

Rapid Removal of Dissolved Cr(VI) Using a Polycationic/ di-metallic Adsorbent Synthesized with Fe³⁺/Al³⁺ Recovered from Actual Acid Mine Drainage

Khathutshelo L. Muedi^{1*}, Vhahangwele Masindi^{2,3}, Jannie P. Maree⁴, Hendrik G. Brink¹

¹University of Pretoria, Department of Chemical Engineering, School of Engineering, Faculty of Engineering, Built Environment and Information Technology, Private Bag X20, Hatfield, 0028, South Africa, Email: deon.brink@up.ac.za;

²Magalies Water, Scientific Services, Research & Development Division, Erf 3475, Stoffberg Street, Brits, 0250;

³University of South Africa (UNISA), Department of Environmental Sciences, School of Agriculture and Environmental Sciences, P. O. Box 392, Florida, 1710, South Africa;

⁴ROC Water Technologies, P O Box 70075, Die Wilgers, 0041, Pretoria, South Africa

Abstract

In this study, Cr(VI) was rapidly removed from an aqueous solution using a polycationic/di-metallic (PDFe/Al) adsorbent synthesized using Fe³⁺/Al³⁺ recovered from actual acid mine drainage. Optimal conditions for the removal of Cr(VI) were 50 mg/L initial Cr(VI), 3 g of PDFe/Al, initial pH = 3, 10 min to 95% of equilibration time and temperature = 40°C. Under these optimised conditions, ≥95% removal of Cr(VI) was observed. The synthesised material shows great potential for the removal of dissolved Cr(VI).

Keywords: Chromium removal; acid mine drainage; wastewater streams; circular economy; wastewater beneficiation; polycationic/di-metallic adsorbent (nanocomposite)

Introduction

Mining has always been crucial to the development of the South African economy due to the relative abundance of mineral and coal reserves. Mining, however, has the propensity for detrimental impacts to both the environment and humans due to the formation of highly acidic and metalliferous wastewater termed acid mine drainage (AMD). Pollutants such as Fe²⁺, Fe³⁺, SO₄²⁻, Al³⁺ and Mn are commonly found in acid mine water – with Cu, Mg, Ca, Zn and Na in traces (Muedi, Masindi *et al.* 2022).

The search for an efficient, effective, and economic technology to remediate AMD has been a global priority for as long as mining has been practiced. Various technologies have been developed for the treatment and recovery of valuable minerals, but the challenge is the production of heterogeneous, highly mineralised, and toxic sludge that pose secondary pollution and disposal challenges (Ighalo *et al.* 2022). An eco-friendly approach would be to recover major mine water contaminants, i.e. Al, Fe, Mn, and sulphate,

from actual AMD and explore their potential beneficiation and valorisation (Muedi *et al.* 2021, 2022). In our previous studies, we demonstrated the valorisation of AMD for the recovery of Al/Fe tri-valent metals that could be used to synthesise an adsorbent that was subsequently used to remove arsenic from wastewater (Muedi *et al.* 2021). Furthermore, the sequential and staged recovery of metals and sulphate has also been demonstrated (Masindi *et al.* 2019). However, an Al/Fe di-metallic nanocomposite has never been used for the removal of hexavalent chromium from aqueous solutions. This is the first study to explore the feasibility of recovering Al³⁺ and Fe³⁺ from actual AMD and using them to synthesise an adsorbent (nanocomposite) that can be used to remove hexavalent chromium from an aqueous solution.

The U.S. Geological Survey reports that South Africa and Kazakhstan are the world's largest producers of chromium with approximately 95% of global chromium reserves (Papp 2017). Chromium is a crucial component of chemical production,

metallurgical industries, refractories, and foundries (Dhal *et al.* 2013). However, these production processes release chromium-rich effluents to different spheres of the environment. This toxic and hazardous chemical species can emanate from natural (geogenic) and man-made (anthropogenic) sources. The natural milieus comprise water, soil, plants, animals, rocks, volcanic eruptions and minerals, while anthropogenic sources include mining, tanning, and manufacturing of paints, plastics, ceramics, glass, salts, dyes and dietary supplements. These sources release chromium rich effluents to different spheres of the environment (Jobby *et al.* 2018).

