Zero-valent Iron-aluminium Co-corrosion: A potential Comprehensive Low-cost Method for Water Defluoridation

***Lema, E.S.[1] and H.T. Mwakabona[2]**

[1]Department of Chemistry and Physics, Sokoine University of Agriculture,
P.O. Box 3038 Morogoro
[2]Department of Earth Sciences, Mbeya University of Science and Technology,
P.O. Box 131 Mbeya

*Corresponding author e-mail: emmy@sua.ac.tz

Abstract

Climate change coupled with population increase has forced communities in fluoride rich areas to turn to fluoride contaminated groundwater to fill in the water deficit created by drying of water sources and increasing water demand. Application of low-cost materials such as iron and aluminium hydroxides in the field is limited by expensive preparation steps involved. This study investigated the applicability of Fe and Al, in their metallic states, in water defluoridation by allowing simultaneous corrosion of zero-valent aluminium (ZVA) and iron (ZVI) to form in situ hydroxides. The effect of time, dose, concentration and pH was studied by varying one parameter at a time while controlling others. Findings reveal that, mixing the two materials in their metallic state have the same synergistic effect on their fluoride removal properties as their corresponding (hydr)oxides. Whereas in their pure metallic states, iron and aluminium lowered the concentration of fluoride from 15 - 13.09 mg/L and 15 - 14.9 mg/L respectively, their mixture lowered fluoride levels from 15 - 7.74 mg/L in the period of seven (7) days. Spiking the fluoride solution with Fe3+ ions was found to enhance fluoride removal by lowering Fluoride levels from 15 - 0.8 mg/L in the same period. This could imply that a fluoride removal mechanism in this process involves precipitation of fluoro-complexes of iron rather than those of aluminium. These findings, therefore, suggest that a step involving conversion of ZVA and ZVI into their (hydr)oxides can be skipped in water defluoridation without significantly affecting their fluoride removal capacities.

Keywords: co-precipitation, zero-valent aluminium, zero-valent iron, defluoridation

Introduction

The increasing dependence on groundwater for water-supply (Foster *et al.,* 2011; Bierkens and Wada, 2019), driven by population growth and the impact of climate change, has a potential of increasing the risk of fluorosis in fluoride rich areas due to higher fluoride levels in groundwater (Yadawe *et al.,* 2010). This makes the on-going search of low-cost methods for water defluoridation a worthwhile endeavour (Tolkou *et al.,* 2021), to provide water solutions, especially in rural areas where the centralised water treatment systems are not available (Nde-tchoupe *et al.,* 2015; Noubactep, 2020). Some of the low-cost materials which are widely studied for water defluoridation include biomass materials, aluminium compounds, natural rock materials and iron-based materials (Mwakabona *et al.,* 2017; Gai *et al.,* 2021; Tolkou *et al.,* 2021). Interestingly, iron-based materials, especially, zero-valent iron (Fe0), are known for their ability to purify microbial contaminants among other contaminants in water and were successfully used in central Europe and America in the 19th and early 20th centuries (Bischof 1877; Anderson, 1884; Mwakabona *et al.,* 2017). However, their fluoride affinity is low (Chesworth, 2008; Mwakabona *et al.,* 2019), thus, in most cases, their application in water defluoridation has involved preparation of composite materials of iron and aluminium hydroxides (Wendimu *et al.,* 2017; Mondal and Purkait, 2019; Girma *et al.,* 2020; Mahfoudhi and Boufi, 2020). However, when these composite hydroxides are used instead of their metallic states, the microbial decontamination power of iron, which depend on the oxidation of Fe0 is reduced (Devonshire, 1890; Anipsitakis and Dionysiou, 2004; Yang *et al.,* 2021) due to reduced formation of Fe(III) ions and their cost is increased. Alternatively, when these materials in their metallic states are used for water defluoridation, their defluoridation efficiency is significantly reduced (Borruf, 1934; Hu *et al.,* 2017). Therefore, the efforts to investigate the methods for increasing the fluoride removal properties of zero-valent may help in exploiting its potency in immobilising microbes in water, eventually providing a comprehensive method that can be used to remove both fluoride and microbes from water.

