Induced Breakdown Spectroscopy (LIBS) using a LIBS2500plus spectrometer (Ocean Optics, FL, USA). The experimental set-up consisted of a 200 MJ Q-switched 1064 nm Nd:YAG pulsed laser (Quantel, USA) S-GIANT, with a laser pulse duration of 10 ns. The laser was focused on a stationary target in an enclosed eyewear-safe sample chamber (LIBS-SC, Ocean Optics). The samples were mounted on a manually controlled x-y stage, in an inert gas atmosphere. The detection system consisted of seven high-resolution miniature fiber optic spectrometers with 2048-element linear charge-coupled device (CCD) array. The data was displayed using OOILIBS software (Ocean Optics).

The GE and NE powders were pressed into pellets and laser pulses were focused on the surface of the pellets. The high temperature of the laser formed a microplasma of the sample which, as it cooled, emitted the characteristic wavelengths of the comprising elements. Qualitative data were collected from these experiments.

5.2.2 Morphology

5.2.2.1 Transmission Electron Microscopy (TEM)

Mucilage samples were prepared for transmission electron microscope (TEM) imaging by suspending 100 mg in 50 mL DI water to make a stock of 2000 mg/L suspension and diluting the stock suspension to the desired concentration. Approximately 20 μL of sample was mounted on a formvar (polyvinyl formal) coated copper TEM grid, stabilized with evaporated carbon film (Electron Microscopy Sciences, Hatfield PA). The samples were allowed to air dry. The dry samples were stained with 1% uranyl acetate; approximated 20 μL of 1% uranyl acetate was pipetted unto the sample and allowed to air dry. The electron microscope used was a Morgagni 268 (FEI, Hillsboro OR). The images were observed at an accelerating voltage of 60 kV.

5.2.3 Surfactant properties

5.2.3.1 Surface tensiometry

Surface tension was measured in water at the air-water interface by the du Noüy ring method using a Sigma 701 force tensiometer (KSV Instruments Ltd, Finland) and a 0.37 mm wire diameter, 60 mm circumference platinum–iridium ring. The temperature was 20 ºC. The instrument was calibrated before each set of experiments against freshly drawn samples of Milli-Q water. Samples of mucilage (both GE and NE) suspended in water with concentrations ranging from 500 to 3000 mg/L were prepared. Sample volume was 25 mL. Between the measurement runs, the ring was cleaned with acetone, isopropanol, ethanol and ultra-pure water then dried in a stream of nitrogen. Surface tension data were recorded as the average values of 1,000 measurements and were automatically corrected using Huh and Mason formula (Huh and Mason 1975).

5.3 Results and discussion

5.3.1 Composition

5.3.3.1 Sugars

The determination of the sugars in the GE and NE is important to distinguish the two materials and thus to account for differences in behavior toward the As. The sugars composition by mass of GE and NE is shown in Table 5.1 below. NE has a higher percentage by mass of neutral sugars than GE. The most abundant sugar for NE is arabinose while that of GE is glucose. These results show some similarities and differences from what has been reported in the literature and summarized in Table 4.1. It is notable that the literature reports arabinose as the most abundant sugar in the mucilage which corroborates the result found in this study for NE. However, two notable differences are observed: rhamnose was not detected in the current study but it was reported in the literature, while glucose was detected in the current study but not reported in the literature.

Cardenas et al. (2008) reported the composition of the cactus pectin as 85.4% uronic acids, 7.0% galactose, 6.0% arabinose and minor quantities of rhamnose and xylose. Compared to our analysis of GE, we see higher neutral sugar content and, as with NE, the apparent substitution of rhamnose with glucose.

Uronic acids were not directly determined, but in Chapter 7, it will be shown that the higher uronic acid content of GE is responsible for its greater reactivity toward As. Indirectly, it may be inferred that the GE with a lower mass composition of neutral sugars would have a higher mass composition of galacturonic acid than NE.

Table 5.1 Sugars composition by mass (%) of GE and NE

Sugars	**Composition by mass (%)**	
	Gelling extract (GE)	**Non-gelling extract (NE)**
Glucose	9.89	1.03
Xylose	3.95	10.80
Galactose	7.35	14.66
Arabinose	8.90	24.38
Sum	**30.10**	**50.86**

5.3.1.2 Inorganic elements

Qualitative data were obtained on the mineral composition of the GE and NE fractions from LIBS. The maximum lines in GE, as well as NE, were for calcium (Ca). GE also showed significant lines for sodium (Na) and magnesium (Mg). Apart from Ca, NE showed significant lines for Na and potassium (K).

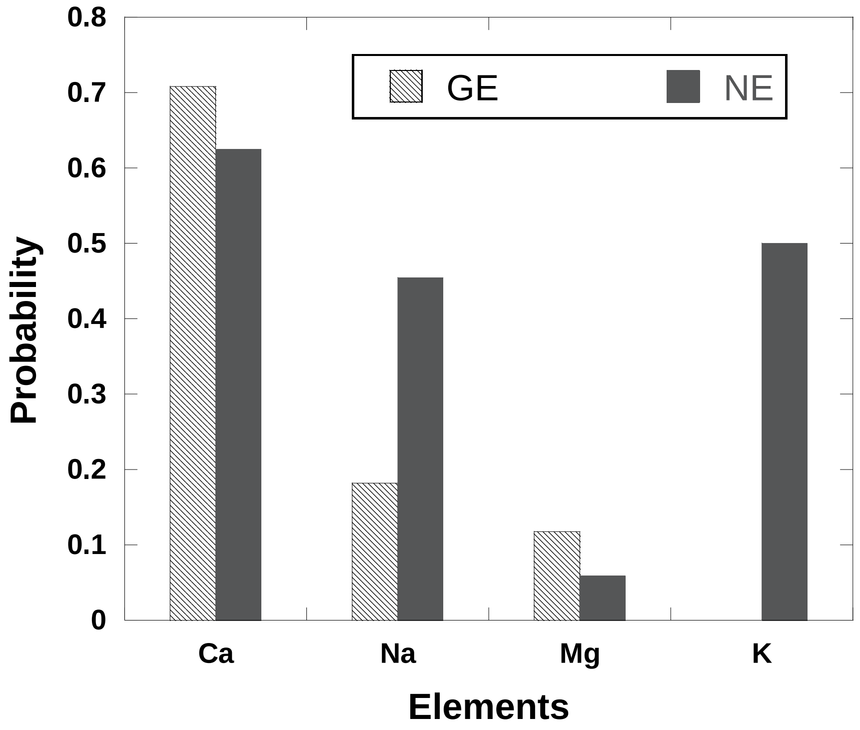


Figure 5.1 Major inorganic elements in extracts of cactus mucilage

5.3.2 Morphology

GE and NE show noticeable morphological differences when observed with TEM; this is shown in Figures 5.2 and 5.3 respectively. GE has a lace-like network with significant separation, seen as spaces, between the polymer strands while NE has a much denser packing, with smaller spaces, like a fishing net.

The lace-like structure arrangement of GE suggests conformational restrictions imposed by an orderly arrangement of a repeating monomer; steric hindrances may dictate the closeness of approach of polymer strands. This may be a result of the typical structure of pectins having linear or "smooth" α-D-galacturonic acid backbone supporting neutral sugar residues branches referred to as "hairy" regions (Schols and Voragen 2002). The branches may impede the how closely the linear regions can align. By contrast, the smooth featureless appearance of NE suggests an undifferentiated, random arrangement of the heteropolysaccharide polymers with no restrictions on aggregation.

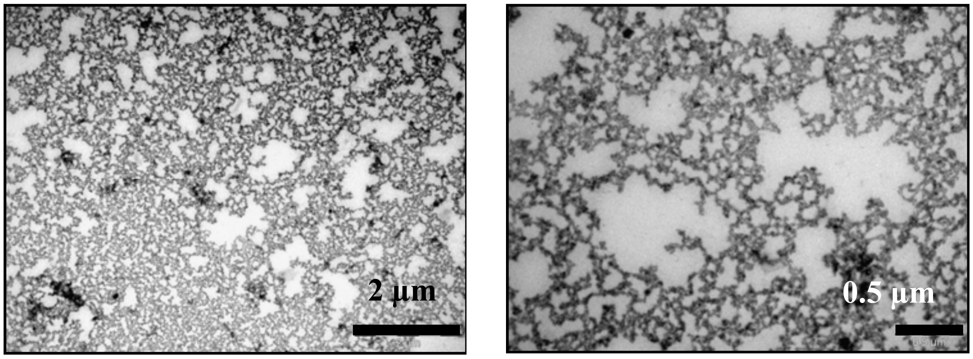


Figure 5.2 TEM images of GE at magnifications of 11kx (l) and 28 kx (r), showing a lace-like network with noticeable spaces between the strands.

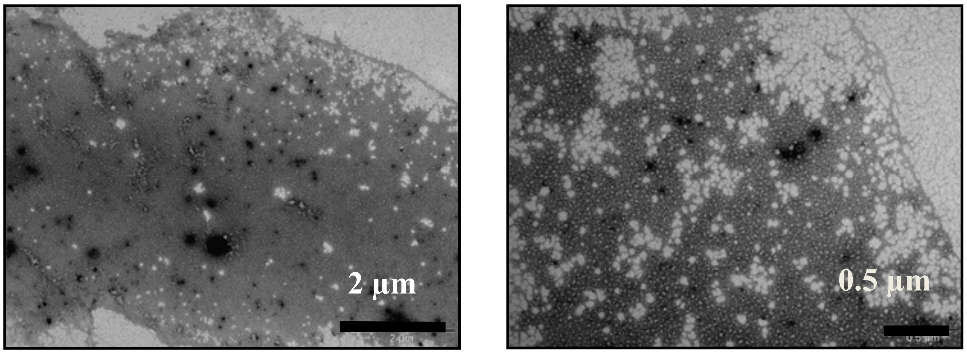


Figure 5.3 TEM images of NE at magnifications of 11kx (l) and 28 kx (r), showing a smoother, denser polymer network than GE.

5.3.3 Surfactant properties

Cactus mucilage showed surfactant properties as evidenced by their ability to lower the surface tension of water. The decrease in surface tension increased with mucilage concentration. However, no change was noted at concentrations below 750 mg/L. A maximum surface tension decrease of 30% was observed with GE but only 16% was observed for NE. The lowering of surface tension is characteristic of amphiphilic molecules and is accounted for by migration of the solute molecules to the air-water interface (van Oss 2006). It should be noted however, that the concentrations used to effect the surface tension lowering are much higher than those employed to interact with As. The mucilage interacts with and transports As to the air-water interface at concentrations between 5 and 100 mg/L. However, with the mucilage suspensions, no surface tension lowering is noted below concentrations of 750 mg/L. It therefore means that the interaction with As was responsible for causing a change in the mucilage such that, even at the low concentrations employed, it was sufficient to effect movement to the air-water interface.

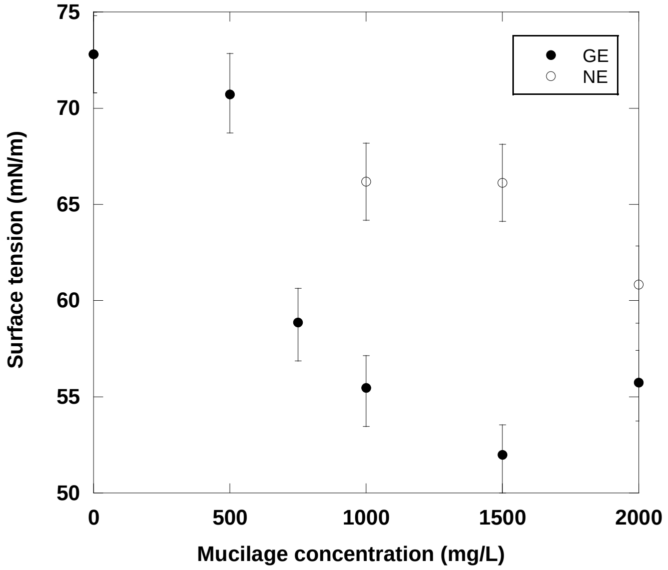


Figure 5.4 Surface tension as a function of mucilage concentration. GE has the greater surface tension lowering effect.

5.4 Summary and conclusions

Based on the sugar and mineral composition, morphology and surfactant properties, there are sufficient characterization differences to distinguish the GE from the NE and so one would expect to observe differences in their chemical and physical behavior. The chemical differences imply that the extracts will behave differently toward the As species while the both chemical and physical differences are important in accounting for differences in flocculating behavior. As will be shown in Chapter 7, the difference in sugar content is a critical factor for the behavior of the mucilage. This is because the mucilage interacts with As by using its CO and OH functional groups. GE was more reactive toward As and this was linked to a higher carboxylic acid content. Other researchers have shown that the NE is a better flocculant than GE for bacteria and kaolin particulates (Buttice, Stroot et al. 2010), and this was linked to the morphological differences between the extracts. It is clear that the distinguishing characteristics in composition and morphology between GE and NE are directly linked to their performance or suitability as water purifying agents.

CHAPTER 6

MUCILAGE EXTRACTION METHODS

6.1 Introduction

The critical selling point for mucilage technology is accessibility. The author's intention is that economically challenged or developing communities should be able to implement this technology starting from the raw material of the cactus plant itself. The extraction methodology used for this research was modified from the literature (Turquois, Rinaudo et al. 1999; Cardenas, Goycoolea et al. 2008) for quality control purposes, and requires facilities found in a conventional laboratory. As such, it is not accessible to the global target audience. The aim of this chapter is to explore simplified modifications of the extraction procedure that require little or no fossil fuel or electrical energy and utilize materials and equipment that are globally accessible and can be found in almost any kitchen. Three alternative extraction methods will be used and they will be compared with the original method of extraction by FTIR.

6.2 Experimental

6.2.1 Materials

Mucilage was extracted from the modified stems (pads) of the *Opuntia ficus-indica* cactus. Fresh pads were obtained from the private nursery of Dr. Norma Alcantar in Tampa, Florida, USA. The plants were grown from pads originally purchased from Living Stones Nursery, Tucson AZ. Water intake was controlled to ensure they all grew at the same rate. No other controls were necessary since different growing conditions only affect the mucilage and pectin content of the pads (Valdivia and Urdaneta 2004). There was no significant variation from plant to plant. All chemicals used were analytical grade or better and purchased from Fisher Scientific (Pittsburgh, PA).

For the alternative extraction methods, pads from the same cultivars were used. For sodium chloride, ordinary (non-iodized) table salt was purchased from the local supermarket, and rubbing alcohol (isopropanol 95%) was purchased from the local pharmacy.

6.2.2 Mucilage extraction (Original method)

6.2.2.1 Cactus pad preparation

Two mucilage fractions were extracted from the cactus pads; a pectic gelling extract (GE) and a non-gelling extract (NE). The NE extraction was done following a modification of the method used by Goycoolea et al. (Goycoolea and Cardenas 2003). The pads were first cleaned by removing thorns and brown spots, washed, dried and weighed. The pads were diced and heated for 20 min at 80 to 85 ºC in 1% NaCl solution (1:1 mass to volume ratio) in order to inactivate enzymes. After cooling, the mixture was liquidized for 45-50 s at the highest speed in a commercial blender (Osterizer ^{TM}), then neutralized with 1M sodium hydroxide (NaOH). The mixture was then centrifuged (Fisher Scientific accuSpin 400) at 4000 rpm for 10 min to separate the liquid from the solids. The supernatant, containing the NE was decanted leaving the solid residue for GE extraction.

