

# Magnetite Synthesized from Acid Mine Drainage: A Novel Approach for Chromium (VI) and Fluoride Removal

Netshedzo Tshikosi<sup>1</sup>, Vhahangwele Masindi<sup>2</sup>, Nomcebo Mthombeni<sup>3</sup> and Munyadziwa Ramakokovhu<sup>4</sup>

**Abstract**— In order to remove hexavalent chromium (Cr(VI)) and fluoride ions from water solutions, this study investigates the extraction of ferric iron from acid mine drainage (AMD) and the synthesis of magnetite (FeO<sub>4</sub>) nanoparticles. In particular, ferric iron was extracted from AMD at pH 3.7, redissolved, and used as a precursor to magnetite. Co-precipitation was used to create magnetite nanoparticles, and X-ray diffraction (XRD) confirmed that the high-purity magnetite had a cubic spinel structure. The synthesized magnetite's surface charge characteristics were demonstrated by its point of zero charge (pHpzc) of 6.5. At pH levels 2 and 8, respectively, clearance rates of 90.5% for Cr (VI) and 81.5% for fluoride were achievable. Electrostatic attraction and ligand exchange were involved in the adsorption process; for each pollutant, the optimal adsorption occurred at different pH values. Fluoride levels reached the WHO recommendation limit when the amount of magnetite employed as an adsorbent was increased, improving removal efficiency. However, excessive amounts of Cr (VI) were still present, suggesting that the procedure needed to be adjusted further. The results highlight the potential of AMD-derived magnetite nanoparticles to successfully remove dangerous metals and fluoride from contaminated water, offering a promising solution to the problem. Batch experiments revealed that pH levels had a substantial impact on the removal of fluoride and Cr (VI). Acid mine drainage (AMD) is a toxic and persistent wastewater containing high levels of harmful chemical species, particularly iron (Fe) and sulfate, along with traces of other elements. The high concentrations of Fe and sulfate make AMD a viable source of valuable minerals, especially when considered within the frameworks of the circular economy, beneficiation, and resource valorization. This study focuses on the recovery of Fe-based minerals from AMD and their potential applications across various industries. It explores the techniques and mechanisms involved in extracting valuable minerals from AMD, as well as the synthesis and beneficiation of Fe-based minerals derived from these recoveries. The study also addresses the challenges, research opportunities, and future perspectives related to this process, with an emphasis on sustainability and the circular economy. By demonstrating how valuable minerals can be extracted from toxic mine drainage, this work highlights the potential to significantly reduce environmental impacts while promoting resource recovery. Additionally, the study investigates the innovative use of magnetite synthesized from AMD for the removal of hexavalent chromium (Cr

(VI)) and fluoride (F<sup>-</sup>) from contaminated water. The method involves recovering ferric iron from AMD and converting it into magnetite through chemical precipitation. The resulting magnetite shows a strong capacity to adsorb Cr (VI) and fluoride ions due to its large surface area, magnetic properties, and high affinity for these contaminants. This approach offers a promising solution for water purification while advancing the principles of the circular economy by transforming waste into valuable resources.

**Keywords**— Acid mine drainage; Chromium(VI); Fluorides, Magnetite; minerals Valorization.

## I. INTRODUCTION

Mineral resources and energy have gained more attention in research fields and all countries around the world. Acid mine drainage (AMD) remains one of the prime pollutants of water bodies especially in coal and gold mining area [1], [2]. There are four types of mine drainages (namely: acid, neutral, saline, and basic mine drainage) depending on the hydrogeology of the mine spaces [1], [3]. Among these mine drainages, acid mine drainage has been considered as an issue due to its acidic pH (pH<sub>≈</sub> 2 – 3) and pre-dominated by ferric and ferrous iron (Fe (III)/(II)), hydrogen ions (H<sup>+</sup>), sulfates (SO<sub>4</sub><sup>2-</sup>), aluminum (Al<sup>3+</sup>), and manganese (Mn<sup>2+</sup>) [4]. These present elements, whereby iron and sulfates exist at high concentrations, justify that AMD is generated from the oxidation of pyrite minerals in the presence of oxygen and water. This renders AMD a feasible option for the valorization of valuable minerals. The solubilization of the metals present in the AMD and surrounding geologies on contact is accelerated by sulphuric acid generated during the oxidation of pyrite and bacteria present. A hazardous impact to terrestrial and aquatic eco-systems are mainly caused by the metals, metalloids, and non-metals in AMD [2], [3], [5], [6]. Due to all the negative impacts AMD has on the environment, active treatment of AMD is essential and involves the addition of alkaline agents (e.g. brucite, hydrated lime[3], sodium hydroxide[7], calcium oxide commonly known as quicklime, calcined, and ball-milled cryptocrystalline magnesite[2], and sodium carbonate[1], [4]) to neutralize the AMD pH and to aid with the precipitation of dissolved metals as hydroxides. Most industries have opted for active treatment as an effective remediation for AMD, however, there is a few throwbacks associated with the method including high operational cost,

