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# Arsenic Removal from Drinking Water Using Enhanced Biochar

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#### **Abstract**

Naturally occurring arsenic, in the soluble form of arsenate, contaminates groundwater resources for millions of people worldwide (WHO, 2018). While there are several technologies available to remediate arsenic contaminated water, the most effective approaches are expensive to implement and maintain, especially for people who are living in poverty. This research studied an inexpensive method for removing arsenate from drinking water by using enhanced biochar. The treatment method was developed by simulating a process that could be adopted by a low-income family. Aspen wood chips were treated with a 10% (by mass) MgCl2 or MgSO4 solution and were then pyrolyzed in low emission cookstoves. Biochar from the MgCl2 and MgSO4 treatments were determined to have arsenic adsorption coefficients (Kd) of 36.7 and 53.2 L/kg, respectively. In column tests, enhanced biochars were able to achieve 95 percent removal of arsenate from 2 mg/L solutions. However, the treated water exceeded the 10 ug/L maximum contaminant level (MCL) for arsenate, and it averaged an unpotable concentration of total dissolved solids.

#### Introduction

Arsenic is a naturally occurring element in groundwater around the world. It is usually found in the form of either arsenite (As(III)) or arsenate (As(V)) (Amen et al., 2020). Arsenic is most toxic and mobile in the environment when it is in its reduced form as As(III), but under aerobic soil conditions, it takes the form of the less toxic As(V) species (Flora, 2014). Human exposure to arsenic generally occurs through drinking water, the consumption of food such as rice that has been grown in arsenic-laden water, or through the inhalation of contaminated soil or dust (Riaz et al., 2022). Arsenic is carcinogenic and exposure can cause short-term and long-term health issues such as skin lesions, cirrhosis, Haff's disease, and other chronic diseases (Amen et al., 2020; Gupta et al., 1978; WHO, 2018). The World Health Organization (WHO) has established a maximum contaminant level for arsenic in drinking water of  $10 \mu g/L$  or  $10 \mu g$  parts per billion (ppb) (WHO 2018). It has been estimated that over 200 million people are at risk to arsenic exposure from contaminated groundwater worldwide (Shakoor et al., 2015).

In the United States, arsenic contamination is a common problem that results from two main sources: arsenic leaching into groundwater from the soil and the continuous residual effects from the historical application of lead arsenate (PbHAsO4) pesticides for a variety of agricultural crops (Riaz et al., 2022). However, the United States is not the only country affected by arsenic contamination.

Bangladesh is on the priority list of countries with arsenic contaminated drinking water, where drinking water is already in short supply (WHO, 2018). For millennia, the people of Bangladesh have gathered water from rivers such as the Padma River, which is an extension of India's Ganges River (Britannica, 2022). The surface waters have increasingly become poor sources of drinking water due to industrial pollution, pathogenic bacteria, and viruses from animal waste (Haque et al., 2019). Beginning in the 1970s, to reduce the health risks associated with surface water sources, the United Nations Children's Fund (UNICEF) partnered with the Bangladesh government to install tube wells (aka groundwater wells or boreholes). With the help of private partners, hundreds of thousands of wells were installed throughout the country by 1990 (Hoque et al., 2006; Kahn, 1997; Smith et al., 2000). In 1993, researchers first discovered that naturally occurring arsenic from the soil was a significant threat to groundwater resources (Smith et al., 2000). With the majority of the population using groundwater as their primary source of drinking water, it quickly became clear that the systematic switch from contaminated surface water to 'safe' groundwater had resulted in the unintended poisoning of up to 77 million people (Smith et al., 2000).

By 2012, it was estimated that 39 million people (approximately 25% of the population) continued to be exposed to arsenic contaminated water in excess of the 10 ppb MCL (WHO, 2018). Drinking water treatment options for the removal of arsenic include various

technologies such as coagulation-flocculation, oxidation, reverse osmosis, and adsorption, among others (Nicomel et al., 2016). However, these options can be prohibitively expensive (Amen et al., 2020) and are not necessarily feasible in rural areas due to availability of resources and people with the knowledge to run them (Hasina, 1999).

In recent years, researchers have begun to study the removal of arsenic from drinking water with biochar. Biochar can be made by burning an organic waste feedstock such as wood, corn husks, or coconut shells. Biochar preparation usually begins with shredding or crushing the feedstock, followed by drying until it is ready to burn. The feedstock can burn in a kiln where it undergoes pyrolysis, which is heating between 550-750 °C with little to no oxygen present (Amen et al., 2020; Yakout 2017; Yang et al., 2020; Zhang et al., 2015).

