

Hexavalent Chromium Reduction by Mineral Olivine

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Abstract

Hexavalent chromium (Cr(VI)) is toxic and generally mobile in groundwater, unlike Cr(III) which is nontoxic and typically precipitates out of the water. Zerovalent iron (ZVI) or iron filings are commonly used in groundwater remediation to reduce Cr(VI) to Cr(III). This study was designed to investigate whether mineral olivine (which has historically been commercially mined in western North Carolina) could be employed as a reducing agent in the remediation of Cr(VI). Batch experiments were conducted by mixing Cr(VI) solutions (0.5-5ppm) with two different sources of olivine as well as iron filings, and measuring the chromium remaining in solution. Samples were analyzed for Cr(VI) using the AA spectrometry. Results showed that both the iron filings and two olivine samples were effective in reducing chromium at a pH of 4. However at a pH of 6, only one of the olivine types and the iron filings were effective at reducing Cr(VI).

1. Introduction

Chromium belongs to the heavy metals group on the periodic table. While its oxidation states range from -2 to 6+, the most stable forms of chromium in the environment are trivalent (Cr(III)) and hexavalent (Cr(VI)). Cr(III) is a nutrient commonly found in multivitamins and is a trace element in vegetables (Alvarez, et. al., 2021). In fact, the Food and Drug administration suggests a daily intake of about 120 mcg (Alvarez, et. al., 2021). Chromium can be absorbed through the skin, by inhalation and by ingestion. Oxidized hexavalent chromium (Cr(VI)) is commonly used in industrial applications, but is toxic and hazardous to human health (Alvarez, et. al., 2021). Long term exposure to Cr(VI) can cause many different forms of cancer as well as kidney and liver problems. Occupational exposure to Cr(VI) is often through aerosols, as it is frequently used in tanneries, pigments and paints, and welding. Many places do not have the proper safety equipment for their employees making Cr(VI) inhalation a very large occupational hazard. While there has not been an extensive amount of research done on the mechanisms for the carcinogenicity or the cytotoxicity of Cr(VI), evidence indicates that transition metals act as catalysts in oxygen deterioration in biological molecules (Alvarez et. al., 2021). Because Cr(VI) has a tetrahedral structure, it resembles sulfate molecules allowing it to pass through ion channels as well as phosphate and sulfate transport systems (Alvarez et. al., 2021).

Although Cr(III) was originally viewed as beneficial to a person's health because of its role in metabolic pathways of glucose, proteins and lipids; recent studies have shown that Cr(III) does not have an effect on the human body at all (Alvarez et. al., 2021). A study done on Zucker rats showed that out of the groups of rats that consumed chromium and the groups of rats that did not consume chromium, there was not a major difference (Alvarez et. al., 2021). This finding contrasts previous notions on Cr(III) being a nutrient; however, it does show that Cr(III) does not affect the body in an adverse way.

While inhalation of Cr(VI) remains the most common form of exposure, contact with Cr(VI) through water is becoming more and more common, including here in North Carolina. In 2014, a Duke Energy coal ash spill contaminated water in the Dan River (Coyte, et. al., 2020), sparking an awareness all over the state for residents living near other coal ash ponds. Studies conducted by researchers at Duke University identified numerous groundwater

wells contaminated with Cr(VI) and other heavy metals (Duke University, 2019). Two local wells located near the Lake Julian power plant in Arden, NC, were found to have Cr(VI) concentrations that exceeded the EPA drinking water standard (Williams, 2015).

Studies done by Duke University identified the different areas of North Carolina that are more susceptible to Cr(VI) contamination in groundwater (Figure 1)(Coyte et. al., 2020). The values in Figure 1 were determined by the geology of the area, as well as by easily accessible chemical parameters such as pH, oxygen content and salinity (Duke University, 2019). According to Figure 1, areas closer to the coast were the least susceptible to Cr(VI) contamination whereas the piedmont region was most susceptible to Cr(VI) pollution.

