

Thesis research project

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Developing a low-cost filter medium for remediation of arsenic in contaminated groundwater



Mexican woman who just received her ceramic water filter from Caminos de Agua. Picture by W. Thurston.

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Colophon

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Summary

Arsenic in drinking water is a threat to human health and affects about 140 million people in at least 70 countries worldwide. Arsenic contaminated drinking water causes a range of health effects, and are due to the acute toxicity of As(III). Long-term health effects are usually observed on the human body, like skin lesions and hard patches on the palms and soles of the feet, and pigmentation changes. In Guanajuato (Mexico), the key factor involved in the formation of arsenic contaminated groundwater is the desorption/dissolution of arsenic from arsenic rich geological sources unto the groundwater. This situation is caused by the declining groundwater level, reaching the arsenic rich geological sources. This results in an increase in arsenic concentration in the groundwater. The water is then pumped to the surface and either used for agricultural irrigation or drinking water. The objective formulated by Caminos de Agua, an NGO in Mexico, is to create a filter medium capable of effectively removing arsenic to below the WHO guideline of 10 µg/L for at least three weeks, treating 25L of drinking water per day, based on a household of five people. In this study, different biochars were prepared and tested on the capacity to remove arsenic from aqueous solutions. Biochar was chosen to work with because of the high surface area and the porosity. Furthermore, the production of biochar is low in costs and easy to make with local materials. All biochars were made by pyrolysis of scrap wood in a biomass gasifier at temperatures above 850 °C and impregnated with iron substances, which were selected after a literature study. Three iron substances with a high affinity towards arsenic have been impregnated unto the wood-char and have been tested in batch experiments: Fe₂O₃, FeCl₃ and Fe(OH)₃. With these substances, seven different filter media were prepared: high-temperature wood-char, wood-char post-treated with Fe₂O₃, wood-char pre-treated with FeCl₃, wood-char post-treated with FeCl₃, base-ash treated wood-char, base-ash treated wood-char post-soaked with FeCl₃, and iron-coated sand where the working compound was Fe(OH)₃.

The materials were then tested in batch experiments to gain insight in the adsorption kinetics, and to measure the adsorption capacity (AC). The adsorption capacity a filter medium must have to comply with the objective of Caminos de Agua was set at 300 µg/gram. The highest AC reached was wood-char post-treated with FeCl₃ and reached an AC of 55.52 µg/gram. This filter medium was then tested in a column set-up with two cartridge filters filled with the wood-char post-treated with FeCl₃. The cartridge filters had a volume of 450 mL and contained 150 gram of filter medium. Influent contained 40 µg arsenic per liter, and after 50 bed volumes (35 liters) the effluent crossed the WHO guideline of 10 µg/L. These results serve as a solid base for Caminos de Agua to continue this study and to achieve the objective. It is recommended to investigate the effect of decreasing the pH of the influent water to 5-7 on the adsorption capacity, and to try more chemical substances such as TiO₂ and MnO₂. Also, different methodologies to impregnate biochar should be tested and compared. Finally, an economic and social feasibility study should be carried out to

investigate whether or not the filter is financially feasible and to understand how the filter should be advertised to communities in the rural areas of Mexico.

Samenvatting (Dutch)

Te hoge concentraties arseen in drinkwater is een grote bedreiging voor de menselijke gezondheid en treft ongeveer 140 miljoen mensen in meer dan 70 landen wereldwijd. Inname van arseen kan resulteren in negatieve gezondheidseffecten vanwege de acute giftigheid van As(III). Effecten op de lange termijn worden aangetroffen op het lichaam, zoals huid letsels, ongewone plekken op de voeten en een verandering van pigment op de huid. In Guanajuato, een regio in Mexico, wordt de arseen vervuiling in grondwater voornamelijk veroorzaakt door desorptie van natuurlijk voorkomend arseen in geologische bronnen. Dit is ten gevolge van de gestage daling in grondwaterpeil die Mexico de laatste jaren ervaart vanwege excessief grondwater gebruik voor irrigatie in de landbouw sector. Caminos de Agua, een ontwikkelingsorganisatie uit San Miguel de Allende, houdt zich bezig met het ontwerpen van water filter systemen en richt zich momenteel op het prepareren van een filter materiaal dat arseen effectief uit water kan adsorberen zodat de arseen concentratie van het water onder het World Health Organization (WHO) limiet van 10 µg/L komt te liggen. Dit filter moet minimaal voor drie weken meegaan en moet minstens 25 liter water per dag kunnen behandelen. In dit onderzoek zijn er verschillende biochars geprepareerd en getest op de capaciteit om arseen te verwijderen uit water. Biochar is gekozen vanwege de hoge oppervlakte en de gunstige porositeit. Daarnaast is de productie van biochar goedkoop en gemakkelijk om te maken met lokale materialen. De biochars waren gemaakt door de pyrolyse van afval hout in een biomassa verbrandingstank in anaerobe omstandigheden met gemiddelde temperatuur boven 850 °C. Om de affiniteit voor arseen vervolgens te verhogen werden de biochars op verschillende manieren geïmpregneerd met ijzer substanties, die geselecteerd werden na een literatuur studie. Drie ijzer substanties met een affiniteit om te binden met arseen waren geïmpregneerd op de biochar en zijn getest in batch experimenten. Fe₂O₃, FeCl₃ en Fe(OH)₃ waren gebruikt om zeven verschillende filter materialen te maken: high-temperature wood-char, wood-char nabehandeld met Fe₂O₃, wood-char voorbehandeld met FeCl₃, wood-char nabehandeld met FeCl₃, base-ash behandeld wood-char, base-ash behandeld wood-char nabehandeld met FeCl₃, en zand met een ijzer coating waarbij het werkende middel Fe(OH)₃ was.

De materialen waren getest in batch experimenten om de adsorptie kinetiek en de adsorptie capaciteit te behalen. Om aan het doel van Caminos de Agua te voldoen moet een materiaal over een adsorptie capaciteit van 300 µg/gram beschikken. De hoogste adsorptie capaciteit die behaald werd was de wood-char nabehandeld met FeCl₃ en die behaalde een adsorptie capaciteit van 55.52 µg/gram. Dit materiaal was vervolgens getest in een kolom set-up met twee kolommen gevuld met het materiaal. De kolommen hadden een volume van 450 mL en beschikten over 150 gram filter materiaal. Het influent had een arseen concentratie van 40 µg/L en na 50 bed volumes (35 liter) werd de WHO guideline van 10 µg/L overschreden. Deze resultaten geven Caminos de Agua een sterke basis voor toekomstig onderzoek en voor het behalen van het doel. Dit onderzoek beveelt aan om het effect op de adsorptie capaciteit te

bepalen na een afname in zuurtegraad in het water naar een pH van 5-7. Daarnaast moeten meerdere chemische substanties getest worden, bijvoorbeeld TiO_2 of MnO_2 . Ook raadt dit onderzoek sterk aan om andere methodologieën voor het impregneren van biochars uit te testen en te vergelijken door middel van het vergelijken van de adsorptie capaciteiten. Uiteindelijk moet een economische en sociale haalbaarheidsstudie uitgevoerd worden om te bepalen of het filter financieel gezien op de markt gebracht kan worden, en om te begrijpen hoe zo'n filter het beste geadverteerd kan worden aan de gemeenschappen in de rurale gebieden van Mexico.

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1 Introduction

In this research project, a student from the University of Applied Sciences Van Hall Larenstein (Leeuwarden, The Netherlands) conducted a research at Caminos de Agua (San Miguel de Allende, Mexico) in the context of a thesis for the bachelor study Environmental Sciences. Caminos de Agua is an organization in Mexico and describes their mission as follows: *“promoting healthier more prosperous lives through practical sustainable solutions along the pathways water travels through our lives and the planet”*. Their work is focused on the water problems of the local communities throughout the Independencia watershed region in Guanajuato, a state in central Mexico. With projects and capacity trainings they enhance the livelihoods of the locals in that region, while cooperating with local communities and grassroots organizations to create long-term sustainable water solutions. Current projects include production and distribution of ceramic water filters for eliminating water-borne pathogens, community-based installations of rainwater harvesting systems, and installing of biochar treatment systems. The main focus of this study was the development and testing of wood-char filters with a strong affinity to arsenic in order to remediate groundwater from this contaminant.

Inorganic arsenic contamination in groundwater is common in Mexico and a number of other countries, and poses a great threat to public health when contaminated water is used for drinking, cooking, and irrigation purposes (WHO, 2011). Arsenic is recognized by the World Health Organization (WHO) as one of the 10 chemicals with a major public health concern. Chemicals such as fluoride, lead, nitrate, selenium and uranium, are also mentioned (WHO, 2011). The recommended guideline concentration of arsenic in drinking water is $<10 \mu\text{g/L}$ (WHO, 2011) and intake of higher concentrations may lead to severe health effects. Arsenic is widely present in the earth's crust, and is usually present in natural waters in concentrations around 1-2 $\mu\text{g/liter}$. However, when there are sulfide mineral deposits and sedimentary deposits from volcanic rocks, the concentrations are typically higher, especially in groundwater. Arsine is the most toxic form of arsenic, followed by arsenite, arsenate and organic arsenic compounds (WHO, 2011). In water it is normally present in the oxidized state as arsenate (+5), but when there is less oxygen, e.g. in groundwater, the more toxic form of arsenite (+3) is likely to be present. The International Agency for Research on Cancer (IARC) classified arsenate and arsenite in drinking water as carcinogenic to humans. Long-time exposure can lead to skin lesions and skin cancer. Other long-term effects include developmental effects, neurotoxicity, diabetes, infant mortality, impaired cognitive development (WHO, 2016).

Caminos de Agua has been doing water quality monitoring throughout the state of Guanajuato and implemented the data in a map (Figure 1) to indicate the extent of arsenic contamination in groundwater. Arsenic concentrations were measured at different locations and marked with a color to present the quality. The green dots adhere to all international standards for arsenic levels in drinking water. The red dots exceed the WHO limit of $10 \mu\text{g/L}$, while the black dots exceed the Mexican government's higher limit of $25 \mu\text{g/L}$. Grey dots

represent wells without data on arsenic concentration. Most of the contaminations found are located in communities in the rural areas of Guanajuato state, however bigger cities as San Miguel de Allende also show significant contamination levels. The water quality monitoring project is an ongoing activity, and the results show an increase in arsenic and fluoride concentration throughout the years due to the overexploitation of groundwater for agricultural purposes (Caminos de Agua, 2017). This results in a decrease in groundwater level and causes the groundwater to mix with natural occurring arsenic and fluoride.

Caminos de Agua is looking for a feasible low-cost alternative to remove arsenic from drinking water, applicable as decentralized small-scale water treatment system for local communities. Adsorption of contaminations with biochar seems a promising and low-cost alternative, while producing less sludge waste and being easy to operate (Mohan, et al., 2014). Furthermore, the pyrolysis of biomass into biochar is an environmentally safe process, when carried out properly, and can be done with multiple materials as feedstock.

Biochar is defined by the International Biochar Initiative as *"a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment"* (IBI, 2012). This technique is not a new phenomenon. Ancient populations in Brazil, Japan and Africa used biochar as soil management for agricultural purposes (Mohan, et al., 2014). Studies have shown that mixing biochar with the soil surface enhances the soil fertility compared to surrounding soils (Lehmann & Joseph, 2009). Many other recent studies have shown the arsenic removal capacity of biochar and used biochar as an adsorbent, effectively removing organic and inorganic contaminants (Ahmed, et al., 2016; Mohan, et al., 2014; Hu, et al., 2014).

The goal of this study was to make and test a biochar with a high affinity for arsenic, which would be able to remove arsenic and get the arsenic concentration in drinking water below the WHO guideline. Research was carried out to see what substances have a strong affinity to arsenic and increase the adsorption capacity of biochar. And therefore also important, how these substances can be impregnated unto the biochar. With this knowledge, Caminos de Agua can help the local people in the Guanajuato region to provide in clean and safe drinking water. To achieve this goal, the following research questions were formulated:

- 1) *Which substances have a strong affinity to arsenic?*
- 2) *What is a suitable way to make an impregnated biochar with a strong affinity to arsenic?*
- 3) *What is a suitable batch- and column methodology to test filter media?*
- 4) *Which impregnated biochar is most promising, in terms of adsorption capacity, in lowering the arsenic concentration in contaminated groundwater to the WHO guideline?*

The outcome of the research questions should give Caminos de Agua a strong base to develop a prototype, and eventually to test it in real-life conditions and solve the arsenic contamination problem in the Guanajuato region. The objective formulated by Caminos de Agua is to create a filter medium effectively removing arsenic that lasts for at least three weeks, treating 25L of drinking water per day, based on a household of five people.

