

ADSORPTIVE REMOVAL OF HEAVY METALS FROM GROUNDWATER BY IRON OXIDE BASED ADSORBENTS



VALENTINE UWAMARIYA



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GROUNDWATER BY IRON OXIDE BASED ADSORBENTS**

**Adsorptive Removal of Heavy Metals from Groundwater
by Iron Oxide Based Adsorbents**

DISSERTATION

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Dedication

This thesis is dedicated to my late father MUNYANGEYO Cléophas.
May his soul rest in peace!

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Foreword

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Abstract

In general groundwater is preferred as a source of drinking water because of its convenient availability and its constant and good quality. However this source is vulnerable to contamination by several substances. Substances that can pollute groundwater are divided into substances that occur naturally and substances produced or introduced by human activities. Naturally-occurring substances causing pollution of groundwater include for example, iron, manganese, ammonium, fluoride, methane arsenic, and radionuclides. Substances resulting from human activities include, for example, nitrates, pesticides, synthetic organic chemicals and hydrocarbons, heavy metals etc.

Acceptable quality limits relative to micropollutant contents in drinking water are becoming increasingly lower and efficient elimination treatment processes are being implemented in order to meet these requirements. Metals contaminants at low concentration are difficult to remove from water. Chemical precipitation and other methods become inefficient when contaminants are present in trace concentrations. The process of adsorption is one of the few alternatives available for such situations. Recent studies have shown that sand and other filter media coated with iron, aluminium, or manganese oxide, hydroxide or oxihydroxide were very good, inexpensive adsorbents which, in some cases, are more effective than the methods usually employed, such as precipitation-coprecipitation or adsorption on granular activated carbon. Selective adsorption can also retain elements that conventional treatment methods are unable to eliminate. This phenomenon was demonstrated after having observed that iron and manganese in particular were more effectively eliminated using old filters than filters containing new sand. This can be explained, in most cases, by a catalytic action of the oxide deposits on the surface of the sand grains.

In this study the adsorption method was used to remove selected heavy metals present as cations (Cd^{2+} , Cu^{2+} and Pb^{2+}) or oxyanions (Cr(VI) and As(V)) using iron oxide coated sand (IOCS) and granular ferric hydroxide (GFH). The effects of pH, natural organic matter (fulvic acid (FA)) and interfering ions (PO_4^{3-} , Ca^{2+}) on the adsorption efficiency were also assessed. The surface complexation modelling for Cd^{2+} , Cu^{2+} and Pb^{2+} adsorption in order to describe the sorption reactions that take place at the surface of the adsorbent was also studied. Batch adsorption tests and rapid small scale column tests (RSST) were used as laboratory methods.

Rwanda uses mainly surface water as drinking water and groundwater remains unexplored field and very limited information is available on the quality of this source of drinking water. In this study, groundwater quality was screened in the Eastern province (Nyagatare District), where groundwater is the main source of drinking. For the determination of physico-chemical characteristics of Nyagatare groundwater, 22 parameters were analysed. The results showed that the turbidity and conductivity for all sampled sites are within the range of acceptable values for drinking water. Among the 20 sampled sites, 12 sites have pH values respecting the norms of drinking water, 6 sites have acidic water and 2 sites have alkaline water. For all

sampled sites, the dissolved oxygen was found to be low, indicating that Nyagatare groundwater is anoxic. The turbidity is low except for one site, and only four sites are within the acceptable ranges of total alkalinity. Total hardness exceeds the limits for 5 sites and the concentration of major cations (Ca^{2+} , Na^+ , K^+ and Mg^{2+}) and major anions (F^- , Cl^- , PO_4^{3-} and SO_4^{2-}) respect the norms of drinking water for all sampled sites. For all sampled sites ammonia concentration is less than 3mg/l except for two sites. NO_2^- and NO_3^- concentrations also respect the WHO (2011) guideline values (2 mg/l and 50 mg/l, respectively). Regarding the concentration of heavy metals, all sampled sites have values of Fe^{2+} exceeding the value of 0.3 mg/l that is the upper acceptable concentration in most national drinking water standards (including Rwanda) and ten sites have values of Mn^{2+} exceeding the value of 0.1 mg/l that is recommended by several national standards to avoid esthetic and operational problems. For other heavy metals, Zn^{2+} respects the norm for all sampled sites except for all Rwempasha and Rwimiyaga sites. Even if the main focus of this research is the removal of heavy metals, the concentrations of Pb^{2+} , Cd^{2+} , Cu^{2+} , As and Cr in Nyagatare groundwater were found to be below the detection limits.