This study therefore, investigated the effect of co-corrosion of iron and aluminium in their metallic states, on water defluoridation. Since these materials are widely available (as scrap and waste aluminium in aluminium material workshops), combining them may provide a cost-effective method for water decontamination in rural areas in Africa.

Materials and Methods

Materials

Granular metallic aluminium was obtained as a waste material from Morogoro Aluminium metal works in Morogoro, Tanzania. It was then sieved to obtain particle size between 400 micron and 1 mm and used without further modification. Anhydrous reagent grade iron (III) chloride used for preparation of Fe (III) solutions was obtained from Loba Chemie (Loba Chemie and Ranken Companies, Mumbai, India). The 1000 mg/L fluoride and total ionic strength adjustment buffer II (TISAB II) solutions were supplied by HANNA services company, Rumania. Metallic iron in form of fine steel wool was obtained from Lakairo Industries in Mwanza, Tanzania and used without further modification. Reagent grade NaOH and HCl were obtained from the local suppliers.

Methods

Preparation of reagents

The 0.5 M iron (III) chloride stock solution was prepared by addition of 81.92 g of (99 %) anhydrous FeCl3 into 700 mL of distilled water in a 1 L volumetric flask. The mixture was shaken vigorously and diluted by distilled water to the 1 L mark. Other different concentrations of iron (III) solution were prepared by appropriate standard dilution of the 0.5 M FeCl3 solution with distilled water. The different concentrations of fluoride solution were prepared by standard dilution of the 1000 mg/L fluoride solution with distilled water in plastic vessels. Solutions of NaOH and HCl were prepared by standard procedures (Smith & Parsons, 1973).

Characterisation of the samples

The percentage elemental composition of the used zero-valent aluminium (Al0) and iron (Fe0) materials and their corresponding corrosion products formed in the experiments were characterised by XRF spectrometer (Tiger S8, Xray Fluorescence, Germany). The concentration of residue ions of Al and Fe in the supernatant solution was analysed by Atomic Absorption Spectrometer (AAS) (919 SOLAAR, UNICAM, UK). The residual fluoride concentration was determined by the portable fluoride meter with an ion-selective electrode (ISE) (HI 98402, Hanna Instruments, Romania). The solution pH was measured by a portable pH meter (PHep supplied by Hanna Instruments).

Determination of the effect of contact time on the concentration of Al, Fe and F ions in the supernatant solution

The effect of contact time on the concentrations of Al, Fe and F in the precipitate and supernatant solution was determined according to the method described by Bischof 1877 and Anderson 1884 with modifications as follows: Firstly, 6 g of the separate materials and their mixture of equal weights was added into 200 mL of 15 mg/L fluoride water in three separate 500 mL plastic beakers. The beakers were swirled for one minute every after one hour for 12 hours in the automatic incubator-shaker at 210 revolutions per minute (RPM) and 25°C. 10 mL of supernatant solution was drawned after 12 hours and every after 24 hours for seven days into the clean and dry 20 mL plastic beakers for analysis of the residual Fe, Al and F by AAS and fluoride meter (ISE). For determination of the concentration of Al and Fe in the precipitated corrosion products, the precipitate were separated from the solution, rinsed in distilled water, dried, crushed and sieved using 150 micron sieve and analysed for its elemental composition by XRF. To determine the role of Fe (III) ions in the fluoride removal process and corrosion reactions, similar experiments were conducted using 200 mL fluoride water spiked with 1 mL of 0.5 M FeCl3 solution using Al^0, Fe^0 and their mixtures in separate containers. All experiments were triplicated and average values used to plot graphs.

Determination of the effect of Fe0 and Al0 dose on the fluoride removal efficiency

The effect of dose of zero-valent materials was determined by varying the weights of the separate individual materials and their mixture (containing equal weights of Fe0 and Al0) from 1 to 6 g. Each weight was added into a separate 500 mL plastic beaker containing 200 mL of 15 mg/L fluoride solution and shaken in the incubator-shaker at 210 RPM and 25°C for seven days. This experiment was triplicated. After seven days, 10 mL of the supernatant solution was drawn from the reactors and analysed for residual fluoride concentration. This was repeated using 200 mL fluoride solution spiked with 1 mL of Fe (III) solution.