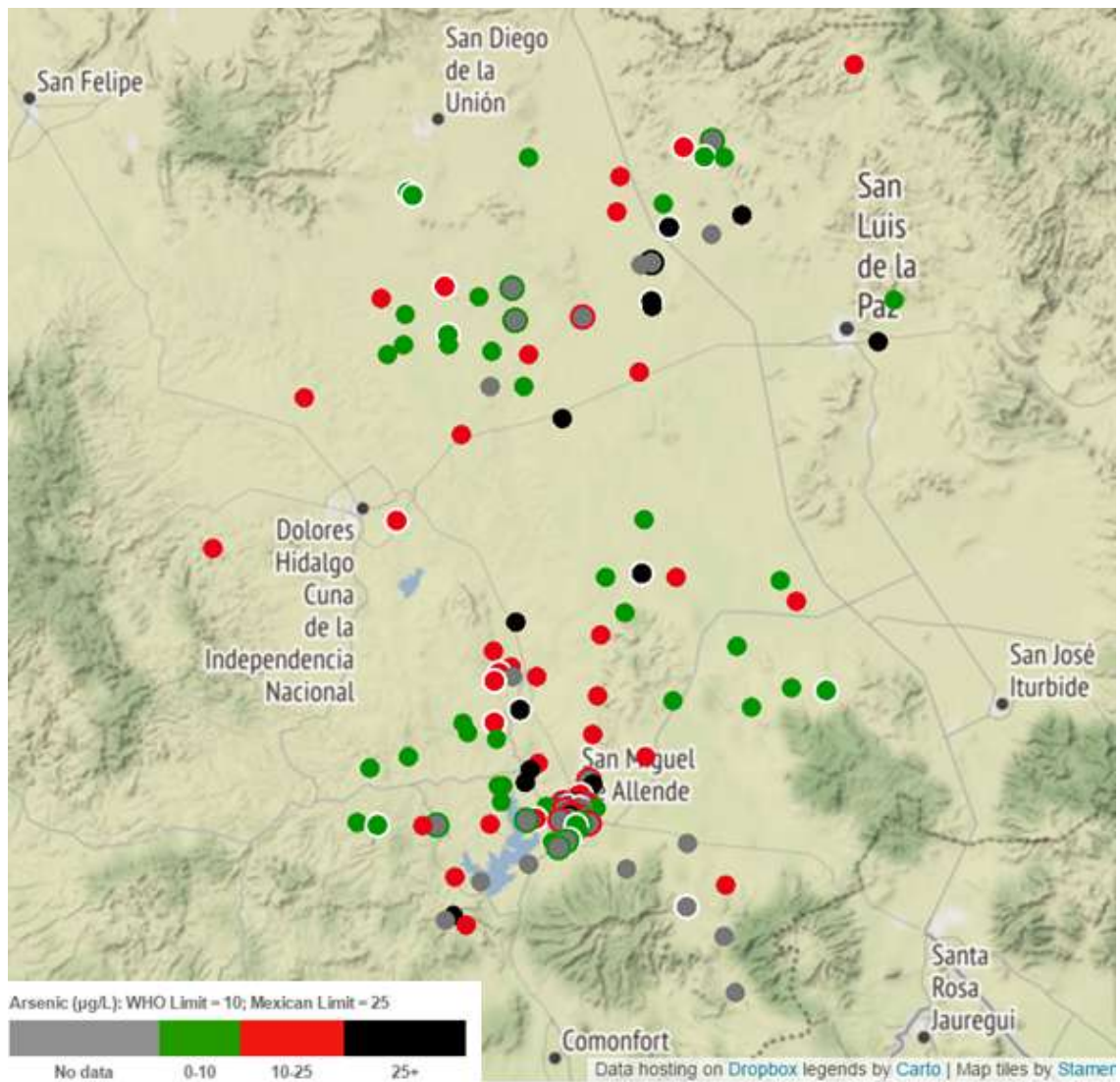


Figure 1: Arsenic concentration in groundwater throughout the Guanajuato region in Mexico (Caminos de Agua, 2017)

2 Theory

2.1 Arsenic in the environment

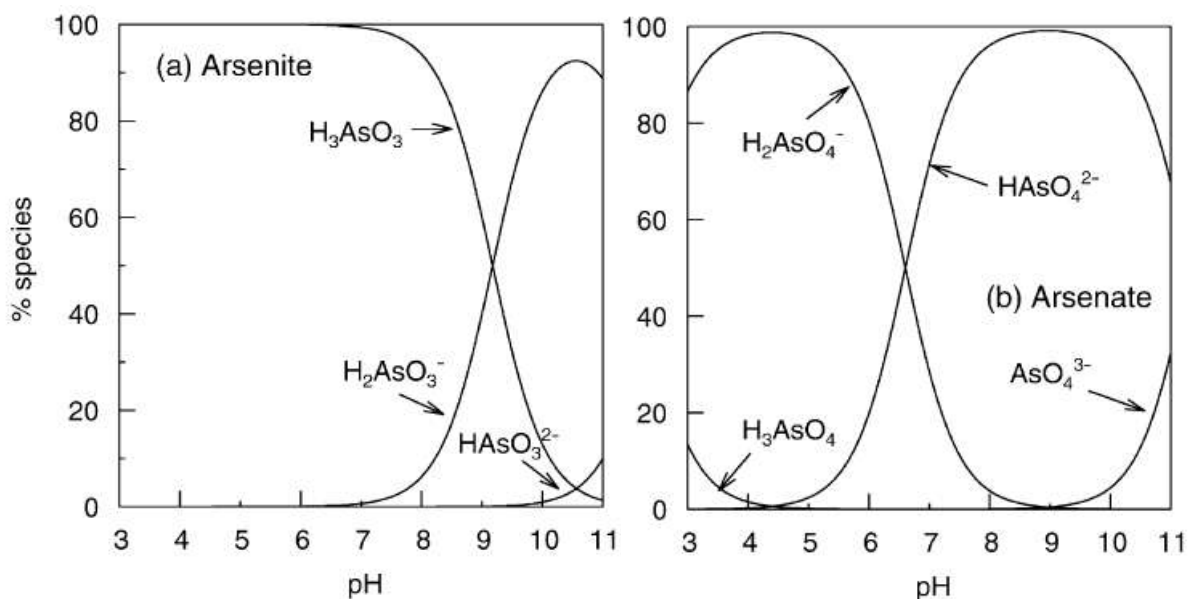
Arsenic in drinking water is a threat to human health and affects about 140 million people in at least 70 countries worldwide (Ravenscroft, et al., 2009). There are two main processes resulting in arsenic contamination of aqueous solutions: natural processes and anthropological processes. Arsenic is present in the atmosphere, soil and rocks, natural waters and organisms. Natural processes as weathering reactions, biological activity, and volcanic eruptions lead to mobilization of arsenic (Smedley & Kinniburgh, 2001). Anthropological activities such as groundwater depletion, mining, combustion of fossil fuels and usage of arsenic containing herbicides and pesticides lead to mobilization of arsenic in the environment as well (Smedley & Kinniburgh, 2001).

Arsenic is most common in nature as arsenate (+V), arsenite (+III) and arsine (-III), dependent on the environmental conditions like pH and oxygen concentration (Panagiotaras, et al., 2012). In aqueous conditions, arsenic is most likely to be present in the oxidation state of arsenate (+V) or arsenite (+III). However, in aqueous conditions arsenic is never present as free ions but forms oxyanions with water:

H_3AsO_3 for As(+III)

H_3AsO_4 for As(+V)

The oxyanions of arsenate and arsenite are further divided in species. It is assumed that arsenic is mainly active as arsenite species in groundwater because of the anaerobic conditions. Arsenate species are more abundant under oxidizing conditions while arsenite species are predominant in reducing environment (Cheng, et al., 2008). A report by WHO also stated that arsenite species are dominant in groundwater and that arsenite species are



more toxic compared to arsenate species (WHO, 2016).

In Figure 2, the different forms of arsenite and arsenate are shown. The pH of the sample water used in this research falls between 7-9. If arsenite is mainly present because of the low oxygen concentration in the groundwater, it is most likely that arsenic is present as H_3AsO_3 . However, the groundwater was pumped to the surface in a water tank, where it was stored for experiments. It is assumed that the mixing with oxygen in the air oxidized the arsenite to arsenate, in the anionic form of HAsO_4^{2-} .

2.2 Arsenic contaminated groundwater and its health risks

Groundwater as part of the hydrological cycle provides water for human consumption, industrial purposes, agriculture, and is crucial for the maintenance of river flows and wetland (Kløve, et al., 2011). The aquifers in the state Guanajuato are critically overexploited, with annual groundwater extractions of around 1200 million cubic meters above recharge (CEAG, 2006). The overexploitation led to a decrease in groundwater levels over the last 50 years with an average drop of around 2 meters per year. In 2004, groundwater levels varied from 10 meters to 250 meters below surface level (Acevedo-Torres, 2004), but has been going down due to a large increase in groundwater irrigation. The groundwater exploitation is caused by cheap diesel pumps and drilling techniques, making the water accessible to the farmers. The farmers can make great use of the groundwater by using it for irrigation purposes, thereby increasing the agricultural growths and increasing their income (Shah, 2009). However, this well-fare turns into ill-fare when groundwater levels keep dropping. This way the small farmers lose access to groundwater and the related well-fare. Ultimately this creates more social differentiation as the rich farmers have more financial advantages to keep up with the declining groundwater levels than the poor farmers, and subsequently leading to more poverty. Besides the state Guanajuato in Mexico, this issue is increasingly affecting areas in India, China, Iran, the Middle East, Northern Africa, Spain, Western USA, and the Peruvian and Chilean Coast (Aeschbach-Hertig & Gleeson, 2012).

In Guanajuato, the key factor involved in the formation of arsenic contaminated groundwater is the desorption/dissolution of arsenic from arsenic rich geological sources into the groundwater. This situation is caused by the declining groundwater level, reaching the arsenic rich geological sources. This results in an increase in arsenic concentration in the groundwater. The water is then pumped to the surface and either used for agricultural irrigation or drinking water. Arsenic contaminated drinking water causes a range of health effects, and are due to the acute toxicity of As(III). However, As(V) is reduced to As(III) in the human body, so the two species are both equally toxic (Johnson & Bretzler, 2015). Acute effects of ingesting arsenic include symptoms as vomiting, abdominal pain and diarrhea (WHO, 2016). Depending on the severity of the arsenic poisoning, these symptoms are followed by feeling numb, or by muscle cramping or even death.

Long-term health effects are usually observed on the human body, like skin lesions and hard patches on the palms and soles of the feet, and pigmentation changes (WHO, 2016). Effects like this occur after a minimum exposure of five years and may introduce skin cancer. Cancer in the bladders and lungs are possible as well. Thereby, as a result of long-term ingestion, other forms of health effects include developmental effects, neurotoxicity, diabetes, melanosis, keratosis, dorsum, gangrene. Symptoms of arsenicosis, a slowly occurring sickness taking 2-20 years to manifest (UNICEF, 2013). Disorders to biological system like the digestive system, the respiratory system, cardiovascular system, hematopoietic system, endocrine system, renal system, neurological system, and reproductive system have also been identified (Mandal, et al., 1996; Maharjan, et al., 2005). While the acute toxicity of arsenic has been known for a long time, the harmful effects of low-level and long-term exposure have only been recognized in recent decades (UNICEF, 2013).

Children are more vulnerable to arsenic and their intellectual development may be inhibited. The higher the arsenic concentration and the longer a person is exposed to arsenic, arsenicosis is more likely to be developed. According to UNICEF, once a person is chronically exposed to arsenic and have developed arsenicosis, the health risks remain for decades and no clear medicine is available (UNICEF, 2013).

2.3 Arsenic removal methods

In order to remove arsenic from the drinking water, a number of water treatment methods are available. The following section discusses in general the advantages and disadvantages of the most common arsenic removal methods, concluding with a table.

Oxidation

Oxidation is used to converse arsenite to arsenate. Therefore, arsenic is not removed, but could be removed more easily in the next step by technologies such as adsorption, coagulation or ion exchange (Johnston & Heijnen, 2015). Below a pH of 9, arsenite is not charged, and hard to remove by the above mentioned technologies. Oxidation by oxygen is a slow process, and may take hours to weeks to complete. That's why chemicals such as chlorine, ozone and permanganate are used to oxidize As(III) to As(V) faster than in normal conditions. However, the oxidant needs to be carefully selected as interfering substances can greatly affect the kinetics of the oxidation (Singh, et al., 2015).

Coagulation and flocculation

Coagulation makes use of positively charged coagulants to reduce the negative charge of colloids. This will make the particles easier collide and get larger (Johnston & Heijnen, 2015). Flocculation is based on the formation of flocs by adding a flocculant to the water. The flocculant makes sure the particles stick together by neutralizing the charge. In these processes, arsenic is converted to a solid, which is later removed by settling or filtration (Mondal, et al., 2013). FeCl_3 is proven to be a good coagulant to reduce the arsenic concentration to the WHO limit (Garelick, et al., 2005; Scott, et al., 1995). Other common coagulants are aluminum, titanium and ferric sulfate (Lakshmanan, et al., 2008). However,

sludge production is a major drawback and needs to be processed accordingly to avoid environmental problems (Mondal, et al., 2013). Treatment of sludge is costly and less feasible for decentralized water treatment and remote communities.

Membrane technologies

Membranes remove particles such as arsenic or other pollutants from water based on size. A membrane consists of millions of pores that act as a barrier and stops particles from passing through (Shih, 2005). To run the influent water through the membranes, a driving force as pressure is needed. There are four major types of membranes with different types of effluent quality, explained in Table 1.

Table 1: Main types of pressure-driven membranes (Shih, 2005)

Parameter	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Permeability (l/h.m².bar)	>1000	10-1000	1.5-30	0.05-1.5
Pressure (bar)	0.1-2	0.1-5	3-20	5-120
Pore size (nm)	100-10000	2-100	0.5-2	<0.5
Rejection Monovalent ions	-	-	-	+
Multivalent ions	-	-/+	+	+
Small organic compounds	-	-	-/+	+
Macromolecules	-	+	+	+
Particles	+	+	+	+
Application	Clarification; Pretreatment; Sterilization	Removal of macromolecules, bacteria and viruses	Removal of organic compounds and some dissolved salts	Removal of salts

A common way of removing arsenic from aqueous solutions is flocculation followed by microfiltration. Microfiltration alone is not enough to stop the arsenic particles, but increasing the particle size with flocculation does (Singh, et al., 2015). The same goes for ultrafiltration. Only nanofiltration and reverse osmosis are both suitable for removal of dissolved compounds such as arsenic (Bruggen, et al., 2003). A major drawback is the high pressure needed for nanofiltration and reverse osmosis. So, costs are higher, the concentrate is produced as a waste product, and electricity is needed.

Ion exchange

Ion exchange works based on positively or negatively charged ion exchangers. In this way, the particle that is desired to be removed is exchanged for a different cation or anion (Crittenden, et al., 2012). So, the present form of arsenic in the aqueous solution needs to be charged in order to be removed. From the arsenic speciation diagram in Figure 3 it can be derived that if As(III) is present, it is in its non-charged form as H₃AsO₃. Therefore, it must be

oxidized to As(V) first to be removed. Then arsenic is present as HAsO_4^{2-} when pH is around 7-9. Common resins used for arsenic removal are so-called strong-base anions (Crittenden, et al., 2012). Another important aspect are the background anions that may compete for the resin exchange sites. Total Dissolved Solids (TDS) should be less than 500 mg/L and sulfate concentration should be less than 120 mg/L (Crittenden, et al., 2012). Then, a reasonable and economic exchange capacity for arsenic can be achieved. However, the resin should be able to be regenerated, used again, and the regenerate should be treated as a waste product.