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not efficient, and high disposal costs of the large quantity of sludge generated [7], [8], [9], [10], [11].

These challenges associated with active AMD treatment have led most industries to advocate for a circular economy phenomenon and zero-liquid-discharge (ZLD) process. Few studies have been conducted to recover, reclaim, and synthesize Fe-based minerals and sulfates. These minerals are recovered for several defined applications. After the recovery of these elements, the remaining supernate can be further treated for remediation of clean water as specified in different water quality guidelines, standards, and specifications [4]. To address the circular economy, involve converting of waste into resources, or by increasing the utilization of natural resources to recover valuable products (precipitated metals from AMD) potentially. AMD sludge has been considered as potential source for the generation of coagulants, inorganic pigments, and magnetic particles such as ferrites. Few studies have been conducted to recover ferric and ferrous iron from AMD for the synthesis of goethite ( $\text{FeO}(\text{OH})$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), and magnetite ( $\text{Fe}_3\text{O}_4$ ) [4]. These ferrites are utilized in several fields such as agriculture, environment, and biomedicine (ferrofluid technology, information and energy storage, coal washing, controlled drug delivery, photo-degradation, photo-anode, catalyst, and magnetic formation). There are several routes of synthesizing magnetite from iron-rich salts such as micro-emulsion, solvochemical, thermal decomposition, hydrothermal, sonochemical synthesis, sol-gel, and chemical precipitation. The precipitation process is the most preferred among these methods due to its versatility. Four mechanisms that are involved during chemical precipitation are (i) co-precipitation of ferric ( $\text{Fe}^{3+}$ ) and ferrous ( $\text{Fe}^{2+}$ ) iron, (ii) oxidation of ferrous ( $\text{Fe}^{2+}$ ) iron to ferric ( $\text{Fe}^{3+}$ ) iron and precipitation of  $\text{Fe}^{3+}$ , (iii) un-aerated precipitation of  $\text{Fe}^{2+}$ , followed by (iv) co-precipitation of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ . This reaction occurs under un-aerated conditions to prevent ferrous iron from oxidizing into ferric iron at the stoichiometric ratio of  $2\text{Fe}^{3+}:1\text{Fe}^{2+}$  under an alkaline medium. Ferric and ferrous chlorides and sulfates are the common salts that synthesize magnetite [12], [13], [14].

Magnetite particles/materials have mostly been used to recover and remove heavy metals and elements from wastewater, including Cr, Pb, As, Zn, Cu, P, and F. Due to its enormous surface area, magnetic properties, and capacity to absorb contaminants from water solutions, magnetite ( $\text{Fe}_3\text{O}_4$ ), a mineral composed of magnetic iron oxide, is gaining popularity as a water cleaning solution [15], [16], [17]. Through adsorption processes, generated magnetite nanoparticles have demonstrated a high level of effectiveness in removing dangerous materials including fluoride ions and heavy metals. In addition to resolving the problem of purifying tainted water, using AMD magnetite enables the recovery of resources from waste streams. The availability of clean domestic and per capita water is decreasing yearly due to population growth and rapid industrialization which generates and utilizes large quantities of effluents and water. Other major components that cause water pollution are chemical fertilizers, pesticides, herbicides, mining activities, refineries, and urban runoff. Contamination of the surface and

