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Electrochemical Treatment of Hexavalent Chromium from Waste Ammonium Nitrate Solution

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# UNIVERSITY OF CALIFORNIA

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Electrochemical Treatment of Hexavalent Chromium

from Waste Ammonium Nitrate Solution

A thesis submitted in partial satisfaction

of the requirements for the degree Master of Science

in Civil Engineering

by

Mark Hoang Khoi Nguyen

2022

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#### ABSTRACT OF THE THESIS

Electrochemical Treatment of Hexavalent Chromium from Waste Ammonium Nitrate Solution

by

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Master of Science in Civil Engineering University of California, Los Angeles, 2022 Professor David Jassby, Chair

The removal of hexavalent chromium (Cr(VI)) from wastewater is an increasing area of concern. Cr(VI) is commonly found in developed water systems and is a frequent contaminant in various wastewaters. Mounting pressure for recycled water usage, along with the consideration of ingested hexavalent chromium as a human carcinogen, is driving the need to develop methods to effectively remove Cr(VI). However, the natural solubility of Cr(VI) and its toxicity at low concentrations presents a challenge to removal. This study aims to apply previously developed electrochemical reduction methods of Cr(VI) to synthetic and real wastewater solutions. Parameters such as current density were evaluated to compare Cr(VI) removal efficiencies. The results demonstrate that Cr(VI) reduction is promising in the synthetic wastewater solutions but

does not translate effectively when applied to the wastewater. Further research is needed to characterize the various parameters in the real wastewater solution inhibiting Cr(VI) removal.

The thesis of Mark Hoang Khoi Nguyen is approved.

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2022

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## **1.0 Introduction**

Fresh water is the most essential natural resource, and there is an ever-increasing pressure on the need for it. As populations continue to increase, combined with climate change and evolving energy considerations, wastewater offers an attractive source for obtaining clean, recycled, and potable water. Recycling wastewaters from industrial, agricultural, and municipal sources presents an opportunity to increase water supply in drought-stricken areas (McNabb 2017). Reclamation wastewater, however, does not come without its obstacles. There are a variety of constituents in various wastewaters that must be degraded before potable and non-potable use (Bohlke 2002). Industrial wastewaters often contain concentrations of metals and toxins, while agricultural wastewaters contain elevated levels of nutrients (Barakat 2011; Pico-Corrales et al., 2020). Municipal wastewaters are polluted with viruses, bacteria, and pharmaceutical chemicals (Kunz et al., 2016).

Metropolitan areas commonly contain industrial, agricultural, and municipal wastewater streams. These regions often rely heavily on groundwater sources to supply the aforementioned activities. Urban developments have drastically changed the natural water cycle, especially in heavily urbanized areas such as Los Angeles, California (Anderson 2003). Paved areas diminish the natural infiltration capacity of the environment, reducing water supplies in the form of groundwater and increasing runoff volumes. Exorbitant use causes groundwater levels to reach uncharacteristically low levels, as well as leading to issues such as seawater intrusion (Bolhke 2002). Natural groundwater replenishment already occurs at an incessantly slow pace; combined with excessive exploitation and reduced infiltration rates, alternative methods of obtaining clean water are a necessity. Furthermore, increased runoff flows also carry with them pollutants from the surrounding areas – bacteria, viruses, microplastics, trash, metals, and other pollutants from nearby industrial and commercial activities (Muller et al., 2020). This leads to potential groundwater contamination where infiltration can occur.

Wastewater from various sources can offer a usable, sustainable water supply. This can significantly aid in meeting the increasing demand for freshwater. For example, the Hyperion Wastewater Treatment Plant of Los Angeles, California treats approximately 260 MGD of municipal wastewater. The plant currently discharges 220 MGD to Santa Monica Bay. The City of Los Angeles plans to convert Hyperion into a 100% recycled water facility, ultimately producing water supplies for both potable and non-potable uses (HWRP 2035). The production of 220 MGD of recycled water is enough to provide one third of the overall potable water consumption of the City of Los Angeles. In this instance, recycling of wastewater increases the local area's water sustainability by diversifying its water resources portfolio.

As the ability to efficiently treat, recycle, and reuse wastewater continues to increase, so too do the challenges in this process. Anthropogenic activities have introduced contaminants of emerging concern, or CECs, into aquatic ecosystems, where they would otherwise not be found. CECs include various classes of constituents such as pesticides, fertilizers, microplastics, pharmaceuticals, cosmetic products, synthetic hormones, and heavy metals (Shah et al., 2020). These pollutants have harmful impacts on the natural environment and human health, even in trace quantities (Yadav et al., 2021). Conventional wastewater treatment methods are often inadequate at treating such compounds which necessitates the need for advanced and novel treatment techniques. However, the potential of these contaminants to have harmful effects in such small concentrations increases energy and monetary considerations, which are integral factors in the development of new wastewater treatment methods. Furthermore, the revolving nature of CECs,

i.e., new compounds and materials are authorized while others are progressively banned, makes identification and testing difficult to consistently perform (Kasonga et al., 2021).