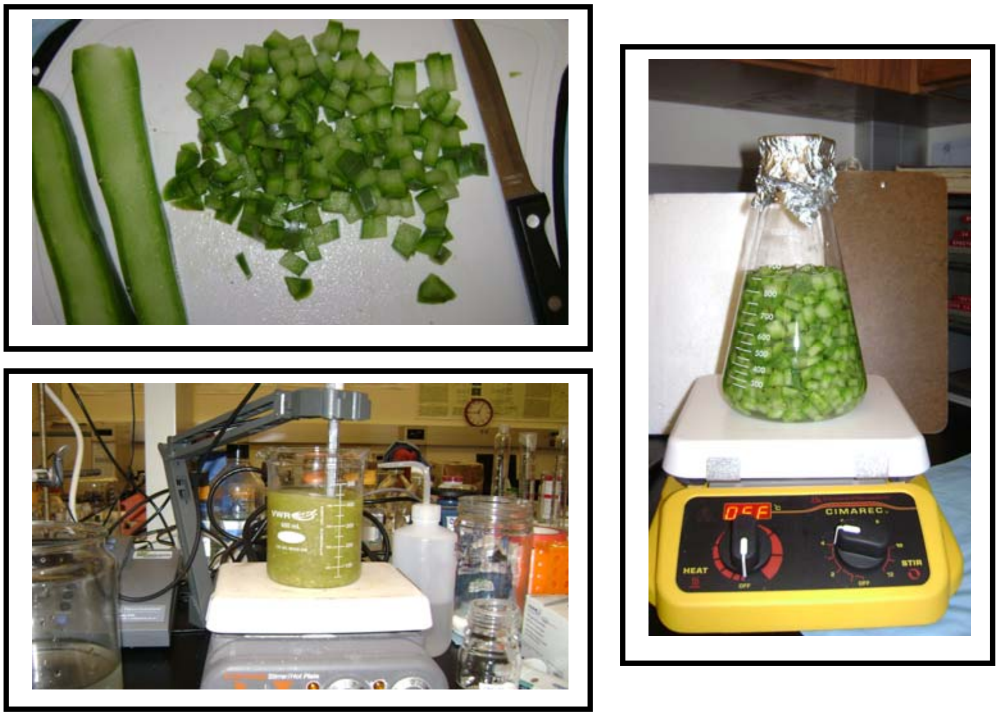


Figure 6.1 Photographs of cactus pad preparation showing diced pads (top left), boiling diced pads (right) and neutralizing the blended pads (bottom left).

6.2.2.2 NE extraction

Sodium chloride (NaCl) was added to the liquid supernatant produced in the pad preparation step to obtain a final 1M NaCl concentration. The liquid was then filtered using Whatman 41 filter paper. By visual observation, if the liquid was too viscous to flow easily through the Whatman 41 filter, then a knitted polyester cloth filter (Polx

1200, Berkshire Corp., Great Barrington, MA) was used. NE was precipitated from the filtrate using acetone or isopropanol in a 2:3 ratio of supernatant to solvent. The precipitate was washed with ethanol-water mixtures in a graded series (70%, 80%, 90%, 95% ethanol and absolute ethanol) to remove any remaining impurities. The precipitate was left to dry at room temperature overnight, followed by an overnight drying in an air oven (Yamato DX-41, Japan). The material was pulverized with a ceramic mortar and pestle and stored in a closed container at room temperature.

Figure 6.2 Cactus pad preparation showing vacuum filtration apparatus

6.2.2.3 GE extraction

The GE extraction procedure was an adaptation of a method developed by Turquois et al. (1999). The differences we used to improve our yield were separating by centrifugation and vacuum filtration, using a different dosage of chelating agent and a shorter sequestering time, and using acetone as the precipitating solvent.

The solid residue from the cactus pad preparation was mixed with 7.5 g/L sodium hexametaphosphate [$(NaPO_3)_6$] in 50 mM NaOH, in a 1:1 mass-to-volume ratio of residue to solution. The mixture was stirred for 1 h, then vacuum filtered with cloth to obtain the filtrate, which contains the dissolved GE. The filtrate pH was lowered to 2.0 by titration with hydrochloric acid (HCl) and refrigerated overnight (~ 5 ºC) in order to precipitate the GE. The precipitate was separated by centrifugation and re-suspended in sufficient DI water to cover it. The pH was adjusted to 8.0 with 1M NaOH to re-dissolve the precipitate. The resulting solution was purified by filtering through a 1.2 μm and a 0.45 μm membrane. The GE was re-precipitated with acetone or isopropanol in a 2:3 liquid-to-solvent ratio, then washed and dried in the same manner as for NE.

6.2.3 Alternative extraction methods

6.2.3.1 Cut-Scoop-Press (CSP) method

Cactus pads were washed, dried and weighed then cut longitudinally in halves. The parenchyma (white fleshy inside) of the pads was scooped out with a spoon and pressed through a potato press. Note that the function of the potato press was to crush the parenchyma in order to break the mucilaginous cells and release the mucilage. This step could be achieved with even simpler tools such as crushing the material with a stone. The pressed liquid was collected and the solids were discarded. Isopropanol was added to the liquid in a 3:2 alcohol to liquid ratio to precipitate the mucilage. The precipitate was washed with three 5 mL to 10 mL aliquots of isopropanol. The precipitate was placed on a petri dish to dry overnight then it was oven dried at 50 ºC overnight. The dry precipitate was then pulverized with a mortar and pestle and stored in an airtight plastic vial.

6.2.3.2 Dice-Boil-Press (DBP) method

Cactus pads were washed, dried, weighed and diced into approximately 1 cm cubes. The cactus cubes were then immersed in 1% sodium chloride solution in a 1:1 mass to volume ratio. At least sufficient liquid was used to cover the cactus. The mixture was boiled for 15 minutes then cooled. The liquid and solids were squeezed through a potato press; the liquid was kept and the residual solids were discarded. Isopropanol was added to the liquid in a 3:2 alcohol to liquid ratio to precipitate the mucilage. The precipitate was washed with three 5 to 10 mL aliquots of isopropanol. The precipitate was placed on a petri dish to dry overnight then it was oven dried at 50 ºC overnight. The dry precipitate was then pulverized with a mortar and pestle and stored in an airtight plastic vial.

6.2.3.3 Grate-Boil-Press (GBP) method

This method was the same as for the DBP method with the exception that the pads were peeled and grated instead of diced.

6.2.4 FTIR characterization of extracts

Mucilage films were prepared by transferring 100 μL of a 5 g/L mucilage suspension directly onto a zinc selenide (ZnSe) crystal for use with a horizontal ATR accessory (Pike Technologies, Madison WI, USA). The suspension was allowed to dry before observing the spectra. ATR-FTIR spectra for the samples were observed using a Nicolet 6700 spectrometer (Thermo Fisher, Madison WI, USA). Each sample was scanned at a resolution of 4 cm^{-1}. Figure 6.3 is a schematic of the deposition of the mucilage film onto the ZnSe crystal.

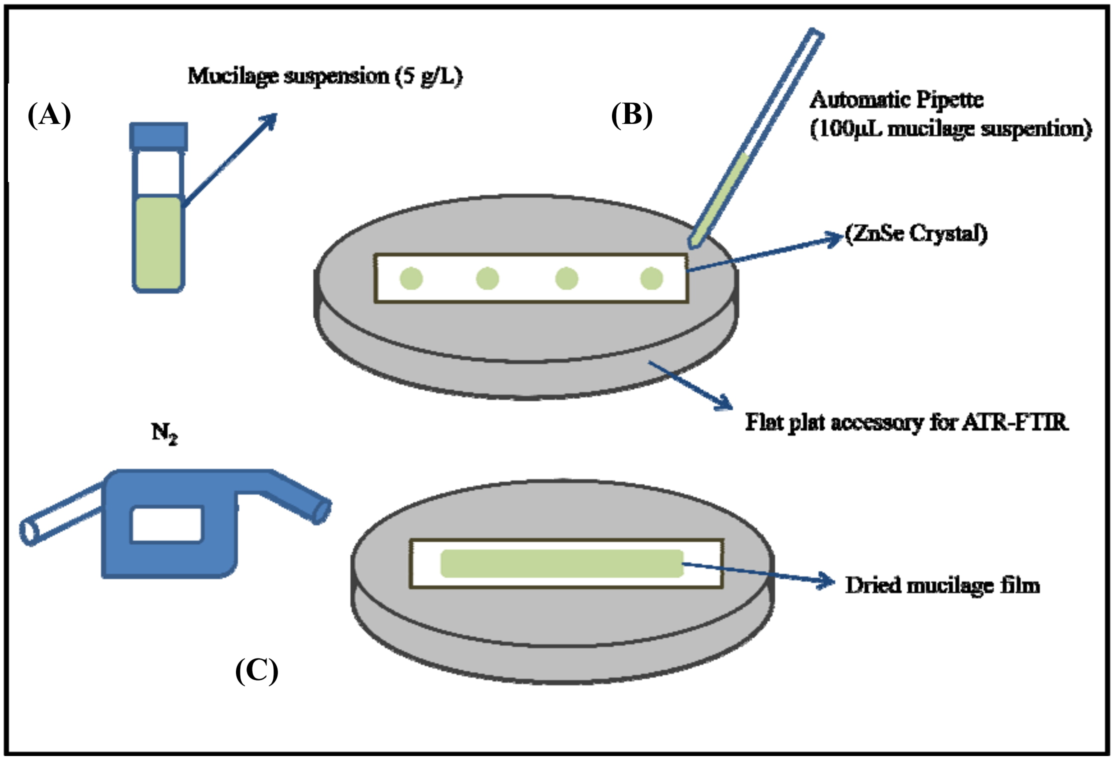


Figure 6.3. Schematic representation of deposition of mucilage film on ZnSe crystal. (A) A concentrated mucilage suspension (5 g/L) is prepared and (B) 100 µL are pipetted unto the ZnSe crystal in a flat plate ATR-FTIR accessory. (C) The suspension is dried in a gentle stream of nitrogen gas taking care to spread the suspension evenly over the crystal.

6.3 Results and discussion

6.3.1 Extraction time and ease of methods

The alternative methods were compared on the bases of time to complete and ease or difficulty. CSP was the best method overall, being both easy to do and taking the least time of two hours. These results are summarized in Figure 6.4. The GBP method was the most difficult because the pads released the mucilage when they were grated and this made the material very slimy and difficult to handle. This difficulty was remedied with the CSP method by scooping the parenchyma (meat of the pad) with a spoon. The mucilaginous cells were kept mostly intact so the material was not as slimy. All the alternative methods were faster than the original method which usually took 24 to 40 h to complete.

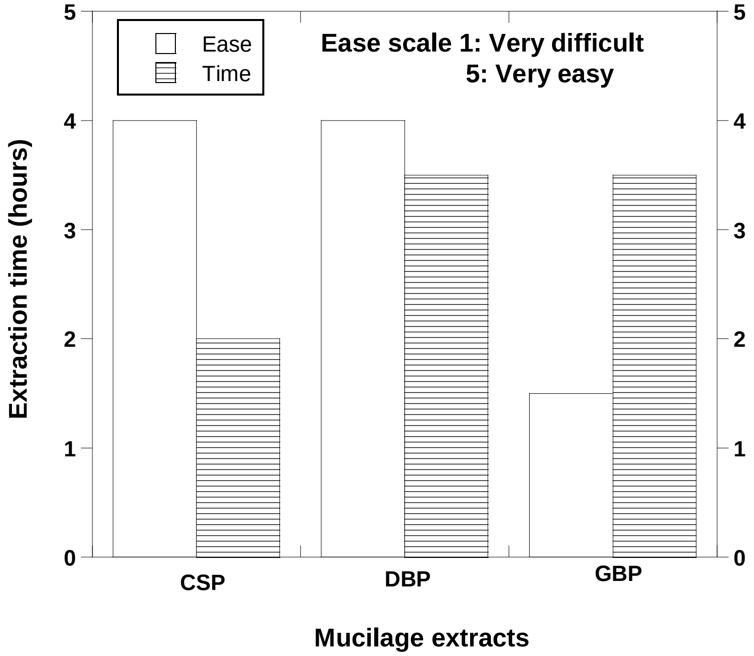


Figure 6.4 Comparison of the extraction methods by extraction time and ease of operation. CSP was the best method.

6.3.2 Comparison of ATR-FTIR spectra

The FTIR spectra of mucilage extracted by the three alternative methods were compared to that of mucilage extracted using the original method (shown in Figures 6.5 to 6.8). Based on the spectra, the mucilage extracted by the alternative methods was clearly Non-gelling Extract (NE). The mucilage extracted by CSP method had the closest spectral match to the original.

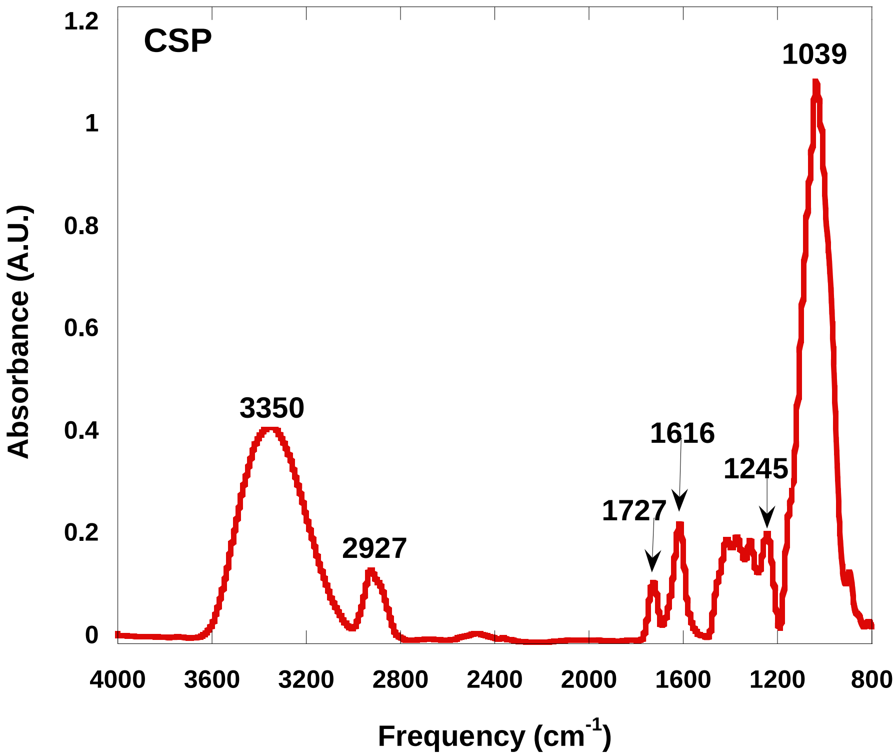


Figure 6.5. FTIR spectrum of mucilage extracted by CSP method showing the main absorbance bands

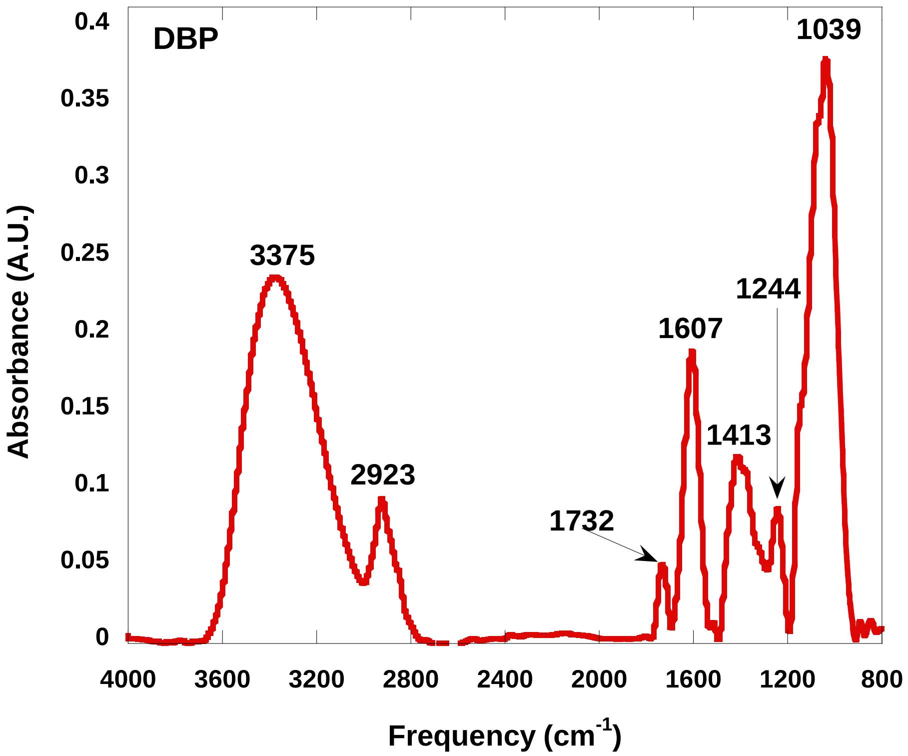


Figure 6.6. FTIR spectrum of mucilage extracted by DBP method showing the main absorbance bands