groundwater has become a prime problem and threat to the environment and health. There are several pollutants in water bodies such as inorganic, organic, heavy metals, microbial, and radioactive species which exist in many forms such as dissolved, suspended, or dispersed materials. The consumption of water regularly is one of the prime modes for a person to inhale fluoride [18]. Chromium can enter the bodies of both people and animals through a variety of routes, mostly through skin contact, breathing, and ingesting. The most common type of chromium that humans and animals encounter is chromium (VI), which is more poisonous and more readily absorbed than chromium (III), which is less dangerous [19], [20], [21], [22]. In order to remove fluoride and chromium (VI) from simulated wastewater, this study explores a novel technique for creating magnetite nanoparticles from AMD. By using waste byproducts from mining operations, this strategy seeks to solve water contamination in areas affected by mining and provides an economical and environmentally responsible way to support sustainable water resource management. With a focus on increasing adsorption efficiency and understanding the underlying removal mechanisms, the potential of synthesized magnetite as an adsorbent for removing fluoride and chromium (VI) is evaluated under various conditions.

## II. MATERIALS AND METHODOLOGY

### *A. Recovery of Ferric Iron (Fe (III)) from Acid Mine Drainage (AMD)*

The raw Acid Mine Drainage (AMD) sample was sourced from the Anglo-American coal mine at Khwezela Colliery in Mpumalanga Province, South Africa. To prevent contamination, it was sealed in high-density polyethylene (HDPE) bottles. To prepare the AMD sample for analysis, filtering and settling were used to remove particulate matter and suspended particles. To ensure stability, the treated samples were then kept at temperatures below  $5^\circ\text{C}$ . Merck Chemicals (Pty) Ltd. supplied sodium hydroxide (NaOH), potassium chromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), sodium fluoride (NaF), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ), while Sigma-Aldrich provided ferrous sulfate heptahydrate. All reagents used in this investigation were analytical grade (AR or GR-grade).

### *B. Mineral Recovery and Synthesis of Magnetite*

Ferric iron recovery was achieved by the selective precipitation of 4500 ml of AMD at a pH of 3.7, the method applied for iron precipitation was adopted from [23], [24]. Hydrogen peroxide was added to raw AMD to facilitate the oxidation reaction. 3.5 mol of sodium hydroxide (NaOH) was utilized to adjust the pH and iron was precipitated as a ferric hydroxide/oxyhydroxide which was further separated by centrifugation at 2500 rpm. The precipitate obtained at pH 3.7 was resolubilized with sulphuric acid resulting in a light brown solution, and further utilized as the feedstock to synthesize magnetite materials. 11.12 g of ferrous sulphate heptahydrate was dissolved in a closed and sealed 2 L beaker of 2M sulphuric acid to make a 0.1M ferrous ion solution.

Nitrogen gas was continuously injected into the reaction vessel to prevent air entrance and delay the oxidation of ferrous ion (Fe (II)) to ferric ion (Fe (III)). After the solids were completely dissolved, the liquid was allowed to settle for 30 minutes to ensure a homogenous solution. The solution was used as a Fe (II) source for magnetite nanoparticles. Magnetite nanoparticles were synthesized utilizing a co-precipitation process, and ultrasonication was utilized to decrease particle clustering. During a typical synthesis, a 2:1 molar combination of Fe (III) and Fe(II) was prepared in a conical flask and subjected to nitrogen gas flow. Later, 4M NaOH was added to raise the pH to 11, forming black precipitates. To ensure consistency, the mix was then ultrasonicated for 30 minutes. The solution was then agitated with a magnetic stirrer at 500 rpm for 45 minutes at 80°C. After cooling the mixture to 25 degrees Celsius, the black precipitate was separated by magnetic separation. The material was rinsed with deionized water and ethanol until it achieved a pH of 7. Next, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dehydrated in a vacuum oven at 70 °C for 12 hours. The dehydrated material was stored in glass vials for further analysis and other uses.