Determination of the effect of initial fluoride concentration on the fluoride removal efficiency

To determine the effect of initial fluoride concentrations, 6 g of the mixture of equal weights of Fe0 and Al0 materials was added into 500 mL plastic beaker containing 200 mL of fluoride solution with varying concentrations (2, 5, 10, 15, 20, mgF/L) spiked with 1 mL of 0.5 M Fe (III) solution in separate beakers as descibed by Mwakabona *et al.,* 2019 with modifications. The mixture was shaken for seven days in the incubator-shaker at 210 RPM and 25°C. After seven days 10 mL of the supernatant was drawn from each reactor for residual fluoride analysis.

Determination of the effect of initial pH on the fluoride removal efficiency of the zero-valent materials

For determination of the effect of initial pH, 6 g of the mixture of Fe^0 and Al^0 was added to 200 mL of 15 mg/L non-spiked fluoride solution adjusted to the pH of 3, 5, 7, 9 and 11 using 0.01M NaOH and HCl solutions according to the method described by Mwakabona *et al.,* 2019 with modifications. The mixture was shaken for 7 days in the incubator-shaker as described in section 2.2.3. After seven days, 10 mL of the supernatant solution was drawn for fluoride analysis by ISE fluoride meter.

Determination of the effect of sequence of mixing on the concentration of residual fluoride

To understand the fluoride removal mechanism, the effect of the order of mixing of the materials was studied. In the first set of reactors, 3 g of Fe^0 materials was added first into the 200 mL of 15 mg/L non-spiked fluoride solution and shaken for one hour at 210 RPM and 25°C in the incubator-shaker. Then 3 g of Al0 was added and shaking continued for seven days. After seven days, 10 mL of the supernatant solution was drawn for fluoride analysis. In the second set of reactors, this procedure was repeated with Al0 added first. All experiments were triplicated.

Results and Discussion

Characterisation of steel wool, granular aluminium and their corrosion products

The XRF analysis results show that, the percentage elemental composition of the steel wool was 95.96% Fe and 4.04% other elements whereas that of granular aluminium was 97.65% Al and 2.35% other elements as shown in Figure 1a and b. These results imply that the percentage elemental purity of the materials used was fairly good and that the observed reactivity is mainly due to the reactions of Al and Fe. Analysis of dry corrosion products, from the reactors that used the mixture, showed a higher percentage of Al (57.72%) than Fe (35.94) in form of oxide as shown in Figure 2. Higher percentage of aluminium in the corrosion products could be an indication of higher rate of corrosion and or wastage of granular Al due to its higher erosion rate in aqueous media (Telfer *et al.,* 2012). This could further indicate the higher rate of in-situ formation active hydroxides of Al than Fe when their zero valent species are mixed in aqueous media. These materials, therefore, can be put to application for water treatment without further modifications (Mondal and Purkait, 2019).

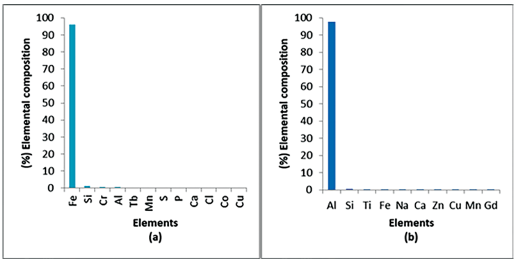

Figure 1: Percentage elemental composition using (a) iron and (b) aluminium materials

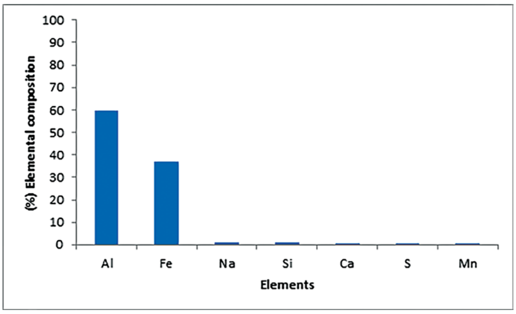

Figure 2: Percentage elemental composition of the formed corrosion products

The effect of equilibration time on the concentration of the residual F, Fe and Al ions in the supernatant solution