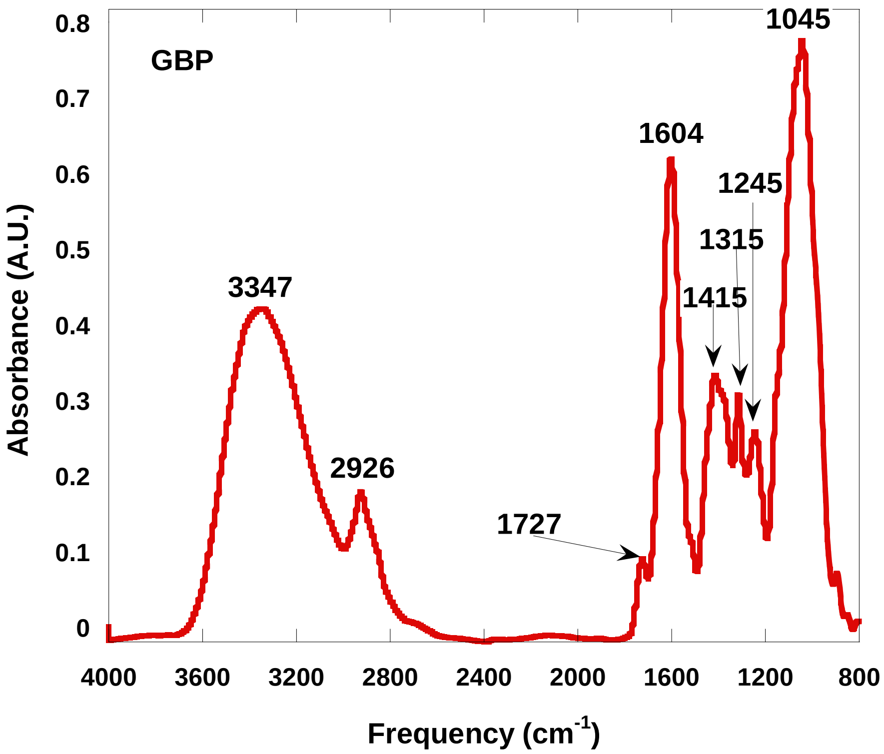


Figure 6.7. FTIR spectrum of mucilage extracted by GBP method showing the main absorbance bands

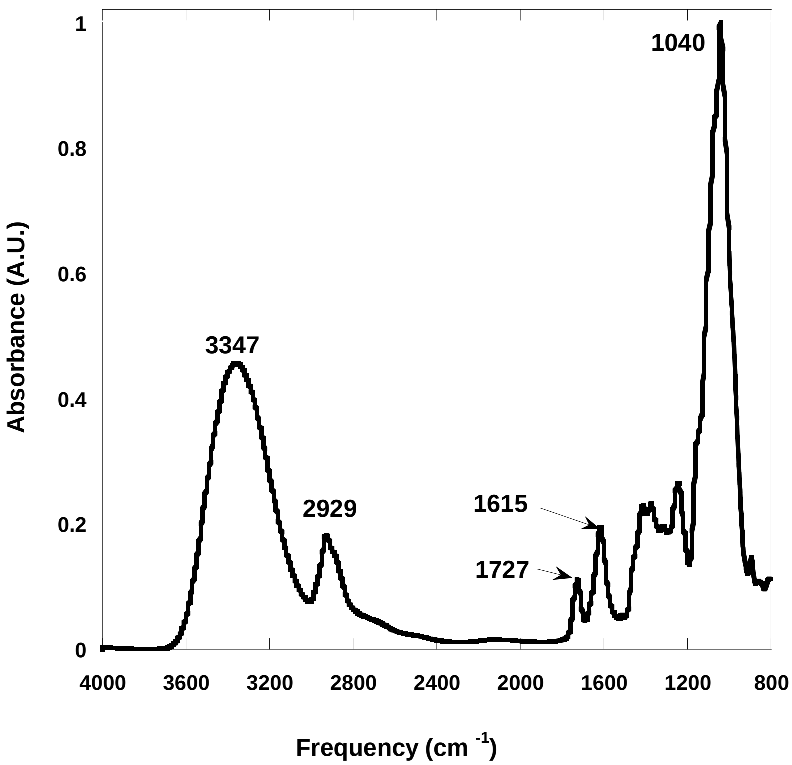


Figure 6.8. FTIR spectrum of NE mucilage extracted by the original method showing the main absorbance bands

6.4 Summary and conclusions

To demonstrate the accessibility of the mucilage technology, three simple alternative extraction methods were developed. These methods required only the use of common kitchen utensils. The extracts by alternative methods were compared with the one from the original method. The alternative methods were faster and cost less than the original method and produced non-gelling extract with very close chemical resemblance to the original (by FTIR). The CSP method was selected as the best alternative method.

CHAPTER 7

BATCH/KINETIC STUDIES: MUCILAGE ONLY AND HYBRID MUCILAGE AND IRON SYSTEMS

7.1 Introduction

Batch studies of the interaction between arsenate (As(V)) and cactus mucilage are presented in this chapter. The reaction conditions were chosen to represent the situation most likely to be encountered in arsenic affected aquifers in Mexico, since Nopal cactus is native to this country. The Region Lagunera of north central Mexico has As in the groundwater. The region is arid with oxidizing groundwater; the average As concentration is 100 μg/L, the pH range was 6.3 to 8.9, and the predominant form was As(V) (Smedley and Kinniburgh 2002). For this reason, As(V) was chosen as the species of interest and the test concentration was 100 μg/L.

These studies demonstrate the fundamental performance of the mucilage; solutions of arsenate (As(V)), which were treated with mucilage, showed differences in arsenic concentration at the air-water interface over time. These concentration differences were attributed to the mucilage binding the arsenic and transporting it either toward or away from the air-water interface. The effect of solution pH and other dissolved species was investigated. Arsenic concentrations were measured with hydride generation – atomic fluorescence spectroscopy (HG-AFS) and inductively coupled plasma – mass spectrometry (ICP-MS). Mucilage concentration was determined by total organic carbon (TOC) analysis.

A second experiment is described where ferric ions were added to the system to capitalize on the strong affinity of arsenate for ferric hydroxides. In batch experiments, arsenate (As(V)) solution was dosed with ferric (Fe(III)) ions as iron (III) nitrate ($Fe(NO_3)_3$), then treated with cactus mucilage in a cylindrical column. After equilibration, sample aliquots were taken from the top and bottom of the column and tested for As and Fe. The mucilage accelerated precipitate formation and settling. Arsenic removal will be shown to be dependent on mucilage concentration, Fe concentration and extent of Fe hydrolysis.

7.2 Experimental

7.2.1 Batch experiments

As(V) solutions, 10 mL of 60 µg/L to 100 µg/L As, were treated with GE and NE to attain final mucilage concentrations of 5 mg/L to 100 mg/L in 15 mL centrifuge tubes. After 24 to 36 hours of equilibration, 1 mL sample aliquots were removed from the air-water interface and the total As concentration was determined by Hydride Generation – Atomic Fluorescence Spectroscopy (HG-AFS) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Total arsenic As concentrations were measured on a PSA 10.055 Millenium Excalibur HG-AFS spectrometer. ICP-MS analysis for total arsenic was carried out using a Perkin Elmer ELAN DRC ICP-MS spectrometer equipped with an autosampler. ^{75}As mass was measured in three replicates. Arsenic calibration solutions (0, 0.5, 1, 5, 10 and 20 µg/L) were run before each sample series. In-between drift monitor checks were performed after each 10-15 samples. Arsenic concentrations in unknown solutions were calculated based on an external calibration curve and error was determined based on the external standard NIST 1064a.

Two types of control experiments were run; As(V) solutions without mucilage, and mucilage solutions without As(V), with all other test conditions and concentrations kept constant. The As(V) stock solution used in the experiments was prepared by dissolving solid sodium arsenate in sufficient de-ionized (DI) water to bring the final concentration to 1000 μg/L. The stock solution was continuously aerated using an aquarium aerator which maintained the dissolved arsenic in the oxidized arsenate form. pH was adjusted using sodium hydroxide and hydrochloric acid.

With conventional sorbents, the concentration of the adsorbate in solution decreases and this decrease is directly related to the removal of the adsorbate. A different scenario was observed with the mucilage; As concentrations increased at the air-water interface as a consequence of mucilage binding and transporting it to this region. Hence, the removal was correlated with this increase in concentration.

Results were reported in terms of increase in As concentration (at the air-water interface), calculated according to:

$$\begin{aligned} &\mathit{Percent\ increase} \\ &= \frac{\mathit{Test\ solution\ concentration} - \mathit{Control\ solution\ concentration}}{\mathit{Control\ solution\ concentration}}\ x\ 100\% \end{aligned}$$

Statistical analysis of variance was done using Student’s t test with $\alpha = 0.1$ to seek significant difference between mucilage-treated solutions and untreated controls.

Variations on the batch tests included the addition of calcium (Ca^{2+}) ions to the test solutions and, in separate experiments, the use of groundwater instead of DI water as the solution matrix. Surrogate groundwater samples were collected from the drinking fountain on the ground floor of the Kopp building in the College of Engineering at the University of South Florida; they were spiked with As then treated with mucilage.

7.2.2 Total Organic Carbon (TOC) analysis

Ten mL samples of 100 µg/L As were treated with 50 mg/L GE in 15 mL centrifuge tubes. Sample aliquots were taken from the top and bottom of the tubes for TOC determination. An automatic pipette was used to remove the sample from the top of the tube then a 1 mL transfer teat pipette was inserted into the tube to remove a sample from the bottom. The TOC of the bulk solution was calculated as the difference between TOC of the entire solution and that of the top and bottom combined. TOC was measured using a TOC analyzer TOC–V equipped with an automatic sample injector (Shimadzu, Japan). Potassium hydrogen phthalate standard solution was used for calibration of the system. The TOC detection limit was 50 µg/L.

7.2.3 Hybrid iron-mucilage system

Batch experiments were performed using a combination of dissolved ferric salt and mucilage to remove As (V) from solution. Ten mL final volume solutions of 100 µg/L

As(V) were prepared and dosed with iron (III) nitrate ($Fe(NO_3)_3$) solution and GE mucilage. The $Fe(NO_3)_3$ concentration ranged from 0 to 50 mg/L while the mucilage concentration ranged from 0 to 500 mg/L. After equilibration, sample aliquots were taken from the top and bottom of the columns and the concentrations of both iron (Fe) and As were determined by ICP-MS.

7.3 Results and discussion

7.3.1 Effect of mucilage type and concentration

Both GE- and NE-treated solutions showed higher concentrations of As at the air-water interface than the control solution, shown in Figure 7.1. The observed increase in As concentration was independent of the mucilage concentration. However, both extracts showed considerable variation in performance, as shown in Figure .7.2.

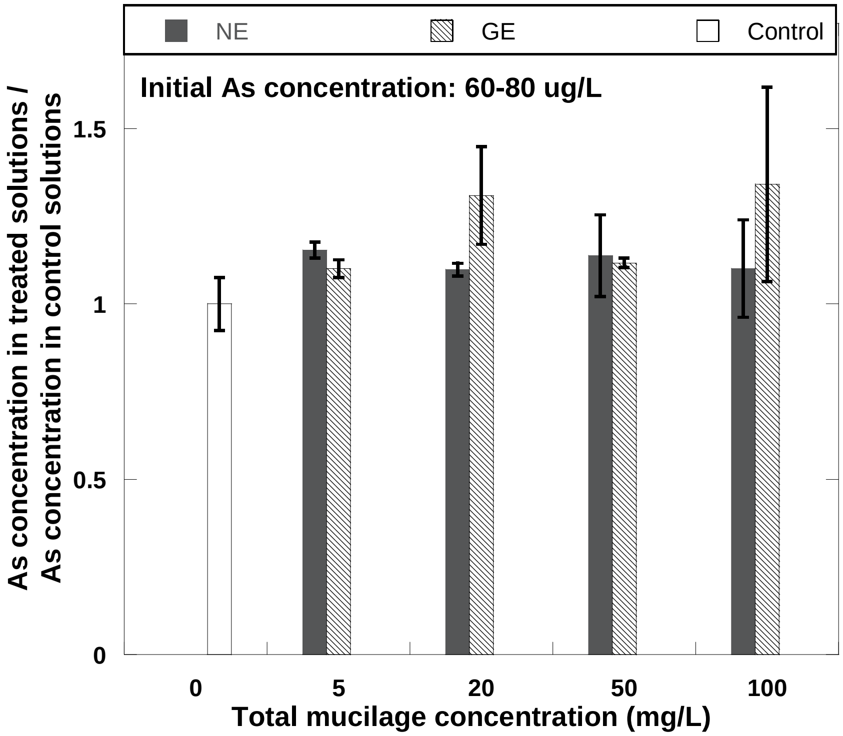


Figure 7.1 As concentrations at air-water interface of mucilage-treated solutions relative to untreated control solutions as a function of mucilage extract and concentration (pH 5.5).

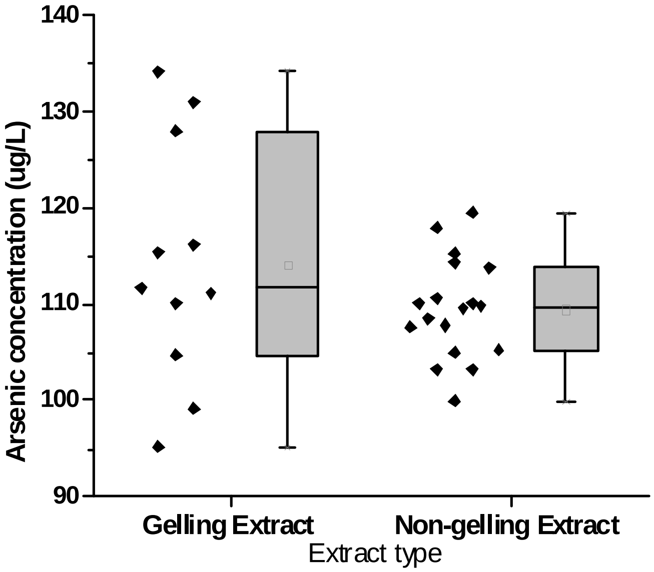


Figure 7.2 Variation in mucilage performance by extract showing mean values (☐), mode (bar inside rectangle), upper and lower quartiles (ends of box) and maximum and minimum values (stems)

The GE showed an average 14% increase in As concentration at the air-water interface, while the NE showed an average 9% increase. GE showed a wider response range and higher maximum increase of 34% than NE, which had a maximum increase of 17%, indicating that the increase in concentration is extract dependent. GE was consequently chosen as the more reactive/responsive extract.

One probable reason for the lack of response to increasing mucilage concentration is that at higher concentrations, the mucilage tends to aggregate and form larger molecular ensembles (Cardenas, Higuera-Ciapara et al. 1997). Aggregation may be hindering the mucilage's interaction with the As(V) ions. This hypothesis requires further investigation, since aggregation may also account for the significant variability in the mucilage performance. Further, the implication is that lower concentrations of both GE and NE may be more effective at transporting As(V) ions to the air-water interface, which will result in lower water treatment costs if mucilage technology is used.

On a mass basis, the 34% maximum increase of As concentration shown by GE converts to 34 μg arsenic (approximately 4%) transported from the bulk solution to 1 mL solution at the air-water interface. While quantitatively modest, these results present an unexplored interaction between pectic polysaccharides and metal oxyanions. Since the mucilage is not a source of As, the increase of As concentration at the air-water interface directly shows an interaction with As, and As transportation by the mucilage.

Pectins have been extensively shown to interact with metal cations. However, interaction of cactus mucilage with As (V) has only been demonstrated by our group (Young, Anzalone et al. 2006). With this research, an understanding of how the mucilage interacts with the As(V) will therefore extend the technological application of pectins to treating new anionic metallic water pollutants and also give insight into how the interaction may be optimized. The transport of the arsenic to the air-water interface is thought to occur due to an increase in the hydrophobicity of the mucilage. The proposed mechanism is that the amphiphilic mucilage binds to the As(V) ions by using its ionizable hydroxyl, carboxyl and carbonyl groups. Normally these ionizable groups would have been used to stabilize the mucilage in the bulk of the aqueous solution by attracting counter ions. On interaction with As the groups are no longer available and, thus destabilized and more hydrophobic, the mucilage-As complex is repelled to the air-water interface.

7.3.2 Effect of pH

Three batch trials were run in triplicate or better at pH 5, 5.5, 6, 7, 8 and 9 to investigate the effect of pH on the interaction between mucilage and arsenic. These pH values were chosen to reflect the pH of natural waters. There are two reasons why pH is expected to be an important variable or factor in the interaction between mucilage and As. Firstly, pH affects protonation of arsenate in solution which in turn affects the charge on the oxyanion. In the pH range of natural waters, the dominant arsenate species are $H_2AsO_4^-$ ($pK_{a,1} = 2.91$) and $HAsO_4^{2-}$ ($pK_{a,2} = 6.94$). Secondly, pH not only affects the protonation and charge on the mucilage but also the conformation. Note that pH 5.5 is the initial solution pH. GE was chosen for pH trials on account of its better interaction with As(V) ions than NE. The initial As concentration was 100 µg/L (as in the previous experiments) and the GE concentration used was 50 mg/L.