With a Piper diagram representation, most of sampled sites are found to be mainly sodium and potassium type and, for few of them, no dominant type of water could be found. In terms of anions, few sites have chloride groundwater type, one has bicarbonate groundwater type and others have no dominant anions. The total hardness varied between 10 and 662 mg/l, 7 samples fall under soft class, 3 samples fall under moderately hard class, 7 samples fall under hard and 3 samples fall under very hard class. The calculation of percentage of Na^+ , the residual sodium carbonate (RSC) and sodium adsorption ratio (SAR) showed that Nyagatare groundwater is suitable for irrigation. The Nyagatare district has abundant granite and granite igneous rocks, and this can explain the source of fluoride found in groundwater. The source of EC, TDS, ammonia and nitrite in Nyagatare groundwater can be related to human activities e.g. application of fertilizers and manure.

Principal component analysis (PCA) results showed that the extracted components represent the variables well. The extracted six components explain nearly 94% of the variability in the original 22 variables, so that one can considerably reduce the complexity of the data set by using these components, with only 6% loss of information. The first component was most highly correlated with fluoride, pH and sulfate; the second component was most strongly correlated with calcium and total hardness, while the third component is most strongly correlated with total alkalinity. The fourth, the fifth and the sixth components are mostly correlated with potassium, iron and magnesium, respectively.

The effects of calcium on the equilibrium adsorption capacity of As(III) and As(V) onto iron oxide coated sand and granular ferric hydroxide were investigated through batch experiments, rapid small scale column tests and kinetics modeling. Batch experiments showed that at calcium concentrations ≤ 20 mg/l, high As(III) and As(V) removal efficiencies by IOCS and GFH were observed at pH 6. An increase of the calcium concentration to 40 and 80 mg/l reversed this trend giving higher removal efficiency at higher pH (8). The adsorption capacities of IOCS and GFH at an equilibrium arsenic concentration of 10 $\mu\text{g/l}$ were found to

be between 2.0 and 3.1 mg/g for synthetic water without calcium and between 2.8 and 5.3 mg/g when 80 mg/l of calcium was present at all studied pH values. After 10 hours of filter run in rapid small scale column tests, and for approximately 1000 Empty Bed Volumes filtered, the ratios of C/C_0 for As(V) were 26% and 18% for calcium-free model water; and only 1% and 0.2% after addition of 80 mg/l of Ca for filter columns with IOCS and GFH, respectively. The adsorption of As(III) and As(V) onto GFH follows a second order reaction irrespective of calcium presence in model water, while the adsorption of As(III) and As(V) onto IOCS follows a first-order reaction in calcium-free model water, and moves to the second reaction order kinetics when calcium is present. Based on the intraparticle diffusion model, the main controlling mechanism for As(III) adsorption is intraparticle diffusion, while the surface diffusion contributes greatly to the adsorption of As(V).

The effect of PO_4^{3-} on the adsorptive removal of Cr(VI) and Cd^{2+} was assessed using IOCS and GFH as adsorbents. Batch adsorption experiments and RSSCT were conducted using Cr(VI) and Cd^{2+} containing model water at pH 6, 7 and 8.5. The best Cr(VI) and Cd^{2+} adsorption was observed at pH 6. GFH showed much better removal of Cr(VI) than IOCS, while IOCS removed Cd^{2+} better than GFH. Increasing PO_4^{3-} concentrations in the model water from 0 to 2 mg/L, at pH 6, induced a strong decrease in Cr(VI) removal efficiency from 93% to 24% with GFH, and from 24% to 17% with IOCS. A similar trend was observed at pH 7 and 8.5. An exception was for Cr(VI) removal with IOCS at pH 8.5, which was not affected by the PO_4^{3-} addition. Cd^{2+} was well removed by both GFH and IOCS, contrary to Cr(VI) which was better removed by IOCS. The effect of PO_4^{3-} is clearly seen at pH 6 when there is no precipitation of Cd^{2+} in the solution. At pH 8.5, the precipitation is the main removal process, as it represents around 70% removal of Cd^{2+} . The isotherm constants K for different combinations confirms the inhibition of Cr(VI) and enhancement of Cd^{2+} adsorption with addition of PO_4^{3-} . The same conclusion is confirmed by the results from rapid small scale column tests. The mechanism of Cr(VI) adsorption by GFH and IOCS is likely a combination of electrostatic attraction and ligand exchange while the mechanism of Cd^{2+} removal at lower pH of 6 was sufficiently energetic to overcome some electrostatic repulsion.