Results indicate that a mixture of Al^0 and Fe^0 have synergistic effect on fluoride removal in aqueous media when compared to their corresponding pure materials (Fig. 3). Whereas pure Al^0 lowered fluoride levels from 15 to 14.9 mgF/L in a non-Fe(III)-spiked fluoride solution, in the studied period, pure Fe0 lowered fluoride from 15 to 13.09 mg/L. The lowest fluoride removal property of Al^0 may be attributed to the formation of soluble fluoro-complex of aluminium in fluoride solution (Motellier and Pitsch, 1994; Noh, 2008; Dubey *et al.,* 2018) which inhibits precipitation and adsorption of fluoride ions. The relatively higher fluoride removal property of Fe^0 may be an indication of the moderate sorption and or coagulation activity of the formed Fe(III) ions and the resulting hydroxides under the conditions of the experiments (Borruf, 1934; Chesworth, 2008; Mwakabona *et al.,* 2019). A mixture of Fe0 and Al0 showed an increased fluoride removal, lowering fluoride levels from 15 to 7.74 mg/L in the studied period. Spiking fluoride solution with Fe(III) solution resulted into a further increase in fluoride removal efficiency of the combined materials, lowering residue fluoride from 15 to 0.83 mg/L.

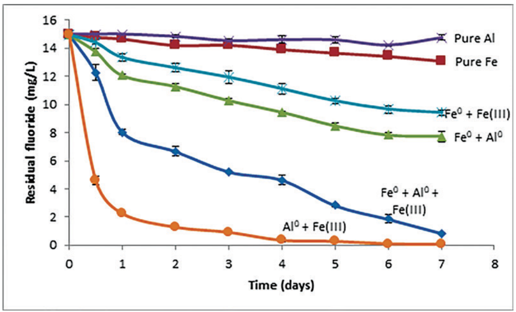

Figure 3: The effect of contact time on the residual fluoride in the supernatant solution

The effect of mixed material dose on the residual fluoride in the supernatant solution

Increasing the dose of the mixture resulted into increase in fluoride removal efficiency (Fig. 4). This could be due to increased concentration of reacting species such as Fe(III) and Al(III) ions in solution media which would eventually result into increased concentration of the formed active hydroxides of aluminium and charged hydroxides of Fe(III) as shown in equation 1, 4 and 5 (Gong *et al.,* 2012). Continuous fluoride removal property with increase of dose may imply that the main removal mechanism is co-precipitation and that increasing dosage may be used to shorten reaction time by increasing the production of active hydroxides in the designs of the water treatment unit. This may also suggest that soluble salts of aluminium and iron (III), when used together, could be effective in removing fluoride ions from water by coagulation. This could be the basis for higher F removal when Fe-Al composite adsorbents are used in water defluoridation (Gong *et al.,* 2012; Alfredy *et al.,* 2023).

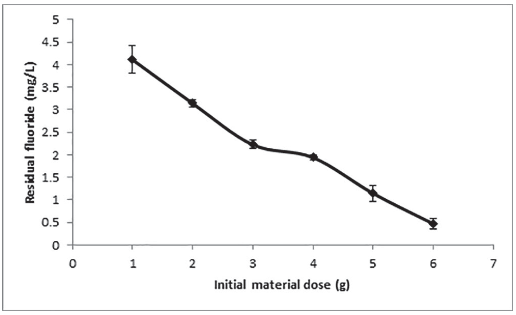

Figure 4: The effect of mixed material dose on the residual fluoride in supernatant solution

The effect of initial fluoride concentration on the fluoride removal efficiency

An increase in the initial fluoride concentration resulted into an increase in fluoride removal efficiency. Whereas in lower concentration of fluoride, the fluoride level was lowered from 2 to 0.02 mg/L, in the higher concentrations, the fluoride level was lowered from 20 to 0.74. This suggests that these materials can be used to lower fluoride levels to acceptable limits even in highly polluted water and that these materials can be used for remediation of water with variable fluoride concentrations. This is common when the main mechanism involved is co-precipitation (Gong *et al.,* 2012).

