



Modelling of sorption of trace elements in an agricultural soil impacted by mining activities

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DECLARATION

I declare that dissertation is my own work, unaided work. It is being submitted for the Degree of Master of Science to the University of the Witwatersrand, Johannesburg, South Africa. It has not been submitted before for any degree or examination to any other University.

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ABSTRACT

The development of the economy of South Africa and many other countries has been highly dependent on mining industries. Minerals such as gold, platinum, diamond and many others have been mined and continue to be mined. Despite the importance of these minerals, their processing comes with social and environmental problems. During the processing of these minerals, trace elements such as copper, chromium, nickel, mercury, uranium, molybdenum and many others are released as wastes into the environment either, directly or indirectly. The release of the elements into the soil is of concern due to the possibility of groundwater system contamination.

The presence of these elements in the groundwater system poses serious challenges to the wellbeing of life forms, due to their toxicity, when they exceed threshold limits. From the processing plants, these elements could be released onto the soil, and mobilise to groundwater, increasing the already existing environmental crisis due to water pollution. Once these elements are in the water, access to living organisms becomes easier through the food chain. Some of these elements are not biodegradable and thus persist in the environment as well as in the bodies of living organisms. They can cause serious health problems because of their toxicity effect. In humans, these elements can be carcinogenic, and also cause chronic disorders, kidney failures, defects in infants, bone and vascular diseases which could also be lethal.

It is therefore of importance that these elements are neither bioavailable nor bioaccessible to living organisms. When these elements are mobile in the soil, the probability of reaching groundwater increases. Water, an important natural resource should always be protected from such pollutants. The demand for unpolluted water has been rising every year in the world due to increasing population, extended droughts and improper disposal.

This research was dedicated to determining the behaviour of elements in an agricultural soil impacted by mining activities. Agricultural soils are sometimes exposed to pollutants that could originate from dust fallout or precipitation; fertilisers and manure; pesticides; and water used for irrigation. Understanding the

processes that control the distribution of these pollutants in agricultural soils is an important risk assessment measure, considering that such pollutants have the potential of being taken up by crops and vegetables or transported to groundwater.

In this study, a soil on a farm that grows vegetables for commercial purpose. Cabbage, spinach, carrots and potatoes are some of the vegetables grown on the plot and sold to markets in Pretoria and Johannesburg. The plot is in the vicinity of smelting operations in the North West Province. The mobility of trace elements in the soil can be controlled, depending on the type and properties of soil. Hence in this research, the ability of the soil to adsorb elements entering the soil is studied.

The batch experimental work was performed to determine the effect of pH, initial concentration (5 - 100 mg/L), competing ions (Fe^{3+} , Ca^{2+} , Co^{2+} , Mg^{2+} , K^+ , Ni^{2+} and Zn^{2+}), fertilisers (ammonium nitrate, ammonium phosphate and calcium chloride) and plant exudates (acetic acid, citric acid and oxalic acid as well as ethylenediaminetetraacetic acid (EDTA) which is often used as proxy organic ligand (found in manure)) on the adsorption of cadmium (Cd), copper (Cu) and chromium (Cr) onto an agricultural soil. The PHREEQC geochemical modelling code was used to complement experimental methods in predicting processes and to further assess the leaching behaviour of the elements. Powder X-ray diffraction (PXRD) and X-ray fluorescence (XRF) were used to determine the mineralization of the soil. The structural features of the soil were determined using Fourier Transform Infrared spectroscopy (FTIR) and the element content was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The point of zero charge (PZC) of the soil was found to be 8.3 and the cation exchange capacity (CEC) of 51.6 meq/ 100g.

In the absence of fertilisers and plant exudates, the soil exhibited a similar high adsorption for elements at all initial concentrations by all the elements. Most (> 90%) of the elements were adsorbed within the first 3 minutes of contact with the soil. Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms were used to describe the experimental data for the elements. Kinetic rates were modelled using pseudo first-order and pseudo second-order equations. Pseudo

second-order gave the best fit for all the elements ($R^2 > 0.999$) indicating chemisorption. The effect of pH on Cd and Cu was insignificant however, the adsorption of Cr decreased with pH. The presence of competing ions decreased the adsorption of cadmium more than that of the other analyte elements. The soil was generally effective in adsorbing and retaining the elements. However, the retention was highly dependent on elemental speciation and prevailing conditions e.g. pH (as in the case of Cu and Cr). Such changes in conditions would have implications for groundwater quality.

The effect of plant exudates and EDTA was studied and the results showed that low molecular weight organic acids (LMWOAs) *viz* acetic acid (AA), citric acid (CA) and oxalic acid (OA) and EDTA significantly ($p < 0.05$) decreased the adsorption capacity of the elements onto the agricultural soil. AA had the least effect on the adsorption capacity of the elements whereas OA and EDTA strongly prevented the adsorption of the elements. Moreover, some of the elements which were already in the soil including those which were not under study such as Ca and Mg were desorbed from the soil by OA and EDTA. Thus, the mobility of the elements was increased by the presence of plant exudates, increasing groundwater contamination and consequently threatening the health of living organisms.

Agrochemicals such as fertilisers, stabilizers and pesticides are constantly applied to agricultural soils to improve the fertility of the soil for better crop production however; their presence may affect the mobility and bioavailability of elements in the soil. The effect of ammonium nitrate and ammonium phosphate as well as calcium chloride on the adsorption of Cd, Cu and Cr onto an agricultural soil was studied. The effects of initial concentrations of the elements (5 – 50 mg/L), concentrations of fertilisers (0.01 – 0.1 mol/L) and pH (3 - 8) on the adsorption of Cd, Cu and Cr were studied. The initial concentration of the elements and the concentration of fertilisers had no significant effect ($p > 0.05$) on the adsorption capacities of Cu and Cr at pH 5. But, ammonium nitrate and calcium chloride decreased the adsorption capacity of Cd. The adsorption of Cd onto the soil was reduced as the concentration of fertilisers increased. The adsorption of Cd was lower than that of Cu and Cr at all pH values. The agricultural soil was found to

be an effective adsorbent in preventing the mobility of Cu and Cr in the presence of fertilisers but not for Cd whose adsorption was significantly affected by the presence of ammonium nitrate and calcium chloride.

A continuous flow fixed-bed column script with specified conditions simulating the natural environment was utilised in PHREEQC for column studies. The geochemical computer model PHREEQC can simulate solute transport in soil surfaces. The effect of initial concentration (100 and 300 mg/L) of the elements, column bed depth (5 and 10 cm) and pH (3, 5, 7 and 10) were considered in this study. The adsorption capacity was affected by initial concentration of the elements since the breakthrough curves at higher analyte concentrations were reached at lower pore volumes than at low concentrations. This can be attributed to the fast occupation of active sites of the soil at higher concentrations. The results from PHREEQC indicated that the conditions used would lead to the oxidation of Cr^{3+} to Cr^{6+} leading to the formation of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ which were not favoured for adsorption by soil surfaces due to high solubility. This could have potential implications on the quality of groundwater in regions with similar conditions. Thus, the leaching of Cr^{6+} onto the agricultural soil will be high in areas where remediation techniques are not applied. The changing of bed depth from 5 to 10 cm did not have an effect on the adsorption of the elements. The ability of the soil surfaces to adsorb Cd and Cu even at lower bed depth implies that the soil will be effective in preventing the leaching of the elements to groundwater due to strong surface interactions of the elements with the soil. The results from PHREEQC showed that the adsorption of Cd and Cr onto the soil surface was not affected by pH. The results for Cr were contradicting with those obtained from laboratory experiments which could be due to the conditions used in PHREEQC. The change in the speciation of Cu at basic conditions decreased the ability of Cu adsorption onto the soil surfaces. The Cu^{2+} was converted to $\text{Cu}(\text{OH})_2$ which were large in size and thus only a small amount could be adsorbed since the other adsorption sites were covered by the large species.

This research had notable outputs in the form of publications which will form an important repository of information.

DEDICATION

This dissertation is dedicated to the following:

First and foremost I would like to give all the glory and honor to my heavenly Father, Jesus and the Holy Spirit for leading me thus far and making it possible to obtain this degree. I therefore dedicate it to them for without them I can do nothing.

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List of abbreviations

CEC	Cation exchange capacity
EDTA	Ethylenediamine tetra-acetic acid
ICP-OES	Inductively coupled plasma optical emission spectroscopy
FTIR	Fourier transform infrared
LMWOA	Low molecular weight organic acid
PXRD	Powder X-ray diffraction
PZC	Point of zero charge
SOM	Soil organic matter
WHO	World health organisation
XRF	X-ray fluorescence

Definition of terms

The following terms are used throughout the study as follows:

Accumulation refers to gathering or increment of something over time.

Adsorption attachment or capturing of a chemical species onto a surface either electronically or chemical by electron capturing.

Anthropogenic addition of substances through human intervention.

Bioavailability refers to the extent and rate at which the active moiety such as elements become available to the target tissue, thereby accessing the site of action.

Contaminant refers to a substance present in the environment, but not causing any obvious harm. It may cause a deviation from the existing environment but is not necessarily a pollutant.

Heavy elements group of elements such as lead, copper, chromium, cadmium, nickel, zinc and mercury and metalloids such as aluminium and arsenic with an atomic density greater than 3.6 g/cm^3 . Heavy elements are also known as trace elements and at trace levels, some of these elements can support life but can become toxic at elevated levels.

Pollutant a substance present in the environment with greater levels of concentrations than natural as a result of human activity. These kinds of these substances have a net detrimental effect upon the environment or upon something of value in that environment

Pollution the introduction of substances into the environment that could be a hazard to human health, living organisms and ecological systems.

Sorption a chemical species may accumulate on a mineral surface either through adsorption, hydrophobic interactions, and /or precipitation.

Toxicity the degree to which something is harmful or poisonous to living organism including humans.

Structure of dissertation

This dissertation was written in a form of research articles which some are sent for review, whilst others are still to be sent. The articles form part of the results chapters (Chapter 4, 5, 6, 7 and 8).

The dissertation consists of the following chapters:

Chapter 1- Introduction

This chapter includes the background and motivation of conducting studies based on the adsorption of elements onto agricultural soils in the vicinity of mining operations. The problem statement and study area are described in this chapter.

Chapter 2-Literature review

The literature review relevant to this study is presented in this chapter. The sorption processes and mechanisms involved between elements and soils were described in detail. Factors affecting adsorption of the elements are presented.

Chapter 3-Aim, objectives and hypothesis

In this chapter, the aim of the study and underlying objectives are clearly stated out. The hypothesis is also presented.

Chapter 4-Batch adsorption studies

In this chapter, the batch adsorption studies are presented in a form of a journal article. The article focuses on the characterization of the agricultural soil used, the effect of initial concentration, pH, and competing ions. The isotherm and kinetic models are also included in this chapter.

Chapter 5-The effect of plant exudates on the adsorption of the elements

This chapter focuses on the effect of plant exudates, namely; acetic acid, citric acid, oxalic acid as well as EDTA on the adsorption of cadmium, copper and chromium onto an agricultural soil. Two research articles are included in this chapter.

Chapter 6-The effect of fertilisers on the adsorption of elements

In this chapter, the effect of ammonium nitrate and ammonium phosphate which are used by farmers are determined. The effect of calcium chloride is also included in this chapter.

Chapter 7-Modelling using PHREEQC – column studies

Column studies performed using PHREEQC geochemical modelling are presented in this study.

Chapter 8-General conclusions

Conclusions are written in each research article but this chapter describes the overall conclusions from this study.

References

References from this study are included in this section but, they exclude those in the research articles unless if they were used also outside of the articles.

Appendices

Supplementary information is included in this section.

This dissertation is based on the following articles:

Adsorption of cadmium, copper and chromium by an agricultural soil impacted by mining activities (South African journal of Chemistry (SAJC) (Ref: Sajc-001495))

Alseno K. Mosai, Elisee N. Bakatula and Hlanganani Tutu

Effect of plant exudates and EDTA on the adsorption of cadmium onto an agricultural soil impacted by mining activities (In preparation to be submitted)

Alseno K. Mosai and Hlanganani Tutu

The effect of plant exudates on the adsorption of copper and chromium in an agricultural soil impacted by mining activities: implications for the shallow groundwater (WaterSA (Water SA 3406))

Alseno K. Mosai and Hlanganani Tutu

The effect of fertilisers on the adsorption of Cadmium, Copper and Chromium on an agricultural soil impacted by mining activities (In preparation to be submitted)

Alseno K. Mosai and Hlanganani Tutu

Modeling the sorption and transport of cadmium, copper and chromium on an agricultural soil impacted by mining activities: a column-based study (In preparation to be submitted)

Alseno K. Mosai and Hlanganani Tutu

CHAPTER 1

INTRODUCTION

This chapter includes the general background and motivation, statement of the problem and study area

1. INTRODUCTION

1.1 Background and motivation

The development of the economy of South Africa has been highly dependent on mining industries. Many minerals such as gold, platinum group elements (PGEs), vanadium and diamond are and have been mined in South Africa for years. South Africa produces the highest quantity of chrome, platinum, vanadium and manganese in the world (Coakley, 1998). Moreover, a number of companies, banks and suppliers of materials and equipment get their profit from mining industries (Coakley, 2000; Northam Platinum limited, 2013). 20% of South Africa's gross domestic product (GDP) is from mining (Coakley, 1998, Cramer *et al.*, 2004). One of the highest employing industries in South Africa and in most parts of the world is mining. The mining industries have also led to the development of urban centres such as Rustenburg (North West Province), Johannesburg (Gauteng Province) and Welkom (Free State province) in South Africa (GDAEC, 2008). Due to the high demand of minerals, mining operations in South Africa such as Anglo Platinum, Lonmin and Impala Platinum have increased the production of minerals to millions of ounces (Cramer *et al.*, 2004).

Despite the importance of mining industries and the minerals they produce as well as the value they add to the country, there are environmental implications that come along with the processing of the elements since, high volume of waste is produced. This waste elements such as copper, chromium, mercury and many others is discharged into surrounding soils and water bodies through direct and indirect discharges (Langston and Bebianno, 1998, Ochieng', 2012). Some of these elements are essential to living organisms but, some are not. Amongst the essentials ones there is copper, zinc, chromium, iron and nickel. The non-essential ones are cadmium, mercury and lead which are very toxic even in low concentrations (Table 1.1) (Langston and Bebianno, 1998). Some of these elements pose serious environmental concerns since they are not biodegradable in nature and thus persist in the environment for long periods of time (Gupta *et al.*, 2001; Navarro *et al.*, 2008). All these elements have become widely distributed due to natural, mining and human activities (Dallas and Day, 2004). It is not only

the environment that is affected but life forms such as humans, animals and plants. Plants can absorb trace elements such as chromium, lead, cadmium and arsenic with many others from the soil on which they accumulate and affect the growth and development of the plants. These elements can also bio-accumulate in humans and other animals causing serious diseases and disorders once they exceed threshold limits (Tarras-Wahlberg *et al.*, 2001; Pehlivan *et al.*, 2009).

The biosphere is continually in danger due to the bio-accumulation of trace elements. Living organisms readily take up these toxic elements *via* processes such as adsorption, breathing and eating foods wherein they are contained. The danger with this especially in humans is that, the elements can be consumed in concentrations above the dietary requirements and thus accumulate in tissues of living organisms due to their inability to biodegrade therefore, harming the human health (Harris *et al.*, 1996; Farsang *et al.*, 2009).

The accumulation of trace elements in the soil is high in regions where there are mining operations nearby (Lim *et al.*, 2008). This accumulation is influenced by many factors such as aerosol input, vegetation, anthropogenic, organic matter content and drainage (Kabata and Pedias, 1993). The elements in the soil can then be prevented from moving around and reaching groundwater aquifers since they can be bound by the soil particles. The physical and chemical properties of these elements are not the only factors that affect their transport but also, the physical and chemical properties of the soil to which they are exposed (Dube *et al.*, 2001). The ability of the soil to perform the adsorbing function is dependent upon the properties of the soil such as pH, humus content, mineralogical composition, ionic strength and the clay content as well as parameters such as metal concentration, contact time and metal speciation which can be influenced by plant exudates and fertilisers (Bradl, 2004; Szegedi, 2007; Farsang *et al.*, 2009). Plant exudates such as low molecular weight organic acids (LMWOA) including citric acid, oxalic acid and tartaric acid (Gao *et al.*, 2003; Li *et al.*, 2014) as well as fertilisers (Matusik *et al.*, 2008) are known to desorb elements bound to the soil.

This study focused on the behaviour of metals (chromium, cadmium and copper) on an agricultural soil impacted by mining activities in Rustenburg (North West

Province). The results of this study will be useful for establishing risk assessment benchmarks for agricultural soils of a similar nature. The study determined the partitioning of pollutants into labile and soil-retained fractions. Geochemical models were, for the first time in such a scenario, applied to study processes determining the interactions of plant exudates and fertilisers with elements as well as their implications on adsorption onto an agricultural soil.

1.2 Statement of the problem

In this study, a soil on a market gardening plot was considered. Cabbage, spinach, carrots and potatoes are some of the vegetables grown on the plot and sold to markets in Pretoria and Johannesburg. The plot is in the vicinity of smelting operations in the North West Province.

A large amount of waste is produced from smelting operations which include pollutants such as chromium, cadmium and copper which could be deposited onto the agricultural soils through dust fallout or precipitation. Fertilisers and manure; pesticides; and water used for irrigation occasionally on the plot could deposit potential pollutants such as cadmium and copper onto the soil.

Understanding the processes that control the distribution of these pollutants in agricultural soils is an important risk assessment measure, considering that such pollutants have the potential of leaching to groundwater and taken up by crops and vegetables hence, find entry into the systems of living organisms including humans where they can cause serious health problems.

Fertilisers, pesticides, sewage sludge and water used for irrigation are constantly applied on agricultural soils and tend to increase the amount of elements in the soil. Due to intense mining and other industrial activities, it has been lately difficult to distinguish between the natural elements and those resulting from anthropogenic sources (Silveira *et al.*, 2003). Thus, the presence of the elements such as Cd, Cu and Cr could be from any of these sources. The main concern with the accumulation of these elements is that they can be toxic to living organisms and due to their persistence, remain so until they are physically removed from the accumulation point. The toxicity of some elements stems from their radioactive

(uranium) and disease causing (cadmium) abilities. Water pollution has been for many years causing diseases and deaths to living organisms. About 14 000 people die daily because of water pollution (West, 2006). Thus, the toxic elements from mining operations and agrochemicals should be controlled. The physical and chemical properties of the soil can affect how elements behave and control their mobility hence bioavailability. The focus of this study was to assess the adsorption of elements onto agricultural soils.

Sludge is often used in agricultural soils to improve soil quality for better crop production. Sludge can achieve this by improving the soil pH, organic matter and nutrients (Tsadilas *et al.*, 1995). The physical properties of the soil such as soil porosity, water retention and aggregation can also be improved by sludge (Karapanagiotis *et al.*, 1991). Despite the importance of sludge, the environment might be in danger of the accumulation of trace elements such as Zn, Pb, Cd, Cu, Cr and Ni (Oliveira and Mattiazzo, 2001; Bradl, 2004).

The concentrations of elements found in sludge are governed by the activities involved where the sludge was taken from. For example, sludge from industrial areas has higher concentrations of elements than sludge from domestic vicinities (Silveira *et al.*, 2003). The concentrations of elements in soils can increase dramatically due to short and long-term use of sludge. Oliveira and Mattiazzo (2001) observed an increase in the concentrations of Cu, Cr, Ni and Zn in soils which were amended for just two years. However in many agricultural soils, the application of sludge has been occurring for many years. Thus, accumulation of elements might be very high in agricultural soil.

Industrial waste also, is often applied on agricultural soils and influences the increase in elemental concentrations. Iqbal *et al.*, (2011) found that the concentration of trace elements (Ni, Cu, Cd, Cr and Pb) in an agricultural soil irrigated by industrial waste water were higher than permissible limits of these elements according to the Netherlands Standard (Denneman and Robberse, 1990).

This therefore, shows that many agricultural soils could have high concentrations of elements due to anthropogenic activities. Table 1.1 shows the permissible amounts of trace elements in soils.

Table 1.1 Permissible amounts of elements in the soil (WHO, 1996)

Elements	Target values of soil (mg/kg)
Cd	0.8
Cu	36
Cr	100

1.2.1 Toxicology

Elevated concentrations of elements in the soil automatically lead to increased concentration of these elements in groundwater and vegetation which will increase the bioaccessibility and bioaccumulation in humans and livestock. These will have long-term negative effects in the species due to health problems that can arise. Some vegetables such as spinach, lettuce and cabbage grown on the plot can easily accumulate high concentrations of elements such as cadmium and arsenic and when ingested, these elements will accumulate in the systems of living organisms (Li *et al.*, 2012; Alloway *et al.*, 1990). Moreover, groundwater and other water bodies such as rivers around the soil will provide water that is high in these elements which, exceed the permissible amounts. Due to the persistence and toxicity of the elements, diseases such as kidney failures, cancer and cardiovascular diseases which can lead to death will arise (Li *et al.*, 2009; Li *et al.*, 2014).

Cadmium can cause skin lesions, renal dysfunction and bone as well as cardiovascular diseases in humans even in low concentrations (Calderon, 2000). The average life expectancy of humans can be reduced by 10 years due to the presence of cadmium (Lacatusu *et al.*, 1996). Once in the body, cadmium is known to affect enzymes responsible for reabsorption of proteins in kidney tubules hence kidney failure. The activities of other enzymes such as alcohol

dehydrogenase, lipoamide dehydrogenase and arylsulfatase which are crucial for normal functioning of the body are also reduced by the presence of cadmium (Manahan, 2003). The continuous application of agrochemicals such as fertilisers and pesticides add to the main sources of cadmium in agricultural soils (Kabata-Pendias and Pendias, 1992).

Despite the importance of copper in the world, it is one of the environmental protection agency's priority pollutants due to its toxicity (Cameron, 1992). It is required by plants and animals for growth. However, when it is above the maximum allowed limits it becomes toxic. It can cause kidney failure, anaemia, liver failure and stomach irritation (Wuana and Okieimen, 2011). Turkdogan *et al.*, 2002 found that copper was one of the elements which increased the levels of upper gastrointestinal cancer rates in the Van region of Eastern Turkey.

In Rustenburg, the most common form of Cr is Cr^{3+} which is considered non-toxic (Ochieng', 2002). However, high concentrations can damage the DNA in cells of living organisms hence only moderate uptake of Cr^{3+} is required (Ochieng', 2002; Eastmond *et al.*, 2008). Cr^{3+} can be oxidised to the toxic Cr^{6+} which is carcinogenic. In the presence of MnO_2 which is present in most soils and in aerobic or anoxic conditions Cr^{3+} can be oxidised to the toxic form (Apte *et al.*, 2006). Thus, through rainfall, runoff and percolation, Cr^{3+} from the mines may result in the formation of Cr^{6+} which can be distributed in the soil and consequently, underground water. The platinum group element (PGE) bearing upper group two (UG2) chromitite layer is mined in Rustenburg hence chromium is considered in this study. The UG2 chromitite has about 42% Cr_2O_3 and this can increase the amount of anthropogenic chromium released into the environment through dust fallout or precipitation (Ochieng', 2002).

1.3 The study area

The soil in an agricultural plot was considered in this study. The plot is in the vicinity of platinum smelting operations in the North West Province (Figure 1.1). The mining operations around the plot constitute important sources of trace elements that can potentially pollute the surrounding soils. The area in which the plot was found, is well known for the mining of platinum group metals (PGMs),

but also has a significant proportion of base metals such as Cu, Fe, Co, Cr, Ni and Zn that are found in the host ores along with PGMs (Ochieng', 2002). The secondary source of contamination to the surrounding soils could be pesticides and fertilisers which are applied to the agricultural soil. Ochieng' (2002) sampled soils from the same area and found that the sites closer to the mining operations had higher concentrations of metals than the sites further away from the mining operations. This suggested that the accumulation of metals in the soils could be increased by these operations. He also found that the concentrations of metals in the soils differ depending on the composition of the soil profile. Some metals were found to decrease in concentration down the soil profiles whilst others were increasing (Ochieng', 2002).

The soils in this area are described as black tuff (podsollic) and are dominated by montmorillonite and illite minerals. The soil composition in this area differs with depth. The top layer (0-2 cm) is fine black, the second (2-20 cm), third (20-40 cm) and fourth (40-50 cm) layers consists of black clay, the fifth (50-60 cm) layer consists of black and white soil interface and the last (60-70 cm) layer is weathered bedrock (norite) (Munsell, 1975; Ochieng', 2002). The soil was found to be alkaline and the alkalinity increased down the soil profile with pH values starting off at around 7.0 in the upper layer and increasing to around 8.9 in the bottom layers. The conductivity of soils near the mining operations was found to be higher than those which are further away (Ochieng', 2002). When considering the soil profile, conductivity is moderate near the surface, high at the middle layers and low at the bottom. The highest concentrations of metals were found in the middle layers of the soil. The middle layers contain much of the clay component of the soil (Ochieng', 2002).

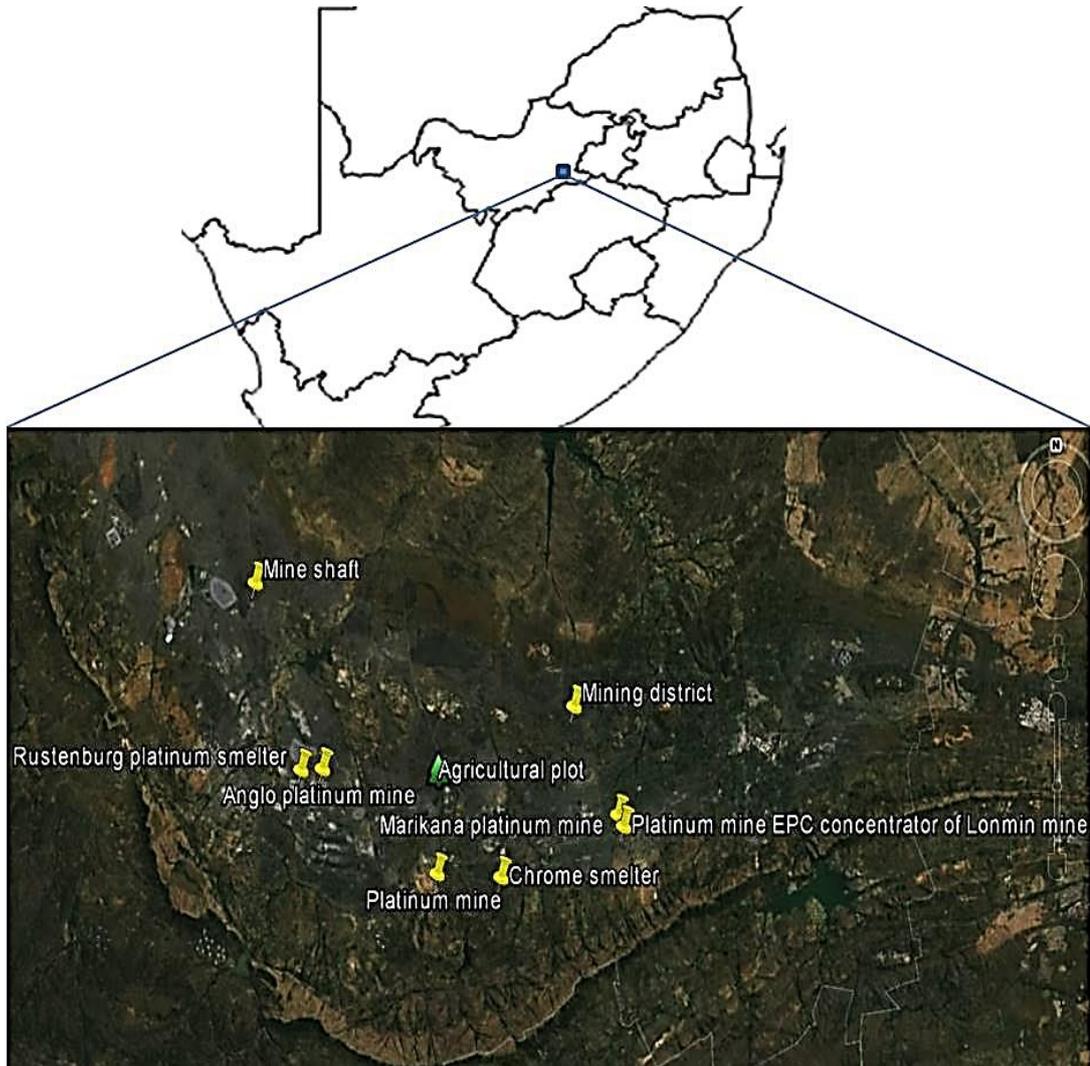


Figure 1.1 Location indicating current mining operations in or near Rustenburg surrounding the agricultural plot considered in this study (Google Earth)

CHAPTER 2

LITERATURE REVIEW

This chapter presents a concise overview of the literature relating to adsorption of trace elements onto soil surfaces.

2. LITERATURE REVIEW

The contamination of the soil and water by trace elements such as Cd, Cu, Cr, As, Hg, U and Pd has been a global problem for many years. Industrial areas, mine tailings, agrochemicals including fertilisers and pesticides, water used for irrigation, sewage sludge, industrial waste waters, atmospheric disposition, animal manures and chemical spillages contain elements which are constantly released into the environment (Hills *et al.*, 1998; Silveira *et al.*, 2003; Zhang *et al.*, 2010). Unfortunately, important natural resources namely soils and water bodies have been the major waste disposal sites for the elements released by the above mentioned sources. Due to the inability to undergo biological and chemical degradation, the elements released persist for long periods in the soils and water bodies (Kirpichtchikova *et al.*, 2006). Their persistence has implications on soil and water pollution which continue to be a problem and costly.

2.1. Soil pollution

The increasing developments of urban, rural and industries have been found to increase soil pollution due to the large amount of waste produced which contains trace elements. The released elements accumulate in the soil where they can be transported to groundwater or even the vegetation around. Remediation techniques such as soil washing, clay linings and phytoremediation have been utilized by developing countries to remove trace elements from the soil and thus reducing soil pollution (GWRTAC, 1997). However, underdeveloped and other developed countries have not yet used these techniques so the accumulation of elements keeps on increasing in the soils. The danger with the accumulation of trace elements is that they can be toxic and cause serious health hazards to humans, livestock and vegetation (Table 2.1). Some of the elements such as mercury, uranium and cadmium are toxic even in low concentrations and only small amounts can be tolerated by the bodies of living systems (Pehlivan *et al.*, 2009). Others such as zinc, chromium, copper and magnesium are required by the

body but as soon as they exceed the permissible limits, they become toxic (Gaur and Adholeya, 2004).

Table 2.1 Sources and toxicity effect of some elements (Adriano, 2001; Resaee *et al.*, 2005; Agarwal *et al.*, 2006; Scragg, 2006; Wuana and Okieimen, 2011)

Element	Sources	Toxicity effect
Cadmium	Fertilisers, refined petroleum products, sewage sludge, mining, smelting, industrial waste and detergents.	Kidney failure, osteoporosis, renal dysfunction, hypertension and affect enzymes responsible for reabsorption of proteins in kidney tubules.
Mercury	Mining, petrochemical, painting, household detergents and fertilisers.	Renal and neurological disorders and kidney damage.
Lead	Ore processing using floating, smelting, roasting and grinding methods. Also pesticides, leaded fuels.	Causes disorder in the nervous and reproductive systems, carcinogenic, kidney failure, brain damage and retardation.
Copper	Mining and pesticides.	Anaemia, liver and kidney damage, stomach and intestinal irritation.
Chromium	Mining, electroplating and disposal wastes.	Allergic dermatitis, lung cancer, skin rash, nosebleeds and genetic material alteration.

Arsenic	Pesticides, herbicides and processing.	DNA breakdown, carcinogenic, and neurological disorder.
Nickel	Mining, electroplating, fossil fuels combustion and plating.	Cancer.

These trace elements have the potential to mobilise to groundwater, leading to water pollution and thus, ease of access to humans and other living organisms.

2.1.1. Agricultural soil pollution

One of the ways of disposing waste produced from mines and industries is through discharge into agricultural land (Silveira *et al.*, 2003). The release of sewage sludge to agricultural soil as a form of nutrient addition has been increasing over the years (Tomlin *et al.*, 1993). In South Africa, 80% of the wastewater treatment facilities release their sewage sludge to land disposal sites which includes agricultural land (Herselman *et al.*, 2006). Despite the importance of nutrient additions into the agricultural soils, sewage sludge have negative impact on soils and groundwater since they may contain high concentrations of trace elements such as Cd, Cu, Cr, Pb, Ni and Zn. Herselman *et al.* (2006) studied soils in which sewage sludge have been applied and found that some trace elements leached from the soil. Moreover, they found that groundwater was high in nitrate ions as a result of sewage sludge. Thus, elements in the sludge can leached through the soil profile and reach groundwater and accumulate hence find entry to living organisms. The content of the elements in the sludge is controlled by the type of industries activities they come from. Sludge due to domestic use is often lower in element (Pb, As, Cu and Cd) content than industrial use (Silveira *et al.*, 2003). The type of sewage treatment is also crucial since the bioavailability can be controlled. Treatment using polymers can increase the bioavailability of elements. The movement of trace elements where sewage sludge has been heavily applied reached a depth of 80 cm down the soil profile, posing serious challenges

should the application of sludge continues as reported by Antoniadis & Alloway (2003). Thus, most agricultural soils may have high concentrations of trace elements exceeding threshold limits due to the application of sewage sludge.

2.2. Water pollution

Water bodies such as rivers, lakes and other streams can accumulate trace elements from a number of sources already mentioned in Table 2.1 through dust fallout. But groundwater can be reached when the trace elements in the soil are mobile and there is no remediation technique applied. Some areas get groundwater directly through boreholes and don't clean it as they ought to in order to remove trace elements that are contained therein. Thus, there are high risks of accumulation of trace elements in humans. However, if the soil is effective in adsorbing the trace elements as soon as they are released then groundwater contamination is reduced since their mobility will be reduced. This study is focuses in the determination of the ability of an agricultural soil to adsorb specific trace elements.

2.3. Adsorption of elements onto soils

The accumulation of trace elements in the soil is largely caused by adsorption onto soil particles. The inorganic colloidal fraction of the soil is responsible for the adsorption of trace elements in mineral particles of the soil such as clay minerals, oxides as well as hydrous oxides of minerals (Dube *et al.*, 2001). Other colloids responsible for adsorption are metal carbonates and phosphates. These colloids are tiny particles in the soil which carry electrical charge (DuPont, 2009). Clay is made up of an array of aluminium and silicon oxides which are negatively charged due to the presence of oxygen atoms. These negatively charged species attract the positively charged ions such as calcium and iron which are dissolved in the soil water. Most nutrients found in the soil are positively charged and thus readily attracted to the negatively charged clay and organic matter surfaces (DuPont, 2009). In addition, the soil also adsorbs other elements such as chromium released as pollutants from mining operations and from pesticides used in agriculture. The solution concentration of these metals is regulated as they are

adsorbed on soil particles and this is also influenced by the organic ligands and inorganic ligands which can be of anthropogenic or biological origin (Bradl, 2004).

The soil has some surface functional groups bound on the solid phase and are responsible for metal adsorption. The nature of these functional groups will determine whether the metal binding is monodentate or bidentate and thus controlling the stereochemistry. There are varying hydrous oxide minerals and organic matter in the soil which possesses surface hydroxyl groups containing protons that can be donated to the surrounding solution which in turn takes up metal ions and thus the adsorption of metals on these sites is a function of pH (Sposito, 1984; Bradl, 2004). Clays, zeolites and manganese oxides are a group of minerals with a permanent structural charge. Just like the hydroxide oxide minerals and organic matter, this group also has surface protons but they also have exchangeable ion-bearing sites in addition (Davis and Kent, 1990). Montmorillonite and bentonite are clays which are readily used for metal adsorption in landfills due to their high specific surface areas and presence in most soils. Montmorillonite is an aluminosilicate mineral with high surface area and fine adsorption performance which make it a good adsorbing material and the regulator of the concentrations of many trace elements in soils (Bradl, 2004; Marco-Brown *et al.*, 2012; Dawei *et al.*, 2015). The ability to adsorb metals is also due to the fact that the cation exchange capacity weakly depends on pH. There are two mechanisms by which metals adsorb on montmorillonite. The first one is the cation exchange in the interlayers due to the interactions between the metals and the permanent negative charge on the surface of montmorillonite and the second is the inner sphere complexes formation (Schindler *et al.*, 1976; Faust and Aly, 1987; Kraepiel *et al.*, 1999).

Inner sphere complexes and outer sphere complexes can be formed depending on how the metal ions are bound on the surface of the solid phase. Outer sphere complexes are formed when there are water molecules between the bound metal ions and the surface functional group leading to the electrostatic bonding. Inner sphere complexes are formed when there are no water molecules between the

bound metal ions and the surface functional group and this leads to a stronger covalent bond (Nordin *et al.*, 1997; Bradl, 2004). Inner sphere complexes will have high adsorption equilibrium constants due to strong bonds formed and will show only poor desorption (Bradl, 2004).

There are several parameters which influence the adsorption of metals in soils. Some of the most important parameters are pH, metal concentration, effect of other ions, contact time and soil composition.

2.4. Sorption mechanisms in soils

The sorption process involves the interaction of the metal ion with the solid phase *via* three mechanisms *viz* adsorption, fixation or precipitation (Apak, 2002). This interaction can be surface complexation reaction (inner-sphere), electrostatic (outer-sphere), surfactant adsorption where metal-polyelectrolyte complexes are adsorbed onto the soils due to the surface tension that is reduced or hydrophobic expulsion of metal complexes which contain non-polar organic solutes. The adsorption of heavy metals can be described by two mechanisms known as specific and non-specific adsorption. The specific adsorption is highly selective and less reversible whilst non-specific adsorption is less selective and highly reversible due to weak interactions (McBride, 1994). Specific adsorption involves the adsorption of heavy metals at hydroxide groups on soil surfaces and edges which becomes negatively charged at higher pH levels and this adsorption is inner-sphere since the metal bonds directly at the surface. The reactions depend largely on pH and can be described as follows (Martinez and Motto, 2000):



where S is the solid particle and Me is the metal ion.

The other mechanism for sorption is fixation whereby the metals diffuse to the solid phase. The metals can become fixed into the pore spaces of the mineral structures after diffusing into the lattice structures of minerals. To remove the heavy metals absorbed, the total dissolution of the particles in which they are incorporated may be required (Bradl, 2004).

