EVALUATING POTENTIAL OF DATE-PALM BIOCHAR FOR ARSENIC REMOVAL FROM WATER, COUPLED WITH SPECTRAL-INDUCED POLARIZATION (SIP) FOR REAL-TIME MONITORING

BY

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This research work is dedicated to my parents, esteemed mentors, and well-wishers

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This research work is a result of contribution of numerous experts in various fields. I shall start by thanking Allah for giving me the privilege and platform to conduct this study. I am sincerely thankful to Dr. Bassam Tawabini who has guided me and helped achieve the set targets. I am grateful to Dr. Pantellis Soupios for his ever-ready support and solutions to the problems that I have encountered during the course of my research. I shall further extend my gratitude to Dr. Dimitrios Ntarlagiannis for his expert advice and lessons that have helped understand the novel technology that we have integrated in this study. I am also sincerely thankful to Dr. Dimitris Kalderis and Dr. Panagiotis Kirmizakis for assisting in determining the appropriate tactics for adopt for achieving research objectives. I am humbly grateful to Mr. Eyad Safi, Mr. Tajaudeen Adeyinka Oyehan and Mr. Tariq Aziz for assisting me in laboratory work. Words cannot express how glad I am to have met all these ever compassionate people.

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ABSTRACT

Full Name : OMER MUHAMMAD SIDDIQ
Thesis Title : **Evaluating Potential of Date-Palm Biochar for Arsenic Removal from Water, Coupled with Spectral-Induced Polarization (SIP) for real-Time Monitoring]**

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In this work, biochar produced from Date-Palm leaves (DPLs) was used as an adsorbent for the removal of arsenic from contaminated water. Initially three biochar formulations were prepared by varying pyrolysis temperature and their ability to adsorb arsenic was investigated. The efficiency of adsorption was enhanced by impregnation biochar with Fe, achieving significant increase in adsorption capacity (20% to 95%). Characterization of biochar produced at 500°C and 800°C was determined using proximate analysis, FTIR, XRD and SEM imaging for determining change in morphology and surface-functional groups after adsorption experiments. Fe-modified biochar was used for further determination of optimal parameters for adsorption(pH, adsorbent dosage, contaminant loading and stirring rate) achieving 99% of arsenic removal in batch sorption study. Water samples spiked with 1.0 ppm arsenic (As) were allowed to saturate through 5% and 10% biochar amended columns . Spectral induced polarization monitoring over the duration of the experiment (16 hours) showed changes in the recorded signals consistent with the As removal as confirmed by chemical analysis.

ملخص الرسالة

الاسم الكامل: عمر محمد صديق

عنوان الرسالة: تقييم فعالية الفحم الحيوي من نخيل التمر في إزالة الزرنيخ من الماء، مقترنًا بالمراقبة بالاستقطاب الطيفي (SIP)

التخصص: ماجستير في العلوم البيئية

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في هذا العمل، تم استخدام الفحم الحيوي (biochar) المنتج من أوراق النخيل (DPLs) في امتصاص الزرنيخ من المياه الملوثة. في البداية تم تحضير 3 تركيبات من الفحم الحيوي عن طريق تغيير درجة حرارة الانحلال الحراري وتم فحص قدرتها على امتصاص الزرنيخ. ثم تم تعزيز كفاءة الامتصاص عن طريق تغليفها بمادة الحديد مما أدى إلى زيادة كبيرة في قدرة الامتصاص (20٪ إلى٪ 95). بعد ذلك تم تحديد خصائص الفحم الحيوي المنتج عند 500 درجة مئوية و 800 درجة مئوية باستخدام اجهزة FTIR و XRD و SEM لتحديد التغيير في التشكل والمجموعات الوظيفية السطحية بعد تجارب الامتصاص. تم استخدام الفحم الحيوي المعزز بالحديد لتحديد الظروف المثلى للامتصاص (الأس الهيدروجيني، تركيز الفحم ، تركيز الزرنيخ ومعدل التحريك) لتحقيق٪ 99 من إزالة الزرنيخ في دراسة الامتصاص. تم السماح لعينات المياه المزودة بـ 1.0 جزء في المليون من الزرنيخ (As) بالتشبع من خلال ٪ 5 و٪ 10 من أعمدة الفحم الحيوي المعدلة. أظهرت مراقبة الاستقطاب الطيفي خلال مدة التجربة (16 ساعة) تغيرات في الإشارات المسجلة المتوافقة مع إزالة As كما أكد التحليل الكيميائي.

CHAPTER 1
INTRODUCTION

1.1 Water Scarcity and Contamination

1.1.1 Water Scarcity and Quality

In Saudi Arabia, we mainly rely on meteoric groundwater resources and desalination of seawater at a very high cost, achieving just enough water to meet the current demand across the country. Therefore, cleaning groundwater is a priority as it can sustain the kingdom's potable water reserves. However, this is usually coming with technical difficulty and at a high cost, as highlighted earlier, which has led many researchers to develop efficient, eco-friendly and cost-effective technologies to treat groundwater sources.

1.1.2 Water Contamination with Arsenic (As)

Arsenic contamination's dominance is variable and assumed to be high in areas where mining and industrial activities are on the rise, as the country plans to expand in current progress in these sectors. Due to its toxicity effect on human health, the removal of arsenic (As) from groundwater becomes a priority for many countries globally. Groundwater contaminated with Arsenic is considered a significant threat to human health. It is backed by the World Health organization that entitles Arsenic in water as Class-I carcinogen where threshold limits are set to 10 $\mu g\ L^{-1}$ for As in drinking water. Arsenic in water can be found in two dominant forms, arsenate (As(V)) and arsenite (As(III)). It is estimated that around 200 million people are affected by drinking arsenic-contaminated water. Countries such as Argentina, Chile, Saudi Arabia, Mongolia,

Kazakhstan, Kyrgyzstan, Bangladesh and China have a high Arsenic concentration in their groundwater where some are thoroughly being surveyed and others are yet to carry out risk assessments for groundwater arsenic contamination. As a general observation, in rural areas where clean water is scarce, there exists large scale, direct utilization of groundwater for drinking and cooking purposes that, if contaminated, will cause larger unaddressed demographic health problems. (Charles F. Harvey, 2002) (Luis Rodríguez-Lado et al, 2013) (R. Brittany Merola et al, 2015).

Sources of arsenic contamination in groundwater are diverse, and the majority of other contaminants can be categorized into two groups: man-induced and natural processes leading to the bioavailability of arsenic. Processes such as slow reduction followed by arsenic mobilization from iron oxyhydroxides are thought to contribute to increasing groundwater arsenic concentration. Another natural contribution is from high alkaline closed basin environment leading to desorption from mineral oxides. Anthropogenic sources mainly burn coal, mining, smelting and improper waste management from domestic, industrial and agricultural activities (Al-Farraj et al, 2013) (Habes Ghrefat et al, 2016). Arsenic in groundwater is found in multiple oxygen states and thus, its toxicity varies accordingly. Inorganic arsenate As(III) being more soluble in water is most toxic followed by inorganic arsenite As(V) and organic arsenate. Thus, for treatment, priority for removal is also given according to their relative toxicity.

1.1.3 Technologies Used for As Removal

Different technologies have been investigated to remove As from groundwater including adsorption, ion exchange, oxidation, coagulation-flocculation, and membrane separation.

However, limited work has been done on the removal of As from water using natural adsorbents. Several adsorbents have been used to remove As, including activated carbon, fly ash, iron-based

oxides and nanoparticles. However, limited work has been conducted on using natural adsorbents such as biochar in removing As. Therefore, this study aims to assess the efficiency of As removal using a natural adsorbent (biochar) combined with a geophysical monitoring technique.

1.1.4 Biochar: Semi-Synthetic Adsorbent for Water Contaminants

Biochar has been widely experimented and proven as a promising product of organic waste carbonization having multiple environmental applications, where decontamination of major groundwater contaminants is one such application that can replace conventional treatment systems at lower costs with either similar or higher removal rates. Biochar derived from Date Palm Biomass has been studied where its tendency to remove dominant contaminants found in most well water is evaluated, stimulating interest to pursue further experiments that can optimize the usage of waste from Date-palm biomass for decontamination purposes. Saudi Arabia being the 3rd largest producer of Date-palms globally after Egypt and Iran, is calculated to generate more than 200,000 tons/year of Date-palm wastes (shrubs, stems and date-seeds). Thus, considering recent experiments utilizing biochar obtained from Date-palms for decontamination by adsorption, there may be a new paradigm shift around the corner where waste is upcycled into useful products.

Modification to biochars can be achieved by chemical, physical, impregnation of metal, and inducing magnetic features in their structures, thus, enhancing their sorption capability. Possible modifications for obtaining favorable biochar properties to achieve high contaminant removal rates can be reviewed in order to achieve removal of high loading rates distinguishing previously used adsorbents as designed biochar functions are achievable.

In recent decades, the use of electrical methods has become increasingly preferred to calculate hydraulic parameters over other methods (Attwa & Günther, 2013; Zisser et al., 2010). Many successful efforts have shown the connection of the hydraulic conductivity with the observed

electrical properties, but taking into account and other assumptions, like porosity and geometry of the pore space as a unique relationship between electrical properties and hydraulic conductivity does not exist (Attwa & Günther, 2013; Hördt et al., 2007; Mazáč et al., 1985). The method of induced polarization (IP) both in the time domain and in the frequency domain (SIP) provides more information about the pore size than other electrical methods, making it the first choice in hydrogeological applications (Slater & Lesmes, 2002).

1.2 Spectral Induced Polarization (SIP)

1.2.1 Induced Potentials

The phenomenon of Induced Potential has been put into application since 1942. Measurements of Induced Potentials are made using conventional electrical resitivity electrode configurations. The response is based upon physical properties of the media that are a form of geophysical anomaly in the general output of data acquisition. When the current applied is switched off, the voltage between finite electrodes takes a quantifiable time to decay to zero because the subsurface stores charges (temporarily) acting as a capacitor for that period in time. Also, as the current is switched back on the voltage increases gradually taking time to reach to its maximum applied voltage.This decay and rise in voltage indicate the properties related to geological and instrumental fators used for focused analysis. Figure.1 below, illustrates the phenomenon of induced potentials in its basic concept.

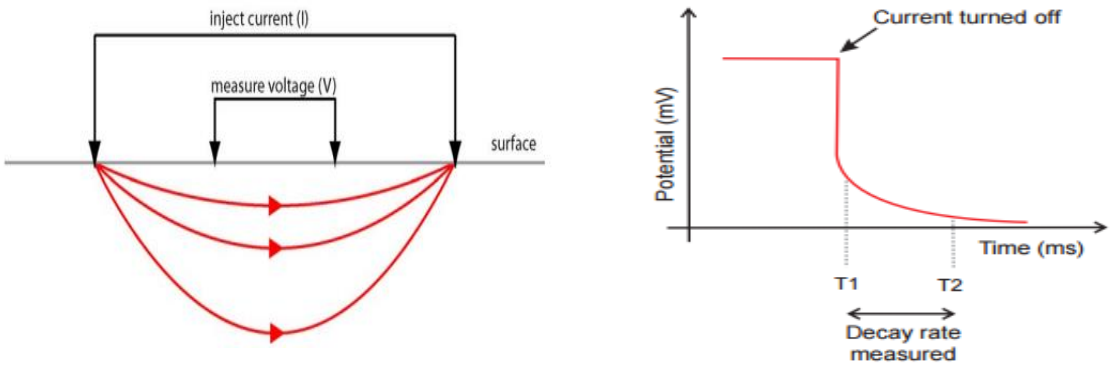


Figure 1 Concept of IP measurements

1.2.2 Types of IP Techniques

The variation in IP technique is based on the variation in the acquisition parameters and the relevant independent variable. These domain variations include:

- **Time-domain** (pulse transient)
- **Frequency-domain** (using harmonic signals)
    - Traditional variable-frequency IP (using two or more frequencies of <10Hz)
    - Phase-domain (measures phase delays between current and voltage)
    - Spectral IP (measures phases and amplitudes of frequencies of 10^{-3} to $4 \cdot 10^{3}$ Hz)

1.2.3 Concept of Spectral Induced Polarization

IP can be measured in the frequency domain by looking at the change in amplitude and phase log of an injected and measured signal. The measurements is thus a complex impedance with magnitude $|z| = {V_p}/{I_p}$ and phase φ, and after calculate a real and an imaginary apparent

resistivity or conductivity. These measurements can be done at different injection frequencies – spectral induced polarization (also called electrical impedance spectroscopy in other fields). Conventional measured parameters include:

$$\text{Phase angle: } \varphi(\omega) = tan^{-1}\left(\frac{\sigma''(\omega)}{\sigma'(\omega)}\right) \cong \frac{\sigma''(\omega)}{\sigma'(\omega)}$$

$$\text{Percent frequency effect: } PFE = \frac{\sigma(\omega_1)-\sigma(\omega_0)}{\sigma(\omega_0)} \cdot 100$$

$$\text{Chargeability: } M \propto \frac{\sigma'_{surf}}{\sigma'_{bulk}+\sigma'_{surf}} \cong \frac{\sigma'_{surf}}{\sigma'_{bulk}}$$

Application of Spectral Induced Polarization (SIP), a mature geophysical monitoring techniques, may provide a valuable monitoring tool for optimal sorbent utilization for on-site groundwater decontamination through providing valuable information that can be used to upscale the application of biochar for decontamination purposes. Overviewing the progress to date, biochar provides an environmentally sustainable alternative for high cost and complex adsorbents, and by merging geophysical monitoring techniques, a reliable treatment system can be developed.

1.3 Statement of Problem

Conventional adsorbents used in groundwater treatment systems are less environmentally friendly as challenges exist in their large-scale repetitive production, using harsh chemicals, and limited sorption capacity, which can be better addressed by utilizing renewable natural adsorbents derived from locally generated organic waste. On the other hand, the large amount of waste produced ends up in landfills requiring more landfills imposing critical concerns across the kingdom to establish an appropriate waste management system. Furthermore, limited groundwater resources and low degree of reservoir recharge rate threaten sustainable resource utilization, which is further intensified as pollution imposes water utilization limitations. Despite being economically stable,

Saudi Arabia has the vulnerability to run out of natural water resources as water demands are significantly on the rise, requiring larger expenditures to meet this demand disturbing the Kingdom's economic stability.

1.4 Significance of this Study

Addressing the current global challenges to obtain clean water with minimum detrimental impact to environment, this work shall streamline a new paradigm shift towards a circular economy where natural and locally available products derived from organic waste can be brought into economic use. Kingdom’s Date palm waste stream has a great potential for commercialization for economic and environmental purposes in Saudi Arabia that requires exploration followed by optimization. Innovative methodology of using geophysical techniques for environmental applications has the capability to ease up the upscaling process of lab-scale experimental findings due to the real-time-monitored decontamination profile of adsorbents that can be obtained by the application of spectral induced polarization (SIP). Monitoring provides further benefit to control the amount of substrates discarded that have reached their respective sorption limits, thus optimizing adsorbent life and introducing new adsorption media. This study's outcome has a great potential for commercialization for economic and environmental purposes in Saudi Arabia.