The effects of pH and Ca^{2+} on the adsorptive removal of Cu^{2+} and Cd^{2+} was also assessed in batch adsorption experiments and kinetics modelling. It was observed that Cu^{2+} and Cd^{2+} were not stable at pH values considered (6, 7 and 8), and the precipitation was predominant at higher pH values, especially for Cu^{2+} . The increase in Ca^{2+} concentration also increased the precipitation of Cu^{2+} and Cd^{2+} . It was also observed that Ca^{2+} competes with Cu^{2+} and Cd^{2+} for surface sites of the adsorbent. The presence of calcium diminishes the number of available adsorption sites of IOCS and GFH, resulting in lower removal of cadmium and copper. Freundlich isotherms for cadmium removal by IOCS showed that the adsorption capacity of IOCS decreased when calcium was added to the model water. The kinetics modelling revealed that the adsorption of Cd^{2+} onto IOCS is likely a second-order reaction.

The effects of fulvic acid on adsorptive removal of Cr(VI) and As(V) was also assessed. Batch adsorption experiments and characterization of IOCS and GFH by SEM/EDS were performed at different pH levels (6, 7 and 8). The surface of the virgin IOCS showed that Fe

and O represent about 60 to 75% of the atomic composition, while carbon concentration was about 10%. The surface analysis of GFH showed that Fe and O represent, about 32% and 28% of the chemical composition, respectively. The adsorption experiments with simultaneous presence of As(V) and FA on the one hand, and Cr(VI) with FA on the other hand, revealed that the role of FA was insignificant at all almost pH values for both IOCS and GFH. Some interference of FA on the removal of As(V) and by IOCS or GFH was only observed at pH 6. It was also found out that organic matter (OM) was leaching out from the IOCS during experiments. The use of EEM revealed that humic-like, fulvic-like and protein-like organic matter fractions are present in the IOCS structure.

Removal of selected heavy metals, namely Cd^{2+} , Cu^{2+} , and Pb^{2+} , by IOCS was also screened in a series of batch adsorption experiments conducted at different pH. Studies metals were present in model water as single or together with some other metals. Results from adsorption experiments using model water with a single metal, and using IOCS as an adsorbent, showed that all metals included in the study can be very effectively removed with total removal efficiency as over 90% at all pH levels studied. XRF analysis showed that IOCS contains mainly hematite (Fe_2O_3) (approximately 85% of the total mass of minerals that could be identified by XRF). Chemical analysis revealed that the main constituent of IOCS is iron, representing 32% on mass basis. Potentiometric mass titration (PMT) gave a value of pH of zero point charge of 7.0. The percentage of metals removed through precipitation was found to be metal specific: the highest for Cu (25%) and the lowest for Cd (2%) at pH 8. Concurrent presence of competing metals did not have a pronounced effect on the total metal removal efficiency, with the observed reduction of total removal efficiency of Cu, Cd and Pb between 1 and 4%. In terms of adsorption capacity, a competitive effect of metals was not observed except for Pb and Cu at pH 8 where the adsorption was decreased for 13% and 22%, respectively.

Complexation modelling showed two type of complexes, one type associated with a weak site (Hfo_wOCd^+ , Hfo_wOCu^+ , Hfo_wOPb^+), and the other associated with a strong site (Hfo_sOCd^+ , Hfo_sOCu^+ , Hfo_sOPb^+), formed for all metals studied. Precipitation of Pb and Cu observed in batch experiments was confirmed in modelling at $\text{pH} \geq 6.75$. IOCS, being an inexpensive and easily available adsorbent, can be used to treat water contaminated with heavy metals like Cd, Cu and Pb. However, pH is an important factor to be considered if one has to avoid precipitated metals which will finish in liquid waste (backwash water), especially for the removal of Cu and Pb.

