ARSENIC OXIDATION ASSISTED BY CARBON-BASED CATALYSTS IN DYNAMIC AND CONTINUOUS CONDITIONS

by

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Abstract

Arsenic is a toxic element and has become a major element of concern in the mining industry. Severe environmental issues may arise if the soluble arsenic species released by mining and extractive metallurgy activities were not responsibly and appropriately managed. Most arsenic immobilization techniques are not efficient for treating trivalent arsenic in solutions. In the cases where soluble trivalent arsenic is predominant in the waters, a first step of oxidation is usually required to yield a desirable overall arsenic removal efficiency.

This thesis presents the results of an investigation on the carbon catalyst assisted arsenic oxidation process with emphasis on the impact of the key process parameters on oxidation efficiency. Rapid small-scale continuous column testing method was employed to simulate dynamic and continuous operations. The process residence time, pH and initial arsenic concentration are demonstrated to be the most crucial operational parameters that have significant impacts on arsenic oxidation. The arsenic oxidation efficiency is proven to be highly sensitive to the change of aqueous pH due to the shift of reaction pathways at various pH scenarios, which is correlated to the specific behaviors of different aqueous arsenic species. Both preloaded and recycled activated carbon are validated for competent capacity to catalyze arsenic oxidation. The reliable long-term performance of activated carbon is demonstrated in a 27 days-long test with a steady arsenic oxidation efficiency of above 97%. Another carbon-based catalyst, Lewatit® AF 5, which has a higher surface area and more active sites than activated carbon, is used in a column test to verify that the functionality of carbon, instead of the specific surface area, has the most catalytic ability of carbon to oxidize arsenic. This is further supported by tests with nitric acid treated activated and AF5, in which the arsenic oxidation is greatly improved at the initial stage, though the efficiency eventually declines to the same level of that of the original carbons. The initial improvement of arsenic oxidation is attributed to the nitric acid exploitation of oxidative function groups on the carbon surfaces.
Acknowledgements

I hope to dedicate this thesis to all those people who have been my mentors, friends, and confidant that always motivate me throughout my pursuit to the master’s degree.

The most generous support from my supervisor Professor Ahmad Ghahreman is greatly appreciated. The lessons I learned from him, on doing research as well as on pursuing advances, will remain a lifetime treasure.

I am grateful for the help of the faculty members and staffs of the Robert M. Buchan Mining Department of Queen’s University, the colleagues and friends in the Hydrometallurgy and Environment Group.

I know my deepest gratitude is felt by my dearest family and the most special one, as sure as I feel them all the time despite the 12 (sometimes 13) hours’ time difference. No word expression of quantity can barely equal to a tenth of how much I own them.

Lastly, thank myself, for being myself, as a whole.
Table of Contents

Abstract ................................................................................................................................. ii
Acknowledgements ................................................................................................................ iii
List of Figures ......................................................................................................................... vii
List of Tables ......................................................................................................................... ix
Chapter 1 Introduction ............................................................................................................. 1
  1.1 Background .................................................................................................................... 1
  1.2 Purposes ....................................................................................................................... 4
  1.3 Scope and importance ................................................................................................. 4
  1.4 Thesis outline ............................................................................................................. 5
Chapter 2 Literature review .................................................................................................. 7
  2.1 Arsenic species ............................................................................................................ 7
    2.1.1 Arsenic occurrence in nature ................................................................................. 7
    2.1.2 Arsenic toxicity ..................................................................................................... 8
    2.1.3 Water chemistry of arsenic .................................................................................. 10
  2.2 Mobilization of arsenic ............................................................................................... 13
    2.2.1 Natural and other anthropogenic sources of arsenic ............................................ 13
    2.2.2 Release of arsenic by mining activities ................................................................. 14
      2.2.2.1 Pyrometallurgical operations ......................................................................... 16
      2.2.2.2 Hydrometallurgical operations ..................................................................... 18
      2.2.2.3 Acid mine drainage (AMD) .......................................................................... 19
  2.3 Arsenic immobilization practices ................................................................................. 20
    2.3.1 Oxidation ............................................................................................................... 20
      2.3.1.1 Conventional oxidation techniques ................................................................. 21
      2.3.1.2 Advance oxidation processes (AOPs) ............................................................. 22
      2.3.1.3 Bio-oxidation ................................................................................................. 23
    2.3.2 Stabilization .......................................................................................................... 26
      2.3.2.1 Adsorption .................................................................................................... 26
      2.3.2.2 Precipitation ................................................................................................. 28
  2.4 Carbon-based catalysts for oxidation .......................................................................... 28
  2.5 Arsenic oxidation assisted by activated carbon ......................................................... 31
    2.5.1 Patent summary .................................................................................................... 32
    2.5.2 Hypothesis proposed on the mechanism ............................................................. 33
Chapter 3 Materials and experimental methods ................................................................. 34
3.1 Raw materials and chemical reagents ........................................................................... 34
  3.1.1 Activated carbon ....................................................................................................... 34
  3.1.2 Lewatit® AF5 catalyst .............................................................................................. 35
  3.1.3 Solution preparation ................................................................................................. 36
  3.1.4 Pretreatment of carbons ......................................................................................... 37
3.2 Experiment design .......................................................................................................... 38
  3.2.1 Rapid small-scale column testing method .............................................................. 38
  3.2.2 Column reactor ...................................................................................................... 38
  3.2.3 Column test matrix ................................................................................................. 40
3.3 Analytical methods ........................................................................................................ 42
  3.3.1 Arsenic speciation .................................................................................................. 42
    3.3.1.1 Trivalent arsenic ............................................................................................... 42
    3.3.1.2 Pentavalent arsenic ......................................................................................... 42
    3.3.1.3 Total arsenic ................................................................................................... 43
  3.3.2 Chemical measurements ....................................................................................... 44
    3.3.2.1 Dissolved oxygen (DO) .................................................................................. 44
    3.3.2.2 pH and oxidation reduction potential (ORP) .................................................. 44
  3.3.3 Hydrogen peroxide determination .......................................................................... 44
  3.3.4 Experimental errors .............................................................................................. 45
3.4 Safety precautions .......................................................................................................... 45
Chapter 4 Preliminary study on the carbon assisted arsenic oxidation process: baseline column test ...... 47
  4.1 Column test procedure ............................................................................................... 47
  4.2 Results and discussion ............................................................................................... 47
    4.2.1 Evolution of arsenic species concentrations ......................................................... 47
    4.2.2 The pH and ORP in the influent and effluent ....................................................... 49
    4.2.3 DO in the influent and effluent ............................................................................ 50
Chapter 5 Kinetics column tests ............................................................................................ 52
  5.1 Parameters study on activated carbon catalyzed arsenic oxidation .............................. 52
    5.1.1 Effect of initial arsenic concentration .................................................................. 52
    5.1.2 Effect of system pH .............................................................................................. 54
    5.1.3 Effect of residence time ...................................................................................... 57
    5.1.4 Effect of oxygen condition .................................................................................. 61
  5.2 Dependence of oxidation efficiency on arsenic speciation ......................................... 67
List of Figures

Figure 2-1. Structural configurations of arsenite (left) and arsenate (right) compounds. ............................. 10
Figure 2-2. Eh-pH diagram for the As-O-H system at 25 °C and 1 bar with 10^6 M As (Brookins, 2012). 11
Figure 2-3. Concentrations of As(III) species as a function of pH (in reducing conditions). ......................... 12
Figure 2-4. Concentrations of As(V) species as a function of pH (in oxidizing conditions). ......................... 12
Figure 2-5. Distribution of documented world problems with As in groundwater in major aquifers as well as water and environmental problems related to mining and geothermal sources (Smedley & Kinniburgh, 2002). ................................................................................................................ 15
Figure 2-6. Arsenic content in concentrate of select mines (Schwartz, Omaynikova, & Stocker, 2017) ... 16
Figure 2-7. Typical paths of arsenic in copper pyrometallurgy (Piret, 1999). .................................................... 17
Figure 2-8. Schematic representation of the generation of arsenic acid mine drainage with dissolved arsenic (Paikaray, 2015) ........................................................................................................................................ 20
Figure 2-9. Microbial transformations of arsenic as (a) a detoxification mechanism; (b) mechanisms to gain energy (Cavalca et al., 2013). ............................................................................................................. 25
Figure 2-10. A typical structure of activated carbon and the common types of surface functional groups (Jahromi, 2019). ........................................................................................................................................... 30
Figure 2-11. The process flow chart of the activated carbon catalyzed arsenic oxidation ............................. 32
Figure 3-1. Pore size distribution of activated carbon-based on BJH adsorption ............................................. 35
Figure 4-1. Arsenic speciation for column test conditions: pH = 1.00; oxygen flow rate = 0.05 LPM; influent As(III) concentration (C_0) = 4.70 g/L As(III); and residence time = 218 min. ......................... 48
Figure 4-2. The pH and ORP in the influent and effluent solutions of the baseline column test ................. 49
Figure 4-3. Concentrations of dissolved oxygen in the influent and effluent samples ............................... 51
Figure 5-1. As(V) concentrations in the effluent of column tests fed with different As(III) solutions (test conditions: pH=0.98; oxygen flow rate=0.05 LPM; residence time=218 min.) ......................... 53
Figure 5-2. The effect of the influent arsenic concentration on the arsenic oxidation efficiency .......... 53
Figure 5-3. pH values of the influent and effluent solution of column tests .................................................. 54
Figure 5-4. The pH and ORP scenario in the column test with pH 5.14 influent (5 g/L As(III)) ............... 56
Figure 5-5. Arsenic oxidation efficiency in column tests at different pH conditions ................................. 57
Figure 5-6. Extending the length of column setup but still pack with same amount of carbon as baseline experiment (left); Arsenic speciation for the test in an extended column reactor with more void volume (other conditions same as baseline experiment; retention time from inlet to outlet = 750 min; equivalent residence time = 218 min) (right) ........................................................................................................ 59
Figure 5-7. Feature curves for column tests with different residence time and same other conditions: feed 5.91 g/L As(III) solution; pH=0.96; oxygen flow rate=0.05 LPM. ................................................................. 60
Figure 5-8. The effect of residence time on the arsenic oxidation efficiency. .......................................................... 61
Figure 5-9. Feature curves for test conditions: oxygen flow rate=0.10 LPM; feed 9.81 g/L As(III) solution; residence time=218 min. ................................................................. 62
Figure 5-10. Feature curves for test conditions: oxygen flow rate=0.2 LPM; feed 5.98 g/L As(III) solution; and residence time=137 min. ................................................................. 62
Figure 5-11. Feature curves for a column test with air flow rate of 0.25 LPM (Other conditions: pH=1.02; feed 5.08 g/L As(III) solution; and residence time=218 min). .................................................. 64
Figure 5-12. Feature curves for a column test with 0.05 LPM air flow (Other conditions: pH=1.02; feed 5.08 g/L As(III) solution; and residence time=218 min). ................................................................. 65
Figure 5-13. Feature curves for a column tests with air flow rate of 0.10 LPM. (Other conditions: pH=1.02; feed 5.08 g/L As(III) solution; residence time=218 min). ................................................................. 66
Figure 5-14. The correlation of arsenic oxidation efficiency and oxidation indexes: dissolved oxygen and hydrogen peroxide level.................................................................................................................. 67
Figure 5-15. The plot of pH and ORP (tested in the effluent of column tests) in the Eh-pH diagram of As-H₂O system (25 ºC and 1 bar)................................................................................................................... 68
Figure 5-16. Calculated As(V) speciation concentrations for 5 g/L (6.67 mM) As solution with 20 ppm dissolved oxygen in the pH range of 0~7 (adapted from OLI software) ................................................................. 69
Figure 6-1. Feature curves for test conditions: oxygen flow rate=0.05 LPM; feed 4.70 g/L As(III) solution; and residence time=218 min; recycled carbon. ................................................................. 72
Figure 6-2. Feature curves for test conditions: pH=1.0; oxygen flow rate=0.05 LPM; feed 1.03 g/L As(III) solution; and residence time=218 min; preloaded carbon .................................................................................................................. 73
Figure 6-3. Feature curves of a long-term column tests with 1 g/L As(III) feed solution. ...................... 74
Figure 6-4. Feature curves of a column test with HNO₃ pretreated activated carbon (feed As(III)=5.06g/L; influent pH=1.0; 0.05L/min oxygen sparging). ................................................................. 76
Figure 6-5. Feature curves for column test with original AF5 (feed As(III)=5.06g/L; influent pH=1.0; 0.05L/min oxygen sparging). ................................................................. 77
Figure 6-6. XPS spectra of O 1s peak for original (left) and nitric acid pretreated AF5 (right) (Jahromi & Ghahreman, 2019) .................................................................................................................. 78
Figure 6-7. Feature curves for column tests with HNO₃ pretreated AF5 (feed As(III)=5.06g/L; influent pH=1.0; 0.05L/min oxygen sparging) .................................................................................................................. 79
List of Tables

Table 1. Authorized arsenic limits in effluents in different countries ................................................................. 3
Table 2. Major arsenic-bearing minerals (Drahota & Filippi, 2009; Riveros et al., 2001) ........................................ 8
Table 3. Column tests matrix ........................................................................................................................................ 41
Table 4. Dissolved oxygen in the test solutions with various oxygen bubbling conditions ................................. 63
Table 5. Relative content of functional groups in O 1s peak (Jahromi & Ghahreman, 2019) ............................ 78
Chapter 1 Introduction

1.1 Background

Arsenic contamination has been a worldwide concern attracting increasing attention from chemists and environmentalists, due to its toxicity and ubiquity (Rumble, 2019). Dissolved arsenic enriched in drinking water causes serious health problems all over the world and particularly in some densely populated regions in developing countries such as Mexico, Chile, Bangladesh, India, and Vietnam. Inorganic arsenic is a Group I carcinogen which is confirmed to be able to induce skin, lung, and bladder cancers (Shi, Shi, & Liu, 2004). Chronic exposures to arsenic contaminated water can also lead to diabetes, hyperpigmentation, skin-thickening, muscular weakness, neurological diseases, and cardiac disorders (Ratnaike, 2003).

Arsenic is abundant in the earth’s crust with an average terrestrial concentration of 5ppm (Riveros, Dutrizac, & Spencer, 2001). A wide range of arsenic containing minerals have been identified in nature, and in most cases these minerals are also associated with those that have commercial value (Anderson, Twidwell, Robins, & Mills, 2014). For example, enargite (Cu₃AsS₄) and tennantite (Cu₁₂As₄S₁₂) are commonly present in sulphide copper ores. Though some natural arsenic bearing minerals are considered stable because of their negligible aqueous solubility under natural conditions, problems may still arise if arsenic in these minerals enters the mining sector, where a mineralogy alteration or phase change could liberate arsenic.

