



Recovery and Synthesis of Al³⁺/Fe³⁺ Polycationic-Nanocomposites from Acid Mine Drainage Treatment Process and their Respective Application in the Removal of Arsenic and Chromium Ions from Polluted Water Resources

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Abstract

As the quest for effective and affordable techniques for the treatment of wastewater continues, this study was therefore designed with the aim of recovering and synthesizing Al/Fe polycationic-nanocomposite from authentic acid mine drainage (AMD) and explore its efficacy in the removal arsenic and chromium ions from an aqueous system. Batch experiments were used to fulfil the goals of this study. The Fe/Al matrix was recovered from coal mine drainage and was then used to synthesize a polycationic-nanocomposite through calcination and vibratory ball-milling. Obtained results revealed > 95 and 99 % removal efficiency for chromium and arsenic ions, respectively. In that regard, preliminary assays from this novel, double-edged and innovative study proved that valorisation of mine water by acceptable treatment and extraction of valuable minerals that has myriads of industrial applications such as contaminated water depollution is achievable.

Keywords: Acid mine drainage, Al/Fe nanocomposite, recovery, adsorption, arsenic ions, chromium ions

Introduction

In recent decades, industries have been discharging water that is rich in potentially toxic and hazardous pollutants such as arsenic and chromium to the environment. This has significantly impaired the quality of the environment and its ability to render endowed intrinsic values (El-Zeiny and El-Kafrawy 2017; Masindi and Gitari 2016). Although arsenic and chromium are important in the society for various uses, they can cause detrimental impacts to the human health, ecosystems, soil and the environment if discharged at high levels since the environment can tolerate a certain range of this pollutants as specified in a number of environmental and toxicological guidelines and standards (Edelstein and Ben-Hur 2018). This is may be attributed to the

fact that these ions can be taken up by plants, consumed by animals and humans via a number of routes and escalate in food chains, thus degrading the environment, and its ability to foster life (Singh and Kalamdhad 2011).

The high carcinogenicity and toxicity nature of As(V) and Cr(VI) have led to a continuous search for amicable and effective depollution technologies. This was further dictated by tight environmental regulations that require industries to clean their water to acceptable standards before they could discharge their effluents to the environment. These technologies include different mechanisms such as adsorption, filtrations, precipitations, ion-exchange, bio-sorption and phytoremediation (Masindi et al. 2014). Amongst these techniques, adsorption has



received paramount attention (Masindi and Gitari 2016). This is attributed to the fact that they rely heavily on locally available materials, cheap and easy to operate and high efficacy. A number of materials have been used for adsorption and they include: carbon nanotubes, aluminium oxide, magnesite-bentonite clay, ceria nanoparticles, and zirconium nanoparticles (Masindi and Gitari 2015). However, there's still a challenge with operational cost and waste disposal which lead to secondary pollution. In light of that, the present study aims at the removal of pollutants from wastewater, and utilizes them to remove other pollutants from contaminated water. This has a binary approach since it is solving an industrial problem by treating AMD and attains materials that can be used to treat another environmental problem that involves the removal of arsenic and chromium.

Materials and Methods

Sampling, feedstock acquisition and preparation

Raw acid mine drainage (AMD) was collected from a Coal mine in Mpumalanga Province, South Africa. Sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) and Potassium dichromate salt ($\text{K}_2\text{Cr}_2\text{O}_7$) salts were 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. All chemicals were used as obtained without processing. 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.

Recovery and synthesis of the nanocomposite

Al^{3+} and Fe^{3+} rich acid mine drainage was used for fractional precipitation of those chemical species using Na-salts as seeding materials. The species were then calcined at 100°C to encourage dehydration and promote reactivity. The dry samples were then milled in a vibratory ball mill to homogenise the samples and ensure efficacy of arsenic and chromium adsorption.

Adsorption studies

To determine the adsorption of arsenic and chromium from an aqueous system, a number of operational parameters that include time, dosage, temperature and pH were evaluated. The results were used to determine the optimum conditions that are suitable to remove arsenic and chromium.

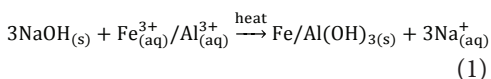
Characterisation

Metal ions in aqueous samples and solutions were analysed using AAS and ICP-MS. Surface area, pore volume and pore size of Al/Fe nanocomposite and resultant residues were determined using a Brunauer-Emmett-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 (QC/QA), all the experiments were carried out in triplicates and the data was reported as mean value as reported in the EPA guidelines.

Results and discussions

Recovery, synthesis and adsorption studies

Caustic soda was added to authentic AMD to elevate the pH for the recovery of Al/Fe nanocomposite via selective precipitation. The interaction of NaOH with Fe^{3+} and Al^{3+} in AMD is shown in equation 1.



The synthesis was done at room temperature. Agglomeration of the particles occurred during heating which was done after precipitation. Synthesis and optimisation parameters are shown in Figure 1 (A – F).