1.5 Research Objectives

The study's main aim is to evaluate the capacity of biochar synthesized from date palms wastes in removing Arsenic (As) from contaminated groundwater. Specific objectives include:

1. To synthesize a biochar formulation from the date palm biomass (DPBs) by pyrolysis method.

2. To identify the main morphological and chemical characteristics of DPBs using SEM, XRD, and FTIR techniques.
3. To model the DPBCs sorption capacity using adsorption modeling techniques.
4. To investigate the removal of As, in lab-scale batch sorption, under various parameters, including the initial concentration, flow rate and pH of As.
5. To evaluate and monitor the breakthrough and exhaust points of contaminant sorption with the SIP geophysical method's aid.

1.6 Summary of the Organization of Thesis

The structure of the thesis is established as follows

Chapter 1: Introduction including the statement, the significance, and the research objectives of the proposed thesis.

Chapter 2|: Gives a thorough literature review of the topic under discussion and covers all previous studies that are relatable. It gives the necessary knowledge background (of the different methods used for this study) and updates on the scientific community's recent progress.

Chapter 3: This chapter elaborates on the experimental procedures employed and the instrument used with respect to their purpose. Further step-wise approach in meeting the research objectives are given in this chapter.

Chapter 4: Illustrates the results obtained and discusses the findings of the research.

Chapter 5: Summarizes the conclusion derived from results and suggests future research opportunities based on knowledge obtained from this thesis

CHAPTER 2

LITERATURE REVIEW

2.1 Occurrence of Arsenic in Groundwater - Sources and its Impact

Arsenic is usually contained in iron-pyrites, ferrous rocks, and the resulting sediments in low quantity. Arsenopyrite (FeAsS) is the most common arsenic-containing mineral found in rocks formed in anaerobic environments (Das et al, 1996) where the As is released into groundwater through desorption. High alkaline and reducing environments are known to favor the rate of desorption from mineral oxides (Mondal et al, 2013). In groundwater, the Arsenic is found in multiple oxygen states, and its toxicity varies accordingly. Inorganic As composites are more dominant in groundwater where arsenite As (III) and arsenate As (V) coexist and vary in abundance according to redox conditions. Arsenite, being more soluble in water is the most toxic form followed by inorganic and organic arsenate As(V) (Jain and Ali, 2000; Mohammed Abdul et al., 2015; Shakoor et al., 2016). In addition to the natural source, anthropogenic sources of As, include the burning of coal, mining, smelting, and improper waste management from domestic, industrial, and agricultural activities (Ghrefat et al., 2016; Usman et al., 2016), mining activities and leachates from mine tailings (Suiling Wang & Mulligan, 2006), can also pose a significant environmental threat.

Millions of people worldwide are directly exposed to As concentration more than the acceptable (Mohammed Abdul et al., 2015) and are mostly affected by drinking As-contaminated water. Moreover, agricultural products that require flooded paddy fields such as rice and maize are more vulnerable to As pollution due to anoxic conditions that are present within paddy soils that are

needed for the cultivation of these crops. These anoxic conditions favor the formation of arsenite As(III) (more soluble) instead of arsenate (V) (less soluble), enabling plants to assimilate and retain As resulting in contaminated crops (Rosas-Castor et al., 2014; Senanayake and Mukherji, 2014). Figure 2 below, summarizes the pathway that leads to presence of arsenic in groundwater.

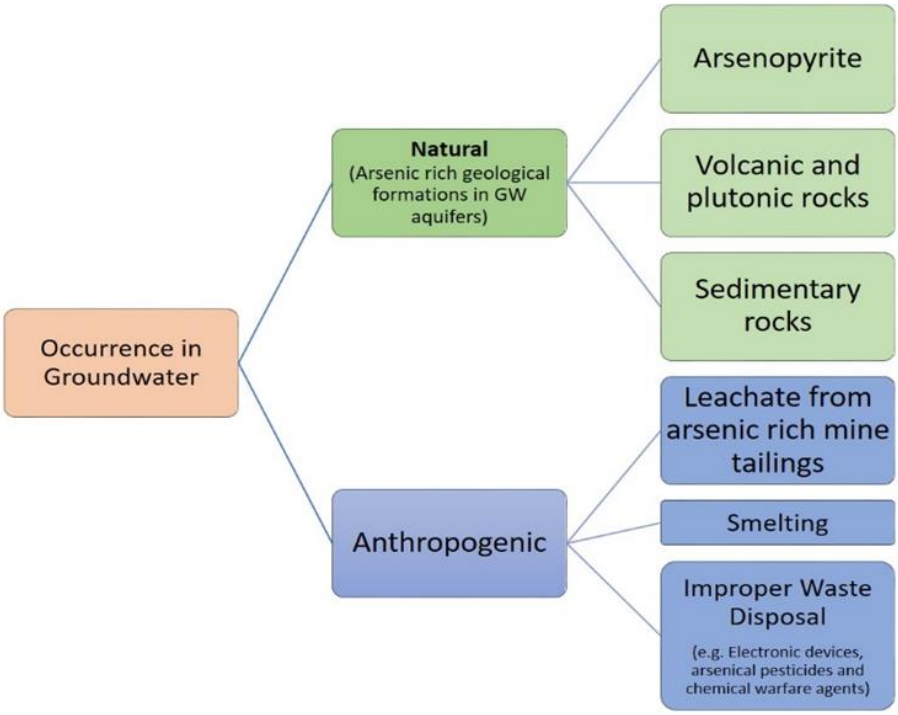


Figure 2 Sources of Arsenic contamination in groundwater

As mentioned above, the exposure to As can either be direct, through drinking contaminated groundwater or indirect, through consuming food irrigated with contaminated groundwater (Senanayake and Mukherji, 2014). The impacts of post-consumption are dependent on two parameters; frequency of exposure and dosage consumed. Acute toxicity leading to fatality has been reported as a result of consuming food or drink having high concentrations >70 mg of monomethylarsenous acid (MMA) or dimethyl arsenic acid (DMA) (Sharma and Sohn, 2009) where vomiting and excessive dehydration are the early symptoms after consumption. Impacts of chronic consumption are more significant in number and have been reported in larger demographic

volumes. The effects of low dose and higher frequency of exposure are prominent only after 2-10 years of consumption, where hypopigmentation (formation of white spots), hypertension, Blackfoot disease, diabetes, and respiratory complications develop over time. NRC-U.S. (1999) noted that "In utero and early childhood exposure has been linked to negative impacts on cognitive development and increased deaths in young adults". The intensity of exposure also depends on the general lifestyle and food consumption patterns. For example, in Bangladesh, an average adult eats 450g of rice contaminated with 0.11mg/kg As per day and 4 L of water contaminated with 10ppb resulting in exceeding the total daily dose limit of 130µg as determined by WHO (Brammer and Ravenscroft, 2009).

2.2 Groundwater Treatment technologies

The remediation of contaminated groundwater requires a complete understanding of the nature of the contaminants involved. A suitable treatment methodology should always be applied to contaminated groundwater to remediate it, ensuring public health safety and sustainability (Fienen and Arshad, 2016; USEPA, 2017). Treatment methodologies of groundwater can be divided into three categories (Wang and Mulligan, 2006);

• pump and treat technique: include technologies that target contaminants that are easily separable (by sedimentation or floatation), prone to volatilization and/or show affinity towards oppositely charged ions (Thiruvenkatachari et al., 2008; Odell, 2010),

• In-situ treatment system: application of specific microbes/chemicals that degrade contaminants within the subsurface, or by utilization of specialized plant species that adsorb specific pollutants,

removing them from suspension (Compernolle et al., 2012; Crittenden et al., 1997; Kao et al., 2008),

• By containment: installation of slurry-walls (physical barrier) that prevent further migration of contaminated plumes (Opdyke and Evans, 2005; Suzumura et al., 2000; Thiruvenkatachari et al., 2008).

2.2.1 Treatment Technologies for Arsenic Removal

Treatment systems that target heavy metals' removal include coagulation-flocculation, oxidation, membrane systems, ion exchange, and adsorption (Nicomel et al., 2015). As is effectively removed by most of these methodologies achieving 80-100% removal. Coagulation-Flocculation effectively removes 90% of As loading upon using alum and titanium (IV) Sulfate as the coagulant. However, the formation of a secondary composition of As-rich sludge limits the effectiveness of the large-scale application of this method. Oxidation is carried out solely to convert the miscible form of arsenite to arsenate, reducing the toxicity. In Membrane Technology, nano-filtration and reverse osmosis membrane systems demonstrated high (up to 85%) removal capabilities for arsenate, but oxidation of arsenite for effective removal prior to treatment is required. Ion-exchange is based on the principle of adsorption, where resins were used to adsorb As ions, achieving removal up to 85% (Oehmen et al., 2011; Pakzadeh and Batista, 2011). The adsorption process has a comparative advantage over other techniques used for As removal. Absorption can achieve high removal rates, has easy operational controls, is cheap, and has minimum secondary hazardous waste materials. Moreover, some adsorbents can be regenerated (Ali et al., 2014; Tangahu et al., 2011).Figure 3 demonstrates various treatment technologies that have been used for the remediation of arsenic in water.

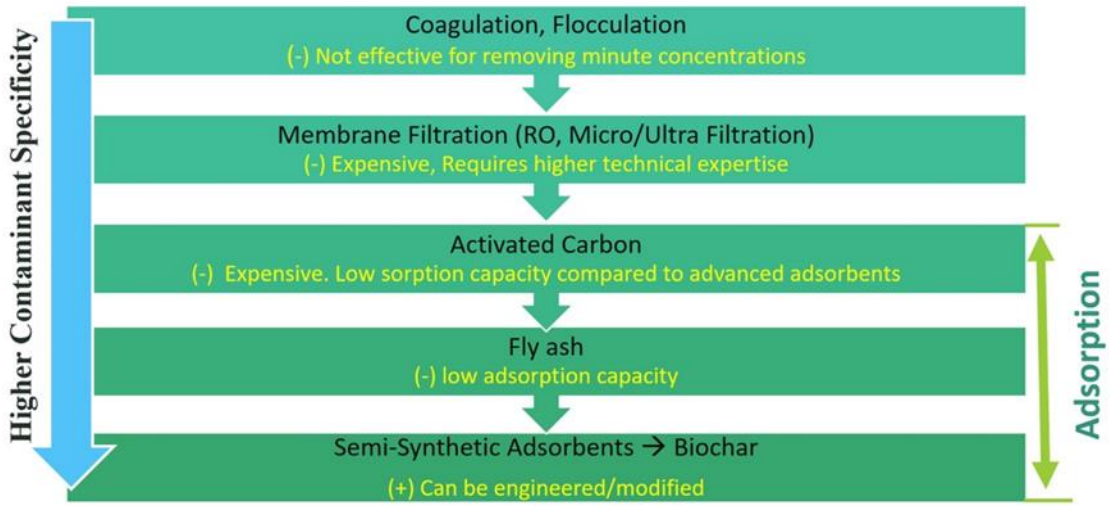


Figure 3 Trend of arsenic treatment technologies that have evolved as contaminant specific applications

2.3 Arsenic Removal by Adsorption

The adsorption process for decontamination of water involves adhesion of contaminants onto a sorbent (solid) surface, removing them from suspension. The adhesion is highly dependent on adsorbent surface properties and characteristics of the initial solution-mixture. The adsorbent's porous structure, where electrostatic attraction and/or Vander Waals forces allow immobilization and capture of the contaminants, is critical for effective decontamination. Adsorption of As is highly dependent on several experimental factors, including; the pH of the solution, presence of other cations (such as phosphate, copper, and silicate), particle size, oxidative state of As (III or V) in the mixture, contact time and adsorbent dosage. These experimental factors vary according to the type of surface functional groups and surface charges present on the adsorbent being used (Wen et al., 2020). The pH of the solution has been reported to be one of the key determining factors for As adsorption. For As (V), a high rate of adsorption is reported at pH lower than the point of zero charges (pzc) of the adsorbent. Due to the presence of positive charges on the adsorbent surface at lower pH range, that favors electrostatic interactions between negatively charged As (V) ions. Whereas As (III) has been reported to exists as non-ionic (H3AsO3) form at

pH <5 and therefore electrostatic attractions don't play a role until pH ≥ 9 of the solution resulting in more dominant As(III) species. Moreover, it is important to note that as pH increases the amount of hydroxyl ions (OH-) present in the solution also increases, competing for surface active sites with As species and hindering As sorption. Therefore, studies have reported surface complexation and ligand exchange as major adsorption processes for As (III) sorption instead of electrostatic attractions (Leng et al, 2019). Ionic radius of As (V) being smaller than As (III) further favors sorption of As(V) in a given adsorbent (Dong et al, 2020). On the other hand, the efficiency of adsorbents can be distinguished in terms of pore space, surface area, thermal stability, and ability to resist the formation of aggregate in suspension. Initially, increasing the dosage of adsorbent increases the sorption efficiency as vacant active sites are occupied. However, the sorption rate eventually plateaus once a certain dose of adsorbent is added in a given mixture, mainly due to the formation of monolayer of As species covering pore channels across the adsorbent (Yusof et al., 2020). Therefore, determining the optimal dosage remains an essential factor in experimental studies. Conventional adsorbents, such as activated carbon, fly ash, iron-based compounds (sulfides, oxides) have been reported as effective As sequesters achieving sorption capacity up to 150mg/g (Hao et al., 2018). Fly-ash in a batch-sorption experiment with initial pH of 7.0, was able to remove 95% of As(V) and 89% of As(III) with a dosage of 3.0g/L and relatively low As loading i.e. 50μg/L in 50 minutes (Ali et al., 2014). 0.4g of Iron-loaded activated carbon removed 97% of As (V) in 1hr from suspension having As loading 100 μg/L. Whereas utilization of activated carbon alone (without iron-loading) achieved 55% of As(V) removal, indicating co-precipitation with iron being the major removal mechanism (Asadullah et al., 2014).

Natural adsorbents made from various organics (egg shell, java plum seed, water chestnut shell, corn cob, tea waste and pomegranate peel) by grounding and sieving (<250μm), have also been

reported to achieve maximum removal of 87% of As(III) at pH 7 and 76% of As(V) at pH 4 in 2h with initial Asloading of 5mg/L (Shakoor et al., 2019).

However, the application of these adsorbents at a large scale involves their consistent use, generating a sustainability-conflict, as factors such as cost of production, relatively limited surface area, ease of recycling/reusing, and utilization of environmentally harsh chemicals limit the feasibility of their application (Sen et al., 2010; Shakoor et al., 2016). Semi-synthetic adsorbents, such as, biochar, made by pyrolysis of organic matter, have gained popularity as being highly porous and easily adjustable to favor the immobilization of specific contaminants (Ahmad et al., 2014). For a further thorough review of advanced adsorbents used for As removal, refer to (Amen et al., 2020; Giles et al., 2011; Lata & Samadder, 2016; Nicomel et al., 2015).