In contrast to the abundant occurrence of arsenic in nature, the market for arsenic consumption is very limited. Historically, arsenic trioxide was sold for the manufacture of chromated copper arsenate (CCA) compounds used in wood preservation; however, this market has been significantly reduced in most countries. Arsenic usage in agricultural domains has declined ever since its being phased out from pesticides, herbicides and fungicides. Arsenic is also used for manufacture of commercial products in the alloy industry, but these consumptions contribute negligible offsets
compared to the amount of arsenic liberated as a byproduct, mostly hazardous wastes, in many other industries. The mining industry contributes a significant portion of arsenic emissions to the total environment (26% of atmosphere emission; 35% of land-disposed wastes; and 72% of arsenic discharged to surface water) (Lowenbach & Schlesinger, 1979). In mining, the arsenic ends up in process streams or waste waters after a series of industrial activities, from mining to metallurgy, and should be immobilized from the solutions before they can be discharged or recycled in order to restrict the detrimental impacts it could impose on the environment.

Arsenic has been subject to increasingly stringent regulations in recent decades (Anderson et al., 2014), because of the high risks that liberated arsenic would pose on human health (Harris, 2000). A series of regulations and detailed guidelines were developed for arsenic environmental scrutiny. Canadian authority defines arsenic as a deleterious substance in the Metal and Diamond Mine Effluent Regulations (MDMER) and prescribes that arsenic in effluents must be removed to a concentration below the limit of 0.50 mg/L. Table 1 summarizes the authorized limit for arsenic concentrations in the industrial effluents in different countries.

Arsenic is one of the unwanted elements that are frequently encountered in sulfide ores. On the one hand, smelting of arsenic-bearing resources may cause serious emission problems since arsenic and its compounds are toxic; on the other hand, arsenic involved in the processes either interfere with the operation of both the smelter and refinery or seriously affects the physical properties of metallic products. In processing of copper, nickel, gold and uranium ores, arsenic is commonly present as an impurity that has to be removed and eventually reports to aqueous processing effluents (Harris, 2000). To minimize the environmental risk of arsenic contamination, the processing effluents from mining and metallurgy operations must undergo treatment to convert the soluble arsenic to a stable form for safe disposal.
The immobilization of arsenic is an essential goal of arsenic-containing effluents treatment. Most proven arsenic immobilization techniques preferentially require arsenic to be in the pentavalent

<table>
<thead>
<tr>
<th>Country</th>
<th>Arsenic concentration limit (Monthly average)</th>
<th>Regulation title/code</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States of America</td>
<td>0.309 ppm</td>
<td>Nonferrous Metals Manufacturing (NFMM) Effluent Guidelines and Standards (40 CFR Part 421)</td>
</tr>
<tr>
<td>China</td>
<td>0.50 ppm</td>
<td>Effluent standards (GB 8978-1996)</td>
</tr>
<tr>
<td>Singapore</td>
<td>0.10 ppm</td>
<td>Environmental Protection and Management (Trade Effluent) Regulations</td>
</tr>
<tr>
<td>Canada</td>
<td>0.50 ppm</td>
<td>Metal and Diamond Mine Effluent Regulations</td>
</tr>
<tr>
<td>Zambia</td>
<td>1.00 ppm</td>
<td>The local administration (trade effluent) regulations</td>
</tr>
<tr>
<td>Chile</td>
<td>0.50 ppm</td>
<td>D.S. 90/2000, 2008</td>
</tr>
<tr>
<td>Malaysia</td>
<td>0.10 ppm</td>
<td>Environmental Quality (Sewage and Industrial Effluents) Regulations</td>
</tr>
<tr>
<td>Brazil</td>
<td>0.50 ppm</td>
<td>CONAMA Directive 357/2005</td>
</tr>
<tr>
<td>Mexico</td>
<td>0.50 ppm</td>
<td>NOM-002-ECOL-1996</td>
</tr>
</tbody>
</table>
form because the higher oxidation state of arsenic typically offers a more stable product that can be safely disposed of in landfill. However, there is a fair amount of cases where trivalent arsenic is the predominant arsenic species in acidic mining solutions, particularly in reducing environments. Hence the arsenical solution needs to be oxidized prior to its removal from process streams. In industrial practice, arsenic oxidation is usually achieved with the use of strong but expensive oxidants. The oxidation process employing hydrogen peroxide as oxidant often accounts for 30% of the process operating cost. To address the dilemma in the industry, a novel process has emerged in which the arsenic oxidation is catalyzed by activated carbon in oxygenated systems using oxygen gas as the only consumable reagent to effectively oxidize arsenic at high concentrations. This economical process promises to be an ideal alternative technology for conventional oxidization process on an industrial scale due to its impressive reaction efficacy and robustness; nonetheless, its application under larger scale dynamics and continuous conditions has not been comprehensively studied.

1.2 Purposes
The purpose of this thesis is to study the effectiveness of the activated carbon assisted arsenic oxidation process and moreover to investigate the feasibility of the process under pilot scale. Different types of carbon-based catalysts are also examined under similar conditions for comparison with original activated carbon. The ultimate objective of this thesis is to facilitate the application of carbon-based catalyst assisted arsenic oxidation technology in the mitigation of arsenic in mining contaminated areas or wastewater treatment in the mining and metallurgy industry.

1.3 Scope and importance
Activated carbon is proven to be able to catalyze arsenic oxidation effectively and efficiently. The desirable efficiency and low expenses of the carbon assisted arsenic oxidation make it possible to develop compact arsenic treatment systems. However, little is known about the design parameters
of this process for industrial use and the basic requirements for the carbon catalysts (i.e. carbon types, pretreatments). The scope of this thesis is to reveal minimum requirements of the activated carbon assisted arsenic oxidation process for acceptable efficacy and to gain an insight into the reaction chemistry by investigating the affecting parameters under dynamic conditions.

This thesis describes how this process works under continuous conditions, by including the following related topics: design of a dynamic continuous column reactor that approaches the goals of the research; validation of carbon assisted arsenic oxidation process under dynamic and continuous conditions; optimization of operating parameters; comparison of different carbon materials; and constructive guidelines for larger scale operations.

1.4 Thesis outline

Chapter 1 introduces the general background of the arsenic concern in mining industry and the importance of this work, defines the objective and scope of this thesis, and outlines the structure of the curation.

Chapter 2 reviews the current state of knowledge in respect to a collection of related topics, including the arsenic occurrence, toxicity, arsenic chemistry, arsenic relation to mining industry, basic concepts in conventional arsenic immobilization processes, typical industrial practiced technologies and the progress of study in the carbon catalyzed arsenic oxidation process.

Chapter 3 explains the main testing and analytical methods and fundamental handling of materials involved in the experiment. Important materials properties, details about the chemical reagents used in the test work, and conceptual experimental design are also laid out in this chapter.

Chapter 4 delivers the results of the baseline column test, which was selected for the preliminary study of the activated carbon catalyzed arsenic oxidation process under dynamic and continuous conditions.

Chapter 5 details the experimental evaluation of the important operational parameters regarding the activated carbon catalyzed arsenic oxidation process. The effects of pH, residence time, aeration
condition, and initial arsenic concentration in the influent solution on oxidation efficiency are studied systematically. The catalytic mechanism of activated carbon is further discussed based on the experimental findings.

Chapter 6 presents preliminary findings on the catalysis of various carbons prepared from different carbon types and/or undergone different alteration and modification of carbon surfaces. A summary discussion is included in this chapter which correlates the findings to the previous proposed mechanism.

Chapter 7 summarizes the experimental findings throughout the thesis and discussions on the catalysis mechanism of carbon assisted arsenic oxidation process. Some pertinent recommendations are highlighted for the future studies in this research area.
Chapter 2 Literature review

2.1 Arsenic species

2.1.1 Arsenic occurrence in nature
Arsenic is the 33rd element in the periodical table symbolized as “As” and is regarded as a metalloid. Arsenic ranks 20th among other elements in crustal abundance and is a constituent of 245 mineral species (Lowenbach & Schlesinger, 1979). Arsenic is also found in the natural environment including soil, water, and air. Man-made sources contribute approximately two thirds of the arsenic present in the environment.

Mineral forms of inorganic arsenic are comprised of approximately 60% arsenates, 20% sulphides/sulphosalts, 10% oxides, and the remainder of arsenite, arsenides, native arsenic and metal alloys (Drahota & Filippi, 2009). In most primary arsenic-bearing minerals, arsenic occurs as anions bonded to metals such as Fe (arsenopyrite), Ni (gersdorffite), Co (cobaltite), or as sulpharsenide anions. Secondary arsenic minerals typically formed via alteration reactions when those primary minerals are exposed to the atmosphere and surface or groundwaters, such arsenic minerals include simple As oxides or more complex phases with As, oxygen and various metals (Drahota & Filippi, 2009). Some most common arsenic-bearing minerals are listed in Table 2.

Arsenopyrite is the most commonly found arsenic mineral, followed by enargite and cobaltite. Apart from arsenical minerals, arsenic is also often present in varying concentrations in other common rock-forming minerals, though not as a major component, in place of sulphur element which possesses similar chemical properties. Elevated arsenic concentrations are commonly found in sulfide deposits associated with nonferrous ores. The highest concentrations of arsenic tend to occur in sulphide minerals, of which pyrite is the most abundant (Smedley & Kinniburgh, 2002).
Arsenate compounds comprise a large class of minerals that have been found in oxidized environments.

**Table 2. Major arsenic-bearing minerals (Drahota & Filippi, 2009; Riveros et al., 2001).**

<table>
<thead>
<tr>
<th>Mineral group</th>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenides</td>
<td>Nickeline</td>
<td>NiAs₂</td>
</tr>
<tr>
<td></td>
<td>Safflorite</td>
<td>(Co,Fe,Ni)As₂</td>
</tr>
<tr>
<td></td>
<td>Skutterudite</td>
<td>CoAs₃</td>
</tr>
<tr>
<td>Oxides</td>
<td>Arsenolite</td>
<td>As₂O₃ (cubic)</td>
</tr>
<tr>
<td></td>
<td>Claudetite</td>
<td>As₂O₃ (monoclinic)</td>
</tr>
<tr>
<td>Arsenates</td>
<td>Olivenite</td>
<td>Cu₂(AsO₄)(OH)</td>
</tr>
<tr>
<td></td>
<td>Arseniosiderite</td>
<td>Ca₂Fe₂O₅(AsO₄)₃·3H₂O</td>
</tr>
<tr>
<td></td>
<td>Scorodite</td>
<td>FeAsO₄·2H₂O</td>
</tr>
<tr>
<td>Sulphides and Sulphosalts</td>
<td>Arsenopyrite</td>
<td>FeAsS</td>
</tr>
<tr>
<td></td>
<td>Arsenical pyrite</td>
<td>Fe(As,S)₂</td>
</tr>
<tr>
<td></td>
<td>Cobaltite</td>
<td>CoAsS</td>
</tr>
<tr>
<td></td>
<td>Enargite</td>
<td>Cu₃AsS₄</td>
</tr>
<tr>
<td></td>
<td>Gersdoffite</td>
<td>NiAsS</td>
</tr>
<tr>
<td></td>
<td>Lollongite</td>
<td>FeAs₂</td>
</tr>
<tr>
<td></td>
<td>Orpiment</td>
<td>As₂S₃</td>
</tr>
<tr>
<td></td>
<td>Realgar</td>
<td>AsS</td>
</tr>
<tr>
<td></td>
<td>Tennantite</td>
<td>(Cu,Ag,Fe,Zn)₁₂As₄S₁₃</td>
</tr>
</tbody>
</table>

2.1.2 Arsenic toxicity

Arsenic has always been attracting significant attention from chemists and environmentalists for centuries because of its notoriety as a poison both in history and in popular literature, despite that arsenic itself may not be the most toxic of elements, particularly in its pentavalent state (Harris, 2000). But arsenic is indeed toxic; and undeniably, improper disposal of arsenic materials can pose disastrous threats on the general environment and human health. Hereafter, the arsenic toxicity is
discussed concerning its poisoning and pathogenic mechanism on causing harmful health effects including cancers.

The inorganic forms of arsenic are found to be more toxic than organic arsenic. Soluble inorganic arsenic species can be absorbed up to over 90% in the human body, while organo-arsenics are absorbed only about 15~40% in most cases (Uthus, 1994). There are two kinds of toxicity in evaluating the harmful effects of toxic substances: acute and chronic toxicity. Acute toxicity describes the immediate effects resulted from the intake of the substance or intensive exposure to the substance within a short period of time; whereas, the chronic toxicity refers to the detrimental effects that usually appear as a result of a long-term exposure (Sarkar & Paul, 2016). Acute toxicity of arsenic occurs from inhalation or ingestion of arsenic compounds. Direct intake of arsenic may cause vomiting and diarrhea, and the symptoms can be resolved within 12 h without any treatment if a dose is no more than 5 mg of arsenic compounds at one time (Ratnaike, 2003). The lethal dose of arsenic for an adult human is estimated to be 1-3 mg/kg (Hughes, 2002). The mostly encountered manifestations of acute arsenic toxicity include nausea, vomiting, severe abdominal pain, etc. (Mazumder, 2008). Chronic arsenic toxicity causes health effects on human body organs such as skin, liver, etc. One of the major symptoms of chronic arsenic poisoning is skin pigmentation and keratosis (Hughes, 2002; Mazumder, 2008). Nervous system, respiration system, and renal system are also vulnerable to arsenic chronic poisoning (Mazumder, 2008). A number of seriously concerned health effects, including DNA impairment, inhibition of enzymatic activities, and tumor promotion, has been reported in some recent studies (Sarkar & Paul, 2016; Shi et al., 2004).

Metabolism of arsenic in human and living organisms plays a decisive role in arsenic poisoning (Ratnaike, 2003). Inorganic arsenic species will undergo methylation processes, where the arsenites and arsenates lose one hydroxyl radical for the addition of each methyl group, once entered human body and being involved in metabolism (Bentley & Chasteen, 2002; Bhattacharya et al., 2007). The metabolized methylation will assist in activating the toxicity of arsenic since it produces MMAIII
(monomethyl arsenous acid) and DMAIII (dimethyl arsenous acid) which have cytotoxic and genotoxic effects (Thomas, Styblo, & Lin, 2001).

Arsenite (As(III)) is known to be of the greatest toxicity among the inorganic arsenic species. The presence of the ionizable hydroxyl group (-OH) on an arsenite oxyanion contributes the most to its notoriety in being problematic. During the metabolic methylation process of arsenic, the hydroxyl group (-OH) of arsenite is replaced by methyl groups (-CH$_3$) giving rise to the methylated species of arsenic which are less electronegative; these methylated species can easily bind to the electronegative biomolecules such as DNA at physiological pH, resulting in impairments of DNA (Tseng et al., 2006).