The last mechanism for sorption is precipitation occurring at the surface of the soil (equation 2). Heavy metals may precipitate as hydroxides, oxides, carbonates, phosphates or sulphites. The pH as well as anions are controlling factors on precipitation of metals in soils (Reed and Matsumoto, 1993; Temminghoff *et al.*, 1997)



2.4.1. Specific adsorption

The adsorption of elements onto the soils can be through specific and non-specific adsorption. Specific adsorption involves specific forces where ions are adsorbed on soil colloidal surface with high bound energy leading to highly stable molecules known as inner-sphere complexes (Sparks, 1995). The stability of adsorption is also due to the absence of waters of hydration between the ion and surface. When trace elements bound through inner-sphere complexation are often irreversible and when they are reversible, the reaction is normally very slow. The ability of trace elements adsorbed through specific adsorption to diffuse to the interior of particles also adds to the irreversibility of adsorption (Barrow, 1985).

Soil constituents which are involved in specific adsorption of trace elements are organic matter and hydrous oxides of Al, Fe and Mg. Moreover, some silicates which are readily available in soils can bind elements through specific adsorption. Cadmium, copper, cobalt and zinc and many other trace elements can be adsorbed through specific adsorption on soils and this is due to the small ionic radius, high polarizability and high electric charge in the nucleus (Yu *et al.*, 1997; Silveira *et al.*, 2003).

2.4.2. Non-specific adsorption

Trace elements can be bound in soils *via* non-specific adsorption, which is adsorption through electrostatic forces between the ion and the surface of the soil. This is also known as cation exchange and is the most dominant type of adsorption on soils. This type of adsorption leads to outer-sphere complexes. Unlike inner-sphere complexes, there is presence of water of hydration between

the ion and the surface (Silveira *et al.*, 2003). The non-specific adsorption have reversible adsorption, thus the adsorbed trace elements onto the soil surface groups can be desorbed. In non-specific adsorption, the adsorbent can selectively bind trace elements depending on their ionic charge and the degree of hydration. Organic as well as inorganic colloids in soils can take part in non-specific adsorption (Silveira *et al.*, 2003).

There are a number of factors that affect the adsorption of trace elements to soil surface colloids such as the valency of elements. The adsorption increases as valency of trace elements increases, thus in the presence of a mixture of elements such Cd, Cu, Cr, Fe and Mg, elements with high valency such as Cr^{3+} and Fe^{3+} will be adsorbed better than Cd^{2+} , Cu^{2+} and Mg^{2+} with lower valency (Silveira *et al.*, 2003). This means that the speciation that the trace elements exist in play a crucial role since they may exist in forms that decrease the overall charge, hence decrease their ability of being selectively adsorbed by soil surface colloids. For ions with the same valency such as Cd^{2+} , Cu^{2+} and Mg^{2+} selectivity and strength of adsorption can be determined by the hydrated radius of the elements (Ji and Li, 1997).

The pH in the soil, concentration of trace elements, anions and surface charge can affect the non-specific adsorption of elements onto the surface colloids. The pH of the soil can affect the speciation of the trace elements hence their adsorption onto the soil. Moreover, the charge on the soil can be affected by pH (Bradl, 2004). Anions such as citrate and acetate can form pairs with trace elements in the soil, thus reducing the overall charge of the elements due to the species formed and consequently decreasing their probability of being adsorbed onto the soils.

2.5. Types of soils

There are different types of soils which are prone to trace element accumulation. Some soils can adsorb trace elements better than others depending on their composition. Studies have shown that coarse-grain soils poorly adsorb elements entering the soil due to their poor holding capacity. This can be attributed to their composition and properties. Coarse-grained soils are known to be characteristic of

low clay content, low organic matter and low surface areas which play a fundamental role in the adsorption of elements (Ochieng', 2002; Bradl, 2004).

Fine-grained soils on the contrary have high clay content, high organic matter and high surface areas and can retain elements better than coarse-grained soils. Thus, fine-grained soils can prevent the mobility of trace elements in the soil better. The high clay content in fine-grained soils plays a major role in trace element retention (Bradl, 2004).

2.5.1. Soil constituents

2.5.1.1. Clay minerals

Clay minerals such as bentonite and montmorillonite are characteristic of many clay soils and responsible for the adsorption of trace elements (Abollino *et al.*, 2003). These minerals are basically alluminosilicates which have permanent structural charge. They possess ion bearing sites on the surface (Davis *et al.*, 1990). These clay minerals can adsorb trace elements through two processes or mechanisms. The first one is through cation exchange where cations such as K, Ca, Mg and Na attached to the negatively charged surface of the soil are substituted by other cations such as Cu and Cd. The second one is through the formation of complexes through the silica and alumina groups on the surface of the soil (Bradl, 2004). Clay minerals are also known as phyllosilicates which are layered silicates, in other words, tetrahedral silicates (Figure 2.1. a) are linked together in infinite two-dimensional sheets and they are condensed with layers of octahedral Al, Fe and Mg (Figure 2.1. b) (Kozák *et al.*, 2010). Figure 2.2 shows how elements e.g. Zn are captured by montmorillonite.

Clay minerals usually have permanent net negative structural charge which influences the sorption properties of the soil (Loughnan, 1969). This charge is due to the hydroxyl groups at the edges and on the outer layers of minerals whose protons can be donated to the surroundings. The deprotonated groups can then take up cations such as Ca and Na (Bradl, 2004). Moreover, clay minerals are made up mainly of silica and alumina groups, the Al^{3+} ion can replace the Si^{4+} ion in the mineral and can thus create a negative charge on the surface of the soil. The

replacement is possible due to the equal size of the ions. Also, the readily available ions, Fe^{2+} and Mg^{2+} can exist at the octahedral layers rather than Al^{3+} , therefore creating negative charges on the surface of the soil (Brown, 1998).

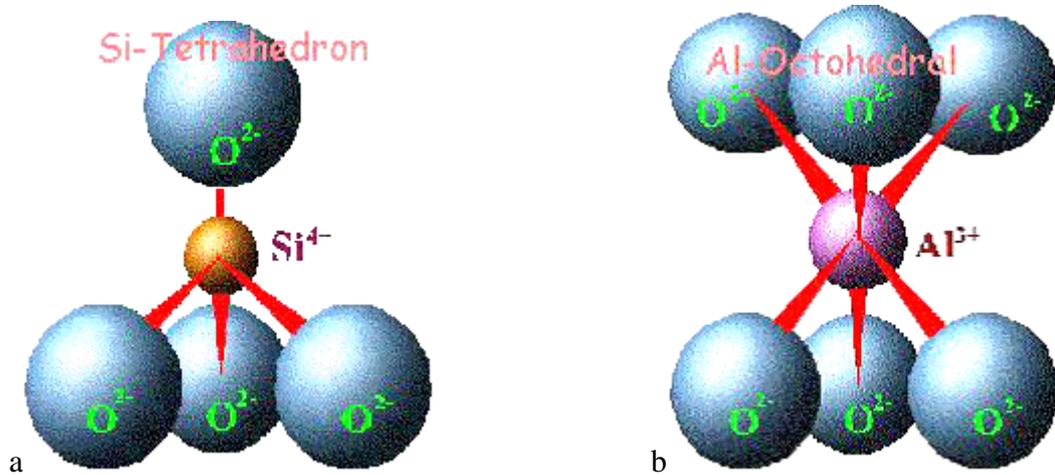


Figure 2.1 The structures of a) tetrahedral silicate, b) octahedral alumina (Brown, 1998)

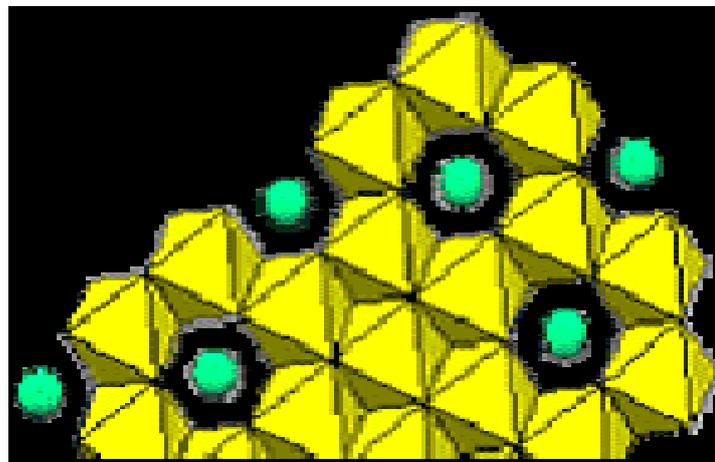


Figure 2.2 Schematic of montmorillonite capturing Zn (shown in green) (Brown, 1998)

There are two major types of clays which are found in soils which are 1:1 and 2:1. The ratios are basically silicates which are tetrahedral to octahedral layers. A 2:1 clay mineral will contain two silicate sheets condensed with octahedral layers (Figure 2.3a) and held together through van der Waals forces, making it possible for elements to enter the interlayer region so as to react with the inner surface

(Dube *et al.*, 2001). A 1:1 clay mineral will have infinite array of one octahedral layer condensing one silicate sheet (Figure 2.3b) held together by strong hydrogen bonds which don't allow for interlayer region, thus preventing the reaction of elements with the inner surface (Dube *et al.*, 2001). Moreover, 2:1. Clay minerals have high surface areas and cation exchange capacity than 1:1 clay minerals which means that they can hold elements stronger and prevent their mobility than 1:1 clay minerals (Table 2.2). Clay mineral such kaolinite exhibit 1:1 type and others such as montmorillonite and illite exhibit 2:1.

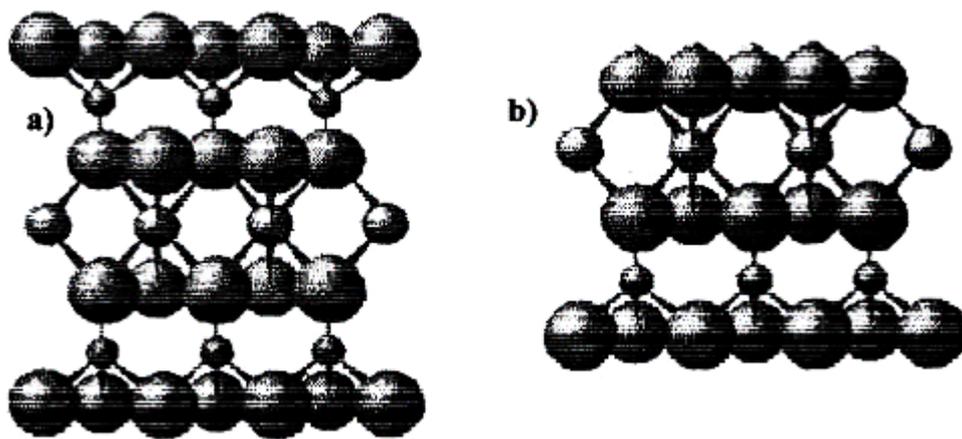


Figure 2.3 The arrangement of silica tetrahedral layers and aluminium octahedral layers in montmorillonite (a) and kaolinite (b) (Loughnan, 1969).

Table 2.2 The characteristics of soil surface groups (Stevenson, 1992; Dube, 2001).

Characteristics	Montmorillonite	Illite	Kaolinite	Hydrous oxides of Fe and Al	Humic acids	Fulvic acids
Type of layering	2:1	2:1	1:1			
Layer charge	0.25 - 0.6	0.6 - 0.9	1.0		485 - 870	900 - 4000
CEC	80 - 120	20 - 50	1 - 10	4		

Surface area	600 - 800	70 - 120	10 - 20			
pH dependent charge	minor	medium	extensive	extensive	extensive	extensive

2.5.1.2. Soil organic matter

Soil organic matter (SOM) which represents the organic constituents in the soil, also plays an important role in trace element adsorption since its presence increases the ability of the soil to adsorb trace elements. SOM is the second main component of the soil solid fraction. SOM includes proteins, polysaccharides, amino acids and humic substances from un-decayed plant and animal tissues, decomposition products of plants, animals and soil biomass (Stevenson, 1992). Carboxyl (-COOH), phenolic (-C₆H₄OH) and carbonyl (C=O) are the most significant functional groups of soil organic matter and responsible for the negative charge when they are deprotonated (Stevenson, 1992). The deprotonated groups are responsible for the adsorption of positively charged elements such as Cd and Cu. Moreover, soil organic matter is known to consist of high amount of humic substances. Humic substances are materials that have high oxygen, carbon, hydrogen and nitrogen atoms and are insoluble at pH <2. In soils, humic substances have very low mobility and are strongly attached to clay minerals (Dube *et al.*, 2001). At acid to neutral pH values, humic substances can be attached to the positively charged soil mineral surfaces such as oxyhydroxides which will result in formation of negatively charged surface which in turn will adsorb positively charged elements (Davis and Bhatnagar, 1995). At higher pH values, the deprotonated anionic forms of humic substances increase and the complexation reaction that can occur between the elements and the humic ligands can lead to increased mobility of elements due to repulsions with the negatively charged soil surface groups (Agarwal *et al.*, 2006). Humic substances consist mainly of phenolic and carboxylic groups which strongly influence the adsorption of trace elements (Figure 2.4). In the presence of humic substances, elements in the soil are attached to soil surface through complexation, thus affecting the mobility of the trace elements which would otherwise reach groundwater but this

is dependent on pH (Benjamin and Leckie, 1981). Figure 2.5 shows how the adsorption of elements by humic substances is dependent on pH. The adsorption of the trace elements increased as pH increased. Cation exchange capacity which is soil's ability to capture or adsorb cations is very high in soil organic matter.

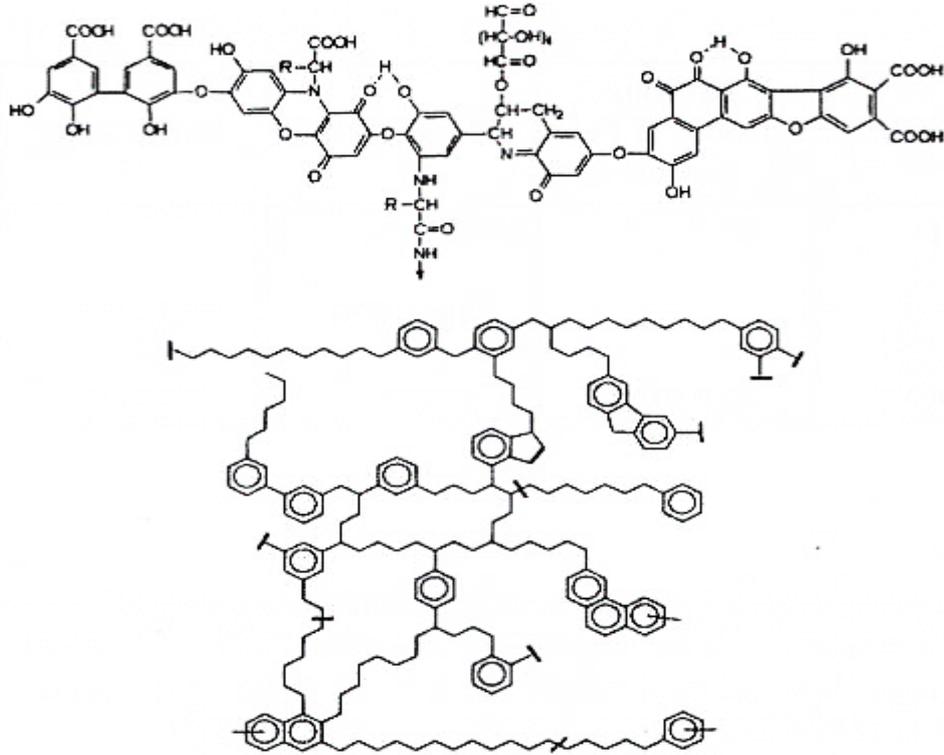


Figure 2.4 Model structures of humic acids according to Stevenson (1982) (a) and Schulten (1991) (b).

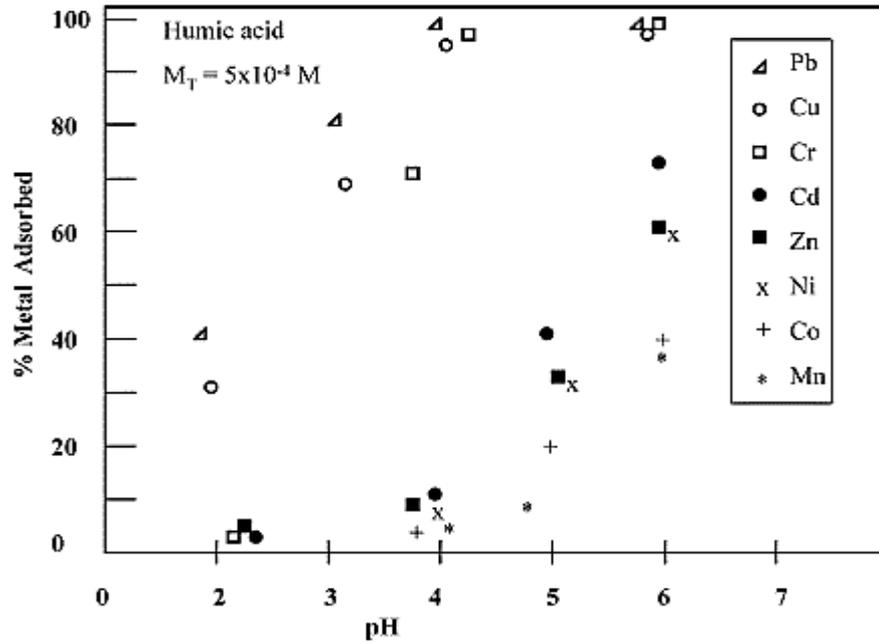


Figure 2.5 Adsorption of some elements onto humic acid as a function of pH (copied from Bradl, 2004).

The silicate groups on soil surface can bind organic substances through Van der Waals forces, hydrogen bonding, hydrous oxides and bridging with Al, Fe, Ca and Mg (Siepak, 1998). Organic materials play very important roles in the soil since they also determine the physicochemical properties of the soil such as the texture of the soil (Dube *et al.*, 2001).

In addition to humic substances, soils also have organic materials known as fulvic substances which are known to be soluble in water at all pH values. Unlike humic substances (Figure 2.4), fulvic substances (Figure 2.6) have small average molecular masses and with high mobility in soils. Fulvic substances have high alkyl groups (Dube *et al.*, 2001). Trace elements can be adsorbed onto soil surfaces with fulvic substances *via* specific adsorption and this can lead to immobilisation of elements in the soil, therefore preventing groundwater contamination. The functional groups in fulvic acid play a role in the adsorption of trace elements since they act as ligands for these elements since each group may occupy two or more of the coordinating positions in elements such as Cd and Cu.

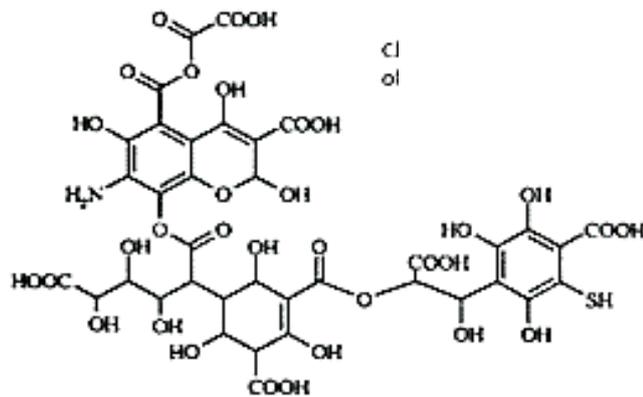


Figure 2.6 Chemical structure of fulvic acid (Dube *et al.*, 2001).

2.5.1.3. Iron oxides

Iron oxides are amongst the most important surface functional groups in soils since they also affect the sorption of trace elements. Iron oxides are present in most soils and influence the structure of soils (Silveira *et al.*, 2003). The stable iron oxides in soils are goethite (α -FeOOH) and hematite (α -Fe₂O₃) and are responsible for the adsorption of elements. These oxides can affect the particle dispersion and aggregate stability of soils (Pinheiro-Dick and Schwertmann, 1996). The concentrations of iron oxides in soils vary from 0.1 – >50% which could be evenly distributed within the soil matrix or concentrated in horizons, mottles, concretions or bands (Schwertmann, 1991). They may exist as the most chemically active portion, amorphous iron oxides which are also important for geochemistry studies in soils (Chao and Zhuo, 1983).

The charge of iron oxides is dependent on pH therefore the concentrations of hydronium and hydroxide ions are crucial. The positive charge that results in soils at lower pH values, is suspected to be due to iron oxides since iron hydroxides (Fe-OH) groups can adsorb hydronium ions to form Fe-OH₂⁺ (Zhang and Zhao, 1997). The adsorption of trace elements at iron oxides sites release hydronium ions to the surrounding solution as shown in equation 3 (Bradl, 2004). Thus, the presence of iron oxides can influence the retention, mobility and bioavailability of elements (Silveira *et al.*, 2003).



2.6. Factors affecting adsorption

2.6.1. Cation exchange capacity

Cation exchange capacity (CEC) also known as soil's ability to hold cations or the capacity of the soil to exchange positively charged ion for others is very crucial in soils. The higher the CEC, the higher the ability of the soil to hold more cations through electrostatic forces. Calcium, sodium, magnesium and potassium are dominant cations in most soils and can be adsorbed through electrostatic forces in soils. These cations can be easily exchanged for other cations in the soil. Soil organic matter and clay minerals are surfaces in soils at which cation exchange sites are primarily found (Ross and Ketterings, 2011). Therefore high organic material in the soil will lead to high CEC. Moreover, high clay content will lead to high CEC. Sandy soils have low CEC due to low clay and therefore CEC decreases with increasing particle size (Table 2.3). Thus, high CEC will prevent the mobility of elements in the soil (Silveira *et al.*, 2003)

Table 2.3 The cation exchange capacity of soil fractions (Schulten, H.R., 2000).

Fraction	CEC cmol(+)/kg
Clay	20.9-110
Fine silt	6.8-41.4
Medium silt	6.3-34.5
Coarse silt	1.2-12.8
Sand	1.0-15.6

2.6.2. Effect of pH

Soils have pH values that can affect the sorption of trace elements in soils. Many studies have shown that the adsorption of elements can be highly dependent on pH (Dube *et al.*, 2001; Silveira *et al.*, 2003; Wu *et al.*, 2003). The charge on the surface of the soil can be influenced by pH due to the abundance of ions present at particular pH. At lower pH values the concentration of hydronium ions are high reducing the negative character of the soil, therefore reducing the ability of the soil to adsorbing positively charged elements. Thus, increasing the mobility of the trace elements in the soil which have the ability of reaching groundwater (Bradl,

2004). This is due to the fact that more hydronium ions will bind to the available negative sites in the soil. Therefore the groundwater contamination is controlled by the pH of the soil. The negative charge of the soil is increased at intermediate pH values. This is due to the increase of hydroxide ions. Thus, the ability of the soil to adsorb positively charged elements is increased. Therefore the mobility of the elements in or entering the soil can be prevented hence reducing groundwater pollution (Bradl, 2004).

Figure 2.7 shows the dependence of the adsorption of some elements on pH. The adsorption of the elements increased as the pH of the sediment composite increased. The pH of the soil can be affected by a number of anthropogenic sources such as fertilisers, pesticides, water used for irrigation and manure. The pH of the soil can lead to net negative, positive or no charge of the soil surface. The pH where the surface of the soil is zero or has no net charge is known as point of zero charge (PZC). The PZC is an important parameter that can be used to determine the sorption trends observed in adsorption processes (Smičiklas *et al.*, 2005). Below the PZC, the charge of the soil will be negative, preferring to retain anions but, above the PZC, the charge of the soil will be positive therefore higher probability of cation exchange. Thus, it is important to know the PZC of the soil.

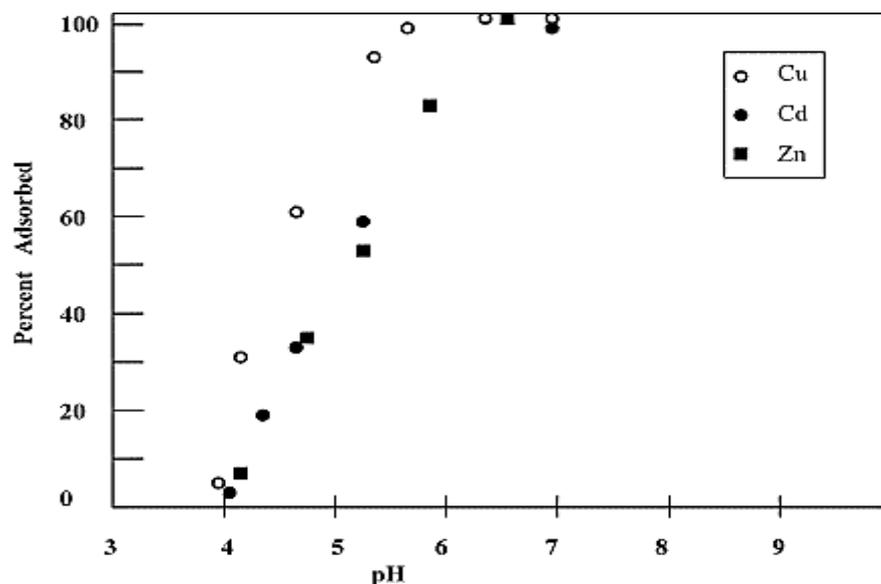


Figure 2.7 The adsorption of Cd, Cu, and Zn onto sediment composite as pH increase (copied from Bradl, 2004).

2.6.3. Fertilisers and pesticides

Farmers always use fertilisers and pesticides for better crop production. Fertilisers are used to improve soil quality and quality crop production since they add nutrients such as N, K and P which are required by plants. These fertilisers such as NH_4PO_3 , NH_4NO_3 , KNO_3 and ZnSO_4 are constantly applied onto the soils. They may contain elements such as Cd, Pb and As in addition to plant nutrients and increase their accumulation in the agricultural soils (Atafar *et al.*, 2010). Parkpian *et al.* (2003) reported that commercial farms where large quantities of fertilisers were added onto the soils had high accumulation of elements than cooperative farms. In addition to elemental content they may contain, fertilisers also affect the speciation and influence complexation of trace elements they may be in contact with. Thus, affecting their mobility (Wångstrand *et al.*, 2007) hence, bioavailability.

The properties of the soil such as pH may also be affected by the continuous application of fertilisers. High volume of fertilisers increases the acidity of the soil and studies have shown that low pH values increase the bioavailability of heavy elements in soils (Batchelor, 1998).

The anions from fertilisers such as Cl^- and NO_3^- are known to complex elements in the soil and affecting their mobility and increasing their solubility hence enhanced mobility of the elements (Sherene, 2010). Moreover, cations; NH_4^+ , Na, Ca and K from fertilisers can adsorb onto the soil surfaces and block the adsorptive sites which will prevent the adsorption of other elements onto the soil.

2.6.4. Exudates

Plant exudates such as citric acid, oxalic acid, acetic acid, tartaric acid and salicylic acid are released by plants into the soil. These plant exudates are excretion products of plant roots and are known as low molecular weight organic acids (LMWOA). These exudates can chelate elements in the soil and thus affect their solubility and mobility (Chen *et al.*, 2003). That is to say, the presence of plant exudates in the soil can increase the concentration and bioavailability of

elements in the soil. Chen *et al.* (2003) found that the presence of citric acid in the soil increased the amount of Cd and Pb in the soil and decreased the adsorption rate. The decrease in adsorption rate was due to the complexes formed between Cd and Pb with citric acid. Gao *et al.* (2003) found that citric and tartaric acids desorbed Cd and Cu from the soil and that the desorption was promoted as the concentration of the acids increased.

In agricultural soils, crops are responsible for releasing exudates. More exudates are released as a form of defence mechanism by the plant to element toxicity. Xu *et al.* (2006) found that Chinese cabbage secreted citric acid, oxalic acid, malic acid, lactic acid, succinic acid, acetic acid and tartaric acid under Zn stress to reduce Zn bioavailability and toxicity in the roots. Therefore more exudates are expected to be secreted where there is high element accumulation from different sources. Due to the ability of the exudates to form complexes with the elements in the soil, some of the adsorbed elements can be removed from the adsorption sites whose mobility will be enhanced down the soil profile, therefore, increasing the probability of reaching groundwater. It was found that under Al stress buckwheat roots secreted oxalic acid to reduce the Al toxicity through ligation of Al with oxalic acid to form chelate complex (Ma *et al.*, 1997).

The widely used chelating agent for elements is EDTA. It is known to be a strong complexing agent for different elements in soils. EDTA can effectively remove elements such as Pb, Cd, Cu and Zn from contaminated soils. The effect of LMWOA and EDTA on element accessibility was studied by Wu *et al.* (2003) and found that EDTA had the greatest effect on element concentration. Thus, the labile concentrations of elements in the soil increased. EDTA was found to increase the total organic carbon content in the soil which is known to enhance the solubility of elements in the soil (Wu *et al.*, 2003).

2.7. Element-ligand affinity

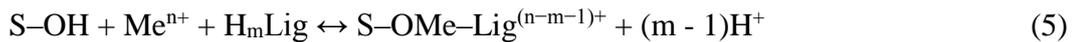
The affinity of elements to ligands depends on a number of factors which have been touched on in the previous sections such as the valency and electron configuration of the elements, pH, stereochemistry, the concentration of the

elements and the speciation of the elements. Heavy elements normally act as Lewis acids, thus accepting electrons whereas surface functional groups acts as Lewis bases and donate electrons. For oxides such as iron oxides (Fe-OH), the deprotonated form, Fe-O⁻ act as Lewis base and donate electrons to positively charged elements such as Cd²⁺ and Cu²⁺ leading to Lewis salt-type compounds as shown in Equation 4 (Bradl, 2004).



Moreover, the complexation of trace elements in the soil with natural ligands such as humic, fulvic, citric and acetic acid as well as anthropogenic ligands such as EDTA and many others is always occurring and changes the reactivity of the elements and thus affecting the mobility of the elements in the soil (Benjamin and Leckie, 1981).

Hydrous oxide surface have amphoteric properties since they can coordinate with positively charged elements and with ligands. A ternary complex is formed between the positively charged element, ligand and the reactive surface which can be very stable than the individual component species. There are two ways in which a ternary complex is formed. The first one is through the bonding of the positively charged element to the surface as shown in Equation 5.



where S-OH is the hydroxyl group on the surface of the soil, Meⁿ⁺ is the positively charged element such as Cd²⁺, Lig represents the ligand. The adsorption is known to increase with increasing pH when the ternary complex is formed with the element directly bonded to the surface (Figure 2.8) (Bradl, 2004). Therefore the ternary complex can increase or suppress the adsorption of elements onto soil surfaces due to the pH and complexing agent presence. It is very crucial to know the types of complexing agents in the soil as well as their effect on element adsorption as this will determine the transport and fate of these elements.

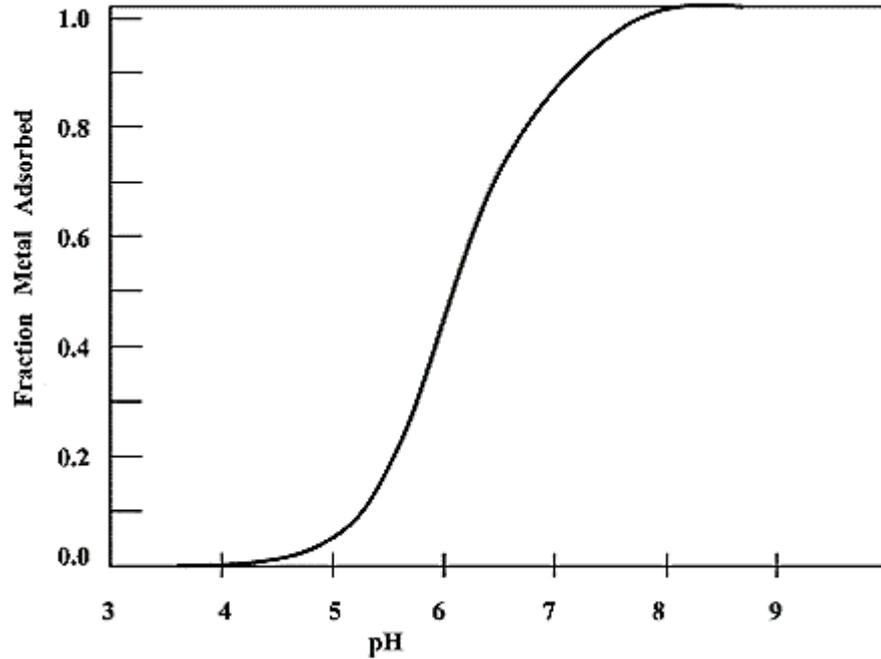
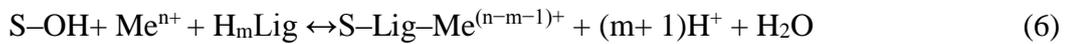


Figure 2.8 Schematic representation of metal-like adsorption (copied from Bradl, 2004).

The second one is through the bonding of the ligand to the surface of functional group as shown in equation 6.



Adsorption with this type of bonding is highly favoured at low pH values as shown in Figure 2.9 (Bradl, 2004).. This can be attributed to the charges that the components possess. The negatively charged soil will prefer to bind positively charged components hence the more negative the surface the higher the adsorption of elements. However, the binding of the negatively charged ligand such as EDTA to the surface of the soil will be preferred when the negative character of the soil is reduced hence adsorption is favoured at low pH values where the surface of the soil is covered with hydronium ions

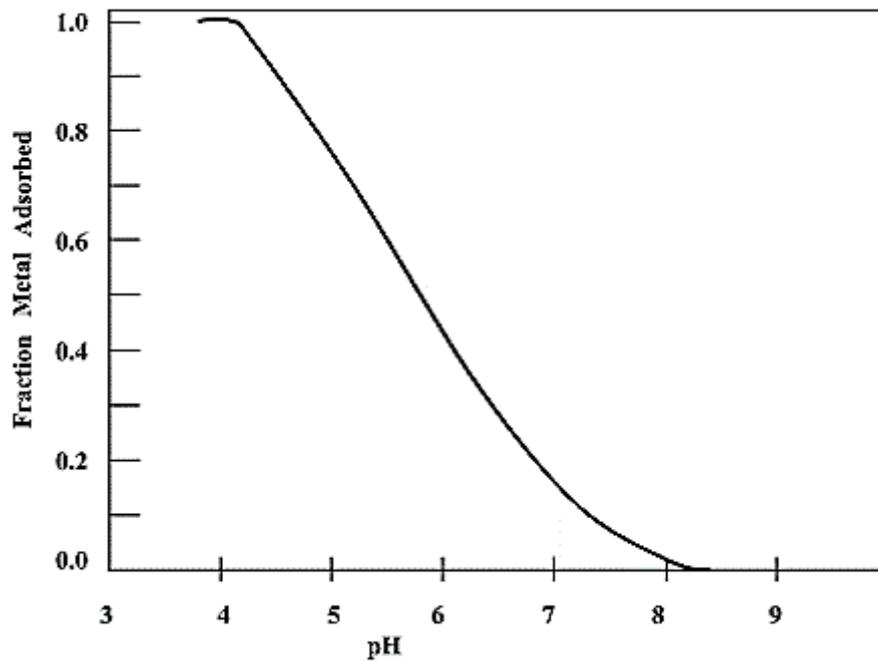


Figure 2.9 Schematic representation of ligand-like adsorption (copied from Bradl, 2004).

2.8. Adsorption isotherms

There are empirical models used to describe the adsorption of trace elements in soils. These models are based on mathematical relationships known as isotherms between the concentrations of trace elements in the liquid phase and the solid phase at equilibrium which can be defined by the chemical potentials of the phases being equal and where the temperature is constant (Toth, 2002; Bradl, 2004). In other words, adsorption isotherms describe the retention or the mobility of elements in aqueous media to a solid phase. The equilibrium can be reached when the liquid and the solid phases have been contacted for sufficient amount of time. The physicochemical parameters obtained in the models can provide information about the affinity of the elements to the surface of the soil, surface properties and adsorption mechanisms (Bulut *et al.*, 2008).

The adsorption of trace elements onto surfaces can be through monolayer or multilayer adsorption. In 1916, Langmuir mathematically explained the monolayer adsorption of gases onto homogenous planar surfaces. In his theory, at equilibrium, the numbers of adsorbed and desorbed molecules on the surface per

unit time are equal (Langmuir, 1916; Vermeulan *et al.*, 1966). However, this model did not take into consideration, the lateral interactions and the horizontal mobility of the adsorbed molecules. It was concluded that adsorption occurs onto finite number of definite localized sites which are identical and equivalent. Statistical thermodynamics were incorporated later and new models were developed for homogenous surface (Volmer, 1925). Brunauer *et al.* (1938) came up with a model that describes the multilayer adsorption.

The equilibrium sorption data can be evaluated using the adsorption isotherms such as Langmuir, Freundlich, Dubinin-Raduskevich and Temkin isotherms.

The most commonly used isotherm is the Langmuir isotherm which was originally used to describe the gas-solid phase adsorption onto carbon. This isotherm has been found to describe the adsorption of metal elements onto soil surfaces and can be described as follows.

$$q_e = b \left(\frac{KC_e}{1+KC_e} \right) \quad (7)$$

where q_e is quantity of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is concentration of adsorbate at equilibrium (mg/L), b is maximum monolayer coverage capacity (mg/g) and K is Langmuir isotherm constant (L/mg) and can be described as the measure of the elements for the surface (Langmuir, 1916; Vermeulan *et al.*, 1966).

Freundlich isotherm is a recently known isotherm which describes the non-ideal and reversible adsorption of elements onto the heterogeneous surface (Hutson and Yang, 2000). This isotherm can be applied to multilayer adsorption. Also, there is no uniform distribution of adsorption heat and affinities over the heterogeneous surface (Adamson and Gast, 1997). In this isotherm, the adsorption of elements onto the surface of the soil is the summation of adsorption on all soil sites with specific bond energy. The isotherm assumes that stronger binding sites of the soil are occupied first until adsorption energy is exponentially decreased upon the completion of adsorption process (Zeldowitsch, 1934). Freundlich isotherm is expressed as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (8)$$

where K_f is Freundlich isotherm constant (mg/g) and n is adsorption intensity or surface heterogeneity ranging only between 0 and 1. For $n = 1$ the linear type isotherm would be produced. As the n value gets closer to zero, the surface becomes more heterogeneous (Bradl, 2004).

Dubinin-Radushkevich is also a widely used empirical model which expresses the adsorption mechanism with a Gaussian energy distribution onto heterogeneous surface (Dubinin, 1906; Gunay, et al., 2007). It is usually applied to distinguish between the physical and chemical adsorption of metal elements onto surfaces using the mean free energy (E) (Equation 11). Dubinin–Radushkevich isotherm model is different to other models since it is temperature-dependent. Thus, when this model is used, the adsorption data must be plotted at different temperatures as a function of logarithm of amounts of elements adsorbed on the surface against the square of potential energy and all suitable data will lie on the same curve, called the characteristic curve (Dubinin, 1906; Gunay, et al., 2007). The equation used for this model is as follow:

$$\ln q_e = \ln q_s - K_{ad} \varepsilon^2 \quad (9)$$

$$\text{where } \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (10)$$

The free energy change, E (kJ/mol) required to transfer one mole of ion from infinity in the solution to the solid surface can be obtained from the equation:

$$E = \frac{1}{\sqrt{2B_D}} \quad (11)$$

where K_{ad} is Dubinin-Radushkevich isotherm constant (mol^2/kJ^2), q_s is theoretical isotherm saturation capacity (mg/g), ε is Polanyi constant, R is the universal gas constant ($\text{J}/(\text{mol} \cdot \text{K})$), T is temperature (K) and $B_D =$ isotherm constant.