2.3.1 Biochar as an Adsorbent for the Removal of Arsenic

Utilizing plant-based organic feedstock (such as pinewood, oak wood, perilla leaf and others) or animal-based organics and subjecting the biomass to high temperatures ranging from 300-800^{o}C under the absence of oxygen, produces a porous, carbon-rich material (Xie et al., 2015) that is called biochar. The applications of biochar are multiple (Kalderis et al., 2018) and often include carbon sequestration, soil amendment to induce vegetative growth (Chen et al., 2010), and sorption of contaminants in soil, water, and wastewater (Kirmizakis et al., 2020).

Biochars can decontaminate heavy metals in soil systems and improve fertility (Park et al., 2011; Zhu et al., 2020). Park et al. (2011) showed that 1% of biochar made from chicken manure and green waste significantly reduced the bioavailability of heavy metals and increased the plant mass by 500%. Saifullah et al. (2018) determined biochars as positive sorption and treatment media for salt-affected soil environments, but the large-scale production and consistent supply is an issue that is yet to be solved. Persistent compounds such as perfluoroalkyl and polyfluoroalkyl (PFAs)

that are used as fire retardants were effectively adsorbed onto biochars (Zhi and Liu, 2018). Biochar made from corn stalk and co-precipitated with various cations forming layered double hydroxides (LDH) composites achieved arsenic sorption capacity of 15mg/g from red and calcareous soils (Gao et al., 2020). Biochar treated with iron was also effective in removing arsenic and other metalloids from farms and industrial soils where 30% of removal was achieved within 24 hours of application (Wan et al., 2020). Likewise, most pot-experiments with different plants and the application of biochar amended soil have shown similar results i.e. low arsenic migration in soil followed by lower accumulation of arsenic in the plant due to adsorption of arsenic onto biochar surface (Vithanage et al., 2017).

An activation process can be applied to enhance the biochar's efficiency (porosity and adhesion potential) by subjecting the biochar to high temperatures in the presence of chemicals (H3PO4, KOH) and/or gases (CO2, steam) (Braghiroli et al., 2018). Contaminant removals up to 100% may be achieved based on electrostatic attractions (Wang et al., 2015a). The activated biochar is a sustainable alternative of activated carbon that is widely used for various environmental applications (Tan et al., 2017).

Specifically, activated biochars carry a surface charge (positive or negative) that can be altered by varying the pH of the solution. At higher pH, the biochar surface is reported to exhibit negative charges. Repulsive forces between negatively charged As (AsO_3^-) ions and biochar result in low sorption rates. Only weak Vander Waal's forces exist that are canceled out by higher repulsive forces of the same charge (negative-negative) interactions. Whereas, at lower pH, the positively charged surface of biochar favors the sorption of As oxyanions. Thus, most experiments have stated higher sorption rates at slightly lower pH 5-6.5 for the removal of As(III) and As(V) due to the attraction of As oxyanions onto positively charged biochar surface (Li et al., 2013; Niazi et

al., 2018; Wang et al., 2015b). It is also observed that the biochar produced at the highest temperature had the highest porosity and surface area (Song et al., 2019), indicating the potential of possibilities for designing and enhancing its properties (Alhashimi and Aktas, 2017). Other experimental aspects such as As-adsorption capacities of various feedstock used for biochar production and models (kinetic and thermal) used for determining the reaction rates and controlling parameters are reviewed by Vithanage et al. (2017). It is worth noting that higher As loadings (>50 mg/l) tend to precipitate on the biochar surface at a very early stage. Such high concentrations are too high compared to the concentrations found in groundwater. Therefore, opting for initial concentrations for optimization studies should be done considering the range of concentrations that are to be tackled in real-life applications.

2.3.2 Biochar Feedstock and Production Conditions

Generally, the feedstock and the production parameters used, control the characteristics of the produced biochar (Zhao et al., 2013). It is shown that higher temperatures produce biochars that are more suitable for the adsorption of organics and lower temperatures, products are good for the sorption of inorganic contaminants (Sun et al., 2014; Zhou et al., 2013). Biochar yield depends on temperature, residence time, and the heating rate at which the pyrolysis is carried out (Tripathi et al, 2016). A higher yield is achieved at lower temperatures, whereas greater porosity is achieved at higher temperatures. A wide range of organic feedstock have experimented with, from sewage sludge, crop residues to wood chips, all demonstrating distinctive morphology and characteristics of the respective product (Pongkua et al., 2018; Racek et al., 2019; Zhao et al., 2013). Lignocellulose based organic wastes produce suitable biochars for decontaminating toxic elements from aqueous solutions (Chemerys and Baltrėnaitė, 2018). Attempts have also been made to evaluate chars obtained from a range of plastics, such as polypropylene-PP, polyethylene

terephthalate-PT and high-density polyethylene-HDPE (Jamradloedluk and Lertsatitthanakorn, 2014). However, sizes of pores formed to lie in mesoscale, which is suitable for immobilizing larger contaminants such as inorganics (Anuar Sharuddin et al, 2016), restricting large scale application as an adsorbent.

Characterizing an adsorbent is a fundamental step before its application that illustrates the physical and chemical profile of the adsorbent and its probable performance in immobilizing contaminants. Adsorbents are thus distinguished based on their structure, surface area, and ability to act as a medium for adhesion of target contaminants. A variety of analytical techniques can be used to identify these characteristics. Elucidating the morphology and the functional groups involves the use of scanning electron microscope-SEM and Fourier-transform infrared spectroscopy-FTIR analysis (Choudhary et al., 2019). Brunauer-Emmett-Teller (BET) surface area analysis determines the surface area available for adsorption indicating the capability to deal with high contaminant loadings. The characterization of biochar involves assessing the ratio of moisture content, fixed carbon, volatile matter, and ash content in the final product. These ratios tend to vary as per the operational parameters and affect the effective yield of biochar that is obtained (Leng et al., 2019). Biochar stability is also an important parameter that examines biochar's ability to prevent sequestered contaminants from leaching out/ desorbing. International Biochar Initiative (IBI) has listed techniques and variables to determine biochar stability (Budai et al., 2013). Molar ratios (O/C, N/C, and H/C), along with the characterization results, outlines the characteristics of biochar (Chemerys and Baltrėnaitė, 2018).

2.3.3 Modification to Biochar to Enhance Sorption

Biochar adsorption can also be improved significantly during, or even after, the original production. Wang et al. (2016) showed that higher sorption capacity (6.52 g/kg) can be achieved

by post-pyrolysis modification of Ni/Mn than to pre-pyrolysis modification (0.549 g/kg). Depending on the target contaminant, chemical, physical, steam activation, gas purging, and impregnation of metals or their oxides are carried out to enhance biochar sorption (Arevalo-Gallegos et al., 2017; Rajapaksha et al., 2016). Chemical modification involves the use of acids, bases and/or strong oxidants such as KMnO4 and H2O2 aimed to alter the functional groups on the surface of biochar. Organic solvents have also been used to modify the surface functional groups. Metal impregnation is another chemical modification option that is targeted to remove inorganics and anions (Rajapaksha et al., 2016). Chitosan (Zhou et al., 2013) and a wide range of metals (Mg, Mn, Fe, Al) (Akgül et al, 2019) have proven as highly effective modifications for removal of high inorganic loadings. Most studies have conducted impregnation of iron-based composites due to the specific reaction of As with iron. Despite the relatively low surface area of some biochars, iron modification has reported achieving significant increase in removal rates for As (Wu et al, 2018). A comparison of other biochar modifications for arsenite removal has been evaluated (Xia et al., 2016), where the same biochar with ZnCl2 achieved the highest removal rates, followed by NaOH, FeCl3, AlCl3, and KOH, respectively.

Physical modification can also be achieved by introducing steam or air to produce a more porous structure, often carried out with NaOH or KOH for activating biochar surfaces, discussed previously. A more widely used approach involves the magnetic modification of biochar which is mainly carried out for two reasons; one, to enhance the sorption of anionic contaminants, and second, to facilitate the recollection of contaminant-saturated biochar from treatment (Ahmed et al., 2016; Rajapaksha et al., 2016). Magnetic characteristics are developed by iron-enriched modifications, efficiently adsorbing a wide scale of heavy metals and other highly persistent chemicals such as PFAs (Silvani et al., 2019).

CHAPTER 3

Research Methodology

The research was conducted in two distinctive parts.

Part-1 involved Batch-sorption experiments and optimization study for arsenic removal using biochar in suspension.

Part-2 comprised of SIP setup and corresponding analysis for monitoring. The methodology shall further be elaborated for each part.

3.1 Part-1: Batch Sorption study

3.1.1 Biochar Preparation

Dried Date-palm leaves (DPL) were collected from King Fahd Park in Khobar, KSA and used as Feedstock. The leaves were washed with water and dried under sun for one day. Upon drying the leaves were cut to 1-2 inches and subjected to pyrolysis. For pyrolysis, DPLs were transferred into iron column-rods and compacted using steel rod as an effort to minimize residual oxygen within the column. The filled rods were then placed in muffle-furnace at desired temperatures for 4hrs. The muffle-furnace was auto-programmed to stop after 4hrs. Once the furnace's internal temperature reached close to room temperature, the biochar was extracted from iron rods, subjected to grounding by means of pestle and mortar. The grounded biochar was then sieved, and the particle size range of $\leq 300\mu m$ was utilized to conduct further experiments.

3.1.2 Modification of Biochar

The modification was conducted after pyrolysis. Biochar was mixed with Fe $(NO_3)_3$ (High purity Lab grade) and Deionized water (Milli-Q) in the ratio 10g: 7g: 250ml.The pH of mixture was raised to 11 using 0.1M NaOH. The mixture was stirred overnight on a hot-plate at 40^{O}C. Multiple washing rounds were then conducted using DI water until the pH reached to neutral(7). The remaining liquid was decanted, and biochar was kept for oven drying at 105^{O}C.

3.1.3 Characterization of Biochar

Proximate analysis of biochar was conducted by employing ASTMD 1762-84-1990 method. Further determination of Total Nitrogen (N) and Hydrogen (H) content of both raw and modified biochar was carried out using Elemental analyzer (PerkinElmer EA - 2400). Surface morphology of both types of biochar was determined using SEM imagery (Tescan Lyra-3). Surface Functional groups in raw and modified biochar for both pre and post-sorption analysis were identified using FTIR using IR spectrophotometer (Smart iTR NICOLET iS10) with attenuated total transmittance within wavelength of 4000-500cm^{-1}. Crystallographic structure was determined using XRD (Ultima IV) whereby reflection data was collected in the form of a survey scan by applying PANalytical vertical diffractometer, copper Kα radiation. The scan was conducted from 5-80 degrees (2θ) using 0.03 degree step size. X-ray generator setting of 40kV and 40mA were applied. Dry powder was used in carrying out all characterization analysis.

3.1.4 Reagents Used for the Preparation of Chemical Composites

Arsenic standard stock was prepared using lab-grade arsenic standard 1000µg/ml (Ultra SCIENTIFIC) and 2-3 drops of 0.1N HNO_3 (ACS Reagent Grade, 70%, Ricca Chemical) were added to prevent any reaction with container walls.Iron nitrate (Fisher Chemical, 98% purity) was for modification. HCl (Fisher Chemical 36.5 to 38%) and NaOH (RPI pellets) were used for pH adjustments. De-ionized water (Milli-Q ultrapure Type 1 water) was used for preparing stock solutions.

3.1.5 Batch Sorption Experiment

Experiments were conducted in 50ml glass vessels. 0.2g of Biochar dosage was used in all analysis with varying Arsenic concentrations. Experiments were conducted on an automatic shaker at 200 rpm. After reaching equilibrium, the mixture was allowed to settle and 2ml of sample was collected using pipette for conducting further analysis. These samples were analyzed by using ICP-OES (Plasma Quant 9000; Analytik Jena GmbH) following EPA method 1632. Figure 4 shows the ongoing adsorption experiment being on an automatic shaker.

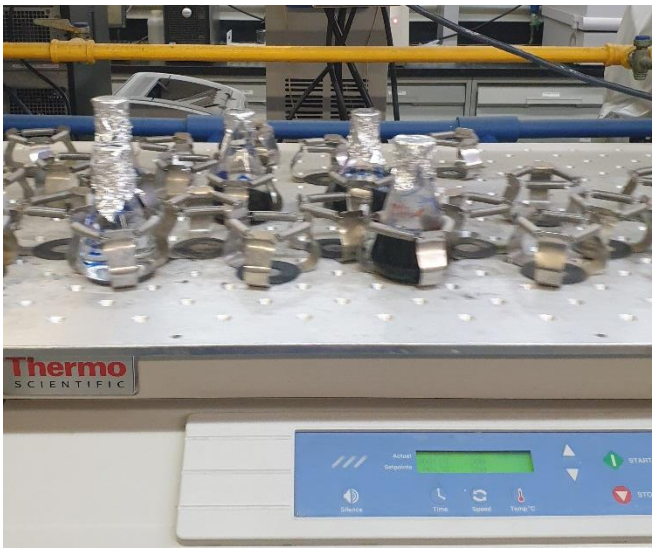


Figure 4 ongoing batch sorption experiment on shaker (Thermo Scientific)

3.1.6 Adsorption Kinetics

To evaluate rate of reaction of both pristine and modified biochar, 0.2g of adsorbent dosage was used, reaction was conducted at same initial concentration, pH, temperature and pressure. After every 30 min interval, 2ml of samples were extracted for 2hrs. The adsorbent and solute mixture was then kept for 12hrs and the final sample was extracted to ensure equilibrium concentration has been achieved. Statistical analyses were carried out employing Pseudo 1st and 2nd Order reactions to analyze the diffusion rate and mechanism of adsorption.

The following equation were used for evaluating the Kinetics of sorption:

$$Q_t = Q_e(1 - e^{-k1t}) \quad (4)$$

$$\frac{t}{q} = \frac{1}{K_2 qe^2} + \frac{t}{qe} \quad (5)$$

Where Eq.1 is for Pseudo 1st Order and Eq.2 determines Pseudo 2nd Order reactions. Q_e is adsorbed quantity (mg/g) and Q_t is for concentration at equilibrium (mg/l). K1 is constant for pseudo 1sr order. K_2 is constant for pseudo 2nd order.

3.1.7 Evaluation of Optimal pH for Adsorption

In order to determine the favorable pH for adsorption of Arsenic, 0.2g of biochar was added in 50ml galss vessel keeping the initial concentration of As, stirring rate, temperature constant. Initial pH of As solute mixture (without adding biochar) was adjusted, ranging from 3-11. The samples were collected for As analysis once the equilibrium time was achieved and mixture settled. Graph of pH vs Removal percentage (%) was plotted and the optimum pH values were determined.

3.1.8 Effect of Stirring Rate on Adsorption Efficiency

Determining the effect of stirring rate on the adsorption efficiency can help in further optimizing the experimental parameters. The evaluation was done by placing duplicate samples on shaker at various shaking speeds (100,150,200,250) rpms for 2hrs. Once the mixture settled, 4 ml of samples were extracted for chemical analysis.