2.1.3 Water chemistry of arsenic

Arsenic is defined as a metalloid which has some of the properties of a metal but is not actually a metal. The element arsenic itself is not soluble in water. However, arsenic in combination with other elements has a wide range of solubility depending on the aqueous acidity as well as the presence of other species. Arsenic can exist in the environment in several oxidation states (−3, 0, +3 and +5) but in natural waters is mostly found in inorganic form as trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Under reducing conditions, arsenite is the dominant form; arsenate is generally the stable form in oxygenated environments. The molecular structures of the two primary arsenic valency states are depicted in Figure 2-1.

![Figure 2-1. Structural configurations of arsenite (left) and arsenate (right) compounds.](image-url)
Redox potential (Eh) and pH are the most important factors controlling As speciation in solutions. The Eh-pH diagram (Figure 2-2) provides the view of stability area of metal/metalloid species in terms of the solution pH and Eh. Oxidative condition is indicated as positive Eh values on the diagram, higher values signifies stronger oxidative condition. It is worth mentioning that the Eh-pH diagram only provides theoretical information on the arsenic speciation based on thermodynamic properties, both arsenite and arsenate can coexist in either redox condition due to slow kinetics.

![Eh-pH diagram](image)

**Figure 2-2.** Eh-pH diagram for the As-O-H system at 25 °C and 1 bar with 10^6 M As (Brookins, 2012).

The specific As(III) and As(V) speciation over pH range 0-14 are depicted in Figure 2-3 and Figure 2-4. Arsenite (As(III)) species exist at reducing conditions. Lower Eh represents a stronger reducing condition, where the uncharged arsenite species H₃AsO₃ will predominate at pH lower than 9.2 while H₂AsO₃⁻ with single negative charge will be present at higher pH.
Different arsenate [As(V)] species are expected at oxidative conditions depending on the pH: $\text{H}_3\text{AsO}_4^0$ and $\text{AsO}_4^{3-}$ may be present in extremely acidic and alkaline conditions respectively, $\text{H}_2\text{AsO}_4^-$ is dominant at pH lower than 6.9, while $\text{HAsO}_4^{2-}$ becomes dominant at higher pH. The speciation of arsenic in the solution remarkably affects its behavior when in contact with other ions or particles, either through electrostatic bonding or chemical reactions that form precipitates.
2.2 Mobilization of arsenic

Arsenic and its compounds usually occur in trace quantities in rocks, soil, water and air. However, higher level of concentration may appear in certain areas as a result of weathering and anthropogenic activities, which mobilize arsenic from its original stable forms in the earth’s crust. Arsenic is transported between different parts of the environment where it may change its form. After being released from the earth’s crust into soluble forms, arsenic is easily transported through water flow and becomes difficult to be immobilized under natural conditions. In comparison to other oxyanion-forming elements, arsenic is the most problematic to the environment due to its mobility over a wide range of redox conditions. Both As(III) and As(V) are soluble in water over a broad range of pH and Eh (Sarkar & Paul, 2016). The mobilization of arsenic arise under certain natural conditions, or via some human activities including metal mining and metallurgy operations.

2.2.1 Natural and other anthropogenic sources of arsenic

As reviewed earlier, arsenic occurs in sediments, soils, and ore deposits, and could be liberated via natural processes, including biotic activities (metabolism) and chemical reactions. Much of the arsenic in the environment comes from high-temperature processes, such as burning vegetation and volcanic activity. Some geothermal activities can contribute soluble arsenic to the water. Arsenic along with other elements like antimony (Sb), boron (B), mercury (Hg), thallium (Tl), selenium (Se), lithium (Li), those do not fit easily in the lattice of common rock minerals, are commonly found in high-temperature hydrothermal vents together with hydrogen sulfide (Sarkar & Paul, 2016). Arsenic level in geothermal fluids has been found to be ranging from 0.1 to 50 ppm (Ballantyne & Moore, 1988).

Low-temperature biological reaction involving microbes also release arsenic into the environment. Microbes act on arsenic in soils and sediments generating soluble or volatile arsenic compounds. Arsenic is distinctive in being relatively mobile under reducing conditions as compared to most other toxic trace metals that occur in solution as cations (e.g. Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+})
which generally become increasingly insoluble as the pH increases (Sarkar & Paul, 2016). It can be found at concentrations in the mg/L range when all other oxyanion-forming elements are present in the μg/L range.

Although mining and smelting of non-ferrous metals and burning of fossil fuels being the major industrial processes that contribute to anthropogenic arsenic sources, the historical use of arsenic in agriculture as pesticides and in timber treatment as copper chrome arsenate has also led to large amount of contamination to the environment in the past.

2.2.2 Release of arsenic by mining activities

Despite the increasing awareness of arsenic toxicity and the advances in arsenic controlling techniques, arsenic in the minerals entered mining sector will inevitably be liberated. The arsenic contamination to the surrounding environment, particularly waterbodies, caused by improper management of arsenic-bearing process effluents or acid mine drainage is a global issue prevailing in almost every primary copper mining country. Figure 2-5 depicts the distribution of arsenic contaminated waterbodies affected by mining and metallurgical activities.
Figure 2-5. Distribution of documented world problems with As in groundwater in major aquifers as well as water and environmental problems related to mining and geothermal sources (Smedley & Kinniburgh, 2002).

Arsenic needs to be removed from ores and concentrates during mineral processing and metallurgical operations for certain technical reasons: the smelter conditions can deteriorate if arsenic circulates and finally accumulates at the top of the reactor. Smelters set a penalty threshold of ~0.2% for arsenic content in copper concentrates, and China has imposed a restriction of 0.5% arsenic on imported copper concentrates containing arsenic. As shown in Figure 2-6, due to the depletion of low-arsenic resources, many existing mines that used to produce clean concentrates a few years ago have to confront the problem of handling arsenic levels above the penalty limit now.
The concentration of arsenic in mineral processing streams can be many orders of magnitude higher than that in naturally arsenic contaminated water sources (R. L. Radzinski, 2017). Techniques to remove arsenic from wastewater at low concentrations may not be as effective as at higher concentrations (Leist, Casey, & Caridi, 2000).

2.2.2.1 Pyrometallurgical operations

The by-product residues that come from pyrometallurgical operations of non-ferrous metals, including roasting, converting and smelting, can contain unfavorable toxic arsenic materials. In the case of copper processing, most of the arsenic can be volatilized as As$_4$O$_6$ vapour and then collected in the gas cleaning section, i.e. electrostatic precipitator and baghouse, and a relatively small amount of arsenic enters the electro-refining section and finally ends up in the final slag (Piret, 1999). Due to the similar electrodeposition potentials of arsenic and copper, it is harder to separate
arsenic from copper products in electro-refining. In practice of improving arsenic evaporation, fluxes such as Na$_2$CO$_3$ and CaO can be added in converting or anode furnacing section to aid in arsenic removal from blister copper (Nakamvra, Ueda, Noguchi, & Toguri, 1984). The main paths of arsenic in the smelting process of copper are presented in Figure 2-7.

During smelting, some of the arsenic volatilizes together with sulfur and reports to the flue dusts as sulfide (As$_2$S$_3$) or oxide (As$_2$O$_3$) while the rest deports to the slag and off-gas. The arsenic compounds must be eliminated from the SO$_2$ gas prior to the sulfuric acid production, as the arsenic level adversely influences the quality of the produced sulfuric acid. In order to have sufficiently low levels of arsenic in the gas before entering acid plant, the gases are cooled and the majority of arsenic is removed as arsenic trioxide (As$_2$O$_3$) dust. Since there is a limited market for this and because its high solubility makes it unsuitable for long-term disposal, smelters tend to cycle it through the smelter, thus increasing the overall arsenic levels in the system. In order to restrict the arsenic input and recycling in the system, smelters usually set penalties on concentrates with arsenic

![Figure 2-7. Typical paths of arsenic in copper pyrometallurgy (Piret, 1999).](image-url)
content higher than 0.5%. There have been attempts to reduce the arsenic content in the ores by roasting in order to drive off arsenic and produce a clean feed for copper smelters (Safarzadeh, Moats, & Miller, 2014). Roasting of arsenic-containing concentrates (400 °C–700 °C) leads to the volatilization of most of the arsenic in form of As$_4$O$_6$, which is cooled and captured as arsenic trioxide dust (As$_2$O$_3$) in the bag-house filters (Nazari, Radzinski, & Ghahreman, 2017). However, this option has generally been viewed as unacceptable due to environmental conflicts and the lack of a market for arsenic trioxide.

As an important sulfide mineral source of copper, chalcopyrite (CuFeS$_2$) is frequently associated with arsenic-containing sulfidic minerals such as enargite (Cu$_3$AsS$_4$) and tennantite (Cu$_{12}$As$_4$S$_{13}$) (Filippou, St-Germain, & Grammatikopoulos, 2007). The arsenic can be removed from these sulfidic minerals as arsenic sulfide via heating in a reducing or inert atmosphere since the Cu-As-S phase has a relatively low melting point (640–690 °C) and is easily volatilized (Johto & Taskinen, 2014). The volatile arsenic sulfide is converted to arsenic trioxide via an oxidation reaction. Stockpiling As$_2$O$_3$ flue dusts leads to serious problems due to its high degree of solubility in water and the toxicity of arsenic trioxide (Filippou & Demopoulos, 1997).

2.2.2.2 Hydrometallurgical operations

Various hydrometallurgical techniques concerned with the arsenic in sulphide resources have been proposed in response to the lack of suitable pyrometallurgy options treating high-arsenic concentrates (Safarzadeh et al., 2014). Attention has been paid to hydrometallurgy processes including alkaline sulfide leach (ASL), sulfate- and chloride-based leach systems, high temperature pressure oxidation, sodium hypochlorite leach, biooxidation, nitrogen species catalyzed pressure oxidation (Safarzadeh et al., 2014).

The hydrometallurgical processing of arsenic-bearing minerals, such as enargite, either selectively dissolve arsenic leaving copper in the residues to produce a clean concentrate or collectively leaching copper and arsenic into a solution.
The leaching of enargite under basic conditions enables selective dissolution of arsenic from enargite with relatively fast kinetics. The leaching residue is an arsenic depleted copper concentrate that can be used for the purpose of smelting.

This arsenical solution must then be treated to obey the regulatory limits. The soluble arsenic resulting from leaching of arsenic-bearing ores under atmospheric conditions often contains a fraction of trivalent arsenic thus requiring a pre-oxidation step in the treatment plant.

2.2.2.3 Acid mine drainage (AMD)

The sulfides are least resistant to weathering and can potentially cause acid mine drainage (AMD) as a result of sulfide oxidation. The mining of arsenic-bearing sulfide ores can extensively expose the arsenic-containing sulfides to air and further subject them to weathering. Oxidation of arsenic sulfides allows arsenic to spread out into the various components of the environment such as soil, water and air (Azcue, Mudroch, Rosa, & Hall, 1994)

Geochemical processes taking place in mine tailing impoundments can eventually cause high concentrations of arsenic and acidity in mine drainage and surrounding aqueous media including stream waters (Figure 2-8). Soils and secondary precipitates also are rich in arsenic because of adsorption and/or co-precipitation (Paikaray, 2015). The migration and mobilization of arsenic from mine wastes into the environment were mostly due to acid mine drainage (AMD) after oxidative leaching of sulfide minerals in mines dumps or waste rocks (Paikaray, 2015).
2.3 Arsenic immobilization practices

The major tasks for arsenic control in mineral processing and extractive metallurgy operations involves preventing arsenic emissions from the gases and aqueous phases, removing arsenic from the metallic phase, and finally disposing in a safe and environmentally acceptable manner preferably as a stable compound (Safarzadeh et al., 2014). However, the removal and immobilization of arsenic, especially from process solutions and wastewaters, has been a great challenge for the mining industry (Riveros et al., 2001). Typical methods for efficient and effective arsenic immobilization follows an oxidation-stabilization pattern: the arsenic-containing solution is subject to a pre-oxidation stage in order to ensure that all the arsenic is present in the pentavalent form; and subsequently to convert the As(V) into stable solid forms using adsorption or precipitation techniques.

2.3.1 Oxidation

In most operations arsenic precipitation and stabilization are designed assuming pentavalent arsenic as the dominant species due to its characteristics of being less toxic, more stable and the ability for
a higher degree of removal from the solution compared to those of trivalent arsenic. Based on thermodynamic calculations, As(V) should be predominant in oxidative conditions. However, such theoretical behavior is not necessarily followed quantitatively in solutions where trivalent arsenic is present originally and the solution redox potentials reflect thermodynamic disequilibrium (Eary & Schramke, 1990; Seyler & Martin, 1989).

Arsenic oxidation is usually the first step to arsenic removal in the mining and metallurgy industries. The weak acid bleed streams obtained from acid plants, smelters and copper tank houses, as well as the re-treatment streams of smelter and roaster dusts contain a significant amount of trivalent arsenic. The oxidation of As(III) is therefore required in order to maximize arsenic removal and the stability of arsenical precipitates.

2.3.1.1 Conventional oxidation techniques

Trivalent arsenic can be oxidized to pentavalent arsenic under ambient conditions with oxygen, however, without catalysts the kinetics of this oxidation reaction is extremely slow. Johnson and Pilson (1975) have studied the oxidation of As(III) by dissolved O₂, so-called oxygenation, and reported half-lives for the oxygenation of As(III) in seawater ranging from several months to a year. Only 25% of As(III) was oxidized during a test bubbling air through the solution containing 200 µg/L As (III) after 5 days (Frank & Clifford, 1986). The oxidation rate is independent of the concentration of dissolved O₂, and is controlled by the rate of a surface reaction (Scott & Morgan, 1995). Therefore, the application of air and oxygen in As (III) oxidation is limited due to a very low oxidation rate (Bissen & Frimmel, 2003a).

Several oxidants have been studied for arsenic oxidation, including SO₂/O₂ mixture (Ociński D., 2014; W. Zhang, Singh, & Muir, 2000), ozone (Bissen & Frimmel, 2003b; Khuntia, Majumder, & Ghosh, 2014) and hydrogen peroxide (Kim, Bokare, Koo, & Choi, 2015; Voegelin & Hug, 2003). The challenge with all the above oxidants is the cost of oxidants and also the practical application of the oxidants. Thus far, hydrogen peroxide has been the most attractive arsenic oxidant, and the
Ecometales arsenic immobilization plant in Chile applies this reagent to oxidize arsenic. Nonetheless, hydrogen peroxide is expensive and the arsenic oxidation efficiency with stoichiometric amount of hydrogen peroxide is only about 65%. At least 100% stoichiometric excess of hydrogen peroxide is required to achieve over 90% arsenic oxidation (Molnar, Vircikova, & Lech, 1994).