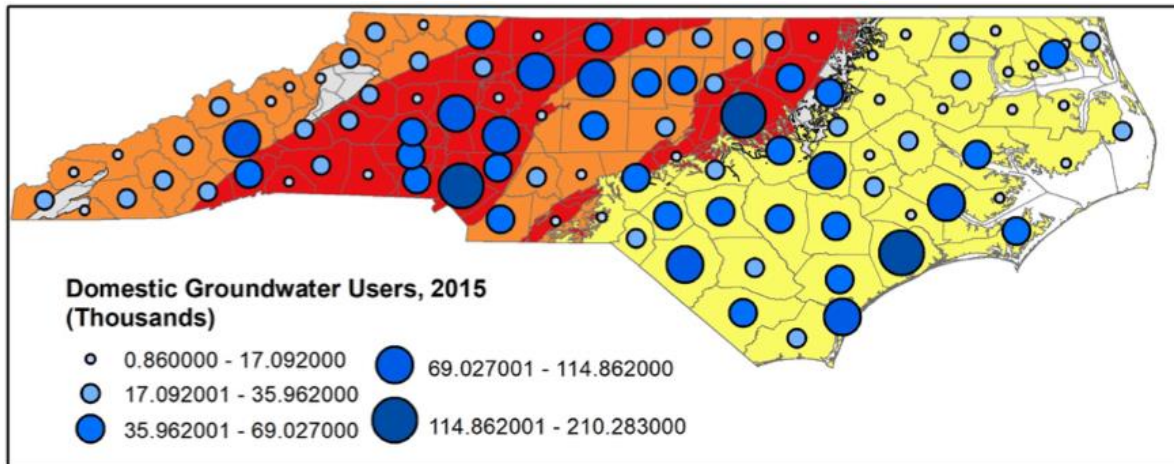


Figure 1: Susceptibility of hexavalent chromium contamination in groundwater due to geology and other chemical parameters. Red means the area is highly susceptible, orange means it is semi susceptible, yellow means it is slightly susceptible and white means it is not susceptible. The blue points represent domestic groundwater usage per thousands of people in each county (Duke University, 2019).

To find out how geology affected the susceptibility of the area, researchers looked at the aquifers. Some aquifers contained innate levels of mineralized chromium, also known as chromite (Coyte et. al., 2020) and were found to have higher concentrations of hexavalent chromium (Figure 2). The researchers also found that in areas with higher pH in the water, chromium was more likely to be present in its hexavalent state (Coyte et. al., 2020). This has also been shown by experiments on the effects of pH on chromium reduction (Gheju & Iovi, 2006).