Like clays, biochar surfaces tend to be negatively charged due to the presence of negative moieties such as carboxylic acid groups. These efficiently remove positively charged ions from water such as copper, zinc, or other metals. Because arsenic is usually present in neutral pH groundwater as the anion arsenate (AsO24–) or arsenite (AsO2–) (Goldberg and Johnston, 2001), biochar surfaces must be modified or enhanced to a positive charge in order to have any significant removal of anions. Examples of biochar enhancement for positively charged surfaces include adding nickel and manganese oxyhydroxides, impregnating the biochar surface with iron, and treatment with calcium carbonate, among others (Amen et al., 2020). A study by Priyadarshni et al. (2020) which treated biochar made from rice husks with stabilized iron and copper oxide nanoparticles for arsenic removal from water concluded that pH, contact time, and interfering ions would determine adsorption efficiency. Critical reviews of studies using biochar for arsenic remediation further identified pyrolysis temperature, surface area, and porosity of the biochar as factors that would affect adsorption (Amen et al., 2020; Yang et al., 2020). The purpose of this research was to develop a method for removing arsenate from drinking water with enhanced biochar that would be inexpensive and that could be done in a rural area. For example, a family could gather and shred a suitable organic waste feedstock (e.g. wood chips, rice husks, etc.). They could then soak the feedstock in a brine solution of MgSO4. In treating wood chips in MgSO4 prior to pyrolization, the goal was to create a more positively charged surface on the biochar and increase the electrostatic attractions for the adsorption of arsenate. We chose magnesium sulfate because it is inexpensive and can be easily acquired around the world in the form of Epsom salts. After soaking in the brine and then drying in the sun, the feedstock would be burned in a low emissions cookstove. The biochar cookstoves as well as cooking can mitigate indoor air pollution (Whitman et al., 2011). The hydrolyzation process burns the treated wood chips at high temperatures in the absence of oxygen which effectively reduces the production of harmful carbon emissions such as carbon monoxide (Whitman et al., 2011). After cooking a meal on the stove, the biochar that remains would be used to treat

arsenic contaminated water. Developed by the Seattle Biochar Working Group (University Place, WA), the prototype for pyrolysis cookstoves was designed to produce low particulate emissions and replace open flame wood stoves that contribute to indoor air pollution and millions of annual deaths worldwide (Younger et al., 2022). Hence, the implementation of this overall process would address the human health challenge of arsenic poisoning. To assess the arsenic removal efficiency of the magnesium sulfate enhanced biochar, we conducted linear isotherm experiments to determine the enhanced biochar's adsorption coefficient (Kd), and we performed experiments with biochar-packed column filters.

#### **Materials and Methods**

To prepare the biochar, aspen woodchips (Small Pet Select, Ellensberg, WA) were soaked in a 10% magnesium sulfate (Mg@SO@\_4) (San Francisco Salt Company, San Francisco, CA) solution for 24 hours. After being dried at ambient temperatures (Figure 1A), they were pyrolyzed in a biochar cookstove (Seattle Biochar Working Group, University Place, WA) (Figure 1B), which took an average of 40 minutes to thoroughly burn the char. The biochar was ground with a mortar and pestle and then sieved so that the granules were between 300-µm and 850-µm in diameter and could meet the American Water Works Association standard for carbon filtration media (Becker et al., 1974). The control biochar was prepared by soaking in tap water from Seattle Public Utilities and then dried, pyrolyzed and sieved in the same manner. Sieved biochar was then packed into three, 24in long, 3-in diameter, polyvinyl chloride (PVC) columns (Figure 2) each containing a Doulton SuperSterasyl (W9121200) ceramic candle filter (Doulton Water Filters, Newcastle-under-Lyme, UK), 1305 g of pea gravel, which was subsequently separated by 100-g of enhanced or untreated biochar with a 3-inch diameter mesh made from 1-mm of 304 stainless steel (Satinior, Chang'an Town, Dongguan Guangdongsheng, China). Columns were fed 1-1.5 liters of a 2 mg/L solution of arsenate in deionized water that was adjusted to pH 7.

