12-2021

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Recommended Citation

Cahill, Joseph E., "Coal fly ash beneficiation for reuse and removal of Boron, Cadmium, Chromium, Copper, and Selenium in wastewater treatment." (2021). *Electronic Theses and Dissertations.* Paper 3905.
https://doi.org/10.18297/etd/3905

Coal Fly Ash Beneficiation for Reuse and Removal of Boron, Cadmium, Chromium, Copper, and Selenium in Wastewater Treatment

By

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B.S., University of Louisville, 2019
M.S., University of Louisville, 2021

A Thesis
Submitted to the Faculty of the
College of Arts and Sciences of the University of Louisville
In Partial Fulfillment of the Requirements
for the Degree of

Master of Sciences

in Chemical Engineering

Department of Engineering
University of Louisville
Louisville, Kentucky

December 2021

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A Thesis Approved on:

8/23/2021

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Abstract

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Joseph E. Cahill

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New regulations on coal-fired power plants make previously used wastewater treatment methods aimed to remove heavy metals obsolete. Therefore, there has been increased interest and investment into new technologies to treat coal-fired power plants effluent in the past few years. Traditionally, heavy metal removal technologies have been broken into three categories: physical, chemical, or biological. However, with the new regulations, each category by itself does not offer an ideal solution to removing acceptable concentrations of heavy metals found in the effluents at the coal-fired power plants. Here we report a novel proof-of-concept utilizing adsorption through ion-exchange/co-precipitation – chemical and physical – using the iron oxide constituents found in fly ash, as an alternative effluent treatment technology. Here we illustrate one of the by-products (fly ash) generated from coal-fired power plants can be effectively employed to treat wastewater effluent. The iron oxide constituent separated from fly ash successfully removed positively charged contaminants during ICP-AES analysis. Based on the results shown, it is proposed that the neutrally charged iron oxide nanoparticles are exchanged with the positively charged contaminants (chromium and selenium), forming insoluble metal hydroxides that are easily separated/removed from the wastewater effluent. These results demonstrate that adsorption through ion-exchange/co-precipitation, using iron oxide constituent, has the potential to be developed as an alternative effluent treatment technology. It is anticipated that the work presented will be a starting point for further development of adsorption by iron oxide constituents derived from fly ash.

Table of Contents

Page

LIST OF FIGURES

Introduction

Burning coal to produce electricity has been the major fuel source of the United States since the early 1960's.[1] Coal-fired generation plants use coal to generate the necessary heat in the furnace boiler to produce steam. The steam is then used to rotate the turbine, and thereby spin a generator, to produce electricity. Through the combustion process of coal and its combustion flue gas treatment for sulfur oxides removal, solid byproducts will be left which are called coal combustion products (CCP's).[2]

Coal combustion products vary based on physical and chemical properties, the combustion method performed, and where the products are reclaimed along the emission control process. The four categories include: coal fly ash (CFA), bottom ash, boiler slag, and flue gas desulfurization material or gypsum.[3] CFA is a fine, powdery material collected in the bag houses and electrostatic precipitators. Bottom ash is a course, angular ash material that is too heavy to be carried to the smokestacks and is precipitated at the bottom of the boiler furnace. Boiler slag or molten bottom ash is a pellet material that is glassy in appearance and is reclaimed at the slag tap. Flue gas desulfurization material or gypsum is a substance leftover from the process of reducing sulfur oxides emissions from the combustion flue gas. The focus of our study is beneficiation of CFA which can be categorized into different classes.

Over 99% of all coal burned in the United States at coal-fired plants can be divided into three major categories: bituminous, subbituminous, and lignite.[4] They are classified by their chemical make-up, namely, carbon content. The American Society for Testing and Materials (ATSM) goes a step further for CFA used in concrete. For CFA containing greater than 20% as calcium oxide or CaO (known as Quicklime), it is classified as class C. For CFA containing less than 10% CaO, it is specified as class F. Class C CFA is derived from subbituminous and lignite coal, while class F CFA is derived from bituminous coal.[5] The coal industry in total produced 78.6 million short tons of CCP's in 2019, of which CFA accounted for 29.3 million short tons.[2] Only 17.8 million tons (60.6%) of that CFA is currently being repurposed for beneficial use. High operational cost needs to be incurred and landfill space/footprint should be allotted for unused CFA's disposal. According to a 2017 report, regional landfill costs for fly ash disposal were $79.30/ton in the Northeast, $57.90/ton in the Pacific, $35.70 /ton in the West, $52.70/ton in the Midwest, and $43.60/ton in the Southeast.[6] Instead of spending that cost and resource for landfilling, there is a large potential for new technologies to beneficiate the unused and disposed CFA and generate revenue.

Landfilled and unused CFA is an abundant source of useful compounds (such as alumina, iron oxides, and silica) that could be used for heavy metals removal within water treatment processes. For compliance with the state and federal permits, industrial facilities need to treat their brine and process water effluent before release to surface waters. The brine effluent could have large quantities of toxic impurities that present public health concerns and ecological damage. When the toxic pollutants are introduced to surface waters, they can cause adverse effects to both aquatic life and people. Toxic heavy metal pollutants that can be found in brine effluents include arsenic, boron, cadmium, chromium, copper, mercury, and selenium, to name a few. Consumption of drinking water or marine life exposed to toxic elements can cause cancer, cardiovascular disease, neurological disorders, kidney and liver damage, and lowered IQ's in children.[7] Treatment techniques are employed by industrial facilities to reduce the discharge of toxic metals to surface waters.

In this study, we targeted boron, cadmium, chromium, copper, and selenium. Boron can be found in wastewater streams attributed to boron containing rocks, volcanic activity, borate containing fertilizer, power generation, seawater (boric acid vapor), and borate mining.[8] Cadmium is found largely in urban wastewater, mainly due to rechargeable batteries, paints, food products, and body care products, but also can be found is waste streams from combustion of coal and storm runoff.[9] Wastewater streams containing chromium include mining processes, power generation, steel and alloy production, paint manufacturing, and wood and paper processing.[9] Copper can be found in waste streams attributed to metal refining, power generation, copper plumbing, used motor oils and brake pads, and pesticide runoff.[10] Lastly, selenium concentrations have been observed in waste streams produced by agriculture runoff, mining operations, power generation, and oil refining.[11]

For staying in compliance regarding heavy metals in process water , industries utilize technologies such as traditional coagulation, flocculation and biological treatment, membrane systems such as Reverse Osmosis (RO) and Ultrafiltration (UF), and thermal evaporation technologies. [7] These technologies could be costly and expensive. Reverse osmosis treatment technologies can range from $6,000-$13,333/GPM for the initial capital cost and start up. An ultrafiltration treatment system ranges from $1,500-$2250/GPM for a high-capacity system (100-200 GPM) and $5,000-$10,000/GPM for a low-capacity system (10-20 GPM). For a boiler feed system capital costs up to start up have been seen to cost $500-$1250/GPM, according to Samco in 2017[12]. In our study, we propose a very cost-effective approach that is to repurpose the CFA that is previously being landfilled and wasted, and instead use it for heavy metals removal. This approach will potentially reduce the previously incurred landfill costs and in return generate revenue for unused CFA and mitigate another environmental problem, process water treatment and disposal.