Treatment of wastewater also utilizes large amounts of energy. Various stages of the wastewater treatment process, including conveyance, physical., chemical., and biological treatment, require significant energy consumption. Different amounts of energy are consumed in the various stages of the wastewater treatment process - in this instance energy consumption is also dependent on factors such as size of plant, water quality, discharge limits, population serviced, and economic status of the service area (Gu et al., 2017). Advanced treatment options such as reverse osmosis, though an effective treatment technology, can consume up to 0.79 kW-h/m<sup>3</sup>, depending on the water quality (Wakeel et al., 2016). As the demand for recycled water continues to grow with population increase, there is a substantial shift to make wastewater treatment systems self-sufficient with respect to the water-energy nexus.

The primary focus of wastewater treatment optimization is to achieve clean effluent water quality. However, challenges from an evolving world are resulting in new and innovative perspectives - a paradigm shift. Related to the water-energy nexus, wastewater treatment processes are considered major contributors to emissions of greenhouse gasses (carbon dioxide, methane, nitrous oxide) (Parravicini et al., 2016). Previous studies estimate the total methane emissions from wastewater management, both municipal and industrial., to be about 5% of the total global methane production (Koutsou, 2018). As new CECs begin to find their way into the wastewater stream, wastewater facilities will have to adjust their treatment processes, subsequently increasing energy consumption along with greenhouse gas emissions.

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#### 2.0 Chromium in Water

Chromium is a naturally occurring metal often found in soil, sediments, rocks, and groundwater (Prasad et al., 2021). Elevated concentrations of chromium found in surface and groundwater are typically due to anthropogenic sources and contamination. Chromium is used in various industries, including, but not limited to, metallurgy, refractory, chemical manufacturing, electroplating, leather tanning, mining, industrial water cooling, and wood preservation (Rahkunde et al., 2012). Chromium can take various forms in the natural environment. In water and soil, chromium typically exists as either Cr(VI) or trivalent chromium (Cr(III)). Hexavalent chromium (CrVI) is commonly associated with chrome plating, where a bright, metallic coating is applied to different consumer and industrial products (Saha et al., 2011). This form of chromium contaminates groundwater as a result of leaching from industrial processes (Rahkunde et al., 2012). Cr(VI), which is quite soluble, is the dominant form in surface and drinking waters (Saha et al., 2011). As a result, Cr(VI) commonly finds its way into drinking water systems. Different Cr(VI) species found in the environment include chromate  $(CrO_4^{2-})$ , dichromate  $(Cr_2O_7^{2-})$ , and hydrogenchromate (HCrO<sub>4</sub>) (Saha et al., 2011). The dominance of any one of these species depends on environmentally specific conditions such as pH, redox potential, and total chromium concentration. Cr(III), conversely, is dominant at low oxygen levels and tends to be extremely insoluble at near neutral pH levels (McNeill et al., 2012). Though the most common form of naturally occurring chromium, its high insolubility renders it considerably immobile in natural waters (Saha et al., 2011). Inorganic Cr(III) may exist in aqueous solutions in various forms. Typically,  $Cr(OH)^{2+}$  and chromium hydroxide ( $Cr(OH)_3$ ) are the most common, with the former dominating at pH ~ 5 whereas the latter is most prevalent at pH 6 - 8 (Figure 1).



(Figure 1. Eh-pH Diagram of Chromium, Huang et al., 2014)