2.3.1.2 Advance oxidation processes (AOPs)
Advanced oxidation processes (AOPs), a concept proposed by Glaze and co-workers in 1987, are defined as the oxidation processes assisted by strong oxidants such as free radicals. These free radical assisted systems can be used in the treatment of contaminants including arsenic. Hydroxyl radical (·OH) is known as a powerful, non-selective chemical oxidant that promotes AOPs. Hydroxyl radicals are able to break a number of chemical bonds such as C-C, C-N, C-S. General methods that can produce hydroxyl radicals include ozonation (O$_3$), activation of hydrogen peroxide (H$_2$O$_2$), catalysis by transition metal ions or noble metal catalysts, and energy-intensive radiation such as light illumination (either ultraviolet light or visible light), ultrasound (US) or electron beam. The generation of hydroxyl radicals in AOPs basically follows a Fenton or Fenton-like reaction pathway. The activation of hydrogen peroxide (H$_2$O$_2$) in the presence of iron to produce hydroxyl radicals was first described by Fenton (1894) on the oxidation of tartaric acid, which being categorized as classical Fenton reaction. The complex reaction sequence of classical Fenton process can be simplified as equation 1.

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 = \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \quad (k = 63 \sim 76 \text{M}^{-1}\text{s}^{-1}) \quad \text{Equation 1}$$

The generation of hydroxyl radicals through classical Fenton reaction is highly restricted to system conditions such as pH and competitive scavenging species. The produced Fe$^{3+}$ ions can react with hydroxide ions to form insoluble ferric hydroxide precipitates in neutral and near-neutral pH conditions. The non-selective and enhanced reactivity of hydroxyl radicals can result in a series of competitive process (Equation 2 - 4).
\[
\ce{Fe^{2+} + HO \rightarrow Fe^{3+} + OH^-} \quad (k = 3.2 \times 10^9 \text{M}^{-1}\text{s}^{-1}) \quad \text{Equation 2}
\]

\[
\ce{H_2O_2 + HO \rightarrow HO_2 \cdot + H_2O} \quad (k = 3.3 \times 10^7 \text{M}^{-1}\text{s}^{-1}) \quad \text{Equation 3}
\]

\[
\ce{HO \cdot + HO \rightarrow H_2O_2} \quad (k = 6 \times 10^9 \text{M}^{-1}\text{s}^{-1}) \quad \text{Equation 4}
\]

The original Fenton system has been investigated with various modifications to improve the oxidation potential of Fenton process; these modified processes are collectively classified as “Fenton-like” reactions. Photo-Fenton (Zepp, Faust, & Jürg, 1992), electro-Fenton (Ding, Ai, & Zhang, 2012), sono-Fenton (Babu, Ashokkumar, & Neppolian, 2016) are the most popular types of Fenton reactions that have been developed later. Generally, photo-AOP techniques involve the use of ultraviolet light in the presence of H$_2$O$_2$, ozone, Fenton’s reagent or a semiconductor surface. Ultrasound is one of the important AOPs, which could be operated either individually or coupled with other AOPs such as O$_3$/US, H$_2$O$_2$/US, UV/US and so on. Even though the classical Fenton reaction alone is not sufficiently effective at oxidizing As(III), it can be coupled with some other following steps such as adsorption to achieve an acceptable removal of arsenic (Holm, Peyton, & Wilson, 2008). A number of modified Fenton processes have been applied on oxidation of arsenic as effective AOPs.

2.3.1.3 Bio-oxidation

Microorganism plays a fundamental role in the reduction-oxidation reaction and circulation of elements in nature. A lot of microorganisms were reported to be able to oxidize chemical species giving proper metabolic conditions. The capability of some particular microbes to generate oxidizing products that can potentially oxidize arsenic gives rise to the biological oxidation, bio-oxidation, of arsenic. The microbial oxidation mechanism typically features an indirect oxidation pathway: the microorganisms oxidize ions, such as ferrous to ferric, which then oxidize other species.
The first record of microorganism being capable of mediating redox transformations of arsenic was reported one century ago (Turner, 1954), bacterial activities related to arsenic transformation have been described by many studies (Cavalca, Corsini, Zaccheo, Andreoni, & Muyzer, 2013). Since the environment of ancient earth was believed to be anoxic, arsenite was probably the primary bioavailable arsenic species in the early time, hence acts as an electron donor in cellular activities to produce energy (Kulp, 2014). To date, microorganisms capable of oxidizing arsenic, including both heterotrophic As(III) oxidizers (HAOs) and chemoautotrophic As(III) oxidizers (CAOs), are found in various groups of Bacteria and Archaea (Oremland & Stolz, 2003; J M Santini, vanden Hoven, & Macy, 2002; Silver & Phung, 2005). Mechanisms for the microbes oxidizing arsenite can be classified as detoxification (Gihring, Druschel, Mccleskey, Hamers, & Banfield, 2001) or respiration (Mohamed & Farag, 2015) or phototrophy (R Budinoff & Hollibough, 2008), depending on the role that arsenic plays in the electron transport chain and the substance bacteria uses as a carbon source. Figure 2-9 illustrates different mechanisms for microbial arsenite oxidation. Arsenite oxidation occurs in many heterotrophic bacteria is generally considered a detoxification process, converts As(III) into less toxic As(V), for their immediate environment (vanden Hoven & Santini, 2004). On the other hand, arsenite was found to be involved in chemoautotrophic arsenic oxidation as an electron donor during fixation of CO₂ coupled with reduction of oxygen (Fisher & Hollibaugh, 2008; Hoeft et al., 2007; Joanne M. Santini, Sly, Schnagl, & Macy, 2000). These arsenic oxidizing bacteria may have an ecological advantage over other microorganisms because of their capability of gaining energy during detoxification by transforming the more toxic As(III) into less toxic As(V) (Cavalca et al., 2013).
Anoxic oxidation of arsenic is a crucial point in industrial scale application of arsenic removal techniques. It is noteworthy that in few of COAs the oxidation of arsenic was performed under anaerobic conditions using nitrate (Rhine, Phelps, & Young, 2006; J. Zhang et al., 2015) or chlorate (W. Sun, Sierra-Alvarez, Milner, & Field, 2010) as the terminal electron acceptor, and arsenite as the electron donor. For the construction of a bioreactor, CAOs are considered to be a better choice than HAOs because of the lower nutritional requirements and lesser possibility of generation of harmful organic by-products during the oxidation reactions (Li et al., 2016).

Oxidation mechanisms that account for the microbial oxidation of arsenite can be differentiated roughly as direct and indirect pathways. The direct oxidation pathway mediated by microorganism attributes to arsenic oxidase which oxidizes As(III) enzymatically. A wide range of bacteria isolated from various contaminated environments were described for their ability to synthesize arsenite oxidases (Lièvremont, Bertin, and Lett 2009). To better understand the source of bacterial oxidation capacity, arsenite oxidases have been studied intensively from a genetic perspective. The name of the gene coding for As(III) oxidase has been changed over time from *aox* to *aro*, and recently it was unified as *aio* (Lett, Muller, Lievremont, Silver, & Santini, 2012). Zhu et al. (2017) have comprehensively concluded known genes involved in arsenic metabolism and noted that the arsenite oxidase is composed of two different subunits named *AioA* and *AioB*, respectively (Stolz,
Basu, & Oremland, 2010). A novel enzyme involved in arsenic oxidation was found by Wang et al. (2017) recently and they revealed a more detailed electron transfer process in arsenic metabolism: arsenite oxidase AioBA may transport electrons to AioE during As(III) oxidation (electron may transfer from AioBA to CytC via AioE). In such case, arsenite oxidation could improve the generation of ATP/NADH to support the growth of Agrobacterium tumefaciens GW4, which provides the evidence of the arsenic contribution to microbial energy generation redox reactions (Oremland et al., 2002; Wang et al., 2015).

There is another plausible mechanism for microbial oxidation of arsenic indicated by a few researchers as an indirect pathway. A number of bacteria have proven capability of generating oxidizing agents, such as ferric ions (Fe(III)) and/or protons in the system, serving as a preliminary step for the biooxidation mechanism (W Sand, Gerke, Hallmann, & Schippers, 1995; Wolfgang Sand, Gehrke, Jozsa, & Schippers, 2001). In an experiment conducted by Hong et al., a mixed culture of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans was adapted for biooxidation of a refractory gold concentrate containing high concentrations of arsenic to observe variations in the ORP resulting from the production of Fe(III) by A. ferrooxidans and the production of Fe(II) in the oxidation of arsenite (Hong et al., 2016). Synergetic effects generated by the mixed culture bacteria was accounted for the indirect oxidation pathway: (i) bacteria produce strong oxidizing agents (i.e., Fe^{3+} and H_2SO_4); (ii) the strong oxidizing agents are then responsible for oxidizing the As (Gonzalez, Gentina, & Acevedo, 2004; W Sand, Gehrke, Jozsa, & Schippers, 1999; Schippers & Sand, 1999).

2.3.2 Stabilization

The oxidized arsenic (i.e. As(V)) should be stabilized for safe long-term disposal. Common practice includes adsorption and precipitation with other ions.

2.3.2.1 Adsorption

26
Dissolved arsenic species can be retained by solid surfaces to which they make contact under certain conditions, so-called adsorption. The adsorption behavior is classified as physical adsorption and chemical adsorption according to the bonding mechanism, physical adsorption through Van der Waal’s force and chemisorption through chemical bonds (Lata & Samadder, 2016; L. K. Wu et al., 2018). Adsorbents with large surface area are preferred for adsorption (Z. Sun, Yu, Pang, & Du, 2013). Physical adsorption is reversible and has low adsorption heat; a decrease in free energy and entropy of the system is also observed in this process and hence it is an exothermic process (Dabrowski, 2001). Transfer of electrons is not assumed to occur between adsorbent and adsorbate in physical adsorption, although; polarization of adsorbate is likely to occur. Physical adsorption is accompanied with the formation of a multilayer of the adsorbate on the adsorbent surface (Dabrowski, 2001; Sarkar & Paul, 2016). The porosity of the adsorbent also influences the adsorption process.

Arsenic species present in water can bind onto the surface of the adsorbents by the van der Waal force. Initial arsenic concentration, adsorbent dose, exposure time or contact time, the solubility of arsenic in water, pH, temperature, presence of other chemical species are found to affect the adsorption process (Eguez & Cho, 1987). A number of adsorbents have been studied for arsenic adsorption in solutions, such as activated alumina (Kunzru & Chaudhuri, 2005; Maliyekkal, Philip, & Pradeep, 2009), granular ferric hydroxide (Badruzzaman, Westerhoff, & Knappe, 2004; Banerjee et al., 2008), iron oxide coated materials (Giles, Mohapatra, Issa, Anand, & Singh, 2011; Katsoyiannis & Zouboulis, 2002; Mohan & Pittman, 2007) and activated carbon (Di Natale, Erto, Lancia, & Musmarra, 2008; Johnston & Heijnen, 2001; Y. Wu, Ma, Feng, & Liu, 2008).

Most adsorbents are more efficient and effective to treat As(V) than As(III). Efforts have been directed to enhancing the removal efficiency of As especially As(III) and reducing the operating cost by modified adsorption or exploration of new methods with acceleration of As(III) oxidation,
for example, Fe-Mn binary oxides (G. Zhang, Qu, Liu, Liu, & Wu, 2007), and Fe-Al bimetallic materials (Meng et al., 2018).

2.3.2.2 Precipitation
Arsenic can be removed from waste streams by precipitation with certain ions. The most common arsenic precipitates from hydrometallurgical processes are: arsenic sulfides, calcium arsenite, calcium arsenate and ferric arsenate (De Klerk, 2008). The solubility of these precipitates is usually dependent on solution pH. Although there are several methods to produce arsenic compounds with very high stability, the processes are either expensive or not efficient (Nazari et al., 2017). The United States Environmental Protection Agency (EPA) has assigned the precipitation of dissolved arsenic with ferric ions as “The Best Demonstrated Available Technology” (Rosengrant & Fargo, 1990). Much research has concluded that a ferric to arsenic ratio greater than three provides acceptable arsenic stability. The stability of disposed arsenic compound is of great concern in arsenic immobilization practise. Arsenic ferrihydride compounds are formed at low temperatures and atmospheric pressure and are acceptable for practical arsenic disposal operations, releasing less arsenic than the regulational limits in many countries (Richmond, Loan, Morton, & Parkinson, 2004). However, since the compounds are amorphous and voluminous, the long-term stability has been a major concern.

In contrast, arsenic can be precipitated as scorodite under high temperature and pressure conditions, which is known to be one of the most stable arsenic minerals (Langmuir, Mahoney, & Rowson, 2006). The arsenic speciation was found to be a limiting factor on the precipitation of scorodite: arsenic must be present as As(V) species in the process solution.

2.4 Carbon-based catalysts for oxidation
Carbon-based catalysts (CBC) are porous catalysts derived from carbon materials with high surface area and chemical resistance. The oxidative property of CBC in the presence of oxygen has been studied intensively and makes the CBC an efficient catalyst in hydrometallurgy and environment
research. Activated carbon (McDougall & Hancock, 1981), engineered biochar (Mohan, Sarswat, Ok, & Pittman, 2014), and carbon-based nanomaterials (Mauter & Elimelech, 2008) are the most common CBCs that are usually used for catalysis of oxidation reactions in metallurgical and environmental engineering fields.

Activated carbon is widely used in catalysis (as catalysts or supports) due to its superior physical and chemical properties, such as high surface area, porous structure, and advanced surface functionalities (Figueiredo & Pereira, 2010; Larsen & Walton, 1940).