Adsorption

Adsorption is the process where an adsorbate is fixed through chemical or physical bonds to an adsorbent. In this process, the adsorbate is transported into the porous adsorbent by diffusion and is then adsorbed to the surface of the adsorbent (Crittenden, et al., 2012). How much arsenic can adsorb to the adsorbent depends on the surface area and the pore size of the filter media. With a given pore volume, the smaller the pores, the higher the surface area and thus the available sites for adsorption. In water treatment there are three types of commercially available adsorbents: zeolites, synthetic polymeric adsorbents, and activated carbon (Crittenden, et al., 2012). Zeolites and synthetic polymeric adsorbents are used in water treatment, but activated carbon is most commonly used because it is a cheaper option. Regarding arsenic adsorption, granular ferric hydroxide and iron-impregnated granular activated carbon (GAC) are commonly used and achieve good removal efficiencies of ~60-100% (Crittenden, et al., 2012). The high removal efficiencies, easy operation, the cost-effectiveness, and the fact that less sludge is produced are all in favor of using adsorption for arsenic removal. However, this technique is pH dependence, adsorbents get saturated and sometimes adsorption is disrupted by competition of other ions for binding sites. The saturated waste product can be dangerous to dispose as well.

Summarizing table

The advantages and disadvantages of the most common arsenic removal methods are summarized in Table 2.

Table 2: Comparison of the different arsenic removal methods in terms of advantages and disadvantages

Arsenic removal method	Advantage	Disadvantage	Literature
Oxidation	Conversion of present arsenite to arsenate	Does not remove arsenic and thus needs a second removal step such as adsorption or ion exchange	(Johnson & Bretzler, 2015)
Coagulation and flocculation	Effective arsenic removal	Sludge production; less feasible for decentralized water treatment	(Mondal, et al., 2013; Lakshmanan, et al., 2008)
Membrane technologies	Effective arsenic removal with nanofiltration and reverse osmosis; feasible	Electricity costs for the high pressure needed; waste product	(Bruggen, et al., 2003; Shih, 2005)

	for decentralized water treatment		
Ion exchange	Effective arsenic removal in; regeneration of resin	Competition at exchange sites with other ions; regenerate waste product; only effective removal if arsenic form is charged	(Crittenden, et al., 2012)
Adsorption	Effective arsenic removal; feasible for decentralized water treatment; easy operation	pH dependent; saturation of adsorbent; competition with other ions for binding sites	(Crittenden, et al., 2012)

2.4 Wood-char as adsorbent

When biomass is heated in a gasifier, a carbon-rich product is created: biochar. At a temperature of 700-1000 °C, the tarry and oily components of biomass are removed and the remaining carbon-rich material is converted to a graphite-like structure (Kearns, 2012). The structure, as can be seen in Figure 3, enables the water to flow through the filter, and increases the total surface area significantly. In terms of porosity and surface area, biochar is similar to activated carbon, a common form of carbon used for adsorption. The technique is especially useful for decentralized water treatment locations, remote areas, communities who are not connected to a collective water treatment system. The gasifier is low in costs and easy to build with local materials. Thereby, compared to similar environmental harmful processes like a traditional kiln, the biomass gasifier is more sustainable in terms of air pollution and efficiency. A proper working biomass gasifier emits minimal gasses, only CO₂ and water vapor because of a complete combustion. The great porosity and surface enhances removal of herbicides and bacteria. The feedstock acts as the energy supplier as well as the final product and in general the technique is user friendly (Kearns, 2012).



Figure 3: Activated carbon vs Biochar as adsorption media

In Appendix F, the biomass gasifier used in this research is displayed and further details are given in Figure 4. The biomass gasifier consists of a 200L reactor body, a 200L combustion zone, and a chimney. The 200L combustion zone is not common for biomass gasifiers, but is there because in other experiments it is used to fulfil secondary pyrolysis of other biomass at

the same time. In terms of this research, the combustion zone is always empty. The 200L reactor body is loaded with the feedstock material, a mixture of scrap hardwood. The wood in the reactor body is set alight at the top. Primary air enters from the bottom and secondary air enters between the reactor and combustion drums, through the small gap caused by the rails. Primary and secondary air allow combustion, but not enough to burn fully. The heat that is generated in this way makes the wood evolve flammable gasses which rise and are burned with the inflowing secondary air in the combustion chamber. Meanwhile, the flame front in the reactor body moves down as more wood fuel is converted to wood biochar. Eventually, all wood is converted to wood-char. A good indicator of well charred wood is a mass loss of 85% of the feedstock. Variables influencing char quality include burning time, average temperature, and type of biomass.

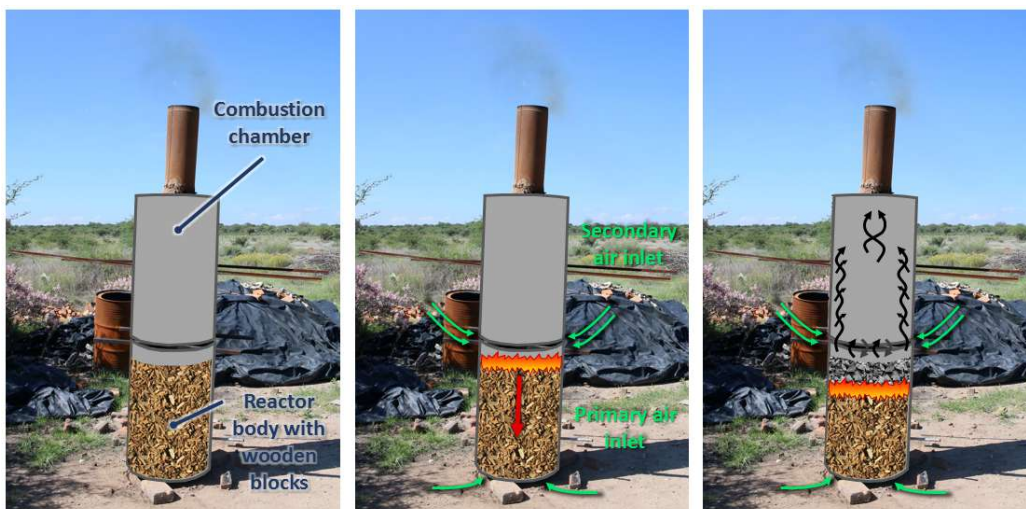


Figure 4: Working principles of the biomass gasifier at the Caminos de Agua's land

Wood-char is known to adsorb organic contaminants from water because of the porosity and the high surface area (Yu, et al. 2009; Yang, et al. 2010; Lou, et al. 2011). Both for water and soil remediation, wood-char is able to adsorb pesticides, herbicides, polycyclic aromatic hydrocarbons, dyes, and antibiotics (Xu, et al., 2012). A research paper by Ahmad, et al., 2013 summarizes the interaction mechanisms of wood-char with organic contaminants in Figure 5. Besides through adsorption, organic contaminants may bind because of polar or non-polar organic attraction. In that case, the organic contaminants bind to H- and O-bonds or hydrophobic sites.

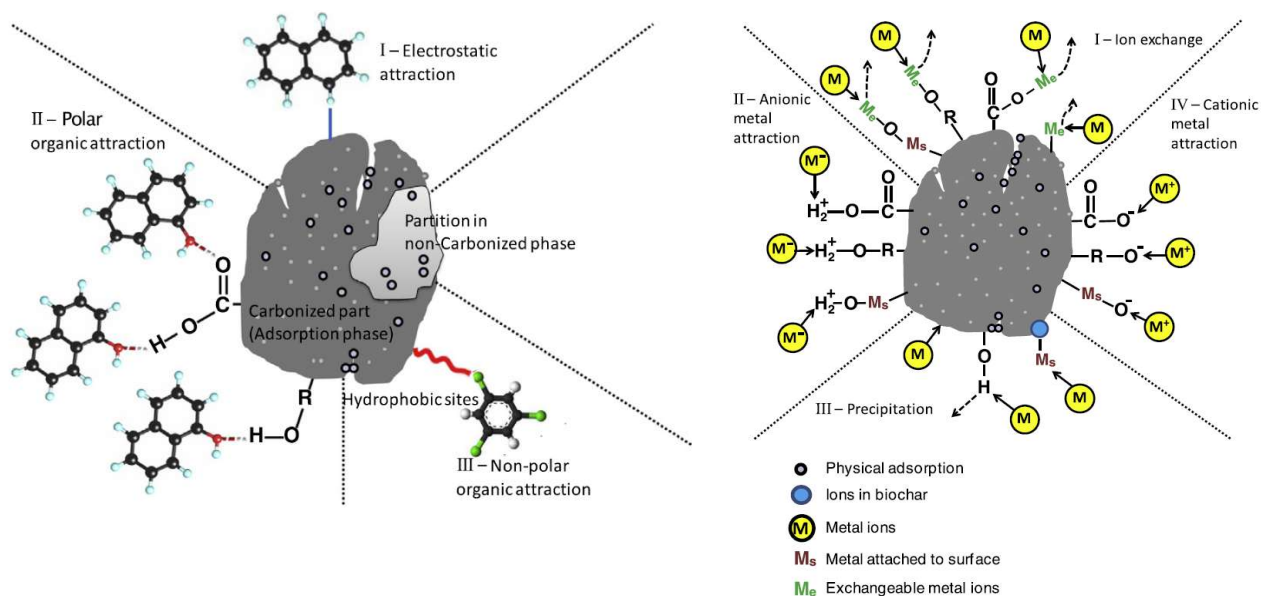


Figure 5 (left): Interaction of biochar with organic contaminants (Ahmad, et al., 2013)

Figure 6 (right): Interaction of biochar with inorganic contaminants (Ahmad, et al., 2013)

Another interaction mechanism that occurs in wood-char is electrostatic attraction. Inorganic contaminants, such as arsenic, lead, zinc, and copper, are bound by other mechanisms. The research paper of (Ahmad, et al., 2013) summarizes those interactions in Figure 6. Underlying mechanisms for inorganic contaminants are: 1) ion exchange between metal-like ions and exchangeable ions in the wood-char; 2) electrostatic attraction of anionic metal; 3) precipitation of inorganic pollutant; 4) electrostatic attraction of cationic metal; 5) physical adsorption of the metal-like ion to the surface of the wood-char.

Wood-char itself is not effectively adsorbing arsenic (Camino de Agua, 2017). However, impregnating chemical substances, with an affinity to bind with arsenic, onto the wood-char may increase the effectivity of arsenic removal. A number of potentially interesting chemical substances to impregnate wood-char with are listed in Table 3.

Table 3: Potentially interesting chemical substances discussed in literature to impregnate wood-char with

Chemical group	Chemical	Effect	Literature
Iron	Fe_2O_3	Adsorption of arsenic onto the adsorption sites provided by iron molecules	(Services, Severn Trent, 2007)
	$\text{Fe}(\text{OH})_3$	Adsorption of arsenic onto the adsorption sites provided by iron molecules	(Saldana-Robles, et al., 2017; Hu, et al., 2014)
	FeCl_3	Adsorption of arsenic onto the adsorption sites provided by iron molecules	(Qiao, et al., 2012; Pan, et al., 2014)
	$\text{Fe}(\text{II})$	Adsorption of arsenic onto the adsorption sites provided by iron molecules	(Shafiquzzaman, et al., 2010)
Titanium	TiO_2	Removal of arsenic by	(Pena, et al., 2005)

		forming particles with agglomerated TiO ₂	
Manganese	MnO ₂	Adsorption of arsenic onto the adsorption sites provided by manganese molecules	(Ouvrard, et al., 2001)
Aluminum	Al(NO ₃) ₃	Removal by precipitation of aluminum and arsenic	(Violante, et al., 2006)

All substances summarized in Table 3 were tried in literature and effectively impregnated onto wood-char and effectively removing arsenic. In this study the following substances will be impregnated onto the wood-char: Fe₂O₃, Fe(OH)₃ and FeCl₃. These substances are common in everyday products as etchants, are cheap, are available in chemical shops in Mexico and were therefore favorable compared to the other chemical substances.

3 Materials and method

3.1 Test water

The water used for testing originated from a well at the rural area near San Miguel de Allende known as Ex-hacienda de Jesus. The arsenic concentration increased since 2013, as displayed in Table 4. At this moment, the well has a arsenic concentration of ~80 µg per liter, which exceeds the WHO guideline of 10 µg per liter significantly. Arsenic concentration measured is the total arsenic in the water, in this case assumed to be mostly arsenate (+5). The well water is pumped to the surface and stored in cisterns, water harvesting tanks. Then it is either pumped to the tap in households or collected at the cistern itself. In some cases the households own biological filters, however it is safe to say the vast majority of the people in the communities do not have any treatment to remove contaminants such as arsenic. In total around 1150 people (230 families) are using this contaminated water. In addition, it is common that the affected people are unaware of their situation and lack knowledge about contamination in water and the impacts of the contamination on their health.

Table 4: Information on test water originated from a well at the Ex-Hacienda de Jesus community

	Ex-Hacienda de Jesus		WHO Guidelines
Date	13-3-2013	19-5-2014	2011
Well depth (m)	275		
Coliform (MPN/100mL)	<1		
E. coli (MPN/100 ml)	<1		
Water Temp (°C)	43,6		
pH	8,61	8,42	
Electronic Conductivity (mS/cm)	579		
Alkaninity (mg/L)	n/d		
Fluoride (mg/L)	16	17,2	1,5
Nitrate (mg/L)	1,18		50
Phosphate (mg/L)	0,2		
Turbidity (NTU)	<2		
Sulfate (mg/L)	63		No health concerns
Arsenic (ppb)	47	60	10

Camino de Agua has been doing quality assessment studies throughout the Guanajuato region in Mexico. Available information about the well in Ex-Hacienda de Jesus is displayed in Table 4. Arsenic and fluoride levels are clearly above the prescribed WHO guideline concentration and increase over time as the groundwater decreases because of groundwater exploitation. For testing, water is pumped to the surface and stored in water storage tanks of one cubic meter. Test water was collected at once at the start of the experiment and throughout this study the same water was used.