3.1.9 Adsorption Isotherms and Dosage Response

Arsenic loading were used (0.25ppm- 30ppm). 0.2g of biochar was used in 50ml glass vessel and other factors such as stirring rate, pH and temperature were kept constant. After 2hrs of shaking, the mixture was allowed to settle and 4ml of solution was extracted using pipette and these samples were then analyzed for residual concentration of arsenic. Isotherm models were then applied and most suitable model that depicts the reaction mechanism was determined by comparing the R^2 (regression) values from each model. Langmuir, Freundlich and Temkin models were applied and the following linear form of equations were used:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

$$\log qe = \frac{1}{n}\log Ce + \log Kf \quad (4)$$

$$qe = \frac{RT}{b} lnKt + \frac{RT}{b} lnCe \quad (5)$$

Eq 3, 4 and 5 are for Langmuir, Freundlich and Temkin models, respectively. Where Ce is the concentration at equilibrium, qm is and K_L are reaction constants for Langmuir. Kf is Freundlich

constant. R is the universal gas constant 8.314 J $mol^{-1}K^{-1}$, Kt is Temkin constant, T is the absolute temperature in Kelvin and b is related adsorption heat.

Moreover, Separation factor for Langmuir was calculated using the equation below for determining its favorability.

$$R_l = \frac{1}{1+K_L C_i} \quad (6)$$

where C_i is the initial concentration of the contaminant.

3.2 Part-2: SIP analysis

3.2.1 Instrument Setup and Configuration

PSIP has the capability of simultaneously measuring more than one column, as it can be delivered with multiple, independent current channels (shown in Figs. 5). Connections are made following the user guide from the manufacturer (Ontash & Ermac) and based on the block diagram as depicted in Figure 6.

Figure 5 Portable Field/Lab Spectral Induced Polarization (PSIP) instrument

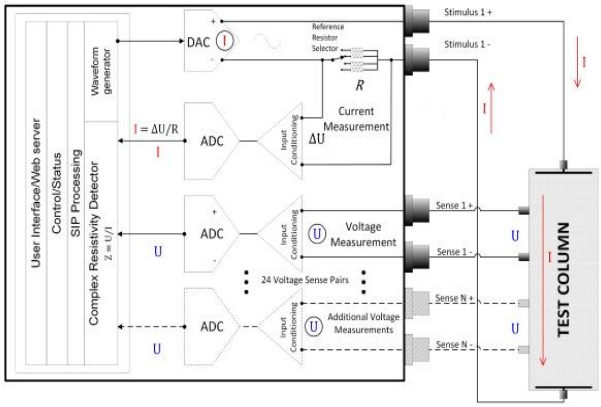


Figure 6 Block diagram of the laboratory Spectral Induced Polarization

3.2.2 Column Setup

Prior to the start of experiments, the electrode wires (made of silver) are soaked in a solution of 5% Hypochlorite for 2-3 hrs and color change from silver to black/purple is observed. Chloriding the wires reduces the reactivity that may result from silver electrodes. Columns made of polyamide were prepared according to our earlier work (Kirmizakis et al., 2020). One column was filled with sand and used as a reference. The other two were filled with biochar amended sand at 5% and 10% wt biochar, respectively (Figure 7). To ensure complete saturation of the columns and avoid flow

channeling, the solutions were pumped from the bottom to the top of the columns at a constant flow of 0.16 ml.min^{-1} for 16 h. SIP measurements were obtained continuously in the frequency range of 0.01-10 kHz, collecting five measurements per logarithmic decade. Eluates from the outflow were obtained at specific time intervals and the residual As concentration was determined by using ICP-OES (Plasma Quant 9000). All experiments were performed in a controlled laboratory environment, at a temperature of 23.5 ±2°C. Figure 7 a) and b) illustrate the column setup.

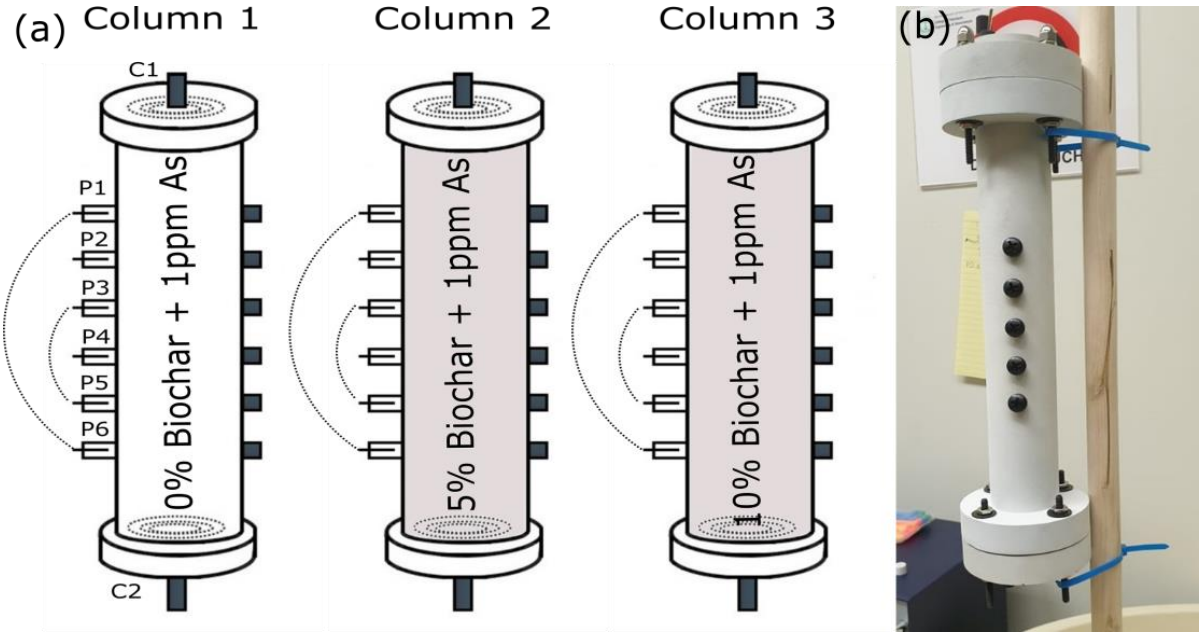


Figure 7 a) Schematic presentation of the experimental set-up, b) image of one column.

3.2.3 Determination of Geometric Factor

Geometric factor (G.F) for each column is required to have greater precision in experimental findings. Accurate GF is needed for accuracte estimation of resistivity based on the measured resistance This can be achieved by the graph of the Fluid Conductivity (μS/cm) VS conductance (μS). The conductance in μS is resulted from:

$$Conductance = \frac{1}{Resistance} \cdot 1.000.000:$$

Taking the inverse of the slope (1/slope) of the graph and replacing in the equation that it follows we can calculate the real fluid conductivity in μS/cm for all measurements that we have to do with the under-study fluid:

$$Fluid\ conductivity = \frac{1}{Resistance} \cdot K(geometric\ factor) \cdot 1.000.000$$

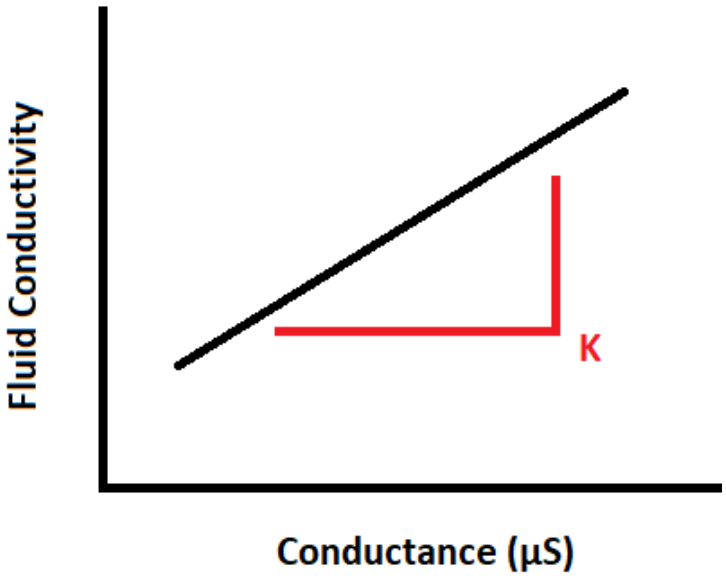


Figure 8 typical graph for measuring geometric factor *K*.

In order to obtain accurate GF estimations, three KCl solutions of known concentration (70 μS/cm, 300 μS/cm, 900 μS/cm) should be prepared using the ASTM D1125-95 method to calculate the exact concentration of the solutions. Through the proposed method, which defines precisely the molarity which must have certain standard solutions, the amount of KCl required for the preparation of the standard conductivity solutions can be estimated as shown in Table 1.

Table 1 Prepared solutions and relative conductivity

KCl concentration		**Conductivity**		**Tolerance at 25°C**
0.00047 M	→	16.75μS/cm	→	± 5 μS/cm
0.00200 M	→	280.6μS/cm	→	± 12 μS/cm
0.00610 M	→	622.4 μS/cm	→	± 0.11 mS/cm

These solutions were analyzed in each column and the geometric factor for each column was calculated. The potential electrodes were connected as shown in the schematic diagram in Figure 9 below.

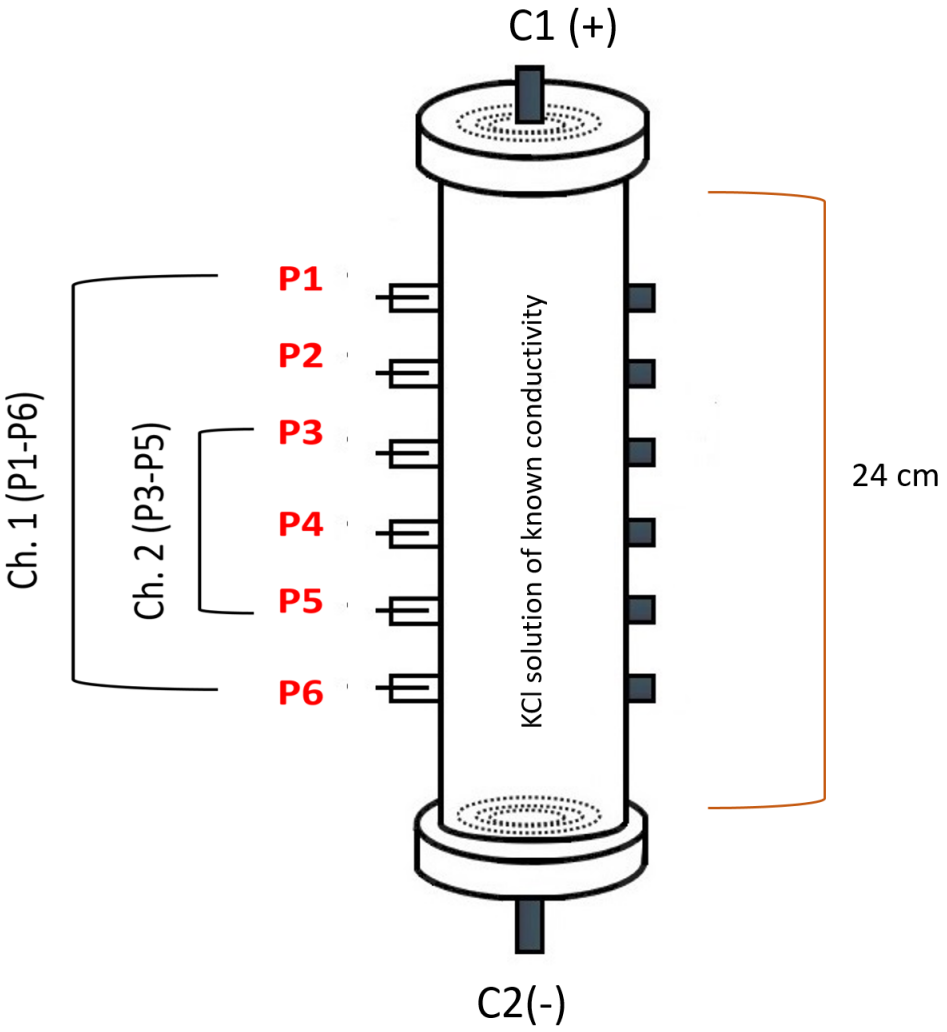


Figure 9 Column setup and potential electrode connections

3.2.4 Preliminary Assessment of Column Dynamics

The objectives in this stage was :

1. To determine the flow rate
2. The time required to saturate the column
3. Evaluate the extent to which buffer media adsorbs arsenic
4. Determine the sensitivity of SIP towards 1ppm and 5ppm solution of arsenic

The columns were washed and dried prior to use. Local sand was used as porous media to fill the column. Sand was collected from a remote dune in Riyadh-Dammam road. This sand was then acid washed for removing any impurities present, using HNO_3 followed by HCl, dried under the sun and sieved. The size of sand particles used to fill the columns ranged from 280 µm to 160 µm. To check for possible leakages a pure solution of salt having predetermined conductivity (KCl in this study) was used to saturate the column before starting the SIP measurements. The time required to fully saturate the column was noted. The SIP measurement run was then initiated along with the injection of contaminant (arsenic) solution.

3.2.5 Biochar Addition and SIP Response

This was the key stage where the effect of biochar adsorption on SIP data was analyzed. Two columns were setup as shown in the previous section. The volume required to fill the potential electrode was determined by measuring the diameter and height of the column as shown in Table 2. 10% and 5% of biochar by volume (using a measuring cylinder) was added and mixed thoroughly with sand (background porous media).

Table 2 Column dimension

Total volume of the column $V=\pi r^2 h$ (cm^3)	**The volume of measurement zone (potential electrodes) (cm^3)**	**Biochar : sand ratio (ml)**
272.19	147.43	7.4:140 (5%Fe-BC500)
		14.8:132.6 (10%Fe-BC500)

The data acquisition parameters were adjusted according to the requirement based on the sensitivity required. SIP acquisition parameters in each stage were employed as as shown in Table 3 below.

Table 3 SIP data aquisition parameters

Stage#	Frequency range (Hz)	Loop count	Resistivity (ohm)	Number of steps
1	1000-0.1	1	1000	21
2	10,000-0.001	5	100	41
3	10,000-0.01	30	100	36

CHAPTER 4

Results and Discussion

4.1 Results and Discussion for batch Sorption Study

4.1.1 Biochar Characterization

Three biochar formations were initially analyzed. Biochar produced at 300 (BC-300), 550 (BC-550) and 800°C (BC-800). Preliminary experiments conducted using all three biochar along with Raw Date-Palm Leaves (DPL) and their potential to adsorb As was found to be very marginal as illustrated in the graph below (Figure 10).