As shown in Figure 7.3, only at pH 5.5 and 9, were small but statistically significant differences observed between mucilage-treated solutions and non-mucilage treated controls. Further significant difference was observed between the mucilage-treated solutions at these two pH levels. These results indicate that solution pH does affect the interaction between the GE and arsenate and further, gives insight into the nature of the interaction. GE, an anionic polyelectrolyte, becomes increasingly negatively charged with increasing pH due to ionization of –OH groups from alcoholic and carboxylic groups (Cardenas, Higuera-Ciapara et al. 1997; Medina-Torres, Brito-De La Fuente et al. 2000; Cardenas, Goycoolea et al. 2008).

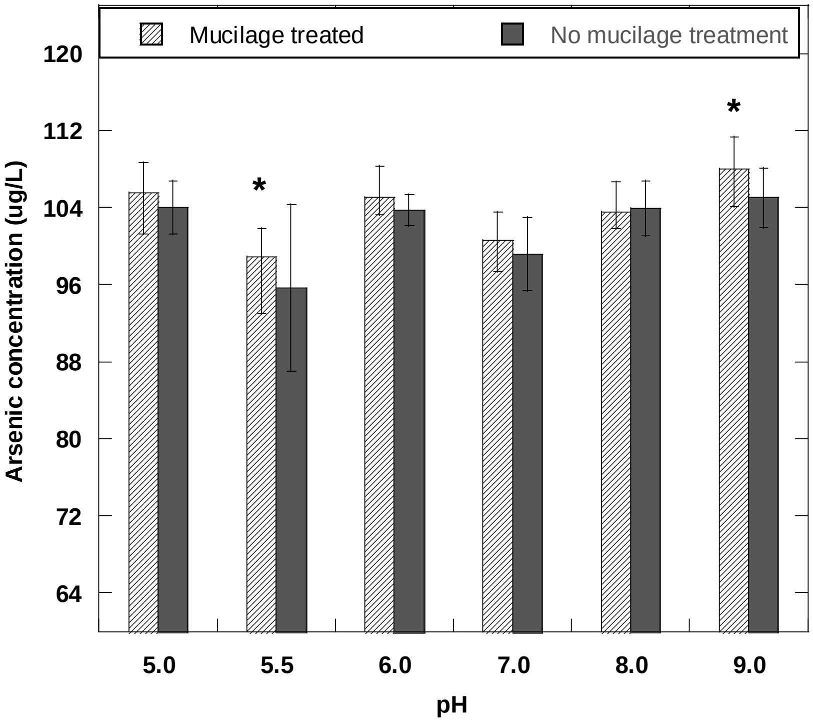


Figure 7.3. As concentrations at the air-water interface of mucilage-treated solutions (GE) relative to untreated control solutions as a function of initial solution pH. Significant difference ($\alpha = 0.1$) between control and treatment is indicated by (*)

The As (V) oxyanion is polyprotic and changes protonation level with pH. In weakly acidic conditions such as pH 5.5 it exists as dihydrogen arsenate $H_2AsO_4^-$, while in weakly basic conditions (such as pH 9) it exists as hydrogen arsenate $HAsO_4^{2-}$ (Benjamin 2002). Our proposed mechanism of interaction is via hydrogen bonded bridging between the protons associated with the As species and the ionized carbonyl and carboxyl groups on the mucilage. It appears that there is a compensation between less ionized groups on the mucilage at lower pH with the higher number on protons on the $H_2AsO_4^-$ to make the interaction comparable to the higher pH scenario where the mucilage is more ionized but the arsenate has less protons. The activity in these pH regions versus the lack of activity from pH 6 to 8 may be due to poorer charge transfer as the pH is in the neutral region. The mucilage is therefore expected to perform better in solutions with higher ionic strength to facilitate charge transfer.

7.3.3 TOC analysis

TOC analysis was done to determine the distribution of the mucilage in the solutions in order to definitively link the mucilage to the transport of As to the air-water interface. As shown in Figure 7.4, the TOC concentration in the entire solution, which correlates to the total mucilage concentration, does not change on addition of As. However, the distribution of mucilage in the solution does change in the presence of As. The TOC in the bulk solution was determined by subtracting the TOC of the combined top and bottom of the solution from that of the entire solution. Figure 7.4 shows a larger proportion of TOC in the bulk of the control solutions than in the mucilage-treated As solutions. This means that mucilage migrated from the bulk of the solution primarily to the air-water interface due to the presence of As.

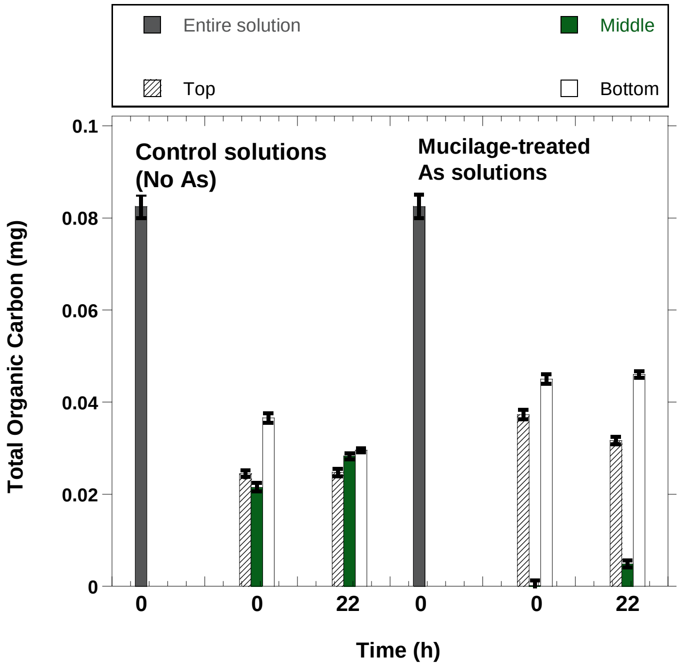


Figure 7.4 Mass distribution of mucilage (reported as Total Organic Carbon) in solution

7.3.4 Mucilage performance in groundwater

Both extracts showed notably different behavior with groundwater than with DI water; the As concentrations at the air-water interface of experimental solutions were all either significantly lower than or showed no significant difference from the control solutions (Student's t-test, $\alpha = 0.10$).

The main difference between the groundwater samples and the DI water samples was the presence of dissolved ions in the former. Among these is iron which can form precipitates with the As; these precipitates can be subsequently removed by the flocculating and settling action of the mucilage, which can account for the lower As concentrations at the air-water interface. As will be shown later in this chapter, the geochemical approach of using iron to bind the As, then flocculating it with mucilage, is a very efficient method of As removal.

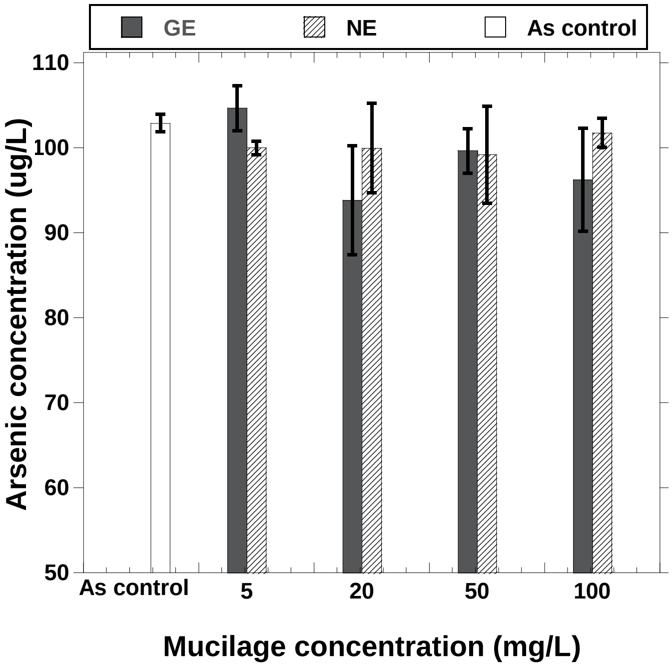


Figure 7.5 Mucilage performance in groundwater as a function of concentration

7.3.5 Hybrid mucilage and iron system

The strong affinity of iron (Fe^0) and iron oxides and hydroxides for As is well-known. Iron oxides and hydroxides form strong complexes with arsenic oxyanions in a number of reactions (Dixit and Hering 2003). These strong interactions have been exploited to remove As from water in coagulation-flocculation-sedimentation treatment systems, described in Chapter 3. One challenge to scaling down these systems for household use is the length of time and large volume reactor required for sedimentation. In this study, the flocculant properties of the mucilage were exploited to improve the efficiency of a bench scale coagulation-flocculation treatment by removing the need for prolonged sedimentation. As solutions were mixed with iron nitrate ($Fe(NO_3)_3$) and mucilage.

The effect of adding cactus mucilage to solutions with iron (Fe) salt and As was easily visible as flocs formed immediately after mixing and standing. Three processes made this possible; the hydrolysis of the Fe salt to iron hydroxide and oxyhydroxide *in situ*, the strong binding of the arsenate by the iron hydroxide and oxyhydroxides to form solid precipitates, and the coagulation of the precipitates to form flocs large enough to settle out of solution. The mucilage enhanced the coagulation and flocculation of the precipitates. Figure 7.6 shows the dense precipitate formed within 10 minutes by solutions containing mucilage, Fe and As. Solutions similarly prepared, but without mucilage, were stable to precipitation for one week. The speed of the flocculation and settling of the solutions with mucilage translates to greater time efficiency and throughput of As removal systems. Further, the low cost and ready availability of the mucilage makes it a potentially competitive alternative to synthetic organic polymers used to enhance coagulation.

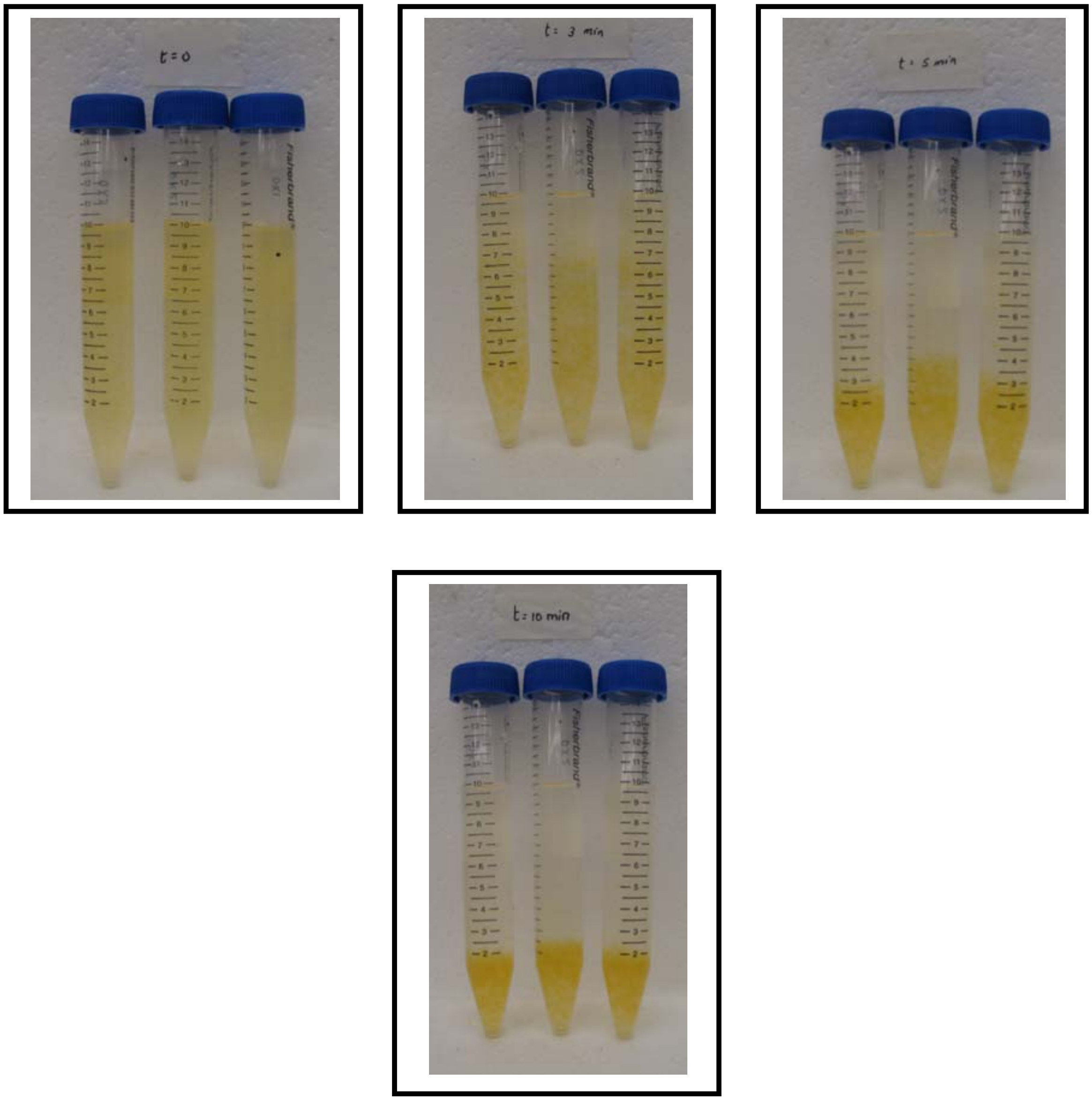


Figure 7.6 Mucilage enhanced settling of iron arsenate. Initially there is no apparent change in solution (top left) but after three min flocs start forming and settling (top middle). The flocs collect at bottom of the tube (top right) and after 10 min all visible flocs have settled (bottom center).

7.3.5.1 Effect of mucilage concentration

Mucilage concentration was varied to deduce the optimal mucilage dosage at high (50 mg/L) and low (5 mg/L) Fe concentrations. These results are shown in Figure 7.7; the species being removed from solution are Fe and As. At high Fe concentration, As removal increased with increasing mucilage concentration reaching a maximum of 96% removed at 100 mg/L GE, then decreasing slightly with further increase in mucilage concentration. It is interesting that further increases in mucilage concentration beyond 100 mg/L were disadvantageous to As removal. This is probably due to the higher mucilage concentrations causing a vertical accumulation of mucilage in the water column and so preventing efficient settling. At low Fe concentration, there was lower As removal, between 10-20%, which did not correlate with mucilage concentration.

The results indicate that precipitate formation is the controlling step in the process; the mucilage appears to provide a framework or surface on which precipitate nuclei can aggregate and form larger flocs. As such, any variable which enhances precipitate formation, such as increasing Fe concentration, will enhance the overall process.

In these experiments, the As challenge was 100 μg/L so at the best performance the As residual was less than 10 μg/L which is the maximum contaminant level proposed by the WHO.

The role of the mucilage was best seen by comparing the As concentrations at the bottom of the tubes of mucilage treated solutions with those treated with only Fe. This is shown in Figure 7.8; the increase in As concentration with time correlates to the settling of the iron-arsenate by the mucilage. By contrast, the As concentration remained fairly constant over that time period in the solutions treated with Fe only.

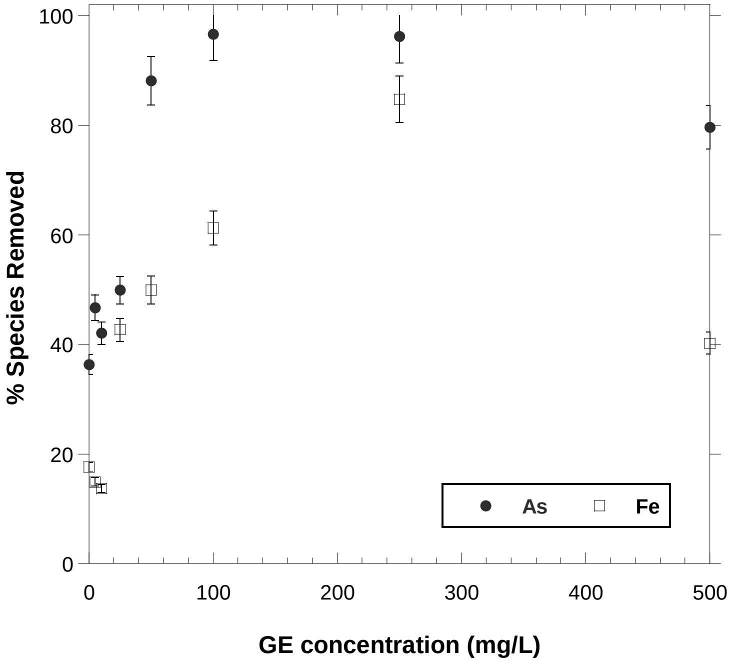


Figure 7.7 Removal of As and Fe as a function of mucilage concentration. The optimum removal occurred at 100 mg/L mucilage. Initial As concentration: 100 µg/L; initial Fe concentration: 50 mg/L; initial pH: 6.5.