(Eco)-toxicological studies have highlighted that the intake of water with elevated levels of chromium ions, specifically hexavalent chromium, can have direct detrimental impacts on human health through bioaccumulation, animals, aquatic organisms, and the environment at large (Shahid *et al.* 2017). The maximum allowed limit in drinking water should be ≤ 0.05 ppm (WHO. 2017). In response to this stringent regulatory framework and standards, various studies have devised numerous ways to treat, remove, and recover chromium ions from water and wastewater matrices. These technologies include electrocoagulation (Wang *et al.* 2020), nano-filtration (Giagnorio *et al.* 2018), freeze desalination (Melak *et al.* 2016), ion exchange (Shao *et al.* 2019), photo-catalysis (Kretschmer *et al.* 2019), adsorption, precipitation, bio-(phyto)-remediation, and crystallization (Kalita and Baruah 2020). However, these technologies still pose a challenge of operational cost and disposal of secondary sludge; hence, they are not used, primarily due to their secondary ecological footprints. Adsorption has emerged as a promising technology due to its effectiveness, affordable costs, and reliance on locally available materials (Muedi *et al.* 2021, Masindi *et al.* 2022).

This study focuses on the use of synthesised iron oxide pigments recovered from AMD emanating from coalmines for the rapid recovery of hazardous Cr(VI) from wastewater. Consequently, it provides a concurrent two-pronged solution to both mining challenges.

Materials and Methods

Sampling, feedstock acquisition and preparation

The adsorbent used was prepared as described previously (Muedi *et al.* 2021, 2022). Potassium dichromate salt ($K_2Cr_2O_7$) was purchased from Sigma-Aldrich and stored until utilisation for stock solution preparation. Caustic soda (NaOH), sulphuric acid (98.5% H_2SO_4) and hydrochloric acid (37% HCl) were purchased from Merck. Aqueous solutions were prepared using ultra-pure water (18.2 M Ω -cm). Experimental vessels (glassware) were carefully and thoroughly cleaned before and after every use to avoid contamination.

Adsorption studies

To determine the adsorption of arsenic and chromium from an aqueous system, several operational parameters (time, dosage, temperature and pH) were evaluated. The results were used to determine the optimum conditions for removing arsenic and chromium.

Characterisation

Metal ions in aqueous samples and solutions were analysed using AAS and ICP-MS. A Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometer (FTIR) with a Perkin-Elmer Precisely Universal attenuated total reflectance (ATR) sampler was used to examine the surface functional groups in the solid samples. X-ray diffraction (XRD) was used to determine the mineralogical composition and the pattern of the synthesised Fe/Al dimetal composite and residue products, which was recorded on a Panalytical X'Pert PRO equipped with Cu-K radiation. The surface area of the Al/Fe nanocomposite was determined using a Brunauer-Emmet-Teller (BET) equipment equipped with micromeritics VacPrep 061 degassing system (Micromeritics Tri-Star II 3020, surface area and porosity, Poretech CC, USA). For quality control/assurance, all the experiments were carried out in triplicates and the data was reported as mean values, per the EPA guidelines.