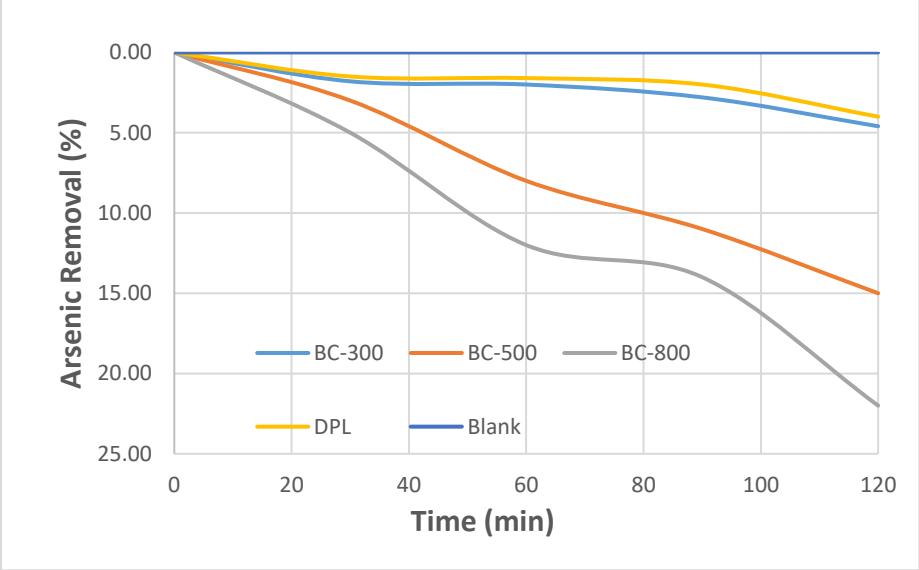


Figure 10 Evaluation of arsenic removal capacities of Date-palm leaves (DPL) and various biochar formulations (raw-biochar)

BC-500 and BC-800 demonstrated the ability to adsorb As by 15% and 22%, respectively. This can be expected due to greater porous structure formed in biochar produced at higher temperatures, as reviewed in by other similar research studies (Xu et al., 2020). These two biochars were then chosen for further analysis of their characteristics by conducting the proximate analysis (see Table 4 below).

Table 4 Proximate Analysis of Raw-DPL and biochar produced at 500 and 800-degree Celcius

Sample	**%Yield**	**%Ash Content**	**% Carbon**	**% Hydrogen**	**% Nitrogen**	**% Sulfur**	**%Oxygen**
Raw-DPL	-	8	48.97	5.28	2.89	0.56	31.16
BC 550	79	11.7	50.19	2.80	1.80	0.26	33.51
BC 800	48	26	55.40	0.83	1.12	0.0	30.95

The ash content and carbon percentage increase as pyrolysis temperatures are raised. Similar trend is found in other studies that have produced biochar from date-palm waste and generally other studies involving the production of biochar (Zhao et al., 2013). However, it is important to highlight that the yield obtained in this study was more significant than that reported in most studies. For example (Usman et al., 2016) reported 32.38% of yield at 500°C and 27.4% at 800°C. This can be due to the additional compaction of feedstock that was carried out in iron-rods, eliminating maximum voids that can contribute in oxidation and subsequent loss of yield obtained. On the contrary, the percentage of carbon is lower in this study than the other study involving analysis of biochar obtained from date-palm waste. It is also important to note that only date-palm leaves/fronds were used as feedstock in this study, whereas a mixture of date-palm waste was used to produce biochar In other studies.

4.1.2 Removal Using Modified Biochar

Fe-modified biochar (BC550 and BC800) demonstrated significant sorption affinity towards arsenic. The comparison with pristine biochar and modified biochar can be clearly observed in]Figure 11below.

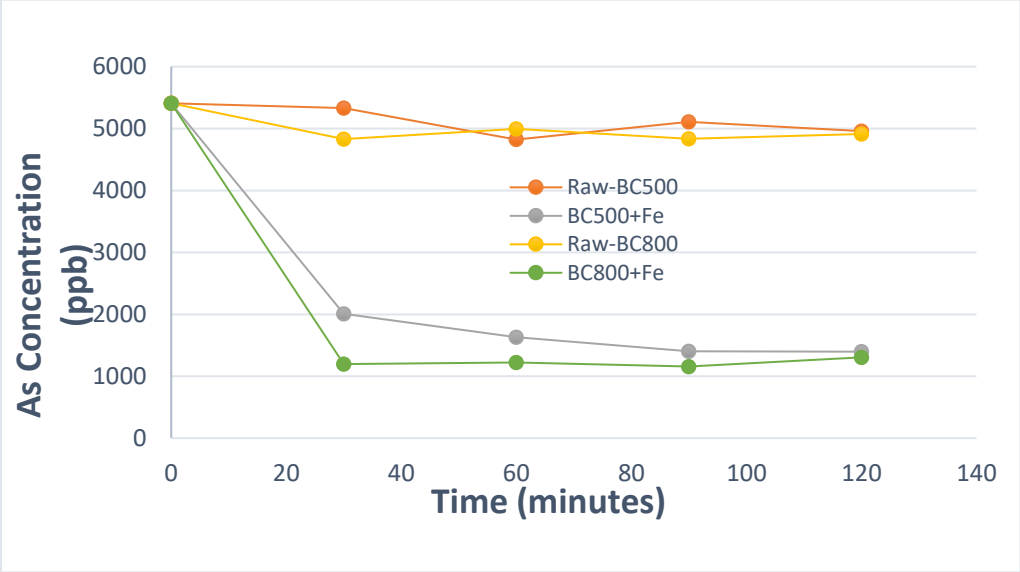


Figure 11 Arsenic sorption of raw and Iron-modified biochar produced at 550° and 800° C.

This indicates that chemical modification dominates adsorption affinity of arsenic. Fe-BC800 achieved sorption capacity in less time due to greater porosity, although no notable difference in final arsenic removal was observed. Hence at equilibrium both biochar (Fe-BC800 and Fe-BC500) formulations removed 76% of arsenic in 2hrs.It was determined that equilibrium time is 2hrs and following experiments for optimizing the parameters for effective sorption shall be conducted accordingly. Optimization analysis was conducted on iron-modified biochar produced at 500°C due to greater yield and approximately same sorption capacity as compared to biochar produced at 800°C. The interactions between As and Fe-functionalized carbonaceous materials have been extensively studied and reported in the literature (Benis et al., 2020; Sizmur et al., 2017). A two-

step process of sorption of As(V) oxyanion on iron oxide hydroxide based on the formation of monodentate and bidentate complexes has been proposed, however pH-dependent, electrostatic interactions such as H-bonding also play a role in the adsorption process.The results of employing pseudo-first-order and pseudo-second-order are illustrated in Table (5).

Table 5 Parameters of Adsorption Isotherms

Adsorbent	Langmuir			Freundlich			Temkin		
	Qm(mg/l)	**K_L (Lg^{-1})**	**R^2**	**n**	**K_F ($mg^{1-n}\ g^{-1}\ L^n$)**	**(R^2**	**b**	**K_T**	**R^2**
Fe-BC500	6.793	0.55	0.9437	14.29	0.448	0.9609	4958.23	9.38	0.8605

4.1.3 Effect of initial pH on adsorption

The pH of solution before the introduction of adsorbent plays a crucial role in determining the adsorption efficiency. Variation in pH influences the presence of surface charge on the adsorbent that determines the degree of electrostatic attraction favoring adoption. Figure 12 below presents the % removal of As at various pH solution levels covering the ranges acidic, neutral and basic.

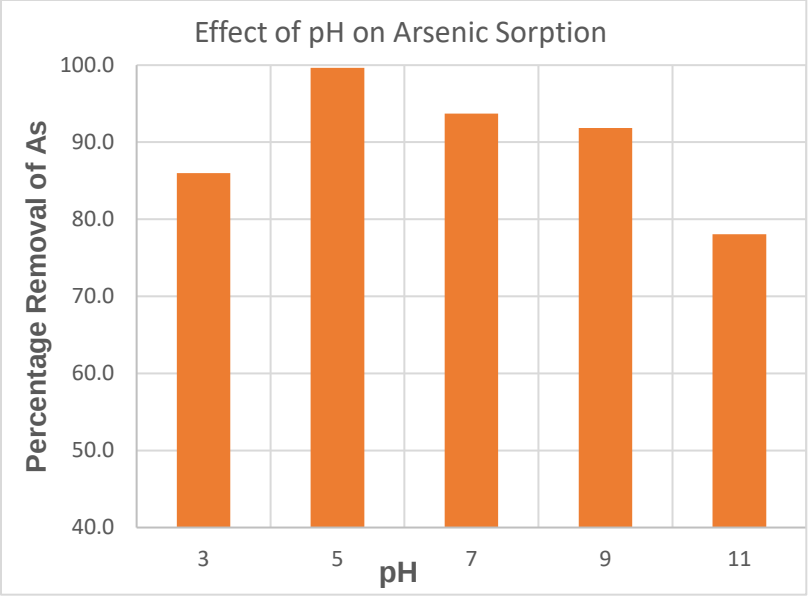


Figure 12 Effect of pH on As sorption

The optimal pH range for arsenic sorption is between 5 and 9. Beyond this range, the efficiency drops below 90%. Similar results have been reported in other research studies where the higher pH (>11) significantly reduces As sorption efficiency due to the domination of OH^- ions that compete with As ions and lower the probability of As binding to surface active sites. At pH 5, 98% of arsenic was removed and further experiments for determining adsorption isotherms were conducted, adjusting the initial pH to 5.

4.1.4 Adsorbent Dosage Response

Adsorption is favored by the number of active surfaces that is available on the adsorbent. In ideal theory, the amount of adsorbent added shall be proportional to the removal of contaminant achieved. However, as seen in Figure (13), from 0.1g to 0.2g the removal efficiency increases rapidly, become stable from 0.2g to 0.6g and a slight increase can be seen upon every 0.2g that is added thereafter. Considering the economical use of biochar, 0.2g/50ml or 4g/L was selected as the optimal dosage for adsorption experiments.

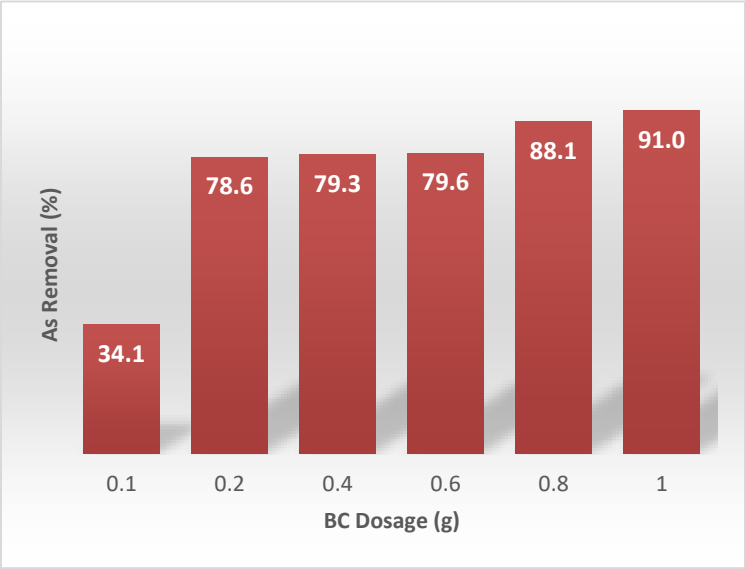


Figure 13 Effect of Biochar dosage on % Arsenic removal

4.1.5 Stirring Rate

Stirring rate ≤100 rpms was insufficient to achieve effective adsorption, whereas increasing the stirring rate from 200-250 had no significant effect in achieving greater removal. It is also noteworthy that most experiments are conducted ≥150rpms as per the literature (Kuśmierek, K., Świątkowski, A, 2015) reviewed for this study. Higher stirring rates increase the frequency of contact of sorbate-adsorbent but reduce the contact time that may be required to achieve the sorption. It is also reported that large-scale variations in stirring rates >250rpms do not affect the

removal efficiency of As sorption (Luengo et al., 2011). Results from the effect of stirring rate on efficiency of arsenic removal are shown in the graph below (Figure 14).

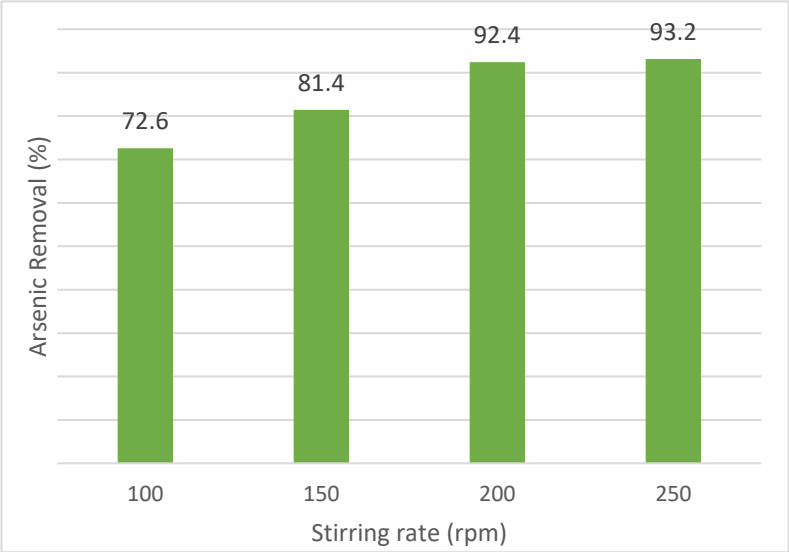


Figure 14 Effect of stirring rate

4.1.6 Adsorption Kinetics

Adsorption of arsenic onto biochar can be best described with a pseudo-second-order model for both adsorbents (Fe-BC500 and Fe-BC800) (Table 6). Therefore, it is inferred that sorption of As is favored by chemisorption on the BC active sites. It can be further interpreted that the rate of sorption with Fe-BC800 is faster initially but the sorption capacities of both adsorbents are the same. These results are similar to other studies that involve iron-modified adsorbents for adsorbing As (Lin et al, 2017).

Table 6 Adsorption Kinetics

Adsorbent	Pseudo 1st Order Parameters			Pseudo 2nd Order Parameters		
	K_1	Qe (mg/g)	R^2	K_2	Qe (mg/g)	R^2
Fe-BC 500	0.0107	4.0205	0.8082	$0.8x10^{-5}$	4.13	0.9657
Fe-BC 800	0.0112	4.14	0.8542	$0.1x10^{-3}$	4.14	0.9657

4.1.7 Adsorption Isotherms

Evaluation and determination of the behavior of adsorbent and adsorbate, isotherm models were employed. 0.2g of Fe-Modified BC500 was added to solutions of various As loadings ranging from 0.25ppm to 30ppm. Three models were applied and the relevancy to the experimental results was examined. Isotherms illustrated that increasing the initial concentration of As results in greater adsorption capacity.

Freundlich model best described the mechanism as it has the highest R^2 (=0.9609) and very similar trend with the actual values obtained from experiments.(see Figue 15 below). Freundlich model suggests that As adsorption is favored by chemical interactions that take place on multilayers (heterogeneous structure). Whereas Langmuir suggests that adsorption is taking place on a homogeneous surface (monolayer adsorption). Further evaluation of separation factor R_L =0.645 indicates that sorption is a favorable process. Typically, if the R_L value is <1 the sorption is favorable whereas in case of R_L>1 sorption is unfavorable. The R^2 value for Temkin were the

lowest indicating that the model is unsuitable for determining the sorption mechanism as shown in Figure 15 below.