The effect of initial pH on the fluoride removal efficiency of metallic materials

When the solution pH was increased from 3 to 9, the fluoride removal tendency of the used materials was increased. The fluoride concentration was lowered from 15 to 9 mg/L at pH 3 and 15 to 7.6 mg/L at pH 9 (Fig. 5). The increase in fluoride removal with increase in solution pH from 3 to 9 could indicate the inhibition of fluoride precipitation at low pH. Further increase of the solution pH from 9 to 11 resulted into a decline in the fluoride removal tendency. This decrease in fluoride removal efficiency could be due to decreased concentration of Fe(III) ions which are involved in precipitation of fluoride ions (Telfer *et al.,* 2012; Mwakabona *et al.,* 2019; Vaddi *et al.,* 2021). The higher fluoride removal property of the mixture of these materials under neutral conditions could suggest that the materials can be used for defluoridation of natural water without necessarily adjusting the initial pH.

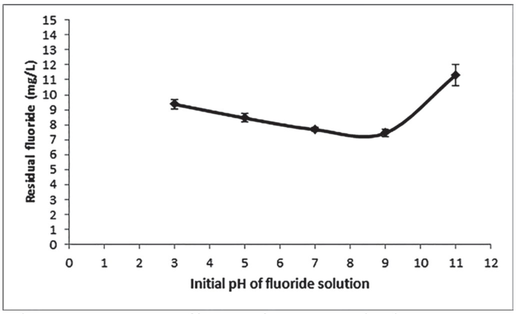

Figure 5: The effect of pH variation on the fluoride removal property by Fe^0-Al^0 mixture

The effect of the order of mixing of materials on the residual fluoride in supernatant solution

Reversing the order of mixing the reacting materials resulted into a significant difference in their fluoride removal property (Fig. 6), when the non-spiked fluoride solution was used. When Fe^0 was added first followed by Al^0, the residual fluoride was lowered from 15 to 7.52 mg/L. On the other hand, addition of Al0 first followed by Fe^0 resulted into a decreased fluoride removal, lowering fluoride concentration from 15 to 14.2 mg/L. From these findings, it can be asserted that, addition of Al^0 before Fe^0, leads to the formation of the soluble fluoro-complexes of aluminium which may be responsible in the inhibition of the fluoride removal process. This may imply that precipitating the fluoro-complexes of aluminium is not favoured in the conditions of this experiment (Dubey *et al.,* 2018; Dubey *et al.,* 2021). Therefore, this observation provides

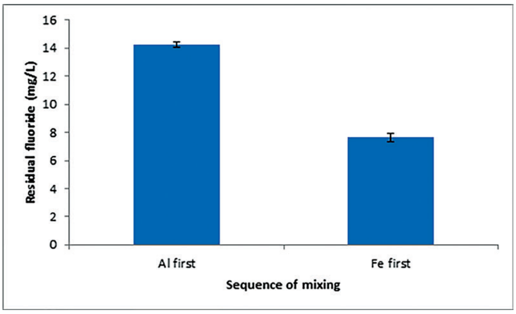

Figure 6: The effect of sequence of mixing on fluoride removal properties of Fe^0-Al^0 mixture

important information on the fluoride removal mechanism, where the fluoro-complexes of iron seems to play an important role. Moreover, this information reveals the sequence of packing the active materials in the designed Fe^0-Al^0-based fluoride treatment facility.