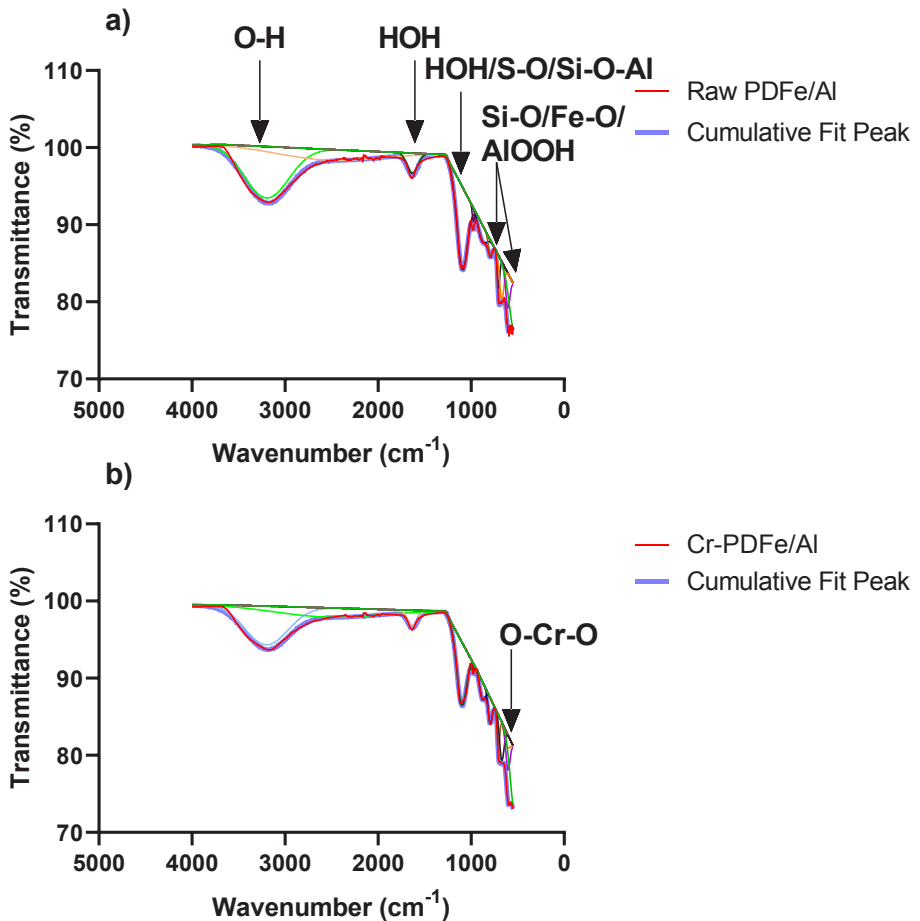


Figure 1 Functional groups of the synthesised PDFe/Al dimetal composite before (a) and after (b) Cr(VI) adsorption

Results and Discussions

Characterisation of the Fe/Al dimetal composite before and after Cr(VI) adsorption

Figure 1 depicts the functional groups of the synthesised Fe/Al dimetal composite before and after Cr(VI) adsorption using a FTIR. Bands of the synthesised Fe/Al dimetal composite are shown before and after Cr(VI). For the raw Fe/Al dimetal composite, high stretching of -OH group is observed between 4000–3500 cm⁻¹. At 1668 cm⁻¹, HOH stretching is observed, which further increases at 1113 cm⁻¹ (Bordoloi, Nath *et al.* 2013). After Cr(VI) adsorption, a change in the stretching of O-H group is observed as a shift of wave band 1138 to 1151 cm⁻¹ (Tarun Kumar Naiya, Biswajit Singha *et al.*

2011). In addition, a new absorption band at, corresponding to O-Cr-O, is observed at 606 cm⁻¹ (Bhatt, Sreedhar *et al.* 2017, Ablouh, Hanani *et al.* 2019).

An XRD diffractogram of the synthesised Fe/Al dimetal composite before and after Cr(VI) adsorption is shown (Figure 2). Iron (Fe) is observed to be the dominant species in the synthesised Fe/Al dimetal composite in the form of goethite/ iron(III) oxide hydroxide (FeO(OH)) with clear diffraction peaks showing the crystallinity of the adsorbent and some amorphousness. Crystalline structures are observed to have formed at the surface of the material. In addition, aluminium is present as aluminium oxide (Al₂O₃), confirming the composite nature of the material. After adsorption, the

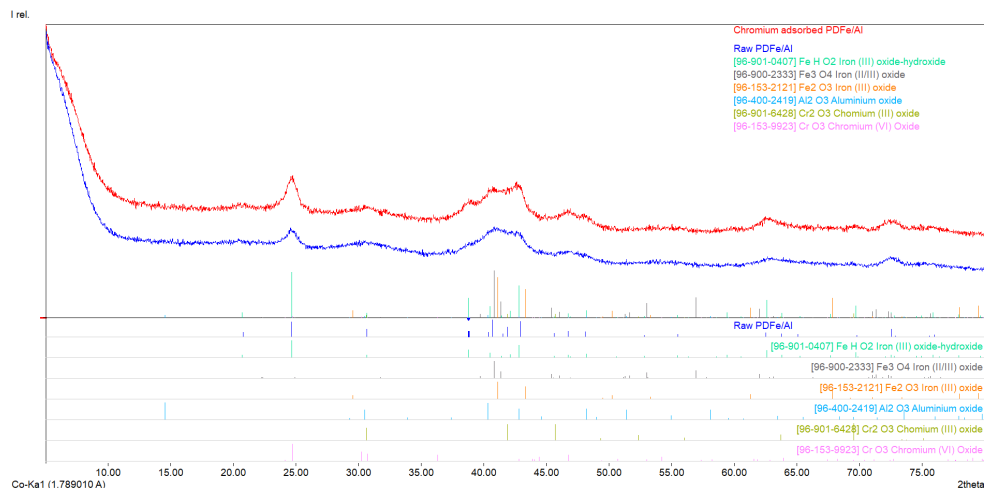


Figure 2 XRD diffractogram of the synthesised Fe/Al dimetal composite before (Blue) and after (Red) Cr(VI) adsorption

significant peaks between $2\theta \approx 35^\circ$ to 50° are observed to have increased. This is attributed to the diffusion of Cr(VI) ions into the pores of the Fe/Al composite adsorbent through chemisorption, with subsequent reduction to Cr(III) (as confirmed by the presence of CrOOH) (Ou *et al.* 2020). The total BET surface area of the raw Fe/Al composite was reported to be $37.5841 \text{ m}^2/\text{g}$.