### C. Batch Adsorption Studies

Adsorption of Cr (VI) and F was conducted in the batch mode in duplicate. 1000 ppm of simulated solutions of hexavalent chromium (Cr (VI)) and fluorides(F) used in this work were prepared in the laboratory by dissolving 3.74 g of potassium chromate(K<sub>2</sub>CrO<sub>4</sub>) and 2.21 g sodium fluoride in two different 1 L of deionized water, respectively. The Cr (VI) and F stock solutions were utilized to prepare Cr (VI) and F solutions of various desired concentrations. A definite quantity of Fe<sub>3</sub>O<sub>4</sub> particles was added into synthetic solutions containing Cr (VI) and F with initial concentrations of 50 ppm and 10 ppm, respectively. The effect of the pH was evaluated by varying the pH value ranging from 2.0 to 12.0, it was adjusted with HCl or NaOH. The effect of dosage concentration (5-400 mg) on the removal of Cr (VI) and F with initial concentration of 100 ppm and 20 ppm for particular periods (up to 24 hours), respectively. After the equilibrium was reached the solutions were filtered(Whatman filter paper No. 1)and IC and UV-IS determined the concentration of metal ions in the filtrate. Metals uptake per unit of adsorbent was calculated by (2) and removal efficiency (R, %) at equilibrium were calculated by (3):

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$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (3)$$

Where V(L) is the volume of the solutions, and M(g) is the mass of Fe<sub>3</sub>O<sub>4</sub> particles, C<sub>0</sub>(mg/L) and C<sub>e</sub>(mg/L) are the initial and equilibrium concentrations of fluoride in the solution.

### III. CHARACTERIZATION TECHNIQUES

The pH<sub>pzc</sub> of the Fe<sub>3</sub>O<sub>4</sub> adsorbent was determined by adjusting the pH of a 0.01M sodium chloride solution. The pH in 50 mL conical flasks was changed with 0.1M hydrochloric acid or sodium hydroxide solutions ranging from pH 2 to 12. Following pH correction, 0.2 grams of magnetite nanoparticles were put in each flask, and the final pH was measured 48 hours later. The final pH was plotted against the beginning pH to determine the point at which the curve meets a straight line, known as the pH<sub>pzc</sub>. X-ray Diffraction (XRD) is used to study the crystalline properties of both natural and manmade materials, including atomic arrangement, mineral content, and molecular structure. A Panalytical X'pert PRO diffractometer was used to conduct XRD analysis on the adsorbents in this study. The device used a Cu K $\alpha$  radiation source ( $\lambda=0.154$  nm) with adjustable slits and operated at 45 kV/40 mA.

The Cr (VI) content was measured using the 3500-Cr B colorimetric technique described by the Federation Association (Association et al., 1915). The beginning and residual Cr (VI) levels at a 540 nm wavelength were measured using a WPA, LIGHT Wave, Labotech UV-vis spectrophotometer (South Africa). A UV-VIS Spectrometer was used to evaluate Cr (VI), along with common reagents such as 1,5-Diphenyl Carbazide (DPC) and 1 N sulphuric acid. 125 mg of DPC was dissolved in 250 mL of ethanol to yield 1.5 DPC, and 13.60 mL of 98% w/w H<sub>2</sub>SO<sub>4</sub> was combined with 500 mL of deionized water in a volumetric flask to yield 1 N of sulphuric acid.

### IV. RESULTS AND DISCUSION

The XRD pattern of both Fe-hydroxides precipitated, and magnetite synthesized with ferric iron from acid mine drainage are revealed at Fig 1. The results of magnetite and Fe-hydroxides showed the same patterns as the same as (wei, Masindi). Peaks 21, 24, 35, 40, 50, 61, 63, 69, and 74 theta degrees confirms that synthesized iron oxide is indeed

magnetite [25], [26], [27]. The existing literature review fully agreed with the results obtained in this study (Masindi, beneficia). There is no other peaks presence on the magnetite diffraction pattern, which, if existed, could suggest the existence of other impurities in the matrices of synthesized magnetite. Therefore the synthesized magnetite is of high purity and good crystallinity, which makes this material viable for wastewater treatment.

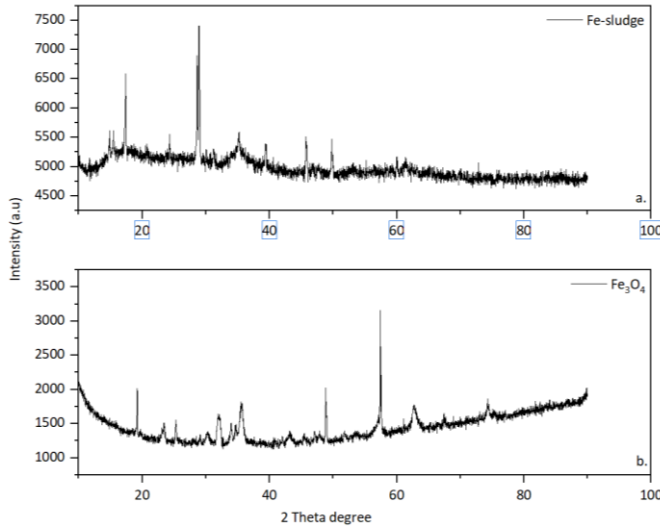


Fig. 1 X-ray diffraction patterns of Fe (III) and  $\text{Fe}_3\text{O}_4$  particles