The synergistic effect of the mixture and fluoride removal mechanism

When Fe^0 and Al^0 materials were used separately, the observed fluoride removal property was lower than when the mixture was used as indicated in Figure 3. This increase was higher than that observed when Fe^0 was used in the Fe(III)-spiked fluoride solution, a modification which resulted into increased formation of the charged hydroxides of iron (Mwakabona *et al.,* 2019; Nyangi *et al,* 2021). This may imply that the synergistic effect in fluoride removal properties of the mixture in aqueous media could be due to in situ formation of the Fe(III) and Al(III) ions catalysed by presence of Fe(III) ions in solution (Pillai *et al.,* 2020). This could be confirmed by higher fluoride removal, when pure Al0 was used in fluoride solution spiked with Fe(III) solution (Fig. 3). The higher concentration of Al (observed by XRF analysis) in the separated corrosion products (Fig. 2) may also suggest that the in situ formation of hydroxides of aluminium is favoured. Presence of the Fe(III) in fluoride solution appears to increase the rate of corrosion reaction of the used materials (Tamura *et al.,* 1976; Tamura *et al.,* 1980). In their study, Tamura *et al.* (1980) showed that the presence of Fe(III) ions increased the oxidation of iron and that the formed Fe(OH)3 adsorb Fe(II) ions which in turn makes the surface of the hydroxides positively charged. This, therefore, suggests an additional fluoride removal mechanism by adsorption of fluoride onto the formed hydroxides. In presence of Al^0, Fe(III) ions catalyse the formation of hydroxides of aluminium according to equations 1, 4 and 7. These in situ formed hydroxides of aluminium could be playing an important role in removal of fluoride ions in these conditions. The slow fluoride removal process (requiring seven days to bring fluoride ions to acceptable levels) may be due to the slow rate of formation of the active Fe(III) and Al(III) ions from their respective. This could be confirmed by the higher rate of fluoride removal when Fe(III) solution was added.

$$2Fe^{3+}(aq)+Al^0(s)==>Al^{3+}(aq)+4e\text{-}+2Fe^{2+}(aq) \quad (1)$$

$$2Fe^{3+}(aq)+Fe^0(s)==>3Fe^{2+}(aq)\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$O_2(g)+2H_2O(l)+4e\text{-}==>4OH\text{-}(aq)\ldots\ldots\ldots\ldots\ldots(3)$$

$$Al^{3+}(aq)+3OH\text{-}(aq)==>Al(OH)_3(s)\ldots\ldots\ldots\ldots(4)$$

$$Fe^{3+}(aq)+2OH\text{-}(aq)+H_2O(l)==>Fe(OH)_2(H_2O)_4^{+}(aq)\ldots\ldots\ldots\ldots(5)$$

$$Fe(OH)_2(H_2O)_4^{2+}(aq)+F\text{-}(aq)==>Fe(OH)_2(F)(H_2O)_4(s)\ldots\ldots\ldots\ldots(6)$$

$$Al(OH)_3(s)+F\text{-}(aq)==>Al(OH)_2F(s)+OH\text{-}(aq)\ldots\ldots\ldots\ldots(7)$$

Conclusion

Combining Al^0 and Fe^0 materials have synergistic effect in their fluoride removal properties. Enhanced fluoride removal properties of the mixture are influenced by the presence of Fe(III) ions which appears to increase the rate of corrosion of the reacting metallic. Two possible fluoride removal mechanisms can be proposed; (i) precipitation of fluoro-complex of iron and (ii) adsorption of fluoride ions on the charged hydroxides of iron and aluminium in the corrosion products. The formation fluoro-complexes of aluminium significantly lowered the fluoride removal properties of the mixture by either inhibiting F-hydroxide interaction or formation of fluoro-complexes of iron. Therefore, effective application of these materials for water defluoridation will depend on the proper design of the treatment unit in ways that will reduce the possibility of formation of fluoro-complexes of aluminium.

Acknowledgments

We express our sincere gratitude to the Sokoine University of Agriculture Research and Innovation Support (SUARIS) for the financial support that made this work possible. Without their invaluable support, this project (Project name: [Modified Iron Corrosion for Water Defluoridation], Funding Number: DPRTC/R/126/SMCOSE/5/2021) could not have been realized. Their contribution has been instrumental in advancing our understanding and contributing to the field of water treatment. We distinctively acknowledge SUARIS for their

noteworthy support.

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