## 2.1 Chromium health effects

Cr(VI) is classified as a known human carcinogen by the United States Environmental Protection Agency (EPA), and decades of epidemiological studies have indicated occupational exposure of workers to airborne Cr(VI) increases risks of lung cancer (McLean et al., 2012). Cr(VI) typically enters the body through inhalation or ingestion, with the latter being the main source of human exposure (Moffat et al., 2018). Because of the exposure in various industrial workplaces, the health effects of chromium on humans have been studied extensively. Cr(VI) in drinking water gained notoriety in 1993, when Erin Brockovich, a legal clerk by profession, brought to light contamination of local groundwater aquifers in Hinkley, California by PG&E, an electricity and natural gas utility. There are differing opinions on the carcinogenicity of Cr(VI) on humans through the route of drinking water ingestion (McLean et al., 2012). Various arguments have been made that at certain concentrations, Cr(VI) may be safe to ingest because of its reduction to Cr(III), which is considerably less toxic than Cr(VI), at the cellular level. However, it has been argued that there is not a complete and consistent conversion of Cr(VI) to Cr(III) in the body (Costa and Klein, 2006). Nevertheless, there are still a variety of deleterious health effects correlated to exposure of Cr(VI). Several studies have proven high levels of genotoxicity and mutagenicity at low levels of chromium exposure. For example, formation of chromium-DNA adducts, a type of DNA damage where the DNA structure binds to a chemical molecule and is associated with cancer risks, were evident in human cells after exposure to a 2 micromolar solution of chromium and even lower concentrations of Cr(VI) (Zhitkovich 2011). The United States Department of Health and Human Services, along with US EPA, have classified Cr(VI) compounds as carcinogens due to correlation of increased lung cancers, kidney and liver damage, and ulcerations within intestinal organs in chromium workers and others having occupational exposure (Cohen et al., 1998). With respect to chromium ingestion through drinking water, a significant, commonly cited study in China investigated stomach and lung cancer rates in rural villages near JinZhou, China, where a chromium ore smelting facility was contaminating the local groundwater (Zhang and Li, 1987). The authors concluded a higher cancer mortality rate in villages with elevated Cr(VI) levels. The same authors returned a decade later to reanalyze the findings of their study, ultimately concluding that there was no statistically significant increase in cancer mortality rates in the villages adjacent to the source of contamination (Zhang and Li, 1997). However, the reanalysis study was retracted by the journal in July 2006, due to the authors' failure to disclose financial and intellectual input

to the paper, as well as evidence supporting unethical involvement of chromium polluting corporations (Brandt-Rauf 2006; EWG, 2006) . Other studies reanalyzing the data from the Jinzhou, China investigation have concluded that, despite the data limitations, results are consistent with increased stomach cancer risk in the population exposed to Cr(VI) in their drinking water (Beaumont, 2008).

Notwithstanding the differing contentions of the Jinzhou, China study, ingestion of Cr(VI) in drinking water has proven to be carcinogenic in animal studies. The National Toxicology Program, under the United States Department of Health and Human Services, performed a 2-year study of sodium dichromate dihydrate ingestion from drinking water in groups of male and female rats and mice. Male rats, female rats, and female mice were given concentrations of 0, 14.3, 57.3, 172, or 516 mg/L sodium dichromate dihydrate, whereas male mice were given concentrations of 0, 14.3, 28.6, 85.7, or 257.4 mg/L. The study concluded clear evidence of carcinogenicity from chronic sodium dichromate dihydrate ingestion, showing squamous cell neoplasms of the oral cavity, small intestine neoplasms, pancreatic and mesenteric lymph nodes, and epithelial hyperplasia in the small intestine (NTP, 2008). The US EPA is currently using this assessment as a marker for health regulation in drinking water and its possibility as a human carcinogen via ingestion. Currently, the federal maximum contaminant level for Cr(VI) sits at 100 ppb.

## **2.2 Chromium Treatment Methods**

Since chromium laden wastewaters are ubiquitous across numerous industries, different treatment methods exist for the reduction and removal of Cr(VI). Each technique has its own respective advantages and disadvantages and must be individually tailored to the specific wastewater chosen for treatment.

Adsorption is a popular treatment technique for the removal of Cr(VI). Adsorption is a process by which molecules in the liquid are concentrated onto the surface of a solid phase sorbent through physisorption or chemisorption. Activated carbon is an attractive sorbent choice, as it can be derived from various sources and exhibits exceptionally high surface areas ranging from 500 to 1500 m<sup>2</sup>/g, well developed porous internal structure, and a wide spectrum of surface functional groups that act as adsorption sites for the target pollutant (Owlad et al., 2008). It is produced from carbonaceous source material by exposure to excessively high temperatures in the absence of oxygen (i.e., pyrolysis) and then activated to develop its porous structure by oxidizing at high temperatures in the presence of air, steam, or other chemicals. Heavy metals such as chromium are removed through surface complex formation between the metals and surface functional groups. Activated carbon can be classified into four different groups based on size and shape: power activated carbon, granular-activated carbon, activated carbon fibrous, and activated carbon cloth, with each having inherent pros and cons (Babel and Kurniawan, 2003). Though it exhibits high efficiency, fast kinetics, and ease of operation, cost is usually a barrier that must be overcome for treatment, as performance and expense is dependent on the type of carbon used, along with high reactivation costs.