3.2 Filter media recipes

This section provides a brief description on how the different filter media were prepared. Detailed step-by-step methodologies to make the filter media are described in Appendix C. The tested combinations are summarized in a flowchart in Figure 7. However, not all possible combinations were tested.

3.2.1 High-temperature wood-char

Wood-char was made by filling a 200L drum with wooden blocks (~5 cm x 7 cm x 15 cm). The wood used was a mixture of scrap hard wood. The wood-char was made at a temperature range of 700-1000 °C in the biomass gasifier, and combustion took 120 minutes (+/- 15 minutes). This applies to the biomass that was charred in the biomass gasifier. It was decided to put the average burning temperature in three different ranges: low, middle and high (<600 °C; 600-850 °C; >850 °C). All chars were made with high temperature burns: >850 °C. Pyrolysis was stopped by pouring water in the drum and quenching the wood. The charred wood was collected and dried for 48 hours and afterwards crushed and sieved through a sieve with pores of 600 µm for batch test, and to a granular size (8 by 30 mesh) for column testing. All other (impregnated) wood-char filter media were made with this material and burned at high temperature.

3.2.2 Wood-char impregnated with Fe₂O₃

2.5 gram Fe₂O₃ was impregnated into 7.0 gram wet high-temperature wood biochar, with fines washed out with demineralized water (DI). 75 mL DI water was mixed with 2.5 gram Fe₂O₃ and 7.0 gram high temperature wood-char in a 90 mL test tube. This method was repeated for 10 test tubes. The whole solution was then mixed for four days. Afterwards the impregnated char was collected and washed with DI to wash the fines away and to make sure all Fe₂O₃ present was effectively impregnated. Then it was air dried for 2 days. Methodology was set-up by A. Krupp, a researcher at Caminos de Agua.

3.2.3 Iron-coated sand

Iron-coated sand was made by following a recipe inspired by earlier research (Benner, et al. 2002; Brooks, et al. 1996). First, a 500 mL solution was made with 0.1M ferric chloride and DI. This solution was titrated to a pH of 7.5 with 1M NaOH. The following reaction occurred:

The ferrihydrite flocs were settled for 24 hours and the supernatant was decanted. The flocs were then washed with a NaCl solution of 0.01M until a pH of 7.0 was reached. It then settled again for 24 hours followed by decanting of the supernatant. The flocs were resuspended in 200 mL 0.01 M NaCl and 270 gram of quartz sand was added. Then the slurry was mixed and the excess supernatant decanted. The iron-coated sand was then dried for 4 days at room temperature and was ready for use. Ferric chloride (0.4 %w/w) and sodium hydroxide were obtained at a local chemistry shop. Pure salt (NaCl) was used.

3.2.4 Pre-soaked FeCl₃ impregnated wood-char

An experiment described in literature (Tchomgui-Kamga, et al., 2009) was used to prepare wood impregnated with FeCl₃, which was then charred. Firstly, a drum was filled with wooden blocks (~5 cm x 7 cm x 15 cm) unto a volume of 100L. Then a 100L 0.1M solution of ferric chloride was made. Then, the solution was poured into the drum with the wooden blocks. It is important that the water level was higher than the wooden blocks. The wooden blocks were then drenched for 48 hours in the drum and then separated and sun dried for 4 days. Then the impregnated wooden blocks were charred in a biomass gasifier following the procedure described in section 2.4 and 3.2.1 above.

3.2.5 Post-soaked FeCl₃ impregnated wood-char

Based on the same literature as the above described method, post-soaked FeCl₃ impregnated was made. 200 gram of wood-char was soaked for 48 hours in a 2L solution of 0.1M FeCl₃ and then air-dried at room temperature for 48 hours.

3.2.6 Bayoxide® E33 arsenic removal media

Bayoxide® E33 is a commercial granular arsenic removal media and tested in this research to compare to the other filter media. The working component in this media is iron oxide (Fe₂O₃) as adsorptive media, and is claimed to reduce arsenic levels to below 4 µg/L. Thereby, the product is approved for use in potable water treatment by the UK secretary of State, the French Ministry of Health and the US National Sanitary Foundation. Technical details of Bayoxide® E33 are: (Severn Trent Services, 2007).

- Chemical designation: synthetic iron oxide
- Fe₂O₃ content >70%
- Specific surface area: 120 – 200 m²/g
- Sieve analysis: <0.5 mm, 20% max >2.0 mm, 5% max
- Bulk density: Approx. 0.4 – 0.6 kg/litre

A 1 kg jar of bayoxide® E33 was purchased and used for testing. All technical data was found online and is available through the website of Severn Trent services.

3.2.7 Ash-base wood-char

1.5 kg of ash from combustion with wood was mixed with 60 liters of tap-water in a 100L drum. Then, the pH was raised to 12.5 with sodium hydroxide. Finally, the drum was filled to the top with wooden blocks (~5 cm x 7 cm x 15 cm). The wooden blocks were then drenched for 24 hours in the drum and then separated and air dried for 4 days. Then the impregnated wooden blocks were charred in a biomass gasifier following the procedure detailed in section 2.4 above.

3.2.8 Ash-base wood-char post-soaked in FeCl₃

The ash-base wood-char described in section 3.2.7 was impregnated with FeCl₃, following the same methodology as section 3.2.5.

Figure 7: Flow-chart of the possible combinations of char preparations tested in this paper

3.3 Experiment set up

Assumptions for filter design

The objective (as discussed in chapter 1) formulated by Caminos de Agua was to create a filter medium effectively removing arsenic that lasts for at least three weeks, treating 25L of drinking water per day, based on a household of five people. This study first focused on testing the different filter media in batch mode, to understand the adsorption kinetics and to select the material with the highest adsorption capacity. Then the filter media with the highest adsorption capacity was tested in a column set-up, representing real-life conditions and test the life expectancy of the filter medium. It was decided that the volume of the column should be 0.450L, and fits ~150 gram of filter media. With the given dimensions and influent, it was decided that the filter media should have an adsorption capacity of 300 µg/gram in order to work effectively for 21 days (Figure 8). The adsorption capacity was calculated by dividing the amount of arsenic per sample volume adsorbed by the filter media and is based on an influent concentration of 80 µg/L.

Where,

q = Adsorption capacity (µg/g)

C_i = Initial concentration (µg/L)

C_f = Final concentration (µg/L)

V = Sample volume (L)

W = Amount of adsorbent (gram)

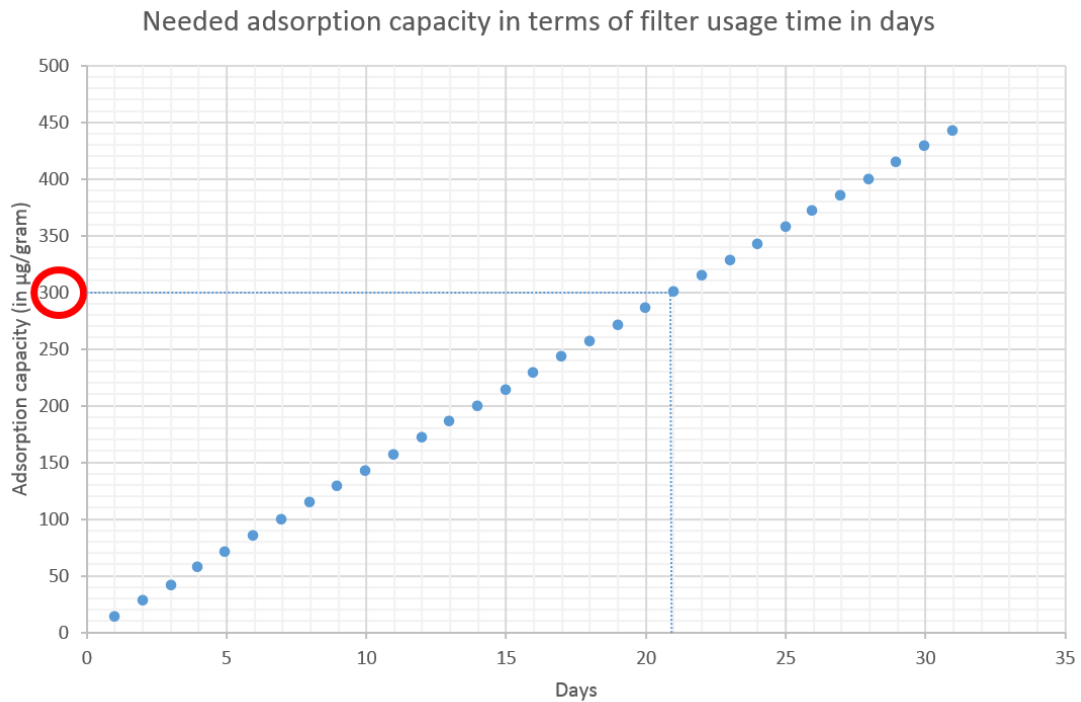


Figure 8: Desired adsorption capacity in terms of filter usage time of days

The batch test

The objective of the batch test was to gain insight in the adsorption kinetics, how fast arsenic is adsorbed, and how much arsenic (the adsorbate) can be adsorbed on a certain mass of filter medium (the adsorbent).

Batch tests were conducted to measure the adsorption capacity of a filter medium. To calculate the medium's capacity, it is crucial that (a) the media is saturated with contaminant and (b) some but not all of the contaminant has been removed from the solution. To ensure that the contamination level is reduced by 80-90% in the batch test, dose tests were performed. In each dose tests, 4-5 different doses (normally: 0.05; 0.1; 0.2; 0.5 and 1 gram) of char were tumbled with sample water with 80 µg/L arsenic for 24 hours. The dose that removed 40-50% of the arsenic after 24 hours was selected for the week-long batch test.

In the batch and dose test, the wood-char was crushed to a powder size around 600 µm (<30 mesh). An increased surface increases the available adsorption sites of the wood-char.

Batch testing took place in sample tubes with 93 mL well water and the mass of filter media determined by the aforementioned dose test while continuously stirred with a velocity of ~30-40 rpm by the rotator (Figure 9). Amount of filter media in grams per sample were decided upon after the dose test. For every filter media, arsenic concentration was measured over time at 0 minutes; 15 minutes; 30 minutes; 1 hour; 1,5 hour; 3 hours; 6 hours; 12 hours; 24 hours; 3 days; 7 days; 10 days and 14 days in duplicate, in separate sample tubes.

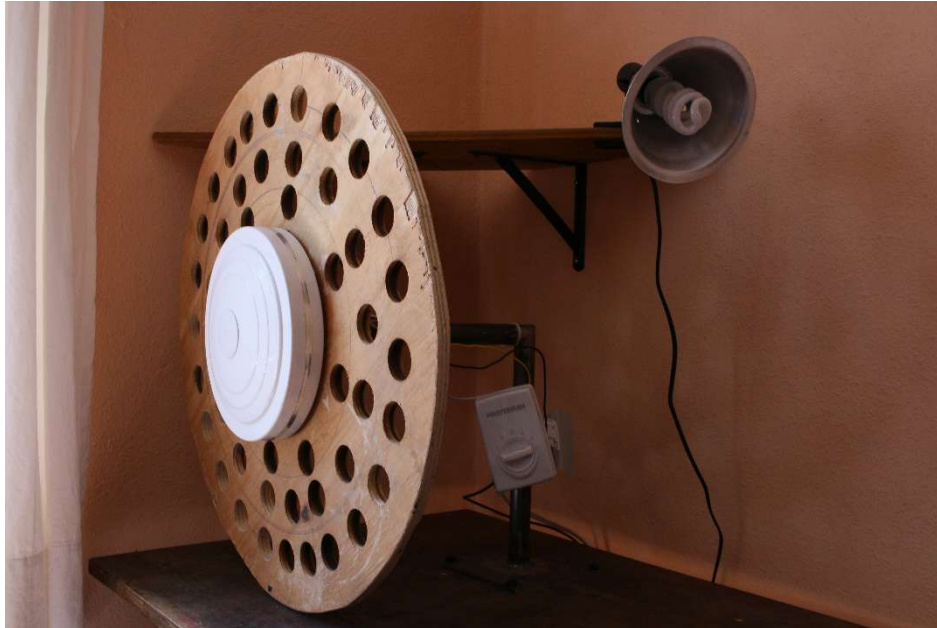


Figure 9: Rotator at the laboratory of Caminos de Agua

After the period of stirring the contact time was stopped by pouring the mixture of test water and filter media in a paper filter (ordinary coffee filter), separating the filter media from the water. Then the arsenic concentration was measured. pH and TDS were also measured. Analytical devices that were used in this research were discussed in the analytical methods part of this chapter.

From the observed data, a 95% confidence interval was computed to estimate the range in which a certain value was true. The upper bound and lower bound ranges were calculated with the formula for the 95% confidence interval:

Where,

CI = Confidence Interval

= Average

σ = Standard deviation

n = Sample size

The column test

In the column the char was crushed to a granular size (between a 8 x 30 mesh), still having a high surface area but avoiding drawbacks like fouling and maintaining an appropriate flowrate.

With the results from the batch tests, Caminos de Agua knows which filter medium is most promising for further research. The filter medium should be able to fulfil the WHO standard for arsenic concentration in drinking water of 10 $\mu\text{g}/\text{liter}$. However, only in real-life conditions it can be tested for how long a filter media may be used until the WHO guideline is exceeded. Therefore, filter media should be tested in a column test, which represents continuous usage.