Research has been performed into synthesizing iron oxide-based nanoparticles in the past. Techniques for synthesizing these nanoparticles include: hydrothermal synthesis, thermal decomposition, co-precipitation, sol-gel method, and colloidal chemistry method.[13] In a study conducted by Zoulian Cheng and his team, maghemite nanoparticles were synthesized using iron chloride, urea, and D.I. water, through a co-precipitation method. The maghemite nanoparticles were used to remove Pb^{2+} ions from aqueous solutions at varying concentrations.[14] Iron oxide constituents have also been obtained by hydrothermal synthesis. T.J. Daou and his research team synthesized maghemite nanoparticles by heating magnetite at 300°C for 12 hours in a freeze dryer. The team synthesized the magnetite through co-precipitation of ferric salts and tetramethylammonium hydroxide.[14]

In this paper we demonstrate a novel proof-of-concept utilizing an iron oxide constituent separated from fly ash to remove heavy metals in coal-fired power plants brine waters. The method successfully removed the heavy metals from the brine water through an ion exchange-adsorption and co-precipitation techniques, followed by filtration. It has been shown that the iron oxide constituent from fly ash can successfully remove the heavy metals in varying degrees, over a wide range of pH. We propose the iron oxides reduced the heavy metals in solution, allowing for adsorption in pH dependent environments.

Material and Methods

2.1 Coal-Fired Power Plant Fly Ash

Fly ash sample was collected from a midwestern coal-fired plant that burns both bituminous and sub-bituminous coals. The sample was collected from the electrostatic precipitator used to capture fly ash before the flue gas reach the chimney.

2.2 Separating Fly Ash into Constituents

Fly ash was added to a beaker containing D.I. water and placed on a stir plate with a magnetic stir bar and stirred for 15 minutes. After, the stir bar was removed, and the remaining fly ash solution was vacuum filtrated to remove the D.I. water. The stir bar and left-over fly ash were dried in an oven with the at 120°C for 24 hours to remove any moisture. The magnetic residue was removed from the stir bar and analyzed. The dried fly ash had to be ground up using a mortar and pestle to form a fine powder.

2.3 Mock Wastewaters

a) Single-ion trial

Reagent grade Potassium Dichromate was dissolved In DI water to create a low 15-ppm concentrate solution of water. pH of the mock wastewater was 5.17.

b) Multi-ion trial

Reagent grade Boric Acid, Cadmium Chloride, Copper (II) Acetate, Potassium Dichromate, and Sodium Selenate were dissolved in DI water to create a 15-ppm concentrate solution of water. pH of the mock wastewater was 5.96.

2.4 Preparation of Metal Reduction Samples

Samples were generated by adding 10 mL of mock solution, containing 15 ppm each, of the heavy metal in question for this study, to a glass vial with a magnetic stir bar. The pH of the mock solution was measured using a SevenCompact S221 pH/Ion Meter. The fly ash component under evaluation was weighed out to 50 mg and was added to the mock solution. The mixture was stirred using a INTLLAB stir plate for 15 minutes and no heat. The pH level and ORP was then measured. For samples that needed pH adjustments, pure acid/caustic 5M HCl and 9M NaOH was used in µmL increments. The samples were left on the stir plates for 24 hours under ambient room conditions. After the stirring was complete the pH and ORP were measured and recorded as the equilibrium values. The mixture was then transferred to a 15 mL centrifuge tube, via a 2mL pipet, and centrifuged in an IEC Fischer Marathon 3200R Refrigerated Tabletop Centrifuge (Thermo Scientific, Waltham, MA) for 30 minutes at 4000 rpm. 5-6 mL of the liquid portion was removed and filtered using a 0.45µm syringe filter.

2.5 Analytical Methods

Material characterization was performed using spectroscopic methods, X-Ray Diffraction (XRD) and Inductively Coupled Plasma Atomic Emission (ICP-AES).

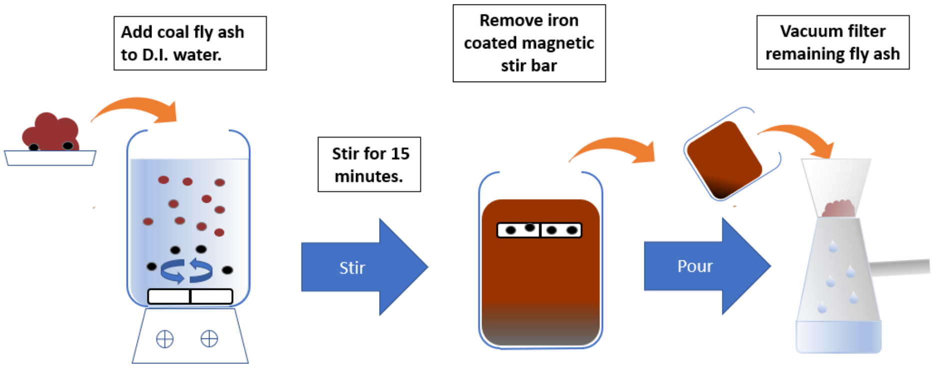
2.6 XRD Analysis

Raw fly ash and its two constituents were mortared with a pestle before placing on sample tray. The three samples were analyzed using a Bruker AXS D8 Advance 2-Series X-Ray Diffraction machine. The samples were run at scan step 2Θ from 20-80°, and the scan speed was 0.7 sec/step. Utilizing a database with previously run samples, peaks could be identified, before post-analysis confirmation.