Chapter 1: Introduction

Water is generally obtained from two principal natural sources: surface water such as fresh water lakes, rivers, streams and groundwater such as borehole water (McMurry and Fay, 2004; Mendie, 2005). Water is one of the essentials that supports all forms of plant and animal life (Vanloon and Duffy, 2005) and it has unique chemical properties due to its polarity and hydrogen bonds which means it is able to dissolve, absorb, adsorb or suspend many different compounds (WHO, 2007). Groundwater is the major source of drinking water in the world because of its availability and constant quality. Groundwater is also the preferred source of drinking water in rural areas, particularly in developing countries, because no treatment is often required and the water source is often located near consumers. However, in nature, water is not pure as it acquires contaminants from its surroundings and those arising from humans and animals as well as other biological activities (Mendie, 2005). This chapter reviews the literature on the quality, the problems related to groundwater pollution, and the different techniques used in the analysis and removal of heavy metals from groundwater. This chapter also provides the scope of the thesis.

1.1 Overview of groundwater availability and quality

Groundwater is water below the land surface that fills the spaces between the grains or cracks and crevices in rocks. It is derived from rain and percolation down through the soil. Groundwater has a number of essential advantages when compared with surface water: it is of higher quality, better protected from possible pollution, less subject to seasonal and perennial fluctuations, and much more uniformly spread over large regions than surface water. Groundwater also can be available in places where there is no surface water. Putting groundwater well fields into operation is also less costly in comparison to what is needed for surface water which often requires considerable capital investments. These advantages coupled with reduced groundwater vulnerability to pollution particularly have resulted in wide spread groundwater use for water supply. Currently, 97% of the planet's liquid freshwater is stored in aquifers. Many countries in the world consequently rely to a large extent on groundwater as a source of drinking water. Table 1.1 shows that 2 billion people rely on groundwater as the only source of drinking water (Sampat, 2000).

Table 1.1: Groundwater use for drinking water production by region

Region	Share of drinking water from groundwater (%)	People served (million)
Asia and Pacific	32	1000-2000
Europe	75	200-500
Latin America	29	150
United states	51	135
Australia	15	3
Africa	?	?
World		2000 (2.0 billion)

(Source: Sampat, 2000)

Groundwater is the major source of drinking water in many countries all over the world (Table 1.2). Unfortunately little is known about use of groundwater for drinking water in Africa. Table 2 shows that groundwater is extensively used as an important source of public water supply in Europe, especially in Denmark where groundwater represents 100% of the

drinking water production. In rural areas of the United States and India, groundwater also represents the primary source of potable water (96 % and 80 % respectively). Groundwater meets over 75% of the water needs of Estonia, Iceland, Russian Federation, Jamaica, Georgia, Swaziland, Mongolia, Libya and Lithuania (Vrba, 2004). Groundwater in Tunisia represents 95% of the country's total water resources, in Belgium it is 83%, in the Netherlands, Germany and Morocco it is 75%. In most European countries (Austria, Belgium, Denmark, Hungary, Romania and Switzerland) groundwater use exceeds 70% of the total water consumption (Vrba, 2004). In many nations, more than half of the withdrawn groundwater is for domestic water supplies and globally it provides 25 to 40 % of the world's drinking water (UNEP 2003).

Table 1.2: Groundwater use for drinking water production by selected countries

Region	Country	Percentage (%)
Europe	Denmark	100
	Germany	75
	Slovakia	82
	The Netherlands	75
	Belgium	83
	The United Kingdom	27
Asia	India (rural)	80
	Philippines	60
	Thailand	50
	Nepal	60
Africa	Ghana	45
	Morocco	75
	Tunisia	95
America	United States (rural)	96

(Source: Vrba, 2004)

Various human activities can result in significant changes in the conditions of the groundwater resources formation, causing depletion and pollution. Groundwater pollution in most cases is a direct result of environmental pollution. Groundwater is polluted mainly by nitrogen compounds (nitrate, ammonia and ammonium), petroleum products, phenols, iron compounds, and heavy metals (copper, zinc, lead, cadmium, mercury) (Vrba, 2004).

Groundwater is closely interrelated with other components of the environment. Any changes in atmospheric precipitation inevitably cause changes in the groundwater regime, resources and quality. Vice versa, changes in groundwater cause changes in the environment. Thus, intensive groundwater exploitation by concentrated water well systems can result in a decrease in surface water discharge, land surface subsidence, and vegetation suppression due to groundwater withdrawal. Groundwater pumping can extract mineralized groundwater not suitable for drinking in deep aquifers, and can draw in saline seawater in coastal areas. All of these circumstances should be considered when planning groundwater use. Even if groundwater is less vulnerable to human impacts than surface water, once groundwater is polluted, remediation can be relatively long term (years), technically demanding and costly (Vrba, 1985).