As shown in Figure 1A, it is clear that molecules and particles in AMD slowly gain kinetic energy between 20 °C and 75 °C. This can be attributed to an exponential growth in the time trend graphs with temperature. After 80 °C, collision of molecules and particles increases. As particles continue absorbing heat with time, they start moving faster and kinetic energy increases, hence temperature increases, as the reaction is endothermic. The rate at which particles collide increased and led to coagulation of small particles which



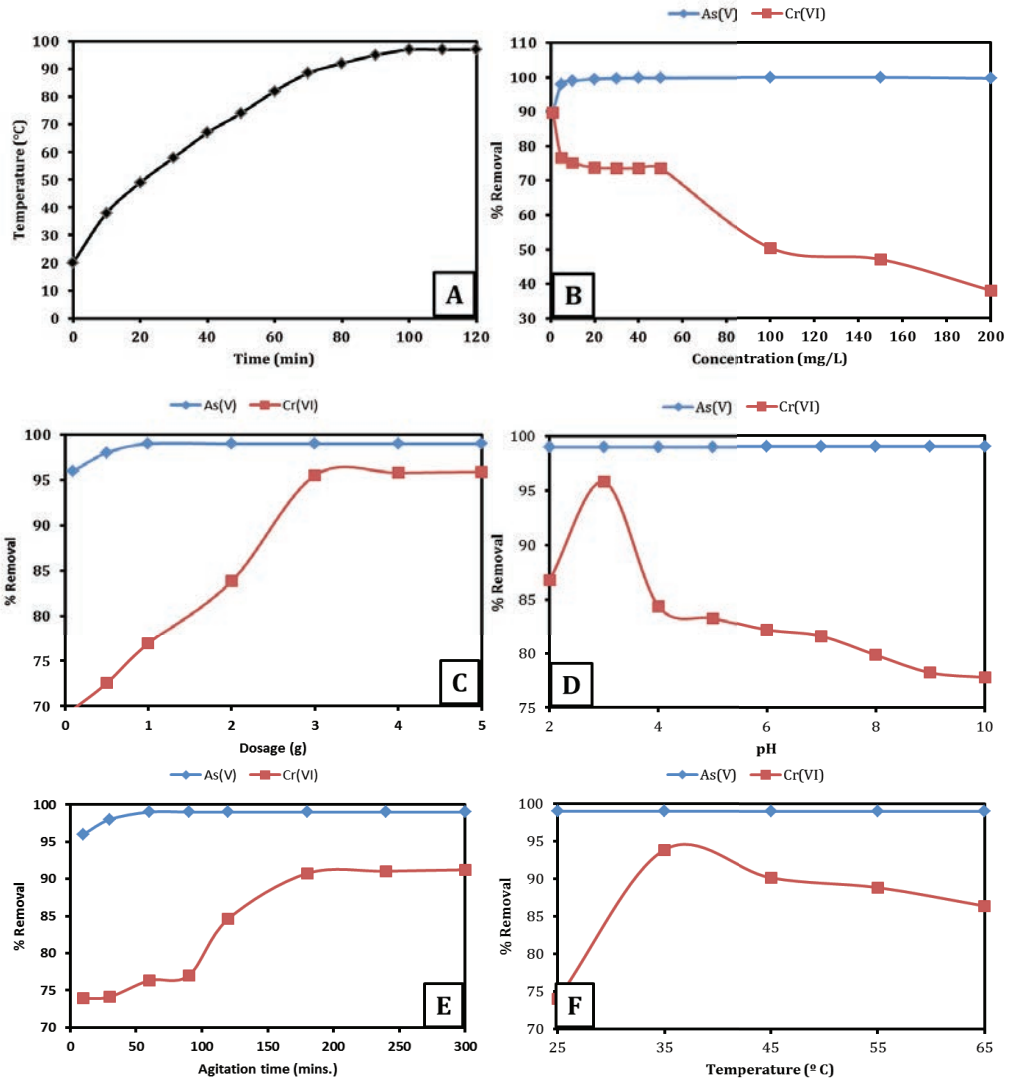


Figure 1: Synthesis of Al/Fe nanocomposite (Figure 1A) and Variation of parameters for the adsorption of As(V) and Cr(VI) onto Al/Fe nanocomposite in a 250 mL aq solution (Figures 1B – 1F)

formed agglomerates of Al/Fe nanocomposites with high surface area and pore volume. This was due to the precipitation of metal cations during neutralisation of AMD. This behaviour is also in agreement with the Le Chatelier's Principle and Collision theory because the reaction favoured the formation of products.

Effect of initial concentration

As shown in Figure 1B, the removal of arsenic from aqueous solution using the synthesized nanocomposite was observed to increase

with an increase in concentration. This justifies that the adsorbent was enough for the removal of arsenic whereas for Cr(VI), the removal efficacy was observed to decrease with an increase in Cr concentration. This is an indication that the adsorption sites were saturated with the Cr ions from aqueous solution. Moreover, this study further proved that As has high affinity for Al/Fe nanocomposite as compared to Cr. Although a decrease in the percentage removal of As(V) was observed between 150 mg/L and 200 mg/L, it was, however, insignificant. Further variation on



As(V) would clearly indicate a clear decrease on the graph. From this results, 150 mg/L and 50 mg/L are optimum initial concentrations for As(V) and Cr(VI), respectively, and they were taken as the optimum and they will be used in subsequent experiments.