2.7 ICP-AES Analysis

Metal reduction elemental analysis was performed with an IRIS Intrepid II XSP Inductively Coupled Plasma Atomic Emission Spectrometer (Thermo Scientific, Waltham, MA). ICP-AES analysis precisely determines elemental concentration by exciting the analyte in question through high energy plasma. The excited-analyte's moves to a ground state due to the electrons trying to dissipate. The energy emitted during this process is light, and the output wavelength(s) is specific due to the number of electrons present which determines the element(s) that are present. Samples were passed into a concentric nebulizer (Meinhard Corporation, Golden, CO) and vertical rotary spray chamber at a rate of 1.3 mL/min and the resulting aerosol was swept into the plasma with a 1.0 L/min argon flow. The ICP-AES was operated at a RF power of 1.15 kW.

2.8 Methods



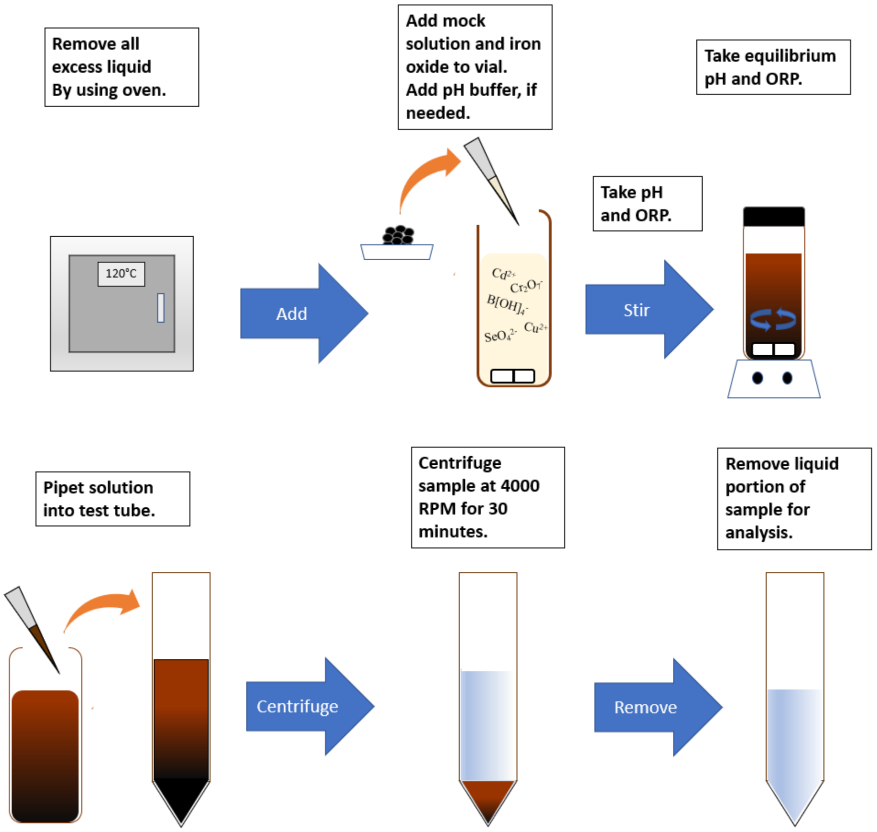


Figure 1 - Schematic showing synthesis of CFA constituents, and the heavy metal removal using the iron oxide constituent.

A schematic of the novelty process used to separate iron oxide constituents from CFA is shown in Figure 1. A small percentage of superparamagnetic iron oxide (maghemite and magnetite) can be found in CFA. A magnetic stir bar will attract the magnetic material suspended in solution. The remaining non-magnetic fly ash was vacuum filtered to remove the D.I. water. After, the constituents were dried in an oven at 120°C, to remove any moisture for a more accurate analysis. Figure 1 also shows the process used to remove heavy metals from solution. The pH and ORP were taken after 15 minutes and 24 hours to determine the ion species of each metal in solution at initial stirring and at equilibrium. The samples were then transferred into test tubes for centrifugation. The liquid portion was then extracted and filtered through a syringe for analysis.