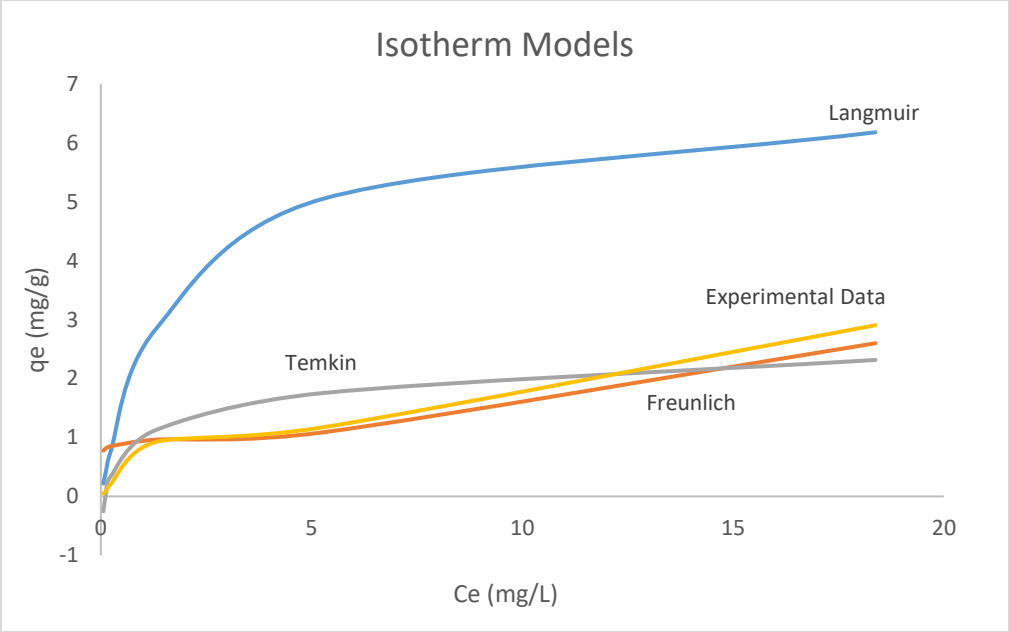


Figure 15 Fe-BC500 Adsorption Isotherm models and experimental results

Comparison of actual experimental data further confirmed that Freundlich model best describes the sorption mechanism. On the contrary, Langmuir model's sorption capacity is too high from the actual values, validating that Langmuir model does not define the sorption mechanism that is taking place.

4.1.8 FTIR analysis

The FTIR spectra of Raw, Fe-BC (before sorption) and Fe-BC(after sorption) show almost same similar wavenumbers. Peaks obtained at wave numbers 700-800 cm^{-1} indicate vibrations due to Fe-O. Iron-modified BC indicate different functional groups that are otherwise not observed in raw-BC. Various peaks appearing at wavenumbers 1050 to 1300 cm^{-1} correspond to C=O and C-O peaks which are related to carboxyl functional groups. Further consideration of transmittance of these functional groups indicate that modification has enhanced the intensity of pre-existing functional groups which are now more "active" and have the tendency to contribute in adsorption. Peaks observed at wavenumbers 1500-1350 indicate change of surface functional groups after sorption. Peak around 3000 cm^{-1} is attributed to the addition of –OH groups after modification. Figure 16 summarizes the variation in surface functional groups with varying peaks at same wavenumbers.

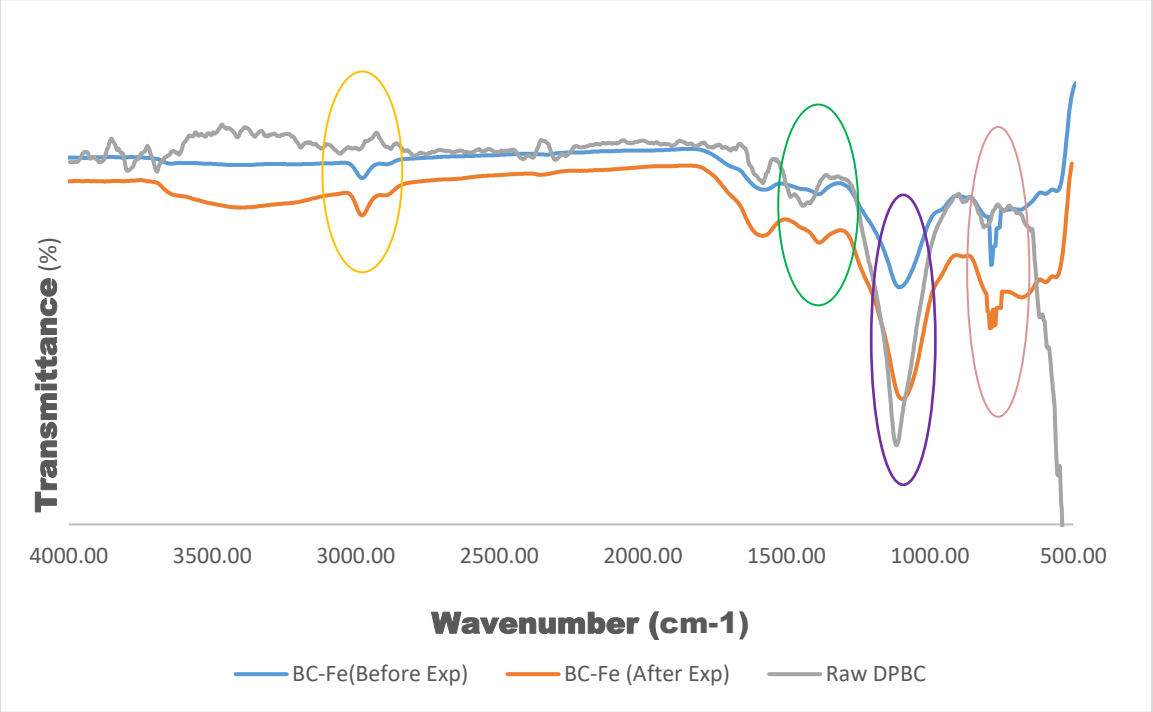


Figure 16 FTIR spectra

4.1.9 XRD analysis

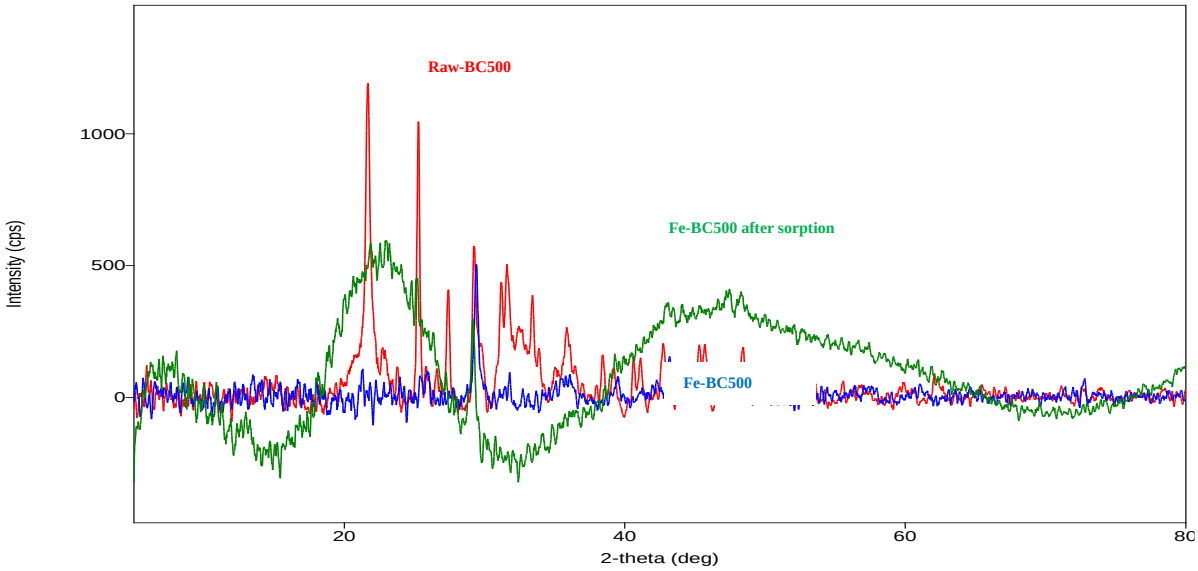


Figure 17 XRD spectra of Raw-BC and Fe-BC before and after sorption

The X-ray diffractometer (Figure 17 above) of powdered biochar samples indicates crystallographic structure for both raw biochar and Fe-modified biochar. Post-adsorption results indicate that the structure is amorphous as the biochar surface is covered by forming a smooth layer. Peaks for raw biochar are intense and are associated with $CaCO_3$ as reported by other research involving a more thorough review of XRD spectra of biochar form date-palm waste (Usman et al., 2016). Peaks for Fe-modified biochar prior to sorption show less intense and broader reflection, which indicates disordered stacking of layers. Other studies related to biochar modification with Fe(III) describe this staking as an indication of intercalation with monomeric and polymeric Fe(III) species (Luengo et al., 2011). It can be assumed that the peak at 35 2-theta indicates the formation of Fe(III) hydroxide coating the surface. The shifting of peaks and subsequent appearance at different degrees illustrates change in crystal structure due to the modification with Fe(III) composites.

4.1.10 SEM Imaging

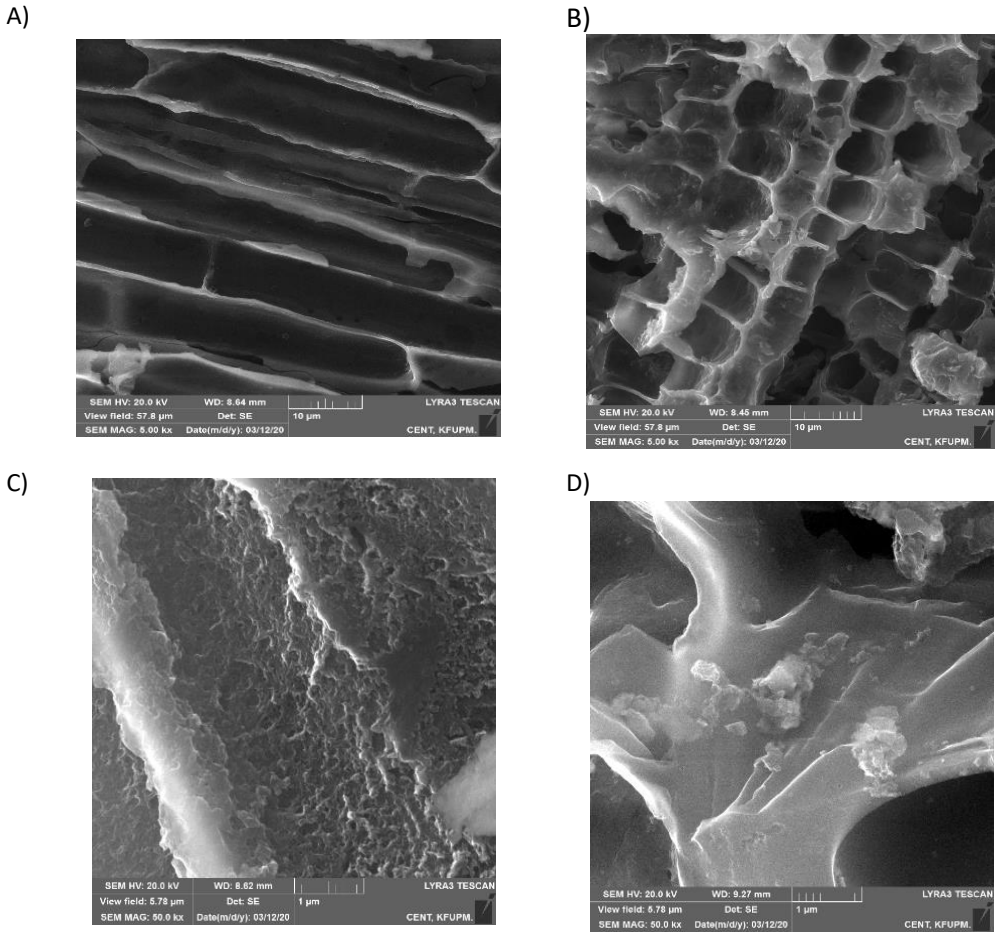


Figure 18 SEM Images of A)Raw-BC500 B) Raw-BC800 C) Fe-BC500 before adsorption and D)Fe-BC500 after sorption

Images obtained from scanning electron microscope (as shown in Figure 18 above) indicate the porous structure for both biochar as observed in all images in Figure16. Images A and B indicate uniform morphology, horizontally stretched pores for BC-500 and heterogeneous porous structure but greater number of pores per area for BC-800. This trend is generally observed in other studies with biochar where biochar produced at higher temperatures have more number of pores (Pongkua et al, 2018; Racek et al, 2019; Zhao et al, 2013). Image of Fe-BC500 indicate formation of iron layer on the pores followed rough surface that further increases the surface area for adsorption. Post adsorption image of Fe-BC500 shows covering of the surface in a form of smooth layer that

may inhibit adsorption, as active sites are saturated. The structure post adsorption is amorphous and morphologically less favorable for further adsorption. Similar conclusion was also drawn by observing XRD spectra in Figure16. A summary of As removal capacity is presented in Table 7 below:

4.2 Results from SIP analysis

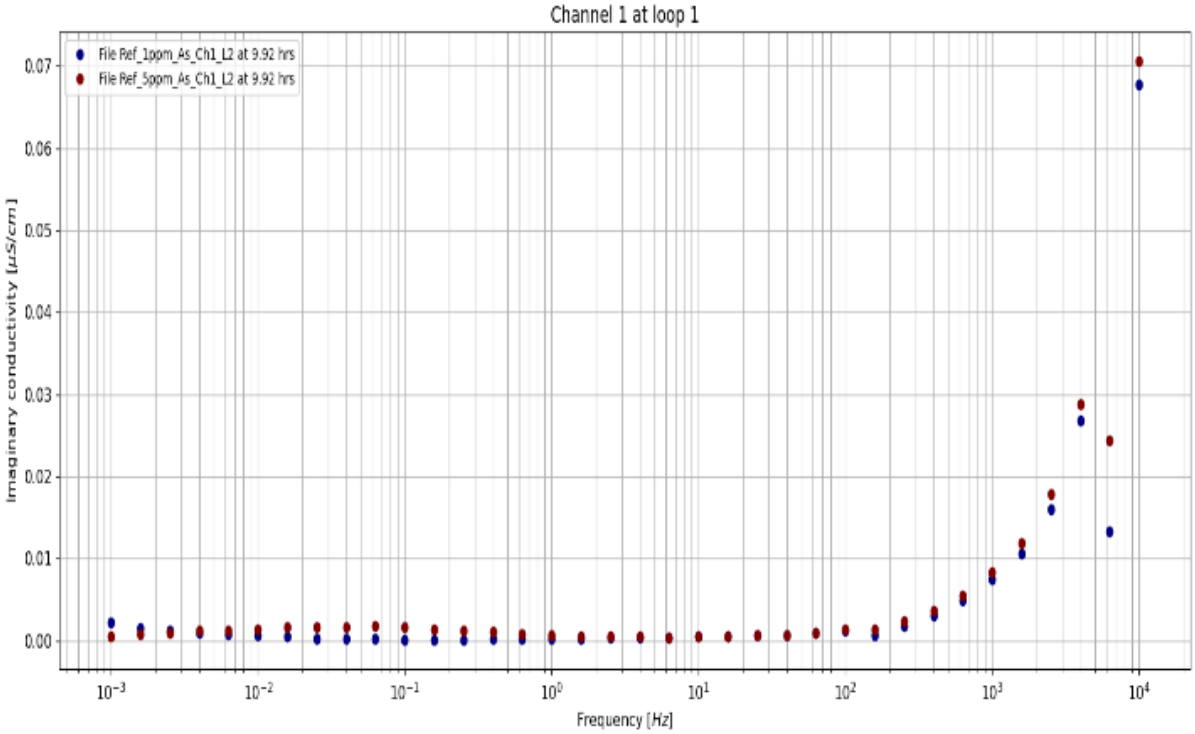
4.2.1 SIP response with porous media and As

Response from SIP measurements for experiment with buffer media indicate high sensitivity towards both arsenic concentrations (5ppm in red and 1ppm in blue).SIP response is both sensitive and distinctive towards the analyzed concentrations of arsenic. Based on the observed response it was decided to proceed with 1 ppm of arsenic for conducting further analysis with biochar. 1ppm of As is closer representation of real-life groundwater contamination reported in survey studies (Jain and Ali, 2000; Mohammed Abdul et al, 2015; Shakoor et al, 2016). The time required to saturate each column was 3 hrs±15minutes. The flow-rate of fluid through the column is 0.16 ml/min. The same flow rate was maintained in further analysis by fixing the control valve from the feed-solution. Samples were taken at intervals for chemical analysis to determine the adsorption potential of buffer-media. The results for chemical analysis of residual arsenic are illustrated in the following section series of images (A→ D). SIP response from loop1 for 2 columns with different arsenic concentration (5ppm and 1 ppm) and same buffer media (acid washed sand) as shown in Figure 19.