Temkin isotherm is also widely used for the adsorption of trace elements on soil surfaces. The origin of this model stems from the adsorption of hydrogen onto platinum electrodes within the acidic solutions. It contains a factor that explicitly

takes into account adsorbent–adsorbate interactions. The model assumes that the heat of adsorption of all the molecules in the layer would decrease linearly and not logarithmic with coverage (Temkin and Pyozhev, 1940). The following equation is used to identify the adsorption of elements on soils that follow Temkin isotherm.

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (12)$$

where A_T and b_T = Temkin isotherm binding constants (L/g)

2.9 Kinetic models

In addition to adsorption isotherms, kinetic models have been widely used in adsorption studies to assess the controlling mechanism of the adsorption process between elements and adsorbents (Bakatula *et al.*, 2015). The intraparticle diffusion, pseudo first- and second-order kinetic models have been used and the equations are shown below respectively.

$$q_t = K_p \cdot t^{0.5} + I_d \quad (13)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (14)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (15)$$

where q_t and q_e are the adsorbed amounts (mol/kg) at time t (experimentally obtained) and at equilibrium, k_1 , k_2 and k_p are the rate constants, I_d is a constant used to examine the relative significance of the two transport mechanisms of the solute, intraparticle diffusion and external mass transfer.

2.10. Thermodynamics

When determining the adsorption of elements onto soil surfaces, it is crucial to consider thermodynamic analyses in order to determine the spontaneity, type of reaction (endothermic or exothermic) and feasibility of adsorption. The thermodynamic parameters, namely, the standard Gibbs free energy (ΔG^0), change in enthalpy (ΔH^0), and entropy change (ΔS^0), are estimated using the following equations, respectively:

$$\Delta G^0 = -RT \ln K_L \quad (16)$$

$$\ln \frac{1}{C_e} = \ln K_L - \frac{\Delta H^0}{RT} \quad (17)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (18)$$

where K_L is the empirical constant of Freundlich (Diban *et al.*, 2008).

2.11. The elements under study

Elements such as Cd, Cu, Cr, Ni, Ca, Mg, Na, Fe and Mn are available in the environment. Some of these elements are essential for plants and animals as they are required for proper functioning and survival. In natural conditions, these elements in soils are produced from parent materials such as rocks and sediments (Silveira *et al.*, 2003). These elements can also be introduced into the soil through anthropogenic sources such as fertilisers, pesticides, irrigation water, sewage sludge and industrial emissions. It is often difficult to deduce the elements from natural sources and those from anthropogenic sources (Silveira *et al.*, 2003). Elements in the soil can exist as free ions or adsorbed to soil colloidal articles. Elements which are essential for humans are zinc, selenium, copper, chromium, magnesium, calcium, manganese, cobalt, potassium, iron, sodium and molybdenum. These elements are essential but when they exceed the threshold limits, they become toxic. Other elements such as mercury, arsenic, cadmium and lead are considered toxic even at low concentrations (Berglund *et al.*, 1984). In the soil, these elements can mobilise to groundwater and cause groundwater contamination. They can also be prevented from mobilising through adsorption on soil surface groups. The extent of adsorption is dependent upon the composition of the soil.

2.11.1. Cadmium

The reaction of cadmium (Cd) with the soil is largely due to adsorption. Some studies have been conducted on the adsorption of Cd on soils and it was found that it adsorbs quickly prior to the exposure time (approximately 10 minutes) and equilibrium can be obtained within an hour (Christensen, 1984; Santillan-

Medrano and Jurinak, 1975). The adsorption of Cd is influenced by pH, exchangeable cations and ionic strength (Elliot and Denenny, 1982). As pH increases, the adsorption of Cd increases. Davis and Leckie (1980) adsorbed Cd onto two soils (sandy sand and sandy loam) and found that the adsorption of Cd was very low at acidic pH values but increased drastically at pH > 6 (Figure 2.10). Thus, adsorption of Cd onto soils is a function of pH. Precipitation is another mechanism that controls the adsorption of Cd on the soils. The solubility of Cd decreases as pH increases. The precipitation of Cd (II) ion occurs at higher Cd activities and the lower activities results in ion exchange (Garcia-Miragaya and Page, 1976; Street *et al.*, 1978). In addition to competing ions, the adsorption of Cd onto soils can also be affected by the presence of anions such as carbonates and chloride ions which form complexes with Cd. The adsorption of Cd complexed with anions is lower than that of the free Cd ²⁺. Moreover, the presence of EDTA and other organic ligands can diminish the adsorption of Cd onto soil surfaces (Bradl, 2004).

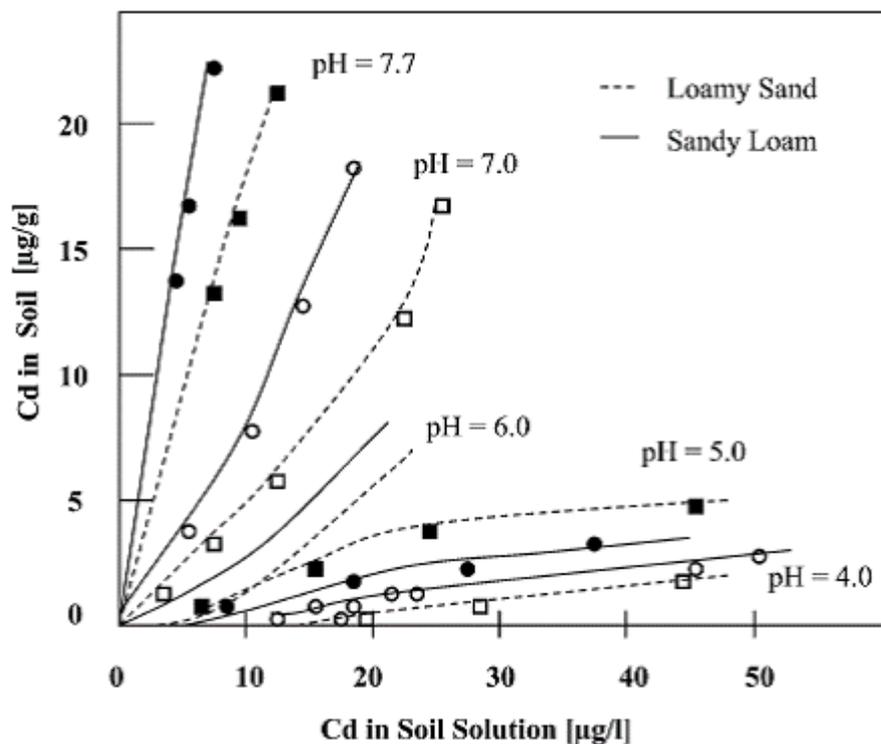


Figure 2.10 The adsorption of cadmium onto two soils as influenced by soil texture and pH (copied from Bradl, 2004).

2.11.2. Copper

The distribution of copper (Cu) on soil constituents is influenced by organic matter in the soil as well as manganese and iron oxides since the affinity for this surface functional groups is very high. Clay minerals and phosphates in soils are not that important on the sorption of Cu (Jenne, 1968; McGrath et al., 1998). The adsorption of Cu in the soil through soil constituents is in the order: Mn oxide > organic matter > Fe oxide > clay minerals (Figure 2.11) (Adriano, 2001; Bradl, 2004). Studies have shown that Cu is highly complexed by humic materials than other metals. In the soil, Cu exists mainly in a form complexed with organic compounds which are soluble (Hodgson et al., 1966). Thus, the retention of Cu in the soil is enhanced in the presence of organic materials such as humic and fulvic acids. Adriano, (2001) studied the adsorption of elements onto humic substances and found that Cu had high affinity for humic acid than other elements. The preference series for humic acid by elements was in the order: Cu > Pb > Fe > Ni = Co = Zn > Mn = Ca. The adsorption of Cu in the soil is mainly through specific adsorption meaning that strong covalent bonds are formed which can immobilise the element in soils (Wu *et al.*, 1999).

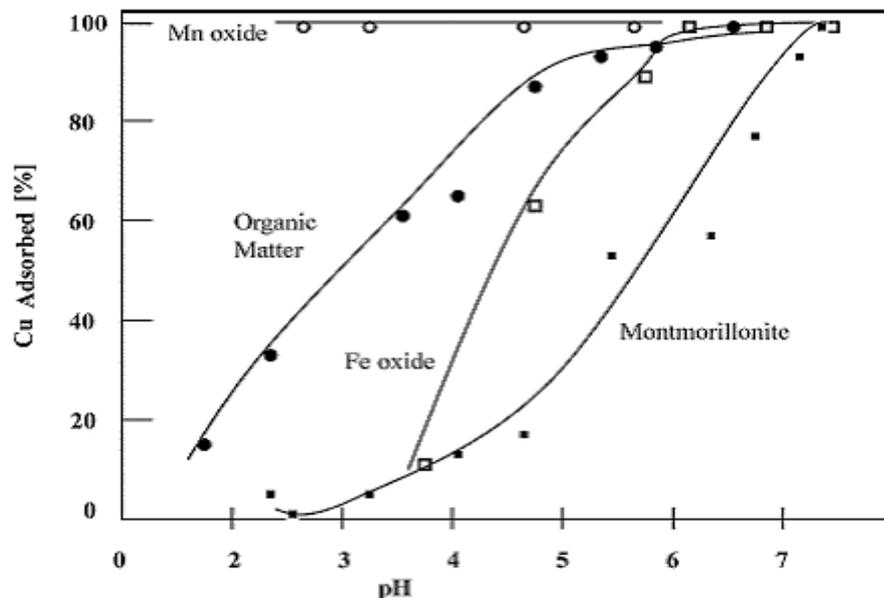


Figure 2.11 Adsorption of Cu by different soil constituents as a function of pH (copied from Bradl, 2004).

2.11.3. Chromium

Chromium (Cr) is an element with a number of oxidation states with +3 and +6 being the commonly observed. Cr^{6+} species are highly adsorbed by a number of soil constituents such as montmorillonite, iron, manganese and aluminium oxides and kaolinite (Griffin *et al.*, 1977; Rai *et al.*, 1989). Cr^{3+} is also readily adsorbed by iron, manganese and clay minerals through specific adsorption. Clay minerals adsorb Cr^{3+} way better than Cr^{6+} . The speciation of Cr is also affected by pH of the solution wherein it is contained (Figure 2.12). As pH increases, Cr binds more hydroxide ions reducing the overall charge and the ability to be adsorbed onto the negatively charged soil surface. As the pH decreases, the adsorption of Cr increases because at lower pH values, the dominant species of Cr are positively charged leading to high affinity for negatively charged soil surface and this was confirmed by Zachara *et al* (1989) where it was found that the sorption of Cr decreased as pH increased with different adsorbents (Figure 2.13). High organic matter also increases the adsorption of Cr in the soil. The presence of organic ligands such as citric and acetic acid and competing ions such as Cd and Cu decreases the adsorption of Cr in the soil. Iron oxides in the soil have the strongest adsorption capacity for Cr than other soil constituents followed by montmorillonite and others (Zachara *et al.*, 1989, Bradl, 2004).

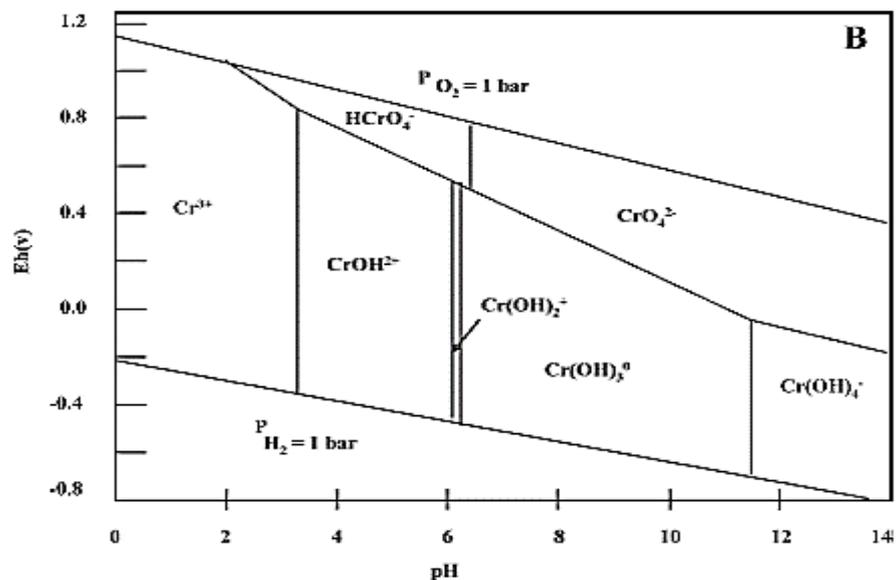


Figure 2.12 The speciation of Cr^{3+} as a function of pH (copied from Bradl, 2004).

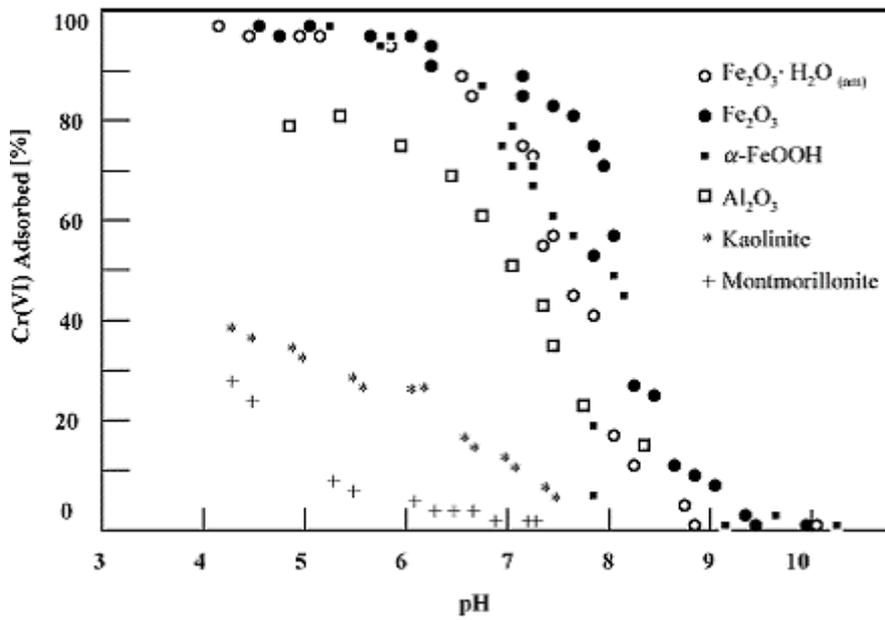


Figure 2.13 The adsorption of Cr⁶⁺ by various adsorbents for a fixed adsorption site concentration (copied from Bradl, 2004).

CHAPTER 3

Objectives and hypotheses

This chapter includes aim, objectives, hypotheses and key questions of the study.

CHAPTER 3

3.1. Aims and objectives

The major aim of the research was to assess the sorption of trace elements in an agricultural soil impacted by mining operations.

This aim was achieved by addressing the following objectives:

- To assess the effect of pH, concentration, time and competing ions on the adsorption of Cd, Cu and Cr.
- To improve the understanding of the percolation processes in relation to elemental distribution in the soil.
- To simulate long term trends of adsorption.
- Determine the speciation of the elements in the presence of plant exudates and fertilisers.
- Assess the ability of geochemical modelling in deducing the patterns followed by the elements on adsorption.

3.2. Research hypothesis and questions

3.2.1. Hypothesis

This study was based on the hypothesis that trace elements such as cadmium, copper and chromium emanating from smelting operations could be deposited onto the agricultural soils in the vicinity of the operations through dust fallout and precipitation. Moreover, elements such as cadmium and copper could be deposited from pesticides and fertilisers that are used occasionally in agricultural plots. These elements can accumulate in the soil and leach to groundwater. Plant exudates and fertilisers can affect the speciation of the elements in the soil, hence, affect their adsorption capacities onto the soil which will consequently affect their leaching into the groundwater. Other factors such as pH and concentration can affect the transport and fate of these elements in the soil. Analytical methods alone are not sufficient to deduce the behaviour of the elements at different

conditions in soils, especially when complexing agents are present, which can change the speciation of the elements. Therefore, geochemical modelling can be applied to better understand the adsorption behaviour of the elements in the soil.

3.2.2. Questions

- Is the soil in the study area effective in the adsorption of trace elements to prevent leaching into groundwater?
- How do different parameters (pH, concentration and competing ions) affect the adsorption of elements by the soil?
- Which elements will be highly adsorbed by the soil and which will be weakly adsorbed (selectivity)?
- Do plant exudates released affect the adsorption of elements?
- What is the role calcium chloride and fertilisers on the adsorption of elements?

CHAPTER 4

Batch adsorption studies paper

This chapter focuses on the paper on batch adsorption studies.

Contribution to the paper: Lead author, conducted the experimental work, analysed and interpreted the results and performed modelling

This paper was submitted to: South African journal of Chemistry (SAJC) (Ref: Sajc-001495)

Adsorption of cadmium, copper and chromium by an agricultural soil impacted by mining activities

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ABSTRACT

Batch adsorption studies for cadmium (Cd), copper (Cu) and chromium (Cr) onto an agricultural soil impacted by mining activities were conducted in single and multi-component systems. The effect of initial concentration, pH and competing ions (Fe^{3+} , Ca^{2+} , Co^{2+} , Mg^{2+} , K^+ , Ni^{2+} and Zn^{2+}) on adsorption was studied. The main constituents of the agricultural soil were SiO_2 (74.7%), Al_2O_3 (11.44%), FeO (5.09%), MgO (3.69%), CaO (2.73%) and Fe_2O_3 (0.63%). The soil exhibited high adsorption capacities for the elements at all initial concentrations with the adsorption process better described by the Freundlich isotherm. Adsorption was found to proceed *via* an ion exchange mechanism. The pseudo second-order kinetic model described the adsorption of the elements ($R^2 > 0.999$), indicating a chemisorption process. The adsorption of Cd increased with pH in both systems whilst that for Cu decreased. The adsorption of Cr decreased with pH in the single-component system, but increased in the multi-component system. The adsorption of Cd was affected more by competing ions while Cu and Cr were not significantly affected ($p > 0.05$). Elemental speciation under varying conditions was studied using the PHREEQC geochemical modelling code. The observed high capacity of the soil for the elements pointed to the soil's potential of being a repository, a feature that would change depending on the speciation of the elements and soil conditions.

KEYWORDS

Agricultural soil, adsorption capacity, Cadmium, Copper, Chromium

1. Introduction

Environmental pollution due to waste from mining industries and agrochemicals has been increasing for years.¹ This waste contains pollutants such as cadmium, copper, chromium, arsenic, mercury, lead and zinc among others.² The soil, air and water have been negatively affected directly or indirectly in most instances as a

result of waste disposal.³ Vegetation, livestock and human beings are also negatively affected especially since they are dependent on these natural resources. The soil is the main disposal site for elemental waste whereas air and water are mainly affected indirectly.⁴ Soils in or near mining areas are prone to elemental waste due to direct and indirect contact. Elements in soils can reach the groundwater where they can accumulate at high concentrations, increasing hazardous risks to public health since some are

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carcinogenic (e.g. cadmium, chromium and arsenic) and can lead to abnormalities in morphology, high mortality and mutagenic effects in humans when ingested.⁵⁻⁷ One of the major challenges with the accumulation of elements in the environment is that they are non-biodegradable and persistent, thus causing long-term effects on the environment.^{1,8}

To prevent elements from reaching the groundwater, their mobility in the soil must be minimised as much as possible. Some soils can retain elements by ion exchange and sorption, minimising the level of groundwater pollution.⁵ These elements can also be bound by the soil into forms which make them biologically inactive, reducing the extent of bioavailability and the possibility of uptake by plants.⁹ Thus, the ability of soils to adsorb elements especially where no remediation method is applied is ideal. Soil is an extremely complex medium which is made up of organic and mineral materials, water, air and living organisms. It can perform a variety of functions such as becoming a medium for plant growth and acting as a hydrologic buffer and an adsorbing surface for elements, this latter function being the focus of this study.^{10,11}

The adsorption of elements by soils has been studied and continues to be an area of interest¹¹. Studies have shown that soils are naturally adsorbing materials with their effectiveness dependent on the prevailing physical and chemical conditions.^{12,13,14} The composition of the soil has a bearing on its adsorption and adsorption capacity. The presence of clay minerals such as montmorillonite, bentonite and illite which have negatively charged layers that attract positively charged ions improve the adsorption capacity of soils due to their high cationic exchange capacity (CEC) and specific surface areas.^{15,16} The presence of natural organic matter such as humic and fulvic acids enhances the adsorption capacity of the soil since these substances have negatively charged groups such as hydroxyls which have high affinity for

most elements.^{17,18} Other factors affecting the adsorption capacity are: pH, concentration of trace elements and elemental speciation.^{11,16}

Studies have reported on the adsorption of metals on materials such as montmorillonite,^{12,15} coconut husk,¹⁹ and dolomite.¹ In this study, an agricultural soil on a market gardening plot was considered. Cabbage, spinach, carrots and potatoes are some of the vegetables grown on the plot and sold to markets in Pretoria and Johannesburg. The plot is in an area where a number of platinum group metals (PGMs) mining and smelting operations are located. As such, the study was predicated on the premise that dust fallout from these activities has potential to deposit some of the constituent elements onto the agricultural soil. Thus, batch adsorption studies were conducted to determine the effectiveness of the soil in adsorbing cadmium (Cd), copper (Cu) and chromium (Cr).

Materials and methods

2.1. Sampling area

The agricultural plot from which the soil was collected is located near Rustenburg (25°39'19.88" S, 27°25'57.51" E), a mining town in the North West Province, South Africa (Fig. 1). Rustenburg is located at 1139 m above sea level with temperatures ranging from -6 to 40 °C with an average of 19°C.²⁰ It is normally a warm to hot area with mean annual precipitation of 600 mm and mean annual evaporation of 1800 mm.²¹ The area is home to the Bushveld Igneous Complex (BIC), which is known to be the richest deposit of PGMs (Pt, Rh and Pd) in the world, but also has a significant proportion of base metals such as Cu, Co, Cr, V, Ni and Zn that are found in the host ores along with PGMs.^{22,23,24}

The soil was collected at a depth of 20-30 cm in a fallow portion of the plot and stored in a polypropylene container after removing large unwanted substances. The

soil was brought into the lab and air dried. The soil pH and conductivity were measured using the soil to water ratio of 1:1 (w/w) with field pH and conductivity meters (Hach, South Africa), respectively.

2.2. Characterisation

The soil collected was manually broken down into smaller particles with mortar and pestle so as to destroy the lumps and was sieved with 2 mm sieve to remove unwanted substances such as stones and mulch. The ground soil was thoroughly mixed for homogeneity before further use. It was characterised using X-ray fluorescence (XRF) (performed in the School of Geosciences at Wits University) (PANalytical, Netherlands) to determine elemental composition of the soil. Powder X-ray diffraction (PXRD) (Bruker D2 Phaser, Germany) was used to determine the mineralogy of the soil. Fourier transform infrared spectroscopy (FTIR)

(Tensor 27, Bruker, Germany) was used for the identification of functional groups present in the soil in the frequency range of $400 - 4000 \text{ cm}^{-1}$. The cationic exchange capacity (CEC) of the soil was determined by the BaCl_2 method.²⁵ Depending on the composition of the soil, it may be positively or negatively charged which will in turn affect the adsorption ability. This charge is due to the functional groups in the soil and it is highly affected by pH. Depending on the values of pH, the charge in the soil can be negative due high amount of hydroxyl groups or positive due to hydronium ions. There is also a pH where there is no net charge in the soil i.e. the concentrations of the positive sites and negative sites are equal. This is known as the point of zero charge (PZC) of the soil and can be used to explain the type of adsorption between trace elements and adsorbents. The PZC for the soil was determined according the method by Smičiklas et al. (2005).²⁶

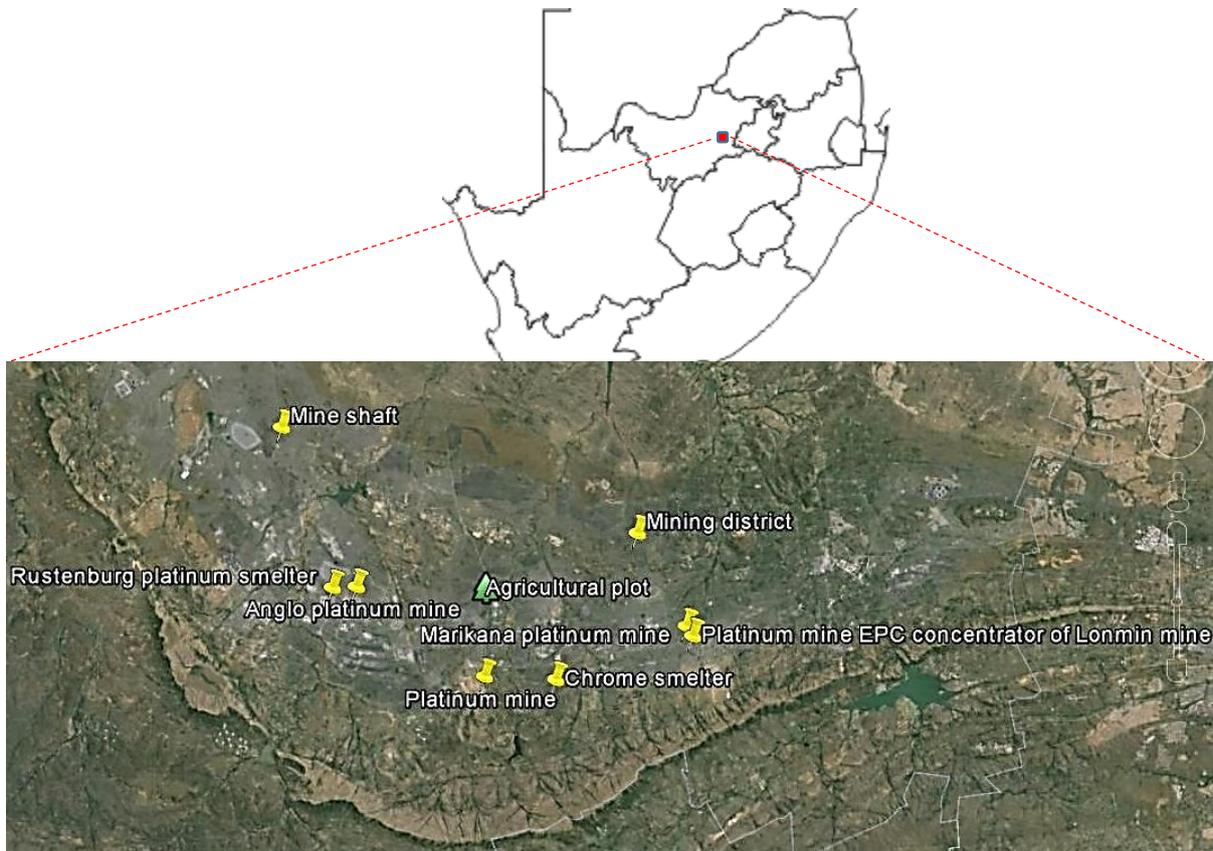


Figure 1 Map of the agricultural plot in Rustenburg, South Africa (map from Google Earth).

2.3. Reagents and standards

All chemicals used were of analytical grade and were obtained from Sigma Aldrich, Johannesburg, South Africa. Stock solutions of cadmium (Cd^{2+}), copper (Cu^{2+}) and chromium (Cr^{3+}) were prepared by dissolving an appropriate amount of nitrate salts in 1 L of deionized water with 0.05% (v/v) HNO_3 . A multi-element stock solution (Fe^{3+} , Ca^{2+} , Co^{2+} , Mg^{2+} , K^+ , Ni^{2+} and Zn^{2+}) was also prepared by dissolving a known mass of nitrate salts in deionised water. Working solutions were then prepared from the stock solution through serial dilutions. The stock solutions were stored in a refrigerator at 4°C when not in use.

2.4. Adsorption experiments

Batch adsorption experiments for single- and multi-component systems were carried out by shaking 0.75 g of soil with 50 mL of analyte solutions in 100 mL polypropylene plastic containers at varying experimental conditions at the speed of 150 r/m using an automated shaker (Labcon, USA) at 25°C. The contents were then centrifuged at 3000 r/m and filtered using filter paper after the adsorption time and the concentrations of the filtrates were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Spectro, Germany). The experiments were done in triplicates. It should be noted here that a single-component system consisted of only one element e.g. Cd only and so on whereas a multi-component system contained a mixture of Cd, Cu and Cr at equal concentrations.

2.4.1. Adsorption kinetic studies

Adsorption kinetic studies were performed by adding 20 g of agricultural soil into 500 mL solution of $\text{Cd}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and $\text{Cr}(\text{NO}_3)_3$ into 1 L polypropylene bottles. The solutions were shaken at 150 r/m and 5 mL aliquots were drawn at

different times and centrifuged at 3000 r/m and the supernatants filtered and analysed.

2.4.2. Effect of initial concentration

The effect of initial concentration on the adsorption of Cd, Cu and Cr was assessed using different concentrations (5, 10, 20, 50 and 100 mg L^{-1}) of the metal nitrates at 25°C. The mass of the adsorbent (0.75 g) and the volume (50 mL) of metal solutions were kept constant. The solutions were centrifuged and filtered after 3 h of shaking at room temperature. Adsorption isotherms were evaluated at these concentrations.

2.4.3. Effect of pH

The effect of pH on the adsorption capacity of Cd, Cu and Cr onto the agricultural soil was investigated by adding 0.75 g of agricultural soil to 50 mL of 10 mg L^{-1} individual metal nitrate solutions at pH 3, 5, 7 and 9. The mixture of the three metals was also used to look at the effect they have on each other at different pH values. HNO_3 and NaOH were used to adjust the pH. After shaking for 3 h, the solutions were centrifuged at 3000 r/m and the supernatants filtered and the metal concentrations determined.

2.4.4. Effect of other ions

The effect of competing ions (Fe, Ca, Co, Mg, K, Ni and Zn) on the adsorption of Cd, Cu and Cr was studied where the cocktail of competing ions was mixed with metal nitrate solutions of individual analytes (Cd, Cu and Cr) at different ratios (1:4, 1:1 and 4:1) and concentrations of competing ions (5, 10, 20 and 50 mg L^{-1}). The multi-component solution (i.e. the mixture of Cd, Cu and Cr) was also used to study the effect that the competing ions have on their adsorption. The mixed solutions were added to 0.75 g of agricultural soil and shaken for 3 h at room temperature. The contents were

centrifuged at 3000 r/m, filtered and analysed.

2.5. Desorption of naturally occurring Cd, Cu and Cr from the soil

The desorption of Cd, Cu and Cr already in the soil naturally was done using nitric acid to determine the concentrations that can be desorbed during the adsorption experiments. These concentrations were subtracted from the equilibrium concentrations obtained during adsorption experiments to get more reliable results for the study. For this study, 50 mL of 0.05 mol L⁻¹ HNO₃ was added to 0.75 g agricultural soil. The experiments were done in triplicates. The solutions were centrifuged and filtered after 3 h of shaking at room temperature. The desorbed concentrations of the elements were determined using ICP-OES. These results were not reported as such here, but only used for correction.

All analyses were done in triplicate with analytical errors or relative standard deviations (RSDs) < 10%.

2.6. Geochemical modelling

Forward geochemical modelling using PHREEQC was done to determine the species that are available and dominant at specific conditions such as solution pH, concentration as well as composition. PHREEQC is a computer program that is designed to perform aqueous geochemical calculations. It uses C and C++ programming languages to perform the calculations implementing the aqueous models found in the software.²⁷

2.7. Data treatment

The amount of adsorbed trace elements in the study at equilibrium i.e. q_e (mg g⁻¹), was calculated using the equation²⁸:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

where C_o and C_e are initial and equilibrium liquid-phase concentrations of metals, respectively and V is the volume of the solution in litres (L) whilst M is the mass of the adsorbent used in grams (g).

The equilibrium sorption data were evaluated using the Langmuir, Freundlich and Dubinin-Raduskevich adsorption isotherms.

The Langmuir isotherm quantitatively describes the formation of a monolayer adsorbate on the surface of the adsorbent, thus no further adsorption takes place.^{29,30} The Langmuir isotherm is defined by the following equation:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

where q_e is the quantity of adsorbate adsorbed per gram of adsorbent at equilibrium (mg g⁻¹), C_e is concentration of adsorbate at equilibrium (mg L⁻¹), b is a constant related to the free energy of adsorption (L mol⁻¹) and q_m is the maximum adsorption capacity (mol kg⁻¹).

The Freundlich isotherm describes adsorption onto a heterogeneous surface and is defined by the following equation.³¹

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

where: K_f is Freundlich isotherm constant (mg g⁻¹) and n is the adsorption intensity.

The Dubinin-Radushkevich isotherm expresses the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface.^{32,33} It is defined by the following equation:

$$\ln q_e = \ln x_m - K_{ad} \varepsilon^2 \quad (4)$$

$$\text{where } \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (5)$$

The free energy change, E (kJ mol⁻¹) required to transfer one mole of ion from infinity in the solution to the solid surface

can be obtained from the following equation:³⁴

$$E = \frac{1}{\sqrt{2B_D}} \quad (6)$$

where: X_m is the maximum sorption capacity of sorbent (mol kg^{-1}), K_{ad} is the Dubinin-Radushkevich isotherm constant ($\text{mol}^2 (\text{kJ}^2)^{-1}$), \mathcal{E} is the Polanyi constant, R is the universal gas constant ($\text{J (mol}\cdot\text{K)}^{-1}$), T is the temperature (K) and B_D is the isotherm constant.

For the kinetic studies, the Elovich³⁵ and pseudo second-order^{36,37} kinetic models were used to describe the adsorption process. The equations of both models are defined below, respectively:

$$q_t = \frac{1}{b} \ln(a \cdot b) + \frac{1}{b} \ln t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where: q_t and q_e are the adsorbed amounts (mol kg^{-1}) at time t (experimentally obtained) and at equilibrium; k_2 is the rate constant; a is the initial adsorption rate and b is a constant related to the extent of surface coverage.

In order to compare the validity of the models, a normalized standard deviation (Δq) was used. The following expression was used to calculate Δq (%):

$$\Delta q(\%) = 100 \cdot \sqrt{\frac{\sum_{i=1}^n \left(\frac{q_{exp} - q_{cal}}{q_{exp}} \right)^2}{n-1}} \quad (9)$$

where q_{exp} is the experimental element uptake, q_{cal} is the calculated amount of element adsorbed and n is the number of data points.³⁸

Comparison of the results was done using analysis of variance (ANOVA) on MS Excel 2010.

3. Results and discussion

3.1. Soil characterisation

The results for XRF measurements are presented in Table 1. The dominant constituents of the agricultural soil were found to be SiO_2 and Al_2O_3 . The significant amount of Al_2O_3 corresponds to the smaller particle sizes of the soil which give it a high surface area.³⁹ This also points to the clayey nature of the soil. The results from PXRD also confirmed that SiO_2 was the most dominant mineral of the soil. The minerals: Al_2O_3 , Montmorillonite and CaO were detected, further confirming the clayey nature of the soil. The results obtained from FTIR showed that there were N-H peaks at 3600 cm^{-1} and O-H peaks at 3400 cm^{-1} which could imply the presence of nitrogen-containing groups (e.g. ammonia and amino acids) and humic substances. There was a strong peak at approximately 1000 cm^{-1} which was evident for Al-O and Si-O groups further confirming that the soil is highly composed of silanol and aluminol groups. The CEC and PZC were found to be $51.6 \text{ meq } 100\text{g}^{-1}$ and 8.3, respectively. Other chemical properties of the soil are shown in Table 2.

Table 1 Percentages of the main constituents of agricultural soil used ($n = 3$; RSD < 10%)

Compound	Percentage composition (%)
SiO_2	74.7
Al_2O_3	11.44
Fe_2O_3	0.63
FeO	5.09
MnO	0.14
MgO	3.69
CaO	2.73
Na_2O	0.15
K_2O	0.2
TiO_2	0.4545
P_2O_5	0.03
Cr_2O_3	0.2224
NiO	0.0239
TOTAL	99.5
LOI	13.43

LOI – loss on ignition

The concentrations of trace elements before adsorption experiments were determined using XRF and microwave digestion method. The results indicated that the concentrations of trace elements under study were high which could be due to deposition from mining plants agrochemicals used. The concentrations of the elements were as follows: Cd (5.8 mg L⁻¹), Cu (25 mg L⁻¹) and Cr (1307 mg L⁻¹). These levels are high for human consumption and if found in the vegetation and water, serious health issues may arise.^{1,2,19}

3.4. 1. Effect of concentration

The effect of varying initial concentration on the adsorption of Cd, Cu and Cr in single and multi-component systems is shown in Fig. 2a and 2b, respectively. Unlike other isolated adsorbing materials such as montmorillonite¹⁶ and zeolites,⁴⁰ the affinity of the soil for the elements was similar for all elements with no significant differences in the adsorption ($p > 0.05$). SiO₂ and Al₂O₃ which were found to be the main constituents of the agricultural soil used, contain exchangeable ion-bearing sites which are highly responsible for the adsorption of the elements.¹¹ Moreover, the high surface area of the soil and CEC could have resulted in the high adsorption capacities observed. The loss on ignition (LOI) is indicative of the content of organic matter in the soil. This has potential to adsorb high amounts of elements. The combination of these factors likely resulted in an increased number of active sites for adsorption in the soil, a phenomenon observed in the increase of adsorption capacity with an increase in initial concentration. The speciation of the elements in different solutions was determined using PHREEQC. At pH 5 which was the standard pH, the dominant species was the free Cd²⁺ in the Cd solution and Cu²⁺ in the Cu solution. The dominant Cr species that were determined at pH 5 are Cr(OH)₂⁺ and Cr(OH)²⁺, with less positive charge than the free Cr³⁺ which was present in less amounts.