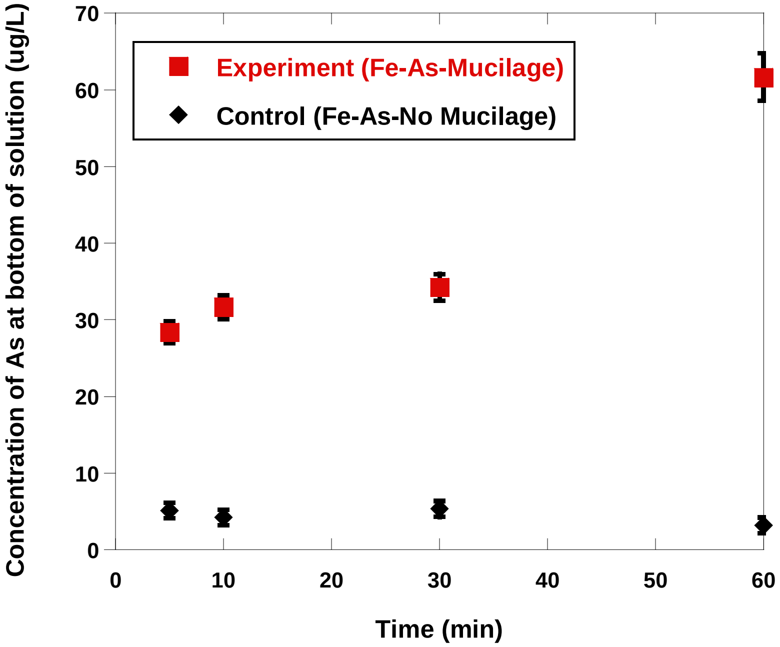


Figure 7.8 Comparison of mucilage-treated solutions with solutions treated with Fe only. Concentrations are 1:10 dilutions of samples taken from bottom of tubes. Initial As concentration: 100 μg/L; initial Fe concentration: 50 mg/L; initial pH: 6.5, GE concentration 100 mg/L.

7.3.5.2 Effect of Fe concentration

The effect of iron (Fe) concentration was also studied. The effect of increasing the Fe dosage from 5 to 50 mg/L is shown in Figure. 7.9. As expected, As removal increased linearly with increasing Fe concentration, reaching a maximum of 90% removal at 40 mg/L. Further increasing the Fe concentration did not yield greater As removal. These results provide proof for the hypothesis that forming the iron arsenate precipitate is the controlling step in the process. The maximum removal was most likely reached because the available As was limited by mass transfer.

The Fe residuals ranged from the best value of 7.5 mg/L at 250 mg/L GE, to 43 mg/L at 5 mg/L GE. The United States Environmental Protection Agency (USEPA) has set the secondary maximum contaminant level for Fe at 0.3 mg/L (Pontius 1992) These residual Fe concentrations can be lowered to potable range by a rough filter such as a sand or cloth filter.

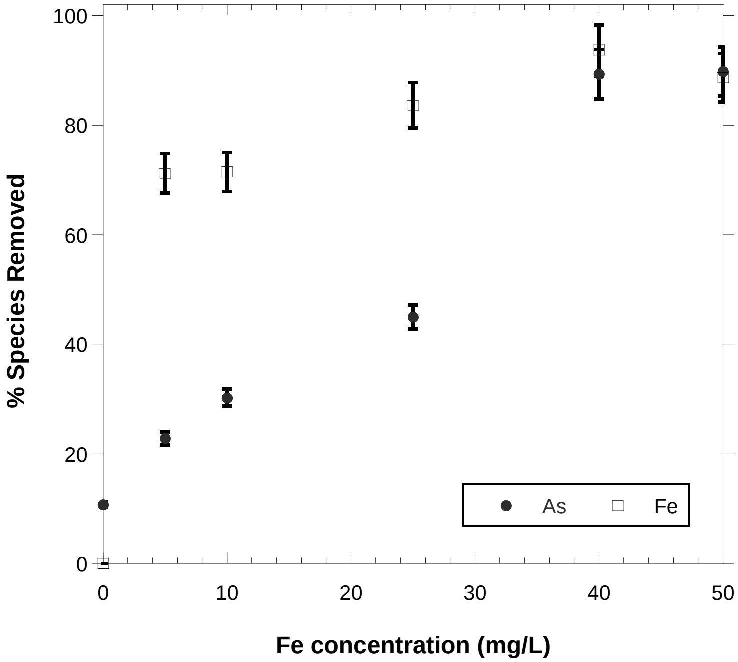
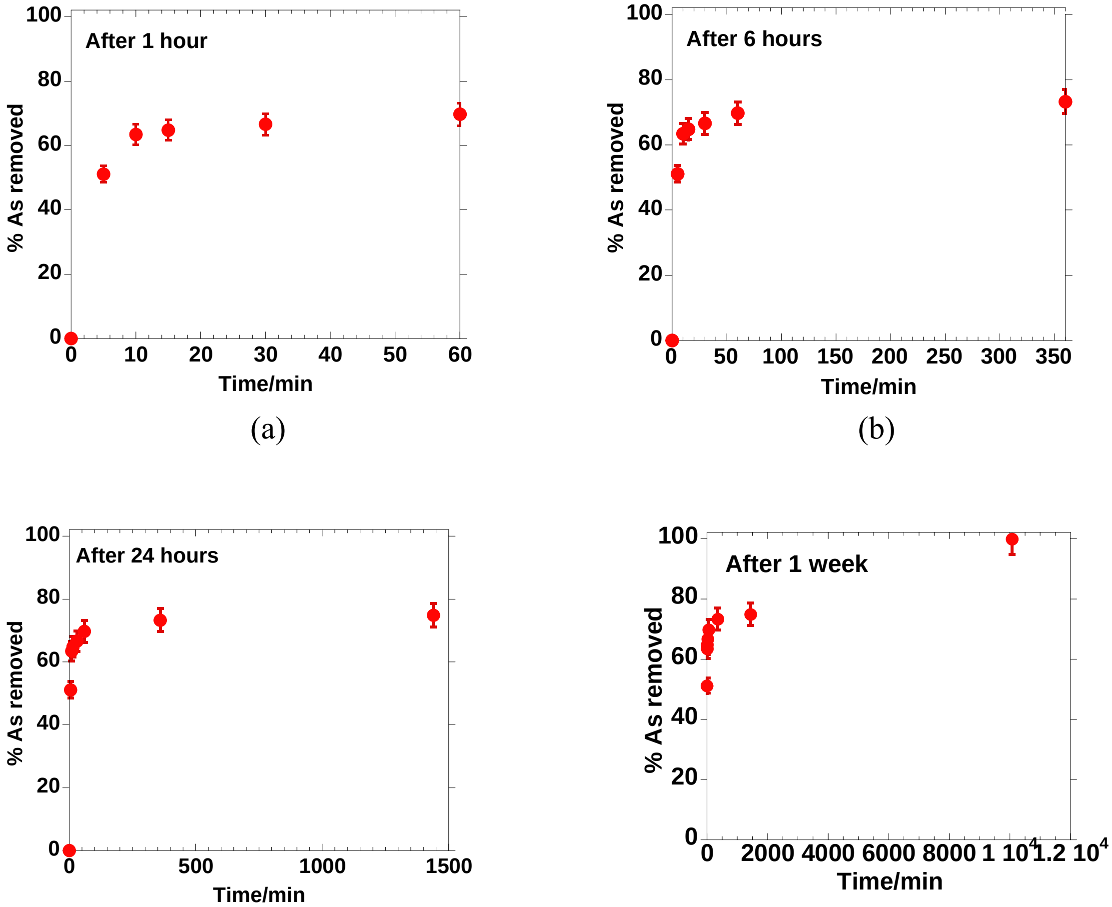


Figure 7.9 Removal of As and Fe as a function of Fe concentration. The optimum removal occurred at 40 mg/L Fe. Initial As concentration: 100 µg/L; GE concentration: 100 mg/L; initial pH: 6.5.

7.3.5.3 Kinetic experiments

In order to study the kinetics of the system, batch experiments were run. Solutions of As were treated with Fe(III) salt (50 mg/L) and 100 mg/L mucilage, stirred, then sampled at the end of different time intervals. The results are shown in Figure 7.10. The plot shows the amount of As removed by the mucilage over time for the optimized initial conditions of 50 mg/L Fe, 100 mg/L mucilage and As challenge of 100 µg/L. The process achieved visual separation within 10 minutes with the majority of the removal being achieved in 30 minutes. There was some variation observed in the endpoint concentrations. That is, removal rates were observed to range from 75 to 96% at 24 h. This may be due to different extents of hydrolysis of the dissolved Fe(III) salt. This hypothesis is supported by lower removal being observed when fresh, unhydrolysed Fe(III) solution was used (shown in Figure 7.11). The shape of the kinetic curve speaks to the adsorption of the iron arsenate precipitate particles on the mucilage surface; equilibrium is achieved when no more surface sites are available or can be accessed by the precipitate. Moreover, the adsorption time is limited by the settling of the mucilage which sinks faster as it gets heavier with adsorbed iron arsenate.



(a) (b)

(c) (d)

Figure 7.10 Kinetics of iron-mucilage system at (a) one hour, (b) 6 hours (c) 24 h and (d) one week. Within 15 min the system reaches equilibrium that is stable up to 24 h. After 24 h, As removal proceeds by normal precipitation. Initial As concentration: 100 µg/L.

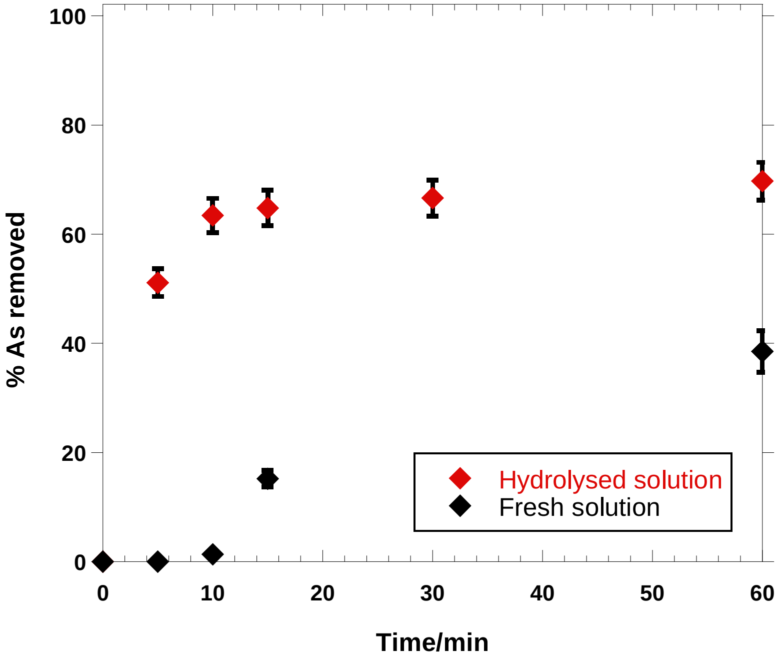


Figure 7.11 Removal of As as a function of Fe hydrolysis. Hydrolysed Fe solution gave higher removal at 24 h. Initial As concentration: 100 µg/L; GE concentration: 100 mg/L; initial pH: 6.5.

7.4 Summary and conclusions

Synthetic As (V) solutions were treated with two extracts, a gelling extract (GE) and a non-gelling extract (NE) in batch trials. The arsenic concentration at the air-water interface was measured after equilibration. The GE and NE treated solutions showed on average 14% and 9% increases in arsenic concentration at the air-water interface respectively (Figure 7.1) indicating that the mucilage bonded and transported the arsenic to the air-water interface. TOC analysis also corroborated this finding by showing a net migration of mucilage to the air-water interface in the presence of As (Figure 7.4). It was observed that solutions containing mucilage and As showed a higher proportion of the mucilage at the air-water interface than solutions with mucilage alone.

This interaction between mucilage and As was affected by solution pH since activity was greater in weakly basic (pH 9) and weakly acidic (pH 5.5) regions (Figure 7.3). These findings suggest that the interaction of the mucilage with the As increases the hydrophobicity of the mucilage by occupying those ionizable groups which would have been stabilized it in the bulk of the aqueous suspension. The mucilage-As complex is consequently repelled to the air-water interface on account of increased hydrophobicity, resulting in the observed increase in As at the air-water interface. It is envisaged that this interaction can be optimized and harnessed for the removal of arsenic from drinking water. This work is the first application of natural pectic substances in the removal of arsenic from drinking water and opens the way for the application of natural pectic materials to the removal of anionic metallic species from water.

In order to capitalize on the strong affinity of iron for As, as well as exploit the flocculant properties of the mucilage, a hybrid iron-mucilage treatment system was investigated. Mucilage was successfully applied as a coagulant aid in the removal of As by Fe(III) salt, achieving between 75% to 96% As removal (Figures 7.7 – 7.11). The process depended on the hydrolysis of the Fe(III) salt to form iron hydroxides and oxyhydroxides which in turn reacted with and adsorbed the dissolved arsenate. The iron arsenate colloidal precipitate formed was then adsorbed onto the mucilage surface forming larger, heavier, denser flocs. The As removal increased with increasing mucilage concentration reaching a maximum at 100 mg/L above which removal declined (Figure 7.7). Increasing Fe(III) concentration increased the As removal reaching an optimum concentration at 40 mg/L above which there was no further increase in removal (Figure 7.9). The As removal had rapid kinetics, achieving visual separation within 10 minutes, while the majority of the removal was achieved within 30 minutes (Figure 7.6). The overall contribution is an accelerated separation of the iron arsenate particles from the bulk of the solution which normally would have required lengthy times and volumes to flocculate and settle on its own. Fe in many forms is widely used in As treatment, particularly at the household level, as discussed in Chapter 3. Its popularity is due to its efficiency in binding As and its accessibility. When combined with mucilage, it forms the basis of a simple, fast, efficient system for arsenic removal from water which meets most of the criteria for accessibility and sustainability. Table 7.1 shows a comparison between the two mucilage technologies explored in this study and with other sorbents. Both systems show moderate performance. However, the hybrid mucilage and iron system is faster, more robust and reliable than the mucilage only treatment.

Table 7.1 Arsenic sorption capacity of selected sorbents

Sorbent	Capacity (mg As /g)	Source
Acacia nilotica powdered stem	50.8	(Baig, Kazi et al. 2010)
Sorghum biomass	2.765	(Haque, Morrison et al. 2007)
Waste tea fungal biomass	0.55	(Mamisahebei, Jahed Khaniki et al. 2009)
Human hairs	0.012	(Wasiuddin, Tango et al. 2002)
Cactus mucilage	2.8 - 0.14	This study
Cactus mucilage and iron	0.99 - 0.75	This study

This work provides fundamental data on two new treatment systems for removing As from water. However, there is room for further work to be done before implementation. Further field testing with real groundwater is needed particularly to evaluate how the systems work with known competitors for As such as phosphates, sulfates and silicates. Also, field testing would provide information on how the systems work with removing As(III), which was not studied in this work. One challenge to the implementation of the hybrid Fe-mucilage system is the local availability of a source of Fe in a target community. Further work needs to be done with more readily available Fe sources, such as rusty nails or lateritic soils, to evaluate the contribution of the mucilage to such systems.

CHAPTER 8

MECHANISM OF INTERACTION BETWEEN MUCILAGE AND ARSENATE

8.1 Introduction

In this chapter, the evidence for interaction of cactus mucilage with arsenic will be presented. The importance of learning the mechanism is that it will enable the optimization of the mucilage-arsenic interaction. Spectroscopy was used to elucidate the mechanism by looking at molecular conformational changes of the mucilage in the presence of the arsenic. Specifically, Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and Ultraviolet-visible (UV-VIS) spectroscopy techniques were used.

8.2 Experimental

8.2.1 ATR-FTIR film method

Mucilage films were prepared to characterize the functional groups by Attenuated Total Reflection (ATR). Mucilage films were prepared by pipetting 100 μL of a 5 g/L mucilage suspension directly onto a zinc selenide (ZnSe) crystal for use with a horizontal ATR accessory (Pike Technologies, Madison WI, USA). The suspension was allowed to air dry before observing the spectra. Films were also prepared to observe the interaction of mucilage with arsenic, made from solutions containing 10 mg/L As(V) and 5 g/L mucilage. ATR-FTIR spectra for the samples were observed using a Nicolet 6700 spectrometer (Thermo Fisher, Madison WI, USA), collecting 100 scans in % Transmittance mode with a resolution of 4 cm^{-1}. The experiment was repeated three times. A schematic of the film preparation is shown in Figure 6.1. Note that, for the experiments, lower concentrations of As and mucilage were used. However, higher concentrations were used for the ATR-FTIR measurements to obtain better spectra.