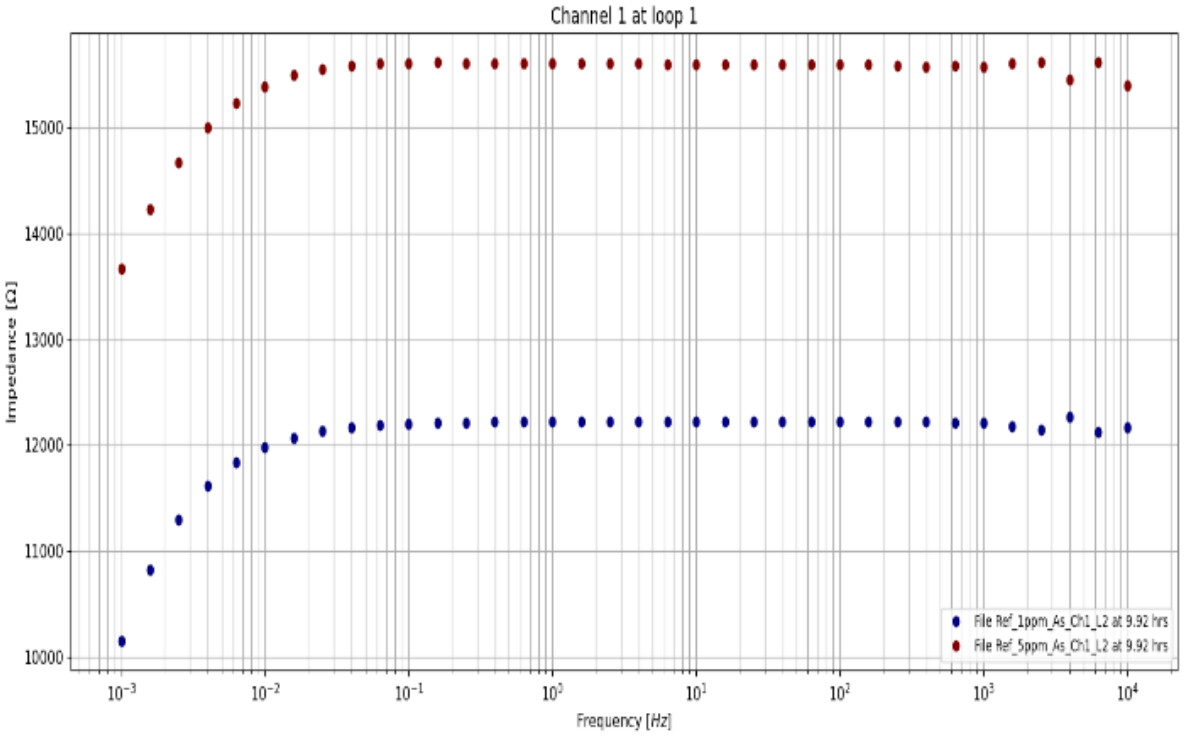
Table 7 Summary of As sorption capacities (SC) achieved by modifying raw biochar (BC)

Biochar Feedstock	**Modification to Biochar**	**SC with Raw BC (mg/kg)**	**SC with modified BC (mg/kg)**	**Reference**
Cotton wood	Impregnation of γ-Fe_2O_3 (post-pyrolysis)	NA	3,147	(Zhang et al, 2013)
Chestnut Shell	Impregnation of Magnetic gelatin	17500	45800	(Z. Zhou et al, 2017)
Corn Stem	Addition of Fe-Mn oxide	2890	8250	(Lin et al, 2017)
Hickory Chips	Impregnation of γ-Fe_2O_3 (post-pyrolysis)	Negligible	2160	(Rajapaksha et al, 2016)
Miscanthus/ Silver grass	Impregnation of $Fe(NO_3)_3$ (post-pyrolysis)	750	5250	(Kim et al, 2019)
Poplar-wood	Addition of $FeCl_3$ (pre-pyrolysis)	133	230	(Xu et al, 2020)
Pinewood	Mixing Natural Hematite (post-pyrolysis)	200	400	(Wang et al, 2015a)
Date-Palm Leaves	Impregnation of $Fe(NO_3)_3$	Negligible	1000	**This Study**

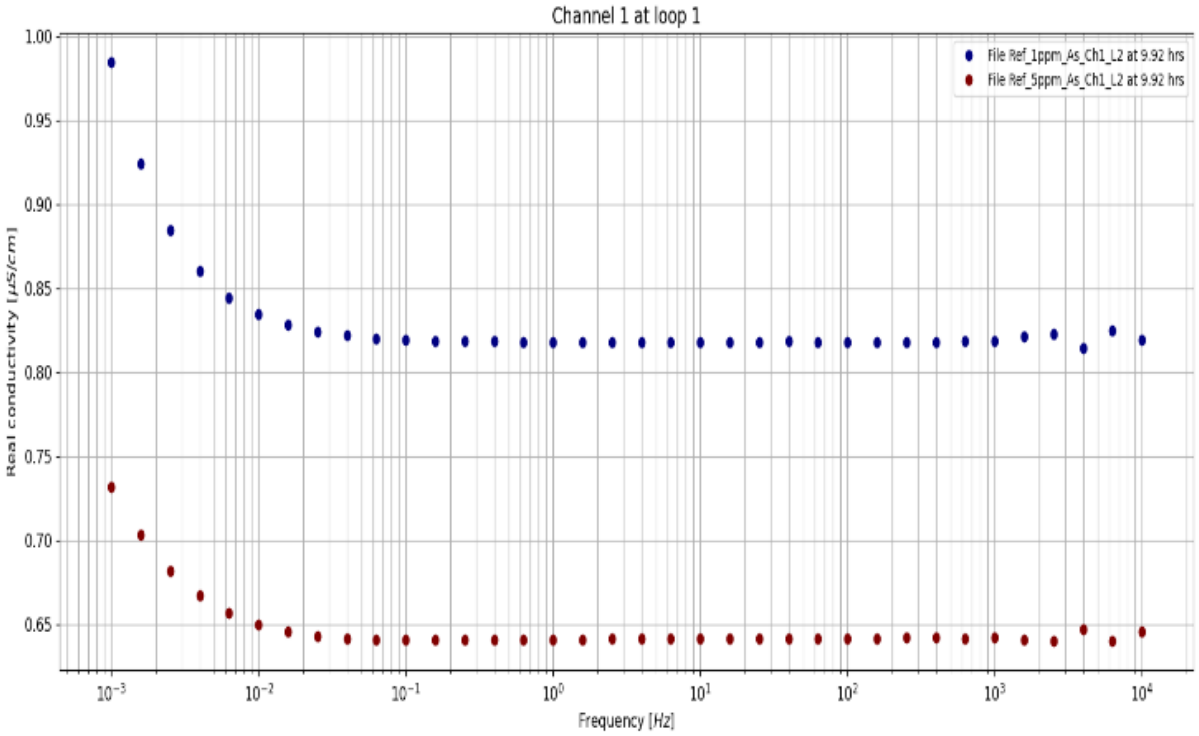
A) Imaginary conductivity



B) Impedance



C) Phase shift



D) Real conductivit

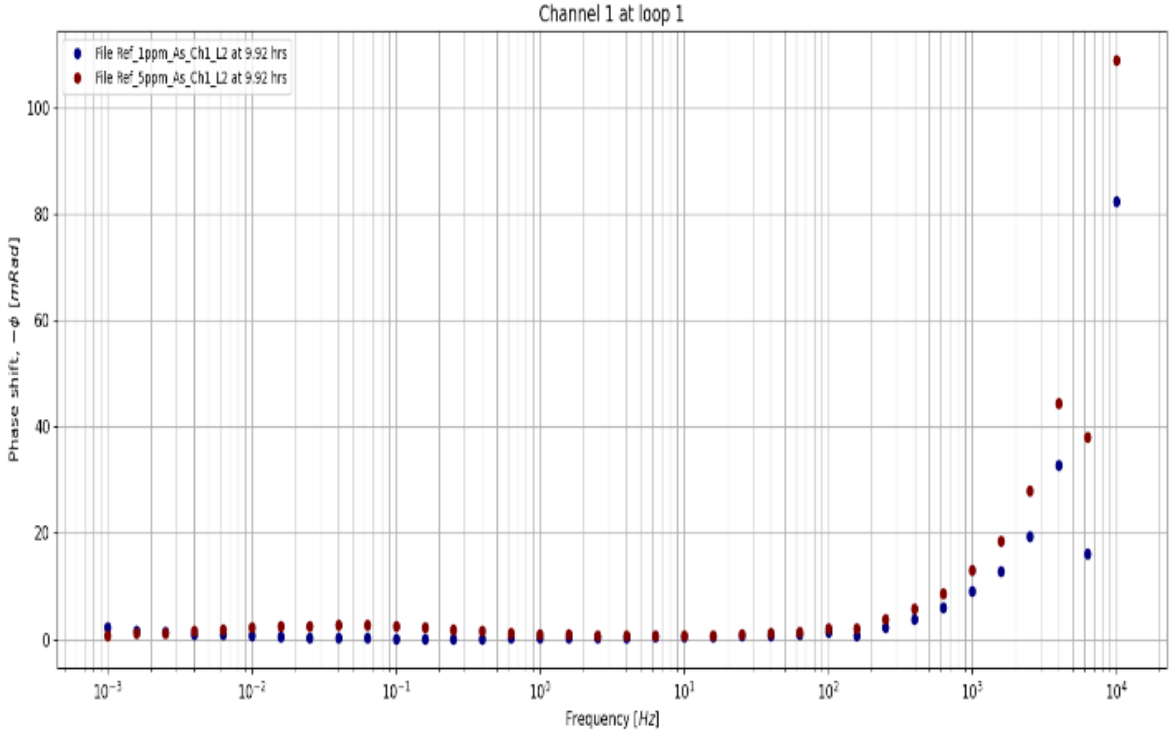


Figure 19: A: Imaginary conductivity B: Impedance C: Phase shift D : Real conductivity .

4.2.2 As removal by biochar and SIP response

Both 5% and 10% biochar-amended columns were successful in removing As from the contaminated water (Figure 20). Compared to the reference column (17% removal), both biochar-amended columns achieved an As removal of >98%. There was no noticeable difference between the biochar columns. Therefore the 5% biochar-amended column can be considered as the optimum. Although a higher biochar quantity practically means a larger number of active sites and functional groups available to interact with As, the packing of the column led to particle aggregation, thus canceling out any additional adsorption of As (Duwiejuah et al., 2020). With respect to the process kinetics and equilibrium, it is clear that As removal mainly occurred in the first 4 h, whereas beyond that time adsorption competed equally with desorption. Based on these observations, it was decided to focus on the SIP response during the first 4 h to attempt and develop a correlation with the % As removal as illustrated in Figure 20 below.

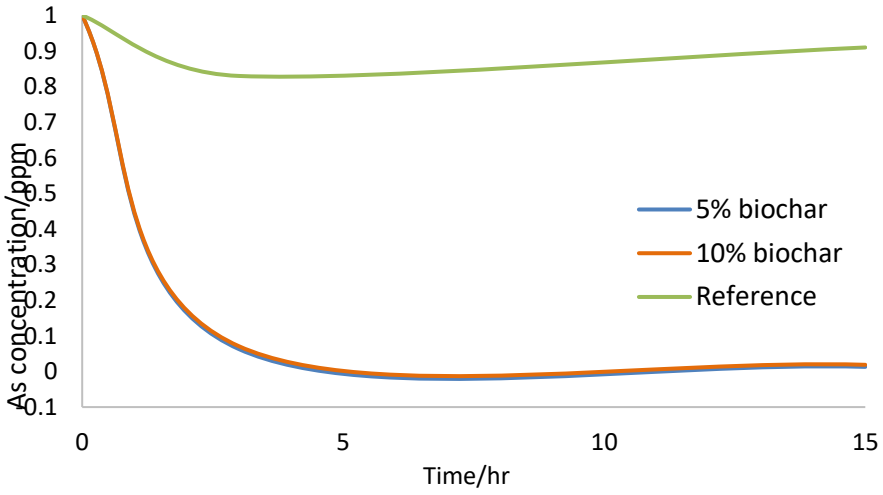


Figure 20 As concentration in effluent from columns measured at time intervals

Looking at characteristic SIP spectra from all three columns we can clearly observe the impact of biochar on the electrical properties of the porous medium (Figure 20). Biochar increased both the

imaginary and real conductivity by ~3 orders of magnitude. To better visualize SIP parameters' temporal behaviour, we focused on the 10 Hz frequency, but other frequencies (up to 100 Hz) showed similar trends. The measured SIP parameters (real and imaginary conductivity) appeared to be impacted by As sorption. Changes in both real and imaginary component appeared to follow As decrease in the effluent (Figure 21).