The point of zero charge (pHpzc) value can be used to derive the surface charge of adsorbent (magnetite) under given condition. Fig 2 demonstrates the graph plotted between change in pH as function of initial pH. Fig 2 was used to determine the pHpzc of the magnetite adsorbent, which indicates the electrical neutrality of the surface and adsorbent at a certain pH value. The pHpzc for this study was found to be 6.5 and the existing literature has found the value ranging from 6 to 8.

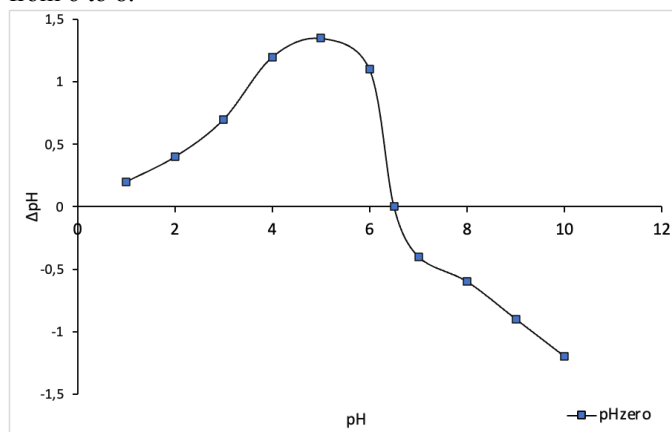


Fig. 2 Zeta potential of  $\text{Fe}_3\text{O}_4$  adsorbent in different pH

The effect of pH in study was evaluated by varying the values from 2.0-9.0, with dosage of 200mg, before addition of the magnetite adsorbent. Fig 3 demonstrate the removal of hexavalent chromium (Cr(VI)) and fluoride (F) by magnetite particles is highly pH-dependent. Maximum removal

efficiency of 90.5% and 81.5% was found at pH 2 and pH 8 with initial Cr(VI) and F concentrations of 50 mL of 100 ppm and 20 ppm, respectively. The quantity of F uptake increased with increasing pH up to a maximum and the drastically decrease, while the other side the Cr(VI) uptake decreases with increase of pH. Considering the adsorption mechanism can explain the different of adsorption efficiency in different pH values. At different pH conditions, the adsorption is combination of electrostatic attraction and ligand exchange. From surface chemistry perspective in aqueous phase, the surfaces of magnetite are often covered with hydroxyl groups that differ in forms at different pH. As illustrated from Fig 2, the surface charge is neutral at the zero point of charge when pH 6.5 is reached and the magnetite surface is positively charged which favored adsorption of anion.

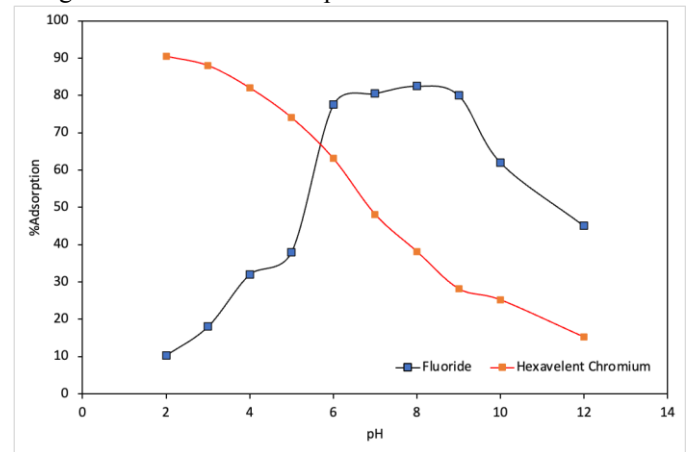


Fig. 3 effect of solution pH on hexavalent chromium (Cr (VI)) and fluorides (F) by magnetite ( $\text{Fe}_3\text{O}_4$ ) particles