Results and Discussion

3.1 XRD Analysis

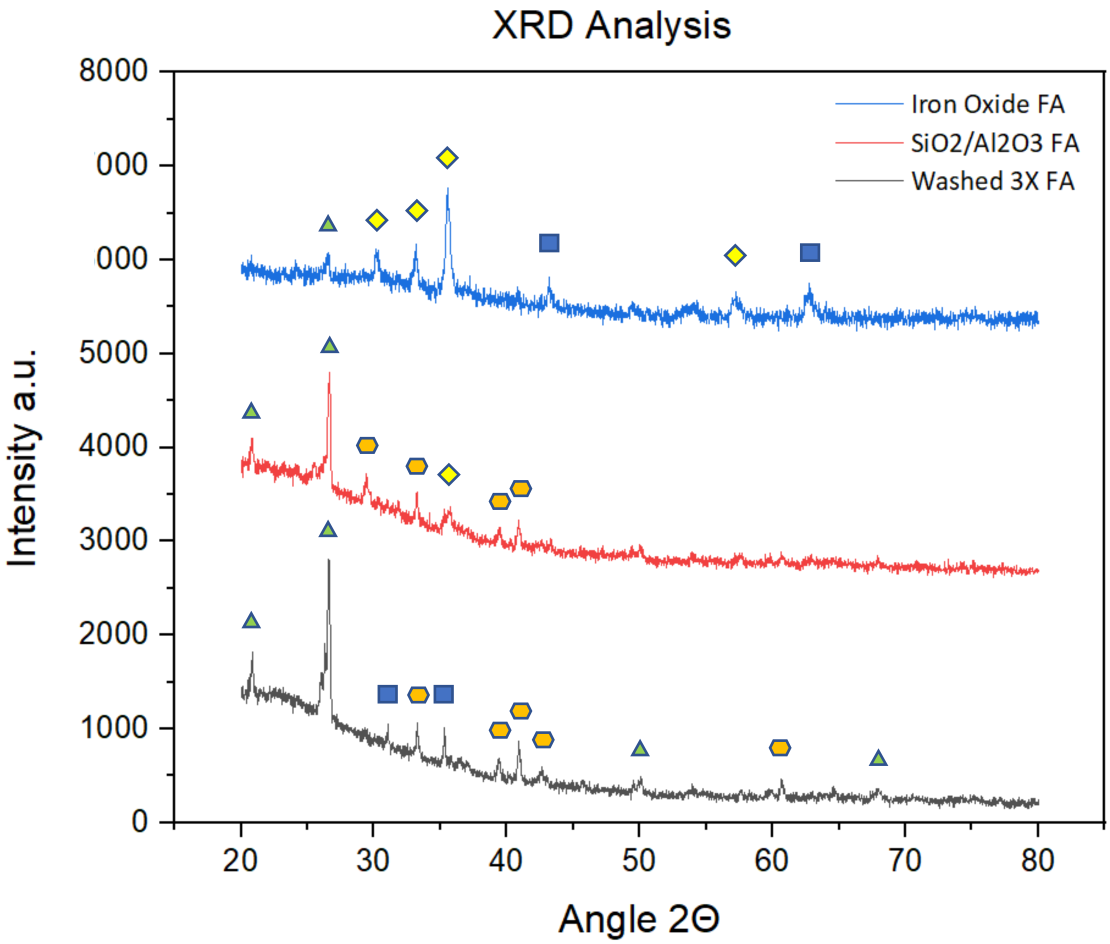


Figure 2 – XRD Analysis removed magnetic material from CFA. It indicates that the particles consist of Fe_3O_4 (peaks denoted by ◇), γ-Fe_2O_3 (peaks denoted by ■) SiO_2 (peaks denoted by ▲), and $Al_2O_3 \cdot SiO_2$ mullite (peaks denoted by ⬢).

CCP's were analyzed through X-ray diffraction to determine the species present before heavy metal removal testing. These specimens were determined to contain silica oxide quartz (SiO_2), aluminum silicate or mullite ($Al_2O_3 \cdot SiO_2$), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4). The bottom sample seen in Figure 2, washed 3X CFA, had peaks of SiO_2-quartz at angles 20.88°, 26.60°, 50.04°, 67.92° with intensity a.u. (counts) ranging from 200-1759. It contained mullite peaks at angles 33.25°, 39.39°, 40.09°, 42.62°, 60.66° which had counts ranging from 191-488. The washed fly ash also contained two maghemites peak at angle 31.03° and 35.31° with a count of 397 and 441, respectively. The SiO_2 / Mullite dominant CFA had SiO_2-quartz peaks at angles 20.78°and 26.66° with counts ranging from 388-1246. The mullite peaks were found to be located at angles 29.42°, 33.23°, 39.41°, and 40.87° and counts ranging from 206-459. The lone iron oxide (magnetite) peak was determined at angle 35.71° with a count of 292. Lastly, the iron oxide dominant CFA had one SiO_2-quartz peak at angle 26.56° with a count of 368. There were magnetite peaks located at angles 30.29°, 35.57°, 37.23°, and 57.22° with counts ranging from 356-1231. There were also two maghemite peaks determined at angles 43.20° and 62.72° with counts 443 and 471, respectively. All XRD samples were labeled using University of Louisville's database cross-referenced with known samples found previously by other researchers.

3.2 Initial running R.F.A and Constituents Against Chromium

The first test conducted utilized the iron oxide constituent, the silica oxide/mullite constituent, and the washed CFA constituent to remove chromium (VI) from mock wastewater. Figure 3 shows the results of chromium removal from a 15ppm concentrated mock solution. The washed CFA and SiO_2/Mullite constituents showed chromium (VI) removal of 27.96% and 37.29%, respectively. The iron oxide constituent showed the most promising removal of 99.69% at near neutral pH.

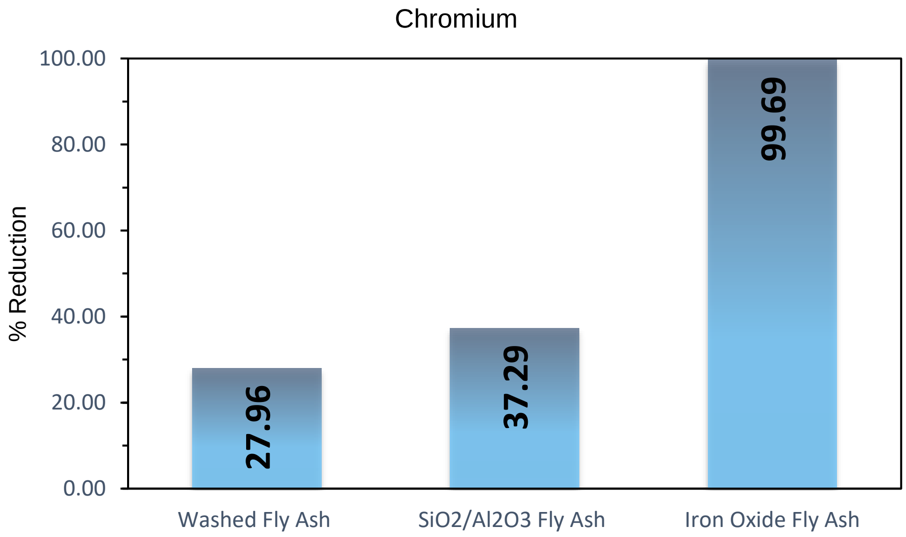


Figure 3 – Initial chromium removal utilizing the iron oxide constituent, the silica oxide/mullite constituent, and the washed CFA constituent – no pH change

3.3 Zeta Potential

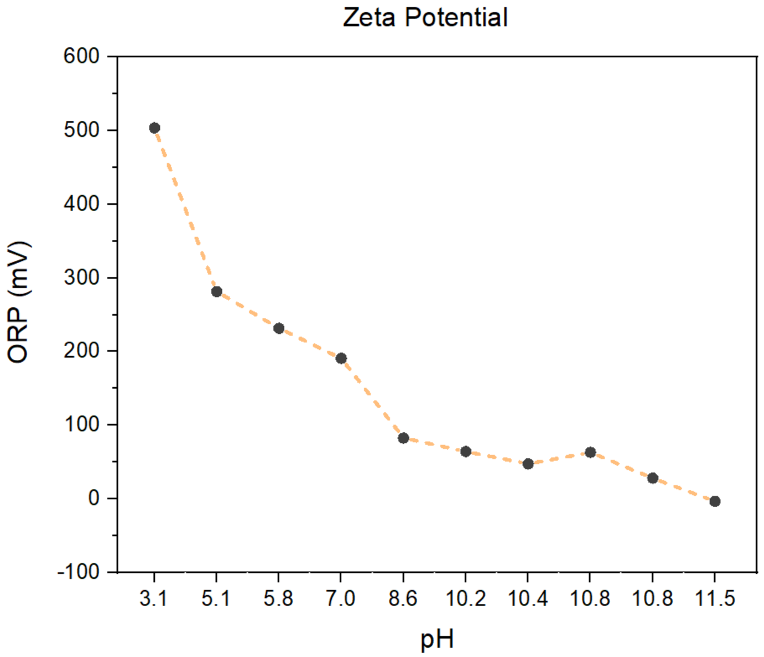


Figure 4 – pH vs. ORP (Oxidation-Reduction Potential) for the iron oxide constituent removing heavy metals in solution.