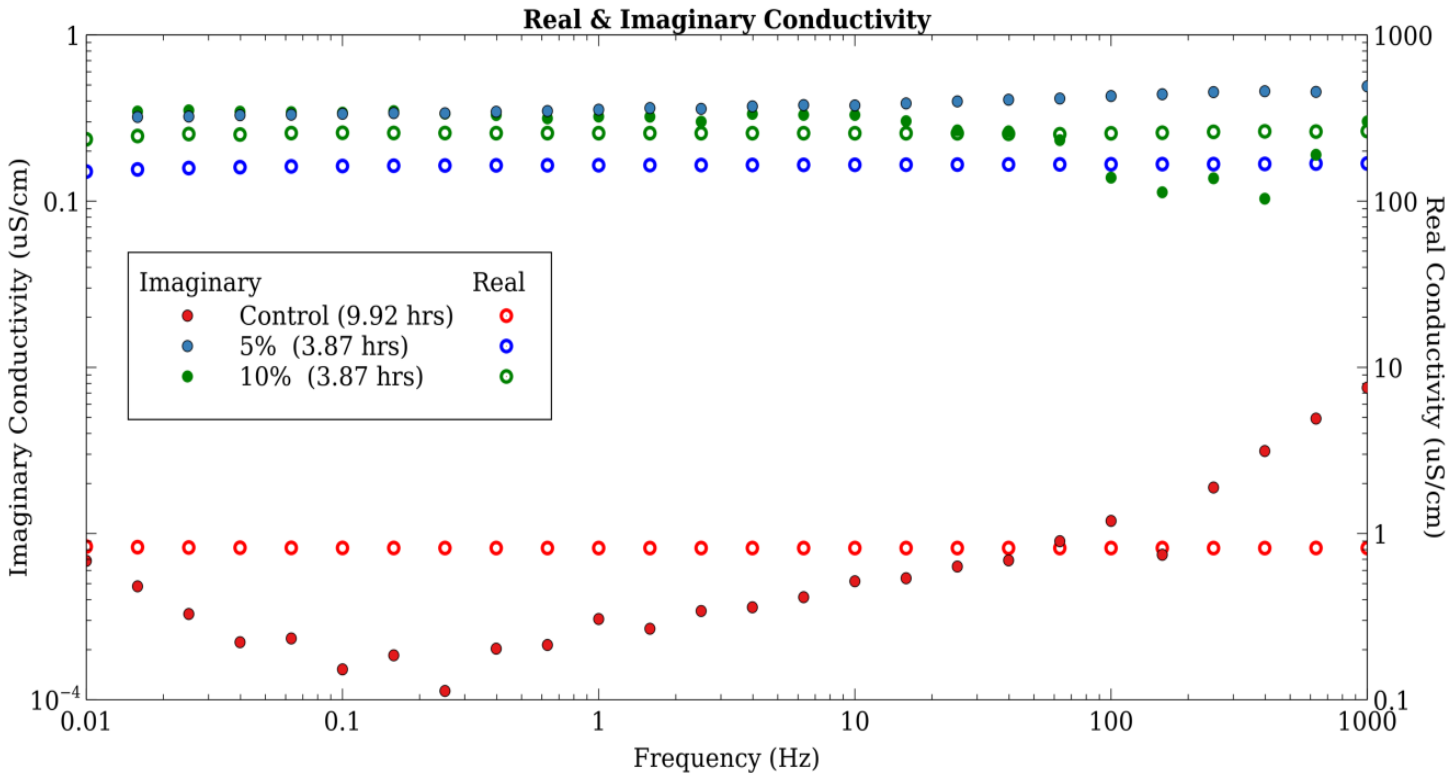


Figure 21 Spectral induced polarization data over a broad frequency range (0.01-1000 Hz) for the control and the amended columns; data shown over same logarithmic range for direct comparison.

The real component, primarily sensitive to the fluid properties in porous media, drops in response to As removal. In both columns, the conductivity drop is steeper at the early stages of the experiment with the behaviour changing at later times; the 5% column appears to reach a plateau,

and even increasing at the end while the 10% continues to decrease, at a much-reduced rate. The imaginary component for the 5% shows a continuous gradual decrease that almost reaches a plateau at the end of the experiment. The 10% shows different behavior, with a dramatic drop early on, followed by an increasing trend with a reducing rate of increase. The removal of As ions from the solution can explain the decrease in real conductivity. The imaginary component appears to be strongly influenced by the real component changes, at least in the early stages. In the 10% column, the imaginary component increases after 5 hrs, becoming a dominant signal probably due to the higher availability of As sorption sites that result in larger changes in the BC surface properties. This is a very important observation, and although more research is needed to establish conclusive links, SIP appears to be a powerful tool to monitor As sorption processes; real conductivity clearly shows the onset, and progress, of early sorption processes, while the imaginary component offers the possibility of long-term monitoring of the process and stability of the adsorbed substance.

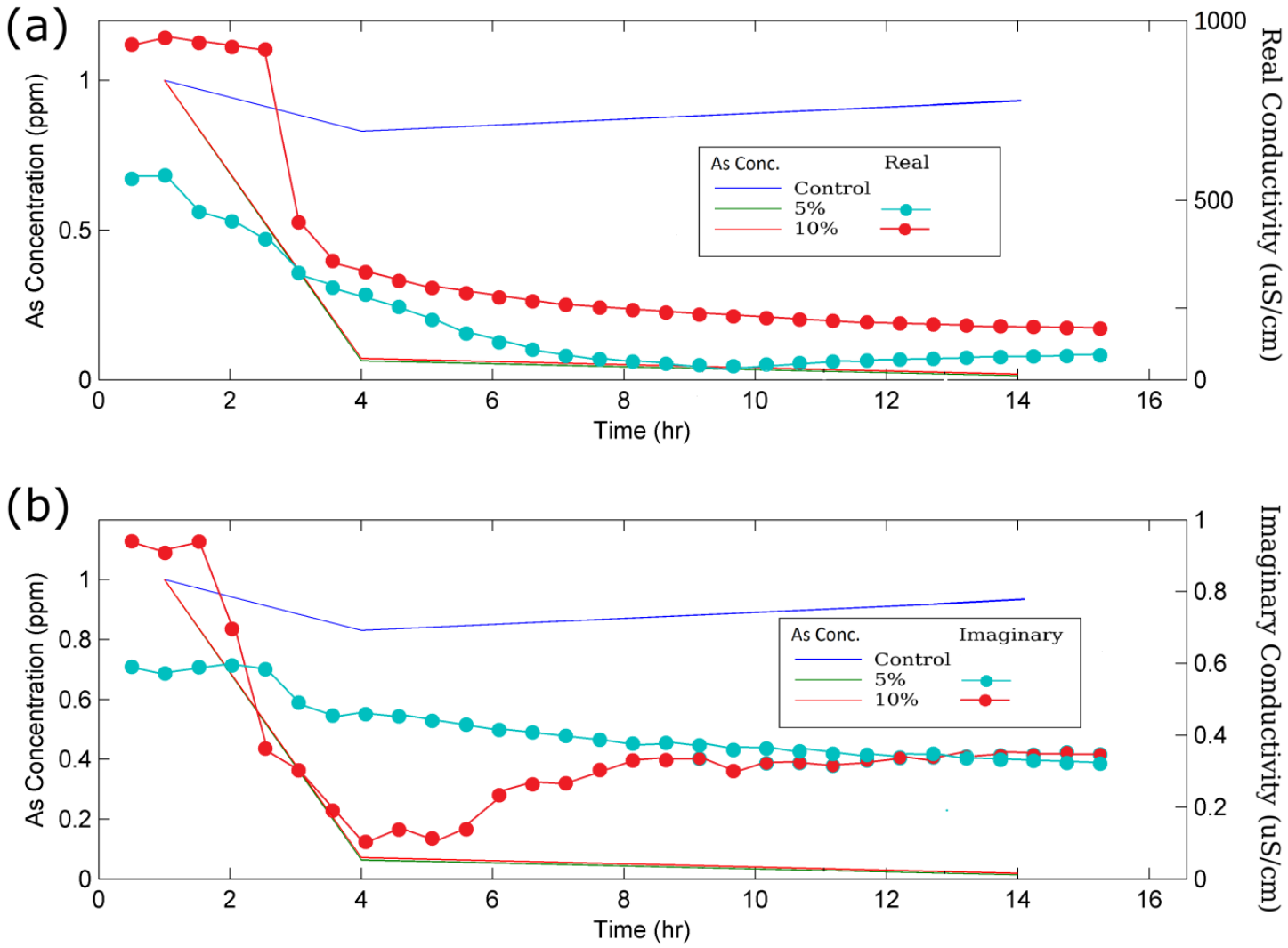


Figure 22 Temporal evolution of 10 Hz signal for real (a) and imaginary (b) conductivity of 5% and 10% biochar columns for the duration of the experiment compared with As concentrations (ppm).

Principle component analysis (PCA) of log-transformed imaginary conductivities was used to redefine the coordinates of the original variables (imaginary conductivity) because of a linear combination and to represent them on a rectangular axis, while the adjacent points maintain a descending order in terms of the variance value. For this reason, the first principal component retains more data information than the second, which does not retain information that was entered earlier (in the first component). The variance on the x-axis is related to the presence of biochar,

with the no-biochar references plotting with negative values and the biochar columns plotting with positive values. The y-axis is attributed to the adsorption of As with the biochar plotting with more negative values as the measurements are increasing while the no-biochar references plotting with positive values. This suggests that despite the signals being found at similar ratios across all measurements, even after a relative short experimental time (16 h) the SIP signal is successfully adapting to carbonized materials and adsorption processes as summarized in Figure 23.

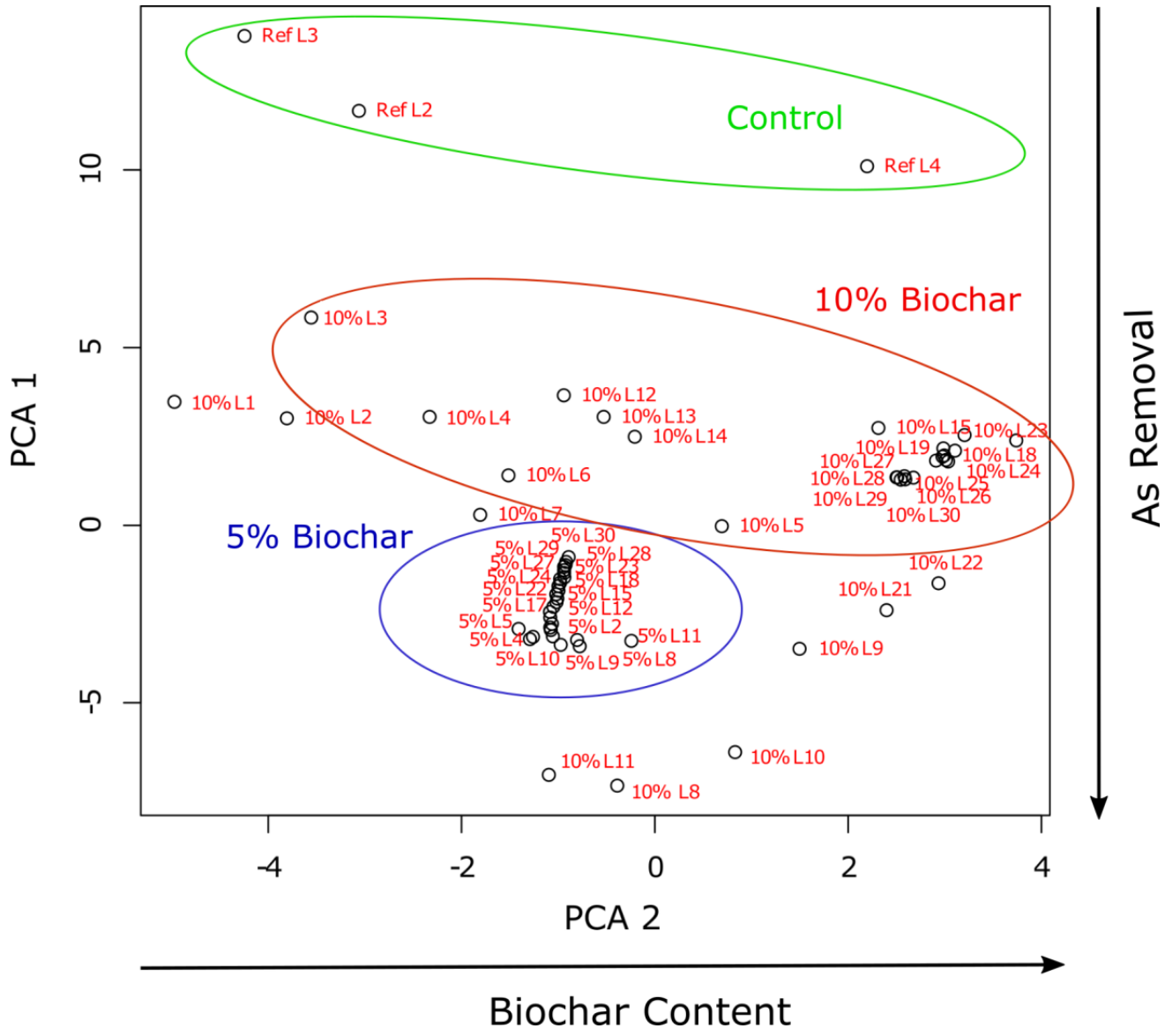


Figure 23 Principal Compnent Analysis (PCA**)** of imaginary conductivities. Principal component 1 (y-axis) is controlled by the adsorption or not of As in biochar with a negative value representing the As adsorption (5% biochar in a blue ellipse). Principal component 2 (x-axis) is controlled by the presence or absence of biochar with positive values representing the higher presence of biochar (10% biochar in red ellipse).

CHAPTER 5
CONCLUSION AND RECOMMENTATION

5.1 Conclusion

This study illustrates how Date-Palm waste can be recycled and applied for As removal in water. Biochar adsorption capacity is limited due to the formation of amorphous layer on biochar surface that inhibits further adsorption of arsenic. SEM and XRD analysis further confirm the previous conclusion drawn. However, results of this study revealed that Fe-modified biochar significantly favors the adsorption of arsenic in comparison to raw biochar. In fact, more than 99% of arsenic removal was achieved at pH 5 using biochar dosage of 0.2 g and stirring rate of 200 rpms. Moreover, the preliminary assessment indicated that both the real and imaginary conductivity values followed the As adsorption on biochar and removal from the contaminated water, providing complementary information. Since As adsorption depends on the electrostatic interactions of the contaminant with the surface functional groups of the adsorbent, it can be suggested that SIP monitoring showed considerable sensitivity for surface sorption processes. This work shows a strong agreement between SIP response and chemical analysis regarding the column adsorption of As.

5.2 Recommendations

Future work should focus on establishing quantitative links between the SIP parameters and the rate of As sorption processes. Modification is the critical factor in formulating biochar for effective adsorption and therefore, comparative evaluation of other forms of biochar modification techniques (steam activation and magnitzation for example) shall be conducted. Only initial analysis have been conducted for analyzing SIP response from ongoing adsorption experiment. Detailed study on precision and reproducibility of SIP response against same experimental conditions is required for strong conclusion. Furthermore, biochar derived from other derivatives of datepalm (date-seeds and trunks) shall also broaden the applicability and economic advantage of upscaling this research findings. Due to the novelty of this concept, new paradigm shifts towards the application of geophysical techniques (of which SIP is one) has emerged.

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