The spectra collected were smoothed and baseline corrected (automatically) using the software OMNIC (Version 7.2a, Thermo Fisher, Madison WI, USA). The spectra were then exported to Kaleidagraph (Synergy Software, Reading, PA) for presentation.

8.2.2 ATR-FTIR layer method

A known volume of water (100 µL) was placed on the ATR crystal and the spectrum was taken. The crystal was dried and the surface was then coated with a mucilage film by spreading 400 µL of 1000 mg/L mucilage suspension on the crystal. The film was dried in a gentle stream of N_2 for 30 min then the spectrum was taken. 100 µL of the test solution, containing known concentrations of arsenic and/or Ca^{2+} were then pipetted onto the film and the spectrum was taken, using the dry film on the crystal as a background. The water spectrum was then subtracted from this spectrum to yield the contribution of the chemical groups of the wet film

8.2.3 UV-VIS spectroscopy

Suspensions of 500 mg/L mucilage (GE and NE), with and without arsenic (100 μg/L) were prepared. The mucilage samples without arsenic were used as the reference for samples with mucilage and arsenic. UV-VIS spectra were collected every 12 h for 48 h over a range of 200 nm to 800 nm using a Jasco V-530 spectrophotometer (Jasco, Japan) outfitted with standard 10 mm x 10 mm quartz cuvettes.

8.3 Results and discussion

8.3.1 ATR-FTIR spectroscopy

The ATR-FTIR spectra of both the gelling extract (GE) and non-gelling extract (NE) show the characteristics of pectic polysaccharides (Figures 8.1 and 8.2). The main difference between them is due to the higher uronic acid content of GE. Pectins have a D-galacturonic acid backbone and various degrees of branching composed of neutral sugars, and methylation of the carboxylic acid functional group. Their spectra show the functionalities associated with the carboxylic acid and carboxylate, ether and alcohol groups that comprise these compounds.

In the GE spectrum, there are four main features: the first is the broad band at 3350 cm^{-1} which corresponds to OH stretching of alcohol and carboxylic acid -OH groups involved in intermolecular hydrogen bonding. The second is two bands at 1609 cm^{-1} and 1416 cm^{-1} corresponding to the antisymmetric and symmetric COO- stretch characteristic of carboxylic acid salts. Thirdly, the bands at 1250 cm^{-1} and 1140 cm^{-1} correspond to

C-O-C ether stretch. Lastly, two strong bands at 1140 cm^{-1} and 1100 cm^{-1} are due to C-O stretch of secondary alcohols and C-O-H stretch in cyclic alcohols, respectively.

Significant similarities exist between the spectra of GE and NE; however, four notable differences distinguish NE from GE. A more pronounced band is observed at 2929 cm^{-1} for the CH stretching. Further, NE shows the expected carbonyl C=O stretch at 1727 cm^{-1} that is absent in GE. The most intense band for NE occurs at 1041 cm^{-1} due to HC-O-H stretch of cyclic alcohols. The most notable difference between the two extracts is seen in the region 1250 cm^{-1} to 850 cm^{-1}. Coimbra et al (1998) showed that the intensity of the bands at 1100 cm^{-1} and 1018 cm^{-1} correlated with the uronic acid content of pectic polysaccharides; on this basis GE is deduced to have a higher uronic acid content than NE.

Table 8.1 Functional groups assigned to major bands in spectra of gelling (GE) and non-gelling (NE) extracts

Functional groups	Gelling extract GE (cm^{-1})	Non-gelling extract NE(cm^{-1})
Hydrogen bonded O-H from alcohol and carboxylic acid groups	3350	3347
CH groups from aliphatic backbone	2937	2929
Carbonyl group (C=O) from carboxylic acid		1727
Carboxyl group from carboxylic acid/carboxylate	1609	1615
	1416 - 1331	1411 – 1317
Ether groups (C-O-C)	1250	1245
	1140	
C-O from secondary alcohol, CHOH from cyclic alcohol	1100, 1019	
Indicative of uronic acid content		
CHOH of cyclic alcohols		1041

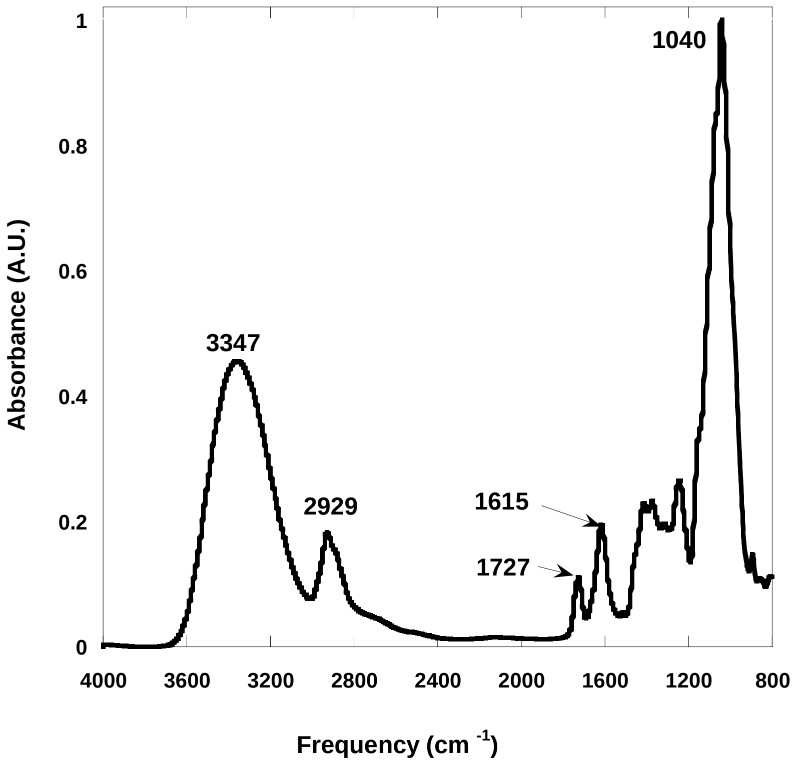


Figure 8.1 ATR-FTIR spectrum of native Gelling Extract (GE) showing the major absorption bands. The labeled bands correspond to OH (3350 cm $^{-1}$), CH (2937 cm $^{-1}$), COO- (1609 cm $^{-1}$, 1416 cm $^{-1}$), COC (1250 cm $^{-1}$) and CO from secondary alcohol (1100 cm $^{-1}$) groups

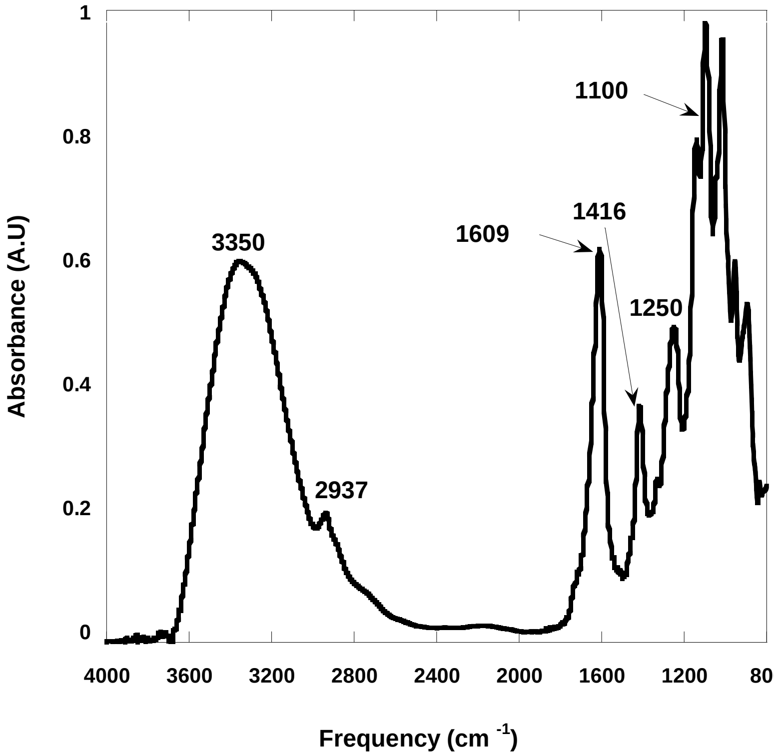


Figure 8.2 ATR-FTIR spectrum of native Non-gelling Extract (NE) showing the major absorption bands. The labeled bands correspond to OH (3347 cm $^{-1}$), CH (2929 cm $^{-1}$), CO (1727 cm $^{-1}$, 1615 cm $^{-1}$) and CHOH (1041 cm $^{-1}$) groups

In FTIR absorbance spectroscopy, peak shifts and intensity changes are important for inferring chemical interaction. Peak shifts signify a change in the chemical environment of a functional group. The coupled appearance and disappearance of absorption bands indicate a reaction involving the corresponding functional group.

On reaction with the As(V) oxyanion, significant changes occur in the spectra of GE and NE; shown in Figure 8.3. These changes indicate the participation of the carbonyl, carboxyl and hydroxyl functional groups in the interaction with As(V).

The OH band of GE at 3350 cm^{-1} was shifted higher to 3364 cm^{-1} indicating a change in the hydrogen bonding network probably due to the direct involvement of the alcohol and carboxylic -OH groups. The 1609 cm^{-1} band shifted to 1640 cm^{-1} further corroborating hydrogen bonding as an interaction mechanism (Vidyasagar, Smith et al. 2009). This shift is shown more clearly in Figure 6. The appearance of band at 1733 cm^{-1} coupled with the decreased intensity of the 1640 cm^{-1} band indicate that the –C=O from carboxylic acid is the binding site for the As(V) oxyanion.

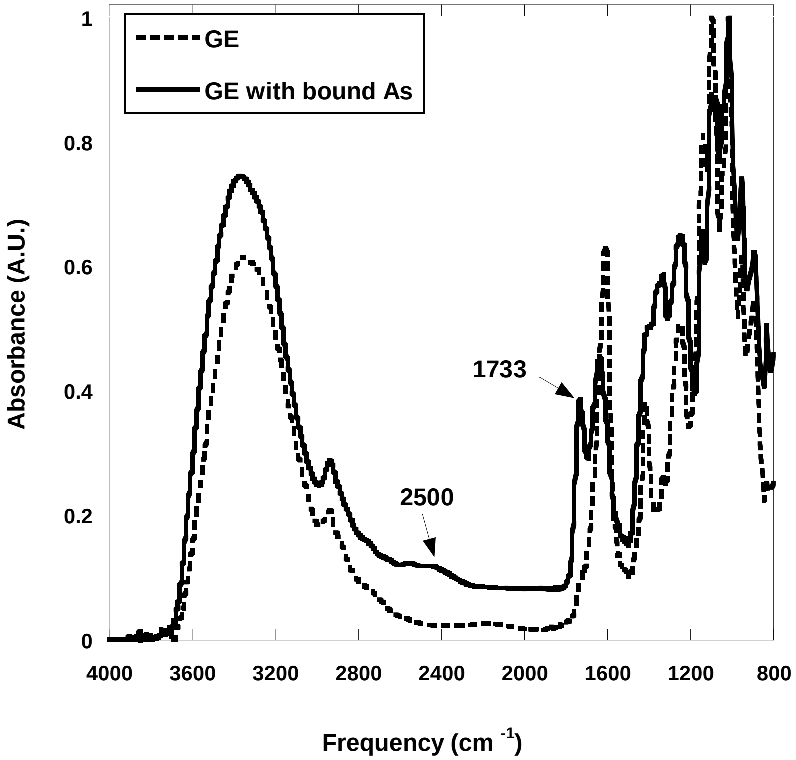


Fig 8.3 ATR-FTIR spectra of GE before (dotted line) and after (bold line) reaction with arsenic. Upon reaction with As, two new bands appear in the GE spectrum at 2500 cm $^{-1}$ and 1733 cm $^{-1}$. The band at 1609 cm $^{-1}$ shifted to 1640 cm $^{-1}$, and its intensity decreased.

Similar changes were observed in the spectrum of NE after reaction. An analogous CO band at 1615 cm^{-1} shifted to 1645 cm^{-1} indicating hydrogen bonding. This band's intensity decreased while the band at 1727 cm^{-1} assigned to C=O stretch shifted to 1735 cm^{-1} and increased in intensity (see Figure 8.4). The band at 1372 cm $^{-1}$ thought to correspond to the carboxylate ion, shifted to 1360 cm $^{-1}$ and showed a dramatic increase in intensity. Taken together, these three changes provide further proof that the C=O group was a binding site for arsenate.

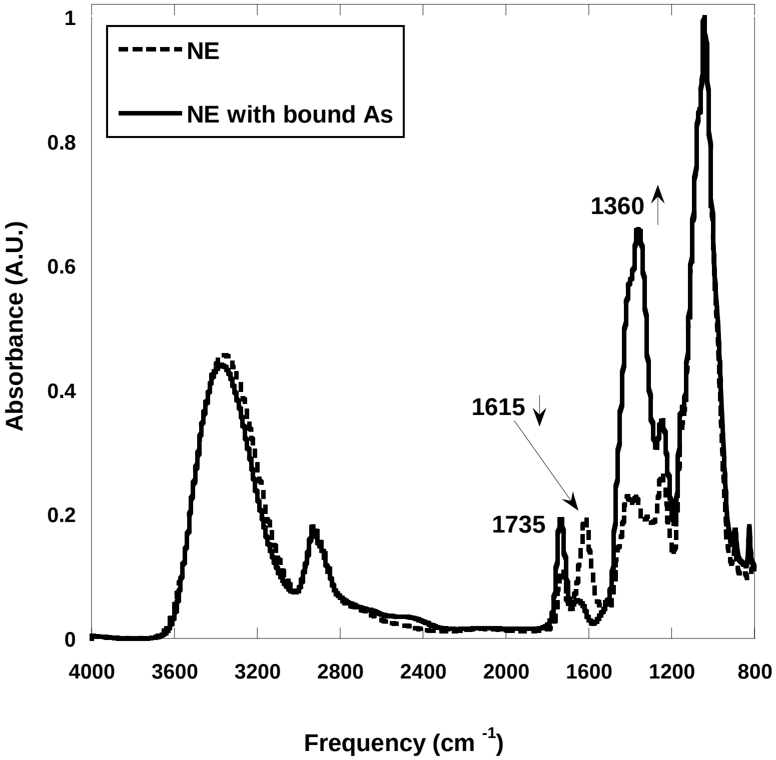


Figure 8.4 ATR-FTIR spectra of NE before (dotted line) and after (bold line) reaction with arsenic. Upon reaction with As, three changes occur: the band at 1615 cm $^{-1}$ shifted to 1645 cm $^{-1}$ and decreased in intensity; the band at 1727 cm $^{-1}$ shifted to 1735 cm $^{-1}$ and increased in intensity and a band at 1372 cm $^{-1}$ shifted to 1360 cm $^{-1}$ and increased in intensity

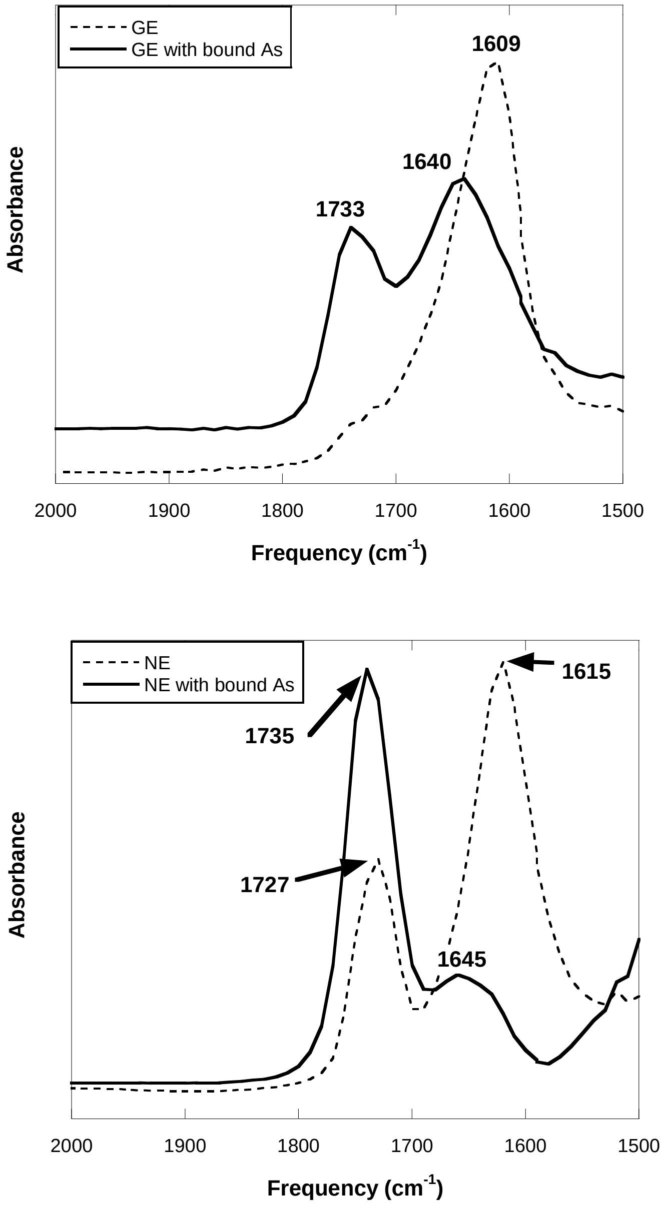


Figure 8.5 Expanded sections of GE spectra (top) and NE spectra (bottom) showing the bands undergoing significant change on account of interaction with As

One limitation of the film method described above for viewing ATR-FTIR spectra of the mucilage is that the chemical environment of the dry mucilage may not approximate well its solvated state. As such, spectra of the mucilage in solution would be ideal. Unfortunately, attempts to acquire spectra of mucilage in solution were unsuccessful due to very strong water absorption which obscured the contributions from the mucilage. However, this challenge was overcome by using the layer method described in section 8.2.2. The objective of the layer method was to observe the spectra of the mucilage at the interface of the film with the covering solution, in order to approximate the solvated mucilage.