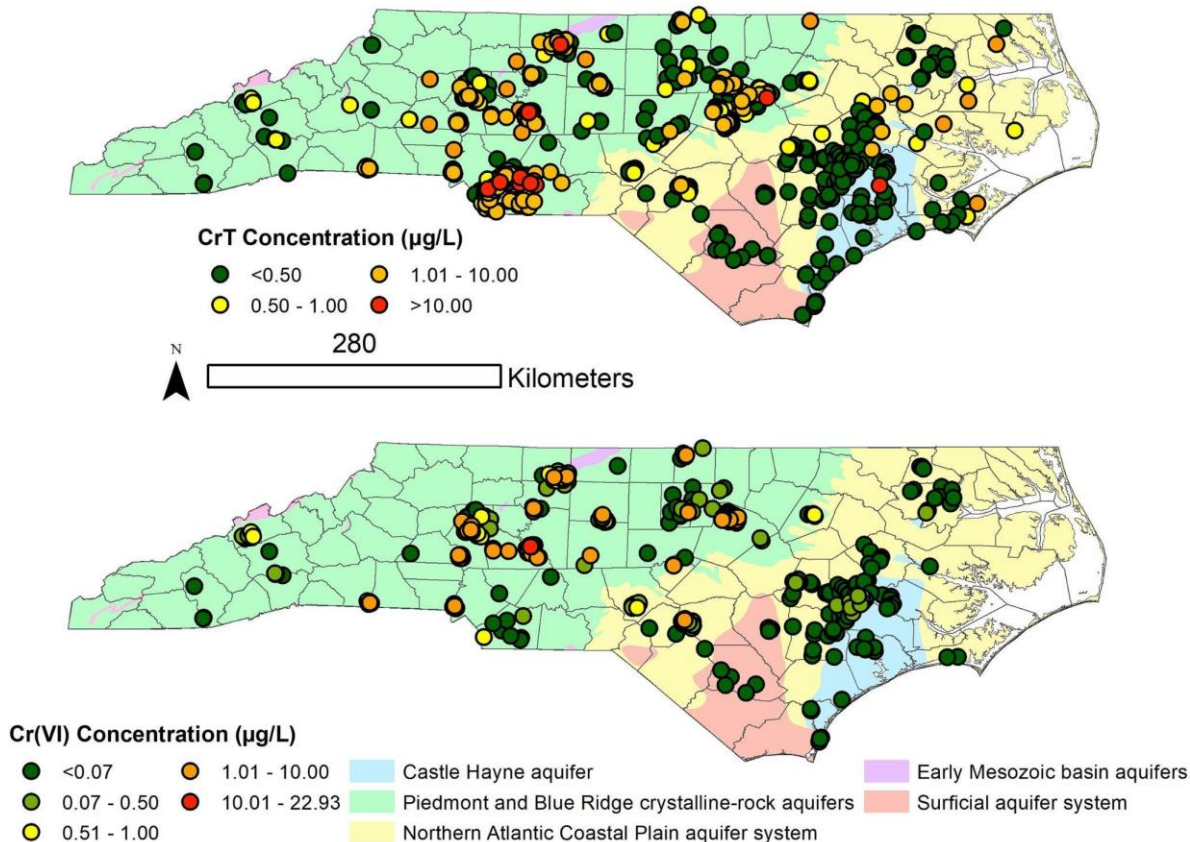


Figure 2: Chromium concentrations in different aquifers in North Carolina (from Coyte et. al., 2020). CrT stands for total chromium (top) and Cr(VI) stands for hexavalent chromium (bottom).

Figure 2 shows there is less susceptibility for Cr(VI) in coastal areas because there is not a lot of innate chromium in the area (Coyte et. al., 2020). CrT (total chromium) and Cr(VI) values are much more concentrated in the piedmont region of North Carolina. This is likely due to the aquifer material. If the aquifer contains chromite or chromate, it is possible for it to change into the +6 oxidation state (Coyte et. al., 2020).

Previous studies have shown that at lower pHs, chromium is more stable in its trivalent state and at higher pHs it is more stable in its hexavalent state (Gheju & Iovi, 2006). Iron has been proven to be useful in reducing Cr(VI) to Cr(III) in many different studies (Gheju & Iovi, 2006). Equation (1) shows how zerovalent iron reduces Cr(VI) to Cr(III) (Gheju, 2011).



This study was designed to investigate whether mineral olivine, a magnesium iron silicate, could also reduce chromium. Olivine ($\text{Mg,Fe}_2\text{SiO}_4$) was mined in North Carolina at the Day Brook deposit between 1941 and 1973 (Fagan, J. M., 1974). This mine is no longer in use but is accessible to the public. The deposit contains trace amounts of chromite and talc but was mostly mined for the olivine (Fagan, J. M., 1974).

2. Methodology

Mineral olivine was collected from the Day Brook deposit in Yancey county, NC. Commercially-available olivine was also purchased from the Teton Supply Company, and iron filings were obtained from American Heritage Industries. Olivine obtained from the Day Brook deposit was crushed at the Mineral Research Laboratory in Asheville,

NC. All three substances were sorted by size using sieve sizes 500 μm , 250 μm , 150 μm , and 75 μm . Only the smallest size (<75 μm) was used in these experiments.

