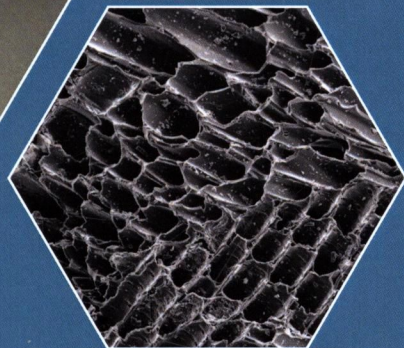
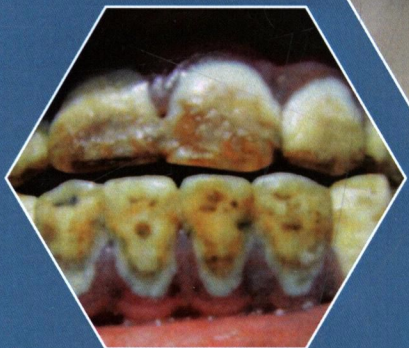
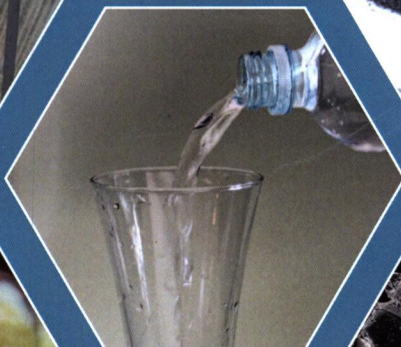


Fluoride Removal from Groundwater by Adsorption Technology

The occurrence, adsorbent synthesis, regeneration and disposal

Abdulai Salifu





UNESCO-IHE
Institute for Water Education



In the Eastern corridor of the Northern region of Ghana, the presence of high fluoride concentration in the groundwater has made many drilled boreholes unusable for drinking. Little is, however, known about the factors contributing to the occurrence of high fluoride in the groundwater. Fluoride-contaminated groundwater can be treated by adsorption, but is hampered by the lack of suitable adsorbents that are locally available. Based on principal component analysis, and saturation index calculations, this thesis highlights that, the predominant mechanisms controlling the fluoride enrichment in the groundwater probably include calcite precipitation and Na/Ca exchange processes, both of which deplete Ca from the groundwater, and promote dissolution of fluorite. The mechanisms also include F-/OH- anion exchange as well as evapotranspiration, which concentrate fluoride ions, hence increasing its concentration in the groundwater. Spatial mapping showed that the high-fluoride groundwaters occur predominantly in the

Saboba, Cheriponi and Yendi districts in the Northern region of Ghana.

The thesis further highlights that, modifying the surface properties of locally available materials by aluminium coating, is a very promising approach to develop a novel fluoride adsorbent. Aluminium oxide coated media reduced fluoride in water from 5.0 ± 0.2 mg/L to ≤ 1.5 mg/L (WHO guideline), in both batch and continuous flow column experiments in the laboratory. Kinetic and isotherm adsorption modelling, thermodynamic calculations, as well as Fourier Transform Infrared and Raman spectroscopy studies, suggest the mechanism of fluoride adsorption onto aluminium oxide coated media involved both physisorption and chemisorption processes. Field testing in Northern Ghana showed that the adsorbent is also capable of treating fluoride-contaminated groundwater in field conditions. The adsorbent also showed good regeneration potential making it a promising defluoridation adsorbent in practical applications in developing countries.

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DISSERTATION

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by

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Cover image:

Photos of severe dental fluorosis, synthesized aluminium oxide coated charcoal (fluoride adsorbent: fine particles and SEM image), house hold defluoridation unit and treated drinkingwater.

(Cover image made by Yness M. Slokar, IHE Delft)

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This thesis is dedicated to the blessed memory of my beloved brother Ahmed Mohamed Salifu and also to all persons exposed to fluoride-related health hazards.

Abdulai Salifu

20 December 2016

Delft, The Netherlands

Summary

It was estimated as late as 2015 that, 663 million people worldwide still use unsafe drinking water sources, mostly in the least developed countries/regions including, sub-Saharan Africa and Southern Asia. A vast majority of the affected population are poor and live in rural areas. At the start of this research (2009), the population across the developing world without safe water sources was estimated at 884 million, and even though a lot was achieved by the end of the Millennium Development Goals (MDGs) deadline (2015), it is clear that a great deal still has to be done.