Redox potential is a measure of a system's affinity for electrons, and the measurement of redox potential will only have meaning when there are reduced and oxidized species, called the redox couple, in the liquid media. The redox couple undergoes a redox reaction, in which the reduction (gain of electrons) of one redox species is accompanied by the oxidation (loss of electrons) of another.[15] The movement of electrons, governed by kinetics (e.g., transport limitations of the redox species to the electrode), creates an electric potential. The potential measured is determined by the ratio of activities of oxidized and reduced species, as defined by the Nernst equation; this is a thermodynamic property.[16] The redox potential can be directly measured using a potentiometer (high impedance voltmeter) with an oxidation-reduction potential (ORP) electrode.[17] This is the recommended technique under the current OECD guidelines for the testing of nanomaterials (NMs).[18] As seen in Figure 4, the ORP values decrease from ~500 to 0mV as pH values increase from ~3-12. Inversely, the potential to gain or lose electrons lowers as pH rises. The results shown below will give an understanding as to why.

3.4 Results of Iron Oxide Constituent Removing Heavy Metals

The promising result of the iron oxide constituent removing chromium from wastewater made us look further into iron oxides synthesized from CFA to remove heavy metals. The next experiment performed was to look at removing five (5) different heavy metals simultaneously over a range of pH. The heavy metals in solution were boron, cadmium, chromium, copper, and selenium, all at 15ppm each.

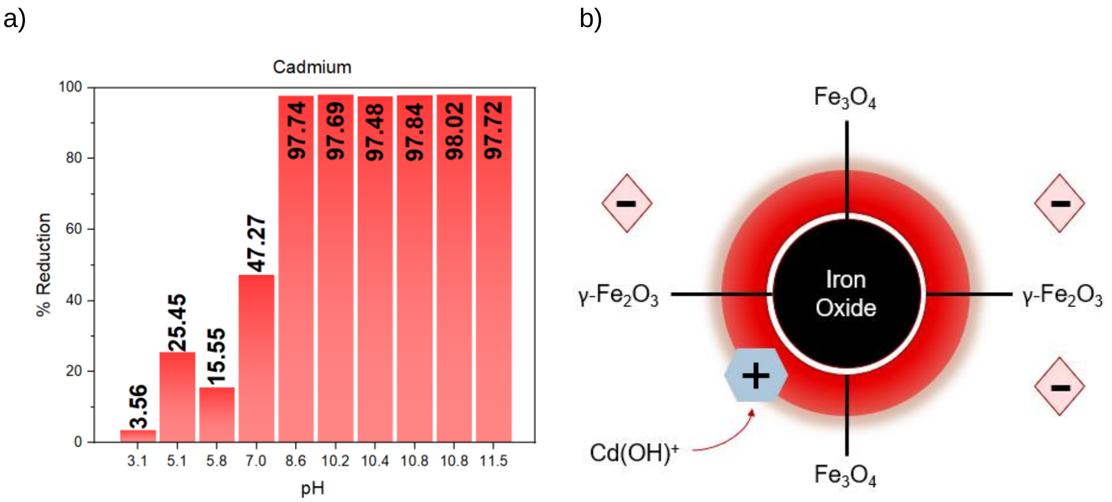


Figure 5 – a) Cadmium removal as a function of pH change utilizing the iron oxide constituent b) Graphic of proposed cadmium removal through co-precipitation .

Cadmium^{2+} removal greater than 97% was achieved at basic pH's, Figure 5. When cadmium in solution transitions to $CdOH^+$, and at higher pH's $Cd(OH)_2$, $Cd(OH)_3^-$, and $Cd(OH)_4^{2-}$, the cadmium precipitates out of solution efficiently. At acidic pH's cadmium exists in solution solely as Cd^{2+}, which is soluble in water at low to near neutral pH. Due to this fact, cadmium removal will not be favorable in pH ranges deemed acidic. The sample at pH 8.58 had no pH buffer added and resulted in a cadmium reduction of 97.74%. A study performed by Ehrampoush et al. (2015) examined cadmium removal using iron oxide nanoparticles in conjunction with tangerine peel extract. The results showed increasing cadmium removal (87-89.5%) with increasing cadmium concentrations 5-20 mg/L. A similar study performed in 2014 utilizing zinc oxide nanoparticles showed with increasing pH, removal of cadmium ion increased in tandem. At pH 4 cadmium removal efficiency was 38% while at pH 7 removal efficiency was 89.6%.[19] A third study, by Singh et al, in 2018 describes a process using iron oxide nanoparticles to remove heavy metals (Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}) from aerated municipal sludge wastewater. The maximum adsorption of cadmium from this study was determined to be 14.7 mg/g.[20]

a) b)

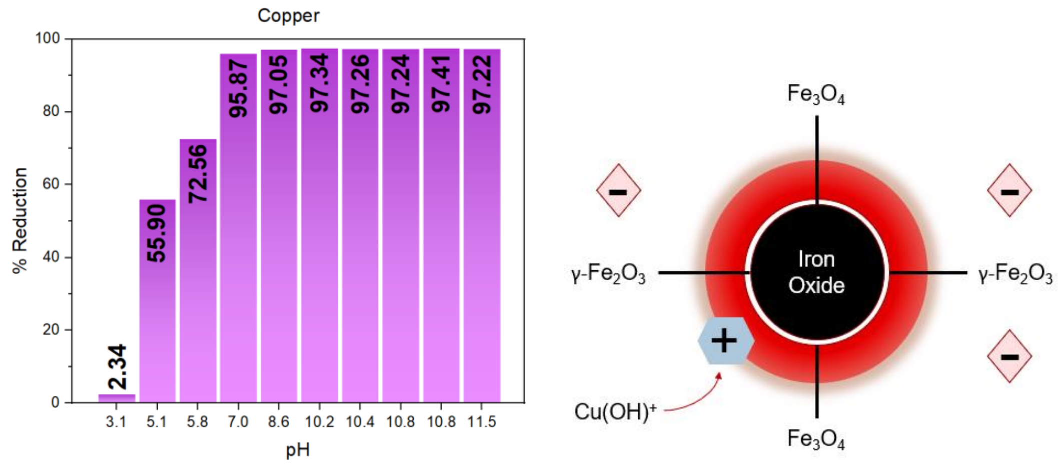


Figure 6 – a) Copper removal as a function of pH change utilizing the iron oxide constituent. b) Graphic of proposed copper removal through co-precipitation.