The FTIR spectrum of GE did not change much using the layer method as against the film method; the same functional groups were observed with some shifts in peak position. Table 8.2 is a summary of the observed groups. The most notable difference between the spectra for the two different methods was seen between the bands attributed to hydrogen-bonded OH groups (around 3200 cm $^{-1}$) , and this was thought to be due to the higher degree of hydration when using the layer method.

Table 8.2 Functional groups assigned to major bands in spectra of gelling extract (GE), before and after reaction with arsenic, using the layer method

Native GE		GE reacted with As	
Wavenumber/ cm $^{-1}$	Assignment	New wavenumber/ cm $^{-1}$	Comment
3228	Intermolecular bonded OH from alcohol (OH stretch)	3389	Disruption of the mucilage hydrogen bonding network by interposing arsenate molecules
2919	CH_3 and CH_2 groups from aliphatic compounds (CH antisymmetric and symmetric stretch) groups	2937	Aliphatic groups more pronounced
1627	Asymmetrical stretching COO- from carboxylate ion	1604	Interaction A-electron donation; reduced bond strength; lower frequency and lower intensity
1391	Symmetrical stretching COO- from carboxylate ion	1416	
1302	Ether COC group	1249	Interaction A electron donation from O
1165	Ether COC group	1098	Interaction A: electron donation from O
1064	CHOH in cyclic alcohols	1018	Interaction A: electron donation from O
		959	

Several frequency changes are seen in the spectrum of GE following reaction with arsenate. With the formation of hydrogen bonds, the OH stretching bands move to lower frequencies and usually have increased intensities and broadening of the band (Silverstein et al, 2005). The opposite trend was observed in the OH stretching band of the mucilage, i.e. it shifted to higher frequency, when comparing the native form and the one reacted with arsenate. This could be the result of disruption of the mucilage hydrogen bonding network by the interposing arsenate molecules. Note that a similar shift was seen with this band using the film method.

The bands assigned to COO^- (1391 cm^{-1}, 1627 cm^{-1}), CHOH (1064 cm^{-1}) and COC (1165 cm^{-1}) all shifted to lower frequencies indicating electron donation by the electron rich oxygen atoms and subsequent electron depletion of the CO bonds. These shifts could be due to any kind of interaction which provides an electron sink such as hydrogen bonding with electron deficient protons from another species or direct binding to a positive metal centre such as the arsenic d-orbitals in arsenate

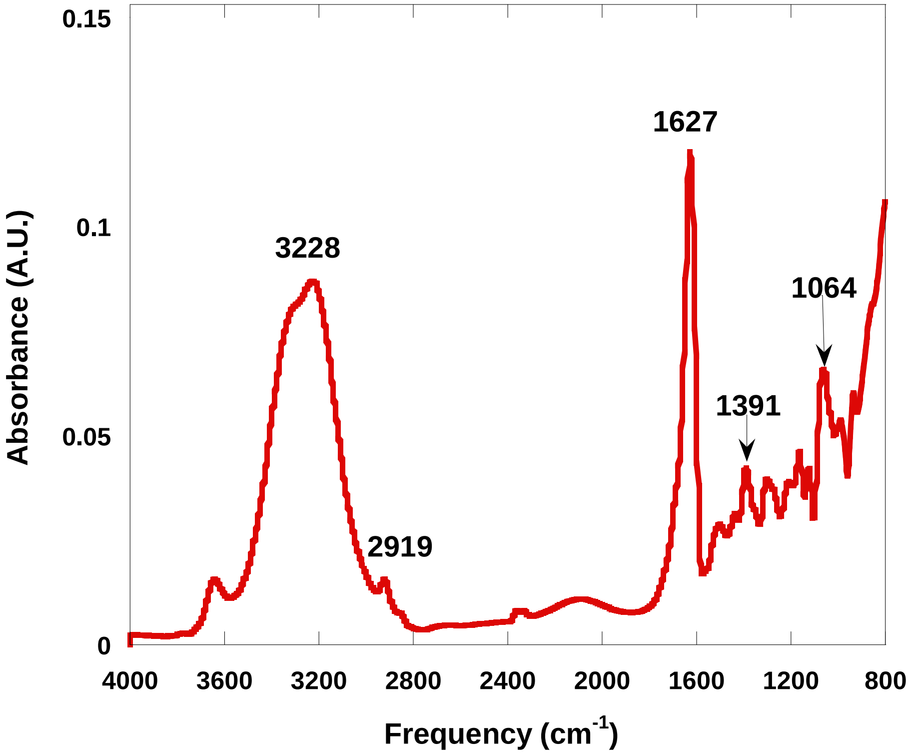


Figure 8.6 An ATR-FTIR spectrum of native gelling extract (GE) in aqueous environment (using layer method)

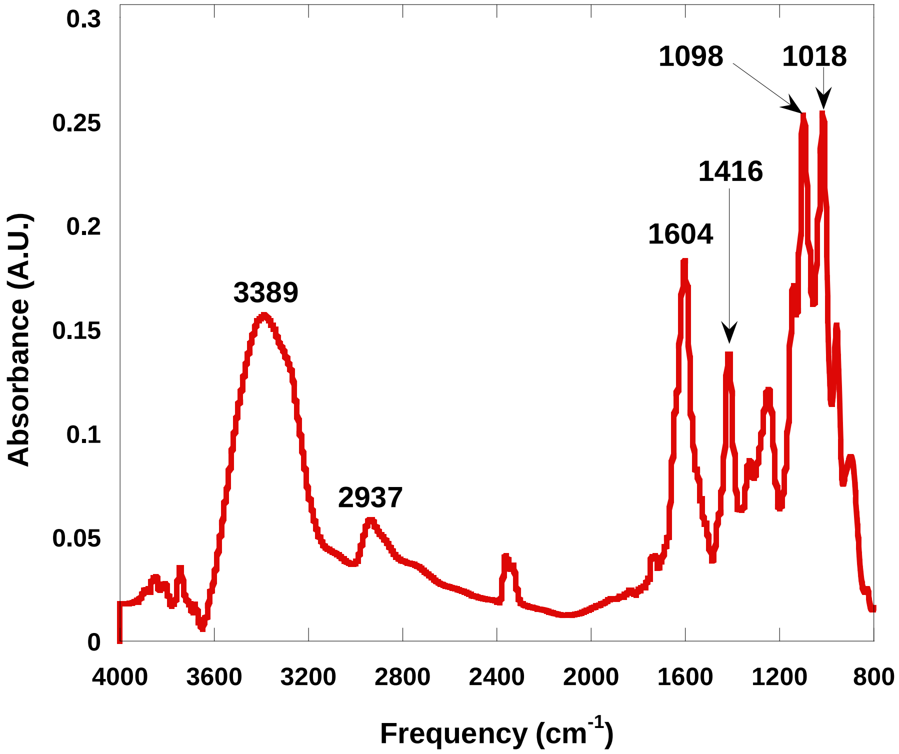


Fig 8.7 ATR-FTIR spectrum of gelling extract (GE) in aqueous environment with arsenic (using layer method)

8.3.2 Mechanisms of interaction

Three interactions are possible to account for the interaction of mucilage with arsenate:

(i) hydrogen bonding/bridging,

(ii) cation-mediated electrostatic attraction and

(iii) direct bonding (donor-acceptor) interaction.

In hydrogen bonding/bridging, the proton on an -OH group on the mucilage polymer (from either alcohol or carboxyl) is attracted to an O atom on the arsenate anion thus binding the anion to the mucilage polymer.

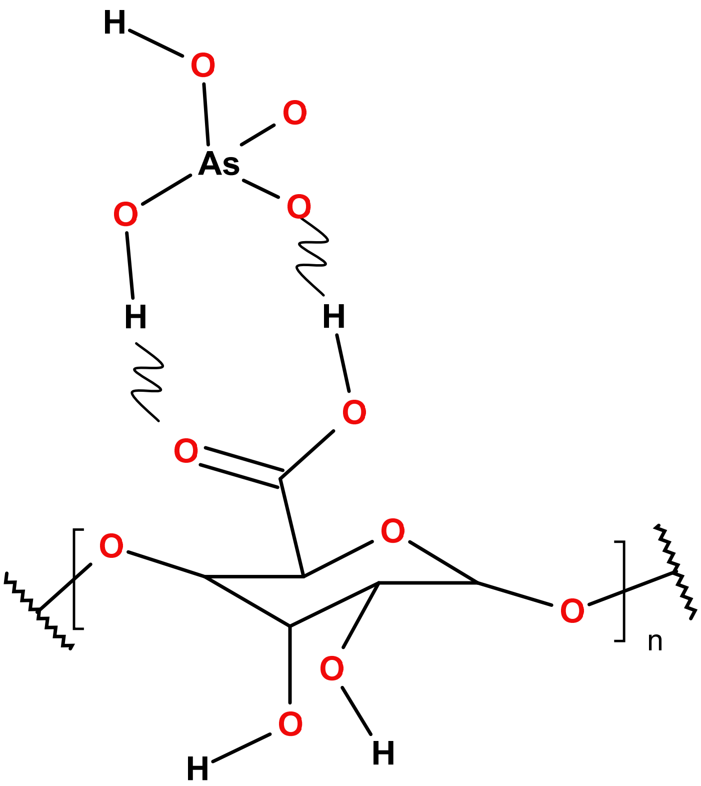


Figure 8.8 Schematic representation of hydrogen bonding/bridging interaction

The appearance of hydrogen-bonded –OH in the spectra of GE and NE and subsequent changes to these bands on interaction with arsenate suggest that hydrogen bonding is a mechanism of interaction. The spectra obtained by the layer method (refer to figures 6.5 and 6.6) give more insight; the changes to the OH bands suggest a disruption to a hydrogen bonded network present between mucilage polymer chains that occurs in the presence of arsenate. These pieces of evidence indicate that hydrogen bonding is important in mucilage-mucilage bonding and that, in the presence of arsenate, the arsenate competes for hydrogen bonding sites.

Additionally, both carbonyl and carboxyl groups are able to use their electron rich oxygen atoms to form hydrogen bonds with the proton from the hydroxyl group on arsenate. Their FTIR spectra show predominantly shifts to lower frequencies indicating electron donation which is consistent with lower electron density on the oxygen atoms involved in hydrogen bonding. However, this observation is also consistent with electron donation to the positive arsenic metal centre of the arsenate oxyanion.

In cation-mediated electrostatic attraction, a cation, such as Ca^{2+} forms a charge bridge between the mucilage polymer and the arsenate anion. Ca^{2+} binding by pectic polysaccharides is well documented (Dronnet, Renard et al. 1996; Harel, Mignot et al. 1998; Melo and D'Souza 2004; Serguschenko, Kovalev et al. 2004; Arslanoglu, Altundogan et al. 2008; Balaria and Schiewer 2008; Schiewer and Patil 2008; Mata, Blazquez et al. 2009; Schiewer and Balaria 2009).

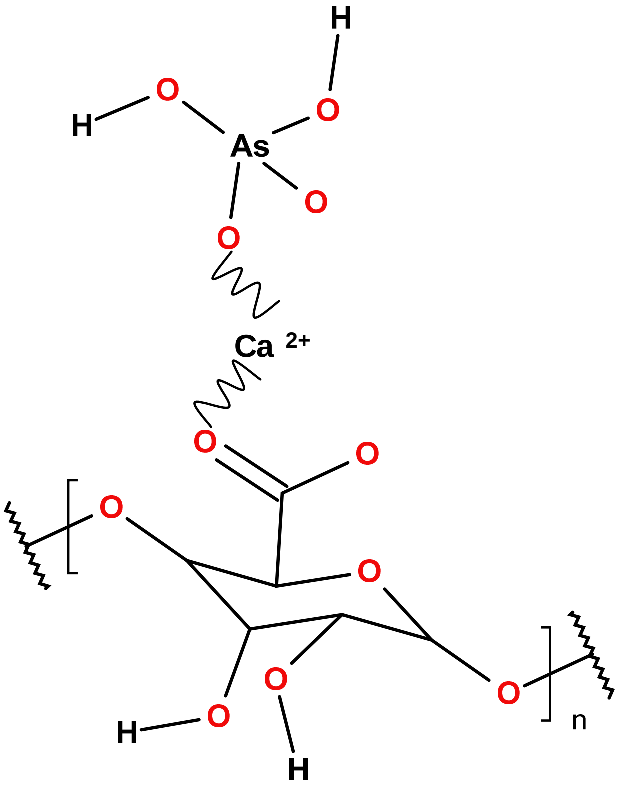


Figure 8.9 Schematic representation of cation-mediated interaction

For cation mediation to be an important mechanism, the presence of cations was expected to improve the efficiency of the mucilage at removing arsenic on the basis of reducing electrostatic repulsion between these species. The opposite was observed; the presence of Ca^{2+} ions hindered the mucilage performance. This may have been due to the competition of Ca^{2+} acting as a bridge between adjacent strands of mucilage polymer and thereby occluding attachment sites for the arsenate.

Direct binding involves the transfer of electrons from the electron-rich carboxyl O atoms directly to the available d-orbitals on the positive As(V) metal centre with loss of an OH group from the arsenate (Huheey, Keiter et al. 1993).

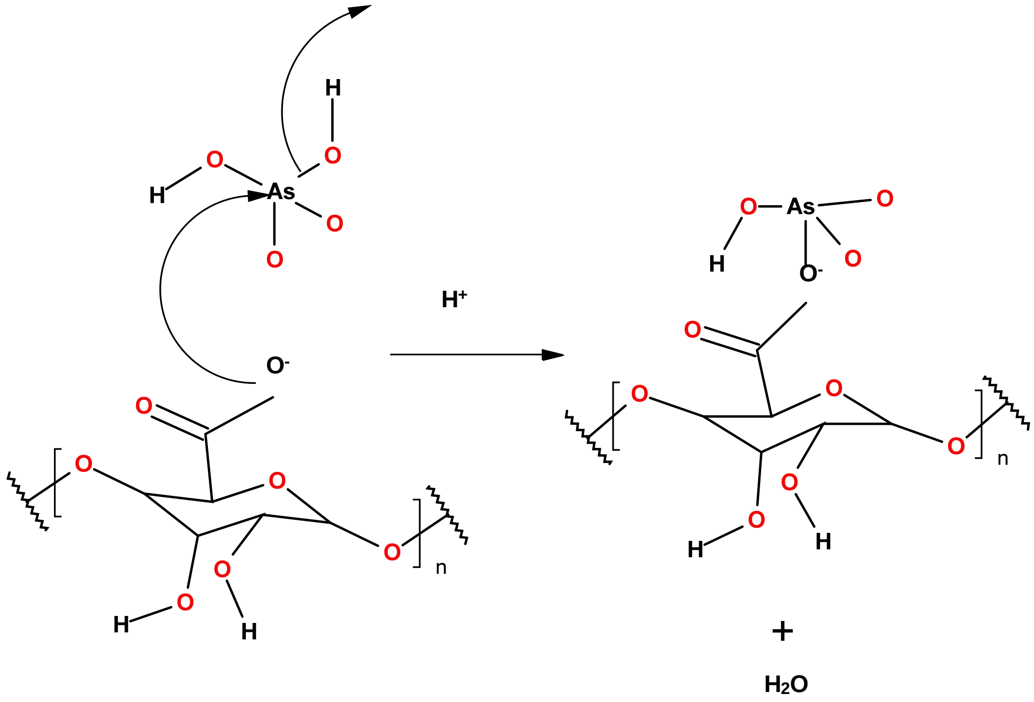


Figure 8.10 Schematic representation of donor-acceptor interaction

It is expected that this reaction would become important in mildly acidic pH where protons are available in solution yet allowing the carboxyl groups to be ionized. Given the pH dependence of this reaction, it may be expected that decreasing pH should improve the efficiency of the mucilage at removing arsenic. However, this correlation was not observed and could be due to the reactive ionizable carbonyl groups becoming protonated and unavailable for reaction at low pH. The mucilage performed best at specific pH (5, 5.5 and 9) which suggest that this is a response to changes in charges on both species with pH.