Access to safe drinking water is not only fundamental to human development and well-being, but is also recognized as a human right. The provision of safe potable water is considered critical and pivotal to the achievements of overall development, including adequate nutrition, education, gender equality and especially eradication of poverty in less developed countries.

Groundwater sources are generally known to be of good microbiological and chemical quality, and mostly require minimal or no prior treatment for use as safe drinking water sources. Hence its use for water supply is associated with low capital, as well as low operation and maintenance cost. It is therefore the most attractive source for drinking water supply in the often scattered, rural communities in developing countries. Problems can, however, occasionally arise with the chemistry of groundwater and render it unsafe, due to elevated concentrations of some elements that can have negative health impacts on the user. Provision of safe drinking water from groundwater sources in such situations therefore, requires some level of treatment. Fluoride is one of the water quality parameters of concern, the excess (beyond 1.5 mg/L, the World Health Organization (WHO) guideline value) of which contaminates groundwater resources in many parts of the world, and renders it not potable for human consumption, due to the related adverse health effects.

Even though an optimum concentration of fluoride (0.5 - 1mg/L) in drinking water is good for dental health and good bone development, the toxic effects on human health when

consumed in excess amounts (beyond 1.5 mg/L), for long periods, have been known for centuries. The human health hazards of the consumption of excess fluoride include: the incidence of fluorosis, changes of DNA structure, lowering of IQ of children, interference with kidney functioning and even death when doses reach very high levels (about 150 - 250 mg/L).

Over 90 % of rural domestic water requirements in the Northern region of Ghana for instance (which was the area of focus of this study), is met from groundwater resources. Fluoride contamination of the groundwater in some parts of the region has, however, exposed the population in the fluoritic communities to fluoride-related health hazards. This has also resulted in the closure of otherwise many very useful drilled boreholes (wells) for water supply, in order to avoid the incidence of fluorosis and other related health effects. The closure of drilled (expensive) boreholes due to presence of excess fluoride do not only represent huge economic cost, but also hampers efforts of providing safe drinking water to the populace. As a consequence the population is forced to use unsafe surface water sources that are associated with the incidence of otherwise preventable, diseases such as cholera and diarrhea. Even though groundwater remains the most important source for rural water supply in the Northern region of Ghana, little is known about the factors (natural and/or anthropogenic) that control the groundwater chemistry and, hence the quality and source of fluoride contamination as well as its distribution.

Due to the permanent risk as well as the lack of known effective treatment for fluorosis and other related health hazards, defluoridation of fluoride-contaminated groundwater sources intended for drinking is a necessity, to avoid the ingestion of excess fluoride as a preventive measure. Several defluoridation technologies have been developed in many places around the world, some of which are described as “Best Available Technologies” (BATs). The current methods, however, mostly have some limitations which generally make their use unsustainable and/or unacceptable under most conditions, particularly in remote areas in developing countries. This include for instance: (i) the Nalgonda technique, which is popular in some Asian countries but is known to have limited efficiency (up to about 70 %), requires careful dosing of chemicals and close monitoring to ensure effective fluoride removal, hence demanding labour, skills and time that are usually problematic

under rural conditions in developing countries; (ii) the contact precipitation process, which is still under study, and moreover the reaction mechanism for the defluoridation process is thought only to be feasible with use of bone charcoal as a catalyst. Bone charcoal is however not culturally acceptable in some societies due to local taboos and beliefs; (iii) adsorption using activated alumina as adsorbent media, which is known to be expensive especially for developing countries, (iv) adsorption with bone charcoal as adsorbent media, which is not acceptable in many places as earlier mentioned, and, (v) reverse osmosis (RO), which has high capital and operational cost, require specialized equipment, skilled labour and a continuous supply of energy.

Due to the negative health impacts of excess fluoride in drinking water, however, the search for an appropriate technology for its removal from contaminated-groundwater still remains very critical. Among the available fluoride removal techniques, the adsorption process is generally considered as one of the most appropriate, particularly for small community water source defluoridation. This is due to its many advantages including flexibility and simplicity of design, relative ease of operation, and cost-effectiveness as well as its applicability and efficiency for contaminant removal even at low concentrations. The appropriateness of the adsorption technology, however, largely depends on availability of a suitable adsorbent. Several adsorbent materials have been developed and tested, mostly in the laboratory, for the treatment of fluoride-contaminated water including: manganese-oxide coated alumina, bone charcoal, fired clay chips, fly ash, calcite, sodium exchanged montmorillonite- Na^+ , ceramic adsorbent, laterite, unmodified pumice, bauxite, zeolites, fluorspar, iron-oxide coated sand, calcite, activated quartz and activated carbon. While some of these adsorbent materials have shown certain degrees of fluoride adsorption capacity, the applicability of most is limited either due to: lack of socio-cultural acceptance, non regenerative nature, and therefore may not be cost-effective, high cost and/or effectiveness only under extreme pH conditions. This may require pH adjustment and consequently additional capital, operation and maintenance cost, and could limit feasibility of such a fluoride removal technology in remote rural areas of developing countries. Some of the studied defluoridation materials are also available in the form of fine particles or powders, with the potential of clogging and/or low hydraulic conductivities when applied in fixed bed