Hydrogen and oxygen are often found on carbon compounds, and other elements such as sulphur, nitrogen and chlorine are commonly associated with carbon (Salame & Bandosz, 2001). The elements found on the carbon surface influence the catalytic characteristics of the carbon compound (Jansen & van Bekkum, 1995). When activated carbon is hydrated, hydroxyl groups which behave amphotERICally are formed on the surface (Jahromi & Ghahreman, 2019).
Surface oxides are a common functional group on activated carbon which are formed via the chemisorption of oxygen. Carboxyl, phenol, quinone, hydroxyl groups and ester groups have been found on the carbon surface (Jahromi & Ghahreman, 2019). Figure 2-10 shows some common
types of surface functional groups. The oxygen functional groups such as hydroquinone and quinone groups on carbon surfaces have been shown to facilitate a reversible redox reaction (Equation 5). The catalytic activity of carbon is dominated by the surface oxidation degree, in particular chromene or quinone groups on the carbon surface, which can form hydrogen peroxide or a hydroperoxyl in solution (Ahumada et al., 2002).

\[
C_{\text{Red}} + \frac{1}{2}O_2 + H_2O \rightarrow H_2O_2 + C_{\text{Ox}}
\]  
\text{Equation 5}

In addition to activated carbon, biochar is an emerging carbonaceous material produced mainly from the thermal decomposition of low-cost biomass residue under limited oxygen conditions. Biochar has similar properties as activated carbon and can be engineered for intended catalytic capacity. Biochar was found to be able to generate reactive oxygen species (ROS), especially hydroxyl free radical (•OH) for degradation of organic contaminant, via the activation of hydrogen peroxide (H$_2$O$_2$) and molecular oxygen (O$_2$) (Fang et al., 2014; Fang, Zhu, Dionysiou, Gao, & Zhou, 2015). A study looked into the catalyzed oxidation of arsenic by biochar has concluded a reaction pathway (Equation 6-8, unbalanced, only presenting the reactants and products) where O$_2$ is activated by biochar to produce ROS, especially H$_2$O$_2$ and •OH for the promotion of As(III) oxidation (Zhong et al., 2019).

\[
C - OH + O_2 + H^+ \leftrightarrow C = O + \cdot HO_2
\]  
\text{Equation 6}

\[
C - OH + \cdot HO_2 + H^+ \leftrightarrow C = O + H_2O_2
\]  
\text{Equation 7}

\[
C - OH + H_2O_2 \leftrightarrow C = O + \cdot OH + OH^-
\]  
\text{Equation 8}

2.5 Arsenic oxidation assisted by activated carbon

As an alternative to the conventional oxidation process consuming costly oxidants, a novel catalysis process was discovered to oxidize high concentration acidic arsenite solutions in the presence of activated carbon and oxygen. The novel and robust carbon catalyzed process, with oxygen being the only consumable reagent, enables the effective and economic arsenic oxidation without requiring noble metal catalysts and expensive chemical additives.
2.5.1 Patent summary

This process, patented by Choi et al. (2014), is carried out in acidic conditions at ambient temperature and pressure in 24 h and has an oxidation efficiency of up to 99%, thus providing a promising solution to the arsenic issue in mining wastewaters. Figure 2-11 presents a process flow chart of the activated carbon catalyzed arsenic oxidation. The idea described in the patent was to use activated carbon to catalyze the arsenic oxidation reaction with arsenic in its pentavalent state. The arsenic bearing solution stream firstly pass through an oxygenated system where some activated carbon was added as a catalyst to expedite the arsenic oxidation. The oxidized As(V) will go through a further arsenic precipitation stage where all the arsenic could be immobilized in a stable form. The key technological claim of the patent is the catalytic oxidation of arsenic with activated carbon in oxygenated systems.

![Process Flow Chart](image)

**Figure 2-11. The process flow chart of the activated carbon catalyzed arsenic oxidation.**

A series of operating parameters have been advised in the patent. The system was suggested to acidified to a relatively low pH for good oxidation efficiency, and oxygen source has to be supplied consistently either using air, or pure oxygen. Ambient temperature and pressure are proven suitable for the process. To treat 10g/L As(III) a minimum of 100 g of activated carbon is required. And the redox potential was preferably kept above 350 mV.
2.5.2 Hypothesis proposed on the mechanism

Some activated carbons are able to produce in-situ \( \text{H}_2\text{O}_2 \) and \( \text{HO}_2^- \) in the presence of oxygen and water according to Ahumada et al. (2002). This phenomenon can be explained by the availability of chromene and quinone groups on the surface of the carbon catalysts.

Two important properties of the activated carbon are believed to contribute to the efficient catalysis. Large surface area can provide sufficient adsorption and active sites that enable the formation of some oxidative species; and abundant oxygen functional groups are potentially capable of producing oxidizing reagents such as hydrogen peroxide.

Activated carbon catalyzes the oxidation reaction of arsenite and oxygen to arsenate (Bissen & Frimmel, 2003a). It was shown that 90% of As (III) was oxidized using 5-10 g/L of activated carbon in 20 to 30 min when the initial concentration of As (III) in the water was 40 μ/L (Bissen & Frimmel, 2003a).

To account for the arsenic oxidation, Radzinski and coworkers (2016) proposed a reaction mechanism where hydrogen peroxide is formed in situ on the carbon surface and then the newly formed peroxide either desorbs into the aqueous phase to oxidize arsenic or directly reacts with the As attached on the carbon surface and subsequently desorbs into bulk solution as As(V).
Chapter 3 Materials and experimental methods

3.1 Raw materials and chemical reagents

3.1.1 Activated carbon

A commercially available granular activated carbon (AC) was used as the catalyst in the experiments. The activated carbon used was “Gold Plus” supplied by Calgon Carbon Corporation, which was derived from coconut shells with a minimum ash content of 5% by weight. The surface area of the activated carbon determined by Brunauer-Emmett-Teller (BET) method (Brunauer, 1938) is 921 m$^2$/g, and the Barrett-Joyner-Halenda (BJH) (Barrett, 1951) adsorption cumulative volume of pores between 1.7 nm and 300 nm width is 0.045116 cm$^3$/g. The BJH pore size distribution of activated carbon on the pore width sizes basis is illustrated in Figure 3-1. Before its use in the tests, the activated carbon underwent an attrition process being stirred with deionized water at 350 rpm for 24 h. The coarse carbon particles were then wet screened with a 16-mesh sieve and stored in deionized water until it was used in the experiments.
3.1.2 Lewatit® AF5 catalyst

Lewatit® AF5 is a microporous carbonaceous bead type material derived from a synthetic polymer. AF5 is originally designed to be used for adsorption and ion-exchange for downstream process separation and purification. The AF5 beads are spherical with diameters between 0.35 and 0.80 mm. AC and AF5 are carbon-based catalysts and have similar structures, however, different carbon-based catalysts have varying properties and they can have different effects on the carbon assisted arsenic oxidation. The AF5 has a BET surface area of 1154 m$^2$/g and BJH pore volume of 0.45631 cm$^3$/g (Figure 3-2).
3.1.3 Solution preparation

Diluted sulphuric acid solution and arsenic solution are prepared for the washing and testing of the carbon loaded column.

Diluted sulphuric acid solution was made by adding 10 mL of concentrated sulphuric acid (Fisher Scientific®) to 2 L de-ionized water in an Erlenmeyer flask under mixing with a magnetic stirrer. The pH of the diluted sulphuric acid solution was then adjusted to the desired value by slowly adding concentrated sulphuric acid using a Pasteur pipette in a dropwise. The pH of the solution was monitored constantly during the dilution until the targeted final pH value was reached.

A high-concentration arsenic stock solution was first made by dissolving arsenic trioxide powders (99.5% on a metal basis from Alfa Aesar). Arsenic trioxide powder, As₂O₃, was added to 2 L de-ionized water in a high dosage so that the stock solution contains a high-concentration of arsenic and can be diluted to different concentrations. The arsenic trioxide powders are mixed in water at 75°C for dissolution. The dissolution stays for at least 2 days to the reach best dissolution of arsenic.
trioxide powders. The mixture of high-arsenic solution and residues that do not dissolve either because of the saturated arsenic concentration in the solution or the impurities carried in the arsenic trioxide powders is then filtrated through 2 micron filter paper into a glass container for arsenic stock solution. The stock solution is measured for arsenic concentration prior to being diluted to lower concentrations. The dissolution of arsenic trioxide in water yield a solution with slight acidity and a pH of 2.7. Arsenic solutions of specific concentrations that are needed for the tests are prepared by diluting the arsenic stock solution. For those needed to be adjusted to a pH lower than 2.7, a volume, that is calculated based on the need for the dilution, of arsenic stock solution is taken from the stock container and acidified to the target pH by adding sulphuric acid. Then the acidified high-concentration arsenic solution is diluted using sulphuric acid solution which was previously adjusted to the same pH into a 2 L volumetric flask. For the arsenic solutions with a pH higher than 2.7, the stock solution is first adjusted to the target pH by adding 0.5 N NaOH (from Sigma-Aldrich) and then diluted using sulphuric acid or sodium hydroxide solution of a same pH into a 2 L volumetric flask.

### 3.1.4 Pretreatment of carbons

Surface modification of carbon-based catalysts can be implemented at low costs usually via treating the carbon catalysts with an oxygenated acidic solution (Chingombe, Saha, & Wakeman, 2005). Nitric acid pre-treatment of activated carbon and AF5 are conducted to further enhance their catalytic properties. The pretreatment process is performed as per the same procedures. 250g of the original carbon catalysts are first subjected to 500mL of 1M HNO₃ solution in a 1000mL beaker. The slurry of carbon solids and nitric acid solution is stirred for 24 hours at 25 °C. The carbon catalysts undergo two washing stages following the treatment with concentrated nitric acid: each washing step involves slowly flushing the carbon particles with 1L deionized water for 10min. The coconut shell based activated carbon was screened using 16-mesh sieve to remove the fine particles from stirring attrition. AF5 features a strong mechanical strength so that there is barely any attrition
during the pretreatment process. The nitric acid pretreated AF5 is then stored for the column tests after washing.

3.2 Experiment design

3.2.1 Rapid small-scale column testing method
In order to validate the effectiveness of activated carbon catalysis on arsenic oxidation under continuous conditions and to study the effect of different parameters on the oxidation, a series of kinetic tests were conducted in column reactors. Compared to shake tests and batch tests, column tests have the advantages of operating on a relatively larger scale (both in size and the amount of stream flow) and simulating a constant flow dynamic condition. Rapid small-scale column tests (RSSCTs) are inexpensive methods originally designed to evaluate the adsorption capacity of absorbents (Critenden, 1991). A study of arsenic removal in RSSCTs was reported for by Wsterhoff in 2005, which represents the first use of RSSCTs to simulate pure adsorption of inorganic ions onto porous absorbents. RSSCTs are preferred in scaling up processes since this method can effectively simulate and predict the performance of the investigated materials under dynamic and continuous conditions and does not require extensive isotherm or kinetics studies. The rapid small-scale column test (RSSCT) was developed to simulate the performance of carbon-based arsenic treatment system in a small to pilot scale reactor.

3.2.2 Column reactor
The RSSCTs have been conducted in aerated column reactors filled with carbon-based catalysts. Column tests can provide a constant flow test results, which are more representative as compared to the batch tests. Sampling from column reactors can exclude attrition of carbon catalysts. A column setup was designed to realize the experiments that aim to study the arsenic oxidation catalyzed by carbon. The column diameter of the reactor and gas and solution ports location comply with the principles of reactor design. Figure 3-3 shows a schematic diagram of the column setup.
Figure 3-3. Schematic diagram of the column setup where: (A) is the gas cylinder, (B) is the regulator, (C) is the gas flow meter, (D) is the gas inlet port, (E) is the solution inlet port, (F) is the fine filter supporting the mass of carbon, (G) is the carbon filled portion of the column, (H) the fine filter restricting the carbon in the column, (I) is the outlet port, (J) is the peristaltic pump, (K) is the reservoir for feed solution, (L) is the effluent waste. (The sizes of different portions in this diagram are not to scale).

The configured column reactor is a fix-bed up-flow setup. The oxygen sources used in the experiment were industrial grade oxygen (> 99.5% O₂) and industrial grade air. The sparging flow rate of the gases ranged from 0.05 L/min to 0.30 L/min, and the flow rates of the solution were between 0.35 mL/min and 0.50 mL/min, both depending on the tests and the column sizes. The gas and solution entered the column through an inline T-adapter with two inlet ports at the bottom and mixed to pass through a fine filter. The fine filter supports the weight of the activated carbon loading in the column and also distributes the gas into mini gas bubbles for better oxygen mass transfer.
within the column. Both the solution flow rate and the void volume in the column loaded with activated carbon dictates the solution residence time in the column system. In reality, the residence time describes the period that the solution requires to pass through the porous spaces within and between the activated carbon of the column reactor. Solutions samples are taken from the top of the columns (open end to atmosphere) by a tube connected to a syringe and were analyzed for pH, dissolved oxygen (DO), and arsenic speciation. The column uses an open top to allow the extra oxygen gas to vent out the column and maintain an ambient pressure inside the column.

### 3.2.3 Column test matrix

A test matrix was designed as a guideline for the column tests. Table 3 shows the key operational parameters and conditions regarding different column tests. The first row in Table 3 signifies the baseline condition which was selected based on previous studies in a small scale (Radzinski, 2017) and industrial practice. The conditions for the baseline test were as follows: a column with a height of 530 mm and an inner diameter of 25.4 mm (268.6 cm$^3$ active column volume) was filled with 129.4 grams of carbon (dry based weight). With this condition, 66.5% of the active column volume was filled with carbon, and another 33.5% was available for the solution to fill. Oxygen was sparged from the bottom of the column at 0.05 LPM and an arsenic solution containing 4.70 g/L As(III) in pH = 0.80 (adjusted with sulfuric acid) was pumped into the column from the bottom at a controlled flow rate of 0.35 L/min; the solution flow rate in the baseline test corresponds to a solution residence time of 218 min in the column.
Table 3. Column tests matrix.

<table>
<thead>
<tr>
<th>Carbon type</th>
<th>Influent As(III) concentration (g/L)</th>
<th>Residence time (min)</th>
<th>Influent pH</th>
<th>Oxygen condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td><strong>0.10 L/min oxygen</strong></td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td><strong>0.15 L/min oxygen</strong></td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td><strong>0.20 L/min oxygen</strong></td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td><strong>0.05 L/min air</strong></td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td><strong>0.10 L/min air</strong></td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td><strong>0.25 L/min air</strong></td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>0.80</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>1.47</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>1.64</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>2.09</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>3.18</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>4.01</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>5.14</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>8.29</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>9.3</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>10.5</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>11.0</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>137</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>300</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td>5</td>
<td>218</td>
<td><strong>567</strong></td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td><strong>1</strong></td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td><strong>2</strong></td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AC</td>
<td><strong>10</strong></td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Pre-loaded AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Recycled AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>HNO₃ pretreated AC</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>Original AF5</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
<tr>
<td>HNO₃ pretreated AF5</td>
<td>5</td>
<td>218</td>
<td>1.0</td>
<td>0.05 L/min oxygen</td>
</tr>
</tbody>
</table>
The parameters or conditions in bold are the ones different from the baseline. To ensure the tests’ results are comparable to the baseline and to other parallel tests, no more than two parameters were changed in each column test. The change of carbon type includes alteration to the same original carbons and carbon catalysts from different sources. In particular, the pre-loaded AC and recycled AC are both prepared from activated carbon that has been used for a previous column test. The recycled AC undergoes a desorption process where the adsorbed arsenic species are washed off from the carbon surfaces, whereas the pre-loaded AC is directly used for the new column test.