Ion exchange is a treatment method by which anions or cations in a solution are replaced with ions of the same charge from the ion exchange resin. In this way, the target wastewater is now rid of the toxic heavy metal and substituted with a more benign molecule. Researchers in California utilized strong base anion exchange columns at the pilot scale to treat groundwater with elevated Cr(VI) concentrations above the maximum contaminant level (Korak et al., 2017). Three columns in parallel were operated until exhaustion, when equal influent and effluent concentrations were measured. Utilizing different regeneration schemes, the authors were able to reduce Cr(VI) from 40 ug/L to below the California MCL of 10 ug/L at 36,000 bed volumes, or total volume until breakthrough occurred. Installation of ion exchange columns are suitable for small and large operations. However specific drawbacks include regeneration of the column resins with chemical reagents resulting in a waste brine, concentrate treatment and disposal., required pre-treatment for high total suspended solids (TSS) levels, and the effect on removal efficiencies by other ions present in the water (Sharma et al., 2008). This often leads to high operational costs, limiting the use of ion exchange treatment at the industrial level (Kerur et al., 2021).

Conventional water treatment processes use the coagulation-filtration-precipitation process to remove chromium from water. Using alum or ferric coagulants, chromium precipitates out as Cr(OH)<sub>3</sub>. Co-precipitation of Al(OH)<sub>3</sub> or Fe(OH)<sub>3</sub> also occurs. However, different chemicals must be used if the reduction of Cr(VI) is needed. Using Fe (II) sulfate, the removal of Cr(VI) is observed to be nearly 100 %, due to the fast reduction of Cr(VI) to Cr(III) by the Fe(II) ion, followed by the coagulation precipitation step by Fe(III), which is formed through oxidation of the Fe(II) compounds in-situ (Sharma et al., 2008). Reduction to Cr(III) occurs at low pH ranges, followed by precipitation at higher pH levels. Though easy to operate and exhibiting high removal efficiencies, the two-stage process presents issues due to high chemical doses – this leads to production of high sludge volumes, increasing operating costs from disposal. Furthermore, precipitation may be ineffective if the metals are complexed, preventing the necessary chemical reactions from taking place.

## **2.3 Electrochemical Transformation of Chromium**

Electrochemical techniques for Cr(VI) removal, specifically electrochemical reduction, are attractive because of their versatility and effectiveness. The process relies on electron transfer from

a charged cathode to the toxic Cr(VI), reducing it from Cr(VI) to Cr(III). This can lead to the formation of a solid Cr(OH)<sub>3</sub> precipitate (Duan et al., 2017). Electrochemical reduction processes are highly dependent on a multitude of factors such as pH, electrolyte species and concentration, current density, and electrode material. Importantly, since the main reagents in the redox reactions are electrons generated from an electrolytic cell, the process does not generate significant sludge volumes like in conventional processes – this makes electrochemical reduction a sustainable and environmentally friendly option for Cr(VI) removal (Velazquez – Pena et al., 2011). Furthermore, electrodes used in the electrochemical reduction processes are non-sacrificial and stable, i.e. they are not consumed to form reagents, unlike electrocoagulation processes (Jin et al., 2016). Thus, considerable efforts have been made to develop efficient electrode material for electrochemical Cr(VI) reduction.

Following the application of a potential., hydrogen evolution, reduction of water, and Cr(VI) reduction occur at the cathode:

 $2\mathrm{H}^{+}(aq) + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(g) (1)$ 

 $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)(2)$ 

$$Cr_2O_2^{7-} + 14 H^+ + 6e^- \rightarrow 2 Cr^{3+} + 7 H_2O(3)$$

Ultimately, Cr(III) reacts with hydroxide ions in solution to form solid chromium hydroxide:

$$Cr^{3+} + 3OH^{-} \rightarrow Cr(OH)_3(s)(4)$$

$$5 \text{ H}^+ + \text{CrO}_4^{2-} + 3e^- \rightarrow \text{Cr(OH)}_3(s) + \text{H}_2\text{O}(5)$$

The production of hydroxide ions raises the pH of the solution, inducing the formation of the Cr(III) precipitate.

At the anode, an oxidation reaction occurs generating oxygen gas:

$$2 \text{ H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{ H}^+(aq) + 4e^-$$
 (6)

## **3.0 Ammonium Nitrate Solution**

Ammonium nitrate solution, or ANSOL, is an aqueous solution containing elevated concentrations of ammonium and amine nitrates. A byproduct of explosive manufacturing, it is generated in excessively large volumes at military facilities and also contains residual high energy compounds such as RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). The solution also contains trace concentrations of Cr(VI), which, in addition to the presence of other constituents, complicates its disposal as waste, effluent discharge, and reuse for recycled water applications. To safely dispose of the ANSOL, an integral part of the waste handling is eliminating the toxic Cr(VI) as to prevent its leaching into the natural environment.