adsorption systems. The search for appropriate alternative fluoride adsorbents therefore remains of interest.

The overall goal of the study was therefore twofold: (i) to study the groundwater chemistry in the Northern region of Ghana with focus on the occurrence, genesis and distribution of fluoride-contaminated waters in the eastern corridor of the region (which is the most fluoritic part), and (ii) to contribute to the search for an appropriate and sustainable fluoride removal technology for the treatment of fluoride-contaminated groundwater for drinking water production in developing countries.

In order to accomplish the first component of the research goal, the climate, geology, mineralogy and hydrogeology of the study area was reviewed in a desk study. Three hundred and fifty seven (357) groundwater samples taken from boreholes drilled in the study area, were analyzed for the chemical data using standard methods. Univariate statistical analysis, Pearson's correlation and principal component analysis (PCA) of the chemical data, using the SPSS statistical software package, as well as Piper graphical classification using the GW chart software, and thermodynamic calculations with PHREEQC, were used as complementary approaches to gain an insight into the groundwater chemical composition, and to understand the dominant mechanisms influencing the occurrence of high-fluoride waters in the area. The geo-referenced groundwater chemical data were further analyzed using ArcGIS software to determine the spatial distribution of fluoride in groundwater at the sampled points of the study area. Inverse distance weighting interpolation (IDW) (using ArcGIS), was also used to examine the fluoride distribution in the study area and to help predict the fluoride levels at non-sampled points as well.

The fluoride concentrations in the 357 groundwater samples taken from the area were found to range between 0.0 and 11.6 mg/L, with a mean value of 1.13 mg/L. A relatively high percentage (23%) of the samples were found to have fluoride concentrations exceeding 1.5 mg/L, the WHO guideline value for drinking water. Based on the piper graphical classification, six groundwater types were identified in the study area: Ca-Mg-HCO₃, Ca-Mg-SO₄, Na-Cl, Na-SO₄, Na-HCO₃ and mixed water type. PCA performed on the groundwater chemical data resulted in 4 principal components (PCs) explaining 72% of

the data variance. The PCs, which represented (or explained) the predominant geochemical processes controlling the groundwater chemistry in the study area, showed that the processes include: mineral dissolution reactions, ion exchange and evapotranspiration. PHREEQC calculations for saturation indices of the groundwater samples revealed that they were largely saturated with respect to calcite and under-saturated with respect to fluorite, suggesting that dissolution of fluorite may be occurring in the areas where the mineral is present. A review of the principal component analysis (PCA) results, coupled with an evaluation of the equilibrium state of the groundwater based on the calculated saturation indices, suggested that the processes controlling the overall groundwater chemistry in the area also influenced the fluoride enrichment. The fluoride-rich groundwaters in the study area were found to occur predominantly in the Saboba and Cheriponi districts, and also in the Yendi, Nanumba North and South districts of the Northern region of Ghana. These areas are underlain by the Obossom and Oti beds, comprising mainly of sandstone, limestone, conglomerate, shale, arkose and mudstone. Results of the conducted hydrochemical analysis showed that apart from the boreholes with high concentrations of fluoride (beyond 1.5 mg/L), groundwater in the study area, based on the limited parameters analyzed is chemically acceptable and suitable for domestic use.

GIS analysis of the geo-referenced groundwater data resulted in a map showing the spatial distribution of fluoride in groundwater at the sampled points of the study area, and also a prediction map that may help determine the fluoride levels at the non-sampled parts of the area. The information provided by the study may help in strategic planning for the provision of improved water sources to the populace in the study area, in either case of high fluoride groundwater, or groundwater wells with insufficient fluoride (for prevention of dental caries).