Adsorbent dose is a prime parameter for both hexavalent chromium (Cr (VI)) and fluorides (F) removal, Fig 4 shows that the %removal of both Cr (VI) and F increases gradually with increases of adsorbent dose. While on the other Fig 5 reveals that the residual Cr (VI) and F concentrations decreases gradually with increases of the adsorbent dose of magnetite. From the Fig 5 it was observed that F was able to reach minimum permeable concentration by WHO guideline, which is 1.5ppm and Cr (VI) with high residual concentration of 3.2 ppm which is high than the permeable concentration of 0.5 ppm. Sharp decrease in both Cr (VI) and F was due to the greater surface area and availability of more adsorption sites of magnetite. The number of active sites of adsorbent and bulk Cr (VI) and F concentrations were declining and reached in equilibrium.

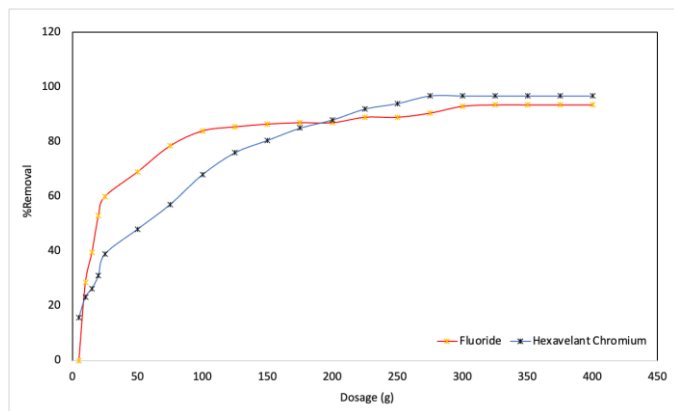


Fig 4 Effect of the  $\text{Fe}_3\text{O}_4$  particles dosage on the hexavalent chromium and fluoride removal

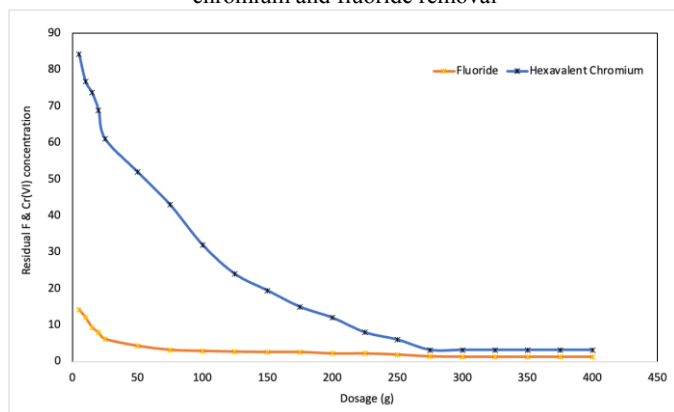


Fig 5 Residual hexavalent chromium and fluoride concentrations

## V. CONCLUSION

In order to remove Cr (VI) and F ions from wastewater, this study successfully recovered ferric iron from acid mine drainage (AMD) and created magnetite nanoparticles. In order to separate ferric iron from AMD in a controlled way, ferric hydroxide/oxyhydroxide was created using hydrogen peroxide and sodium hydroxide. This was then redissolved with sulphuric acid to produce magnetite. In order to obtain uniform particle size, magnetite nanoparticles were produced by a co-precipitation process with the aid of nitrogen gas and ultrasonication. XRD measurements confirmed that pure magnetite with a cubic spinel structure was created. The surface characteristics of the magnetite were disclosed by its  $\text{pH}_{\text{pzc}}$  of 6.5. With removal efficiencies of 90.5% and 81.5%, respectively, at pH 2 and 8, the magnetite nanoparticles showed great efficacy in removing Cr (VI) and fluoride during adsorption testing. Both ligand exchange and electrostatic attraction were used in the elimination procedure. By increasing the amount of magnetite, the removal efficacy improved, and the fluoride levels reached the 1.5 ppm WHO recommended limit. However, the levels of Cr (VI) that remained were more than what was considered acceptable, suggesting that further process optimisation is required. Overall, the study highlights AMD's magnetite nanoparticles' potential as an effective, environmentally responsible water treatment solution.

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