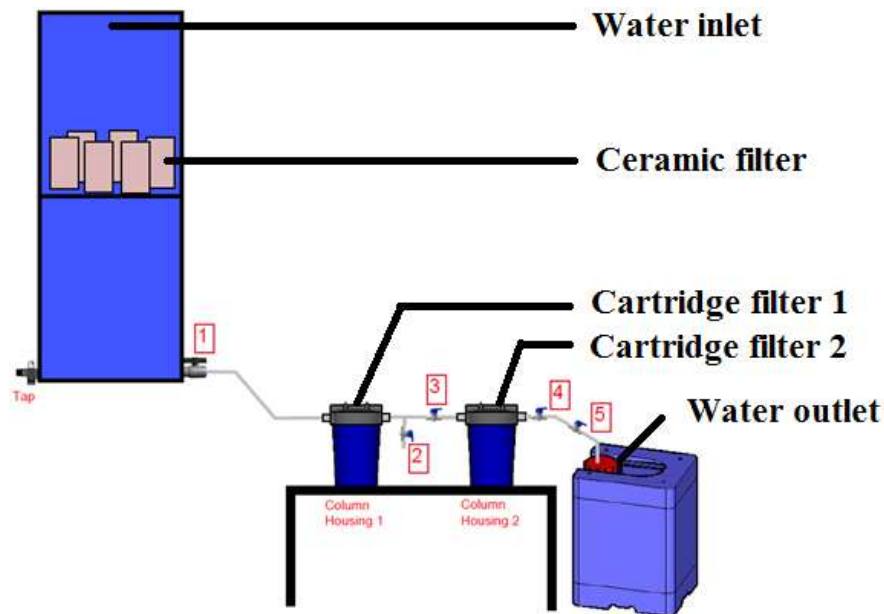


Figure 10: Technical drawing of the column set-up used in this research. Drawing by Caminos de Agua's volunteer S. Mitchell

The column test setup is designed to fulfil the daily drinking water needs for a family of five, and is able to treat 25L of water per day. One setup consists of two cartridge filters in series with a volume of 450 mL packed with 150 gram of filter medium. In the test phase, the two cartridge filters were connected to a ceramic filter, as designed by Caminos de Agua, to get rid of pathogens and bacteria. A technical drawing of the column test setup is given in Figure 10. Via a lid at the water inlet point the influent is put in the set-up, then the water flows through the ceramic filters and through tap 1 the water enters the column set-up. The column set-up uses the lead/lag configuration, a configuration to get a higher removal and usage efficiency out of the cartridge filters. Cartridge filter 1, the lead filter, is removing arsenic to acceptable levels, but when the effluent of cartridge filter 1 is above limits cartridge filter 2, the lag filter, will ensure that the final effluent is at acceptable levels. At the moment when the effluent of cartridge filter 2 is above the acceptable limit, it will replace cartridge filter 1 and a new cartridge filter 2 is placed into the set-up (Denning & Dvorak, 2009). The lead/lag configuration is visualized in Figure 11.

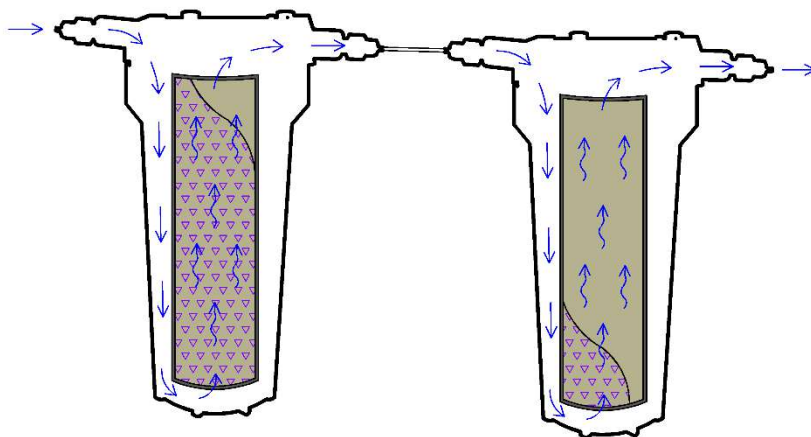


Figure 11: The lead/lag configuration. Drawing by Caminos de Agua's volunteer E. Diek.

A control with reverse osmosis treated water was run for one week, to check if any arsenic was coming off from either the ceramic filter

or the cartridge filters. The flow was set at 25L/day with valve 5. At valve 2 and 4 (see Figure 9), respectively after cartridge filter 1 and cartridge filter 2, water samples were taken every day at 8:00; 16:00; 0:00. At 16:00, a post-ceramic sample was taken from valve 1, and every three days a pre-ceramic sample was taken of the influent. On top of the ceramic filter is a lid, where 25L of water was poured in daily. The water samples were then tested for arsenic concentration, TDS, and pH.

After the control time, the column test was run with test water from the well at Ex-Hacienda de Jesus. As for the water sampling, the same methodology was applied. The experiment stopped when the water at valve 4 started showing concentrations of arsenic above the WHO limit of 10 µg/liter. With the results of the column test it was investigated how the filter media behaved over a period of time, and when they reached saturation. A detailed description of the column test methodology is added in Appendix B.

Analytical methods

Arsenic concentration in influent and effluent was measured with a Hach Dual Range Arsenic Test Kit, a color-change test-strip. Two reagents (zinc and sulfamic acid) were mixed with the sample, and the mixture gives off arsenic gas which causes a color change. Concentrations between 0 and 100 micrograms/liter can be measured. Figure 12 shows the test kit.



Figure 12: Hach Dual Range Arsenic Test Kit

Once the sample was taken, it was run through a paper filter (coffee filter), to stop the adsorption process by separating the solution from the adsorbent. A detailed methodology for arsenic testing is described in Appendix A.

pH and TDS were both measured with a simple pH-meter and TDS-meter, and were always well calibrated.

4 Results and discussion

For both the batch and column test, the arsenic concentration, TDS and pH were measured. Complete data sheets can be found in Appendix D, E and F for respectively the batch results and the column results. The most important data will be discussed in this section.

Adsorption kinetics

In total, eight different filter media were tested. The data on these filter media are summarized in Table 5. The post-treated wood-char and the ordinary wood-char all come from the same burn. The ash-base treated wood-char and pre-treated wood-char with FeCl₃ originate from separate burns. Notable adsorption capacities were reached when wood-char was post-treated with FeCl₃. The proprietary media bayoxide® E33 sets a control value.

Table 5: Summary of the prepared and tested arsenic removal filter media

Arsenic removal filter media	Material	Chemical pre-treatment	Burning temperature	Chemical post-treatment	Dose test highest adsorption capacity in µg/gram (After 24 hours)	Functional compound
Wood-char	Biomass: wood	None	>850 °C	None	8.77	Carbon
Wood-char with Fe₂O₃	Biomass: wood	None	>850 °C	Fe ₂ O ₃ addition	16.03	Carbon and Fe ₂ O ₃
Iron-coated sand	Sand	None	None	Fe(OH) ₃ addition	13.95	Carbon and Fe(OH) ₃
Wood-char with FeCl₃	Biomass: wood	FeCl ₃ addition	>850 °C	None	18.60	Carbon and FeCl ₃
Wood-char with FeCl₃	Biomass: wood	None	>850 °C	FeCl ₃ addition	55.52	Carbon and FeCl ₃
Bayoxide® E33	Proprietary media	None	None	None	>290.63	Fe ₂ O ₃
Wood-char with ash-base	Biomass: wood	Sodium hydroxide and addition of ash	>850 °C	None	16.32	Carbon and minerals
Wood-char with ash-base and FeCl₃	Biomass: wood	Sodium hydroxide and addition of ash	>850 °C	FeCl ₃	52.64	Carbon, minerals and FeCl ₃

From the eight filter media summarized in Table 5 only six were tested in batch: wood-char, iron-coated sand, wood-char pre-soaked in FeCl₃, wood-char post-soaked in FeCl₃, wood-char with ash-base and wood-char with ash-base and FeCl₃. Bayoxide E33® was excluded because it is a proprietary media and only tested in the dose test to compare with the other filter media. Wood-char with Fe₂O₃ was excluded in the batch test because the dose test showed very poor results and because of time limitations. The adsorption capacity of normal high temperature wood-char reached 8.77 µg/gram, but arsenic adsorption was very limited and didn't improve much when higher dosages were tried. The same applies to wood-char pre-

treated in FeCl_3 and ash-base treated wood-char, which were both tried in batch and reached respectively adsorption capacities of 18.60 and 16.32 $\mu\text{g}/\text{gram}$ in the dose tests. Because of similar results for Fe_2O_3 treated wood-char in the dose test, it was excluded from the batch test. The iron-coated sand reached adsorption capacities of 13.95 $\mu\text{g}/\text{gram}$. However, different from the above discussed filter media, when dosage was increased the arsenic was effectively removed.

All batch results data are included in Appendix E. Figure 13 displays the adsorption capacity of the filter media over a time period of 160 hours. High temperature wood-char did not efficiently remove any arsenic. When impregnated with ash and sodium hydroxide, the efficiency was not effectively improved. However, when FeCl_3 was impregnated onto the charred wood, the arsenic removal efficiency increased significantly from an adsorption capacity of ~ 3 $\mu\text{g}/\text{gram}$ towards ~ 55 $\mu\text{g}/\text{gram}$. Soaking the wood in FeCl_3 before pyrolysis proved have a smaller effect on the adsorption capacity compared to post-soaking. The functional compound in iron-coated sand, $\text{Fe}(\text{OH})_3$, effectively removed arsenic. However, the adsorption capacity only reached ~ 3 $\mu\text{g}/\text{L}$. It is believed that $\text{Fe}(\text{OH})_3$ impregnated on wood-char will have a higher adsorption capacity because of the high surface of wood-char compared to sand. However, impregnation of $\text{Fe}(\text{OH})_3$ into the pores of wood-char is hard because of the size of the iron hydroxide flocs. Further research should be carried out to come up with a methodology on how to effectively impregnate the iron hydroxide unto the wood-char. Figure 14 shows the effective arsenic removal with iron-coated sand. Figure 15 shows the effective arsenic removal with wood-char post-treated with FeCl_3 . In Appendix E, the other results are summarized. Base-ash treated wood-char post-treated with FeCl_3 shows similar results to wood-char post-treated with FeCl_3 . Bash-ash treated wood-char and normal wood-char show similar results as well, arsenic removal from 80 to 70 $\mu\text{g}/\text{L}$ after a few hours and does not change for 180 hours.

Figure 13: Comparison of the different filter media by comparing adsorption capacity

Figure 14: Arsenic adsorbed by iron-coated sand

Figure 15: Arsenic adsorbed by wood-char post-soaked with FeCl_3

The pH of the influent ranged between 8.5 and 9.3 throughout the research period of three months. Effluent pH decreased over time when high temperature wood-char and base-ash treated wood-char were used, respectively from 8.5 to 8.0 and 8.6 to 8.2. The filter media post-treated with iron substances had a bigger effect on pH. Iron-coated sand treated effluent changed from 9.3 to 8.2; wood-char post-soaked in FeCl_3 changed from 8.5 to 7.3; base-ash treated wood-char post-soaked in FeCl_3 changed from 8.6 to 7.3. It is believed that the decrease in pH contributes to a higher arsenic removal efficiency due to the arsenic species present at lower pH, as earlier research pointed out (Qiao, et al., 2012). The wood-char pre-soaked in FeCl_3 had a minor effect on pH, throughout time it fluctuated between 9.2 and 8.9.

TDS of the influent was around 280 mg/L and increased towards 300 mg/L for high temperature wood-char and wood-char pre-soaked in FeCl_3 . The filter media post-treated with iron substances resulted in a higher TDS around 320-330 mg/L. It is assumed that some solids were washed from the filter media over time resulting in a higher TDS.

Column test results

The results of the used wood-char post-soaked in FeCl_3 inside the cartridge filters are shown in Figure 16. A complete summary is displayed in Appendix F. This filter medium was chosen to test in the column set-up because it proved to be the most promising material after the batch tests. Arsenic concentrations rose above the acceptable limit of 10 $\mu\text{g/L}$ after 16 bed volumes in column 1, and after 50 bed volumes in column 2. 35 liters of contaminated groundwater were effectively treated with influent concentrations $\sim 40 \mu\text{g/L}$. That represents for 1,5 days' worth of drinking water for a household of 5 persons. The adsorption capacity reached in the batch test (55 $\mu\text{g/L}$), should be sufficient for at least 4 days treating an influent arsenic concentration with 80 $\mu\text{g/L}$. The influent arsenic concentration in the column test was twice as low, so it was estimated that the filter medium would last for 8 days instead of 1,5 days. There was no comparable literature study found to compare the results with and it is uncertain why the results turned out lower than expected. pH fluctuated around 8.4 and TDS slightly increased over time from 253 mg/L to 297 mg/L in column 1 and from 198 mg/L to 328 mg/L in column 2.

5 Conclusion

The four research questions from the introduction section are answered in this chapter.

Which substances have a strong affinity to arsenic?

The chemical substances FeCl_3 , Fe_2O_3 and $\text{Fe}(\text{OH})_3$ were investigated in this study because they proved to have worked in other studies in terms of removing arsenic by adsorption. FeCl_3 was effectively impregnated onto the wood-char and removed arsenic. Fe_2O_3 was not effectively impregnated onto the wood-char or/and did not substantially remove any arsenic. $\text{Fe}(\text{OH})_3$ was effectively coated onto sand and proved to remove arsenic efficiently. The other chemical substances that came out of the literature study were not tested due to time limitations.

What is a suitable way to make an impregnated biochar with a strong affinity to arsenic?

FeCl_3 and Fe_2O_3 were impregnated onto the wood-char by soaking the wood-char after/before pyrolysis in a solution concentrated with the iron substances. FeCl_3 proved to be more efficiently impregnated onto the wood-char after pyrolysis. When Fe_2O_3 was tried to be impregnated onto the wood-char after pyrolysis no substantial arsenic removal efficiently was observed. It is believed that the poor efficiency of Fe_2O_3 depends on the impregnation method, which clearly didn't work. The described methodology to make iron-coated sand with $\text{Fe}(\text{OH})_3$ proved to result in the making of a efficient filter media, although sand worked poorly as filter media material.