Batch isotherm experiments with biochar and arsenic were performed by adding either 0.0, 0.1, 0.3, 0.5, 0.8, 1.2 or 1.6-g of enhanced (or control) biochar to 40-ml centrifuge tubes along with 40-ml of a 2 mg/L arsenate solution that was adjusted to pH 7. Feedstock for the isotherm experiments were treated using magnesium sulfate(Mg®SO®\_4)or magnesium chloride (Mg®Cl®\_2) (MilliporeSigma, Burlington, MA, USA) as described above. The samples were placed in a shaker table at 25°C and incubated at 135 rpm for eight hours. After centrifugation at 3000 rpm for 10-min and at 10,000 rpm for 5-min, the water samples were decanted into nitric acid-prepared bottles from Fremont Analytical Laboratories (Seattle, WA) which analyzed all samples for total arsenic using EPA Method 200.8 and inductively coupled plasma mass spectrometry (ICP-MS).

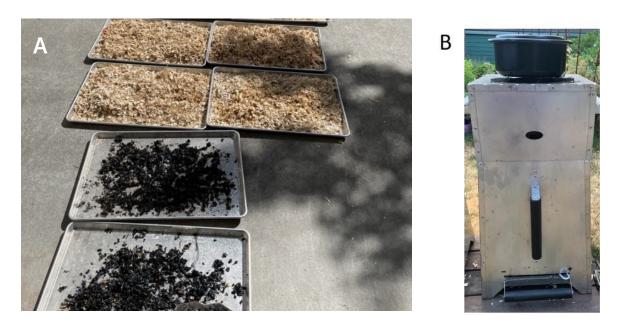


Figure 1 (A) Aspen wood chips drying outdoors and pyrolyzed biochar. (B) Low-emissions biochar cookstove.

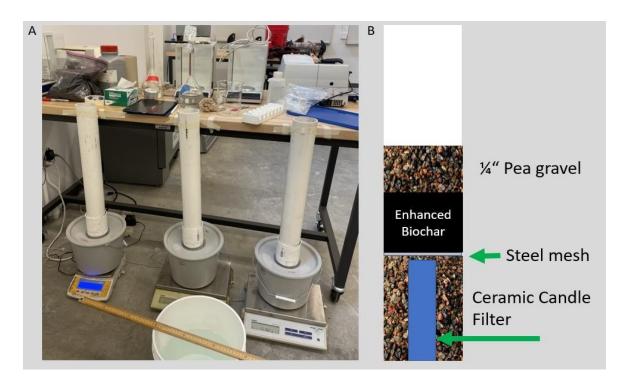


Figure 2 (A) Packed column filters and (B) filter media detail for each column.

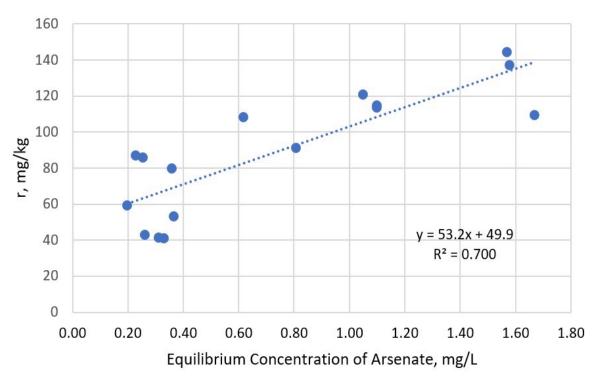
#### **Results and Discussion**

The cookstoves yielded 20 to 30 percent biochar for the untreated and treated aspen woodchips, respectively (Table 1). The dried magnesium sulfate salts slowed the pyrolysis rate which resulted in the higher yields. These results indicated that enough biochar could be produced from a single 40-min cooking period (which we confirmed was long enough to prepare two cups of rice) to pack a single filtration column with 100-g of biochar. A linear adsorption isotherm was conducted to produce a graph to represent the variation in absorbance across the columns where the slope represents the adsorption coefficient. Results from the linear adsorption isotherm with magnesium sulfate (Figure 3) or magnesium chloride (Figure 4) enhanced biochar indicated adsorption coefficients (K<sub>d</sub>) of 53.2 L/kg and 36.7 L/kg, respectively. The adsorption coefficient for the magnesium sulfate enhanced biochar was slightly higher but on the same order of magnitude as the magnesium chloride enhanced biochar. This slight advantage in adsorption combined with the greater availability and lower cost of Epsom salts would, thus, make magnesium sulfate (Mg®SO®\_4) the preferred salt for producing enhanced biochar for the removal of arsenate.