Batch experiments were conducted by mixing the three different substrates with various concentrations of Cr(VI) and then measuring how much Cr(VI) was reduced to Cr(III). To create standards to use in batch experiments, a 1000 ppm Cr(VI) standard solution was diluted to different concentrations to be used in batch experiments as shown in Table 1.

Table 1: Dilution factors for chromium standards.

Concentration of initial chromium	mL of initial chromium	Final mL in flask	Final Concentration
1000ppm Cr(VI)	2.5 mL	25 mL	100ppm Cr(VI)
100ppm Cr(VI)	10 mL	200mL	5ppm Cr(VI)
100ppm Cr(VI)	5mL	200mL	2.5ppm Cr(VI)
100ppm Cr(VI)	2mL	200mL	1ppm Cr(VI)
100ppm Cr(VI)	1mL	200mL	0.5ppm Cr(VI)

To begin the batch experiments, 0.5g of each mineral substance were added into a series of centrifuge vials before the four different hexavalent chromium standards (0.5ppm, 1.0ppm, 2.5ppm, 5ppm) were added. The vials were then mixed for 6 hours and centrifuged for 10 minutes. The samples were then filtered using 0.45 μm nylon syringe filters and acidified with 50 μl of 67-70% Nitric acid. Samples were then placed into the fridge until they could be analyzed with the Atomic Absorption Spectrometer.

Two different batch experiments were performed, one at pH=6 and the other at pH=4. To obtain the difference in pH, a 1:19 dilution of 67-70% HNO₃ made. To obtain a pH of 6, nothing was added to the solution as it was already at a pH of 6. To obtain a pH of 4, 20 μl of the 1:19 diluted Nitric acid was added to each sample. All experiments were performed in triplicate.

3. Results

In each batch experiment, a standard curve (Figure 3) was created using eight standard solutions (0.025-5ppm).

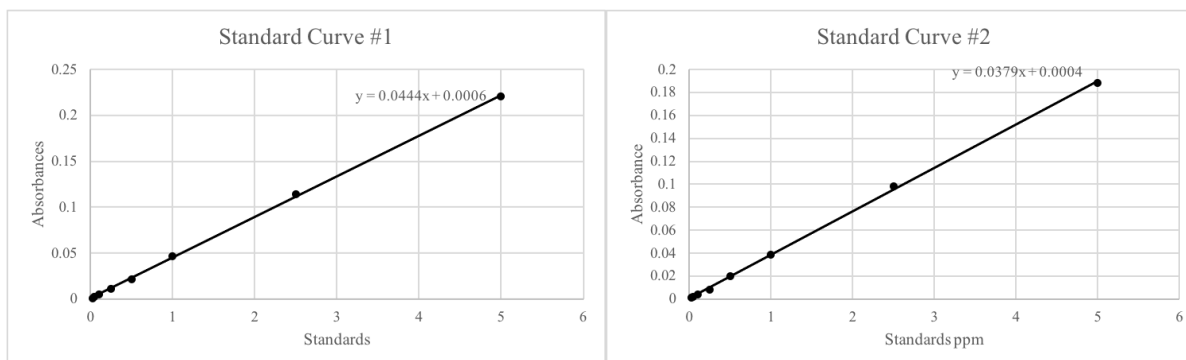


Figure 3: Standard curve for the pH=6 batch experiment (left, #1) and pH=4 batch experiment (right, #2).

Each experiment also included a control batch, where standard solutions (without olivine or iron) were mixed, centrifuged and filtered like the rest of the samples. The final control solutions could then be compared to those that were mixed with each of the test mineral substances (Figure 4 and 5).