Previous research in electrochemical reduction of Cr(VI) has been performed using electrically conducting carbon nanotube composite membranes with polyvinyl alcohol (PVA) as a crosslinking polymer to control pore size (Duan et al., 2017). The authors reported efficient Cr(VI) removal (> 95%) from synthetic Cr(VI) solution (potassium dichromate with sodium sulfate salt as an electrolyte) and tap water spiked with Cr(VI). Following this study, we applied the principles of electrochemical reduction with CNT/PVA membrane to examine Cr(VI) removal from a synthetic wastewater solution, mimicking that of the ANSOL from an ammunition facility. Furthermore, we applied the removal mechanism to actual ANSOL obtained from the ammunition facility. Ultimately, Cr(VI) removal from the synthetic wastewater shows promising efficiency. Cr(VI) treatment from the ANSOL is, however, variable; further research must be done to analyze specific irregularities in treatment efficiency.

#### **4.0 Materials and Methods**

PS-35 polysulfone ultrafiltration membranes were used as the support layer. Dodecylbenzenesulfonic acid (DDBS), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), and RDX (1,3,5-Trinitroperhydro-1,3,5-triazine) were purchased from Sigma-Aldrich and used as is to make synthetic wastewater. Multi-walled carboxylic group functionalized CNTs, PVA (polyvinyl alcohol), glutaraldehyde (Sigma-Aldrich, 50% purity), and hydrochloric acid (Fisher Chemical, 35% purity) were used for membrane fabrication. Following the membrane fabrication method from Duan et al., 0.01 wt.% CNT powder and 0.1 wt.% DDBS were suspended in DI water using a horn sonicator. 450 mL of the suspended solution was pressure deposited onto a PS-35 polysulfone membrane support layer, along with .15 mL of PVA. It was then cross linked with hydrochloric acid and glutaraldehyde solution for 1 hr. at 80 °C, then dried at the same temperature for 5 minutes. New membranes were prepared for each experiment.

Experiments with synthetic wastewater solution, containing 1ppm Cr(VI), 65% NH<sub>4</sub>NO<sub>3</sub>, and 15 mg/L RDX were carried out in a dead-end filtration cell unit. This cell contained the CNT/PVA fabricated membrane and acted as the cathode. Wastewater solution was pumped through the membrane using a vacuum pressure peristaltic pump and collected into a permeate chamber (Figure 2). Solution was recirculated through the anode and back into the feed chamber to prevent pore clogging. The filtration cell had an active surface area of 21.4 cm<sup>2</sup> with a substoichiometric titanium oxide (Ti<sub>4</sub>O<sub>7</sub>) anode located approximately 0.5 cm from the cathode. Due to time constraints, the experiments were conducted in duplicates with each lasting at least six hours – the first three hours, no potential was applied, followed by the application of 7 V for the final three hours. Average volumetric flow rate into the permeate chamber was calculated at (8.06 mL/hr.). Current density was calculated at 9.34 mA/cm<sup>2</sup> for the first set of experiments and 23.364 mA/cm<sup>2</sup> for the second set. Samples were collected at hourly intervals to measure Cr(VI) removal using a HACH (DR 1900) Spectrophotometer.

Experiments with the real ANSOL were conducted in triplicate. No supporting electrolyte or additional constituents were added to the solution. Application of 7 V was applied to the entire duration of the experiment (5 hours), average flux of 13.5 LMH, and current density was 233.64  $A/m^{2}$ .



(**Figure 2.** Experimental setup showing Cr(VI) reduction/precipitation at the cathode (CNT membrane) and titanium dioxide anode recirculating solution in the feed chamber. Solution is pumped through the cathode and collected into a permeate chamber)

#### 5.0 Results & Discussion

Figure 3 displays change in Cr(VI) concentration and mass over time in the synthetic wastewater solutions performed with current density of 9.34 mA/cm<sup>2</sup>. At time t=4 to t=5, the largest decrease in Cr(VI) concentration occurred in the feed stream. However, permeate concentrations stayed relatively consistent, hovering at approximately 0.7 - 0.8 mg/ L. Feed and permeate concentrations at time t=4 were nearly identical. Permeate concentrations at t=1, t=3, t=5, and t=6 measured higher than that of feed concentrations. Operating at the selected current density of 9.34 mA/cm<sup>2</sup> may have resulted in the unexpected permeate concentrations at these times, as well as explaining inhibited Cr(VI) reduction throughout the experiment. Current density was likely not high enough to induce the Cr(VI) reduction and precipitation. Variations between the duplicate experiments at 9.34 mA/cm<sup>2</sup> were significant, explaining the large standard deviation measurements for each sample point.