Effect of adsorbent dosage

As shown in Figure 1C, the removal of arsenic was observed to increase with an increase in adsorbent dosage. Similar trend was observed for chromium. For As(V), it can be noted that more than 1 g of the adsorbent leads to over-saturation of the system. The % removal of As(V) from water remains constant between 1 g – 5 g, which means that, 1 g is enough for the removal of 10 mg/L As(V) ions from 250 mL of aqueous solution. This stability of the curve tells that the surface of the adsorbent can accommodate more of As (V) onto its interlayers and matrices. For Cr(VI), an even increase in percentage removal of Cr (VI) is observed from 0.1 – 3 g of Al/Fe nanocomposite dosage. After 3 g, the graph took a gentle slope. This could indicate saturation of the adsorbent; hence it could not take any more of Cr (VI) ions. Therefore, 3 g was adequate for the removal of chromium from aqueous solution. The challenge is the affinity and ionic strength of these toxic elements.

Effect of initial pH

In colloidal science, the adsorption of pollutants is firmly dependent on the supernatant pH. pH governs the state of chemical components in aqueous solution and dictate the charge and elements that are going to be adsorbed in aqueous solution. As shown in Figure 1D, there was no effect on the behaviour of initial pH of As (V) solution on the adsorption of As(V) by Al/Fe polycationic-nanocomposite. This could be attributed to: [1] As (V) salt is dibasic and makes its solution alkaline; [2] Sodium arsenate dibasic heptahydrate ((Na₂HAsO₄·7H₂O) salt is a conjugate base of arsenic acid, which is why the pH of its aqueous solution is within 7 – 9; [3] Al/Fe nanocomposite was precipitated using NaOH which is a strong base, hence the pH does not have much effect as the adsorption process is accommodated within a wide pH range; [4] As(V) ions are more dominant between

pH of 2 – 11, according to arsenic Pourbaix diagram, where the probability of removing them from water is high. This is when they are in solution as dihydrogen arsenate (H₂AsO₄⁻) and hydrogen arsenate (HAsO₄²⁻). This zone accommodates the adsorption of As(V) onto Al/Fe nanocomposite as the adsorbent was also synthesised within that pH range. Ferric iron also plays an important role in anionic exchange within this pH range. On the other hand, for the removal of Cr (VI), the highest removal occurred at a pH of 3. This could better be explained by the value of point of zero charge of the adsorbent which was found to be pH_{PZC} = 3.02. A pH_{PZC} indicates that at pH below the PZC the adsorbent will adsorb anions and above the PZC, the adsorbent will adsorb cations.

Effect of agitation time

As shown in Figure 1E, the % removal of species under study was observed to increase with an increase in contact time. There was a rapid increase in the removal efficiency. After 1 hour (60 minutes) and 3 hours (180 minutes) of agitation, the graphs take a gentle slope for As(V) and Cr(VI), respectively, thus showing that those are the optimum times of agitation for the removal of those heavy metals from water using Al/Fe nanocomposite. The optimum time was observed to be 180 minutes for all the species under study. As such 180 mins will be used for all the subsequent experiments.

Effect of temperature

As shown in Figure 1F, the removal of As was independent of temperature. Furthermore, Cr was observed to be firmly dependent on temperature. From the Cr(VI) graph, it can be noted that the percentage removal increases as temperature increases, but within a range 25 – 40 °C. Temperatures higher than 40 make Cr (VI) go back into solution, hence making 40°C optimum for this study.

Surface area and porosity

The synthesised PTFe/Al nanocomposite has surface area and pore size of 25 m²/g and 8.6 nm, respectively, which serve as basis that the material is a mesoporous nanocomposite material as its pore size falls within the range of 2



– 50 nm (Thommes et al. 2015). After adsorbing As and Cr, the surface area was observed to have decreased, this is an indication that the material adsorption sites are getting saturated with the pollutants that is being scavenged from the solution.

Conclusions and recommendations

From the preliminary studies, it was observed that polycationic (Al^{3+}/Fe^{3+}) nanocomposite can be successfully recovered and synthesised from natural acid mine drainage (AMD). The recovered and synthesised product can be beneficiated by using them in the removal of pollutants from water. In this study, polycationic composites were used for the removal of arsenic and chromium ions from aqueous solution and they showed great potential and high efficiency. The removal efficacy were observed to be >99% and >95% for arsenic and chromium ions. This can be attributed to high surface area, porous nature and composition of the adsorbents. Al/Fe nanocomposite has a high adsorption capacity of $q_e=37.48$ mg/g and 4.17 mg/g which made it effective in removing 150 mg/L As (V) and 50 mg/L Cr(VI), respectively. Researchers should adopt technologies which use natural pollutants to treat wastewater in place of synthetic adsorbents. Future work involves modelling the adsorption of these pollutants from aqueous solution using a number of mathematical models and to test it against authentic water that is rich in arsenic and chromium ions.

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