3.3 Analytical methods

3.3.1 Arsenic speciation

3.3.1.1 Trivalent arsenic

A colorimetric titration method was used to obtain As(III) concentrations in the solutions. The amount of oxidant - ceric sulfate - consumption determined the quantity of As(III) in the solution. The stoichiometric reaction is showed as Equation 9.

\[
\text{As(III)} + 2\text{Ce(IV)} = \text{As(V)} + 2\text{Ce(III)}
\]  

Equation 9

0.01 N Ce(SO₄)₂ solution (Fisher brand certified) is employed as the titrant, 0.1 wt% phenanthroline ferrous sulfate complex (ferroin indicator from Sigma-Aldrich) is used for colour indicator. The titration endpoint was recognized as a sharp color change from orange-red to pale blue.

3.3.1.2 Pentavalent arsenic

As(V) concentrations in the solutions were analyzed by the molybdenum blue method using Ultra-violent visible spectroscopy (UV-Vis). 1 mL of the solution sample was diluted with the 1:1 hydrazine:molybdate (0.04 M) solution into a 10 mL volumetric flask. The mixture was then heated in a 70 °C warm water bath for 2 h to let the As(V) react with the reagent. Then the resulting solution was radiated with an 840 nm wavelength (Talanta, 2003). The absorbance of the solution was read on UV-Vis. A calibration curve, which plots the absorbance of 5, 10, 15, 20, and 40 ppm
As(V) standards, was prepared before the measurement of arsenic in the test solutions (Figure 3-4). The As(V) concentration can be calculated from the absorbance reading by the regression equation of the calibration curve.

![Calibration curve](image)

**Figure 3-4. Calibration curve for As(V) standards of 0, 5, 10, 20, 30, 40 ppm.**

3.3.1.3 Total arsenic

The total arsenic concentrations were calculated by adding the numbers of As(III) concentration and As(V) concentration. Besides, the total arsenic concentration of solutions was measured by Atomic Absorption Spectroscopy (AAS, Thermo Scientific™ iCE 3000) to ensure the above speciation data reliable. AAS was conducted in reference to Method 7000A specified by US EPA. The typical detection limit for arsenic using direct aspiration AAS is 0.002 mg/L. An arsenic solution sample was aspirated into the sample compartment and then atomized in the nebulizer of the AAS instrument. A light beam from a hollow cathode lamp, whose cathode is made of the element being measured, i.e. arsenic, travels through an air/acetylene flame into a monochromator. The atomized sample was directed to the flame to measure the amount of light absorbed, which can
be recorded by a detector installed behind the monochromator. The absorption of the light energy is dependent on the presence of free, unexcited ground-state atoms in the flame. Thus the light energy absorbed by the flame can be correlated to the concentration of arsenic in the sample. Because the AAS is employed for the measurement of total arsenic concentrations, the calibration standards were prepared from 1000 mg/L As(V) standard solution provided by VWR®. The original 1000 mg/L arsenic standard solution was diluted using 5% HNO₃ into 5, 10, 25 ppm arsenic standards. A calibration curve is plotted prior to the analysis of arsenic samples. The detected absorbance will automatically be converted into total arsenic concentration by interpolation.

3.3.2 Chemical measurements

3.3.2.1 Dissolved oxygen (DO)
The concentration of dissolved oxygen in solution samples is measured instantly using Thermo Scientific® Orion 3-Star DO Benchtop Meter.

3.3.2.2 pH and oxidation reduction potential (ORP)
The pH value and ORP of solution samples are measured within 7 days after sampling using Oakton® pH 700 meter. The pH probe was calibrated prior to each use with pH 1.68, 4.01, and 7.00 buffer solutions.

3.3.3 Hydrogen peroxide determination
The concentration of hydrogen peroxide produced in the column was determined by ultraviolet-visible spectroscopy at a wavelength of 353 nm. The UV-Vis tested sample is composed of 1 mL of hydrogen peroxide-containing solution, 1 mL of an iodide solution, and 1 mL of a solution containing potassium hydrogen phthalate (KHP). A calibration curve was created by measuring the absorbance of samples with hydrogen peroxide standards with known concentrations. The sample from the top of the column was taken and subjected to the method described above and then plotted on the calibration curve to read the corresponding hydrogen peroxide concentration.
3.3.4 Experimental errors

There are always some systematic errors associated with different analytical methods. These experimental errors are taken into consideration into the reporting of test results. Analyses using different methods and instruments will give different precisions of the results. For all the analytical methods mentioned before, the systematic errors were assessed specifically by repeating the tests of the same sample at least 3 times. The experimental errors of the results are reported in all the applicable figures as error bars.

3.4 Safety precautions

Arsenic is toxic, so the test work has to be done in a safe way where the handler is ensured not to be exposed to arsenic under any circumstance, and the arsenic waste is not discarded improperly and cause contaminations to the laboratory and general environment subsequently.

Specific safety precautions are clarified in the Standard Operation Procedures (SOPs) of arsenic related test work and are taken during the conduction of arsenic test work. The risk of arsenic contamination includes arsenic oxides powders dusting, airborne arsenic in the working space and spill of arsenic containing solutions. To restrict the unwanted spread of arsenic in order to prevent arsenic contamination in the work space, the weighing of arsenic trioxide (As$_2$O$_3$) and arsenic pentoxide (As$_2$O$_5$) powders and arsenic dissolution into solutions should be done in the fume-hood. The analysis of arsenic concentrations involves colourimetric titration of As(III); UV-Vis spectroscopy for measuring As(V); and AAS for total arsenic determination. The colourimetric titration of arsenic samples should be conducted in the fume-hood. The dilution and preparation of arsenic samples for UV-Vis and AAS tests are performed in the fume-hood and the prepared samples should be stored in sealed containers before taken out for spectroscopy. The column reactors for arsenic tests are secured on a wooden bar attached to the wall so as to ensure the safe positioning of columns. The open top of column reactors should be covered by Parafilm with small holes preventing the splash of arsenic solution as well as allowing the escape of gas. The containers
for arsenic solutions are kept in capped buckets for transportation and storage outside the fume-hood. Spill trays are placed under the column reactors to restrain the spread of arsenic contamination in the event of any incidental spills. Acid spill kits should be used to treat abundant spills of acidic arsenic solution. The glassware used for arsenic tests should be thoroughly washed and rinsed for three times using deionized water prior to the use of other tests. Arsenic wastes are classified and temporarily stored in the fume-hood in liquid arsenic waste containers and solid arsenic waste containers, respectively.
Chapter 4 Preliminary study on the carbon assisted arsenic oxidation process: baseline column test

4.1 Column test procedure
To investigate the efficacy of the activated carbon loaded column reactor to oxidize arsenic in aqueous solutions, a baseline condition was selected (from the past test work experiences) for the experiments. A series of operating parameters regarding arsenic oxidation in carbon columns are studied later in Chapter 5 versus the baseline test.

The arsenic oxidation column tests were conducted in Teflon column reactors configured as described in Chapter 3. A commercial coconut shell based activated carbon was adopted in the baseline column test. The activated carbon is screened and washed prior to the column test, as per description in Chapter 3, then loaded into the column reactor. The activated carbon column reactor is fastened vertically onto a wood bar situated on the wall in order to enable an upward flow of influent solution to provide the maximum interaction between solid carbon catalysts and aqueous As(III) solution. A diluted sulfuric acid solution is prepared for washing activated carbon to an identical pH with that of the influent arsenic solution. The activated carbon in the column is washed with at least 2 L diluted sulfuric acid solution until the pH in the effluent sampling port is measured to be stable at pH = 1 for at least 3 samples with 30 min intervals.

4.2 Results and discussion

4.2.1 Evolution of arsenic species concentrations
The evolution of arsenic species concentrations for the baseline test are plotted in Figure 4-1, where the figure adapts throughput volume (mL) as the abscissa axis instead of time (h), mainly because the test time was not comparable for tests with different flow rates (due to different residence time of the columns). As presented in Figure 4-1, the concentration of total arsenic in the discharge gradually increased up to approximately 5 g/L after treating roughly 3500 mL solution volume.
The arsenic concentration then stabilized at the equivalent arsenic concentration in the influent being fed to the column. The breakthrough of arsenic was observed shortly after the arsenic solution was fed into the column (approximately 100 mL throughput volume) because the adsorption capacity of activated carbon for arsenic was not substantial compared to the accumulative solution being treated.

Figure 4-1. Arsenic speciation for column test conditions: pH = 1.00; oxygen flow rate = 0.05 LPM; influent As(III) concentration (C₀) = 4.70 g/L As(III); and residence time = 218 min.

The instantaneous oxidation efficiency was calculated by dividing As(V) concentration by total arsenic concentration in the effluent. Only when the total arsenic concentration in the effluent rose to the level of the arsenic concentration in the influent, which signifies that the highest adsorption density limit of activated carbon has been reached, the calculated As(V)/As(T) value reflects the
actual oxidation efficiency of arsenic species. Therefore, the steady oxidation efficiency of the column test is expressed by the average of As(V)/As(T) values in the last few samples situated on the plateau of curves shown in Figure 4-1. The steady state oxidation efficiency was 84% in Figure 4-1.

4.2.2 The pH and ORP in the influent and effluent
The pH and ORP of the influent and effluent solutions are measured during the column test, and the results are presented in Figure 4-2. The influent pH and ORP stay constant through the entire column test, the fixed values are marked in Figure 4-2 by dashed lines.

![Figure 4-2. The pH and ORP in the influent and effluent solutions of the baseline column test.](image-url)
Since the column reactor was washed using pH 1 sulfuric acid solution, the initial pH and ORP in the effluent solution are representative to the wash solution. The pH in the effluent solutions experienced a fluctuating between pH=1.00 and pH=1.03. The ORP in effluent samples ratchet down from 342 mV to 336 mV.

4.2.3 DO in the influent and effluent

Dissolved oxygen is believed to play an important role in the oxidation of chemical species in aqueous solutions. The involvement of dissolved oxygen in As(III) oxidation was proved by performing experiments in nitrogen saturated solutions, where oxidation was not observed (Ryu & Choi, 2007). In a study of arsenic oxidation induced by biochar, Zhong-delai (2019) and co-workers suggested that dissolved oxygen can accept electrons from the hydroxyl groups on the carbon surface to produce superoxide anion free radicals (·O₂⁻), then further accept an electron to form H₂O₂. In a study of sono-oxidation of arsenic, the H₂O₂ production was considerably reduced as compared to that observed during the sonication of water alone without As(III) (Neppolian, Doronila, & Ashokkumar, 2010). This suggested that ·OH radicals were involved in the As(III) oxidation process (Neppolian et al., 2010). The concentration of dissolved oxygen in the influent and effluent solutions is monitored throughout the column test. Figure 4-3 presents the exact DO concentrations in influent and effluent samples as well as the difference between influent and effluent DO concentrations. The DO of influent samples are labelled as DO(in); while DO concentrations in the effluent are labelled as DO(out). It can be seen in Figure 4-3 that the initial DO(in) and DO(out) are close to each other at around 5-6 ppm, while the DO(out) surged up to a much higher value of ~13 ppm and was maintained at this high level after the system became oxygenated. The increase of DO concentration in the effluent samples is clearly related to the sparging of oxygen into the system. The plateau of DO concentration in the effluent signifies an abundant amount of oxygen in the solution, which implies that dissolved oxygen is the precursor for the oxidizing reagents that promote arsenic oxidation.
Figure 4-3. Concentrations of dissolved oxygen in the influent and effluent samples.
Chapter 5 Kinetics column tests

5.1 Parameters study on activated carbon catalyzed arsenic oxidation

5.1.1 Effect of initial arsenic concentration

The oxidation efficiency was increased to above 95% in a column test treating the influent solution of 1.03 g/L As(III), without any other changes in the parameters of the experiment versus those of the baseline test (Figure 5-1). The plateaus of As(V) in the effluent samples were observed at different throughput volumes in the cases of different influent As(III) concentrations: the higher the concentration in the influent, the earlier the plateau was reached. This can be attributed to the intrinsic adsorption capacity of activated carbon and a lower adsorption density limit when it is in contact with solutions with lower arsenic concentrations. Moreover, when dealing with an influent solution of 1.98 g/L As(III), the column reactor presents an average oxidation efficiency of 88%, which is lower than the 1.03 g/L As(III) test (i.e. 95% As oxidation) but higher than the baseline test (i.e. 84%). In a column test treating influent solution containing 9.81g/L As(III), the arsenic oxidation is only 76%, which is a far lower oxidation efficiency than that of those tests with lower arsenic concentrations (4.70 g/L, 1.98g/L and 1.03 g/L As(III)). Figure 5-2 summarized the effect of the influent arsenic concentration on the arsenic oxidation efficiency with the activated carbon column reactor. The effect of initial arsenic concentration on the arsenic oxidation is likely related to the dosage of activated carbon.
Figure 5-1. As(V) concentrations in the effluent of column tests fed with different As(III) solutions (test conditions: pH=0.98; oxygen flow rate=0.05 LPM; residence time=218 min.).

Figure 5-2. The effect of the influent arsenic concentration on the arsenic oxidation efficiency.
5.1.2 Effect of system pH

The pH of the feed arsenic solution has a significant impact on the oxidation of arsenic species in the solution, especially because the arsenic species (i.e. As(III) and As(V)) vary within different pH range (Bissen & Frimmel, 2003b). Usually the arsenic oxidation mechanism follows a completely different pathway in alkaline solution as compared to acidic environment (Pettine, Campanella, & Millero, 1999). Thus pH is an important factor in the design and operation of industrial processes (Choi, Ghahremanizhad, & Ahern, 2014).

The performance of the column system was examined under a wide range of pH conditions. It should be noted that the arsenic oxidation reaction is an acid generating reaction thus in the experiments the steady state pH of the column was always lower than the influent solution. This phenomenon is further discussed below. Figure 5-3 shows the difference in influent and effluent pH values of a series of 12 column tests fed with 5 g/L As(III) solutions at different pH in the range of 0.80–10.98.

![Figure 5-3. pH values of the influent and effluent solution of column tests.](image)

54
When the influent pH is lower than 1, the final pH of the solution discharged from the column reactor will stabilize at a very similar pH value to that of the influent, because the acidity of the solution is high and the acid produced during the arsenic oxidation process is not enough to make a significant change in the concentration of total H\(^+\) in the column. Whereas, with higher pH influent solutions (pH higher than 1), the pH of the solution after passing through the carbon column will be depressed and result in a stable effluent pH as depicted in Figure 5-3. It is worth mentioning that even when the influent solution is in alkaline condition (i.e. pH 8.29, 9.30, 10.50, 10.98 in Figure 5-3), the activated carbon column can acidify the solution to an acidic pH range, which can be attributed to the arsenic oxidation and then the arsenic acid (H\(_3\)AsO\(_4\)) dissociation reaction where protons can be released into the aqueous solution and consequently lower the pH (Equation 10-12).

\[
\begin{align*}
\text{H}_3\text{AsO}_3 + \text{H}_2\text{O} & \leftrightarrow 2\text{H}^+ + \text{H}_3\text{AsO}_4 + 2\text{e}^- & \text{Equation 10} \\
\text{H}_2\text{AsO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{AsO}_4^- + 2\text{H}^+ + 2\text{e}^- & \text{Equation 11} \\
\text{H}_3\text{AsO}_4 & \leftrightarrow \text{H}^+ + \text{H}_2\text{AsO}_4^- & \text{Equation 12}
\end{align*}
\]

The pH of solution within the column space presents a descending gradient from the influent high pH to effluent low pH. Samples from different height in the column space were taken to measure the specific pH and ORP. Figure 5-4 presents an example from the column reactor after being tested with pH = 5.14 influent solution and reached a stable effluent pH of 2.18. It can be seen that the actual pH and ORP condition within the column space where the solution is in direct contact with activated carbon particles is close to the effluent pH. The arsenic oxidation and related reactions are presumed to occur under the measured pH and ORP environment.
Figure 5-4. The pH and ORP scenario in the column test with pH 5.14 influent (5 g/L As(III)).