3.2.2. Adsorption isotherms

The results for the Langmuir, Freundlich and Dubinin-Radushkevich isotherms are presented in Table 3. The adsorption of the elements correlated well with the isotherms except for Cr which was poorly described by the Langmuir isotherm ($R^2 = 0.074$). The Freundlich isotherm described the data better for all elements as depicted by the high correlation coefficients, indicating that the surface of the soil is heterogeneous in nature. This means that the energies of the active sites vary (typically a mixture of weak and strong sites), a feature that is plausible given the composition of the soil. The adsorption *via* the Freundlich isotherm was substantiated by the observed increase in adsorption with increasing exposure time. The Freundlich adsorption intensity (n) indicated that adsorption was favourable especially for Cd and Cu, but not that well for Cr. The adsorption energy (E_s) for Cu was higher than that for Cd and Cr. This could be attributed to the high amount of free Cu species (Cu²⁺) available at pH 5. Such species would then interact or react through the inner shell than the outer shell as in the case of hydroxylated species e.g. Cr(OH)₂⁺ in the case of the dominant Cr species. The sorption energy found from the Dubinin-Radushkevich isotherm indicated that the adsorption process proceeds *via* ion exchange mechanism for all the elements.

Table 2: Chemical properties of the studied agricultural soil ($n = 3$; RSD < 10%).

Chemical Value	property
pH	8.32
CEC (meq/100 g)	51.6
Total dissolved solids (TDS) (ppt)	0.37
Electrical conductivity (mS cm ⁻¹)	1.06

Table 3 Langmuir, Freundlich and Dubinin-Radushkevich adsorption model parameters for the adsorption of Cd, Cu and Cr on agricultural soil.

Metal ion	Langmuir				Freundlich				Dubinin-Radushkevich			
	$q_m /$ (mg g^{-1})	$b /$ (L mol^{-1})	R^2	$\Delta q\%$	$K_f /$ (mg g^{-1})	n	R^2	$\Delta q\%$	$X_m /$ (mol g^{-1})	$E_s /$ (kJ mol^{-1})	R^2	$\Delta q\%$
Cd	4.17	23867	0.940	16.97	88.2	1.21	0.974	26.22	0.823	9.22	0.967	21.04
Cu	3.81	67185	0.876	39.38	177	1.29	0.908	49.48	1.84	9.74	0.851	45.00
Cr	87.8	1980	0.074	46.37	6271	0.95	0.914	50.05	19.3	8.08	0.857	46.26

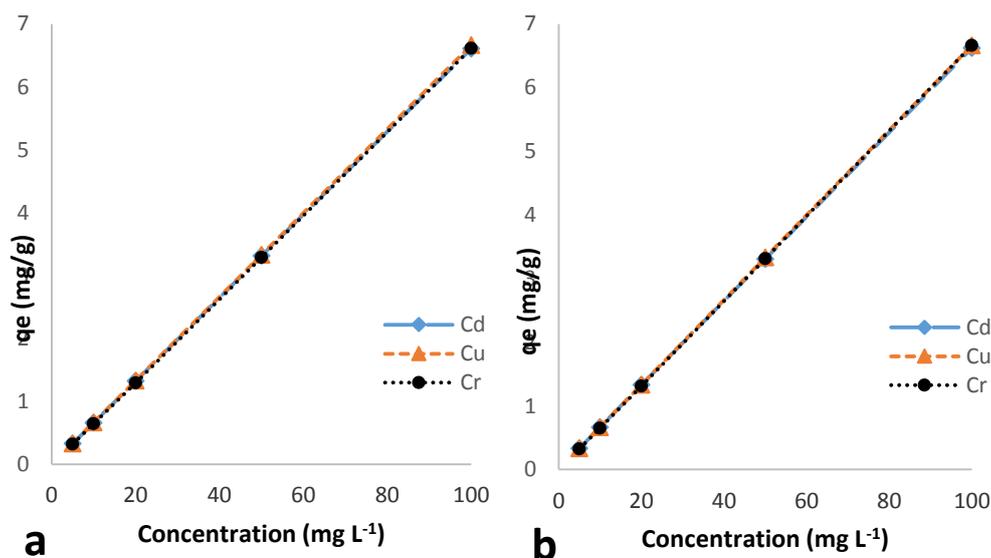


Figure 2 Effect of concentration of the elements in single- (a) and multi-component systems (b) on adsorption ($V = 50 \text{ mL}$, mass = 0.75 g , temp = 25°C , contact time = 3 h , pH 5) ($n = 3$ and RSD < 10%).

3.2.3. Kinetic models

The results for the kinetic studies are presented in Table 4. The results generally pointed to a fast uptake of the metals i.e. >90% uptake within the first 3 min of contact. There was equilibration observed after the 3 min (results not shown here).

Table 4 Pseudo second-order and Elovich kinetic model parameters for Cd, Cu and Cr adsorption on agricultural soil.

Metal ion	Pseudo second-order					Elovich			
	$k_2 /$ $\text{kg mol}^{-1} \text{ min}^{-1}$	$q_e (\text{cal}) /$ $\text{kg mol}^{-1} \cdot 10^{-3}$	$q_e (\text{exp}) /$ $\text{kg mol}^{-1} \cdot 10^{-3}$	R^2	$\Delta q\%$	$a /$ $\text{kg mol}^{-1} \text{ min}^{-1}$	$b /$ $\text{kg mol}^{-1} \text{ min}^{-1}$	R^2	$\Delta q\%$
Cd	3081	1.94	2.00	0.999	1.43	4.23E23	31136	0.489	1.696
Cu	3265	3.43	4.00	0.999	6.28	1.34E24	17698	0.759	1.543
Cr	449.5	8.46	10.0	0.999	16.8	3.39E57	15356	0.706	0.841

The fast adsorption of the elements at the beginning of contact can be attributed to the soil's high affinity for the metals as stated previously. The pseudo second-order gave the best fit for all the elements ($R^2 > 0.999$), indicating that the chemical process is the rate controlling mechanism (Table 4).³⁸ The calculated adsorbed amounts at equilibrium were found to be similar to the ones obtained experimentally which indicated that adsorption was highly dependent on concentration. The Elovich equation is used in chemisorption reactions to show that the rate of adsorption decreases with time since surface coverage increases and adsorption sites available for binding decrease. There was no fit with the Elovich model for all trace elements. Essentially, it pointed to that fast kinetics within the first 3 min.⁴¹

3.2.4. Effect of pH

The effect of pH on the adsorption capacity of the elements was determined since it is an important variable to consider that can change the surface of the soil and the species in solution due to the ions that occur at particular pH values¹¹. Fig. 3a and 3b show the effect of pH on the adsorption of elements in single and multi-component systems of the elements, respectively. Higher pH will make the soil surface more negative due to the presence of OH⁻ groups and a lower pH will make the surface of the soil to be more positive because of the high concentration of hydronium (H₃O⁺) ions. Depending on the types of species dominant at a particular pH, adsorption can increase, decrease or remain the same as pH is increased. In the single-component system, the adsorption of Cd was observed not to be affected by pH since it remained almost the same over a wide range and this might be due to the dominance of the free species, Cd²⁺ which were in significant amount at all pH values. In the multi-component system of the elements, the adsorption of cadmium was low at lower pH values but increased as pH increased although the speciation remained the same as in the single-component system. It is noteworthy that

though the adsorption capacity increases, it is lower than in the single-component system and this can be attributed to competition for binding sites with Cu and Cr. The observed increase in the adsorption capacity for Cd with pH might be due to the increased negative charge on the surface of the soil which is attributed to more hydroxide ions at higher pH values. This is however not a conclusive argument taking into account that in the single-component system the adsorption capacity remained virtually constant. Further studies would be required to elucidate the exact cause.

The adsorption of Cu was seen to be different from that of Cd as its adsorption decreased slightly with increasing pH as observed in the single-component system (Fig. 3a). The species that occur at pH 3 where the maximum adsorption was observed, was predominantly Cu²⁺ but, as pH increased, the species Cu(OH)₂ and CuOH⁺ were observed to increase. In terms of size, these are larger for the same number of Cu ions. Thus, fewer Cu ions would occupy the active sites on the soil compared to the case where only Cu²⁺ was involved. It is also important to note that Cu(OH)₂ would precipitate while CuOH⁺ would adsorb, thus making the adsorption of Cu at higher pH regimes to be a mixture of precipitation and actual adsorption. However, pH only had minimal influence on the adsorption of Cu in the multi-component system of elements since, the free Cu²⁺ species were in significant amounts at all pH values and thus Cu is in the form favourable for adsorption. This can be attributed to the free hydroxide ions in the solution reacting more with other elements in the solution than Cu. More Cu²⁺ species that occur at higher pH in the multi-component system may be due to the ability of chromium to attract hydroxide ions than the divalent elements as the dominant chromium species at higher pH is Cr(OH)₃, making the hydroxide ions to be more available for other elements. The adsorption of Cr in the single-component system decreased with increasing pH (Fig.

3a). Adsorption increased slightly until pH 5 and then decreased due to the negative chromium species (CrO_2^- and $\text{Cr}(\text{OH})_4^-$ as confirmed by PHREEQC), which were dominant at $\text{pH} > 5$. These species would likely lead to lower electrostatic interactions with the soil surface that is becoming negatively charged at higher pH. Moreover, the uncharged species ($\text{Cr}(\text{OH})_3$) also dominated at higher pH, adding to the introduction of larger Cr species compared to the free Cr^{3+} . The adsorption of Cr in the multi-component

system seem to be increasing but, the precipitate $\text{Cr}(\text{OH})_3$ is the dominant species, therefore it may look like there is adsorption when in actual fact it is just precipitation. The adsorption of Cr onto the agricultural soil was observed to be highly affected by pH than by the presence of Cd and Cu.

The decreased adsorption of Cu and Cr as pH increased implies that these elements can be easily leached to the groundwater at these pH values.

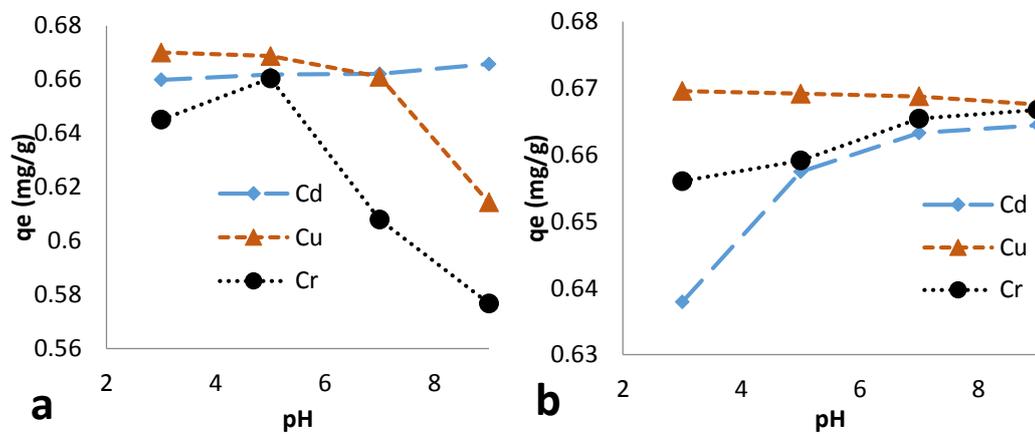


Figure 3 The effect of pH on the adsorption of elements onto the soil in single- (a) and (b) multi-component systems ($V = 50 \text{ mL}$, mass = 0.75 g , temp = 25°C , contact time = 3 h , concentration of elements = 10 mol L^{-1}) ($n = 3$ and $\text{RSD} < 10 \%$).

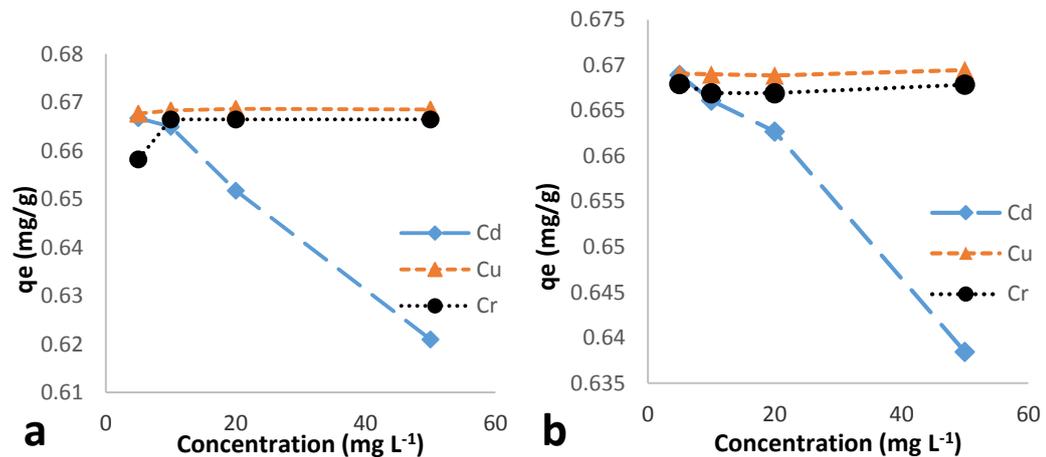


Figure 4 The effect of competing ions at different concentrations on the adsorption of elements in single- (a) and (b) multi-component systems in a 1:4 ratio of analytes to competing ions ($V = 50 \text{ mL}$, mass = 0.75 g , temp = 25°C , contact time = 3 h , pH 5, concentration of elements = 10 mol L^{-1}) ($n = 3$ and $\text{RSD} < 10 \%$).

3.2.5. Effect of competing ions

The dust fallout may contain a number of elements⁴² that occur with the analyte elements (Cd, Cu, Cr), which might enhance, reduce or have no effect in the adsorption of the analytes. The results for the effect of Ca, Mg, K, Ni, Fe, Co and Zn (as competing ions) on the adsorption of Cd, Cu and Cr are presented in Fig. 5 and 6. The competing ions reduced the adsorption capacity of Cd but not of Cu and Cr (Fig. 4, 5 and 6). When the three elements were analysed without competing ions (Fig. 2), their adsorption capacities were similar, which was not the case when other elements were included. The decrease of Cd adsorption as the concentration of competing elements increased could have been due to the competition for binding sites. There are other factors which could play a role on the observed adsorption capacity of Cd such as the atomic radius, valence as well as the hard-soft Lewis acid-base properties.⁴³⁻⁴⁶ Cd is a soft Lewis acid whose binding to a possible hard Lewis base on the surface of the soil was not

highly favourable due to the presence of other hard acids (e.g. Cr^{3+} , Mg^{2+} , K^+ and Ca^{2+}) and borderline Lewis acids (Co^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+}) which would be preferred as they are harder. The effect was slightly higher when a single element solution was contacted with that of competing ions in all ratios, than the multi-component system of the analytes. The ratios showed that there was no difference in the adsorption of the elements when the volume of competing ions was lower (4:1), equal (1:1) or higher (1:4) than that of the analytes (Fig. 4, 5 and 6). However, the effect of the concentration of competing ions became prevalent for Cd as concentration of the competing ions increased for reasons stated previously. The adsorption of Cu is higher than that of other elements in all the ratios and concentrations which might be due to the high electronegativity of the element relative to the others. The presence of competing ions did not show any significant effect on the adsorption of Cu and Cr.

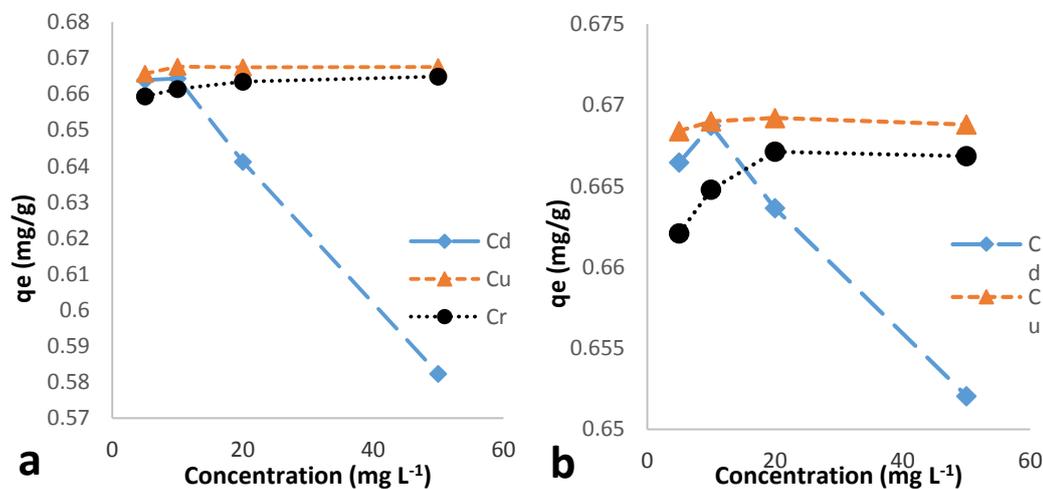


Figure 5 The effect of competing ions at different concentrations on the adsorption the elements in a single (a) multi-component systems (b) in a 1:1 ratio of analytes to competing ions ($V = 50 \text{ mL}$, mass = 0.75 g, temp = 25°C, contact time = 3 h, pH 5, concentration of elements = 10 mol L^{-1}) ($n = 3$ and RSD < 10 %).

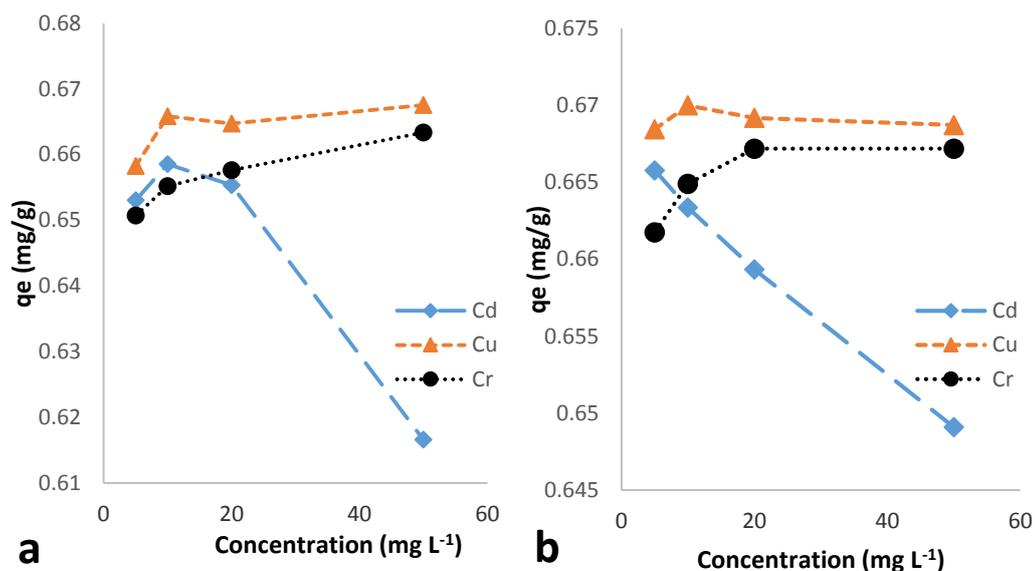


Figure 6 The effect of competing ions at different concentrations on the adsorption the elements in single (a) and multi-component systems (b) in a 4:1 ratio of analytes to competing ions ($V = 50$ mL, mass = 0.75 g, temp = 25°C, contact time = 3 h, pH 5, concentration of elements = 10 mol L⁻¹) (n = 3 and RSD < 10 %).

4. Conclusion

In this study, the adsorption of Cd, Cu and Cr onto an agricultural soil was studied and the effects of initial concentration, pH and competing ions were investigated. The results demonstrated that the agricultural soil is efficient in adsorbing Cd, Cu and Cr. As the concentration of the elements increased, the adsorption capacities also increased. The adsorption of the elements was better described by the Freundlich isotherm. The pseudo second-order kinetic model better described the kinetic data, affirming that adsorption occurred *via* a chemisorptive process. The adsorption of Cr was found to be dependent on pH, a factor that did not significantly affect the adsorption of Cd and Cu. The adsorption capacity of Cu and Cr was not affected by the presence of competing ions while the adsorption of Cd decreased significantly. The soil was generally effective in adsorbing and retaining the elements. However, the retention was highly dependent on elemental speciation and prevailing conditions e.g. pH (as in the case of Cr) and the presence of competing ions (as in the case of Cd). Such changes in conditions would have implications for

groundwater and plants (if the elements become bioavailable). Further work would have to be conducted to assess the effect of other factors such as the presence of agricultural chemicals (e.g. fertilisers and soil texturisers) and plant exudates on the adsorption of the elements.

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CHAPTER 5

Effect of plant exudates on the adsorption of cadmium, copper and chromium

This chapter consists of two papers discussing the effect of plant exudates on the adsorption of Cd, Cu and Cr onto an agricultural soil.

5.1. Effect of plant exudates on the adsorption of cadmium onto an agricultural soil

The following paper focuses on the effect of plant exudates on the adsorption of cadmium.

Contribution to the paper: Lead author, conducted the experimental work, analysed and interpreted the results and performed modelling

This paper will be submitted to: Journal of Environmental Management

Effect of plant exudates and EDTA on the adsorption of cadmium onto an agricultural soil impacted by mining activities

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Abstract

Sorption studies were conducted to investigate the effect of the presence of plants exudates (acetic acid (AA), citric acid (CA) and oxalic acid (OA)) and EDTA on the adsorption of non-essential and toxic cadmium (Cd) element onto an agricultural soil surrounded by mining plants. The effect of concentration and pH on adsorption were investigated. The SiO₂ and Al₂O₃ were found to be the main constituents of the soil as confirmed by power x-ray diffraction (PXRD) and x-ray fluorescence (XRF) and were responsible for Cd adsorption. The agricultural soil used had the following composition: SiO₂ (74.7%), Al₂O₃ (11.44%), FeO (5.09%), MgO (3.69%), CaO (2.73%), Fe₂O₃ (0.63%), TiO₂ (0.455%), Cr₂O₃ (0.222%), K₂O (0.2%) and Na₂O (0.15%) with a loss on ignition (LOI) of 13.4%. The presence of plants exudates and EDTA decreased the adsorption capacity of Cd at all initial concentrations of Cd and the effect followed the sequence: OA < AA < CA < EDTA. The adsorption of Cd onto the soil was best described by Freundlich isotherm model in the presence of all exudates, indicating heterogeneous surface. Cd adsorption in the presence of EDTA was poorly described by Freundlich isotherm due to lack of Cd adsorption. The adsorption of Cd decreased as the concentration of exudates increased and EDTA totally inhibited the adsorption of Cd at all concentrations. AA did not significantly affect the adsorption capacity of Cd at all pH levels ($p > 0.05$) but other exudates and EDTA decreased the adsorption as pH increased from 3 – 9. The soil can effectively adsorb Cd but in the presence of exudates and EDTA and at lower pH levels, the adsorption is lessened.

Keywords: adsorption capacity, agricultural soil, cadmium, acetic acid, oxalic acid, citric acid, EDTA

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Introduction

The accumulation of metals in the soil has been a worldwide problem that a host of researchers have been trying to solve for many decades (Bradl, 2004). Metals such as cadmium, mercury, chromium, uranium and arsenic from anthropogenic sources such as agrochemicals and mining operations can accumulate into the soils. Upon entering the soil, these metals can bind onto soils where their mobility will be reduced but if they do not bind onto the soil, they will leach into the groundwater and cause groundwater contamination which will in turn have a negative effect on aquatic systems. Thus, increasing the time and money required to clean the water before transportation to areas for domestic use. These elements are considered to be toxic even in low concentrations. The cost of remediation of contaminated soils have led many companies to ignore the traditional physiochemical methods for remediation, thus, the accumulation of heavy metals in the soil is still one of the major contributors to soil and groundwater pollution (Garbisu and Alkorta, 2001; Bradl, 2004). When there is no remediation method applied in the soil, the fate of metals entering the soil depends on the ability of the soil to adsorb metals. However other factors of the soil have to be taken into consideration.

In this study, the adsorption of cadmium onto an agricultural soil impacted by mining activities is investigated. There has been no remediation process applied onto the soil and therefore the accumulation of heavy metals from agrochemicals used in the soil and from nearby mining operations is assumed to be high. Cadmium is a non-essential element that can get into the systems of living organisms *via* the food chain since the crops grown on the plot are sold to cities and town in South Africa. Cadmium can easily be absorbed by plants which when ingested by humans can cause health disorders that can lead to death. When it accumulates in plants, it can prevent the uptake of minerals by plants microbes (Moreno et al., 1999). Moreover, photosynthesis was reported to be inhibited by cadmium (Sanitá di Toppi and Gabrielli, 1999; Shi *et al.*, 2010). Also, Cd was seen to interfere with the uptake,

transport and use of other elements (Ca, Mg, P and K) and water by plants (Das et al., 1997; Gouia et al., 2000). Thus cadmium toxicity is of serious concern.

There are a number of factors that affect the leachability and mobility of heavy metals in the soil such as the pH, soil composition, plants exudates, clay content, cation exchange capacity (CEC) and the speciation of the metals in the soil as well as their concentrations (Marschner and Romheld, 1995; Gray et al., 1999; Sukreeyapongse et al., 2002; Bradl, 2004). The pH can affect the constituents of the soil hence, influence adsorption of metals. At pH <4, constituents such as silanol and aluminol groups become protonated and this will make the soil less negatively charged and consequently, there will be reduction in adsorption of metals (Batchelor, 1998). At higher pH values, the soil become more negatively charged and the probability of adsorbing metals increases. The type of soil is very crucial to note as they may lead to high or low adsorption of metals. Coarse-grained soils have poor metal retention abilities whilst fine-grained soils such as clay have high retention abilities due to high surface areas and surface reactivities (Bradl, 2004). Soil with high surface areas also have high CECs. Plants exudates and EDTA have been found to be good complexing agents for metals and have been used in remediation techniques such as phytoremediation to recover metals from soils (Elless and Blaylock, 2000; Chen et al., 2003). Though this is a great initiative, the presence of plants exudates and EDTA might have a negative effect on the adsorption of metals onto soil surfaces where no remediation is applied and they might increase their mobility of the metals in the soil and cause serious health problems in living organisms (Friedly et al., 2002). The concentration of plants exudates is high in soils where plants grow, as they are released by the roots of plants and crops such as spinach, cabbage etc. and they include acetic, citric and oxalic acids which are low molecular weight organic acids. Moreover, plant and animal residues decomposition in soils release exudates (Cristofaro et al., 1998). EDTA on the other hand is contained in agrochemicals and released into the soil through waste waters. It is known as one of the powerful complexing agents for metals leading to stable complexes (Williams, 1998).

The main aim of the study was to evaluate the effect of plant exudates on the adsorption of cadmium. What happens to cadmium upon entering the soil with the presence of plants exudates? Is the soil effective in adsorbing cadmium? What species of cadmium are formed? What about the mobility and bioavailability? What will the findings say about the safety of people and livestock feeding on the crops grown on the plot? These are some of the key questions that this study seeks to address.

Methods and materials

Sampling site

This study is based on the adsorption of cadmium onto an agricultural soil which was collected from an agricultural plot in Rustenburg, a city in the North West Province, South Africa. As can be seen in Fig. 1, the plot is in the vicinity of mining and smelting operations. The elements from these operations as well as from fertilisers and pesticides which are constantly used on the soil can potentially pollute the surrounding agricultural soil. The accumulation of these elements (cadmium, copper, chromium, nickel, lead and many others) onto the soil endangers the wellbeing of living organisms including plants and animals. Rustenburg is located on the southeast of the North West Province at 25-39° 16' S, 27-15° 21' E and 1139 m above sea level with temperatures ranging from -6 to 40 °C with an average of 19°C.

The soil was collected to a depth of about 30 cm below the surface and stored in a plastic container after removing large unwanted substances. The soil was brought into the lab and air dried. The dry soil was stored into the plastic container until used.

Characterization

The agricultural soil was characterized using power X-ray diffraction (PXRD) for mineralogy as well as X-ray fluorescence for elemental composition. Fourier transform infrared spectroscopy (FTIR) was used to identify functional groups in the

soil while the cation exchange capacity (CEC) was determined by the BaCl_2 method (Gillman and Sumpter, 1986). The point of zero charge (PZC), total dissolved solids (TDS) and electrical conductivity of the soil were determined.

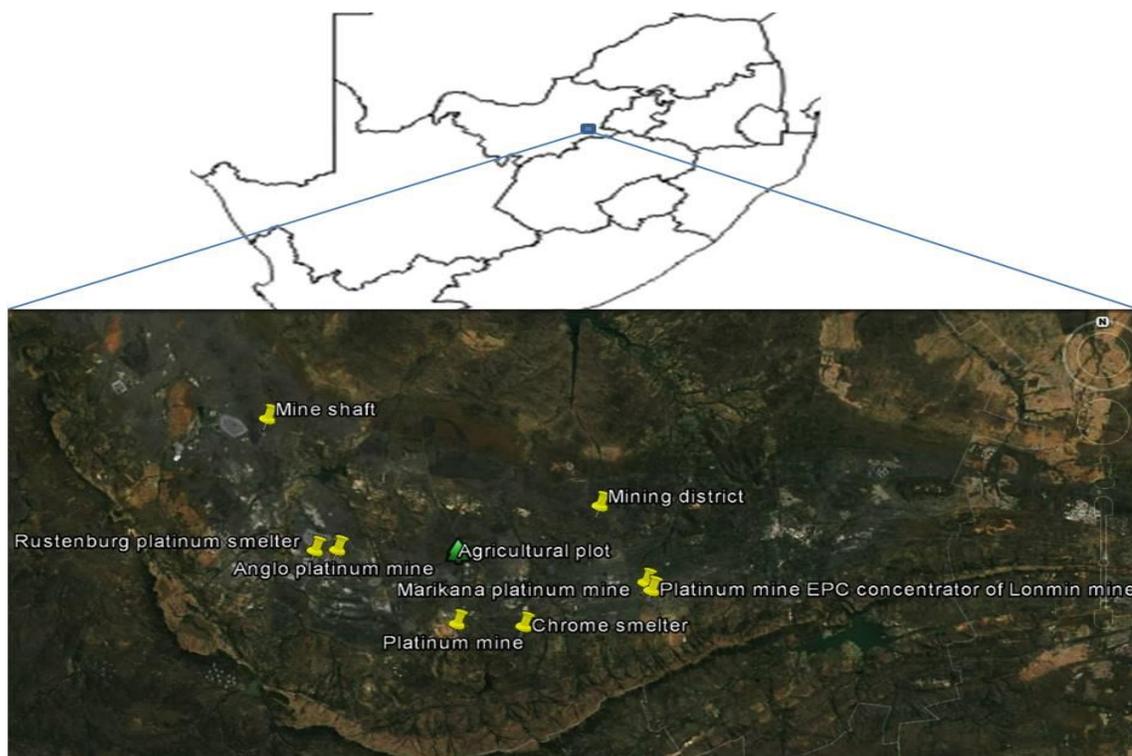


Figure 1: The vicinity of the agricultural plot

Reagents and standards

The chemicals used were of analytical grade, obtained from Sigma Aldrich. 1000 mg L^{-1} stock solutions of nitrate elements ($\text{Cd}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and $\text{Cr}(\text{NO}_3)_3$) were prepared by dissolving appropriate amounts with deionized water and filling to the required volume. 1 mol L^{-1} stock solutions of plants exudates (acetic acid, citric acid, oxalic acid and EDTA) were also prepared by dissolving appropriate amounts of exudates obtained from Sigma Aldrich in deionized water. The stock solutions were stored in a fridge at $4 \text{ }^\circ\text{C}$ when not used. Working solutions were prepared daily by serial dilutions from the stock solutions.

The presence and desorption of Cd in the soil

In order to get accurate results in this study, the presence of Cd in the soil was determined. Microwave digestion was used to determine the concentration of Cd in the soil. 3 mL of concentrated citric acid (99%), 9 mL of concentrated hydrochloric (96%) acid and 1 mL of concentrated hydrofluoric acid (95%) were added to microwave tubes with 0.250 g of agricultural soil and the elements were digested from the soil using the microwave.

The resulting solution with elements was analyzed using ICP-OES (Spectro Genesis, Spectro, Germany). The 50 mL of plants exudates and EDTA were also used to determine the desorption capacities of each. Plants exudates and EDTA with concentrations of 0.05 mg L⁻¹ were added to centrifuge tubes with 0.75 g soil. The contents were shaken at 150 r/m for 3 h at room temperature. They were then centrifuged at the speed of 3000 r/m and room temperature. The contents were filtered with filter paper and the supernatant was analyzed for desorbed amounts of Cd using ICP-OES.

Effect of initial concentration of Cd in the absence of plants exudates

The effect of initial concentration on the adsorption of Cd onto the soil was determined by preparing cadmium nitrate solutions with concentrations ranging from 5 – 100 mg L⁻¹. The prepared solutions were added to 0.75 g soil in polypropylene containers. After shaking for 3 h using the speed of 150 r/m at room temperature, the contents were centrifuged and filtered. The concentrations at equilibrium were determined using ICP-OES (Spectro Genesis, Spectro, Germany).

Effect of initial concentration of Cd in the presence of plants exudates

The initial concentration of cadmium in the presence of plants exudates was studied to determine their effect on adsorption. Concentrations ranging from 5 – 50 mg L⁻¹ were mixed with plants exudates with a fixed concentration of 0.05 mol L⁻¹. The solutions

were added to polypropylene containers with 0.75 g soil. After shaking for 3 h, the contents were centrifuged at 3000 r/m and filtered using filter paper. The concentrations at equilibrium were determined using ICP-OES.

Effect of the concentration of plants exudates

The effect of the concentration of exudates was determined. Plants exudates with concentrations; 0.01, 0.05 and 0.1 mol L⁻¹ were prepared and added to cadmium nitrate solutions to make the final concentration of 10 mg L⁻¹ Cd. The mixtures were shaken with 0.75 g soil for 3 h at 150 r/m and centrifuged. After filtering, the filtrate was analyzed using ICP-OES.

Effect of pH on the adsorption of Cd

The effect that pH has on the adsorption of Cd in the presence of plants exudates and EDTA was studied. The concentrations of cadmium and plants exudates as well as EDTA were kept constant 10 mg L⁻¹ and 0.05 mol L⁻¹ respectively. Nitric acid and sodium hydroxide were used to set the pH of solutions. The solutions were added to polypropylene containers with 0.75 g soil. The contents were shaken for 3 h at room temperature. The contents were centrifuged 3000 r/m and filtered. The concentrations at equilibrium were determined using ICP-OES.

Speciation modelling using PHREEQC

To determine the species that are present in all solutions of the plants exudates or EDTA with defined solution condition, a PHREEQC geochemical modelling was used. PHREEQC is a computer program that uses C and C++ programming languages to perform calculations of specified solution compositions (Parkhurst and Appelo, 2013). The results obtained from PHREEQC can assist in accounting for the observed responses at equilibrium. To do this, the pH, temperature, concentrations of Cd and exudates used in the study were specified.

Results and discussion

Characterization

The main constituents of the soil were found to be SiO₂ and Al₂O₃ as determined by XRF and were responsible for binding positively charged elements (Table 1). The results obtained from PXRD also confirmed that SiO₂ and Al₂O₃ were the main minerals in the soil. The high contents of these minerals are an indication of the high surface area of the soil leading to high adsorption capacities of elements. The CEC and PZC of the soil were found to be 51.6 meq 100g⁻¹ and 8.3 respectively. The FTIR spectrum indicated the presence of Si-O and Al-O groups at ~1000 cm⁻¹ whilst O-H and N-H groups were observed at 3400 and 3600 cm⁻¹ respectively. The N-H group observed might be due to the ammonium fertilisers which are constantly used on the plot or the amino acids due to decaying organic compounds.

Table 1: Percentages of the main constituents of agricultural soil used

Compound	Percentage composition (%)
SiO ₂	74.7
Al ₂ O ₃	11.44
Fe ₂ O ₃	0.63
FeO	5.09
MnO	0.14
MgO	3.69
CaO	2.73
Na ₂ O	0.15
K ₂ O	0.2
TiO ₂	0.4545
P ₂ O ₅	0.03
Cr ₂ O ₃	0.2224
NiO	0.0239
TOTAL	99.5
LOI	13.43

Effect of initial concentration of Cd²⁺

In order to determine the effect that plants exudates have on the adsorption of Cd, an adsorption experiment in the absence of plants exudates was done varying the initial concentrations of the metal element. The results indicated that the adsorption capacity of Cd increased as the concentration increased from 5 to 100 mg L⁻¹ (Figure 2). Thus, the soil is capable of adsorbing high concentrations of cadmium. This can be attributed to the availability of binding sites and the driving force of concentration gradient. Thus, the active sites will be surrounded by more cadmium ions as the concentration increases.

Effect of plants exudates on adsorption

The effect of plants exudates on adsorption was investigated and were found to reduce the adsorption capacity of Cd but with different degrees (Fig. 3). Langmuir, Freundlich and Dubinin-Radushkevich sorption isotherms were plotted to evaluate the equilibrium sorption data. Freundlich isotherm was found to describe the data better than other isotherms (determined by R² values), for all low molecular weight organic acids, indicating isothermal variations of adsorption due to the heterogeneity of the soil surface. There was no evidence for the adsorption of Cd in the presence of EDTA hence was poorly described by the isotherms and only Langmuir gave the best fit. There was a recognizable difference between the parameters of the isotherms of the control (no plants exudates or EDTA) and when plants exudates including EDTA were present (Table 3). Adsorption intensity (K_f) which is indicative of the favourableness of adsorption onto the surface was determined from Freundlich isotherm and confirmed that the adsorption of Cd onto the soil was favoured but, in the presence of plants exudates, the maximum adsorption of Cd was inhibited hence K_f was lower (Table 3). Though the adsorption intensity of Cd was higher in the presence of acetic acid, the n parameter (< 1) clearly confirmed that adsorption was not highly favoured. The adsorption energy (E_s) and maximum adsorption capacities (X_m and q_m) were high for the control and oxalic acid hence higher adsorption

capacities were observed. These parameters were also high for acetic acid, however, it was not described well by the isotherms. The parameters from the isotherms indicated that the adsorption of Cd in the presence of EDTA was not favoured hence no adsorption was observed.