Cu^{2+} removal using iron oxides showed reduction of greater than 95% in all sample with a pH$\geq$ 6.98. At low pH's$\leq$ 6, Cu^{2+} ions are favorable in solution, and are soluble in water. As the pH rises towards basic conditions copper ions in solution transition to larger concentrations of CuO and $CuOH^+$, which are insoluble in water and form precipitates, as with cadmium. A 2007 study conducted by Boukhalfa et al. showed promising copper removal through coprecipitation with hydrated iron oxide. The results showed little to no removal at pH's below 4.5. The group further states that the pH range of 5-6 is where absorption starts to take place due to the predominant copper species of Cu^{2+} and $CuOH^+$. The results show at a pH above 6, 100% copper removal can be achieved.[21]

a) b)

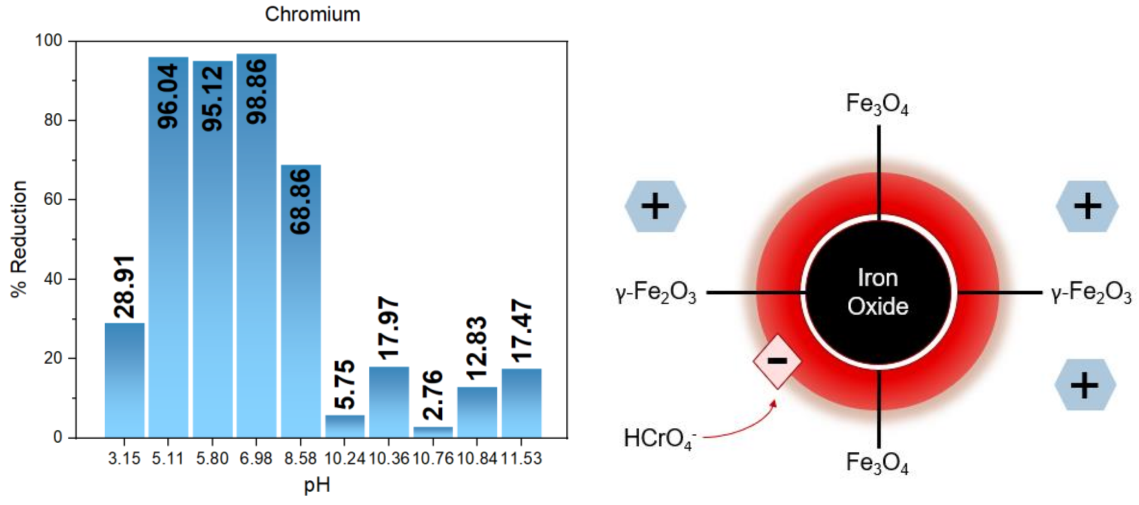


Figure 7 – a) Chromium removal as a function of pH change utilizing the iron oxide constituent. b) Graphic of proposed chromium removal through ion exchange.

Chromium^{6+} removal from mock solution showed removal greater than 95% in the pH range 5-7, Figure 7. At pH 8.58, where no buffer was added a chromium removal of 68.86% was achieved. At high basic condition chromium removal never exceeded 18%. As the ORP values decrease, the reduction potential to gain or lose electrons decreases conversely. High chromium removal in acidic conditions coincides with previous findings from literature. In a 2016 study Gusain et al. and his team synthesized iron oxide nanoparticles from $FeCl_3$ for chromium removal. Adsorption tests were performed over a pH range from 2-12 using potassium dichromate for the mock water solutions. Adsorption of chromium was found to decrease with decreasing pH. Chromium exists in solution primarily in three forms: $HCrO_4^-$, $Cr_2O_7^{2-}$, and $Cr_4O_{13}^{2-}$. The neutral charge of the absorbent increases chromium removal with high concentrations of $HCrO_4^-$ in solution. Results showed chromium removal of greater than 90% at pH 2, around 30% at pH 4 and chromium removal less than 15% an any pH>6. The pH$_{zpc}$, or the point at which the surface potential of the absorbent is zero, of the iron oxide was 7.65. Adsorption that occurred above the pH$_{zpc}$ was governed by a mechanism other than electrostatic force of attraction.[22] In a second study, from 2013, targeting hexavalent chromium, Roy and Bhattacharya utilized maghemite at 6.0 pH. The maximum adsorption capacity was 94.33 mg/g.[23] Similar experiments performed by Karami (2013) and Kumar and Chalwa (2014) utilizing magnetite at 5.5 pH and hematite at 5.0 pH were able to remove Chromium (IV) at maximum adsorption at 88.93 mg/g and 65.00 mg/g, respectively.[24] [25]

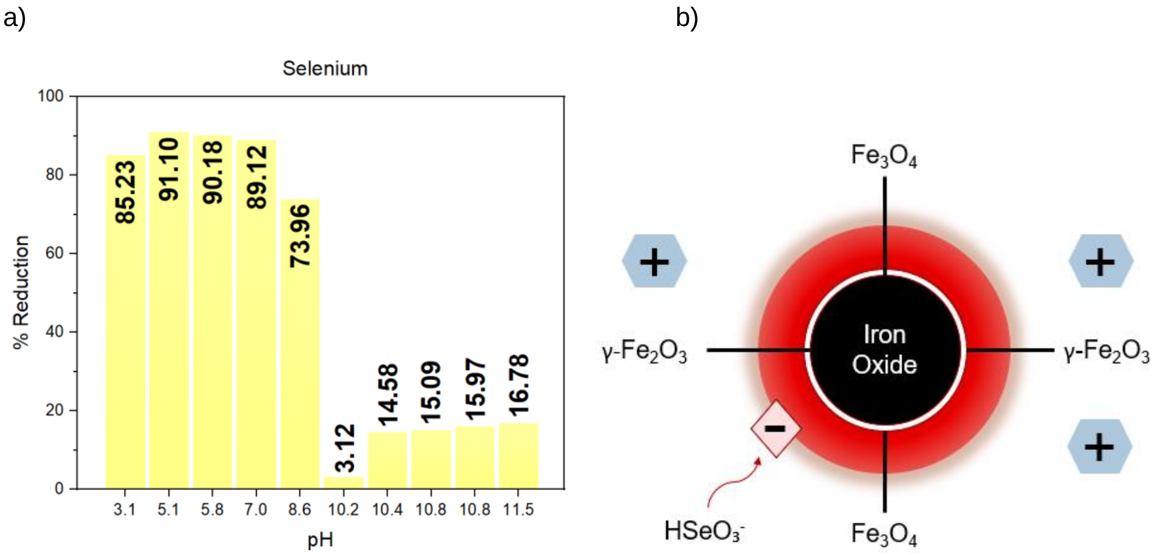


Figure 8 – a) Selenium removal as a function of pH change utilizing the iron oxide constituent. b) Graphic of proposed selenium removal through ion exchange.