The second component of the research goal was accomplished through a combination of studies related to: a laboratory synthesis of alternative fluoride adsorbent materials, an assessment of their fluoride adsorption performance (i.e. kinetics and equilibrium capacity), a study of the mechanisms of fluoride removal and, a comparison of the performance to both activated alumina (AA), the industrial fluoride adsorbent, and also to other developed fluoride adsorbents reported in literature. The study also included the possibility of

regenerating the synthesized materials when exhausted for its economic and practical viability, safe disposal of the spent adsorbent into the environment (when it can no longer be used), and a field screening of the capability of the synthesized adsorbent to treat natural fluoride-contaminated groundwater.

The synthesis of a fluoride adsorbent was accomplished by exploring the possibility of modifying the physico-chemical properties of the surfaces of locally available materials, that contributes to a low cost of adsorbent production and sustainability, when in use in developing countries. Three materials, i.e. pumice, bauxite and wood charcoal, which are indigenous and readily available in many developing countries, were used as base material for the surface modification process. The use of different indigenous materials for the surface modification process was aimed at investigating the influence of the starting base materials on fluoride removal performance of the modified version, and, hence at determining which is more suitable as a precursor material. Surface modification of the indigenous materials was accomplished by an Al coating/Aluminol (AlOH) functionalization process, using 0.5 M $\text{Al}_2(\text{SO}_4)_3$ as the Al – bearing solution, and, exploring the hard soft acid base (HSAB) concept. Due to its characteristics, Al (III) is classified as a hard acid, while F^- is categorized as a hard base. Al (III) therefore has good affinity for fluoride in accordance to the HSAB concept, hence its choice for the modification of the indigenous materials surfaces, as alternative materials for fluoride adsorption. Three different types of Al modified adsorbents were produced, i.e. Al oxide coated pumice (AOCP), granular Al coated bauxite (GACB), and Aluminol functionalized wood charcoal (AFWC). For bauxite, the influence of the synthesis process conditions on the effectiveness of the coating process, and the consequent effect on the fluoride adsorption efficiency of the produced adsorbent (i.e GACB), was investigated, which was aimed at optimizing the synthesis process. These conditions included different coating pH, and different process temperatures for thermal pre-treatment of bauxite prior to the aluminum coating. For wood charcoal, the effect of the source of wood charcoal (i.e. from 4 sources) on the fluoride removal performance of the produced adsorbent was also investigated. Several characterization techniques were employed for studying the physico-chemical properties of the synthesized fluoride adsorbents. These included: X-ray power diffraction (XRD), X-ray fluorescence (XRF) analysis, scanning electron microscopy (SEM), Fourier transform

infrared (FTIR) analysis, Raman spectroscopy, energy-dispersive X-ray (EDX) analysis, BET specific surface area analysis, mass titration and potentiometric titration. This was helpful in informing and guiding the fluoride adsorbent material engineering process. Regeneration of the produced adsorbents, when exhausted, was accomplished by creating new Al-based active sites on the surfaces of the fluoride-saturated adsorbent through an Al re-coating/aluminol re-functionalization process.

Batch fluoride adsorption and/or laboratory-scale continuous flow column experiments were conducted to either evaluate the fluoride removal efficiencies of the produced adsorbents, or to determine their kinetic properties and/or fluoride adsorption capacities. Several kinetic models were used for the interpretation of the kinetic data; which included the pseudo-first-order and pseudo-second-order kinetic models, Banghams equation, Elovich and the Weber and Morris intra-particle diffusion models. Different models give different information which can complement each other for a better understanding of the properties of the synthesized adsorbent as well as the nature of the adsorption process. Similarly, interpretation of the equilibrium data was accomplished using several isotherm models including; Langmuir, Freundlich, Temkin, Elovich, BET, Generalized, Dubinin-Raduskevich and Redilich-Perterson equations. The continues flow column experimental data in the form of breakthrough curves were also analyzed/modelled using three well known models: Thomas, Adams-Bohart and the bed-depth service models. Due to the inherent errors associated with linearization, both linear regression and non-linear optimization techniques (with error analysis), were employed to determine best-fit and the related model parameters. Due to the complex nature of adsorption processes, the kinetic and equilibrium modelling in combination with the Raman and FTIR spectroscopic analysis as well pH_{pzc} measurements and thermodynamic calculations were used as complementary approaches to gain insight into the mechanisms involved in fluoride removal onto the produced materials. The effects of pH and/or co-ions (sulfate, chloride, bicarbonate, nitrate and phosphate) as well as long-term storage of adsorbent on the performance of the three produced fluoride adsorbent materials, were examined in batch adsorption experiments. The effect of particle size on the performance of the Al modified wood charcoal was studied under continuous flow conditions.