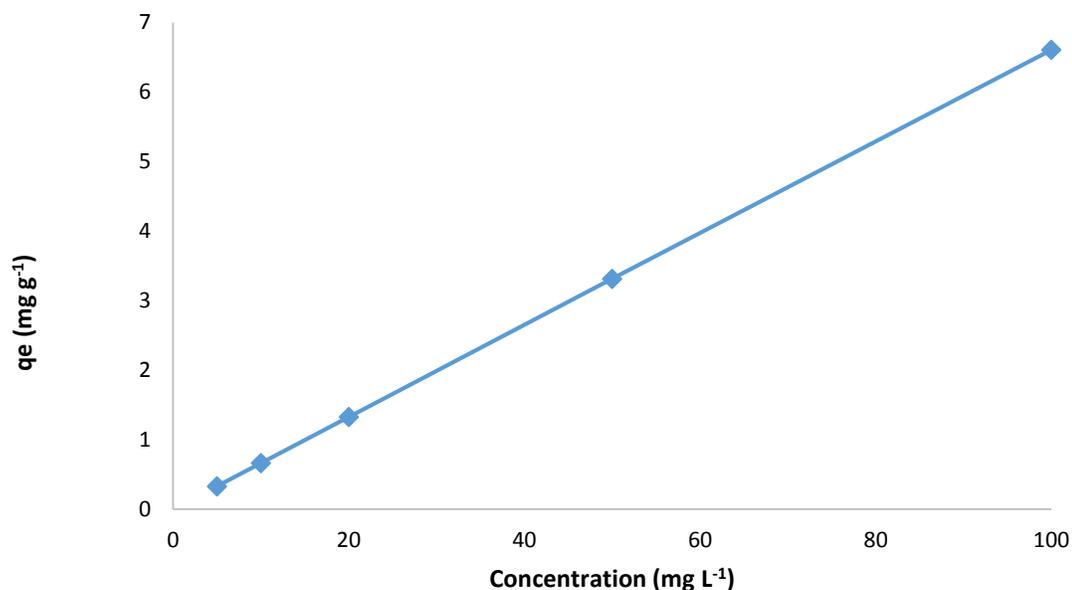


Figure 2: Effect of initial concentration of Cd on adsorption onto an agricultural soil (temp = 25 °C, pH 5, contact time = 3 h) (n = 3 and RSD < 10 %).

Table 2: Chemical properties of the studied agricultural soil

Chemical property	Value
pH	8.32
CEC (meq/100g)	51.6
Total dissolved solids (TDS) (ppt)	0.37
Electrical conductivity (mScm ⁻¹)	1.06

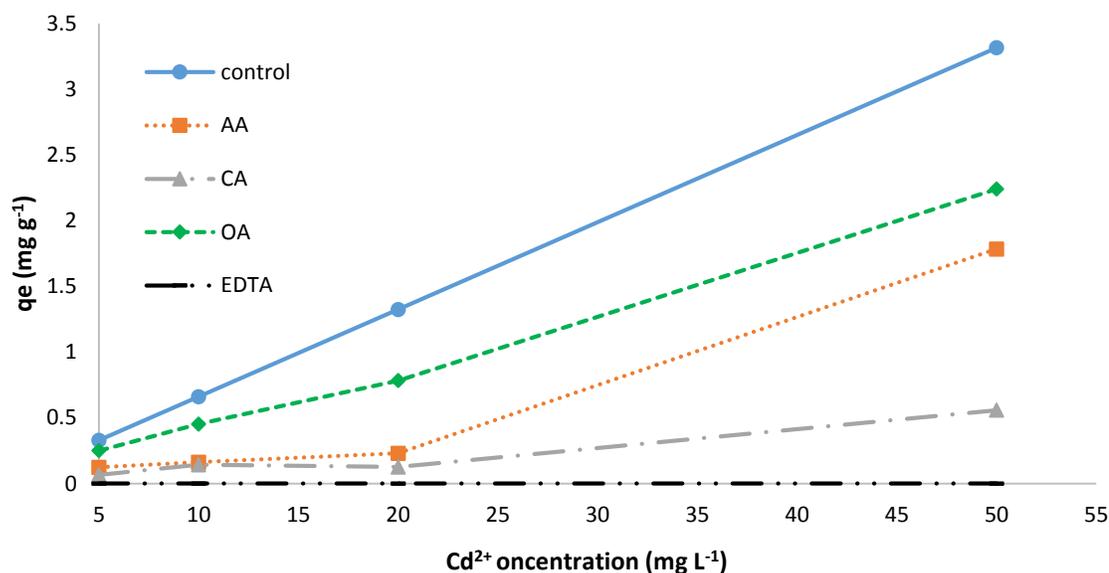


Figure 3: Effect of initial concentration of Cd in the presence of plants exudates and EDTA on adsorption onto an agricultural soil (temp = 25 °C, pH 5, contact time = 3 h, concentration of exudates and EDTA = 0.05 mol L⁻¹) (n = 3 and RSD < 10 %).

Table 3: Adsorption isotherms for Cd in the presence of plants exudates and EDTA

	Langmuir			Freundlich			Dubinin-Radushkevich		
	q _m	b	R ²	K _f	n	R ²	X _m	E _s	R ²
Control	4.17	23867	0.9404	88.23	1.208	0.9740	0.8231	9.22	0.9665
AA	0.0369	640	0.0844	66	0.925	0.7936	0.3698	7.41	0.7801
CA	0.0182	737	0.2012	1.99	1.26	0.9045	0.0542	8.42	0.8955
OA	0.0646	2402	0.4016	18.8	1.24	0.9722	0.3256	8.86	0.9644
EDTA	0	0	0.9999	0	0	0.5811	0	0	0.5596

Acetic acid

In the presence of acetic acid, the adsorption of cadmium decreased significantly and this can be attributed to the formation of cadmium acetate species (Cdacetate⁺ and Cd(acetate)₂). The percentage reductions in adsorption capacities were 62, 75, 82 and 46% at 5, 10, 20 and 50 mg L⁻¹ respectively. The formation of Cd(acetate)₂ and Cd-

acetate⁺ complexes were found to be in high concentrations than the free Cd ion (Cd²⁺) as determined by PHREEQC. These species decreased the ability for the maximum adsorption of Cd onto the soil surface due to large size, hence, more cadmium was detected after the equilibration time. This means that some of the complexed species were not accommodated on the soil surface. Therefore, the remaining Cd species were available and just floating in the solution. This has implications on the safety of groundwater since, when large amount of Cd is complexed with acetate ions, there is a possibility of leaching into the groundwater due to the unavailability of binding sites. Moreover, due to the complexation of Cd species, the shielding of the positively charged Cd will lead to weak adsorption of the species formed. The presence of more acetate ions can attach to the weakly bound Cd(acetate)⁺ to form more Cd(acetate)₂.

Citric acid

The effect of citric acid on the adsorption of cadmium was great as more cadmium was inhibited from adsorbing onto the soil surface (Fig. 3). Citric acid prefers to chelate more with Cd and this can be attributed to the small atomic radii of Cd element, making it is easy for complexation to take place. The Cd complexes formed with citrate ions were not favourable for adsorption onto the soil surface. Thus, the affinity onto the soil surface decreased, leading to more Cd species floating in solution rather than being adsorbed onto the soil. Since cadmium ion have an oxidation state of +2 and the deprotonated citrate will have an overall charge of -3, the complexes formed were Cd(citrate)⁻ and Cd(citrate)₂⁴⁻ as confirmed also by PHREEQC. The adsorption capacity of Cd onto the soil surface was found to be ~70 % at all concentrations. The presence of citrate ions released by plants will prevent the desirable adsorption of Cd onto the soil, thus, increasing the leaching of Cd to groundwater.

Oxalic acid

In the presence of oxalic acid, the adsorption of cadmium element decreased due to complexation reactions with the element. But, the effect was less than that of the other exudates. The adsorption capacity of Cd was reduced by ~ 30% in the presence of oxalic acid at all concentrations greater than 5 mg L⁻¹ (Fig. 3) The species formed in the presence of oxalic acid was Cd(oxalate) which was the culprit that led to the reduction in adsorption capacity observed. The complexes formed were large in size and therefore their adsorption prevented further adsorption of Cd complexes due to lack of adsorption sites onto the soil.

EDTA

The effect of EDTA on the adsorption of Cd was studied and amongst the chelating agents, its effect on preventing the adsorption of cadmium was the greatest since the adsorption decreased more than in the presence of other chelating agents (Fig. 3). The higher effect might have been because EDTA is larger than the other chelating agents and has the highest overall negative charge when it is fully deprotonated hence, the interaction with positively charged cations was greater. Thus, the chelate effect was greater with EDTA. Strong complexes formed between EDTA and cadmium ions had a stoichiometry of 1:1 (Harris, 2010). According to PHREEQC, the species that formed were Cd-EDTA²⁻, which were the only dominant species. This species was not favourable for adsorption onto the soil surface hence adsorption capacity was very low if there was any. Most of the Cd species was just moving around without being adsorbed onto the soil. The concentrations observed for Cd after the equilibrium period were more than the initial concentrations used, which meant that, EDTA desorbed some of the elements which were already adsorbed onto the agricultural soil. Studies have shown that low molecular weight organic acids and EDTA can be used as leaching agents for metals due to the complexation reactions

they undergo with the elements already adsorbed onto the soil surfaces (Chen, 2003; Huaying et al., 2014). The desorption studies using EDTA confirmed that Cd was desorbed from the soil. Thus, when EDTA is released into the soil, it will react with elements such as Cd emanating from fertilisers and nearby mining operations and this will increase their mobility as well as their bioavailability in the soil, increasing the probability of reaching groundwater and living organisms.

Effect of the concentration of plants exudates

The effect of concentrations of plants exudates on the adsorption of cadmium was studied and it was found concentration have a significant effect on the adsorption of cadmium onto the soil

Acetic acid

Fig. 4 shows the effect of concentration of plants exudates on the adsorption of Cd onto the agricultural soil. The adsorption of Cd decreased as the concentration of acetic acid increased. The adsorption capacities of Cd were similar at lower concentrations (0.01 - 0.05 mol L⁻¹), but as the concentration of acetic acid increased, the reduction in adsorption capacity became more prevalent. The adsorption of Cd decreased significantly due to the reduction of the free Cd²⁺ as concentration of acetic acid increased, leading to more Cd(acetate)₂ and Cd(acetate)⁺ species. The complex Cd(acetate)₂ was either weakly or not adsorbed at all since it was not favourable for adsorption, hence an increase in the percentage reduction of adsorption. Therefore, when high concentration of acetic acid is released by plants, the mobility and bioavailability of Cd in the soil will increase. The Cd species will have the potential of being absorbed by plants and also reach groundwater, posing serious challenges in the environment and in the health of living organisms since, there is no remediation process applied on the soil. At higher concentration (0.1 mol L⁻¹) of acetic acid, the adsorption capacity of Cd was reduced by approximately 60%. Thus, higher

concentrations will prevent the satisfactory adsorption of Cd onto the agricultural soil.

Citric acid

The adsorption of Cd decreased with increasing citrate concentration. Since citric acid is a tridentate acid, the species formed with Cd were negative, because, cadmium has a charge of +2. The Cd species; $\text{Cd}(\text{citrate})^-$ and $\text{Cd}(\text{citrate})_2^{4-}$ increased as concentration increased whilst the free Cd^{2+} decreased. These species were not favourable for adsorption, hence, low adsorption capacities were observed. When the concentrations of citrate released by plants are high, more Cd will be available for plant uptake. Moreover, Cd mobilization will increase. The percentage reduction on the adsorption capacities of Cd were 31, 78 and 94% at 0.01, 0.05 and 0.1 mol L⁻¹ respectively. Therefore, the presence of citric acid in the soil will increase the bioavailability of Cd which can end up in groundwater. These species can also be absorbed by plants in the plot hence, find entry to living organisms including human beings.

Oxalic acid

Oxalic acid is a diprotic acid that has been used as a chelating agent so as to desorb some elements from the soil (Luo et al., 2006). In this study, oxalic acid was seen to decrease the adsorption of Cd onto an agricultural soil. The adsorption capacity of Cd decreased linearly unlike the other exudates where different trends were observed. The effect is not as prevalent as the other exudates and this can be attributed to the small size of the chelator. The percentage reductions on the adsorption capacities of Cd were 26, 31 and 56% at 0.01, 0.05 and 0.1 mol L⁻¹ respectively. Therefore high concentrations of oxalic acid will increase the leaching of Cd in the soil.

EDTA

The effect of concentration of EDTA on the adsorption capacity of Cd was also studied. The adsorption capacities of Cd were highly affected by the presence of EDTA. No adsorption was observed in the presence of EDTA and the concentration of Cd was found to be above the initial due to desorption of the Cd which was already in the soil. This was also observed with the effect of the concentration of the elements (Fig. 3) where the concentrations of Cd after the adsorption time were higher than the initial concentrations used. When the concentration of the desorbed Cd was subtracted from the equilibrium adsorption obtained, the adsorption capacity was still found to be around zero. Wu et al. (2003) exposed EDTA to the soil and monitored the desorption capacity of Cd and Cu from the soil and found that the concentrations of the elements increased after the exposing time and also, the solubility of the elements increased, leading to high bioavailability of the elements. Thus, EDTA in this study desorbed some of the Cd from the soil. Even the small concentration (0.01 mol L^{-1}) of EDTA prevented the adsorption of the elements due to chelation and increased their mobility. The higher effect of EDTA on the adsorption of Cd was due to the high number of negative complexes formed. The dominant species for Cd was Cd-EDTA^{2-} , which increased as the concentration of EDTA increased. Thus, the dominant silica and alumina groups which are the main constituents of the soil rejected the complexes formed. The Cd complexes formed with EDTA will be bioavailable and will leach to groundwater leading to contamination. The ability of EDTA to desorb Cd from the soil poses serious challenges on the environment since the high accumulation of elements in groundwater will mean high costs and more time for clean-up.

Effect of pH on the adsorption of Cd in the presence of plant exudates

The effect of pH on the adsorption of Cd onto an agricultural soil in the presence of plant exudates and EDTA was studied and the results are shown in Fig. 5. The

adsorption of Cd onto the soil was not affected by pH in the absence of the exudates and EDTA. However, the effect of pH on the adsorption of Cd varied with the different exudates. Acetic acid had minimal effect on the adsorption of Cd at all pH values. In fact, there was no significant difference ($p > 0.05$) between the adsorption capacities of Cd in the control and in the presence of acetic acid. The adsorption capacities of Cd were found to increase slightly as pH increased from 3 – 9 in the presence of oxalic acid. At lower pH values there was more adsorption inhibition of Cd than at higher or less acidic pH values. The observed effect might have been due to the less negative surface that resulted due to more hydronium ions, therefore the adsorption of dominant Cd species which were positively charged was not highly favourable. At higher pH values, the surface of the soil was negative, resulting in more Cd adsorption.

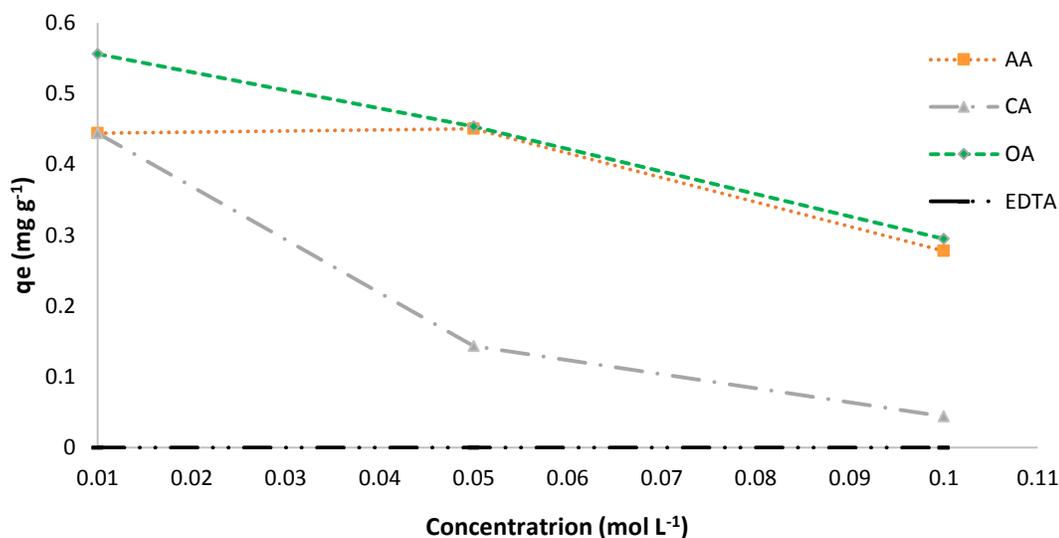


Figure 4: Effect of the concentration of plants exudates and EDTA on the adsorption of Cd onto an agricultural soil (temp = 25 °C, pH 5, contact time = 3 h, concentration of Cd = 10 mg L⁻¹) (n = 3 and RSD < 10 %).

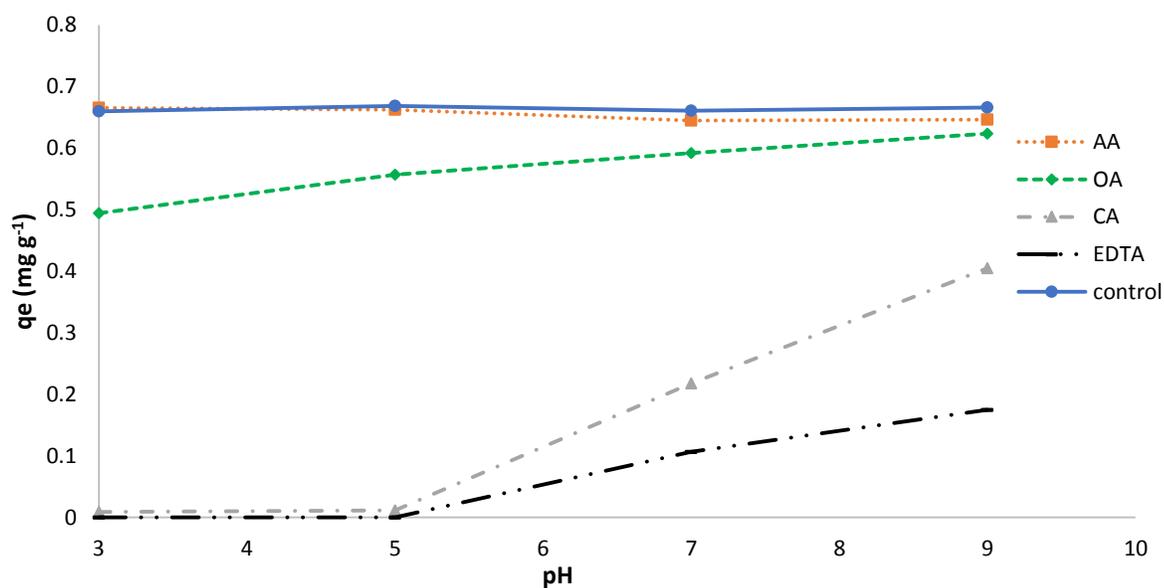


Figure 5: Effect of pH on the adsorption of Cd in the presence of plants exudates and EDTA onto the agricultural soil (temp = 25 °C, pH 5, contact time = 3 h, concentration of Cd = 10 mg L⁻¹) (n = 3 and RSD < 10 %).

There was a significant difference from the control of the adsorption of Cd in the presence of citric acid and EDTA. The adsorption capacities were found to be around zero at pH 3 and 5 for both citric acid and EDTA, which could have resulted due to the occupation of soil surface groups by hydronium ions which have high affinity for ion exchanges and complexing sites (Pehlivan et al., 2009). The surface of the soil could not adsorb the negatively charged Cd species i.e. Cd-citrate⁻ and Cd-EDTA²⁻ that form in the presence of citric acid and EDTA respectively because the soil did not form positive adsorption sites. At acidic pH values, the free Cd²⁺ was also present in significant amount but could not be adsorbed and this might be due to the shielding of the soil functional groups by complexes formed. At higher pH values (7 – 9), the adsorption of Cd was seen to increase. The increase was a result of the adsorption of free Cd²⁺ to the negatively charged soil surface. According to PHREEQC, the non-complexed Cd²⁺ species were not high and decreased as pH increased from 7 – 9 but

more Cd was forced to adsorb onto the soil as the soil was favourable for adsorbing any Cd which was available for adsorption.

Conclusion

The present study showed that the presence of plants exudates and EDTA decreased the adsorption capacity of Cd which can adsorb > 95% Cd introduced in their absence. The reduction in adsorption was higher with CA and EDTA which formed more negative complexes with Cd as confirmed by PHREEQC. These complexes were repelled by the negatively charged surface of the soil. The higher the concentrations of plants exudates and EDTA the lower the adsorption capacities due to the increase in complexes that are not favourable for adsorption. The change in pH will affect the adsorption of Cd in the presence of OA, CA and EDTA since the adsorption was seen to be low at acidic conditions due to the formation of positively charged surface which is not favourable for adsorbing positively charged Cd species or even the complexes formed because of the shielding of adsorption sites of the soil. AA and OA had low effect on the adsorption of Cd due to the formation of either positively charged or uncharged complexes such as Cd acetate⁺ and (Cd acetate)₂ in the presence of acetic acid and Cd oxalate in the presence of oxalic acid. The overall effect of the exudates and EDTA follows the sequence: AA < OA < CA < EDTA. Therefore the presence of exudates and EDTA will decrease the adsorption of Cd onto the agricultural soil used and soils of a similar nature with high adsorbing capabilities. Thus, the likelihood of Cd reaching groundwater will increase when plants exudates released by plants and EDTA from agrochemicals are present.

Acknowledgement

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5.2. The effect of plant exudates on the adsorption of copper and chromium

Contribution to the paper: Lead author, conducted the experimental work, analysed and interpreted the results and performed modelling

This paper was submitted to: WaterSA (Water SA 3406)

The effect of plant exudates on the adsorption of copper and chromium in an agricultural soil impacted by mining activities: implications for the shallow groundwater

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Abstract

The elements emanating from mining operations can enter the soil through dust fallout or precipitation and mobilize to the groundwater if they are not held tightly by the soil. In this study, an agricultural soil in a plot located in the vicinity of mining and smelting operations was studied. Some of the vegetables grown on the plot include spinach, cabbage and tomatoes. The approach of the study hinged on the premise that plants such as the mentioned vegetables release plant exudates that can interact with elements within the soil, thus affecting their mobility. To assess this, batch experiments were conducted to study the effects of surrogate plant exudates including acetic acid (AA), citric acid (CA) and oxalic acid (OA) as well as ethylene diaminetetraacetic acid (EDTA) which is contained in agrochemicals on the adsorption of copper (Cu) and chromium (Cr). The effect of the initial concentrations of elements and concentration of plant exudates and EDTA were studied. The agricultural soil composition was: SiO₂ (74.7%), Al₂O₃ (11.44%), FeO (5.09%), MgO (3.69%), CaO (2.73%), Fe₂O₃ (0.63%), TiO₂ (0.455%), Cr₂O₃ (0.222%), K₂O (0.2%) and Na₂O (0.15%). The PHREEQC geochemical modelling code was used to determine the speciation of the elements. The results showed that EDTA and plant exudates significantly ($P < 0.05$) decreased the adsorption capacity of the elements onto the agricultural soil. AA had the least effect on the adsorption capacity of the elements while OA and EDTA strongly affected the adsorption of Cu. Moreover, these exudates were found to desorb elements which are already present in the soil. Though the adsorption capacity of Cr was reduced, it was found that the adsorption increased slightly with an increase in CA and EDTA concentrations due to an

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increase of free Cr^{3+} species. Thus, the mobility of the elements will be increased by plant exudates that transform them into forms that are not favourable for adsorption hence rendering them mobile to unconfined aquifers and shallow groundwater. The transformations can also make the elements to be potentially bioaccessible and bioavailable to plants.

Keywords: agricultural soil, Cu, Cr, acetic acid, citric acid, oxalic acid, EDTA

Introduction

Agricultural soils in or near mining operations have the potential of accumulating elements emanating from mining and smelting operations as well as from agrochemicals applied onto the soil. These elements include Cd, Cu, Cr, As, Ni, Hg and U and have potential to reach groundwater and subsequently finding entry into living organisms *via* the food chain. When these elements exceed the tolerable limit they become hazardous to living organisms including plants, animals and humans (Abollino et al., 2003). Some of these elements are carcinogenic whilst some are responsible for other serious diseases such as kidney failure and osteoporosis (Kabata-Pendias and Pendias, 1993). Upon entering the soil, these elements can be adsorbed onto the soil surface or mobilise to groundwater. It is thus important to assess the probability of element mobility in soils as well as their stimulants to mobilise as this is indicative of their bioavailability. In some landfills, for instance, clay minerals have been used to prevent the mobility of elements in the soil, thus ensuring protection of groundwater and the environment at large (Bailey et al., 1999). Developed countries have been using remediation techniques such as immobilisation, soil washing and phytoremediation for the remediation of elements in contaminated sites (GWRTAC, 1997). However, underdeveloped and some developing countries are yet to implement these techniques due to increased awareness of their importance. In the meantime, elemental accumulation continues to increase in the soil, causing serious health hazards. It is therefore important to know the effectiveness of soils in adsorbing elements and preventing their mobility especially where there is no remediation technique applied. This would also help in determining the risk assessment benchmark in the impacted area.

In places that are prone to contamination by elements, soils usually act as a buffer to protect groundwater and vegetation. Some soils, depending on their composition, can retard the

mobility of elements by adsorbing them. Soils which are high in clay minerals can effectively adsorb the positively charged elements due to the presence of negative surface charges and high surface areas (Bailey et al., 1999). Organic matter and hydrous oxide minerals present in the soil also promote the adsorption of trace elements onto the soil. They have hydroxide groups whose protons could be exchanged for positively charged elements (Davis and Kent, 1990). Some soils poorly adsorb elements due to the absence of adsorbing minerals and the influence of other factors such as soil pH, element speciation and element concentration. In such cases, a gradual increase of trace elements accumulation in the groundwater is observed (Allen and Torres, 1991; Cavallaro and McBride, 1980; Stahl and James, 1991; Martinez and Motto, 2000). Moreover, soils with high cationic exchange capacity (CEC) have high exchangeable sites leading to better and higher retention of elements, thus reducing the mobility of elements (Silveira et al., 2003; Hadi et al., 2016; Zolfaghari et al., 2016).

In this study, a soil on a market gardening plot in a platinum group element (PGE) mining and smelting area in the North West Province, South Africa was studied. Cabbage, spinach, carrots and potatoes are some of the vegetables grown on the plot and sold to markets in Johannesburg and Pretoria. Dust fallout and precipitation could mean that constituent elements in the host ores from the mining and smelting operations can potentially be deposited on surrounding soils. A study by Ochieng' (2002) pointed to increased element concentrations in soils in the vicinity of such operations. A study by Tutu et al. (2009) pointed to the capability of agricultural soils in the area to retain metals such as Ni and Cu. However, no comprehensive assessment of the behavior of these contaminants within the impacted soils has been done. For instance, plants release exudates such as oxalic acid (common in spinach and cabbage), malic acid, acetic acid and other organic ligands and complexing agents (Cline and Reed, 1995; Wu et al., 1999; Degryse et al., 2008; Li et al., 2012) and these could interact with elements within the soil matrix. This study used batch adsorption experiments to assess the effect of the following exudates: citric acid, oxalic acid, acetic acid and ethylenediaminetetraacetic acid (EDTA) on the adsorption of copper (Cu) and chromium (Cr). It should be noted here that other sources of contaminants to the soil could include fertilisers and manure, pesticides, and water used for irrigation.

Materials and methods

Study area

The agricultural soil sample was collected from an agricultural plot in Rustenburg (25-39° 16' S, 27-15° 21' E), North West Province, South Africa (Fig. 1) which is in the vicinity of PGE mining and smelting operations. The area has a humidity of 43% with temperatures ranging from -6 °C in winter to 40 °C in summer. The mean annual precipitation is 600 mm. Agriculture is a major land use activity in the area with 50 833 hectares of agricultural land (Midgeley et al., 1994).

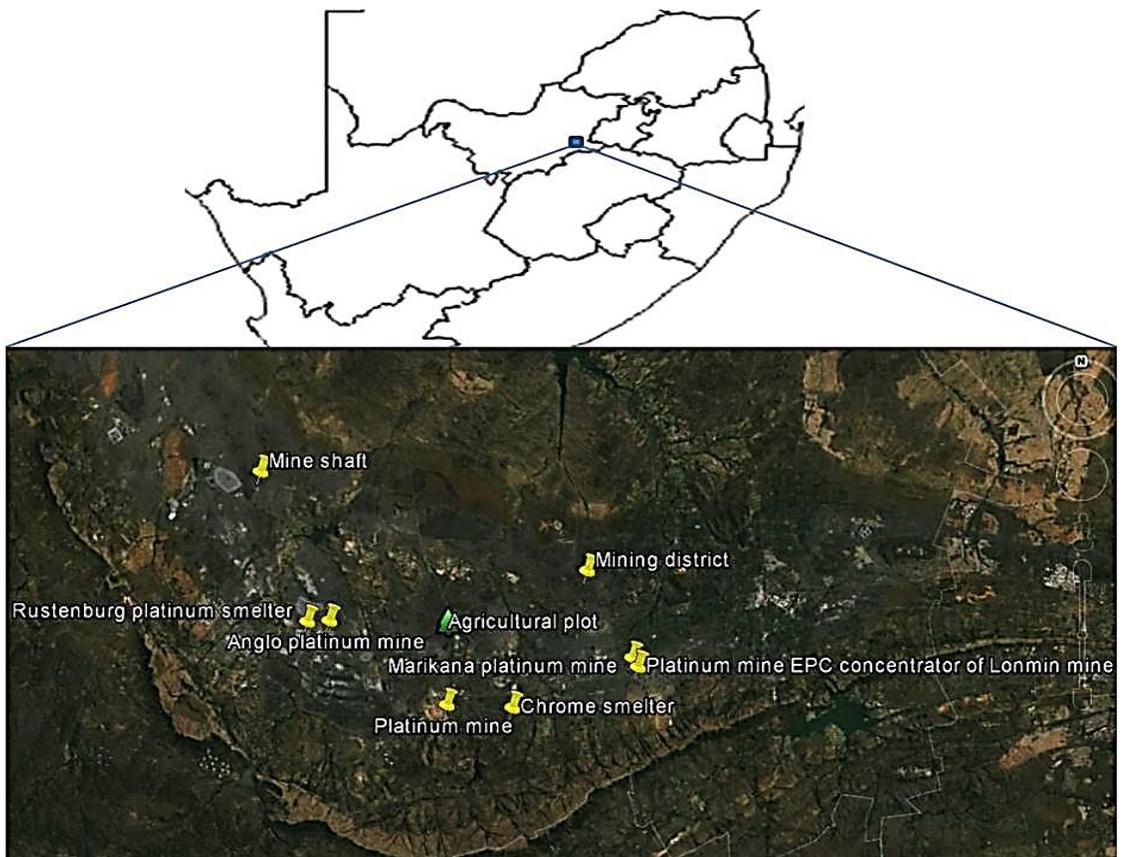


Figure 1: The location of the agricultural plot in the vicinity of mining operations

The soil samples were collected at depths of 20-40 cm at 5 points within a fallow part of the plot. The soil was air dried, ground and sieved using a 2 mm sieve to remove stones, clods and twigs. It was then stored in a polypropylene container at room temperature until it was required.

Characterisation

Characterisation was done using powder X-ray diffraction (PXRD) (Karlsruhe, Germany) to determine minerals in the soil and X-ray fluorescence (XRF) (PANalytical, Netherlands) to determine the chemical properties of the soil. In order to identify functional groups of the soil, a Fourier-transform infrared spectrometer (FTIR) (Tensor 27, Bruker, Germany) was used and spectra in the frequency range of 400 to 4000 cm^{-1} were recorded. The point of zero charge (PZC) of the soil was determined so as to give an indication of the pH range at which the surface of the soil is positive and negative (Smičiklas et al., 2005). The cationic exchange capacity (CEC) was determined using a method described by the BaCl_2 method (Gillman and Sumpter, 1986).

Reagents and standards

The chemicals used were of analytical grade, obtained from Sigma Aldrich, South Africa. Stock solutions (1000 mg/ℓ of $\text{Cu}(\text{NO}_3)_2$ and $\text{Cr}(\text{NO}_3)_3$ were prepared by dissolving appropriate amounts in deionised water. Stock solutions (1 mol/ℓ) of plants exudates (acetic acid, citric acid, oxalic acid and EDTA) were also prepared by dissolving appropriate amounts of exudates in deionized water. The stock solutions were stored in a refrigerator at 4°C prior to use. Working solutions were prepared by making serial dilutions using the stock solutions.

Adsorption experiments

Batch adsorption experiments were carried out by adding 0.75 g of soil into 50 ml solutions of analytes in 100 ml polypropylene plastic containers. The contents were then shaken for 3 h at 150 r/m at 25°C using an automated shaker (Labcon, USA). After shaking, the contents were filtered and the filtrate analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Spectro Genesis, Spectro, Germany).

Effect of initial concentration of elements

The effect of the initial concentrations of elements in the presence of plant exudates was studied. The concentrations of plants exudates were fixed at 0.05 mol/ ℓ. The different volumes of the elements were mixed with the plants exudates to prepare aqueous solutions of the elements with concentrations ranging from 5 to 50 mg/ℓ in both the single- and multi-component systems. The solutions (50 ml) were added to polypropylene containers with 0.75 g soil. After shaking for 3 h, the contents were filtered and the filtrate analysed using ICP-OES.

Effect of concentration of exudates

The effect of the concentration of exudates on elemental adsorption was determined. Elemental solutions of concentration 10 mg/l were mixed with varying concentrations of plant exudates (0.01, 0.05 and 0.1 mol/ℓ). The mixtures were shaken with 0.75 g soil for 3 h at 150 r/m and filtered; the filtrate was analysed using ICP-OES.

Data treatment

The amount of elements adsorbed onto the agricultural soil was calculated using the mass balance equation expression (Chisholm-Brause et al., 2001):

$$q_e = \frac{(C_i - C_e)V}{M}$$

where: q_e (mg/g) is the adsorption capacity; C_i and C_e (mg/ℓ) are the initial and equilibrium metal concentrations, respectively; V is the solution volume (ℓ) and M is the amount of adsorbent (g).

Speciation modelling

The determination of elemental species under varying conditions (pH, solution composition and concentration) was done using the PHREEQC geochemical modeling code (Parkhurst and Appelo, 2013). PHREEQC is a computer program that is designed to perform aqueous geochemical calculations according to the inputs provided that suits the solution of interest. It

uses a C and C++ platform to perform thermodynamic-based calculations of reactions and species dominance. When performing the geochemical modeling, the pH, elements (and their concentrations) and temperature must be specified in the input file. The database used should contain adequate information about the elements and their reactions in order to get appropriate results.

Results

Characterisation

The agricultural soil used had the following composition: SiO₂ (74.7%), Al₂O₃ (11.44%), FeO (5.09%), MgO (3.69%), CaO (2.73%), Fe₂O₃ (0.63%), TiO₂ (0.455%), Cr₂O₃ (0.222%), K₂O (0.2%) and Na₂O (0.15%) with a loss on ignition (LOI) of 13.4%. The results pointed to a clayey type of soil, confirming findings by other researchers on soils in the same area (Ochieng, 2002; Tutu et al., 2009). Clays contain aluminosilicate minerals which have ion exchange sites that make them good adsorbents and ion exchange surfaces (Davis and Kent, 1990). Alumina surfaces have terminal –OH groups which can be deprotonated and bind strongly the positively charged ions (McBride, 1994). Silanols (depicted by SiO₂) can also be deprotonated, leading to the adsorption of elements onto them. The PZC and CEC of the soil were found to be 8.3 and 51.6 meq 100g⁻¹, respectively. The FTIR spectrum had peaks at approximately 3600 and 3400 cm⁻¹, showing evidence of the presence of N-H and O-H functional groups, respectively which can also increase the adsorption capacity of the elements onto the soil. Results from PXRD showed that the dominant minerals in the soil were Al₂O₃, SiO₂, CaO and montmorillonite, the latter further pointing to the clayey nature of the soil.

The effect of the initial concentration of elements in the presence of plant exudates on the adsorption

The adsorption of elements in single-component systems in the absence of exudates were conducted in order to compare with the adsorption in the presence of exudates. The results for the effect of the concentration of elements in the absence and presence of plant exudates are shown in Fig. 2 and Figs. 3 to 6, respectively. The presence of plant exudates was found

to suppress the adsorption capacities of the elements onto the soil. In the absence of plant exudates, the maximum adsorption of elements at equilibrium (Fig. 2) after 3 h, were approximately 0.32, 0.64, 1.29 and 3.3 mg g⁻¹ at 5, 10, 20 and 50 mg/l of elemental concentration, respectively. The adsorption capacities were not significantly different at all. However, these capacities were reduced significantly in the presence of plant exudates. This implied that the mobility of the elements to unconfined aquifers and their bioaccessibility were increased. These findings were substantiated in other studies (Lombi et al., 2001; Wu et al., 2003; Luo et al., 2008). The following sections address the effect of each exudate on the adsorption of the elements.

The effect of acetic acid

The results for the effect of acetic acid on the adsorption capacity of Cu and Cr as the concentration of elements increased from 5 – 50 mg/l are presented in Fig. 3. The adsorption capacity for Cu was reduced significantly by the presence of acetic acid. The dominant species of copper in the presence of acetic acid were: Cu(acetate)₂ (33%), Cu(acetate)⁺ (50.5%), Cu(acetate)₃⁻ (0.33%) and free Cu²⁺ (15.9%) at 10 ppm, as determined by PHREEQC. The percentage reductions on the adsorption capacity of Cu were 7, 24, 33 and 42% at 5, 10, 20 and 50 mg/l, respectively. Thus, the mobility of Cu would potentially increase in the presence of acetic acid. The reductions in the adsorption of Cu can be attributed to the lack of binding sites on the soil since; the Cu complexes formed with acetic acid were large, thus preventing further adsorption of other complexes.

Though acetic acid had a significant effect on the adsorption of Cr ($p < 0.05$), the effect was less than that for Cu and this might be due to the higher free Cr species (35%) which were readily adsorbed by the soil compared to 15% of free Cu species which were available for adsorption. Abdalazeem and Elmugdad (2015) reacted Cr with acetate and found that only ML and ML₂ complexes form, namely Cr(acetate)₂²⁺ and Cr(acetate)₂⁺. This was confirmed by PHREEQC in this study. These species just like the free Cr species can also be adsorbed onto the surface of the soil but due to their large size, some of the species were prevented from adsorbing onto the soil due to the lack of available sites for adsorption as is the case with Cu. The PHREEQC also showed that in the presence of acetic acid, Cr(acetate)₃ was in significant amount and led to the reduction in the adsorption of Cr because it does not have a

charge that can be attracted to the charged soil surface. Thus, in the presence of acetic acid, Cu and Cr will be bioaccessible and reach the shallow groundwater.

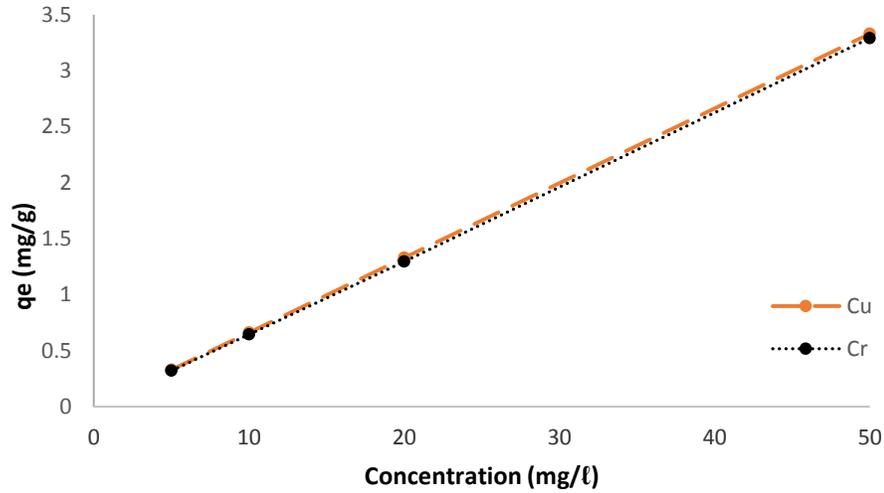


Figure 2: Effect of initial concentration of elements in the absence of plants exudates on the adsorption of elements in an agricultural soil (temp = 25°C, pH 5, mass = 0.75 g, volume = 50 mL, contact time = 3h) (n = 3 and RSD < 10%).