It should be noted that the negative charge on both the arsenate oxyanion and the mucilage carbohydrate polymer presents a common challenge of electrostatic repulsion to all the mechanisms of interaction. However, this repulsion is counteracted by attractive van der Waals forces which are significant for large carbohydrate polymers such as those present in the mucilage, and also by stabilization achieved by interaction. No one mechanism sufficiently accounts for all the observations; it is more likely that a combination of hydrogen bonding and donor-acceptor bonding occur.

8.3.3 UV-VIS spectroscopy

Further evidence for the activity of the carboxyl and carbonyl groups in the cactus extracts was obtained using UV-VIS spectroscopy. The spectra shown in figures 6.10 and 6.11 represent the electronic changes during the interaction of the GE and NE extracts with As. The main features of these spectra are the absorption peaks at 225 nm and 280 nm corresponding to electronic transitions of carboxyl and carbonyl UV chromophores respectively. For both GE and NE subtle hyperchromic shifts at these wavelengths occur, reaching maximum absorbance after 24 h. Given the time frame for the observed UV shifts, they may be linked to conformational changes, such as aggregation, in the systems.

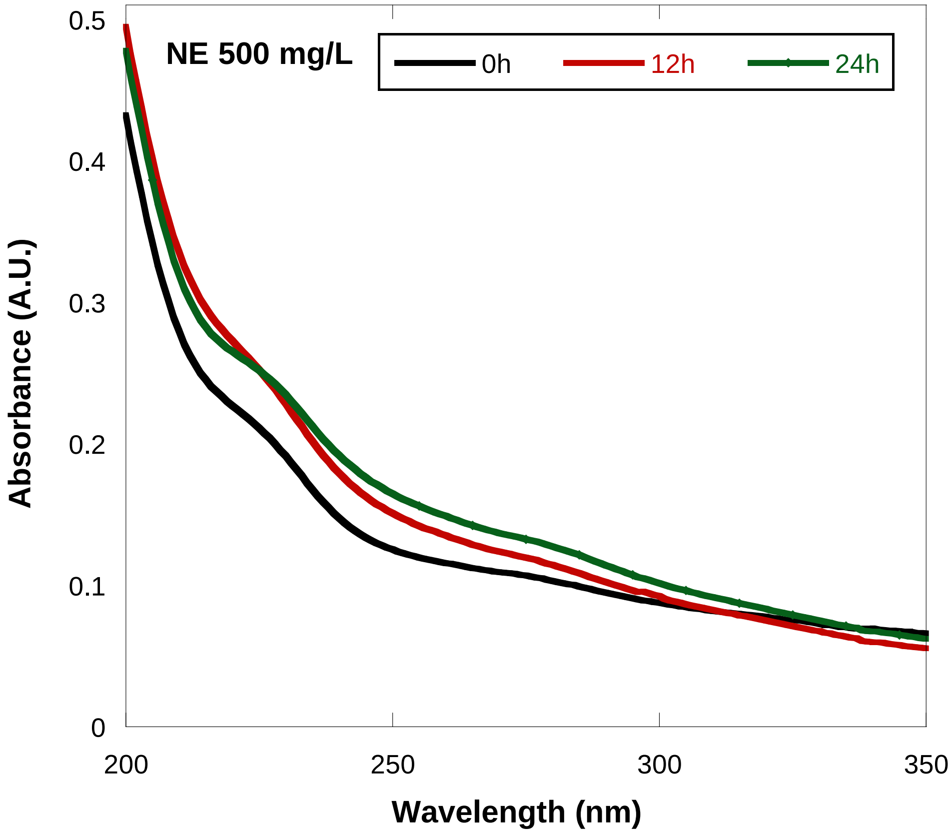


Figure 8.11 UV-VIS spectra of NE with arsenic

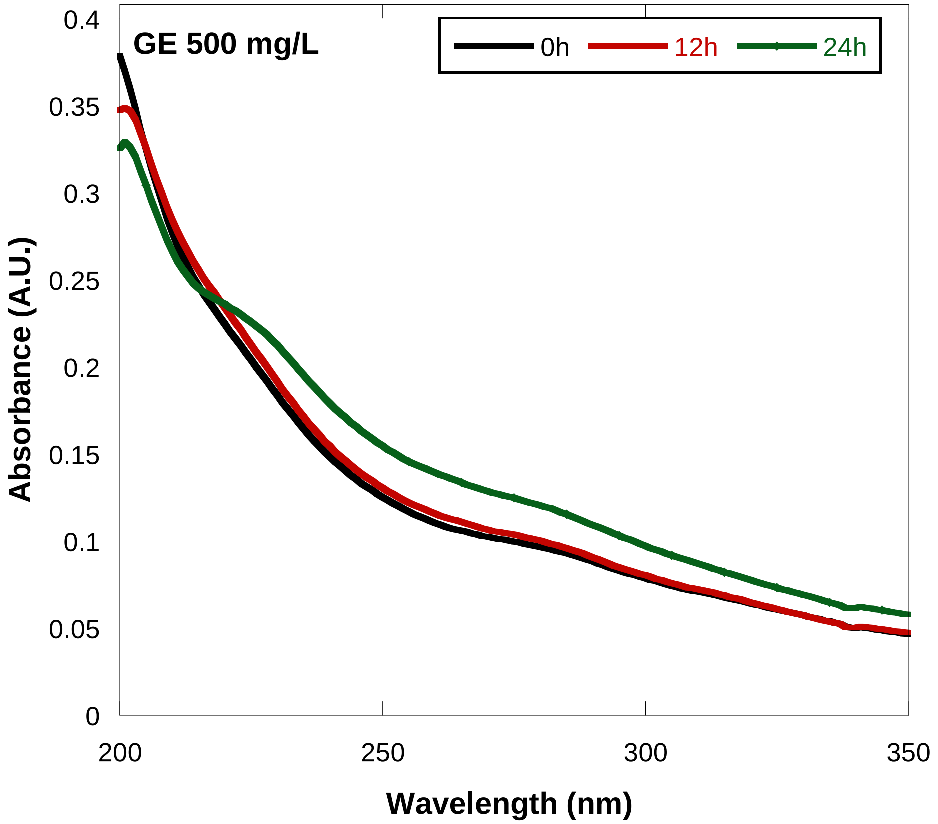


Figure 8.12 UV-VIS absorption spectra of GE with arsenic showing hyperchromic shift at 225 nm and 280 nm

8.4 Summary and conclusions

Spectroscopic studies point to the involvement of CO (carboxyl and carbonyl) and OH (hydroxyl) functional groups of the mucilage in hydrogen bonding and donor-acceptor interactions with arsenate.

ATR-FTIR spectra corroborated the findings of mucilage characterization that the NE and GE differ in uronic acid and neutral sugar content. Reaction with As produced changes in the mucilage ATR-FTIR spectra that were used to identify their active functional groups as CO (carboxyl and carbonyl) and OH (hydroxyl) groups. Two methods were used to obtain the ATR-FTIR spectra, a conventional film method and an alternative layer method, which was developed to provide more realistic *in situ* conditions than the film method. Both methods yielded the same observations. Further, UV-VIS spectra also indicated the activity of CO and OH groups.

Based on these observations, three mechanisms were proposed to explain the observations of mucilage interaction with As: hydrogen-bonding/bridging, cation-mediated electrostatic interaction and donor-acceptor (metal-ligand) interaction. Two of the mechanisms (hydrogen-bonding/bridging and donor-acceptor interactions) were supported by ATR-FTIR.

Having established that the major functionality in the pectic polysaccharides are carbonyl and hydroxyl (carboxyl) groups, it was deduced that mucilage binds As using these groups. At this point, it is proposed that the interaction occurs through a combination of mechanisms: hydrogen bonding between the protons of the OH groups on mucilage and O groups of arsenate, and electrostatic attraction or complexation between the positive metal centre of As (V) and the electron-rich CO groups of the mucilage on account of the tetrahedral geometry of the arsenate oxyanion (Cotton and Wilkinson 1999). FTIR data shows that for both GE and NE, hydrogen bonding, and binding at the carbonyl and carboxyl CO sites were important. Further, other researchers using entirely different biosorbents with similar functional groups have also reported the involvement of CO and

OH groups in As binding (Kamala, Chu et al. 2005; Haque, Morrison et al. 2007; Pandey, Choubey et al. 2009).

In the end, any process, whether extraction or derivatization, or condition that can increase the number and availability of active (CO and OH) groups, should improve the mucilage's ability to interact with As. For instance, the lower the degree of esterification of the GE carboxyl groups, the better it should perform due to a greater availability of carboxyl groups. This can be achieved through having a source of naturally occurring low methoxy pectin or, using a chemical extraction in preference to a physical/enzymatic method (Min, Lim et al. 2011). Further, these mechanisms can be extrapolated to predict the behavior of other pectic polysaccharides with As.

CHAPTER 9

SUMMARY AND CONCLUSIONS

Cactus mucilage from *Opuntia ficus-indica* (OFI) was investigated as an agent for the removal of arsenic (As) from water with the vision of creating an accessible, sustainable technology appropriate for use in developing countries. The mucilage is an effective coagulant (Miller, Fugate et al. 2008; Buttice, Stroot et al. 2010) and was shown to interact with As (Young, Pichler et al. 2008). Further, since the cactus is intrinsically renewable, environmentally-benign and widely accessible, it will transfer these qualities to the technology that incorporates it. In this work, two systems were studied: the cactus mucilage acting alone and a hybrid mucilage and iron treatment system. The mucilage and iron treatment system is especially promising as a scalable, easily implementable and relatively inexpensive method to remove arsenic from drinking water.

The primary objective of this research was to design a filter that used the interaction of mucilage with arsenic, as well as the flocculant properties of the mucilage to remove arsenic and particulates from water. This objective was largely achieved, as the working basis for the filter was demonstrated.

In batch experiments, synthetic As contaminated water was treated with two mucilage extracts, NE and GE. The results are described in Chapter 7. Both cactus extracts showed an interaction with As by binding and transporting As to the air-water interface of the water columns, as shown in Figure 7.1. This unprecedented mode of action was further corroborated by Total Organic Carbon (TOC) analysis, which showed that while mucilage goes to the top and bottom of the treatment container, the net result of the presence of As was the migration of mucilage from the solution bulk to the air-water interface (Figure 7.4). The pH dependence of the mucilage-arsenic interaction was also demonstrated (Figure 7.3). The interaction of mucilage and As can be exploited to remove As from drinking water by decanting the fraction of more contaminated water leaving the cleaner water behind. However, the removal rates were only modest, with GE and NE effecting a 14% and 9% respective increase in As concentration at the air-water interface (Figure 7.2). As such, it would require several stages of cleaning to effect a substantial reduction in As concentration at the expense of the contaminated water and As-laden mucilage which would have to be discarded.

A more efficient process was observed using the geochemical approach whereby the As contaminated water was first treated with Fe(III) salt. The salt underwent hydrolysis to form *in situ* iron hydroxides which adsorbed and reacted with the As forming a colloidal precipitate. When mucilage (GE) was added to this system, the precipitate rapidly coagulated, formed dense flocs and settled out of solution on the surface of the mucilage. As removal rates were typically between 75% to 90% but as high as 99% was observed. Further, As removal was found to be a function of the mucilage concentration, the Fe concentration and the extent of Fe hydrolysis, as shown in Figures 7.7, 7.9 and 7.11. Under the experimental conditions, the optimal mucilage concentration was 100 mg/L, optimal Fe(III) concentration was 40 mg/L and the older the Fe(III) solution, the better the system worked. In the best case scenario, solutions containing 100 µg/L As were reduced to below 10 µg/L. The advantage of using the mucilage over a system with Fe only treatment, is a faster, more efficient removal of the colloidal precipitates - arsenic-laden iron hydroxide precipitate as well as iron arsenate. A filter based on this process would require 1-2 stages for 100% As removal and a rough filter, such as sand or a cloth filter, to remove residual Fe and mucilage.

A supporting objective was to characterize the mucilage extracts in terms of chemical composition and morphology with the goal of relating these to any differences in performance. This objective was achieved as the GE and NE were both characterized by sugar and mineral composition as well as by TEM for their morphology and ATR-FTIR for their functional group composition. The two extracts had a very similar mineral composition; the major mineral component for both of them was calcium. NE had a higher neutral sugar content (50.8% by mass) than GE (30.1%). The GE had a higher proportion of uronic acid as shown by FTIR (Figures 8.1 and 8.2). Further, TEM exposed different morphologies of the two extracts; the GE being more porous and lace-like while the NE was smoother and sheath-like, resembling a fishing net.

These differences are very important in seeking to explain the difference in behavior of GE and NE in the arsenic removal systems studied. The functional group differences between the two extracts gave clues about the mechanism of interaction between As and mucilage. The morphological differences were of more importance to the iron and mucilage system where GE once again proved to be more effective than NE. In this case, it was the more porous structure of the GE that gave it a higher surface area to facilitate flocculation of the colloidal iron arsenate. These results were important to the research because it showed the versatility of the system having different modes of operation for different applications.

Further afield, these results are important to research involving materials of similar composition. This includes pectinaceous polysaccharides, as well as mucilaginous products from plants and animals. Several plants are known to produce mucilage, including Okra (*Abelmoschus esculentus*) , Sijan (*Moringa oleifera*), Aloe vera (*Aloe vera*), Psyllium (*Plantago ovata*) and Slippery elm (*Ulmus rubra*). Also, many microorganisms produce mucilage as exopolysaccharides. These mucilage compounds may become important to water treatment, should they show similar composition and properties to cactus mucilage.

At the heart of this study was the objective of determining the mechanism of the interaction between cactus mucilage and dissolved As. This objective was largely achieved as the carbonyl, carboxyl and hydroxyl groups of the mucilage were identified as active functional groups, and the most probable modes of interaction were discussed (Chapter 8). Coming out of this discussion was the observation that two mechanisms are supported by the experimental results and therefore it is likely that the mucilage interacted with the As by both hydrogen bonding/bridging and donor-acceptor ligand interaction. These results lay the groundwork for optimizing the mucilage-As system;

GE extraction methods which maximize the production of carboxylic and hydroxyl groups as against methylated groups are expected to perform better. Just as the similarities between mucilage functional groups and humic acid functional groups bore fruit in the interaction of mucilage with As, these results are expected to be important for the selection of future materials for interacting with As. A simple comparison of the functional groups can now give insight into the potential of new pectic polysaccharide materials for interacting with As.

These results are important because they demonstrate that the mucilage is versatile, being able to interact as a complexant for the arsenic as well as an effective coagulant aid for iron arsenate precipitate. Further, these results demonstrated that the GE was more important than NE for arsenic removal systems. Thus, the GE is an active component of an alternative treatment for arsenic removal and indeed for water treatment in general. Beyond the scope of this project, these results are important because the GE is a pectin and as such one can expect other pectinaceous polysaccharide polymers such as citrus, beet, and apple pectins to behave in a similar fashion. This is innovative because, to date, these materials are not used in any way in arsenic removal systems and these results can be particularly important in revolutionizing coagulation-flocculation-sedimentation systems. On a large scale, the rapid settling projected by the mucilage translates into smaller reactors, lower retention times leading to faster processing of arsenic contaminated water.

The contribution of this work is that the results herein will inform design and implementation of prototype filters based on mucilage use. The active material, cactus mucilage, is easily obtained from an abundant, adaptable plant. The technology is simple to use and will require no fossil fuel energy to operate. What remains to be done is the building and testing of the prototype both with synthetic challenge water as well as in the field with real As-contaminated water. Overall, this research has accomplished its aim in providing the groundwork for a new, accessible technology for As removal from drinking water.

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