Selenium removal utilizing iron oxide, shown in Figure 8, was greater than 85% for all sample solutions in acidic conditions. ORP values from Figure 4 suggest selenium species predominantly were in elemental Se^0 or $HSeO_3^-$, where selenium retention is expected. Selenium samples in basic conditions had selenium species in SeO_3^{2-} (selenite) form, where selenium removal is not favorable. As with chromium, the reduction potential from (Figure 4) decreases allowing less electron removal to take place, significantly reducing percent reduction. In 2020, a study utilizing iron oxide impregnated hybrid polymers to remove selenium from water by Marjanovic et al. was conducted over a pH range from 2-11 and selenium concentrations of 0.5-5 mg/L. The results showed highest removal efficiency at pH 3-4 with maximum removal ~96%. Sorption removal was 20% or lower for pH values greater than 6. Using a MINTEQ software, selenium (IV) distribution as a function of pH showed a coexistence of $HSeO_4^-$ and SeO_4^{2-} at pH$\leq$4, while at pH$\geq$4 $SeO4^{2-}$ is dominantly in solution.[26]

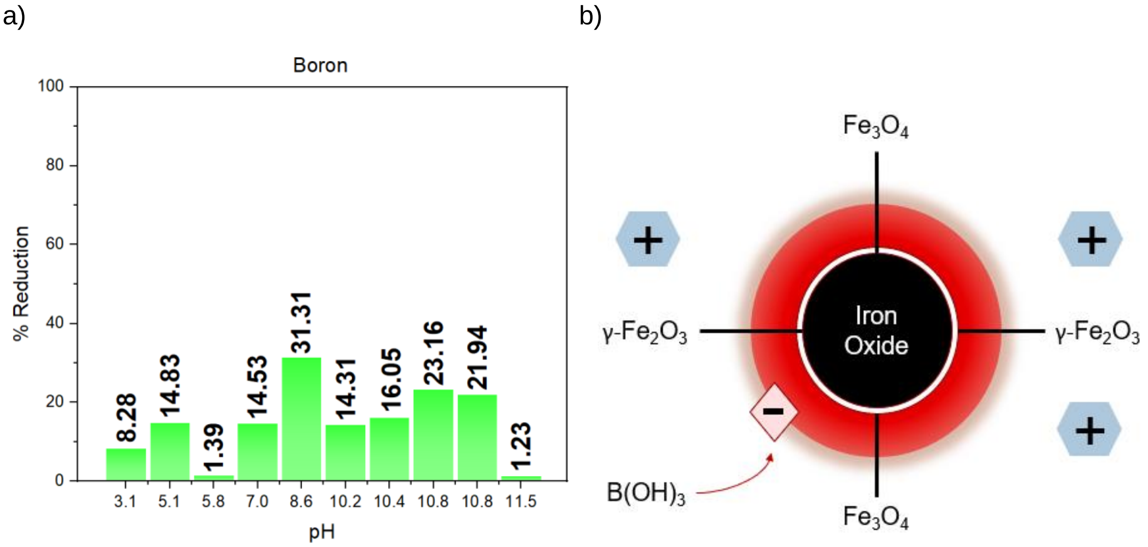


Figure 9 – a) Boron removal as a function of pH change utilizing the iron oxide constituent. b) Graphic of proposed boron removal through co-precipitation

Boron^{3+}, the heavy metal with the lowest percent reduction over the pH range of 3-12 showed a maximum reduction of 31%, Figure 9. The highest removal was attained at a pH of 8.58 and a zeta potential of 0.08V. The highest removal being attained at a pH near 8 was expected based of previous results seen in literature. Although the removal percentage was not in the vicinity of the 70% seen in literature, the boron in this study was competing with four additional metal ions for removal, which was not a variable in the ensuing study. In 2011, Demetriou et al. utilized iron oxide nanoparticles to remove boron from aqueous solutions. The study showed at various molar concentrations 0-1 M, the optimum pH for boron removal through iron oxide nanoparticles is 8. At pH 8.2 the pH$_{zpc}$,, of iron oxide was determined, while the equilibrium point of the two boron species, $B(OH)_3$ and $B(OH)_4^-$ was determined to be pH value 9.1. The study explains the optimum conditions for boron removal occurs when the absorbent surface has no charge and when boric acid is the predominant species in solution. The optimum removal of boron was 70%.[27]

Conclusions

A proof-of-concept of a novel synthesis method has been developed and demonstrated for the removal of heavy metals from wastewater sources. Synthesis of iron oxides occurred using CFA, from a coal burning electrical facility, utilizing magnetic-field attraction of a magnetic stir bar. Heavy metal removal was demonstrated by using a concentrated water solution and the constituents derived from CFA. Through ion exchange and co-precipitation, the heavy metals in the concentrated water solution were removed after a 24-hour stirring step. The final liquid sample showed significant reduction of four out of five targeted heavy metals over a varying pH's, ranging 3-12.

To determine if fly ash constituents could remove heavy metals from concentrated brine samples, an initial test was run using a 15ppm solution of potassium dichromate. Using washed fly ash, and the two derived constituents; SiO_2/Al_2O_3 and iron oxide, results showed the iron oxide constituent removed 99.69% of the chromium in solution. The washed fly ash and SiO_2/Al_2O_3 constituent removed ~28% and ~37% of the chromium, respectively and were not investigated further. Secondary testing into heavy metal removal was pursued for the iron oxide constituent to determine if fly ash derivatives could be used as a stand-alone absorbent. No error bars were correlated to this study as only one run of each testing was performed. Due to cost of ICP analysis and time constraints due to Covid-19 protocols.