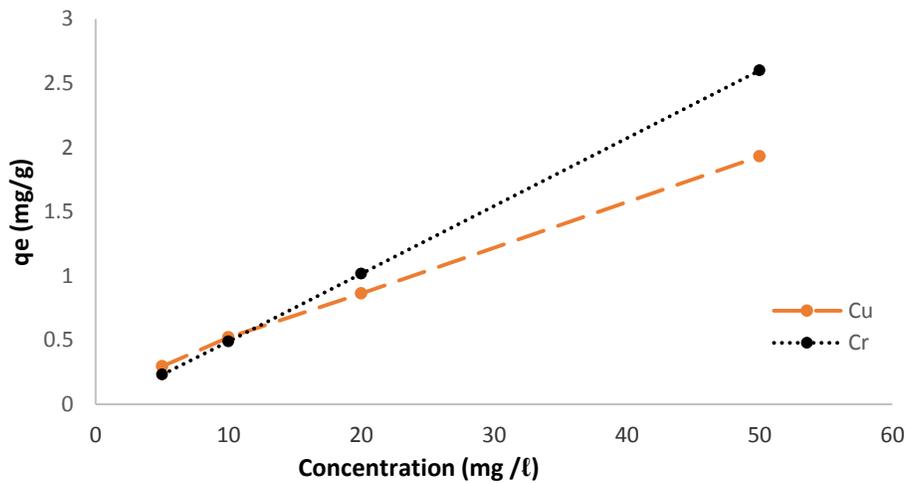


Figure 3: Effect of initial concentration of elements in the presence of acetic acid on the adsorption of elements in agricultural soil (temp = 25°C, pH 5, mass = 0.75 g, volume = 50 mL, contact time = 3 h, concentration of exudate = 0.05 mol/l) (n = 3 and RSD < 10%).

The effect of citric acid

Citric acid, a tri-dentate complexing agent, is one of the readily released exudates from plants and one of the best complexing agents found in soils (Robert and Berthelin, 1994; Harris, 2010). Previous studies have shown that it has the ability to form complexes with positively charged elements (Chen et al., 2003). The results for the effect of citric acid on the adsorption of Cu and Cr are presented in Fig. 4. Citric acid was observed to have a very significant effect on the adsorption of Cu and Cr ($p < 0.05$) for both cases. The percentage reductions were ~70% and ~38% for Cu and Cr, respectively compared to adsorption in the absence of citric acid at all concentrations. The high reduction observed with Cu can be attributed to the higher stability constant of Cu citrate ($\log K = 6.1$) compared to 5.3 of Cr (Furia, 1972; Mabbett et al., 2002). Thus, complexes formed with Cu were more favoured than those formed with Cr. The adsorption in the presence of citric acid was very low. Therefore the presence of citrate in the soil will complex Cu and prevent its adsorption onto the soil. Citric acid can also desorb elements from the soil, thus whilst it was complexing to Cu it was also removing other elements which are already in the soil, since some of the elements such as Ca and Mg which were not in the initial solution were detected by ICP-OES. From PHREEQC, the dominant Cu species in the presence of citric acid were $\text{Cu}(\text{citrate})^-$ (57.8%) and $\text{Cu}(\text{citrate})_2^{4-}$ (42%) at 10 mg/l and the small amount of Cu adsorbed may be the free Cu^{2+} as well as some of the Cu complexes. The percentage reductions were 73, 73, 81 and 88% at 5, 10, 20 and 50 mg/l respectively. The Cr species formed in the presence of citrate were Cr-citrate, $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_2^+$. The low adsorption capacity observed was due to the citrate complexes and the large size of the Cr-OH species formed since the Cr hydroxide species could be adsorbed onto the surface of the soil. The percentage reductions in the adsorption of Cr were 37, 61, 39 and 55% at 5, 10, 20 and 50 mg/l. Thus, the presence of citric acid in the soil will likely increase the metals entering unconfined aquifers and their bioaccessibility.

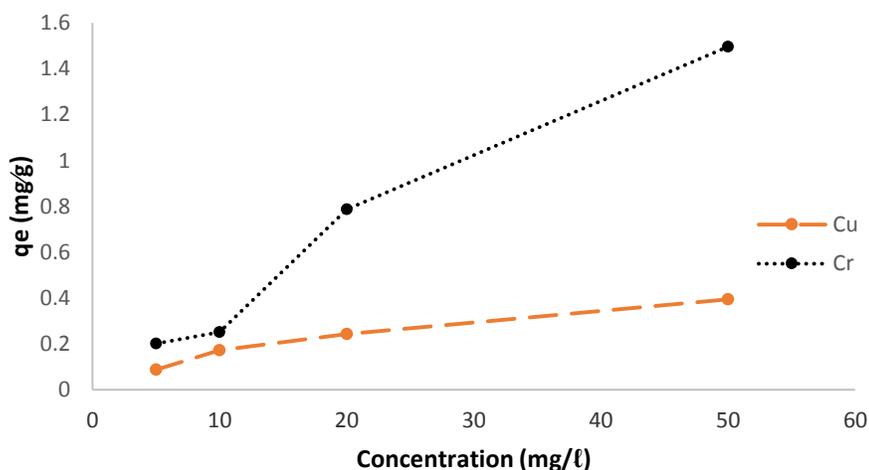


Figure 4: Effect of initial concentration of elements in the presence of citric acid on the adsorption of trace elements in agricultural soil (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 ml, concentration of exudate = 0.05 mol/l) (n = 3 and RSD < 10%).

The effect of oxalic acid

The results for the effect of oxalic acid on the adsorption of Cu and Cr are presented in Fig. 5. The results pointed to a significant difference in the adsorption. The effect was more prevalent with Cu than with Cr. Being a smaller cation, Cu^{2+} was almost all complexed by oxalate hence the effect. The adsorption capacity of Cu was very negligible, if at all, implying that almost all the Cu was solubilised making it mobile to the immediate aquifer and bioaccessible. The critical stability constant for the Cu-oxalate complex ($\log K = 6.23$) is higher than that for the Cr-oxalate complex ($\log K = 3.78$) which means that stronger bonds were formed between Cu and oxalate (Harris, 2010; Abdalazeem and Elmugdad, 2015). The lesser effect of oxalic acid observed on Cr adsorption could have been due to the low stability of the complexes formed as well as larger atomic radius of Cr since oxalate is a very small chelating agent, hence chelation was not highly favoured. Nonetheless, since the adsorption capacity was significantly decreased (by 20% at all concentrations), oxalic acid had a recognisable effect on the adsorption of Cr which can be attributed to the complexed Cr. Therefore, oxalate from plants grown on the plot will increase the probability of Cu and Cr reaching the shallow unconfined aquifers.

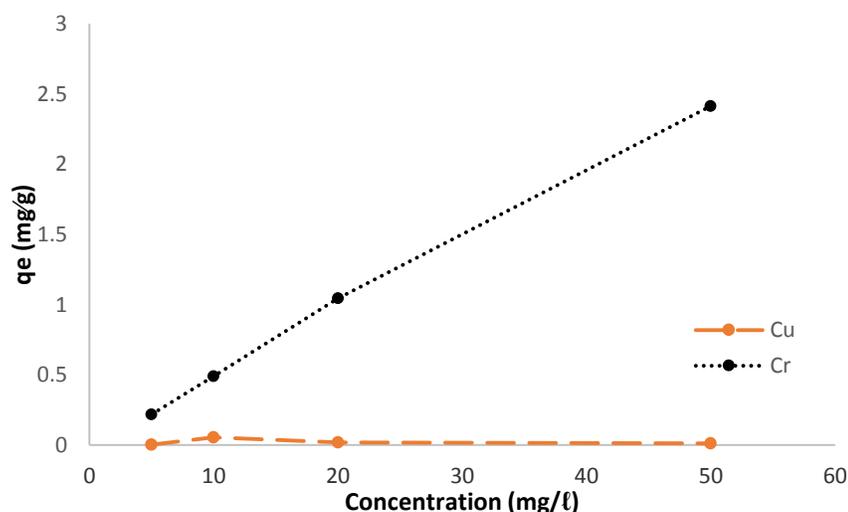


Figure 5: Effect of initial concentration of elements in the presence of oxalic acid on the adsorption of trace elements in agricultural soil (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 ml, concentration of exudate = 0.05 mol/l) (n = 3 and RSD < 10%).

The effect of EDTA

The effect of EDTA on the adsorption of Cu and Cr was studied and its effect on the adsorption of the elements onto the soil is shown in Fig. 6. A greater complexation effect (chelate effect) was observed for Cr than obtained for the other exudates. The great effect was because EDTA is a large chelating agent and it has the highest negative charge when it is fully deprotonated due to the higher number of acidic hydrogens. Hence, the interaction with positively charged cations was high even with the larger Cr ion. EDTA tends to form strong complexes with elements in a stoichiometric ratio of 1:1 regardless of the charge on the element (Harris, 2010). The concentrations observed for Cu after equilibration time were more than the initial concentrations used, meaning that EDTA formed complexes with some of the Cu elements which were already in the agricultural soil, thus removing them from the soil. Studies have shown that EDTA can be used as leaching agents for metals due to the complexation reactions they undergo with the elements already adsorbed onto the soil surfaces (Chen, 2003; Huaying et al., 2014). Thus, whilst EDTA was forming complexes with the elements under study, it was also desorbing the ones which were already adsorbed hence a low adsorption capacity of Cu was observed. Moreover, the results from ICP-OES showed that there were some elements which were not in the initial solution. Thus, EDTA

did not only desorb Cu but other elements such as Ca and Mg. The stability constants ($\log K$) of the complexes formed between the analytes and EDTA are higher than those of other organic acids. CuEDTA has a higher $\log K$ value of 18.80 compared to CrEDTA with a value of 13.61, thus explaining the higher adsorption of Cr. The higher $\log K$ value for CrEDTA is the reason why the greatest effect on adsorption was observed. Even in the presence of Cr, EDTA still desorbed some of the elements which were already in the soil. Therefore, the presence of EDTA in the soil will enhance the mobility of Cu and Cr to unconfined aquifers and increase their bioaccessibility.

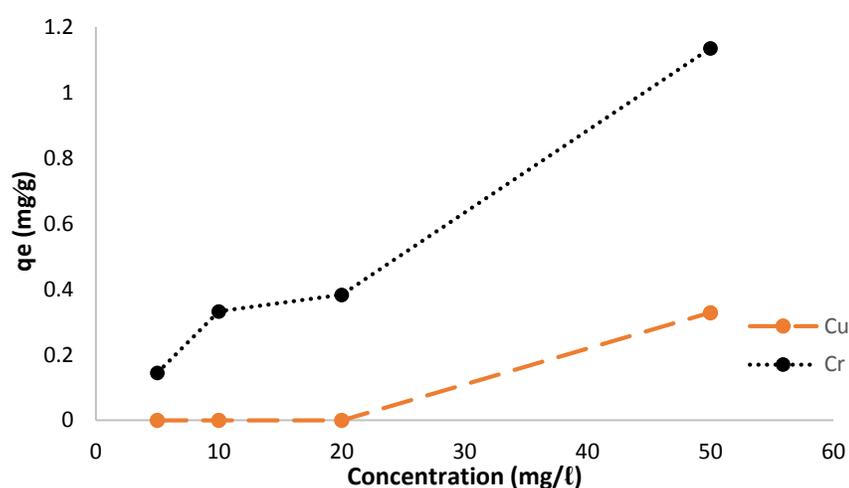


Figure 6: Effect of initial concentration of trace elements in the presence of EDTA on the adsorption of elements in agricultural soil (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of exudate = 0.05 mol/L) (n = 3 and RSD < 10%).

The effect of the concentration of plant exudates on the adsorption of elements

The effect of the concentration of plant exudates on the adsorption of Cu and Cr was studied and the results for individual exudates are presented in Fig. 7- 10.

The effect of acetic acid concentration

Fig. 7 shows the effect of acetic acid concentration on the adsorption of elements onto the agricultural soil. The adsorption of the elements decreased as the concentration of acetic acid increased. The Cu species that increased and dominated as the concentration of acetic acid

increased were $\text{Cu}(\text{acetate})_2$, $\text{Cu}(\text{acetate})^+$ and $\text{Cu}(\text{acetate})_3^-$. The increase of these species led to the reduction in the adsorption of Cu onto the soil due to the reduction of the free Cu species and an increase of large species. The large species prevented further adsorption of other species due to the lack of adsorbing sites. The $\text{Cu}(\text{acetate})^+$ species was likely to be adsorbed onto the surface of the soil just like Cu^{2+} but occupied more space than when there is just Cu^{2+} hence the reduction in adsorption. The adsorption capacity of Cu decreased as the concentration increased from 0.01 to 0.1 mol/l, therefore, the higher the concentration of acetic acid, the higher the mobility and bioaccessibility of Cu. The percentage reductions at 0.05 and 0.1 mol/l of acetic acid were 25 and 28%, respectively. For Cr, the species: $\text{Cr}(\text{acetate})_3$, $\text{Cr}(\text{acetate})_2^+$ and $\text{Cr}(\text{acetate})^{2+}$ increased as the concentration of acetic acid increased whilst the concentration of Cr^{3+} decreased. The percentage reduction on adsorption capacity of Cr in the presence of acetic acid was found to be 5, 22 and 38% at 0.01, 0.05 and 0.1 mol/l, respectively. Therefore the higher the concentration of acetic acid the more mobile and bioaccessible will the Cr be.

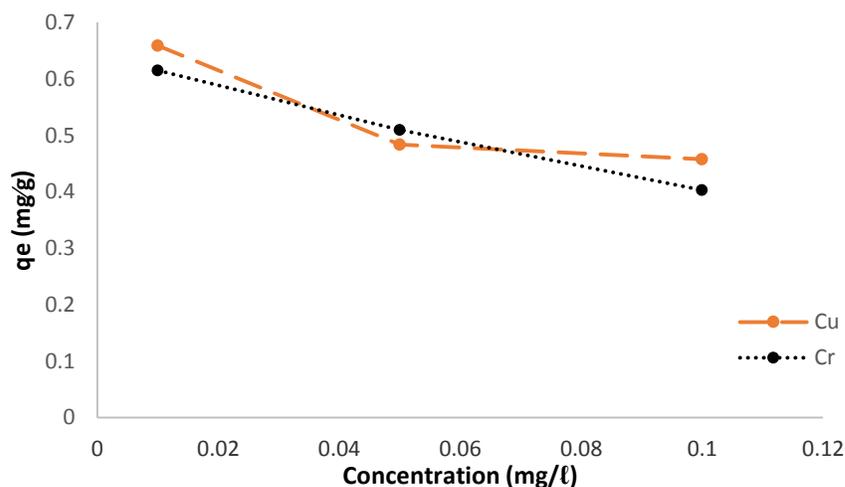


Figure 7: Effect of the concentration of acetic acid on the adsorption of elements onto the agricultural soil (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of trace elements = 10 mg/l) (n = 3 and RSD < 10%).

The effect of citric acid concentration

The results for the effect of citric acid concentration on the adsorption of Cu and Cr are presented in Fig. 8. The effect of changing the concentration of citric acid on the adsorption of elements was found to be different for both elements. The adsorption of Cr decreased while Cu was hardly affected. Thus, the adsorption of Cu was not significantly affected by the increasing concentration of citric acid. Though the adsorption did not depend on the concentration of citric acid, the effect that the acid had on adsorption capacity of Cu was high as observed also in Fig. 4. As the concentration of citric acid increased, the concentration of free Cu^{2+} species which can be adsorbed did not change significantly hence the adsorption capacity was almost the same throughout. The adsorption capacities of Cu decreased by approximately 74% for all concentrations of acid. The adsorption capacity of Cr was seen to increase with increasing concentration of citric acid. The species $\text{Cr}(\text{OH})^{2+}$, Cr^{3+} and $\text{Cr}(\text{OH})_2^+$ increased as concentration of the acid increased and these were likely more capable of adsorbing onto the soil surface. However, it should be noted that the adsorption of Cr decreased greatly from when there was no citric acid, thus, the presence of citric acid reduces the adsorption of Cr but, the effect becomes slightly less as concentration of citric acid increases. Thus, the probability of Cr reaching groundwater will be high in the presence of acetic acid, but will be slightly less when the concentration of citric acid is high. The reduction of Cr adsorption was due to the complexation that occurred between citric acid and Cr. The mobility of Cu and Cr to unconfined groundwater aquifers will be enhanced in the presence of citric acid.

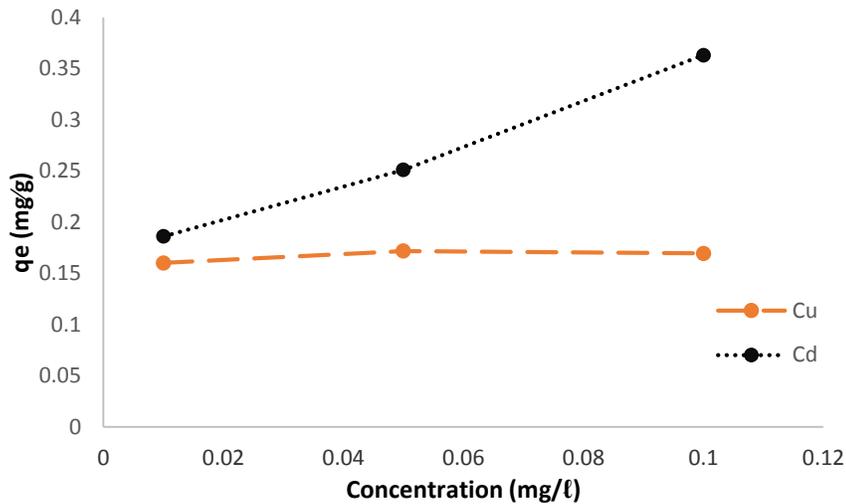


Figure 8: Effect of the concentration of citric acid on the adsorption of elements onto the agricultural soil (temp=25°C, pH 5, contact time=3h, mass = 0.75 g, volume = 50 mL, concentration of trace elements = 10 mg/l) (n=3 and RSD < 10%).

The effect of oxalic acid concentration

Oxalic acid is a diprotic acid that has been used as a chelating agent so as to desorb some elements from the soil (Luo et al., 2006). The results for the effect of oxalic acid concentration are shown in Fig. 9. In this study, oxalic acid was seen to decrease the adsorption of Cu and Cr. The adsorption capacity of Cu onto the soil was affected more than that of Cr. This observation can be attributed to the interaction of Cu with oxalate being highly favoured due to the small ionic radius of Cu; since, oxalic acid in itself is small. The stability constant of Cu:oxalate in 1:1 ratio is around 6.23 but, the ratio of 1:2 is also possible with a stability constant of 10.3. Thus, the higher probability of preventing the adsorption of Cu onto the agricultural soil was due to the complexes formed in the ratio of 1:2 leading to strong interactions between Cu and oxalate. The species formed in 1:2 ratio was $\text{Cu}(\text{oxalate})_2^{2-}$ as predicted by PHREEQC. These species were increased as the concentration of the acid increased and prevented the adsorption onto the soil. Even small concentrations of oxalic acid had a significant effect on the adsorption of Cu due to the strong complexes formed. The concentration of 0.01 mol/l did not have much effect on the adsorption of Cr, but as the concentration increased, the effect became more pronounced. As the concentration

increased, more oxalate ions increased and reacted with more of the Cr species thus, decreasing the free Cr ions that could be adsorbed onto the soil. The percentage reductions on the adsorption capacity of Cr were 17, 24 and 50% at 0.01, 0.05 and 0.1 mol/l, respectively. The adsorption of Cr was higher than that of Cu because of its lower stability constant with oxalate. The results obtained agreed with those for the effect of concentration of elements where the adsorption of Cr was higher than that of Cu which was found to be around zero in the presence of oxalic acid (Fig. 5). The exuded oxalic acid by plants will reduce the adsorption of Cu and Cr onto the soil hence increase their concentrations in groundwater.

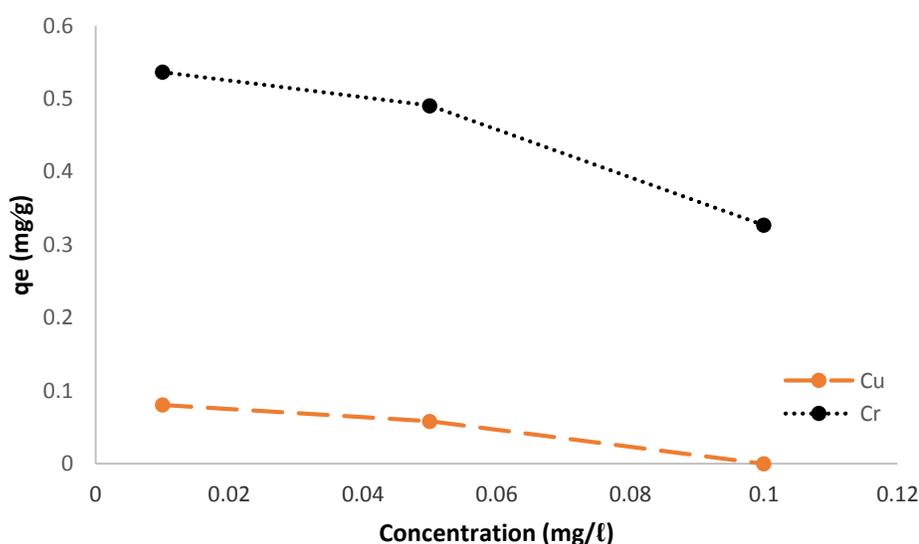


Figure 9: Effect of the concentration of oxalic acid on the adsorption of elements onto the agricultural soil (temp = 25°C, pH 5, contact time = 3h, mass = 0.75 g, volume = 50 mL, concentration of trace elements = 10 mg/l) (n=3 and RSD < 10%).

The effect of EDTA concentration

The results for the effect of EDTA concentration on the adsorption of Cu and Cr are presented in Fig. 6. The adsorption capacity of Cu was highly affected by the presence of EDTA. The concentration of Cu after equilibration time was observed to be more than the initial at 0.1 mol/l meaning, that the concentration was also due to the desorbed Cu which was already in the soil. This was also observed with the effect of the concentration of the elements (Fig. 6) where the concentrations of Cu after the adsorption time was higher than

the initial used at 5 – 10 mg/ℓ, indicating the desorption of the elements from the soil. Wu et al. (2003) exposed EDTA to the soil and monitored the desorption capacity of Cd and Cu from the soil and found that the concentrations of the elements increased after the exposure time and that the solubility of the elements increased, leading to high bioavailability of the elements. As observed in this study, even a small concentration (0.01 mol/ℓ) of EDTA significantly decreased adsorption of Cu and Cr through chelation and increased their mobility. The dominant species for Cu was CuEDTA^{2-} , which increased as the concentration of EDTA increased as confirmed by PHREEQC. The adsorption of Cr increased slightly as the concentration of EDTA increased. The dominant species of Cr were: $\text{Cr}(\text{EDTA})^-$ and $\text{CrOH}(\text{EDTA})^{2-}$ which were in higher amounts especially at higher EDTA concentrations (confirmed by PHREEQC) and led to the reduction in the adsorption capacity of Cr. The species: Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$ which were adsorbed onto the soil due to their small size, increased as the concentration of EDTA increased, thus leading to a slight increase in the adsorption of Cr. It is noteworthy that though the adsorption of Cr increased, the complexation affected the overall concentration of the free Cr species, hence the adsorption was lower than in the absence of EDTA. Therefore, the mobility of Cu and Cr in the soil to groundwater will increase in the presence of EDTA.

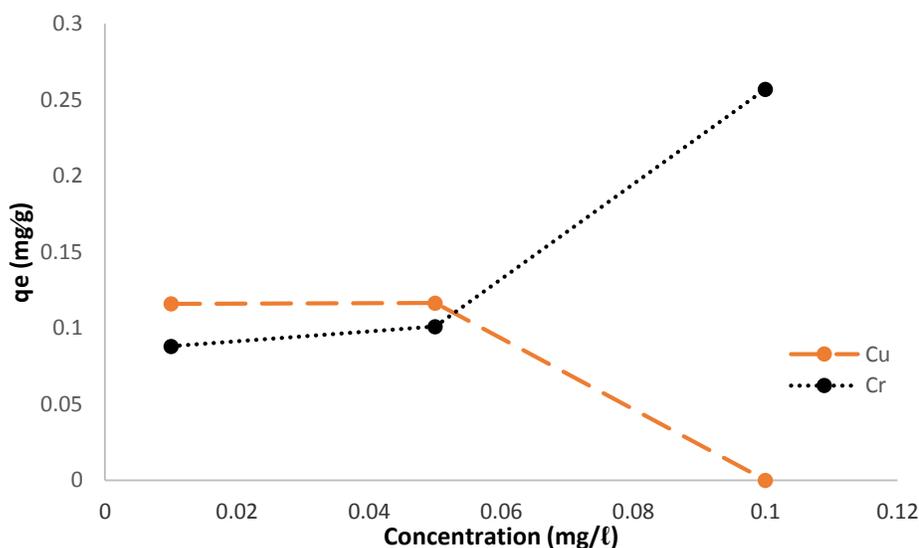


Figure 10: Effect of the concentration of acetic acid on the adsorption of elements onto the agricultural soil (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of trace elements = 10 mg/ℓ) (n=3 and RSD < 10%).

Conclusion

This study demonstrated that the presence of plant exudates such as acetic acid, citric acid, oxalic acid and EDTA decrease the adsorption capacities of Cu and Cr. The sequence that they followed in terms of their effect was: acetic acid < citric acid < oxalic acid < EDTA for Cu and acetic acid < oxalic acid < citric acid < EDTA for Cr. At similar concentrations of the exudates, EDTA was found to have more effect in complexing the metals, thus rendering them more mobile. The adsorption of Cu decreased as its concentration increased. Some of the elements that were already in the soil were desorbed by oxalic acid and EDTA.

Overall, the study pointed to the possibility of mobilising Cu and Cr and possibly other elements to the nearby groundwater as a result of reduced adsorption of the elements in the presence of exudates. This mobilisation also implies that the elements become more bioaccessible.

Acknowledgement

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CHAPTER 6

Effect of fertilisers on the adsorption of cadmium, copper and chromium

The following paper focuses on the effect of fertilisers on the adsorption of cadmium, copper and chromium

Contribution to the paper: Lead author, conducted the experimental work, analysed and interpreted the results and performed modelling

This paper will be submitted to: South African journal of Chemistry (SAJC)

The effect of fertilisers on the adsorption of Cadmium, Copper and Chromium on an agricultural soil impacted by mining activities

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Abstract

Agrochemicals such as fertilisers and pesticides are constantly applied to agricultural soils to improve the fertility of the soil for better crop production. The presence of fertilisers may affect the mobility and bioavailability of elements in the soil which in turn, can affect living organisms. In this study the effect of fertilisers (ammonium nitrate, calcium chloride and ammonium phosphate) on the adsorption of cadmium (Cd), copper (Cu) and chromium (Cr) onto an agricultural soil from a plot was considered. The plot is in the vicinity of smelting and mining operations which increase the accumulation of the elements in the soil. These elements can be absorbed by plants and also reach groundwater. The effect of certain parameters on the adsorption of trace elements by the soil studied: initial concentrations of the elements (5 – 50 mg/L), concentrations of fertilisers (0.01 – 0.1 mol/L) and pH (3 - 8). The composition of the agricultural soil was; SiO₂ (74.7%), Al₂O₃ (11.44%), FeO (5.09%), MgO (3.69%), CaO (2.73%), Fe₂O₃ (0.63%), TiO₂ (0.455%), Cr₂O₃ (0.222%), K₂O (0.2%) and Na₂O (0.15%) with a loss on ignition (LOI) of 13.4%. The results indicated that the initial concentrations of the elements had no significant effect ($p > 0.05$) on the adsorption capacities of Cu and Cr when fertilisers are present at pH 5 but, ammonium nitrate and calcium chloride decreased the adsorption capacity of Cd. The adsorption of Cd onto the soil was reduced as the concentration of fertilisers increased. Cu and Cr adsorption was insignificantly ($p > 0.05$) decreased by the increase in concentration of ammonium phosphate. The adsorption of Cd was lower than that of Cu and Cr at all pH values. Ammonium nitrate and calcium

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chloride affect the adsorption of Cd at all variables under study and Cr was affected slightly by ammonium phosphate at different fertiliser concentrations and pH of the solution. The agricultural soil was found to be an effective adsorbent in preventing the mobility of Cu and Cr in the presence of fertilisers but not for Cd whose adsorption was significantly affected by the presence of ammonium nitrate and calcium chloride.

KEYWORDS: adsorption, agricultural soil, Cd, Cu, Cr, fertilisers.

Introduction

Soil is an important natural resource which plays a number of vital roles. It is used for food production, regulating the storage of water and solutes, filtering, protecting the quality of water etc. The soil's ability to perform its roles can be decreased due to some factors such as erosion and pollution. There are a number of factors leading to soil pollution such as mining activities, agriculture (through the application agrochemicals such as fertilisers and pesticides) as well as industrial activities. Agrochemicals are continually added to agricultural soils to increase the levels of nitrogen, sulfur and phosphorus to improve crop growth and production (Jones and Jarvis, 1981; Wuana and Okieimen, 2011). Despite the importance of agrochemicals, studies have shown that their continued application leads to the accumulation of elements in agricultural soils which can be absorbed by plants and can also reach groundwater (Li et al., 2016). These elements become highly toxic to living organisms when they exceed threshold limits as set out by the World Health Organization (WHO) and the European Union (Kabata-Pendias, 1995; Selene et al., 2003; Chen et al., 2006; Nouri et al., 2008). The toxicity nature of these elements is very alarming especially to humans, as some are carcinogenic whilst others are responsible for disorders such as impaired development in infants, kidney failure, mental deterioration, insomnia as well as problems with the circulatory system (Scragg, 2006; NSC, 2009). Soil pollution caused by trace elements in the presence of fertilisers has been one of the major concerns in some countries due to their continued application and the persistence of these elements (Alloway, 1990). Mining activities are one of the major culprits of elements accumulation in soils whose mobility and bioavailability can be influenced by fertilisers applied in the soil.

Adsorption and dissolution of elements in soils determine their leachability and mobility. Adsorption is a process whereby elements attach to the surface of the soil and depending on the properties of both the soil and the elements, the adsorption can be weak, leading to reversible adsorption of the elements or strong leading to irreversible or slightly reversible adsorption. Strong adsorption of elements to the soil prevents their mobility in the soil, thus, reducing the probability of groundwater contamination (Grant et al., 2010; Christine et al., 2006). Soil pH, composition of the soil and clay content, competing elements and fertilisers in the soil are important factors that determine the strength of adsorption of the elements onto the soil (Brümmer, 1986; Ross, 1994; Gray et al., 1999; Sukreeyapongse et al., 2002; Zhu *et al.*, 2011; Gupta *et al.*, 2014). It is therefore crucial, in agricultural areas where no remediation techniques are applied, to determine the effectiveness of the soil is in adsorbing elements, taking into account the factors stated.

Grant *et al.* (1999) found that the concentration of cadmium was increased upon addition of NPK fertiliser which led to high uptake in Canola, oil seed flax and spring wheat. Phosphate fertiliser was found to increase the mobility of arsenic in the soil (Li *et al.*, 2016). Other factors such as the application of sewage sludge which is constantly applied in agricultural areas also affect the mobility of elements due to the presence of dissolved organic matter (DOM) and high organic strengths of soil solutions (Ashworth and Alloway, 2004). Thus the adsorption studies of elements onto an agricultural soil in the presence of fertilisers are of importance to determine the fate of the elements, hence, the risk assessment measure.

Depending on the composition of the soil, the rate of mobility of trace elements can be reduced as they can be strongly adsorbed on the soil. The adsorption of elements in sandy soils (low organic matter and clay content) is low compared to clay soils (high organic matter and clay content). Also, soil properties such as pH, conductivity, point of zero charge and others can determine the extent of adsorption (Chen *et al.*, 2006). Functional groups on the surface of the soil are also very crucial for adsorption. Hydroxyl groups on the surface can donate their

protons to the surrounding solution and take up trace elements. Clay minerals and metal oxides strongly adsorb positively charged trace elements (Bradl, 2004). Studies have shown that adsorption of trace elements is dependent on pH (Heidemann, 1959). Generally, low pH ranges lead to low adsorption of trace elements whilst intermediate pH ranges lead to high adsorption due to the increase of negatively charged surface sites (Bradl, 2004). Some fertilisers such as lime affect the pH of the soil, hence the adsorption of trace elements. Thus, the effect that pH has on adsorption should be studied to speculate what could be happening in the actual environment with their presence. The type of soil in which trace elements are present is also very important as it determines the extent of adsorption. The presence of clay minerals and humic substances in the soil leads to better adsorption of elements than coarse-grained soils due to their high surface area. The holding capacity of the soil for trace elements also known as cation exchange capacity (CEC) determines the extent of adsorption. Since clay minerals have high surface area, they have high CEC hence high ability of holding trace elements (Crawford *et al.*, 1993; Bradl, 2004).

Trace elements under study are believed to be in higher quantities in the agricultural soil used in the study due to the application of fertilisers. Li *et al.*, (2016) reported that the concentrations of cadmium (Cd) and copper (Cu) were higher in a greenhouse land where manure and fertilisers were used but other lands where no fertilisers were used had less concentrations. Cd and Cu are well known impurities in fertilisers and they are also found in the water used for irrigation, but also occur with the processing of platinum and other minerals found in the area under study. Though they may be introduced into the soil, they are also naturally present in the soil and thus the anthropogenic activities add to the already available concentrations. Cr is very high in the platinum ore. These elements are very toxic especially when inhaled or ingested. Cu is one of the most widely used elements in the world but when it is in high doses and uncontrollable, it becomes dangerous to life forms.

This study will focus on the behavior of elements (Cd, Cu and Cr) in the presence of fertilisers (ammonium phosphate, ammonium nitrate and calcium chloride) on

an agricultural soil impacted by mining activities. The agricultural plot is in the vicinity of mining operations (platinum and Platinum Group Elements (PGEs)). Thus the quantity of the elements in the soil is influenced by both the mining operations as well as agrochemicals used. The objective is to determine how the soil will adsorb elements in the presence of fertilisers since previous studies have shown that mobility of the elements can be influenced by their presence (Caoa et al., 2003). This can occur *via* reactions that increase the adsorbent-adsorbate interactions or precipitation as well reactions that prevent trace elements from dissolving (Agarwal et al., 2006; National Research Council, 1994). The study will determine the partitioning of pollutants into labile and soil-retained fractions. Geochemical models will be applied to study processes determining the interaction of nutrients and trace elements with an agricultural soil.

The results of this study are expected to be useful for establishing risk assessment benchmarks for agricultural soils of a similar nature.

Materials and methods

Study site

The soil used in this study was collected from an agricultural plot in Rustenburg, a city in the North West Province, South Africa (Figure 1). The plot is in the vicinity of mining operations whereby fertilisers, manure and water used for irrigation are constantly applied. The smelting operations surrounding the plot produce platinum group elements (PGEs), furthermore, base metals such as Cu, Cr and Zn are found in host ores of PGEs and thus there are trace elements that reach the agricultural soil and have the potential to harm the health of people living near the area and those eating the crops.

Ochieng' (2002) sampled soils from the same area and found that the sites closer to the mining operations had higher concentrations of metals than the sites further away from the mining operations. This suggested that the accumulation of metals in the soils could be increased by these operations. He also found that the concentrations of metals in the soils differs depending on the composition of the

soil profile. Some metals were found to decrease in concentration down the soil profiles whilst others were increasing (Ochieng', 2002). Another secondary source of contamination to the surrounding soils could be pesticides and fertilisers.

The soils in this area are described as the black tuff (podsollic) which are dominated by montmorillonite and illite minerals. The soil composition in the area differs with depth. The top layer (0-2 cm) is fine black, the second (2-20 cm), third (20-40 cm) and fourth (40-50 cm) layers consists of black clay, the fifth (50-60 cm) layer consists of black and white soil interface and the last (60-70 cm) layer is weathered bedrock (norite) (Munsell, 1975; Ochieng', 2002). The soil was found to be alkaline and the alkalinity increased down the soil profile with pH values starting off at around 7.0 in the upper layer and increasing to around 8.9 in the bottom layers. The conductivity of soils near the mining operations is higher than those which are further away. When considering the soil profile, conductivity is moderate near the surface, high at the middle layers and low at the bottom. The highest concentration of metals were found in the middle layers of the soil. The middle layers contain much of the clay component of the soil (Ochieng', 2002).

Characterization of agricultural soil

The soil collected was air dried and ground to remove lumps. The ground soil was then passed through a 2 mm sieve. The chemical and physical properties of the soil were determined. The mineralogy of the soil was determined using Powder X-ray diffraction (PXRD) (Karlsruhe, Germany) and X-ray fluorescence (XRF) (PANalytical, Netherlands) was used to determine mineral composition of the soil. FTIR (Tensor 27, Bruker, Germany) was used for the identification of functional groups present in the soil. The point of zero charge (PZC) of the soil was determined.