What is a suitable batch- and column methodology to test filter media for?

The methodology for testing filter media in batch- and column methodology as described in chapter 3 proved to be suitable for this study and was set-up after a period of trial and error. Although there are a few minor changes recommended, in general the methodology was good to work with, reliable and replicable. These recommendations will be discussed in the next chapter.

Which impregnated biochar is most promising, in terms of adsorption capacity, in lowering the arsenic concentration in contaminated groundwater to the WHO guideline?

From the filter media tested, wood-char post-soaked in FeCl_3 proved to have the highest adsorption capacity with 55 $\mu\text{g}/\text{g}$. The results of the column test however show that it only functioned for 1,5 days, providing 35L for a household of five people. Therefore, the main objective of this study to make a filter medium appropriate for treating 25L per day of contaminated groundwater for three weeks was not reached. However, this study set the foundation for future research into this problem, which is discussed in the recommendations chapter.

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6 Recommendations

Recommendation for methodology of testing

The methodology summarized in this research was corrected throughout and set-up at the time previous to testing. Even though limited by the technologies and laboratory luxuries at hand, the methodology proved to work well. The methodology for both batch and column testing described in this paper serves as a solid foundation for future research. A view minor recommendations for the methodology are in place:

- filters: the coffee filters used in the batch experiment are not always 100% effective separating the filter media from the water;
- arsenic test kits: if possible, it is recommended to use techniques like chromatography and spectrophotometry to measure arsenic concentrations because it is more reliable;
- characterization of the filter media: comparing internal surface and pore volume between the filter media.

Recommendation for making the filter media

The filter media are made in a few steps, as displayed in Figure X. The following section deals with the different steps and the associated recommendations.

The filter media material

The first step in the process of making a filter media fit for adsorption of arsenic is the selection of the filter media material. Although the focus of this research is on wood-char as the main filter media base, other materials like bone-char, sand, and a proprietary media have been tested as well. The proprietary medium was tested to compare the different filter media with once they were tested. Sand as an adsorbent media was tested to see if a certain method of impregnation with iron, the iron-coated sand, worked or not. Because the recipe for that particular media already existed it was decided to follow the same methodology. The methodology of iron-coated sand should be adapted so that it could be applied with wood-char. Other than that, the main focus was on biomass and especially wood-char. For future research, it is recommended to investigate a broader range of biomass feedstock for pyrolysis and compare them. The wood-type used in this research was a mixture of scrap wood, chopped in wooden blocks to a size of (~5 cm x 7 cm x 15 cm). Different wood types should be tested with the same methodology and be compared, and should always be locally available.

Chemical pre- and post-treatment

This section applies to biomass being pre- or post-treated with chemicals before or after being charred, so proprietary media and sand are not involved in that exact way. However, the iron-coated sand was made by chemical impregnation with $\text{Fe}(\text{OH})_3$. Chemical pre-

treatment and chemical post-treatment were both implemented in the process to investigate the difference it makes in terms of structural- and chemical change inside the char.

In this study, impregnation by iron addition was investigated. FeCl_3 was tested for both pre- and post-treatment, but proved to be more effective in terms of arsenic removal when the chemical was impregnated after the charring. Fe_2O_3 was only tested when impregnated after charring. Although the results weren't promising, it is recommended to try the pre-treatment with Fe_2O_3 step to compare the results. This information is important for understanding the underlying processes behind chemical addition and the structural, physical, or chemical changes it causes. With the iron-coated sand, the effectivity of $\text{Fe}(\text{OH})_3$ was tested and the results seem promising. However, this methodology should be applied to wood-char and tested for both pre- and post-treatment with $\text{Fe}(\text{OH})_3$ impregnation.

There are big differences in terms of arsenic removal efficiency when comparing normal wood-char to wood-char pre- or post-treated with chemicals. In future research more chemicals should be tested and compared. In the literature study previous to this research, a number of promising chemicals were found to impregnate the biochar with: Fe^{2+} , TiO_2 , MnO_2 and $\text{Al}(\text{NO}_3)_3$.

Acid and base treatment was not carefully investigated in this paper and is strongly recommended to be tested in future research. Impregnation by a base or an acid might change the structure of a biochar resulting in a higher surface area and improving the arsenic removal efficiency.

Burning temperature

This applies to the biomass that was charred in the biomass gasifier. It was decided to put the average burning temperature in three different ranges (<600 °C; 600-850 °C; >850 °C). All wood-char burns were carried out in the highest range. Future research should to investigate the differences in arsenic removal efficiency for wood burned at all three ranges, for the burning temperature may have an impact on the porosity and thereby effectivity of the wood-char.

Recommendations for future research in a nutshell

- Testing more different filter media as described in the section above:
 - $\text{Fe}(\text{OH})_3$ impregnated wood-char;
 - Acidic modified wood-char;
 - Trying different molar concentrations of FeCl_3 ;
 - Trying other chemical substances as: TiO_2 and MnO_2 .
- Oxidation of the test water to transform all arsenic to arsenate, and check how the removal efficiency differs from non-oxidized test water.
- pH control: research showed that arsenic removal is strongly influenced by pH (Qiao, et al., 2012). When pH was increased in Qiao's study, arsenic removal decreased. This

is associated with the different arsenic species at different pH levels. The same study showed that removal at a pH around 5-7 resulted in the highest removal rate (Qiao, et al., 2012). It should be investigated how decreasing the pH of the test water to pH 5-7 would improve the results

- Literature study on different methods of impregnation, to increase the effectivity of impregnation from the chemical towards the wood-char.
- When a filter media is effectively removing arsenic for the desired time:
 - Economic feasibility study;
 - What is the water price per liter? Is that feasible?
 - Social study;
 - How can you tell the people in the Mexican communities that they should not drink dirty water and that they should use the filter?
 - How can we design the system best to make it easy to use?
 - What happens after saturation of the filter medium?
 - Recovery: find out how to desorb arsenic from the filter medium so that it can be reused. But what to do with the arsenic concentrate?
 - Selling: is there a market for arsenic concentrate?
 - Dumping: disposal of arsenic in a landfill? What would be the impact?
 - Reuse: how can it be reused?
 - Dumping: disposal of the filter material and arsenic in a landfill?
- Safety study: the effluent was only evaluated on arsenic, pH and TDS. It is important to know if any iron substances were leaching from the impregnated char.

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Appendix A – Arsenic testing methodology

- 1) Rinse test tubes and the lid with deionized water (3 times);
- 2) Separate the lid from the test tube and wash the test tube with sample water (3 times);
- 3) Shake the lid vigorously and let them dry by air;
- 4) Once the lid's surface is visibly dry, carefully put the paper strip where the color change will occur on in the lid;
- 5) Fill the test tube with 50 ml sample water;
- 6) Set timer and open reagents 1 and 2 so they can be used immediately;
- 7) Put it the reagents 1 and 2 (zinc and sulfamic acid), and close the test tube with the lid. Then start the timer.
- 8) Carefully swirl the test tube by hand for 30 seconds so that the reagents will mix with the sample water, make sure the paper in the lid doesn't get wet;
- 9) Rest until 6:30 minutes, then swirl until 7:00 minutes. Rest until 13:00 minutes, swirl until 13:30. Stop timer at 20:00.
- 10) Remove the lid from the test tube and take out the paper, the paper will be colored. Read off the arsenic concentration with use of the appropriate table of colors and the corresponding concentration;

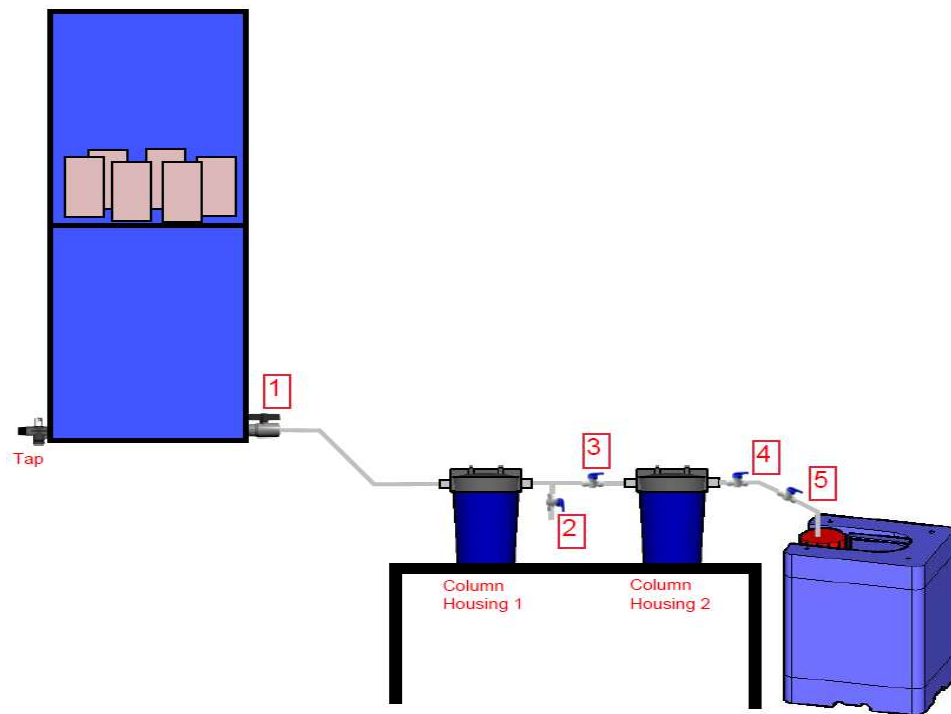
11) Note time and arsenic concentration. Multiple samples can be done at the same time by using multiple test tubes.

Appendix B – Column testing methodology

I. *Pre-start and start of column test*

Preparing the filter cartridges:

1. Fill two empty cartridge filters with the appropriate char as much as possible. The char should be about half a centimeter from the top of the cartridge.
1. Close the filters and compact the char by shaking them thoroughly for roughly 30 seconds.
2. Reopen the filters and add more char to within a few millimeters from the top.
3. Weigh the full cartridge filters to check they are roughly the same. If not, try to compact the lighter filter further by shaking and add more char. It is important not to break the grains of char, so do not compact the filter by hand. Shaking should suffice. Then weigh again. Repeat this until the cartridge filters weigh roughly the same.
4. Make a note of the weights and place the cartridges into the column housings.
5. Connect the column housings to the set-up.
6. Label the first column, closest to the influent water, “column 1.” Label the second column, closest to the effluent, “column 2.”



Running the column tests:

1. Before starting a column test with new char, baselines need to take place by running RO through the system. This also has the additional advantage of settling the char which is needed even if baselines do not need to take place.
1. Ensure that for each column set-up: valves 1, 2 and 4 are closed and that the tap on the lower container is closed.
2. Empty any water that is present in the top tub and place aside, on its side, so as not to dirty the underside of the ceramic filters. This may need the help of a second person.
3. Open the tap on the bottom tub until as much water as possible is drained. Scoop out any remaining water by tilting the tub.
4. Close the tap on the bottom tub, secure its lid and place the upper tub back in place.
5. Fill the upper container with RO water.

6. With the electric mixer, mix the water for 30 seconds and then take a pre-ceramic filter sample following the instructions under the 'taking samples' section.
7. Whilst waiting 30min until the following step, weigh each container that will be receiving flow from the column set-ups.
8. 30 minutes after step 7, take a post-ceramic filter sample following the instructions under the 'taking samples' section.
9. For each set-up, open valve 1, ensuring that valves 2, 3 and 4 are open. Valve 5 should be partially open or open to allow water to flow through.
10. As soon as water flows out the tube, close valve 4.
11. Press down on the red button on the top of column housing 2 to release air.
12. Without reopening valve 4, press down on the red button every few minutes to release air that is inside the column. Repeat this step until water is released.
13. When water is released upon pressing the red button, close valve 3.
14. Apply steps 12 & 13 to column housing 1 without adjusting any valves.
15. When water is released upon pressing the red button on column housing 1, open valve 3 and valve 4 so that flow enters the containers and make a note of the time.
16. Determine the flow rate of the column set-up and adjust valve 5 until a flowrate between the range of 17.5ml/min and 18.5ml/min is measured. Tip: this flowrate will typically occur when the valve is over half way closed therefore a good starting point is to set valve 5 to approximately half way closed and adjust accordingly from there.
18. Once satisfied that all column set-ups are operating within the correct flow range specified, **DO NOT** touch or adjust valve 5 at any subsequent time unless it's to readjust the flowrate back to within the range stated above.
19. The first set of samples should be taken as detailed in the following section as soon as all the set-ups are up and running at the correct flow rate.
20. If not carrying out baselines, only 50 bed volumes of RO water need to pass through the system.
21. After running RO water through the system for the desired period of time, close valve 4 followed by valve 1, ensuring valve 2 is already closed.
22. Repeat steps 3-5.
23. Fill the top tub with the diluted community water prepared earlier into the upper container.

24. Repeat steps 7-9.
25. For each set-up, open valve 1 and ensure that valves 2 and 4 are closed.
26. Press down on the red button on column housing 2 in case any air has gotten into the system.
27. If water is not released, press down on the red button every few minutes to release air that is inside the column. Repeat this step until water is released.
28. When water is released upon pressing the red button, close valve 3 and repeat the process for column housing 1.
29. When water is released upon pressing the red button on column housing 1, open valves 3 and 4 while ensuring that the end of the tubes are positioned above their respective containers to receive the outflow from column 2.

I. *Taking samples*

Instructions on how to label sample bags can be found on tab “Sampling Timetable” in the data collection spreadsheet.