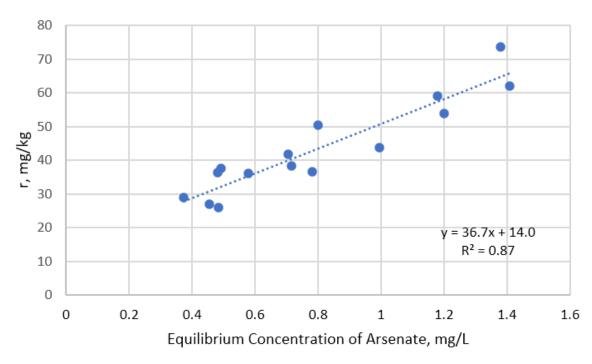
Column tests showed that 100-g of untreated biochar could remove approximately 75 percent of the arsenate from a 2 mg/L solution, and 100-g of treated biochar was able to remove approximately 95 percent for a final concentration of 40  $\mu$ g/L (Figure 5. In addition to exceeding arsenic's  $10\mu$ g/L MCL, the treated water had levels of sulfate and total dissolved solids that were similar to seawater and therefore undrinkable (Table 2). The enhanced biochar's adsorption capacity for arsenic was approximately 0.015 g/g. This was on the low end of the range of adsorption capacities that have been reported for other biochar-based adsorbents (Amen et al., 2020; Yang et al., 2020).

**Table 1** Biochar yields from 300 g of untreated (n = 17) and enhanced (n = 16) aspen wood chips at an average pyrolysis temperature of  $450 \, ^{\circ}$ C.

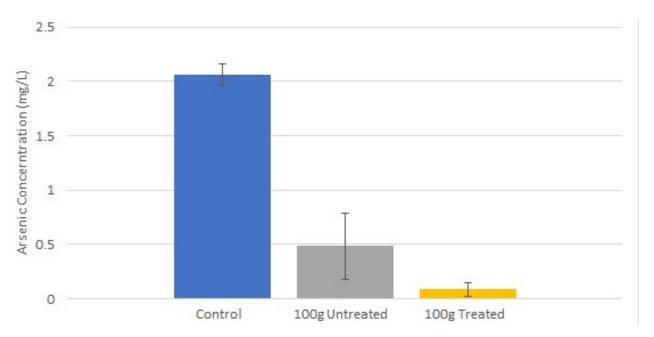
Biochar Type	Average Yield Weight (g)	Percent Yield
Untreated	61.4± 15	20.5%
Enhanced with 10% MgSO <sub>4</sub>	91.0± 27	30.3%



**Figure 3:** A linear isotherm for arsenate with biochar enhanced in a 10%  $MgSO_4$  solution had an adsorption coefficient ( $K_4$ ) of 53.2 L/kg.



**Figure 4** A linear isotherm for arsenate with biochar enhanced in a 10% 10%  $MgCl_2$  solution had an adsorption coefficient ( $K_d$ ) of 36.7 L/kg.



**Figure 5** Columns with 100 g of untreated biochar had 75 percent removal of arsenate compared to 95 percent removal by biochar treated with a 10% MgSO<sub>4</sub> solution.

Table 2 Total dissolved solids for water filtered with untreated and treated biochar.

Biochar Type	Total Dissolved Solids (mg/L)	
Untreated	2,072 ± 466	
Enhanced with 10% MgSO <sub>4</sub>	29,136 ± 16,587	

## Conclusions

Arsenic contamination of drinking water is a global issue that is particularly challenging for countries such as Bangladesh because modern treatment technologies can be too expensive for the average household to purchase. This research developed an arsenic removal process that could be implemented in rural areas for a cost of approximately \$0.25 per liter (excluding the cost of labor), which is low even with the average income of someone in Bangladesh being 141.58 USD/month, according to Bureau of Statistics data for 2017 (Take-Profit.org, 2023). Experimental results indicated that enhanced biochar could achieve 95% arsenic removal, but the process could not meet the 10 ppb MCL needed to meet potable water standards. While effective at removing arsenic, the enhancement process increased the total dissolved solids concentration to unpotable levels. Because the MCL is so small and arsenic is so toxic, it is not

possible to achieve potable drinking water using simple enhanced biochar removal. It may be possible to use enhanced biochar to remove other contaminants with higher MCL such as fluoride, but arsenic remediation requires more advanced technologies such as reverse osmosis, oxidation, or coagulation-flocculation techniques, which all require drinking water treatment plants. Until a suitable, inexpensive water treatment process can be developed, arsenic removal from drinking water will need to be done with proven technologies. However, the issues with these processes remain the same: they are expensive and difficult to maintain. To help families (especially those in rural areas) who cannot afford to purchase more expensive treatment technologies, microfinancing strategies for community-level drinking water treatment systems could be implemented (Water.org, 2018).

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