Secondary testing into the iron oxide derivative was pursued utilizing 5-metals in solution simultaneously. The metals included for testing were Cd^{2+}, Cu^{2+}, Cr^{6+}, Se^{6+}, and B^{3+}. After testing was complete, results cadmium was removed at 97% and above for all pH's $\geq$8.58. Coinciding with cadmium copper was removed at 95% or greater at pH's $\geq$8.58. Chromium achieved 95-97% removal over the pH range 5-7. Selenium was removed the best at acidic pH's 3-7, achieving removal percentages 85-91%. Boron achieved 31% removal at pH 8.58, with no buffer adjustment.

Utilizing iron oxide constituents from CFA to treat wastewater gives financial benefits versus purchasing absorbents from outside vendors. Fly ash intended for disposal would now have an additional use in saving power plants disposal costs, along with absorbent costs needed to clean processed waters to generate electricity.

Additional investigation would be needed for scale up costs as well as removal efficiencies into other metals not investigated in this study. Separating the iron oxide from large quantities of CFA would become another issue to tackle in further investigation to utilizing fly ash as an absorbent replacement. A study into brine samples containing salts and chlorides would need to be studied in further research to determine removal efficiency differences due to electrostatic interactions with the iron oxide. Further development may also be considered to the recyclability of the iron oxide as a one-off absorbent. Spent iron oxide with a one-time use would be costly due to sludge maintenance needed frequently. The recyclability would add cost benefit to any consumer wishing to utilize iron oxide derived from CFA in the future.

References

1) "Fossil Energy Study Guide: Coal". *Energy,* www.energy.gov/sites/prod/files/Elem_Coal_Studyguide.pdf.
2) "How a Coal Plant Works". *Tennessee Valley Authority,* www.tva.com/energy/our-power--system/coal/how-a-coal-plant-works#:~:text=Coal-l- fired%20plants %20produce%20electricity,to%20start%20the%20process%20over.
3) "About Coal Ash: What are Coal Combustion Products?". *ACAA*, www.acaa-usa.org
4) "Coal Explained". *US Energy Information Administration*, 08 Oct. 2020, ww.eia.gov
5) W. Bouguerra, A. Mnif, B. Hamrouni and M. Dhahbi, Boron removal by adsorption onto activated alumina and by reverse osmosis, Desalination, 223 (2008)

6) Szilagyi, Jessica. “The Financial Incentives for Private Landfills to Take Coal Ash”. *AllOnGeorgia*, 05 Jul. 2019, www.allongeorgia.com

7) “Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category”. *Federal Register*, PDF, 2019-24686. EPA, 11 Nov. 2019, 64620-64677. www.federalregistrer.gov

8) “Boron”. *GreenFacts*, 15 Dec. 2004, www.greenfacts.org

9) Tchounwou, P. B., et al. (2012). "Heavy metal toxicity and the environment." Experientia supplementum (2012) **101**: 133-164.

10)Flemming, C.A., Trevors, J.T. Copper toxicity and chemistry in the environment: a review. *Water Air Soil Pollut* 44, 143–158 (1989)

11) P. Ježek, P. Škarpa, T. Lošák, J. Hlušek, M. Jůzl and P. Elzner (October 3rd 2012). Selenium – An Important Antioxidant in Crops Biofortification, Antioxidant Enzyme, Mohammed Amr El-Missiry, IntechOpen, DOI: 10.5772/50356.

12) Marshall, Kimberly. “How Much Does an Industrial Water Treatment System Cost?” *Samco Tech*, 28 Nov. 2018, www.samcotech.com

13) Cheng, Z., et al. (2012). "Synthesis and Characterization of Iron Oxide Nanoparticles and Applications in the Removal of Heavy Metals from Industrial Wastewater." International Journal of Photoenergy **2012**: 608298.

14) Daou, T. J., et al. (2006). "Hydrothermal Synthesis of Monodisperse Magnetite Nanoparticles." Chemistry of Materials **18**(18): 4399-4404.

15) Schüring, H. D. Schulz, W. R. Fischer, J. Böttcher, and D. Schüring, *Redox: Fundamentals, Processes and Applications*, Springer, Berlin, Germany, 2010.

16) S. S. Judd and T. Stephenson, *Process Science and Engineering for Water and Wastewater Treatment*, IWA Publishing, 2002.

17) W. D. Weight, *Hydrogeology Field Manual*, Mcgraw-Hill Professional Publishing, 2008.

18) ENV/JM/MONO, “Ref: no. 27–46 list of manufactured nanomaterials and list of endpoints for phase one of the sponsorship programmed for the testing of manufactured nanomaterials: revision,” 2010.

19) Salmani M, Zarei S, Ehrampoush M, Danaie S. Evaluations of pH and high ionic strength solution effect in cadmium removal by zinc oxide nanoparticles. J Appl Sci Environ Manag. 2014;191:123–131.

20) Singh P, Tiwary D, Sinha I (2015) Chromium removal from aqueous media by superparamagnetic starch functionalized maghemite nanoparticles. J Chem Sci 127(11):1967–1976

21) Boukhalfa, C., et al. (2007). "Removal of copper from aqueous solutions by coprecipitation with hydrated iron oxide." Asian Journal of Chemistry **19**: 4267-4276.

22) Gusain, D., Srivastava, V., Sillanpää, M. *et al.* Kinetics and isotherm study on adsorption of chromium on nano crystalline iron oxide/hydroxide: linear and nonlinear analysis of isotherm and kinetic parameters. *Res Chem Intermed* **42,** 7133–7151 (2016)

23) Roy A, Bhattacharya J (2013) A binary and ternary adsorption study of wastewater Cd (II), Ni (II) and Co (II) by γ-Fe2O3 nanotubes. Sep Purif Technol 115:172–179

24) Karami H (2013) Heavy metal removal from water by magnetite nanorods. Chem Eng J 219:209–216

25) Kumar R, Chawla J (2014) Removal of cadmium ion from water/wastewater by nano-metal oxides: a review. Water Qual Expo Health 5(4):215–226

26) Marjanovic, V., et al. (2020). "Selenate Adsorption from Water Using the Hydrous Iron Oxide-Impregnated Hybrid Polymer." Metals **10**(12): 1630.
27) Demetriou, A. and I. Pashalidis (2012). "Adsorption of boron on iron-oxide in aqueous solutions." Desalination and Water Treatment **37**(1-3): 315-320.

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