(**Figure 3.** Average Cr(VI) concentration and mass over time with 0.2 A constant current in synthetic wastewater)

Synthetic wastewater experiments performed at 23.364 mA/cm<sup>2</sup> showed much higher removal efficiencies (Figure 4). Final permeate concentrations were measured just above the federal MCL of 100 ppb for Cr(VI). After the application of the potential at t=3, average Cr(VI) concentrations dropped significantly in both feed and permeate streams, with the highest concentration decrease observed from t=4 to t=5. The 23.364 mA/cm<sup>2</sup> current density, compared to 9.34 mA/cm<sup>2</sup>, resulted in the higher removal efficiency, likely due to the increase in current. Furthermore, upon application of the 7 V potential, pH values in the permeate range from pH 6 to pH 8, coinciding with the pH range in which Cr(OH)<sub>3</sub> is precipitated as the dominant form of Cr(III). The high concentration of NH<sub>4</sub>NO<sub>3</sub> within the synthetic solution acted as an excellent electrolyte, inducing high electrical conductivity in the solution and ultimately aiding in Cr(VI) reduction. Additionally, synthetic wastewater experiments performed at a current density of 23.364 mA/cm<sup>2</sup> exhibited the higher flux of the synthetic experiments at 4.34 LMH. Though not significantly higher than the average flow rate of the 9.34 mA/cm<sup>2</sup> experiments, the increased flow rate could be a factor in displaying higher removal efficiency.



(Figure 4. Average Cr(VI) concentration and mass over time with 0.5 A constant current in synthetic wastewater)

Applying the same experimental methods to the real wastewater solution did not achieve similar results. Cr(VI) concentrations were measured using inductively coupled plasma mass spectrophotometry (ICP-MS). Experiments using real ANSOL, performed in triplicate, displayed non-uniform trends in overall removal efficiency. During the experiment, several samples for both feed and permeate concentration read higher than the initial measured concentration. Notably, the final permeate concentration at t=5 was higher than that of the initial feed concentration at t=0. Furthermore, the lowest permeate concentration was measured at t=1, only an hour after the application of the potential; the following samples then proceeded to increase and display

measurements at approximately 4.85 mg/L. Accounting for the lack in Cr(VI) reduction could be the chemical constituency of the ANSOL. The ANSOL sample is known to have trace concentrations of Cr(VI) along with other unknown constituents in the wastewater sample. These additional constituents could be interfering with the chemical reactions necessary to reduce Cr(VI) to Cr(III). Average pH range of the permeate was approximately 3-4, outside that of which Cr(OH)<sub>3</sub> is formed as a precipitate.



(Figure 5. Average Cr(VI) concentration over time in real ANSOL experiment)

## **6.0** Conclusion

This work is an extension of previously developed electrochemical reduction methods for Cr(VI). Here, we demonstrate that these methods are successful at converting Cr(VI) to Cr(III) in a synthetic wastewater solution. Using CNT/PVA coated ultrafiltration membrane, direct

application shows promising removal efficiencies. High electrolyte concentration of NH<sub>4</sub>NO<sub>3</sub> facilitates application of the potential and, consequently, effective reduction of soluble Cr(VI) to soluble Cr(III) species. When different current conditions were applied, experiments performed at 23.364 mA/cm<sup>2</sup> current density exceeded 95% removal efficiency and delivered higher removal efficiencies compared to experiments at 9.34 mA/cm<sup>2</sup>.

Utilizing real ANSOL to examine electrochemical Cr(VI) reduction did not achieve notable, consistent results. No additional electrolyte was added, and experiments were performed at 23.364 mA/cm<sup>2</sup> current density. Upon measuring samples using ICP-MS, final permeate concentrations were measured at higher values than that of the initial feed concentration. In order to fully recognize the obstacles in achieving Cr(VI) via electrochemical reduction, it is necessary to establish the chemical constituency of the ANSOL obtained from the ammunition facility, as well as the approximate concentration of each chemical species (though it is likely that the ANSOL has a variety of organic molecules that can chelate then Cr(VI) and prevent its reduction). This will allow for focused investigation as to why high removal efficiencies of Cr(VI) were not observed in the real wastewater solution, despite application of previously developed methods and successful experimental conditions from the synthetic wastewater experiments. Due to time constraints, membrane characterization was not performed for these experiments. In the future, membrane characterization should be performed to examine surface characterization, membrane resiliency, and analysis of chromium precipitates formed during experimentation.

## References

Anderson, J. (2003). The environmental benefits of water recycling and Reuse. *Water Supply*, 3(4), 1–10. https://doi.org/10.2166/ws.2003.0041

Babel, S. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: A Review. Journal of Hazardous Materials, 97(1-3), 219–243. https://doi.org/10.1016/s0304-3894(02)00263-7

Barakat, M. A. (2011). New trends in removing heavy metals from industrial wastewater.
 Arabian Journal of Chemistry, 4(4), 361–377.
 https://doi.org/10.1016/j.arabjc.2010.07.019