Pre-Ceramic samples:

1. A pre-ceramic sample should be taken every time the large upper tub is filled with water as detailed in the following procedure.
1. Label a sample bag with the corresponding code (01 for a pre-ceramic sample, followed by the correct letter) and the date. Instructions on how to label sample bags can be found on tab “Sampling Timetable” in the data collection spreadsheet.
2. Fill the large upper tub to the top and mix for 30 seconds using the electric paint mixer.
3. Scoop enough water from the tub to fill $\frac{3}{4}$ of the bag, then close.
4. Weigh the bag and write the weight on the bag.
5. The final label on the bags should be as follows: LABELCODE - DATE – WEIGHT
e.g. 32C - 17/3 - 198

Post-Ceramic samples:

1. A post-ceramic sample should be taken prior to every time samples are taken from columns 1 and 2.
2. Label a sample bag with the corresponding code (02 for a post-ceramic sample, followed by the correct letter) and the date. Instructions on how to label sample bags can be found on tab "Sampling Timetable" in the data collection spreadsheet.
3. Open the tap on the large lower tub and fill $\frac{3}{4}$ of the sample bag, then close.
4. Weigh the bag and write the weight on the bag.
5. The final label on the bags should be as follows: LABELCODE - DATE – WEIGHT
e.g. 32C - 17/3 - 198

Column samples:

1. As soon as the correct flowrates for each column have been achieved, the first set of samples can be taken. However, the total volume of water passed through each column should be captured in each set-ups' respective containers while trying to achieve this flow.
1. Samples should be taken from column 1 first, then 2.
2. Label all sample bags with the corresponding code and the date. Instructions on how to label sample bags can be found on tab "Sampling Timetable" in the data collection spreadsheet.
3. Prepare the corresponding sample bags for columns 1 on the hooks and place them over valve 2 for each respective set-up. The outlet of the tube from valve 2 should be positioned in the sample bag.

4. For each set-up, operate the valves as follows: close valve 4 followed by valve 3 so that no air gaps are formed. Make a note of the time to enter into the data collection spreadsheet afterwards.
5. Consecutively for each set-up, open valve 2 as slowly as possible until the flow rate appears similar to that which flows out of column 2 (no flow should be coming from column 2 at this time).
6. While the sample bags are filling, weigh the containers in the same order that valves 2 were operated in order to ascertain how much water has passed through the columns since the last sample was taken. *Note: it may be safer to take samples from two set-ups at a time (rather than all 4) so that there is sufficient time to measure the containers before the sample bags are full. This will depend on the amount of time since the last sample was taken, and the capacity of the scale.*
7. Weigh the empty container (to deduct from the volume weight at the next sampling time) and place back under the outlet of its corresponding set-up.
8. Place the pre-labelled sample bag for column 2 of the corresponding set-up into the opening of the jerry can whereby the handles of the bag are sitting over the edge.
9. When the sample bags are $\frac{3}{4}$ full from column 1, operate the valves in the following order: close valve 2, open valve 3, open valve 4. Ensure that the outflow is going directly into the sample bag for column 2.
10. Carefully remove the bag and hook from valve 2 and close the bag.
11. Repeat this procedure for each set-up.
12. When all samples have been taken, weigh the bags and write the weights on the bags.

Appendix C – Char Recipes

High temperature wood char

Materials

- 200L Biomass gasifier
- Wooden blocks (~5 cm x 7 cm x 15 cm)
- ~50L water
- Collection bag
- (Temperature probe)

Method

- 1) Cut wooden blocks in pieces of around 5 cm x 7 cm x 15 cm;
- 2) Fill the 200L reactor body of the biomass gasifier with the wooden blocks;
- 3) Light a fire on top of the wooden blocks and carefully place the chimney on the reactor body;
- 4) Wait until the pyrolysis is completed, normally this takes around 120 minutes. Pyrolysis is done when all biomass is charred, the fire will turn from normal campfire color to pale blue;
- 5a) Take off the chimney and pour water over the char and the reactor body to stop burning and lower the temperature. Afterwards the char can be collected right away in a bag.

Or

- 5b) Take off the chimney and put a lid on the reactor body and make it airtight with mud to stop the burning. After 12 hours, the char will be cooled down and ready to collect.

Note: for e.g. academic purposes it might be useful to know at what temperature the pyrolysis is done, because the temperature says something about the quality of the char. Place a temperature probe in the top, the middle, and the bottom of the reactor body and measure the temperature of each place throughout time.

Wood-char impregnated with Fe₂O₃ – Recipe

Idea by Aaron Krupp

Materials

- 75mL DI water
- 2.5 gram Fe₂O₃
- 7.0 gram high temp wood biochar

Method

- 1) Mix all ingredients in 90mL tumbler tube;
- 2) Close lid tightly with teflon tape;
- 3) Tumble on speed 1 for 4 days;
- 4) Collect char on a mesh and wash with DI until the water coming off is clear (some Fe_2O_3 will be washed away);
- 5) Air dry the char for 1 days.

Iron-coated sand – Recipe

Experiment inspired by research of (Benner, et al. 2002; Brooks, et al. 1996)

Materials

- NaCl solution (0.01 M, pH adjusted to 7)
- FeCl₃ solution (ferric chloride, 500 ml of 0.1M)
- NaOH solution (1M)
- Stirrer
- Clean sand
- pH measuring device
- Containers (minimal 1L)

Method

- 1) Make a solution of 500 ml with 0.1 M ferric chloride;
- 2) Titrate with NaOH (1M) to a pH of 7.5;
Reaction: $3 \text{NaOH} + \text{FeCl}_3 \rightarrow 3 \text{NaCl} + \text{Fe(OH)}_3$
- 3) Let the ferrihydrite floc settle for 24 hours, then decant the supernatant;
- 4) Wash flocs with a diluted NaCl solution of 0.01 M, adjust to a pH of 7;
- 5) Repeat settling, decanting and resuspend in 200 ml 0.01 M NaCl;
- 6) Add 270 gram of quartz sand;
- 7) Mix the slurry and finally decant any excess solution;
- 8) Dry at room temperature for 4 days;
- 9) Collect the iron-coated sand.

Pre-soaked FeCl₃ wood-char – Recipe

Experiment inspired by research of (Tchomgui-Kamga, et al., 2009)

Materials

- 3L of ordinary ferric chloride solution (0.4 m/m)
- 97L of tap water
- A drum full of wooden blocks (~5 cm x 7 cm x 15 cm), around 200L
- Drying plates
- Biomass gasifier
- 2 containers of 150L/200L

Method

- 1) Fill a container with wooden blocks unto a volume of 100L;
- 2) Make a 0.1M solution of ferric chloride for 100L. In most cases, with an ordinary ferric chloride solution of 0.4 m/m, pour 3L of ferric chloride solution in 97L of ordinary water;
- 3) Pour the ferric chloride solution into the container with the wooden chips. Make sure that the water level is higher than the wooden chips, in order to completely soak all the chips;
- 4) Let it rest for 48 hours, so that the wooden chips are completely drenched;
- 5) Separate the wooden chips from the solution and dry the wooden chips for 4 days;
- 6) Burn the wooden blocks in a biomass gasifier until the char is ready;
- 7) Collect your pre-soaked FeCl₃ impregnated wood-char.

Post-soaked FeCl₃ wood-char – Recipe

Experiment inspired by research of (Tchomgui-Kamga, et al., 2009)

Materials

- 50 mL of ordinary ferric chloride solution (0.4 m/m)
- 2L deionized water
- 200 g high temperature wood-char
- 10L bucket
- Stirring stick

Method

- 1) Fill a 10L bucket with 2L deionized water;
- 2) Pour 50 mL ferric chloride into the deionized water to make a 0.1M FeCl₃ solution and mix to homogenize the solution;
- 3) Pour 200 gram of high temperature wood-char into the solution and mix for 5 minutes;
- 4) Soak the wood-char like this for 48 hours and cover the bucket with a lid;
- 5) Air-dry the wood-char at room temperature for 48 hours;
- 6) Collect your post-soaked FeCl₃ impregnated wood-char.

Base/ash wood-char – Recipe

Materials

- Sodium hydroxide
- Wooden blocks (~5 cm x 7 cm x 15 cm)
- 200L drum
- 60L of tap water
- pH probe
- 1.5 kg of wood ash
- Biomass gasifier

Method

- 1) Fill a 200L drum with 60L of tap water;
- 2) Add sodium hydroxide to the drum with tap water and raise the pH to 12.5, then add 1.5 kg of ash and mix the solution for 10 minutes;
- 3) Add the wooden blocks into the solution until the drum is filled with wooden blocks, while maintaining a higher water surface;
- 4) Soak the wood like this for 24 hours and cover the bucket with a lid;
- 5) Air-dry the wood-char at room temperature for 48 hours;
- 6) Then, fill the biomass gasifier and start the pyrolysis as any other;
- 7) Collect the base/ash wood-char

Base/ash wood-char post-soaked in FeCl₃ – Recipe

Experiment inspired by research of (Tchomgui-Kamga, et al., 2009)

Materials

- 50 mL of ordinary ferric chloride solution (0.4 m/m)
- 2L deionized water
- 200 g base/ash wood-char
- 10L bucket
- Stirring stick

Method

- 1) Fill a 10L bucket with 2L deionized water;
- 2) Pour 50 mL ferric chloride into the deionized water to make a 0.1M FeCl₃ solution and mix to homogenize the solution;
- 3) Pour 200 gram of the base/ash wood-char into the solution and mix for 5 minutes;
- 4) Soak the wood-char like this for 48 hours and cover the bucket with a lid;
- 5) Air-dry the wood-char at room temperature for 48 hours;
- 6) Collect your base/ash post-soaked FeCl₃ impregnated wood-char.

Appendix D – Dose test results

Wood-char pre-soaked in FeCl₃										
Initial concentration: 80 µg/L										
Dosage (gram)	0,033	0,033	0,1	0,1	0,15	0,15	0,3	0,3		
Concentration after 24 hours (ppm)	80	80	20	50	60	60	50	25		
Arsenic adsorbed (ppm)	0	0	60	30	20	20	30	55		
Adsorption capacity	0	0	55,8	27,9	12,4	12,4	9,3	17,05		
Iron-coated sand										
Initial concentration: 80 µg/L										
Dosage (gram)	0,2	0,2	0,5	0,5	1	1	2	2		
Concentration after 24 hours (ppm)	60	50	50	50	50	40	20	25		
Arsenic adsorbed (ppm)	20	30	30	30	30	40	60	55		
Adsorption capacity	9,3	13,95	5,58	5,58	2,79	3,72	2,79	2,56		
High temperature wood-char										
Initial concentration: 60 µg/L										
Dosage (gram)	0,1		0,2		0,5		1			
Actual dosage (gram)	0,106	0,122	0,217	0,207	0,529	0,52	0,967	1,022		
Concentration after 24 hours (ppm)	50	50	50	45	60	50	50	45		
Arsenic adsorbed (ppm)	10	10	10	15	0	10	10	15		
Adsorption capacity	8,77	7,62	4,29	6,74	0	1,79	0,96	1,36		
Wood-char post-soaked in FeCl₃										
Initial concentration: 60 µg/L										
Dosage (gram)	0,05		0,1		0,2		0,5		1	
Actual dosage (gram)	0,051	0,067	0,103	0,109	0,201	0,213	0,518	0,503	1	1,001
Concentration after 24 hours (ppm)	30	20	15	15	5	5	2	0	0	0
Arsenic adsorbed (ppm)	30	40	45	45	55	55	58	60	60	60
Adsorption capacity	54,71	55,52	40,63	38,39	25,45	24,01	10,41	11,09	5,58	5,57
Base-ash treated wood-char post-soaked in FeCl₃										
Initial concentration: 80 µg/L										
Dosage (gram)	0,05		0,1		0,2		0,5		1	
Actual dosage	0,053	0,055	0,1	0,102	0,193	0,205	0,417	0,503	1,115	1,001

(gram)											
Concentration after 24 hours (ppm)	50	50	35	30	10	10	0	0	0	0	0
Arsenic adsorbed (ppm)	30	30	45	50	70	70	80	80	80	80	80
Adsorption capacity	52,64	50,73	41,85	45,59	33,73	31,76	17,84	14,79	6,67	7,43	
Wood-char impregnated with Fe2O3											
Initial concentration: 80 µg/L											
Dosage (gram)	0,05		0,10		0,20		0,50		1,00		
Actual dosage (gram)	0,058	0,064	0,109	0,113	0,201	0,214	0,514	0,505	1,016	0,987	
Concentration after 24 hours (ppm)	70	70	70	70	70	70	60	60	60	60	
Arsenic adsorbed (ppm)	10	10	10	10	10	10	20	20	20	20	
Adsorption capacity	16,03	14,53	8,53	8,23	4,63	4,35	3,62	3,68	1,83	1,88	
Bayoxide E33®											
Initial concentration: 80 µg/L											
Dosage (gram)	0,025		0,05		0,1		0,2		0,5		
Actual dosage (gram)	0,024	0,026	0,055	0,059	0,098	0,102	0,211	0,206	0,537	0,521	
Concentration after 24 hours (ppm)	5	5	0	0	0	0	0	0	0	0	0
Arsenic adsorbed (ppm)	75	75	80	80	80	80	80	80	80	80	80
Adsorption capacity	290,63	268,2	135,2	126,1	75,92	72,94	35,26	36,12	13,85	14,28	
Base-ash treated wood-char											
Initial concentration: 80 µg/L											
Dosage (gram)	0,05		0,10		0,20		0,50		1,00		
Actual dosage (gram)	0,049	0,057	0,115	0,125	0,222	0,179	0,472	0,502	1,062	1,021	
Concentration after 24 hours (ppm)	75	70	70	70	60	60	50	50	40	40	
Arsenic adsorbed (ppm)	5	10	10	10	20	20	30	30	40	40	
Adsorption capacity	9,49	16,32	8,09	7,44	8,38	10,39	5,91	5,56	3,50	3,64	

Appendix E – Batch test results

High temperature woodchar						
Time (in hours)	pH A	pH B	Average pH	TDS A (mg/L)	TDS B (mg/L)	Average TDS (mg/L)
0,00001	8,5	8,5	8,5	285	285	285
0,25	7,7	7,7	7,7	291	286	288,5
0,5	7,7	7,7	7,7	294	296	295
1	7,8	7,7	7,75	293	291	292
1,5	8	8	8	295	295	295
3	8	8,1	8,05	301	294	297,5
6	8	8	8	297	297	297
12	8	8,1	8,05	302	299	300,5
24	8	8	8	299	302	300,5
48	8,1	8	8,05	301	301	301
72	8	8	8	296	295	295,5
86	8	8	8	301	298	299,5
168	8	8	8	301	300	300,5