Figure 5-5 shows the effect of pH on the arsenic oxidation efficiency of the column tests. The oxidation of arsenic was highly sensitive to pH in the range of 0.96~2.26. The steady-state arsenic oxidation efficiency can be improved from 80% at pH = 0.96 to 97% at pH = 1.84, and further pH increase above 1.84 will reduce the efficiency of As oxidation in the column. The amount of produced protons can be calculated by comparing the influent and effluent pH values. When the arsenic oxidation culminates at 97% at pH=1.84, the ratio of H⁺ produced and arsenic oxidized was 2:1, which is generally in accordance with the stoichiometry in Eq. 8 (the pH in the effluent dropped from pH=3.18 in the influent, indicating that 1.379×10⁻² M H⁺ were produced theoretically, which results in 6.499×10⁻³ M of As(III) being oxidized.). The As oxidation at pH 2.26 decreases to about 80% only. However, column tests at pH conditions higher than 2.26 yielded an almost complete
oxidation of As(III). The arsenic oxidation efficiency at pH 2.82 was 97%, 96% at pH 4.74, and at pH 5.8 it was 98%.

![Figure 5-5. Arsenic oxidation efficiency in column tests at different pH conditions.](image)

The solution pH plays a crucial role in determining the extent and pathway of redox reactions between functional groups on carbon-based materials and redox-sensitive species such as arsenic. Most studies suggested that arsenic oxidation is generally promoted under alkline conditions versus acidic conditions. For example, Jiang et al. showed that a model HS quinone (9,10- anthraquinone-2,6-disulfonic acid, AQDS) could oxidize 0.5%, 12.6%, and 67.3% of As(III) at pH 3.0, 7.0, and 11.0 under anoxic conditions, respectively. Persistent free radicals PFRs on AQDS were suggested to directly oxidize As(III) at pH values of 3.0 to 11.0 in anoxic solutions. Previous studies in the literature only cover the situations where pH is typically higher than 3.0, the arsenic oxidation assisted by AC under highly acidic conditions (pH < 3.0) in our cases is proved to follow a different pattern mainly involving the change in As(V) speciation. The different reaction patterns under varying pH conditions are further discussed in section 5.2.

5.1.3 Effect of residence time
Residence time can be a critical factor in the design of dynamic tests since it also dominates the
time span allowed for the chemical reactions to proceed. Long leaching residence time for a process
is not desirable, since it directly impacts the capital cost of the plant development. In order to
investigate the effect of residence time on the activated carbon assisted arsenic oxidation, the
column reactors was altered in length and the feed solution flow rate is adjusted to vary residence
time in column tests.

Residence time indicates the general duration for the flowing solution to be treated in the activated
carbon loaded column system. In other words, the residence time of a column test is the period of
time when a single drop of arsenic solution is in direct contact with the activated carbon catalyst.
It should be noted that in all the column tests the ratio of total solution volume inside the column
to the total activated carbon volume inside the column was designed to remain the same. The
residence time in the column tests is determined jointly by the influent flow rate and the void
volume in the activated carbon filled column reactor. Only the period of time for arsenic solution
in direct contact with activated carbon can be regarded as effective residence time. A column test
was conducted, in comparison with the baseline test, in a modified column setup with extended
length but still with the same volume loaded with activated carbon. The volume of the upper
compartment is one third of that of the lower compartment, thus the retention time for arsenic
solution in the column was extended from 218 min to 750 min. Figure 5-6 shows that the arsenic
oxidation efficiency still stabilized at approximately 82%, similar as the case in the baseline test
with 218 min residence time.
Figure 5-6. Extending the length of column setup but still pack with same amount of carbon as baseline experiment (left); Arsenic speciation for the test in an extended column reactor with more void volume (other conditions same as baseline experiment; retention time from inlet to outlet = 750 min; equivalent residence time = 218 min) (right).

In a column test the influent flow rate was raised from 0.35 mL/min to 0.5 mL/min, consequently the residence time was reduced to 137 min. A steady oxidation efficiency of 67% was reached with 5.91 g/L As(III) in the influent solution (Figure 5-7). The oxidation was significantly depressed with a smaller residence time of 137 min as compared to the baseline value of 218 min, which is likely due to the relatively slow kinetics of the arsenic oxidation reaction.
Figure 5-7. Feature curves for column tests with different residence time and same other conditions: feed 5.91 g/L As(III) solution; pH=0.96; oxygen flow rate=0.05 LPM.

On the contrary, extending the residence time has a positive impact on the steady oxidation efficiency. Higher oxidation efficiencies of 87% and 97% were achieved at a steady state of the column tests with 300 min and 567 min residence time, respectively. The effect of different residence time on the arsenic oxidation efficiency are summarized in Figure 5-8. The efficiency is only related to the time rather than the amount of carbon.
5.1.4 Effect of oxygen condition

An oxidation efficiency of 80% was observed at the steady state of a column test where the oxygen aeration was increased to 0.10 LPM, and the influent solution contained 9.81 g/L As(III). The feature curves of the effluent arsenic concentrations are shown in Figure 5-9. The increase of oxygen flow rate did not show significant improvement in the arsenic oxidation, compared with the test under similar conditions but with only 0.05 LPM oxygen sparging (Figure 5-1). This is also backed up by a column test treating 5.91 g/L As(III) influent solution with 137 min residence time and a higher oxygen flow rate of 0.2 LPM (Figure 5-10). The oxidation efficiency calculated based on the data from Figure 5-10 is 66%, which is similar to the steady oxidation efficiency of the column test with 0.05 LPM oxygen bubbling as depicted in Figure 5-8.

Figure 5-8. The effect of residence time on the arsenic oxidation efficiency.
Figure 5-9. Feature curves for test conditions: oxygen flow rate=0.10 LPM; feed 9.81 g/L As(III) solution; residence time=218 min.

Figure 5-10. Feature curves for test conditions: oxygen flow rate=0.2 LPM; feed 5.98 g/L As(III) solution; and residence time=137 min.
Increasing oxygen sparging rate does not present a significant impact on the arsenic oxidation efficiency. An oxygen flow rate of 0.05 L/min seems sufficient to achieve the optimal conversion of As(III) to As(V) since the arsenic oxidation with higher oxygen flow rates was not improved accordingly. Dissolved oxygen (DO) could play an important role in the arsenic oxidation reaction because oxygen and water can react on the activated carbon surface generating a strong oxidant, such as hydrogen peroxide, and subsequently oxidize As(III) to As(V) (Equation 13-14) (R. Radzinski et al., 2016). Thus, the DO would be a critical parameter controlling H₂O₂ formation and consequently, arsenic oxidation.

\[
\frac{1}{2} O_2 + H_2O \xrightarrow{\text{Activated carbon surface}} H_2O_2 \quad \text{Equation 13}
\]

\[
H_3AsO_3 + H_2O_2 \leftrightarrow H_3AsO_4 + 2H_2O \quad \text{Equation 14}
\]

Table 4 shows the measured DO concentration in the test solutions from the column tests fed 4.8 g/L arsenite solutions with different oxygen flow rates.

<table>
<thead>
<tr>
<th>Oxygen sparging rate (L/min)</th>
<th>DO in the influent (ppm)</th>
<th>DO in the effluent (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>5.14</td>
<td>12.45–16.31</td>
</tr>
<tr>
<td>0.10</td>
<td>5.36</td>
<td>13.30–16.56</td>
</tr>
<tr>
<td>0.15</td>
<td>5.13</td>
<td>12.35–16.17</td>
</tr>
<tr>
<td>0.20</td>
<td>5.28</td>
<td>13.72–17.14</td>
</tr>
</tbody>
</table>

Since the influent solutions were measured for DO before the oxygen sparging through the system, the values of initial DO ensure that the enhancement of DO concentration should be attributed to oxygen addition. DO concentrations in the effluent solutions are not noticeably correlated with the oxygen flow rate and the fluctuation range of DO concentrations in these cases shows a good overlap in general. Excessive oxygen addition to over 0.05 L/min flowrate does not seem to aid the
arsenic oxidation, which is likely due to the saturation level of DO in the column system that was reached with such oxygen sparging rate.

Moreover, switching the injection gas from pure oxygen to compressed air can decrease the oxidation efficiency that can be reached within the column system. A column test treating an influent solution containing 5.08 g/L As(III) presents 62% arsenic oxidation at its steady state with 0.25 LPM air sparging (Figure 5-11). It should be noted that an air sparging rate of 0.25 LPM quantitatively provides the same total amount of oxygen input into the column system as with 0.05 LPM pure oxygen sparging rate; thus the results of Figure 5-11 are comparable with those of the baseline test. Similarly, an arsenic oxidation efficiency of 59% was reached after the total arsenic discharge stabilized at a plateau in the column tests with 0.05 LPM air flowrate (Figure 5-12), and in the case of 0.10 LPM air flow rate, the steady oxidation efficiency of arsenic was 60% (Figure 5-13).

![Figure 5-11. Feature curves for a column test with air flow rate of 0.25 LPM (Other conditions: pH=1.02; feed 5.08 g/L As(III) solution; and residence time=218 min).]
Similarly, an arsenic oxidation efficiency of 59% was reached after the total arsenic discharge stabilized at a plateau in the column tests with 0.05 LPM air flow rate (Figure 5-12), and in the case of 0.10 LPM air flow rate, the steady oxidation efficiency of arsenic was 60% (Figure 5-13). The decrease in the oxidation of arsenic, resulted from the switching of pure oxygen to compressed air, can be correlated to the DO level and hydrogen peroxide concentration (Equation 13-14).
Figure 5-13. Feature curves for a column tests with air flow rate of 0.10 LPM. (Other conditions: pH=1.02; feed 5.08 g/L As(III) solution; residence time=218 min).

Figure 5-14 summarized the DO and hydrogen peroxide concentration measured from the discharge of column tests with different gas flow scheme. There is a clear correlation between the hydrogen peroxide concentration and the oxidation efficiency, which complies with the carbon-catalyzed arsenic oxidation mechanism proposed by Radzinski. & Ghahreman (R. Radzinski et al., 2016): there is an oxidizing agent (i.e. H$_2$O$_2$) produced in situ at the activated carbon catalytic sites facilitating the oxidation of arsenite. This is in conformity with Scott and Morgan (1995) that the rate of arsenic oxidation is independent of the concentration of dissolved O$_2$, the rate being controlled instead by the rate of a surface reaction.
Figure 5-14. The correlation of arsenic oxidation efficiency and oxidation indexes: dissolved oxygen and hydrogen peroxide level.

5.2 Dependence of oxidation efficiency on arsenic speciation

To develop an insight into the arsenic speciation under the conditions of the tests of the present study, more specifically the pH and ORP conditions, and to correlate that with our test results, the pH and ORP values of the column tests are plotted in the Eh-pH diagram of As-H2O system (Figure 5-15). All the pH and ORP plots fall in the areas pertaining to As(V) species, meaning that As(III) is less stable than As(V).
Figure 5-15. The plot of pH and ORP (tested in the effluent of column tests) in the Eh-pH diagram of As-H₂O system (25 °C and 1 bar).

Figure 5-16 depicts the As(V) speciation in the conditions of the tests over the pH range of 0 to 7. It’s evident that H₃AsO₄ is the dominant As(V) species in pH values up to 2.4, and at greater pH values the dominant As(V) species is the HAsO₄⁻.
Figure 5-16. Calculated As(V) speciation concentrations for 5 g/L (6.67 mM) As solution with 20 ppm dissolved oxygen in the pH range of 0–7 (adapted from OLI software)

The considerable difference in the oxidation efficiencies between the solutions with pH < 2.26 and those with pH > 2.82 likely is connected to the As(V) speciation under the different pH ranges (Figure 5-16). This also complies with the information from Figure 5-15 where the fitting line for all the sporadic (pH, ORP) points presents a less negative slope than the slope of H$_3$AsO$_4$/H$_2$AsO$_4^-$ boundary, meaning that the higher the pH, the further the oxidation overpotential will be on As(III) species.

5.3 Chapter conclusions

Concentrated As(III) solution can be oxidized effectively in column reactors loaded with activated carbon in an acidic environment. An oxidation efficiency of 84% is achieved in the column test treating 5 g/L As(III) influent solution with 0.05 L/min oxygen flow rate. Longer residence time is desired to reach a higher oxidation efficiency: 218 min residence time was proven to be effective and efficient for the activated carbon column reactor, shortening the residence time will depress the arsenic oxidation by activated carbon catalysis. On the contrary, a higher oxidation efficiency
can be reached with a longer residence time. With a residence time of 567 min, the oxidation efficiency can be improved to over 97%. pH condition is critical in the conversion from As(III) to As(V). The oxidation of arsenic was highly sensitive to change in pH in the range of 0.80–2.26. The steady-state arsenic oxidation efficiency culminated in 97% at pH 1.84. pH higher than 2.26 will yield almost complete oxidation of As(III) because of the formation of negatively charged As(V) species. Aeration is required during the operation to facilitate oxidation of arsenic: when the sparging gas is pure oxygen, an oxygen flow rate of 0.05 L/min is sufficient to achieve a relatively high oxidation efficiency, and the increase in oxygen flow rate does not have a significant effect on promoting the oxidation efficiency; whereas, when the column reactor is bubbled with air, the oxidation efficiency is restricted to above 60%. The oxidation efficiency can be correlated to the hydrogen peroxide concentration in the column reactor.
Chapter 6 A study of column tests with various carbons

6.1 Altered activated carbon

6.1.1 Recycled activated carbon

In the column tests stated before, a fresh activated carbon filled column reactor was proven effective and efficient on converting As(III) to As(V). However, the longevity of carbon catalyst is also of great concern for the industrial application of the activated carbon catalyzed arsenic oxidation process. The recyclability of activated carbon is tested accordingly in the column reactors. Figure 6-1 shows the results of a column test employing recycled activated carbon (instead of fresh activated carbon). The recycled activated carbon was prepared by washing the old activated carbon left from a previous arsenic oxidation column test. The activated carbon after long term contact with concentrated arsenic solution has adsorbed arsenic species to presumably saturation. The activated carbon was then washed by a pH = 1 sulfuric acid solution for 24 hours until the total arsenic concentration in the strip solution was below 0.5 g/L. The recycled activated carbon shows remarkable efficacy in catalyzing arsenic oxidation with a steady oxidation efficiency of 87% in the column test.
Figure 6-1. Feature curves for test conditions: oxygen flow rate=0.05 LPM; feed 4.70 g/L As(III) solution; and residence time=218 min; recycled carbon.