- Beaumont, J. J., Sedman, R. M., Reynolds, S. D., Sherman, C. D., Li, L.-H., Howd, R. A., Sandy, M. S., Zeise, L., & Alexeeff, G. V. (2008). Cancer mortality in a Chinese population exposed to hexavalent chromium in drinking water. *Epidemiology*, 19(1), 12– 23. https://doi.org/10.1097/ede.0b013e31815cea4c
- Brandt-Rauf, P. (2006). Editorial retraction. *Journal of Occupational and Environmental Medicine*, 48(7), 749. https://doi.org/10.1097/00043764-200607000-00019
- Böhlke, J.-K. (2002). Groundwater recharge and agricultural contamination. *Hydrogeology Journal*, 10(1), 153–179. https://doi.org/10.1007/s10040-001-0183-3
- Cohen, M. D., Kargacin, B., Klein, C. B., & Costa, M. (1993). Mechanisms of chromium carcinogenicity and toxicity. *Critical Reviews in Toxicology*, 23(3), 255–281. https://doi.org/10.3109/10408449309105012
- Costa, M., & Klein, C. B. (2006). Toxicity and carcinogenicity of chromium compounds in humans. *Critical Reviews in Toxicology*, 36(2), 155–163. https://doi.org/10.1080/10408440500534032

- Duan, W., Chen, G., Chen, C., Sanghvi, R., Iddya, A., Walker, S., Liu, H., Ronen, A., & Jassby,
  D. (2017). Electrochemical removal of hexavalent chromium using electrically conducting carbon nanotube/polymer composite ultrafiltration membranes. *Journal of Membrane Science*, 531, 160–171. https://doi.org/10.1016/j.memsci.2017.02.050
- Gu, Y., Li, Y., Li, X., Luo, P., Wang, H., Robinson, Z. P., Wang, X., Wu, J., & Li, F. (2017).
   The feasibility and challenges of energy self-sufficient wastewater treatment plants.
   *Applied Energy*, 204, 1463–1475. https://doi.org/10.1016/j.apenergy.2017.02.069
- Jin, W., Du, H., Zheng, S., & Zhang, Y. (2016). Electrochemical processes for the environmental remediation of toxic cr(vi): A Review. *Electrochimica Acta*, 191, 1044–1055. https://doi.org/10.1016/j.electacta.2016.01.130
- Kasonga, T. K., Coetzee, M. A. A., Kamika, I., Ngole-Jeme, V. M., & Benteke Momba, M. N. (2021). Endocrine-disruptive chemicals as contaminants of emerging concern in wastewater and Surface Water: A Review. *Journal of Environmental Management*, 277, 111485. https://doi.org/10.1016/j.jenvman.2020.111485
- Kerur, S. S., Bandekar, S., Hanagadakar, M. S., Nandi, S. S., Ratnamala, G. M., & Hegde, P. G. (2021). Removal of hexavalent chromium-industry treated water and wastewater: A Review. *Materials Today*: Proceedings, 42, 1112–1121. https://doi.org/10.1016/j.matpr.2020.12.492
- Korak, J. A., Huggins, R., & Arias-Paic, M. (2017). Regeneration of pilot-scale ion exchange columns for hexavalent chromium removal. *Water Research*, 118, 141–151. https://doi.org/10.1016/j.watres.2017.03.018

- Koutsou, O. P., Gatidou, G., & Stasinakis, A. S. (2018). Domestic wastewater management in Greece: Greenhouse gas emissions estimation at country scale. *Journal of Cleaner Production*, 188, 851–859. https://doi.org/10.1016/j.jclepro.2018.04.039
- Kunz, N. C. (2020). Towards a broadened view of water security in mining regions. Water Security, 11, 100079. https://doi.org/10.1016/j.wasec.2020.100079
- LA Sanitation and Environment. (n.d.). Hyperion Water Reclamation Plant. Retrieved from https://www.lacitysan.org/san/faces/home/portal/s-lsh-wwd/s-lsh-wwd-cw/s-lsh-wwd-cw-rw-

h2035?\_afrLoop=5724535120656267&\_afrWindowMode=0&\_afrWindowId=null&\_adf .ctrl-

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- McLean, J. E., McNeill, L. S., Edwards, M. A., & Parks, J. L. (2012). Hexavalent Chromium Review, part 1: Health effects, regulations, and analysis. *Journal - American Water Works Association*, 104(6). https://doi.org/10.5942/jawwa.2012.104.0091
- McNabb, D. E. (2017). Managing recycled water. *Water Resource Management*, 283–306. https://doi.org/10.1007/978-3-319-54816-6\_12
- McNeill, L. S., McLean, J. E., Parks, J. L., & Edwards, M. A. (2012). Hexavalent Chromium Review, part 2: Chemistry, occurrence, and treatment. *Journal - American Water Works Association*, 104(7). https://doi.org/10.5942/jawwa.2012.104.0092
- Moffat, I., Martinova, N., Seidel, C., & Thompson, C. M. (2018). Hexavalent chromium in drinking water. *Journal - American Water Works Association*, 110(5). https://doi.org/10.1002/awwa.1044