Effects of operation conditions

As shown in Figure 3A, the Cr(VI) removal efficacy was observed to decrease with an increase in Cr(VI) concentration. This is an indication that the adsorption sites were saturated with the Cr(VI) ions from aqueous solution. It can be observed that 50 mg/L is the optimum initial concentration for Cr(VI), so this was used in subsequent experiments.

Figure 3B demonstrates that an initial pH of 3 optimised Cr(VI) oxyanion adsorption, as previously reported (Yang *et al.* 2015). Also, as shown in Figure 3C, the removal of Cr(VI) was observed to increase with an increase in adsorbent dosage. A similar trend was observed for Cr(VI); an even increase in percentage removal of Cr(VI) is observed from $0.1 - 3 \text{ g}$ of Al/Fe nanocomposite dosage. After 3 g , the trend flattened; therefore, 3 g was adequate for the removal of chromium from the aqueous solution.

As shown in Figure 3D, the % removal of species under study was observed to increase with an increase in contact time. There was a rapid increase in the removal, with up to 95% of the equilibrium adsorption capacity reached after 10 minutes of contact time. This result is of prime importance to the study as it demonstrates the rapidity of the Cr(VI) adsorption, which provides great promise for an industrial application.

As shown in Figure 3E, the removal of Cr was observed to be firmly dependent on temperature. From the graph, it can be noted that the percentage removal peaked at 40°C . This is of particular interest industrially, as an operational temperature of 40°C is realisable within most industrial settings.

Conclusions and Recommendations

PDFe/Al was successfully used to remove Cr(VI) from water. The removal efficacy was observed to be $>95\%$ for Cr(VI) ions, which can be attributed to its high surface area, the surface composition of the adsorbents, and reduction of Cr(VI) to Cr(III) by the PDFe/Al. The study provides strong evidence for the potential of the recovered adsorbent for the removal of Cr(VI) for solution. Future work involves modelling the adsorption of these pollutants from aqueous solution using mathematical models and to test it against authentic water that is rich in chromium ions.

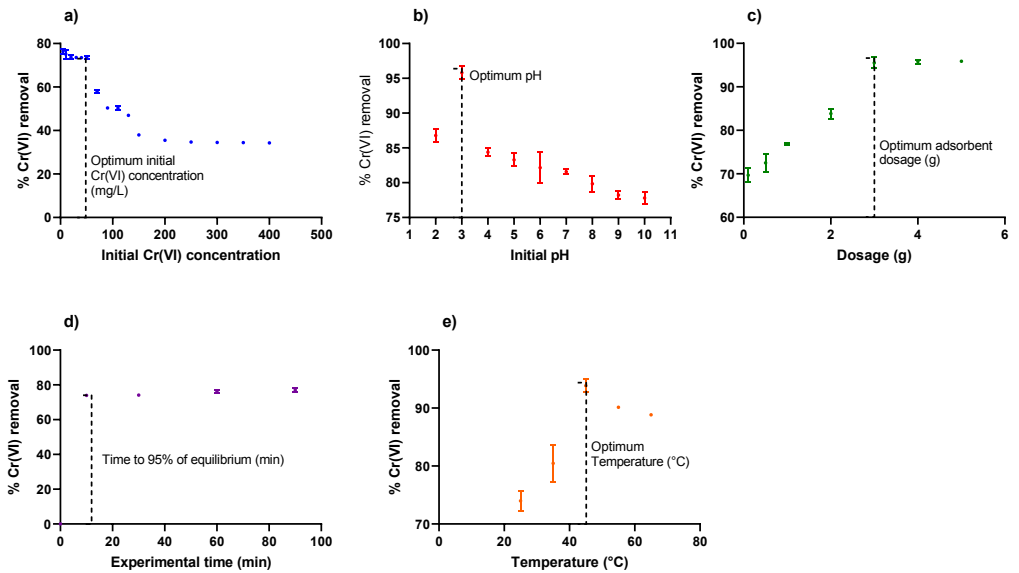


Figure 3 Effects of different operational parameters on the adsorption of Cr(VI)

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