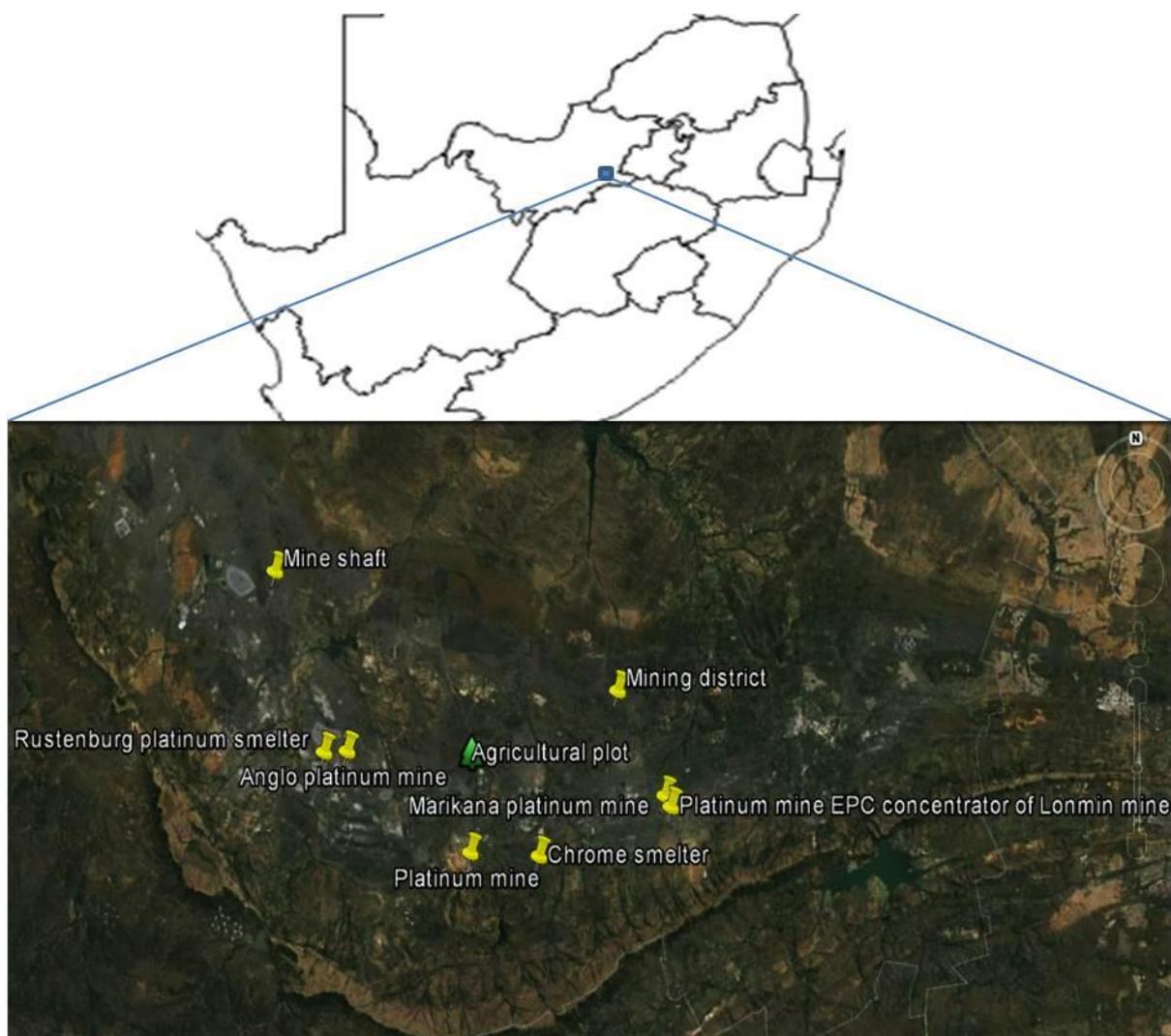


Figure 1: The vicinity of the study area

Reagents and standards

All chemicals used were of analytical grade and bought from Sigma Aldrich, South Africa. Stock solutions of 1000 mg/L of analytes were prepared by dissolving appropriate amounts of nitrate forms with deionised water and filling to the required volume. Required concentrations were prepared by serial dilutions from the stock solutions. 1 M stock solutions were prepared by dissolving appropriate amounts of the salts with deionized water.

Adsorption experiments

Batch adsorption experiments were conducted in this study by shaking 0.75 g of soil with 50 mL of a mixture of analytes and fertiliser solutions in 100 mL polypropylene plastic containers. The contents were shaken at the speed of 150 r/m using an automated Shaker (Labcon, USA). The contents were then centrifuged and filtered after the adsorption time and the concentrations of the filtrates were measured using ICP-OES (Spectro, Kleve, Germany).

Determination of concentration of trace elements desorbed from the soil.

In order to get the exact concentration of trace elements at equilibrium, the concentrations of the elements (Cd, Cu and Cr) already in the soil that could possibly be desorbed from the soil due to the presence of fertilisers had to be accounted for. This was done to determine if the fertilisers would desorb the elements from the soil during the study since it was reported before that elements can be desorbed by fertilisers (Li *et al.*, 2016; Yamaguchi *et al.*, 2009; Grant *et al.*, 2010). However, the main focus of this study is based on the reaction of trace elements and fertilisers with an agricultural soil. To determine the concentration of desorbed elements, 50 mL of 0.1 M of fertilisers (ammonium nitrate, ammonium phosphate and calcium chloride) were mixed with 0.75 g of an agricultural soil in polypropylene containers. The contents were then shaken at 150 r/m for 3 hours and centrifuged at the speed of 3000 r/m at room temperature (25°C). The solution was filtered and analyzed using ICP-OES. The results are not included in this study but they were used to determine the exact concentration adsorbed by the soil.

Effect of initial concentration of trace elements

Since the concentrations of trace elements introduced to the soil may vary, it is important to determine how they will be affected by the presence of fertilisers. To accomplish this, the concentration of fertilisers was fixed at 0.05 M and only that of trace elements was varied. The concentrations used were; 5, 10, 20 and 50 mg/L both the individual and a mixture of trace elements. The mixtures were

separately prepared with 0.05 M of individual fertilisers into 50 mL volumetric flasks which were added into polypropylene containers with 0.75 g soil. After shaking at room temperature (25°C) at the speed of 150 r/m for 3 hours, the contents were centrifuged and filtered. The concentrations at equilibrium were determined using ICP-OES.

Effect of fertilisers at different initial concentrations

The effect of initial concentration of fertilisers on adsorption of cadmium, copper and chromium onto the agricultural soil was determined by preparing 10 mg/L of analyte (Cd, Cu, Cr and a cocktail) solutions with fertilisers at different concentrations (0.01, 0.05 and 0.1 M) at room temperature. 50 mL of the mixtures of trace elements with fertilisers were added to 0.75 g soil in polypropylene containers. The solutions were centrifuged at 3000 r/m and filtered using filter paper after 3 hours of shaking at 150 r/m at room temperature (25°C) and analyzed.

Effect of pH

The effect of pH on the adsorption capacity of cadmium, copper and chromium onto the agricultural soil with the presence of fertilisers was investigated. 50 mL of 0.05 M individual fertilisers were prepared with individual trace elements or the mixture of trace elements and the pH was adjusted (3, 5 or 8) using 0.01 M nitric acid and sodium hydroxide. The contents were poured into polypropylene containers containing 0.75 g of soil. The mixture of the three metals was also used to look at the effect that the elements have on each other at different pH values. The solutions with the soil were shaken at room temperature of 25°C using the speed of 150 r/m for 3 hours and they were centrifuged at 3000 r/min for 5 min after equilibrium and the supernatants were filtered and the metal concentrations were determined.

Data treatment

The amount of elements adsorbed onto the agricultural soil was calculated using the mass balance equation expression (Chisholm-Brause *et al.*, 2001):

$$q_e = \frac{(C_i - C_e)V}{M}$$

where q_e (mg g^{-1}) is the adsorption capacity, C_i and C_e (mg L^{-1}) are the initial and equilibrium metal concentrations, respectively; V is the solution volume (L) and M is the amount of adsorbent (g).

Results and discussion

Characterization

The agricultural soil used had the following composition, SiO_2 (74.7%), Al_2O_3 (11.44%), FeO (5.09%), MgO (3.69%), CaO (2.73%), Fe_2O_3 (0.63%), TiO_2 (0.455%), Cr_2O_3 (0.222%), K_2O (0.2%) and Na_2O (0.15%) as well as loss on ignition (LOI) of 13.4%. The high silica content may be the driving force in the adsorption of trace elements. Aluminosilicates (minerals composed of aluminium, silicon and oxygen) in soils are major components in clay minerals. Hence, the soil used was composed of high clay content which had a permanent structural charge and high surface area. Aluminosilicate minerals have ion-bearing sites which hold tightly the positively charged ions (Davis and Kent, 1990). Alumina surfaces have terminal $-\text{OH}$ groups which can be deprotonated and bind strongly the positively charged ions (McBride, 1994). Aluminol and silanol can be deprotonated and bind ions and since their contents are significant, there is a higher probability of trace elements adsorbing onto the agricultural soil. The PZC and CEC of the soil were found to be 8.3 and 51.6 meq/100g respectively. The results from the FTIR had peaks showing evidence of the presence of N-H and O-H functional groups which also influence adsorption of elements onto the soil. There were strong peaks of Si-O/Al-O which also lead to higher adsorption of

trace elements. PXRD was used to determine the minerals in the soil. The dominant minerals of the soil were Al_2O_3 , SiO_2 , CaO and montmorillonite.

Effect of initial concentrations of elements

The effect of initial concentration of trace elements with the presence of fertilisers (ammonium nitrate, ammonium phosphate and calcium chloride) on the adsorption of Cd, Cu and Cr was studied. Fertilisers are annually applied in agricultural soils and tend to increase the amount of trace elements in the soil along with smelting operations around. In this study, the focus was more on how the presence of these fertilisers affect the mobility of elements which are introduced into the soil. In order to determine the effect of fertilisers, adsorption studies were conducted in the absence of fertilisers and the results are shown in Figure 2. The results on how fertilisers affect the adsorption of elements at different initial concentrations are shown in Figures 3-5. Single and multi-component element systems were used. The multi-component systems were used to determine the effect that the elements may have on each other during adsorption processes.

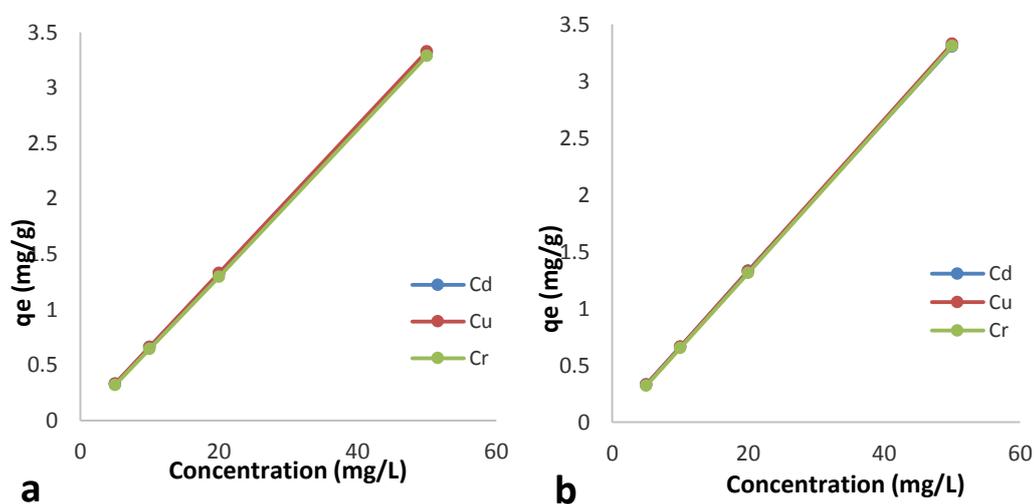


Figure 2: Effect of initial concentration of elements in the absence of fertilisers on the adsorption of elements onto an agricultural soil in the single (a) and multi-component (b) systems (temp = 25°C , pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of fertiliser = 0.05 mol L^{-1}) ($n = 3$ and $\text{RSD} < 10\%$).

Ammonium nitrate did not have an effect on the adsorption of Cu and Cr ($p > 0.05$) in both the single- and multi-component systems (Figure 3) and their adsorption was increased linearly with increasing initial concentration as in the absence of fertilisers (Figure 2). Calcium chloride and ammonium phosphate also did not affect the adsorption capacities of these elements. Only Cd was affected by the presence of the fertilisers (ammonium nitrate and calcium chloride). The Cd adsorption increased as initial concentration increased but not as much as it was in the absence of the fertilizer. This could be due to the reactions that the ions of the fertiliser undergo with the Cd ion leading to the formation of CdNO_3^+ as observed from PHREEQC. These species formed were large in size and therefore prevented some of the species from adsorbing onto the soil due to unavailability of binding sites. The decrease in adsorption of Cd was more prevalent in the multi-component system and this could be due to the occupation of binding sites by smaller Cu and Cr. Thus, Cu and Cr were more favourable for adsorption onto the soil than CdNO_3^+ which are large. Therefore CdNO_3^+ had to compete for binding sites. Moreover, studies have shown that the NH_4^+ species can be adsorbed on soil surfaces (Bruggenwert and Kamphorst, 1979; Phillips and Sheehan, 2005). Depending on the surface groups available in the soil, the monovalent cation, NH_4^+ can be highly preferred by some soil surface groups than the divalent trace elements (Phillips and Sheehan, 2005). The species formed had more effect on adsorption of Cd than the possibility of competing for binding sites.

Calcium chloride suppressed the adsorption of Cd more than fertilisers used. Just like with ammonium nitrate, the type of species formed with the elements had more effect on their adsorption onto the surface of the soil. The PHREEQC geochemical modeling showed that the chloride ions from calcium chloride reacted with Cd to form species such as CdCl^+ , CdCl_2 , CdCl_3^- and CdOHCl which prevented high adsorption of Cd onto the soil. Most of the Cd species was in the form CdCl^+ followed by the free Cd^{2+} which will be adsorbed onto the surface of the soil but also CdCl_2 and CdCl_3^- were in significant amounts. Saeki and Kunito (2012) found that in the presence of NaCl, about 83% of Cd species was in the form CdCl^+ . They also found that the free Cd^{2+} is preferred by solid surface than

the monovalent Cd hence low Cd adsorption capacity was observed (Swedlund *et al.*, 2003; Saeki and Kunito, 2012). The free divalent species naturally have higher selectivity in ion exchange reactions with the surface ions of the soil than monovalent species (Bruggenwert and Kamphorst, 1979). The larger size of the species formed was also the contributing factor to the low adsorption capacity observed. Thus, the adsorbed species took more space on the surface of the soil, preventing further adsorption of other species. There were no element mononitrate species that were observed with Cu and Cr in the presence of ammonium nitrate hence unaffected linear adsorption. The amount of chloride and phosphate species formed with the elements were not significant as confirmed by PHREEQC. Hence the adsorption of Cd, Cu and Cr was not affected by the presence of ammonium phosphate.

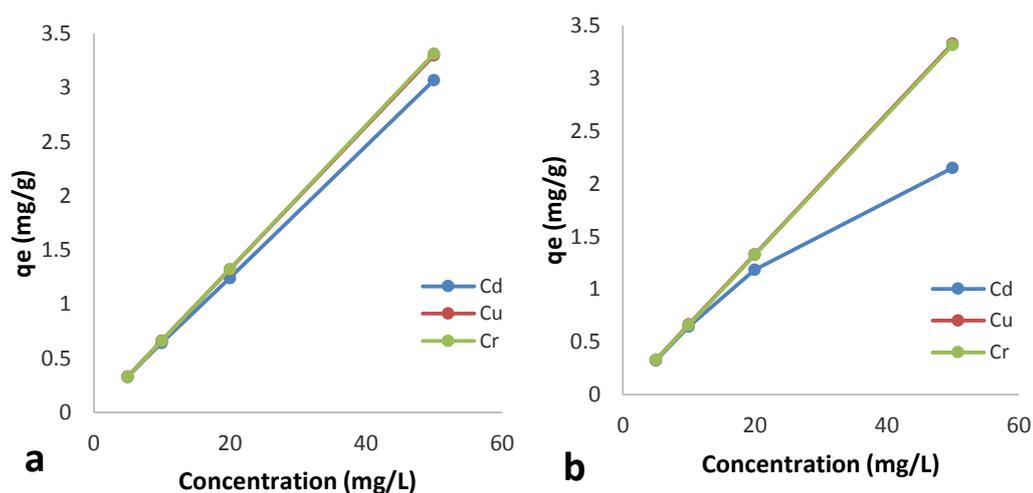


Figure 3: Effect of initial concentration of trace elements with ammonium nitrate fertiliser on the adsorption of trace elements in agricultural soil in the single (a) and multi-component (b) systems (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of fertiliser = 0.05 mol L⁻¹) (n = 3 and RSD < 10%).

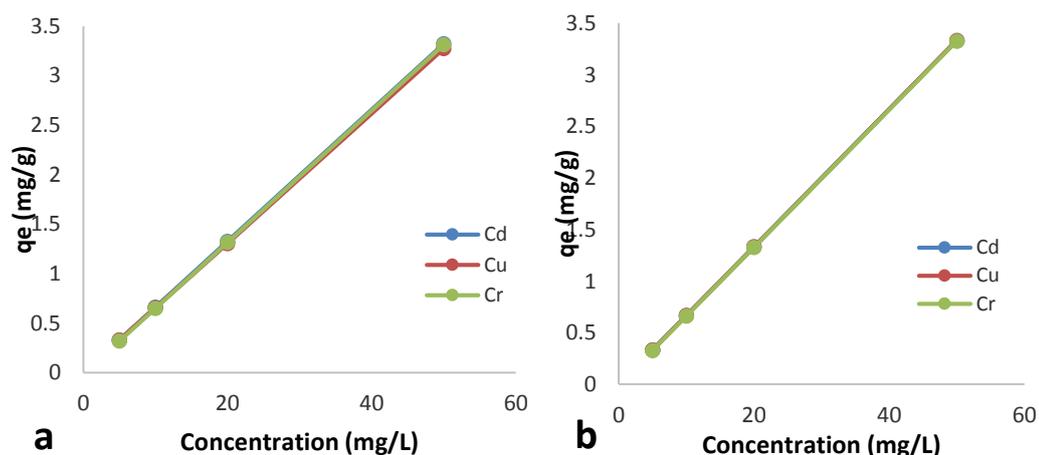


Figure 4: Effect of initial concentration of trace elements with ammonium phosphate fertiliser on the adsorption of trace elements in agricultural soil in the single (a) and multi-component (b) systems (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of fertiliser = 0.05 mol L⁻¹) (n = 3 and RSD < 10%).

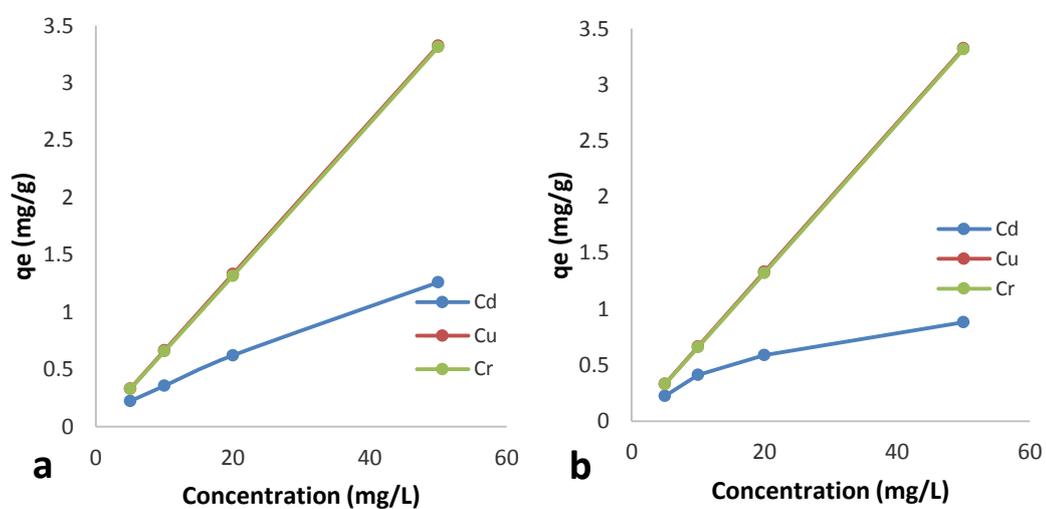


Figure 5: Effect of initial concentration of trace elements with calcium chloride fertiliser on the adsorption of trace elements in agricultural soil in the single (a) and multi-component (b) systems (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of fertiliser = 0.05 mol L⁻¹) (n = 3 and RSD < 10%).

Effect of the concentrations of fertilisers on the adsorption of elements

The effect of the concentration of fertilisers was studied to determine what happens as the concentration increases. The results are shown in Figure 6-8 for both the single and multi-component element systems. The results showed that the adsorption of Cd decreases as the concentration of ammonium nitrate and calcium chloride increases. The effect is more prevalent in single-component than in multi-component systems. The decrease in the adsorption of Cd as the concentration of ammonium nitrate increases is due to the loss of free Cd ion as more mononitrate species (CdNO_3^+) formed. The formation of the Cd mononitrate species could be due to nitrates preferring to react with Cd than ammonium ion and thus leaving the free ammonium ion which can adsorb on the soil surface. Ammonium nitrate is a well-known and widely used fertiliser due to the high nitrogen content from both the ammonium ion and nitrate which plants need. When ammonium nitrate enters the soil, the nitrate is readily taken up by plants but the ammonium ion will be taken up by roots or converted to nitrate form by microorganisms found in the soil, which will then be available for plant uptake. The decrease in the adsorption of Cd may be due to the readily available nitrate ions in ammonium nitrate as well as from nitrification which then react with the free Cd to form mononitrate cadmium (Bremner and Blackmer, 1978). The adsorption of Cd decreases dramatically in the presence of calcium chloride than that of ammonium nitrate. This is due to the more cadmium chloride species that are formed as the concentration of chloride increases. The PHREEQC script shows that as the concentration of chloride ions increase, the negative cadmium species (CdCl^-) as well as the cadmium chloride (CdCl_2) species increased. Thus, the presence of calcium chloride in the soil will prevent the maximum adsorption of cadmium by the soil due to the formation of these species. Thus, the high concentration of chloride ions in the soil will make Cd mobile and bioavailable. This will increase the probability of Cd reaching groundwater.

The presence of ammonium phosphate did not show any significant effect ($p > 0.05$) if any, on the adsorption of cadmium since, there was no difference observed in adsorption as the concentration increased. The free Cd species were

very high and only a small amount of Cd that reacted with the phosphate group to form $\text{CdP}_2\text{O}_7^{2-}$ was seen from PHREEQC.

Ammonium phosphate concentration affected the adsorption of Cu and Cr. The adsorption of the two elements was affected more in single systems than in multi-component systems. The dominant species of Cu in the presence of ammonium phosphate were in the order: $\text{CuH}_2\text{PO}_4^+ \approx \text{CuHPO}_4 > \text{Cu}^{2+} > \text{CuPO}_4^- \approx \text{CuNH}_3^{2+}$. The higher Cu-phosphate species formed led to the reduction in adsorption of Cu onto the agricultural soil. The free Cu species were reduced as the concentration of ammonium phosphate increased whilst, the Cu-phosphate species and Cu-ammonia species increased, hence the decrease in Cu adsorption. Thus, the more large species present, the lesser the adsorption on soil surfaces, which increases the mobility of Cu and consequently, its bioavailability. In the presence of ammonium phosphate, Cr reacted with phosphate groups to form CrPO_4 which increased as the concentration of the fertiliser increased. More hydroxide species are also formed and increase as the concentration of the fertilisers increases. PHREEQC also showed that $\text{Cr}_3(\text{OH})_4^{5+}$ and CrOH^{2+} were formed and led to reduction in adsorption of Cr onto the soil. The high concentration of ammonium phosphate will slightly increase the mobility of Cu and Cr onto the soil.

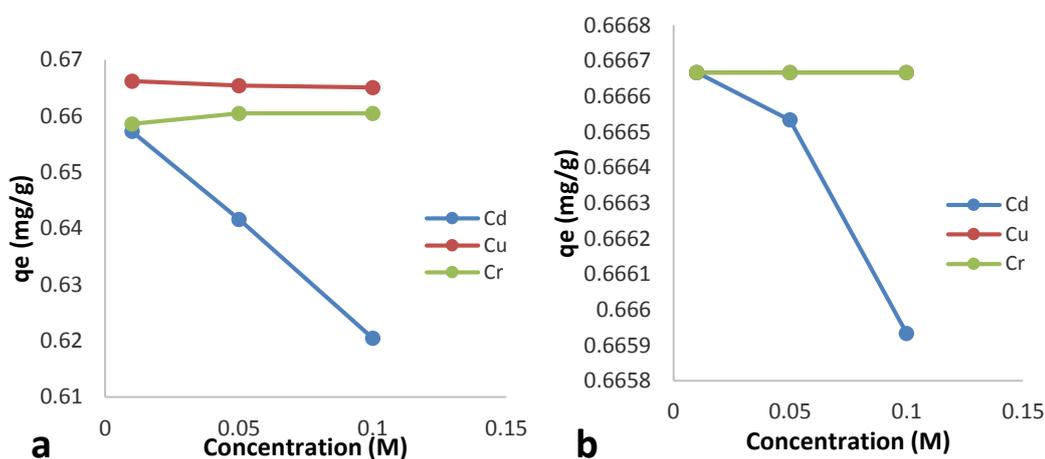


Figure 6: Effect of concentration of ammonium nitrate fertiliser on the adsorption of trace elements in agricultural soil in the single (a) and multi-component (b) systems (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of elements = 10 mg L⁻¹) (n = 3 and RSD < 10%).

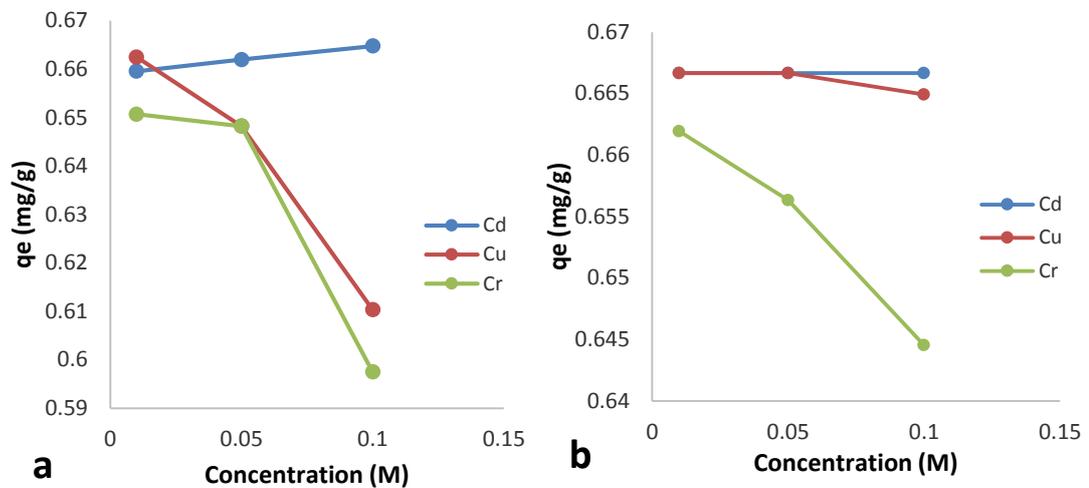


Figure 7: Effect of concentration of ammonium phosphate fertiliser on the adsorption of trace elements in agricultural soil in the single (a) and multi-component (b) systems (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of elements = 10 mg L⁻¹) (n = 3 and RSD < 10%).

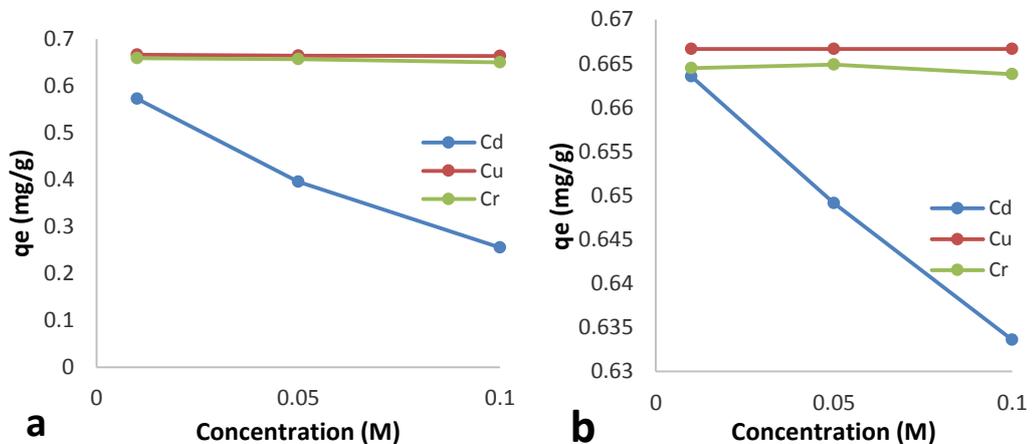


Figure 8: Effect of concentration of calcium chloride fertiliser on the adsorption of trace elements in agricultural soil in the single (a) and multi-component (b) systems (temp = 25°C, pH 5, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of elements = 10 mg L⁻¹) (n = 3 and RSD < 10%).

Effect of pH on the adsorption of elements

The effect of pH on the adsorption of trace elements in the presence of fertilisers was studied and the results are shown in Figures 9-11. The adsorption of Cd onto the soil was affected by solution pH due to the affected solubility and speciation. Cd showed a significant change in adsorption capacity with increasing pH of the solution. The effect of pH on the adsorption of Cd is prevalent with calcium chloride than other fertilisers. The effect of fertilisers with increasing pH on the adsorption of Cd was in the order: calcium chloride > ammonium nitrate > ammonium phosphate in single-component system and calcium chloride > ammonium phosphate > ammonium nitrate in the mixed system. The results showed that the adsorption of Cd increases with pH but it is noteworthy that the adsorption capacity is lower than that of Cu and Cr. At acidic conditions, there are more hydronium ions (H_3O^+) leading to low adsorption of Cd due to the surface of the soil being less negatively charged thus, reducing the ability to bind the positively charged elements. The concentrations of the free elements (e.g. Cd^{2+}) were high at low pH values as observed from PHREEQC but, due to the protonation of silanol and aluminol groups which are dominant components of the soil, the adsorption was low. Therefore, the protonation of these soil components makes them less available for adsorption. Elements with high ionic radius have lower charge densities and will therefore be highly affected by the protonation of surface functional groups (Abollino et al., 2003). At higher pH values there are more OH^- groups which increase the negative character of the soil hence, the adsorption of Cd increased. If the pH is in the acidic region, the mobility of Cd element to groundwater in the presence of calcium chloride will be enhanced. The presence of calcium chloride on its own decreases the pH of the soil and thus, inhibits high adsorption of Cd in addition to the species formed due to its presence (Kissel and Vendrell, 2004). The presence of ammonium nitrate also had a significant effect on the adsorption of Cd with increasing pH since, the adsorption of Cd increased as pH increased (Figure 9). Concentration of ammonium phosphate fertiliser did not have a significant effect on the adsorption of Cd (Figure 7) but the pH at which the fertiliser and Cd are present in, will have a

significant effect on the adsorption capacity of Cd (Figure 10). Thus, pH plays a major role in adsorption of Cd.

The pH did not have a significant effect on the adsorption of Cu and Cr since the differences in the adsorption capacities of the elements were not significant. Thus, the presence of the three fertilisers in the soil will not affect the mobility of Cu and Cr. The insignificant effect observed with Cu does not mean that there was no change in the species as the pH changed. The dominant species at different pH values were in the order: $\text{Cu}^{2+} \gg \text{CuNH}_3^{2+} > \text{CuOH}^+$ at pH 3, $\text{Cu}^{2+} \gg \text{CuNH}_3^{2+} > \text{CuOH}^+ > \text{Cu}(\text{NH}_3)_2^{2+}$ at pH 5 and $\text{Cu}(\text{NH}_3)_2^{2+} \approx \text{Cu}(\text{NH}_3)_3^{2+} > \text{CuNH}_3^{2+} > \text{CuOH}^+$ at pH 8 as determined by PHRREQC. The adsorption of Cu was seen to be decreasing only slightly as pH increased which could be due to CuOH^+ species.

In the presence of ammonium phosphate, the adsorption of Cu decreased slightly at low pH 3-5 but increased at pH 8. The slight increase at basic pH values might have been due to more hydroxide ions which increased the negativity of the soil surface and thus increasing its ability to adsorb positively charged Cu species. Phosphate ions from the fertiliser can adsorb onto soil particles whilst some react with the elements in the soil since, phosphate ions have strong interactions with the soil. The Cu phosphate species, $\text{CuH}_2\text{PO}_4^+$ were dominant at pH 3 and 5 and were adsorbed onto the soil. However due to the large size of the species, the adsorption was lower than at pH 8 where $\text{Cu}(\text{NH}_3)_3^{2+}$ species were dominant.

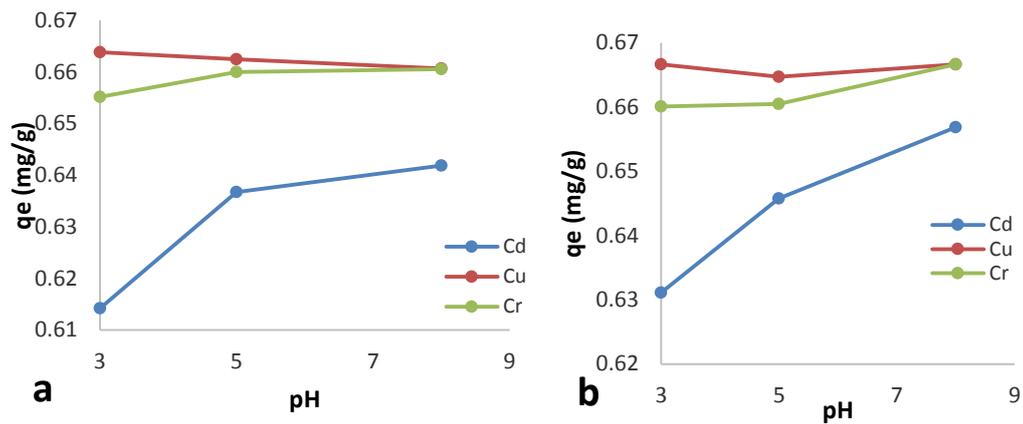


Figure 9: Effect of pH on the adsorption of trace elements on an agricultural soil in the presence of ammonium nitrate in the single (a) and multi-component (b) systems (temp = 25°C, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of elements = 10 mg L⁻¹, concentration of fertiliser = 0.05 mol L⁻¹) (n = 3 and RSD < 10%).

The adsorption of Cr onto an agricultural soil was not affected by pH in any of the fertilisers and there was no difference in adsorption ($p > 0.05$) in the single- and multi-component systems. The dominant Cr species formed at all pH values were positively charged hence no effect was observed on adsorption.

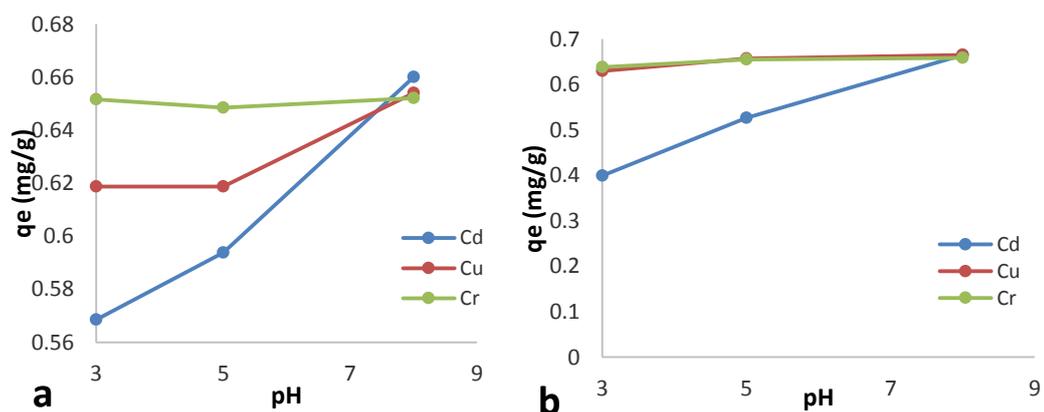


Figure 10: Effect of pH on the adsorption of trace elements on an agricultural soil in the presence of ammonium phosphate in the single (a) and multi-component (b) systems (temp = 25°C, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of elements = 10 mg L⁻¹, concentration fertiliser = 0.05 mol L⁻¹) (n = 3 and RSD < 10%).

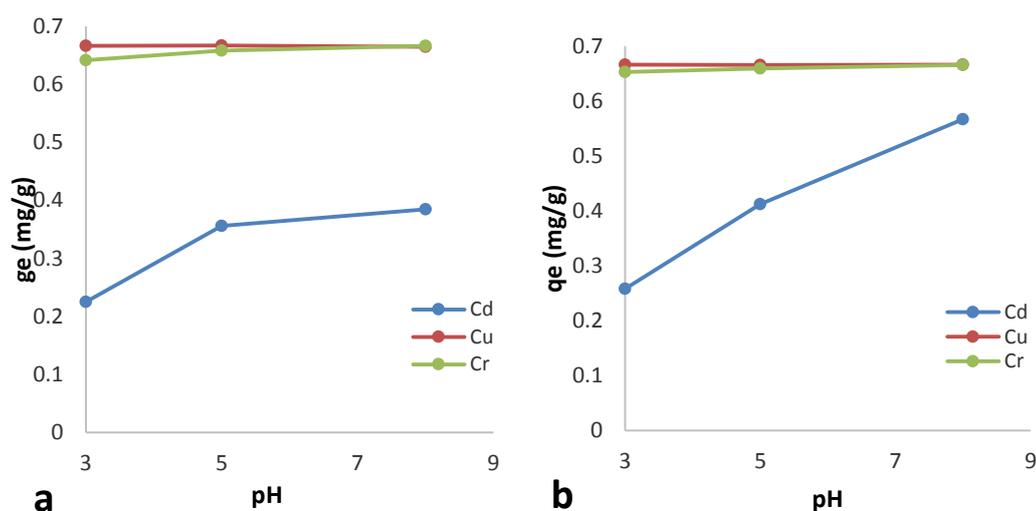


Figure 11: Effect of pH on the adsorption of trace elements on an agricultural soil in the presence of calcium chloride in the single (a) and multi-component (b) systems (temp = 25°C, contact time = 3 h, mass = 0.75 g, volume = 50 mL, concentration of elements = 10 mg L⁻¹, concentration of fertiliser = 0.05 mol L⁻¹) (n = 3 and RSD < 10%).

Conclusion

The continual use of fertilisers by farmers and smelting operations increase the accumulation of elements in the soil. These elements have the potential of reaching groundwater if the soil is not effective enough to hold them and prevent their mobility. The effect of fertilisers on the adsorption of Cd, Cu and Cr in an agricultural soil was studied. The adsorption of Cd was found to be decreased by the presence of calcium chloride due to the formation of cadmium chloride species, which led to poor adsorption of the element. Ammonium nitrate also decreased the adsorption of Cd but with lower degree than calcium chloride. The effect of concentration of fertilisers, pH and initial concentration of elements under study affected the adsorption of Cd. Concentration of fertilisers and pH did not show any significant effect on the adsorption of Cu and Cr. Thus, the application of fertilisers into the soil will prevent the adsorption of Cd and probably other elements of a similar nature and this will pose challenges on the health of living organisms.

The effect of fertilisers was in the order: calcium chloride >>> ammonium nitrate > ammonium phosphate for Cd, ammonium phosphate > ammonium nitrate \approx calcium chloride for Cu and ammonium phosphate > ammonium nitrate \approx calcium chloride for Cr.