- Müller, A., Österlund, H., Marsalek, J., & Viklander, M. (2020). The pollution conveyed by urban runoff: A review of sources. *Science of The Total Environment*, 709, 136125. https://doi.org/10.1016/j.scitotenv.2019.136125
- National Toxicology Program. Toxicology and carcinogenesis studies of sodium dichromate dihydrate (Cas No. 7789-12-0) in F344/N rats and B6C3F1 mice (drinking water studies). *Natl Toxicol Program Tech Rep Ser*. 2008 Jul;(546):1-192. PMID: 18716633
- Owlad, M., Aroua, M. K., Daud, W. A., & Baroutian, S. (2008). Removal of hexavalent chromium-contaminated water and wastewater: A Review. Water, Air, and Soil Pollution, 200(1-4), 59–77. https://doi.org/10.1007/s11270-008-9893-7
- Parravicini, V., Svardal, K., & Krampe, J. (2016). Greenhouse gas emissions from wastewater treatment plants. *Energy Procedia*, 97, 246–253. https://doi.org/10.1016/j.egypro.2016.10.067
- Picos-Corrales, L. A., Sarmiento-Sánchez, J. I., Ruelas-Leyva, J. P., Crini, G., Hermosillo-Ochoa, E., & Gutierrez-Montes, J. A. (2020). Environment-friendly approach toward the treatment of raw agricultural wastewater and river water via flocculation using chitosan and bean straw flour as bioflocculants. *ACS Omega*, 5(8), 3943–3951. https://doi.org/10.1021/acsomega.9b03419
- Prasad, S., Yadav, K. K., Kumar, S., Gupta, N., Cabral-Pinto, M. M. S., Rezania, S., Radwan, N., & Alam, J. (2021). Chromium contamination and effect on environmental health and its remediation: A sustainable approaches. *Journal of Environmental Management*, 285, 112174. https://doi.org/10.1016/j.jenvman.2021.112174

- Rakhunde, R., Deshpande, L., & Juneja, H. D. (2012). Chemical speciation of chromium in water: A Review. *Critical Reviews in Environmental Science and Technology*, 42(7), 776–810. https://doi.org/10.1080/10643389.2010.534029
- Saha, R., Nandi, R., & Saha, B. (2011). Sources and toxicity of hexavalent chromium. *Journal of Coordination Chemistry*, 64(10), 1782–1806. https://doi.org/10.1080/00958972.2011.583646
- Shah, A. I., Din Dar, M. U., Bhat, R. A., Singh, J. P., Singh, K., & Bhat, S. A. (2020). Prospectives and challenges of wastewater treatment technologies to combat contaminants of emerging concerns. *Ecological Engineering*, 152, 105882. https://doi.org/10.1016/j.ecoleng.2020.105882
- Sharma, S. K., Petrusevski, B., & Amy, G. (2008). Chromium removal from water: A Review. Journal of Water Supply: Research and Technology-Aqua, 57(8), 541–553. https://doi.org/10.2166/aqua.2008.080
- Sharp, R., & Wiles, R. (2006, March 13). Letter to JOEM: Retract fraudulent chromium-6 paper. Environmental Working Group.
- Velazquez-Peña, S., Barrera-Díaz, C., Linares-Hernández, I., Bilyeu, B., & Martínez-Delgadillo,
  S. A. (2011). An effective electrochemical cr(vi) removal contained in electroplating industry wastewater and the chemical characterization of the sludge produced. Industrial & Engineering *Chemistry Research*, 51(17), 5905–5910.
  https://doi.org/10.1021/ie200968s
- Wakeel, M., Chen, B., Hayat, T., Alsaedi, A., & Ahmad, B. (2016). Energy consumption for water use cycles in different countries: A Review. *Applied Energy*, 178, 868–885. https://doi.org/10.1016/j.apenergy.2016.06.114

- Yadav, S., Ibrar, I., Al-Juboori, R. A., Singh, L., Ganbat, N., Kazwini, T., Karbassiyazdi, E.,
  Samal, A. K., Subbiah, S., & Altaee, A. (2022). Updated review on Emerging
  Technologies for pfas contaminated water treatment. *Chemical Engineering Research and Design*, 182, 667–700. https://doi.org/10.1016/j.cherd.2022.04.009
- Zhang, J. D., & Li, S. K. (1997). Cancer mortality in a Chinese population exposed to hexavalent chromium in water. *Journal of Occupational & Environmental Medicine*, 39(4), 315–319. https://doi.org/10.1097/00043764-199704000-00008
- Zhitkovich, A. (2011). Chromium in drinking water: Sources, metabolism, and cancer risks. *Chemical Research in Toxicology*, 24(10), 1617–1629. https://doi.org/10.1021/tx200251t