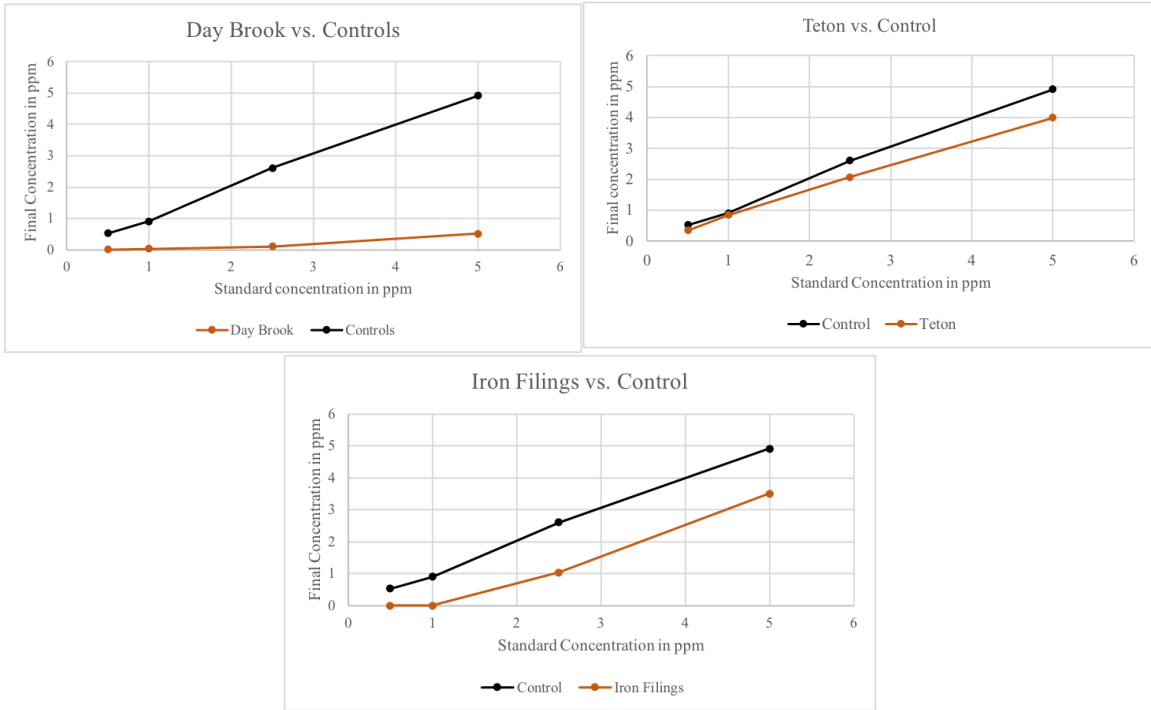


Figure 4: Mineral substances compared to the controls for the pH of 6 experiment.

In the pH=6 experiments, nearly all the Cr(VI) was removed when mixed with Day Brook olivine. The iron filings showed similar removal rates at lower Cr(VI) concentrations but less removal at the 2.5ppm and 5.0ppm Cr(VI) levels. The Teton olivine caused minimal Cr(VI) reduction compared to the controls or other two substrates. .