High temperature woodchar													
Date	Time	Volume (L)	(A) Actual amount of filter media (gram)	(B) Actual amount of filter media (gram)	[As] A (ppb)	[As] B (ppb)	As A removed	As B removed	Average	Sigma (sd)	N (sample size)	Error	
25-5-2017	9:10	0,00001	0,093	0	0	80	80	0	0	0	0,00	2	
	9:25	0,25	0,093	0,498	0,488	70	70	10	10	10	0,00	2	
	9:40	0,5	0,093	0,508	0,507	70	70	10	10	10	0,00	2	
	10:10	1	0,093	0,498	0,524	70	70	10	10	10	0,00	2	
	10:40	1,5	0,093	0,517	0,499	70	70	10	10	10	0,00	2	
	12:10	3	0,093	0,511	0,504	70	70	10	10	10	0,00	2	
	15:10	6	0,093	0,562	0,486	70		10	10	10	0,00	2	
	21:10	12	0,093	0,511	0,5	70	70	10	10	10	0,00	2	
26-5-2017	9:10	24	0,093	0,506	0,494	70	70	10	10	10	0,00	2	
27-5-2017	9:10	48	0,093	0,512	0,546	70	70	10	10	10	0,00	2	
28-5-2017	9:10	72	0,093	0,495	0,5	70	65	10	15	13	3,54	2	
29-5-2017	9:10	86	0,093	0,504	0,496	70	70	10	10	10	0,00	2	
1-6-2017	9:10	168	0,093	0,5	0,548	70	70	10	10	10	0,00	2	

Iron-coated sand						
Time (in hours)	pH A	pH B	Average pH	TDS A (mg/L)	TDS B (mg/L)	Average TDS (mg/L)
0,00001	9,3	9,1	9,2	284	273	278,5
0,25	9	9,2	9,1	295	297	296
0,5	9,1	9,1	9,1	302	299	300,5
1	9	9	9	300	304	302
1,5	9,1	9,1	9,1	290	289	289,5
3	9,1	8,9	9	289	296	292,5
6	8,8	8,9	8,85	308	305	306,5
12	9	9,1	9,05	304	301	302,5
24	8,6	8,6	8,6	288	289	288,5
72	8,4	8,4	8,4	307	309	308
168	8,5	8,4	8,45	318	310	314
240	8,3	8,3	8,3	305	340	322,5
336	8,3	8,2	8,25	320	329	324,5

Iron-coated sand										
Date	Time	Char per sample (gram)	Volume (L)	[As] A (ppb)	[As] B (ppb)	As A removed (ppb)	As B removed (ppb)	Average As removed in ppb	Sigma (sd)	
20-4-2017	11:10	0,00001	2	0,093	80	80	0	0	0,0	
	11:25	0,25	2	0,093	30	40	50	40	7,1	
	11:40	0,5	2	0,093	40	45	40	35	3,5	
	12:10	1	2	0,093	55	35	25	45	14,1	
	12:40	1,5	2	0,093	30	50	50	30	14,1	
	14:10	3	2	0,093	30	40	50	40	7,1	
	17:10	6	2	0,093	20	20	60	60	0,0	
	23:10	12	2	0,093	20	20	60	60	0,0	
21-4-2017	11:10	24	2	0,093	17	19	63	61	1,4	
23-4-2017	11:10	72	2	0,093	15	20	65	60	3,5	
27-4-2017	11:10	168	2	0,093	20	17	60	63	2,1	
30-4-2017	11:10	240	2	0,093	17	15	63	65	1,4	
4-5-2017	11:10	336	2	0,093	15	17	65	63	1,4	

High temperature woodchar presoaked with FeCl3						
Time (in hours)	pH A	pH B	Average pH	TDS A (mg/L)	TDS B (mg/L)	Average TDS (mg/L)
0,00001	9,3	9,1	9,2	284	273	278,5
0,25	9,2	9,2	9,2	302	296	299
0,5	9,2	9,2	9,2	293	294	293,5
1	9,2	9,2	9,2	290	295	292,5
1,5	9,2	9,2	9,2	274	285	279,5
3	9,2	9,2	9,2	288	283	285,5
6	9	9,1	9,05	286	283	284,5
12	9,2	9,2	9,2	292	290	291
24	8,9	8,8	8,85	285	284	284,5
72	9,1	9,1	9,1	290	292	291
168	8,9	8,8	8,85	298	297	297,5
240	9,1	9	9,05	301	304	302,5
336	9	9,1	9,05	300	303	301,5

High temperature wood-char pre-soaked with FeCl3											
Date	Time		Char per sample (gram)	Volume (L)	[As] A (ppb)	[As] B (ppb)	As A removed (ppb)	As B removed (ppb)	Average As removed in ppb	Sigma (sd)	
20-4-2017	11:10	0,00001	0,3	0,093	80	80	0	0	0	0,0	
	11:25	0,25	0,3	0,093	55	55	25	25	25	0,0	
	11:40	0,5	0,3	0,093	55	55	25	25	25	0,0	
	12:10	1	0,3	0,093	60	60	20	20	20	0,0	
	12:40	1,5	0,3	0,093	60	60	20	20	20	0,0	
	14:10	3	0,3	0,093	45	50	35	30	32,5	3,5	
	17:10	6	0,3	0,093	40	45	40	35	37,5	3,5	
	23:10	12	0,3	0,093	40	50	40	30	35	7,1	
21-4-2017	11:10	24	0,3	0,093	40	35	40	45	42,5	3,5	
23-4-2017	11:10	72	0,3	0,093	50	40	30	40	35	7,1	
27-4-2017	11:10	168	0,3	0,093	30	40	50	40	45	7,1	
30-4-2017	11:10	240	0,3	0,093	25	50	55	30	42,5	17,7	
4-5-2017	11:10	336	0,3	0,093	50	50	30	30	30	0,0	

High temperature wood-char post-soaked with FeCl3						
Time (in hours)	pH A	pH B	Average pH	TDS A (mg/L)	TDS B (mg/L)	Average TDS (mg/L)
0,00001	8,5	8,5	8,5	285	285	285
0,25	7,3	7,4	7,35	302	302	302
0,5	7,4	7,5	7,45	297	300	298,5
1	7,5	7,8	7,65	297	300	298,5
1,5	7,9	7,9	7,9	306	309	307,5
3	7,9	7,9	7,9	302	306	304
6	7,8	7,8	7,8	299	304	301,5
12	7,9	8	7,95	312	304	308
24	7,8	8	7,9	305	314	309,5
48	8	7,9	7,95	307	309	308
72	7,9	8	7,95	305	305	305
86	7,8	8	7,9	306	307	306,5
168	7,8	7,9	7,85	309	307	308

High temperature wood-char post-soaked with FeCl3												
Date	Time	Volume (L)	(A) Actual amount of filter media (gram)	(B) Actual amount of filter media (gram)	[As] A (ppb)	[As] B (ppb)	As A removed	As B removed	Average	Sigma (sd)	N (sample size)	E
25-5-2017	9:10	0,00001	0,093	0	0	80	80	0	0	0,0	0,00	2
	9:25	0,25	0,093	0,099	0,108	50	50	30	30	30,0	0,00	2
	9:40	0,5	0,093	0,107	0,101	50	50	30	30	30,0	0,00	2
	10:10	1	0,093	0,099	0,1	40	40	40	40	40,0	0,00	2
	10:40	1,5	0,093	0,098	0,104	40	40	40	40	40,0	0,00	2
	12:10	3	0,093	0,105	0,1	35	40	45	40	42,5	3,54	2
	15:10	6	0,093	0,104	0,109	40	35	40	45	42,5	3,54	2
	21:10	12	0,093	0,124	0,104	30	35	50	45	47,5	3,54	2
26-5-2017	9:10	24	0,093	0,106	0,104	25	25	55	55	55,0	0,00	2
27-5-2017	9:10	48	0,093	0,103	0,112	20	20	60	60	60,0	0,00	2
28-5-2017	9:10	72	0,093	0,118	0,1	15	20	65	60	62,5	3,54	2
29-5-2017	9:10	86	0,093	0,096	0,103	20	20	60	60	60,0	0,00	2
1-6-2017	9:10	168	0,093	0,096	0,113	20	15	60	65	62,5	3,54	2

Base-ash treated wood-char						
Time (in hours)	pH A	pH B	Average pH	TDS A (mg/L)	TDS B (mg/L)	Average TDS (mg/L)
0,00001	8,6	8,6	8,6	287	291	289
0,25	8,5	8,4	8,45	316	314	315
0,5	8,4	8,4	8,4	309	302	305,5
1	8,3	8,3	8,3	314	298	306
1,5	8,3	8,3	8,3	316	298	307
3	8,3	8,3	8,3	319	303	311
6	8,3	8,3	8,3	314	317	315,5
12	8,2	8,3	8,25	315	314	314,5
24	8,4	8,3	8,35	307	302	304,5
48	8,3	8,3	8,3	312	315	313,5
72	8,2	8,3	8,25	312	319	315,5
86	8,3	8,3	8,3	322	314	318
168	8,3	8,2	8,25	317	318	317,5

Base-ash treated wood-char												
Date	Time	Volume (L)	(A) Actual amount of filter media (gram)	(B) Actual amount of filter media (gram)	[As] A (ppb)	[As] B (ppb)	As A removed	As B removed	Average	Sigma (sd)	N (sample size)	
14-6-2017	10:25	0,00001	0,093	0	0	80	80	0	0	0	0	2
	10:40	0,25	0,093	0,464	0,52	70	70	10	10	10	0	2
	10:55	0,5	0,093	0,486	0,498	70	70	10	10	10	0	2
	11:25	1	0,093	0,464	0,464	70	70	10	10	10	0	2
	11:55	1,5	0,093	0,48	0,465	70	70	10	10	10	0	2
	13:25	3	0,093	0,505	0,541	70	70	10	10	10	0	2
	16:25	6	0,093	0,462	0,528	70	70	10	10	10	0	2
	22:25	12	0,093	0,502	0,488	70	70	10	10	10	0	2
15-6-2017	10:25	24	0,093	0,568	0,498	70	70	10	10	10	0	2
16-6-2017	10:25	48	0,093	0,415	0,504	70	70	10	10	10	0	2
17-6-2017	10:25	72	0,093	0,35	0,512	70	70	10	10	10	0	2
18-6-2017	10:25	86	0,093	0,494	0,487	70	70	10	10	10	0	2
21-6-2017	10:25	168	0,093	0,419	0,497	70	70	10	10	10	0	2

Base-ash treated wood-char post-soaked with FeCl3						
Time (in hours)	pH A	pH B	Average pH	TDS A (mg/L)	TDS B (mg/L)	Average TDS (mg/L)
0,00001	8,6	8,6	8,6	287	291	289
0,25	7,5	7,5	7,5		325	325
0,5	7,5	7,5	7,5	329	323	326
1	7,5	7,5	7,5	322	325	323,5
1,5	7,4	7,4	7,4	322	323	322,5
3	7,4	7,4	7,4	330	328	329
6	7,4	7,4	7,4	322	336	329
12	7,4	7,4	7,4	324	326	325
24	7,3	7,3	7,3	318	326	322
48	7,3	7,3	7,3	328	328	328
72	7,3	7,3	7,3	330	333	331,5
86	7,3	7,3	7,3	326	339	332,5
168	7,3	7,3	7,3	326	315	320,5

Base-ash treated wood-char impregnated with FeCl3												
Date	Time	Volume (L)	(A) Actual amount of filter media (gram)	(B) Actual amount of filter media (gram)	[As] A (ppb)	[As] B (ppb)	As A removed	As B removed	Average	Sigma (sd)	N (sample size)	
14-6-2017	10:25	0,00001	0,093	0	0	80	80	0	0	0	0,00	2
	10:40	0,25	0,093	0,107	0,09	50	50	30	30	30	0,00	2
	10:55	0,5	0,093	0,093	0,103	50	50	30	30	30	0,00	2
	11:25	1	0,093	0,097	0,092	35	40	45	40	43	3,54	2
	11:55	1,5	0,093	0,096	0,1	35	35	45	45	45	0,00	2
	13:25	3	0,093	0,107	0,097	35	35	45	45	45	0,00	2
	16:25	6	0,093	0,097	0,117	35	35	45	45	45	0,00	2
	22:25	12	0,093	0,112	0,085	35	35	45	45	45	0,00	2
15-6-2017	10:25	24	0,093	0,09	0,105	30	30	50	50	50	0,00	2
16-6-2017	10:25	48	0,093	0,104	0,114	20	15	60	65	63	3,54	2
17-6-2017	10:25	72	0,093	0,1	0,098	20	25	60	55	58	3,54	2
18-6-2017	10:25	86	0,093	0,104	0,119	15	15	65	65	65	0,00	2
21-6-2017	10:25	168	0,093	0,123	0,106	10	15	70	65	68	3,54	2

Appendix F – Column test results

Date and time	Average flowrate over last period [mL/min]	Total volume treated [L]	Bed volumes treated	Column 1			Column 2		
				pH	TDS [ppm]	As [ug/L]	pH	TDS [ppm]	As [ug/L]
7-6-2017 14:55			0						
7-6-2017 16:30	26,71	2,54	3,65	8,4	253	0	8,2	198	0
7-6-2017 23:43	17,04	9,92	14,27	8,4	279	10	8,4	273	0
8-6-2017 7:43	18,03	18,57	26,72	8,5	276	20	8,4	286	0
8-6-2017 16:19	13,48	25,53	36,73	8,3	289	20	8,4	285	5
9-6-2017 0:05	19,11	34,43	49,55	8,4	291	30	8,5	280	10
9-6-2017 8:27	17,71	43,33	62,34	8,4	294	40	8,4	280	30
9-6-2017 16:05	18,88	51,97	74,78	8,4	297	40	8,1	328	40

Appendix G – Picture of the biomass gasifier used in this research