The recyclability of activated carbon can be attributed to the impermanent adsorption of arsenic species and the reversible nature of the in-situ oxidants generating reactions. The recycled activated carbon can provide similar catalysis for high arsenic oxidation efficiency as the fresh activated carbon. Such a feature makes activated carbon a promising catalyst for industrial application since one time installment of an activated carbon catalyst column can last for a fair long time meaning the replacement of catalyst columns is required less frequently and the maintenance cost is minimum.

6.1.2 Activated carbon preloaded with arsenic

The initial As(III) concentration in the influent solution is proven to be an important factor affecting the arsenic oxidation by activated carbon. To further investigate the influence of arsenic concentration on its oxidation, an activated carbon preloaded with high arsenic content was examined in a column test. Figure 6-2 depicts a column test treating 1.03 g/L As(III) influent with
heavily preloaded activated carbon. Before the column test, the activated carbon was treated with highly concentrated arsenic solution (9.81 g/L As(III)) under acidic condition (pH=1) until the maximum adsorption density was met. The steady oxidation efficiency, in this case, was 95%, which shows no inferiority as compared to the tests with fresh carbon. The result with high arsenic content preloaded activated carbon further shows that it is the initial arsenic concentration in feed solution, rather than that on the carbon surface, that affects the overall oxidation efficiency of arsenic. The reaction of arsenic and in-situ produced oxidants is the limiting step regarding the general arsenic oxidation. Even the carbon surface is assumed to be saturated with adsorbed As(III) and As(V), there is still sufficient active sites to generate the oxidant, i.e. H$_2$O$_2$, irrespective of the arsenic concentration.

![Figure 6-2. Feature curves for test conditions: pH=1.0; oxygen flow rate=0.05 LPM; feed 1.03 g/L As(III) solution; and residence time=218 min; preloaded carbon.](image-url)
The desirable performance of preloaded AC enables a great potential for reliable long term industrial application. A long-term column test treating 1.03 g/L As(III) solution with 0.05 L/min oxygen flowrate was conducted for 27 days, as illustrated in Figure 6-3. The arsenic oxidation efficiency reached above 97% at a steady state and remained at such a high level until the end of the test where a total throughput volume of 14000 mL As(III) solution was treated. The activated carbon exhibits durable and efficient catalysis capacity withstanding an ultra-long-period of operation, suggesting a reliable long-term performance of the activated carbon treatment system.

![Figure 6-3](image)

**Figure 6-3.** Feature curves of a long-term column tests with 1 g/L As(III) feed solution.

### 6.1.3 Pretreated activated carbon

Oxygen-function groups on the carbon surface are essential to the oxidizing ability of activated carbon. Chemical modification of activated carbons is considered to be an effective approach to introduce and further graft new functional groups onto the carbon surface. Through chemical pre-treatment processes, it is possible to increase the density of the functional groups on the activated
carbon surface and improve its catalytic properties. Oxidative acids, such as nitric acid, sulfuric acid, and hydrochloric acid, are commonly used for pre-treatment of carbon catalysts since they enhance the oxygen functionalities on the carbon surface. In addition to the oxygen functionalities, the negatively charged nitrogen functionalities also can participate in the catalysis of the reactions. During a nitric acid pre-treatment process the nitration mechanism and the generation of oxygen functionalities take place simultaneously.

To illustrate the effect of functional groups exploitation on the arsenic oxidation efficiency, a column test is conducted with HNO$_3$ pretreated AC. The nitric acid pretreatment was conducted as described in chapter 3.

The concentration of arsenic species in the effluent samples are presented in Figure 6-4. The HNO$_3$ pretreated AC does not exhibit notable improvements on the arsenic oxidation efficiency (~87% oxidation efficiency is similar as that of the baseline test). This is either because the HNO$_3$ treatment does not yield extra exploitation of key functional groups on the activated carbon or the HNO$_3$ functionality does not aid in the catalysis of arsenic oxidation.
Figure 6-4. Feature curves of a column test with HNO₃ pretreated activated carbon (feed As(III)=5.06g/L; influent pH=1.0; 0.05L/min oxygen sparging).

6.2 Lewatit AF5

Apart from activated carbon, another novel carbon-based catalyst, Lewatit AF5, was also reported to be able to catalyze the oxidation reaction (Cowan, Jahromi, & Ghahreman, 2019). Recently, AF5 has been employed in a hydrometallurgy leach processes to catalyze the oxidative leaching of refractory sulfide minerals such as enargite and pyrite (Jahromi & Ghahreman, 2019).

6.2.1 Original AF5

AF 5 was also tested for arsenic oxidation in the column reactor. The feature curves of AF 5 column test in Figure 6-5 show that the AF5 has the ability to catalyze the conversion of arsenic species however the oxidation of As(III) only proceeded at low rate, 40%-50% as compared to normally over 80% with activated carbon, even though AF5 has higher specific surface area and larger pore volume. Original AF5 is high in surface area and pore volume, but since this catalyst is originally developed as an ion exchange resin, most of the sites on the surface are not activated specifically for oxidation catalysis. The lower arsenic oxidation efficiency of AF5 demonstrates that surface area only provides necessary reaction sites for the reactive oxidative species generation reaction, but it is the surface functional groups that are essential to the generation of ROS.
6.2.2 HNO₃ pretreated AF5

The catalytic effect of carbon-based catalysts in oxidation is attributed to their surface functional groups. It is reported that nitric acid treatment could increase nitrogen and oxygen functional groups to the AF5 surfaces. Johromi (2019) has conducted a characterization of nitric acid pretreated AF5 to investigate the surface chemistry of this carbon-based catalyst. The XPS analysis of AF5 before and after HNO₃ treatment (Figure 6-6, Table 4) shows that the oxygen functional groups shifted from the quinone-like (C=O) and chemo-adsorb oxygen to carboxyl oxygen (C-OH; C-O-C). And the HNO₃ treatment introduced some new functional groups. The newly formed oxygen functional groups results in the formation of more oxygen double bonds such as quinone groups (C=O) which can significantly increase the catalytic capability of AF 5 for oxidation reactions.

Figure 6-5. Feature curves for column test with original AF5 (feed As(III)=5.06g/L; influent pH=1.0; 0.05L/min oxygen sparging).
The nitric acid pre-treatment can also result in surface defects, higher porosities and fresh new surfaces with high potential of activation (Kundu, Wang, Xia, & Muhler, 2008).

Table 5. Relative content of functional groups in O 1s peak (Jahromi & Ghahreman, 2019).

<table>
<thead>
<tr>
<th>O 1s relative concentration</th>
<th>Peak 1</th>
<th>Peak2</th>
<th>Peak3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Quinone like)</td>
<td>(Carboxyl)</td>
<td>(Non-carboxyl)</td>
</tr>
<tr>
<td>Original AF5</td>
<td>36.8</td>
<td>30.7</td>
<td>32.5</td>
</tr>
<tr>
<td>HNO3 pre-treated AF5</td>
<td>23.5</td>
<td>49.0</td>
<td>27.5</td>
</tr>
</tbody>
</table>

Nitric acid pretreatment was applied to AF5 catalysts to compare the oxidation efficiency with original AF5 and HNO3 pretreated AC (Figure 6-7). The arsenic oxidation efficiency at the initial stage of this test was significantly improved to over 99% as compared to less than 50% in the test with original AF5. The enhanced arsenic oxidation efficiency of HNO3 pretreated AF5 is attributed to the exploitation of catalyst surface functionalities by HNO3 treatment. The nitrogen and oxide functional groups are believed to be reactive to expedite the oxidation of arsenic. In the As(III)
feature curve, a breakthrough was observed after treating approximately 4000 mL of 5 g/L As(III) influent solution, meaning that the enhanced arsenic oxidation arising from HNO₃ pre-treatment is related to the direct increase in oxygen and nitrogen functionalities and cannot be sustained simply by oxygen gas sparging. The steady arsenic oxidation stabilized at ~70%, which is lower than that of original AC but higher than original AF5.

![Feature curve for column tests with HNO₃ pretreated AF5](image)

**Figure 6.7. Feature curves for column tests with HNO₃ pretreated AF5 (feed As(III)=5.06g/L; influent pH=1.0; 0.05L/min oxygen sparging).**

### 6.3 Summary discussion on the reaction mechanism of carbon assisted arsenic oxidation

The oxidation of arsenite is examined in column tests with different carbon-based catalysts, including changing the carbon types and alteration methods. It is found that the specific surface area of carbon-based catalysts is an index of potential reaction sites for in-situ reactive oxidative species formation. The reaction sites can be activated via some chemical pretreatment process, such
as nitric acid pretreatment. AF5 has higher surface area than AC, but the original AF5 exhibits lower catalysis in arsenic oxidation since most sites on AF5 surface have not been activated for arsenic oxidation. The arsenic oxidation efficiency is drastically improved after AF5 was treated with HNO$_3$, which was attributed to the oxygen and nitrogen functionalities resulted from nitric acid surface groups’ exploitation. The enhanced arsenic oxidation with HNO$_3$ pretreated AF5 eventually reverted to a level lower than that of original AC but still higher than original AF5. The exploitation of oxygen and nitrogen functional groups can directly improve the arsenic oxidation, but these functionalities introduced by HNO$_3$ is temporary and cannot be sustained under simply oxygenated conditions. The steady oxidation efficiency of pretreated AF5 can still stay at a higher level than that of original AF5 likely because of the formation of surface defects, increased porosities and fresh new surface caused by nitric acid pre-treatment.
Chapter 7 Conclusions and future work

The efficient and effective arsenic oxidation assisted by carbon-based catalysts is validated in column reactors which features a dynamic and continuous influent condition. Concentrated arsenic solution with an As(III) content as high as 5 g/L can be oxidized effectively in activated carbon column system in an acidic environment. A baseline condition for rapid small-scale column test is selected based on previous research and industrial practice: an activated carbon loaded column reactor featuring 218 min residence time fed with 5 g/L As(III) influent solution at pH =1.0 while under 0.05 L/min oxygen gas sparging. The baseline test yields an oxidation efficiency of 84%. A number of operation parameters are examined regarding their effects on arsenic oxidation efficiency. Residence time and initial As(III) concentration are proven to be important in the activated carbon catalyzed arsenic oxidation. In general, longer residence time is desired to reach a higher oxidation efficiency given the relative slow kinetics of the arsenic oxidation. A residence time of 218 min in the rapid small-scale column tests can readily provide acceptable arsenic oxidation efficiency over 84%. The oxidation efficiency can be improved to over 97% with a residence time of 567 min. The effect of initial arsenic concentration on the arsenic oxidation efficiency is related to the amount of carbon catalysts since the catalysts’ dosage defines the active sites for the in-situ formation of reactive oxidative species that can facilitate arsenic oxidation. In our rapid small-scale column tests, 129.4 grams of activated carbon was adapted as the baseline carbon dosage and is corroborated to be sufficient for treating 5 g/L As(III) solution persistently. Same dosage of activated carbon can give an arsenic oxidation of over 95% with 1 g/L initial As(III) concentration.

Activated carbon catalyzed oxidation of arsenite is highly pH dependent. The solution pH plays a crucial role in determining the extent and pathway of redox reactions between surface groups on activated carbon and arsenic. The oxidation of arsenic is sensitive to change in pH in the range of 0.80~2.26. The optimal steady-state arsenic oxidation efficiency reaches 97% at pH 1.84. The
formation of negatively charged As(V) species can yield almost complete oxidation of As(III) at pH higher than 2.26.

Oxygenation of the carbon column is important to maintain the carbon catalysis capability for arsenic oxidation. The oxygen sparging into the system enables the regeneration of key functional groups on the carbon surface and consequently produce reactive oxidative species, i.e. H₂O₂ and hydroxyl radicals (·OH), so as for the redox reaction of arsenic to proceed. Pure oxygen gas is superior to air for sparging at the same oxygen dosage. An oxygen flow rate of 0.05 L/min is sufficient to achieve a relatively high oxidation efficiency, and the increase in oxygen flow rate does not have a significant effect on promoting the oxidation efficiency; whereas, when the column reactor is bubbled with air, the oxidation efficiency is restricted around 60% since the highest dissolved oxygen concentration can be achieved with air is only ~8 ppm and with pure oxygen is ~15 ppm. The oxidation efficiency can be correlated to the dissolved oxygen and hydrogen peroxide concentration in the column reactor. Dissolved oxygen works as a precursor in the carbon column system to produce H₂O₂ and further ·OH in an electron transfer reaction.

Various carbons are tested in the column reactor to investigate the general carbon catalysis mechanism for arsenic oxidation. Recycled activated carbon and activated carbon preloaded with high arsenic content are both validated for competent catalysis capacity on arsenic oxidation. The recyclability of activated carbon and its sustainable catalysis capability for arsenic oxidation make the activated carbon a promising catalysts for arsenic oxidation in industrial application. Nitric acid pretreated activated carbon does not show significant superiority in arsenic oxidation. Original AF5 is also tested for arsenic oxidation while only gives limited arsenic oxidation efficiency of ~40%. Nitric acid pretreatment can drastically improve the arsenic oxidation efficiency at the initial stage of AF5 column test: from ~40% to 99%. However, the improved oxidation efficiency will revert to a level lower than that of activated carbon but still higher than original AF5. The improvement in arsenic oxidation is attributed to the exploitation of surface functionalities on the carbons by HNO₃.
Since molecular oxygen is the only consumable oxidant in the carbon catalyzed arsenic oxidation process and regular oxygen sparging technique will result in a relatively low ceiling concentration of DO in the system which substantially restricts the oxidation, it is of great interest to increase the DO concentration in the solutions as much as possible such as to improve the generation of reactive oxidizing species and to further promote the oxidation of arsenic. The future work of this research field should include investigations into the techniques that can enhance gas diffusion and mass transfer of oxygen molecules into the aqueous solution, which potentially increase the DO concentration significantly. The interactions between arsenic species with some other common cations in mining waters, such as Fe$^{3+}$ and Cu$^{2+}$ ions, may have some promoting effects on the oxidation of arsenic. It is also recommended to study the interference of these ions on arsenic oxidation under continuous conditions in the future.

References


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