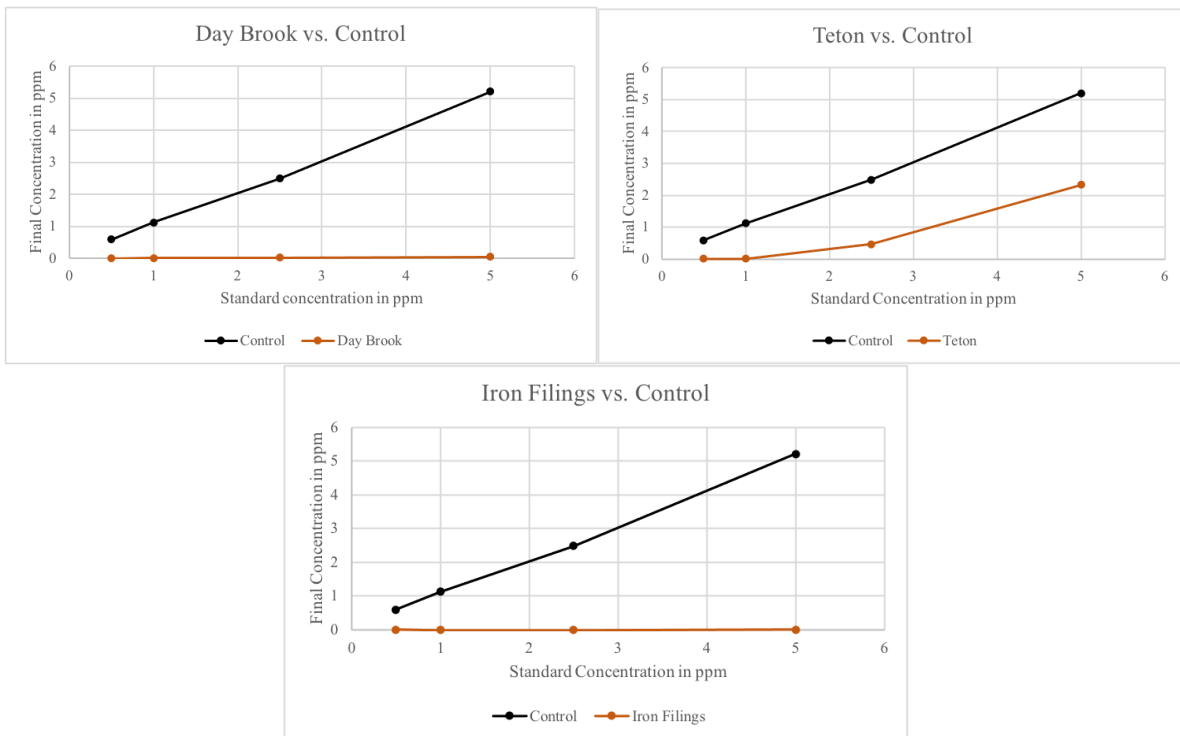


Figure 5: Mineral substances compared to the controls for the pH of 4 experiment.

In the pH=4 experiment, Cr(VI) was completely removed when mixed with Day Brook olivine or iron filings. The Teton olivine had less Cr(VI) removal than the other substrates, but more than at pH=6.

4. Discussion

Iron filings have in previous research been shown to reduce Cr(VI) (Gheju & Iovi, 2006), which was also demonstrated in this study. The Day Brook formation olivine did exceptionally well in removing Cr(VI) at both pH=4 and pH=6. The Teton olivine did a notably poor job of removing the chromium at pH=6, but performed better at a pH=4.

These findings could be useful in developing larger scale remediation processes such as permeable reactive barriers (Figure 6). A permeable reactive barrier is placed in an area where it can intercept a groundwater contaminant plume; as groundwater flows through the permeable barrier, it is treated and comes out clean on the other side (Rad, P. R. & Fazlali, A., 2020). Iron filings are currently used in permeable reactive barriers to treat Cr(VI); this study suggests that olivine obtained from western North Carolina may also be a suitable substrate for this application.

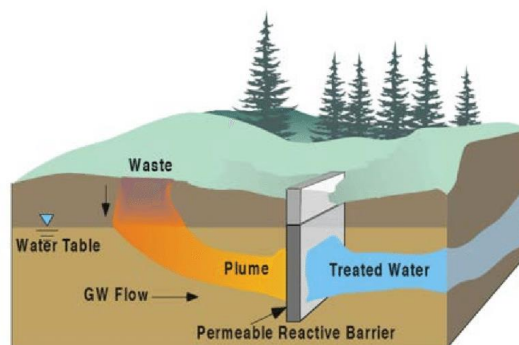


Figure 6: Graphic depiction of groundwater flowing through a permeable reactive barrier (Rad, P. R. & Fazlali, A., 2020).

5. Conclusion

This study examined how Cr(VI) is reduced under different circumstances. Previous research showed that iron filings were an effective way to reduce Cr(VI), which was confirmed in this study. Olivine also proved to be effective in reducing chromium contamination in water. While the result varies with pH and the different types of olivine; nevertheless, olivine can be a useful tool in reducing chromium contamination in groundwater.

6. References

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