The elements under study were also found in the soil used but there was no evidence of desorption for Cu and Cr which meant that the soil constituents held them tightly *via* surface complexation reaction which is selective and irreversible (McBride, 1994). Some of the fertilisers dislocated Cd from its conventional adsorption sites in the soil and hence increasing its bioavailability (Lorenz et al., 1994; Lambert et al., 2007). Thus, the presence of fertilisers will increase the mobility of Cd by forming species which are not favourable for adsorption onto the soil.

According to the results obtained, it was concluded that fertilisers affect the solubility and speciation of Cd and consequently its mobility. The concentration of Cd found in the soil was lower than that of the other elements under study which could be due to the increased lability of Cd in the presence of fertilisers which are constantly applied on the plot. Therefore, the concentration of Cd in groundwater should be highly considered in areas where agriculture and mining industries are dominant.

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CHAPTER 7

Simulation of elemental transport through columns

This chapter contains a paper focusing on column studies using PHREEQC.

Contribution to the paper: Lead author, performed modelling, analysed and interpreted the results.

This paper will be submitted to: Journal of environmental modelling and assessment

Modeling the sorption and transport of cadmium, copper and chromium on an agricultural soil impacted by mining activities: a column-based study

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Abstract

Platinum mining leachates usually contain high concentrations of elements which have negative impact on water quality. Agricultural plot soils near mining areas are prone to element contamination and thus have negative impact on the health of living organisms. Therefore the ability of the soil surface particles to hold elements entering the soil is crucial on the quality of groundwater in that vicinity. It is therefore important to determine the effectiveness of soils in the vicinity of mining areas to prevent the mobility of elements. The adsorption of cadmium (Cd), copper (Cu) and chromium (Cr) onto an agricultural soil surface using PHREEQC geochemical modeling was considered in this study. A continuous flow fixed-bed column script with specified conditions simulating the natural environment was used. The geochemical computer model PHREEQC can simulate solute transport in soil surfaces. The effect of initial concentration of the elements, bed depth and pH were considered in this study. The adsorption capacity of Cd and Cr onto the soil surface was affected by initial concentration of the elements as the breakthrough curves were reached at lower pore volumes at high concentrations (300 mg/L) than at low concentrations (100 mg/L). Due to the conditions used in this study, the initial Cr^{3+} was oxidized to Cr^{6+} leading the formation of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ which were not favoured for adsorption by soil surfaces. The changing of bed depth from 5 to 10 cm did not have an effect on the adsorption of Cd, Cu and Cr. The adsorption of Cd and Cr onto the soil surface was not affected by pH. Basic pH values affected the speciation of Cu converting Cu^{2+} to $\text{Cu}(\text{OH})_2$. The $\text{Cu}(\text{OH})_2$ species were large in size and thus only a small amount of the initial solution could be adsorbed onto the soil surface.

Introduction

Heavy elements such Cd, Cu, Cr, Zn, Ni and many others have been found to accumulate in and contaminate agricultural soils due to anthropogenic sources such as mining activities, smelting operations and agricultural activities (Kadirvelu et al., 2001). Their inability to degrade or be eliminated makes them hazardous to living organism including human beings, livestock and aquatic animals since; they are toxic when they exceed tolerable limits (Vinodh et al., 2011; Agbozu and Emoruwa, 2014). The accumulation of the elements in agricultural soils can lead to increased bioavailability and bioaccessibility of the elements to plants and other organisms feeding on the crops grown in the agricultural plots. Moreover, these elements can reach groundwater as leachates through the soil, leading to water pollution that will eventually affect aquatic life and other organism that depend on water, simply, all life forms in the ecosystem can be affected (Gaur and Adholeya, 2004). The presence of the elements in high concentrations in human beings can lead to cancer, liver and kidney failure, dizziness, renal damage, defects in morphology of infants and many others hence their mobility in soils should be inhibited.

Studies have shown that the mobility of heavy elements can be inhibited by soil particles such as iron oxyhydroxides, organic matter and clay minerals through sorption mechanisms (Veeresh et al., 2003, Bradl, 2004; Chaari et al., 2011; Abat et al., 2012). Upon entering the soil, elements from mining activities, fertilisers and pesticides, smelting operations, water used for irrigation and sewage sludge can be bound by soil particles before seeping to groundwater and consequently, decreasing the bioavailability of these elements. The ability of the soil to prevent the leaching of elements to groundwater is important for the quality of water. The time required for the clean-up of such water will be less and less costly. But, if the elements leach to groundwater and accumulate, the time required for clean-up will be high and expensive. Therefore soils which can adsorb elements and prevent their mobility are of importance especially where there are mining plants around and no remediation techniques applied.

In this study PHREEQC geochemical modelling computer program is used to simulate transport of Cd, Cu and Cr onto an agricultural soil. The full-scale sorption process, continuous-flow fixed bed column will be used. The conditions used were obtained from batch studies which are not included in this study. The results of the study will help understand the leachability of the elements to groundwater. The results of this study will be very crucial since the soil considered in this study was from an agricultural plot which is in the vicinity of platinum mining and smelting plants. Fertilisers, pesticides and water used for irrigation are constantly applied on the plot. Since studies have shown that agricultural substances and mining operations add elements such as Cd, Cu and Cr into the soil, the concentrations of the elements in the plot could be from these sources as well as from natural sources. There are no remediation techniques applied on the plot to reduce contamination of the soil and consequently groundwater and therefore the adsorption of the elements onto the soil is very crucial to prevent contamination of groundwater by reducing the mobility of the elements. Thus, this study seeks to understand the effectiveness of the soil in holding elements which are considered hazardous.

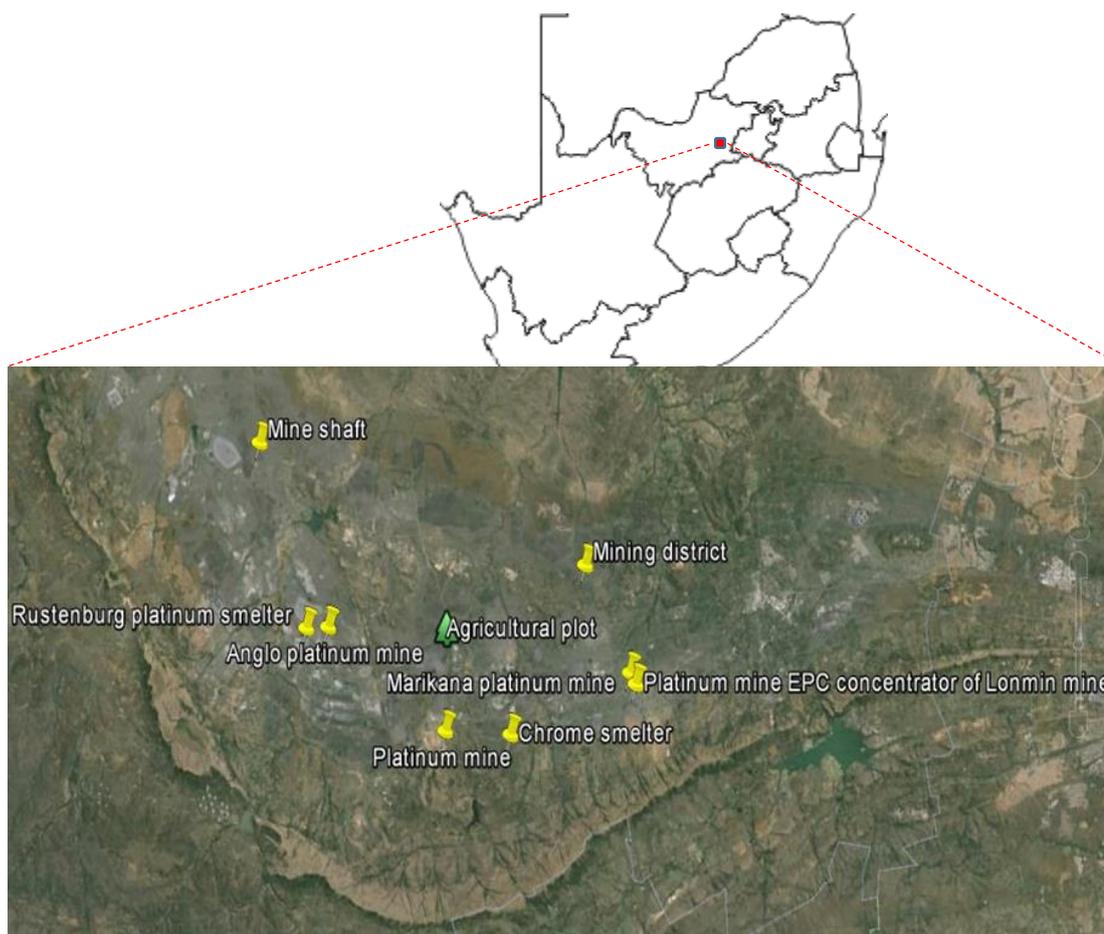


Figure 1 Location plan indicating current mining operations around the agricultural plot in Rustenburg

Materials and methods

The batch analytical results (not shown) were used to establish speciation models using PHREEQC interactive version 2 geochemical modeling code (Parkhurst and Appelo, 2013). The phreeqc.dat data base of the code was used for Cd and Cu but LLNL.dat (Lawrence Livermore national laboratory) was used for Cr since its Cr^{3+} species could not be found in other databases.

Forward modeling was used in this study, which gives the final solution composition after the reaction has completed (Crawford, 1999). The cation exchange capacity (CEC) of the soil which was determined by BaCl_2 method was used to represent the exchange surface (Gillman and Sumpter, 1986). Solution 0

represents the analyte solution with specified conditions. The analyte nitrate solutions were used in batch studies hence considered in this study. In PHREEQC, nitrate ions are represented as N(5) and their concentrations together with the concentrations of the analytes were calculated based on the chemical formula of the chemicals used in batch studies, which were obtained from Sigma Aldrich, South Africa. The conceptual model consists of a column with 10 cells in which the analyte solution will pass through. Shifts represent the number of times the solution passes through each cell as shown in Figure 2. Therefore, when 3000 shifts are used, then Solution 0 will be added to the column 3000 times (Figure 3). The results used in this study were only from cell 10, which was the final cell of the column into which the solution passes.

In this study, the effect of initial concentration (100 and 300 mg/L), pH (3, 5, 7 and 9) and bed depth (5 and 10 cm) on the adsorption of Cd, Cu and Cr onto the specified soil surface was determined. The one-way analysis of variance (ANOVA) was used to determine if there are any statistical differences between some of the different conditions of the same parameter and the same element. The general conditions used for all elements are described on the script in Figure 2.

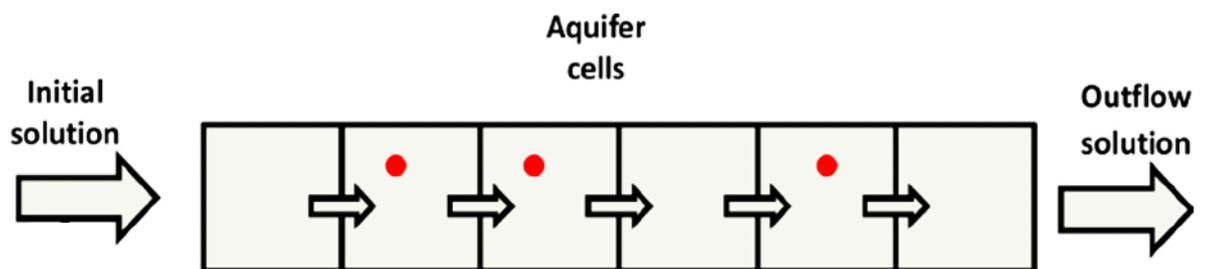


Figure 2 Schematic diagram of a column with 6 cells showing how the analyte (in red) travels through a column

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TITLE The adsorption of analyte (Cd, Cu or Cr) onto an
agricultural soil
SOLUTION 0
Units mg/L
pH 5
pe 4
temp 25
Cd, Cu or Cr (concentration of analytes)
N(5) (Concentration of N(5))
SOLUTION 1-10
temp 25
pH 7
pe 4
Units mmol/kgw
density 1
-water 1 #kg
Na 1
K 0.2
EXCHANGE 1-10
-equilibrate solution 1
X 0.516
USE exchange none
TRANSPORT
-cells 10
-shifts 3000
-lengths 0.0001
-time 40
-dispersivities 0.0
-print_cells 10
END

```

Figure 3: PHREEQC script

The breakthrough curve was used to determine the performance of the packed bed. The breakthrough curves provide important information regarding the adsorption of elements in a flow through system.

Results and discussion

Effect of concentration

PHREEQC was used to determine the effect of concentration on the adsorption of Cd, Cu and Cr. The results are shown in Figures 4, 5 and 6. The results indicated that initial concentration will have a significant effect on the breakthrough curves for Cd and Cu. As the initial concentration of Cd and Cu increased from 100 to 300 mg L⁻¹, the volume at which breakthrough was reached decreased. Thus, the adsorption capacity of the elements was affected by increasing concentration. This can be attributed to the types of species formed with the elements under study. The common and dominant species of Cd was found to be Cd²⁺ which was small in size hence, was easily adsorbed than other elements which formed other species as obtained from PHREEQC leading to breakthrough with high pore volume. Thus, leaching of Cd in the soil with high affinity will occur after a long time in the absence of other factors such as competing ions or plant exudates. However when the concentrations are higher the leaching to groundwater will be faster due to occupation of active sites on the soil by Cd species. The inability to form other species such as CdNO₃⁺ led to the high adsorption of Cd.

The breakthrough curves for Cu occurred at lower pore volumes than those of Cd at both 100 and 300 mg L⁻¹. At 300 mg L⁻¹, the breakthroughs were found to be at ~4000 and ~2000 mL for Cd and Cu, respectively whilst at 100 mg L⁻¹, the breakthrough was found to be at 12800 and 7120 mL for Cd and Cu, respectively. This can be attributed to the formation of other species of Cu such as CuOH⁺ and Cu₂(OH)₂²⁺ other than Cu²⁺, which are relatively large and thus occupying more of the soil surface, preventing further adsorption of Cu species hence the early breakthrough. This phenomenon can be clearly observed on the concentration of 100 mg L⁻¹ since at the volume of ~9600 mL, the soil was already being saturated with Cu species since no further significant adsorption was observed beyond. This was not the case with Cd since other species such as CdNO₃⁺ were not in significant amounts.

The results indicated that the Cr^{3+} which was in the initial solution was oxidized to Cr^{6+} due to the specified conditions which simulate the natural environment. At higher redox potentials, Cr^{6+} predominates in the environment. Thus the incoming Cr^{3+} from mining plants can enter the soil and convert to the harmful and highly soluble Cr^{6+} , which will have implications on groundwater quality. The conversion was possible since water contains oxygen which can be used to oxidise Cr^{3+} to Cr^{6+} . The maximum concentration of Cr^{3+} that leached out under specified conditions was $<2 \text{ mg L}^{-1}$ at both concentrations. The dominant Cr^{6+} species were HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ which are large in size. The results indicated that these species were not favourable for adsorption since the breakthrough was reached within the first few pore volumes (100 mL) indicating that only small amounts were adsorbed. The lower concentrations of Cr observed within the first few pore volumes could be due to the adsorption of Cr^{6+} species on sites which favour their adsorption but it seems as though these sites are few hence saturation was reached in a short space of time. Thus, there is high probability that Cr will leach to groundwater, leading to high bioaccessibility and bioavailability to plants and animals.

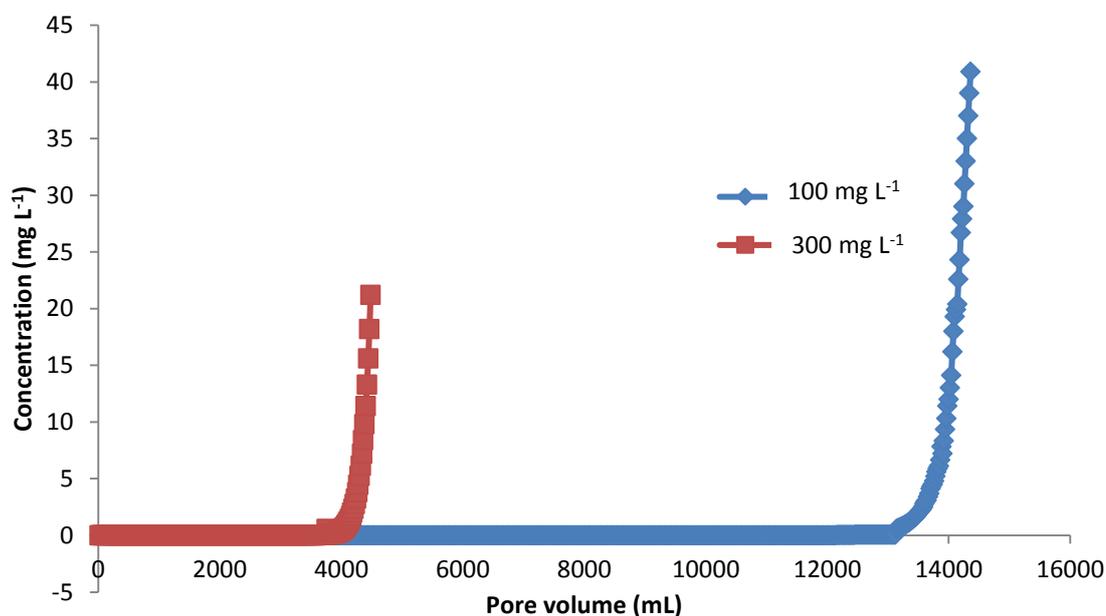


Figure 4 The effect of concentration of Cd on breakthrough curve

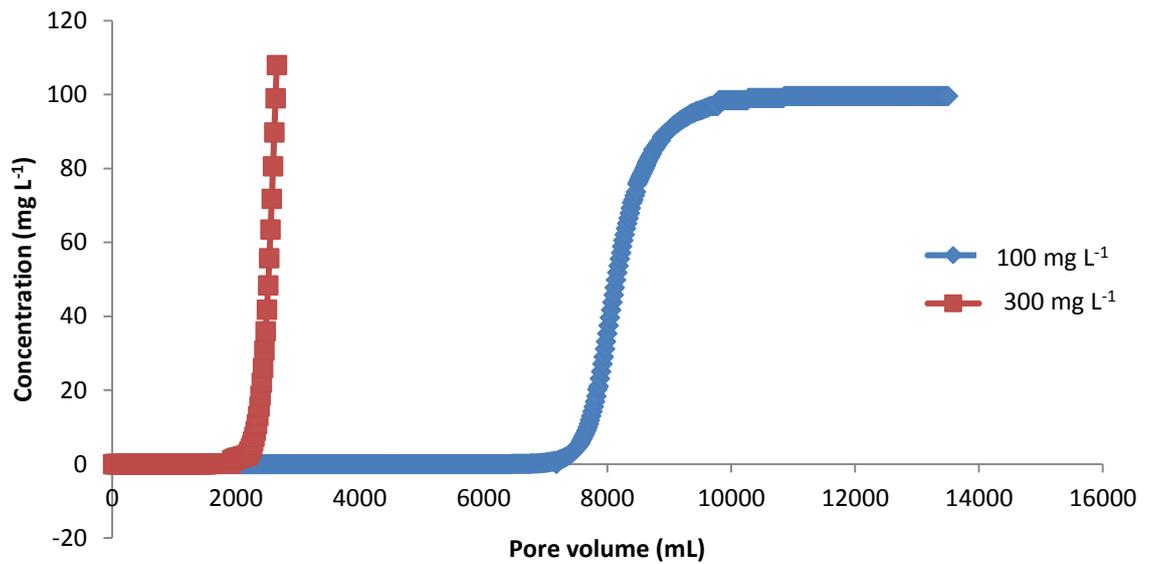


Figure 5 The effect of concentration of Cu on breakthrough curve

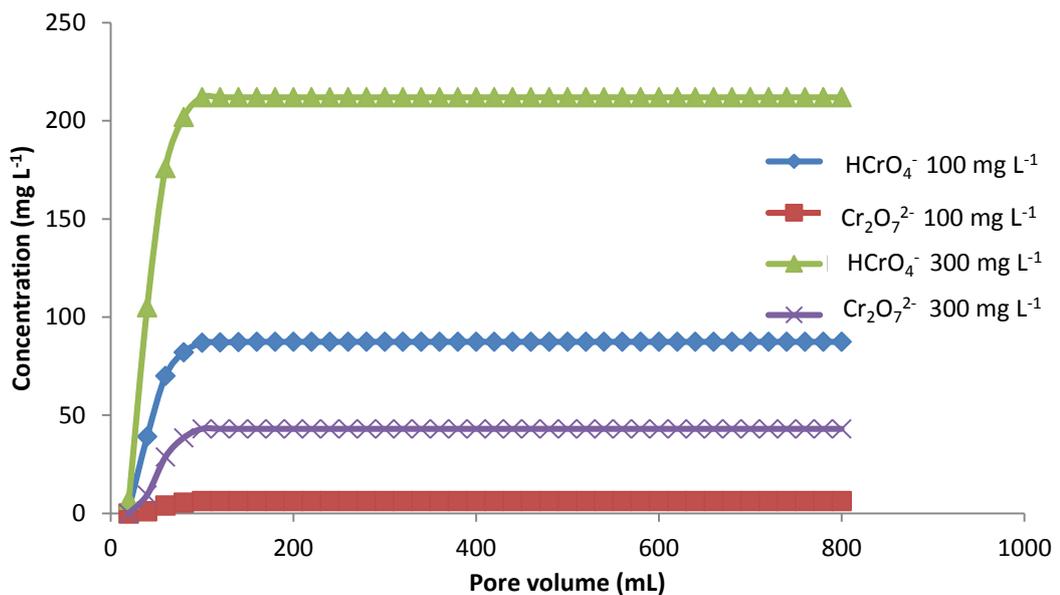


Figure 6 The effect of concentration of Cr on breakthrough curve

The effect of bed depth

Bed depth was studied to determine the effect it has on the adsorption of Cd, Cu and Cr and the results are shown in Figures 7, 8 and 9. There was no significant difference on the breakthrough curves of Cd as confirmed with anova single factor. Therefore, the adsorption of Cd onto the soil will not be affected by the

bed depth (5 or 10 cm) of the soil and this is due to the availability of strong binding sites which have high affinity for Cd^{2+} species and strongly bind them, making the adsorption process very effective even in lower bed length. Therefore, even low soil depth will have enough binding sites to hold high concentrations of Cd species. There was no significant difference on the adsorption of Cu onto the soil with 5 and 10 cm bed length. This can also be attributed to the strong interaction between Cu species and the soil binding sites. The adsorption of Cr onto the soil also showed no significant difference with bed length. The adsorption of HCrO_4^- was similar at both 5 and 10 cm bed length, and the same was observed with $\text{Cr}_2\text{O}_7^{2-}$ species. The breakthrough curves for Cr were very low and this might be due to the low adsorption of Cr onto the soil hence the breakthrough was reached quickly. Thus, the leaching of Cr onto the soil will be high compared to that of the other elements since the species produced will not be favourable for adsorption or attachment onto the soil through complexation.

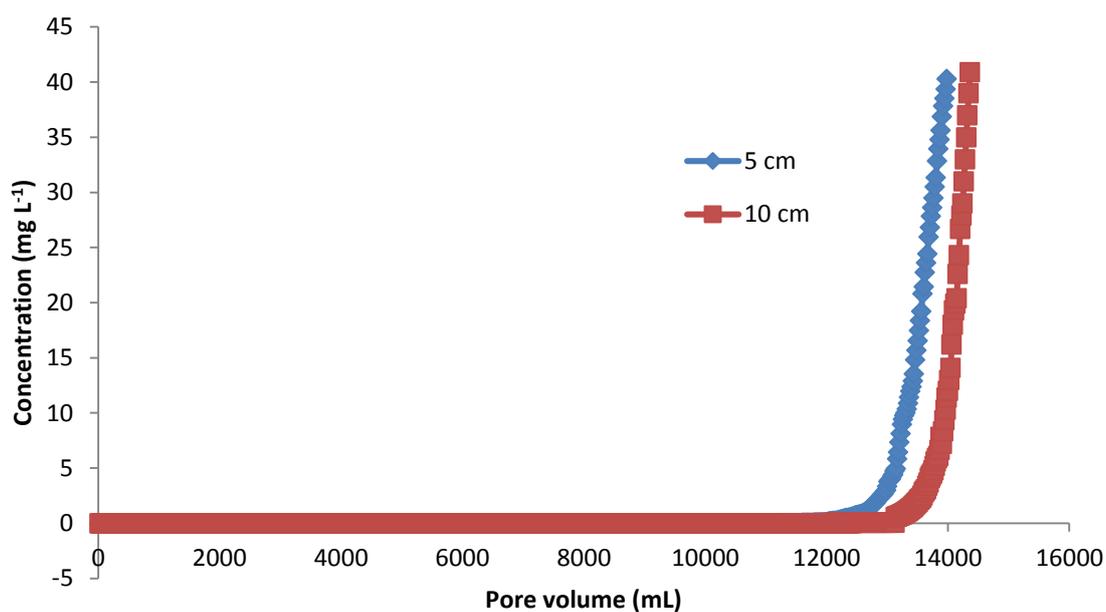


Figure 7 The effect of bed depth on breakthrough curve of Cd (Concentration of Cd = 100 mg L^{-1})

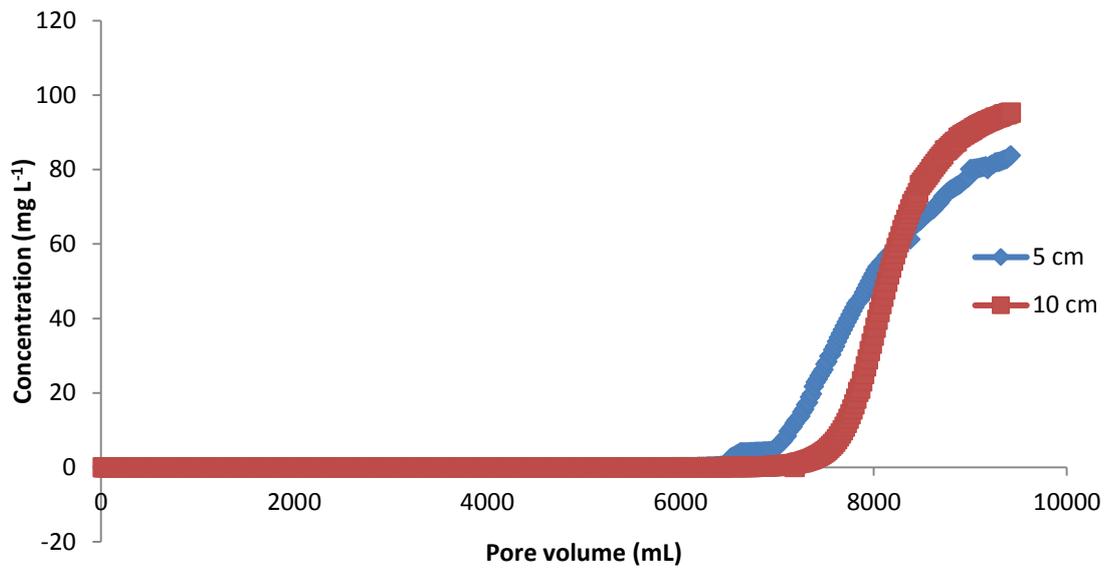


Figure 8 The effect of bed depth on breakthrough curve of Cu (Concentration of Cu = 100 mg L⁻¹)

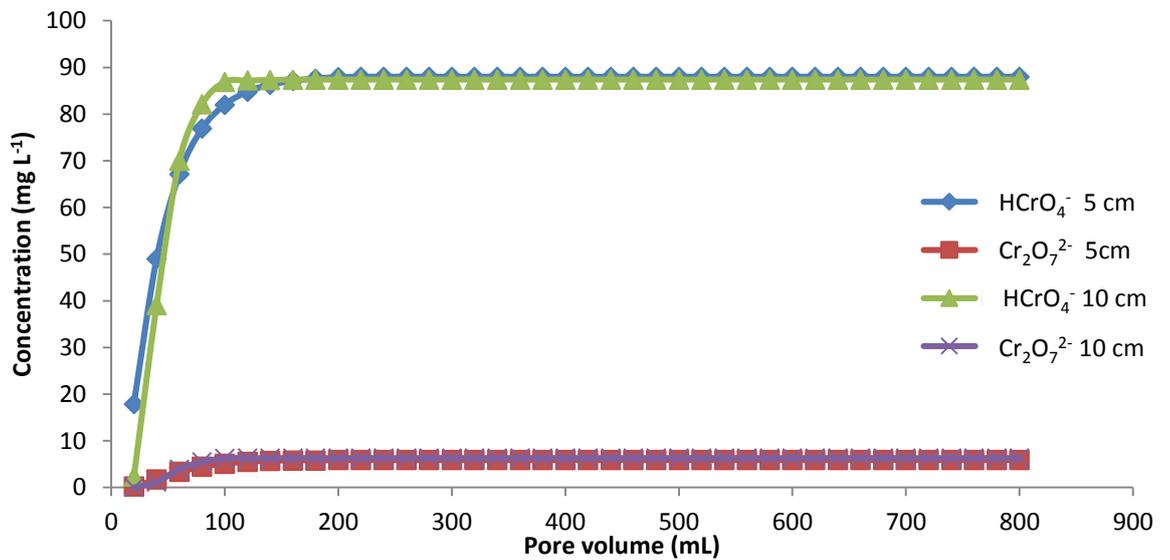


Figure 9 The effect of bed depth on breakthrough curve of Cr (Concentration of Cr = 100 mg L⁻¹)

The effect of pH

The effect of pH on breakthrough curves was studied for Cd, Cu and Cr and the results are shown in Figures 10, 11 and 12. The adsorption of Cd onto the soil

surface was found not to be affected by pH. The breakthrough curves at pH 3, 5, 7 and 9 were all the same. Thus the adsorption of Cd will not be affected by pH. This can be attributed to the lack of change of speciation of Cd with pH. The dominant species of Cd was still Cd^{2+} at all pH values. This observation was seen when batch adsorption studies were conducted (Chapter 4 in this dissertation). This means that the adsorption of Cd onto the mineral surface is independent of pH_{PZC} , implying that adsorption was *via* surface complexation as corroborated by the batch studies. However, the adsorption of Cu was affected by pH and this can be attributed to the speciation of Cu formed as confirmed by PHREEQC. At acidic pH (3 and 5), Cu exist mainly as Cu^{2+} and this led to more Cu species adsorbing onto the soil hence breakthrough was reached at larger pore volumes. At basic pH, the dominant Cu species were found to be $\text{Cu}(\text{OH})_2$ which are larger than Cu^{2+} . The $\text{Cu}(\text{OH})_2$ species were not favourable for adsorption onto the specified soil surface and this might be due to the less positive charge on the species, since the surface of the soil was negative, therefore the attraction or complexation between the soil functional groups and Cu was very low. The maximum amount of Cu that is coming leached out at pH 7 (53.6 mg L^{-1}) was lower than at pH 9 (93.3 mg L^{-1}) at the chosen end pore volume. Thus, more $\text{Cu}(\text{OH})_2$ could still be adsorbed onto the soil surface at pH 7 probably due to less hydroxide species than at pH 9. High pH will increase the leachability of Cu onto the agricultural soil due to the formation of $\text{Cu}(\text{OH})_2$ species.

The changing pH did not affect the adsorption of Cr onto the soil surface. The adsorption capacities at pH 3, 5, 7 and 9 were all the same. The dominant Cr species at all pH values was HCrO_4^- . The breakthrough of Cr was achieved at a very short space of time at pore volume of 20 mL. The Cr^{6+} species formed were very large and unfavourable for adsorption. Therefore, when the Cr^{3+} species from mining plants enter the soil where oxidation prevails, Cr^{3+} will be converted to the more hazardous Cr^{6+} and this will increase the leaching of Cr species to groundwater. This will increase the bioavailability of Cr species which will pose serious challenges on the health of living organisms.

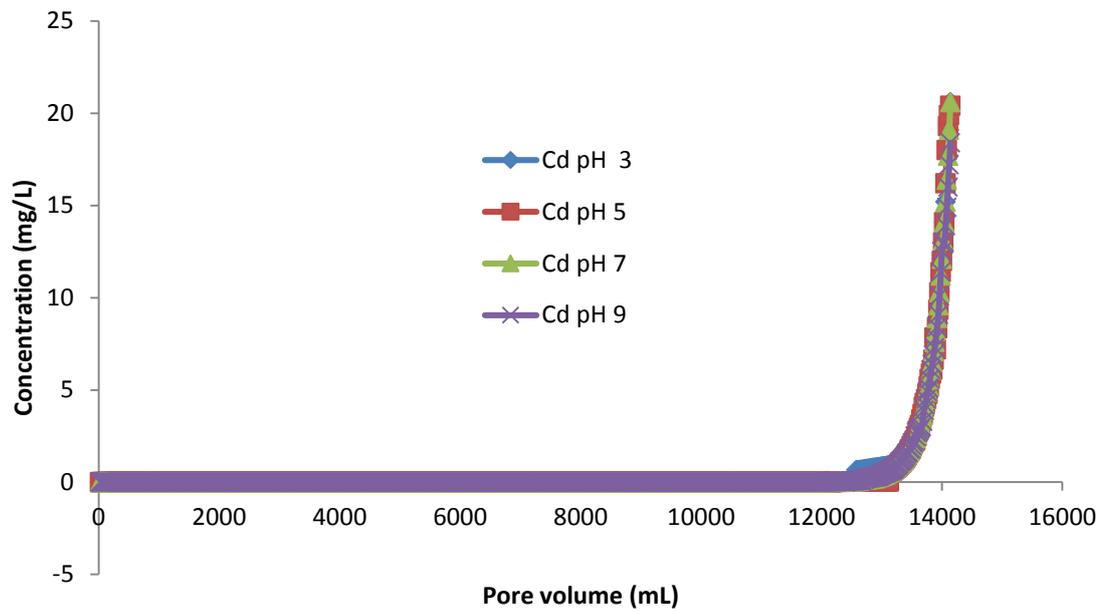


Figure 10 The effect of pH on breakthrough curve of Cd (Concentration of Cd = 100 mg L^{-1})

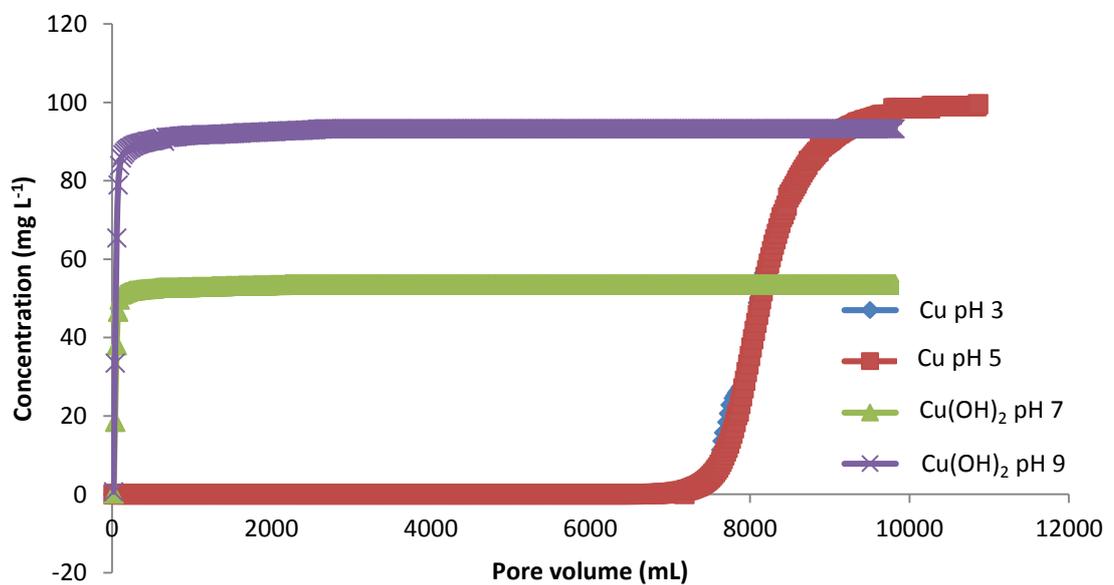


Figure 11 The effect of pH on breakthrough curve of Cu (Concentration of Cu = 100 mg L^{-1})

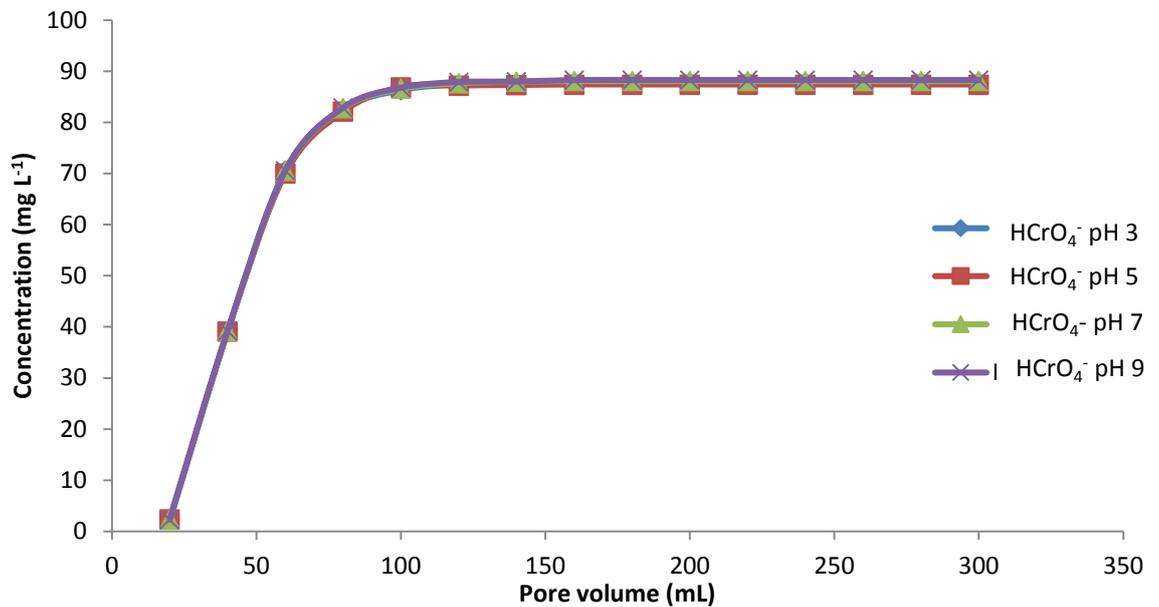


Figure 12 The effect of pH on breakthrough curve of Cr (Concentration of Cr = 100 mg L⁻¹)

Conclusion

PHREEQC can determine the speciation of elements at specific conditions and it is thus an important tool to use, when trying to understand the processes that occur in the natural environment, which would otherwise be difficult to understand with just the laboratory experiments. The adsorption of Cd, Cu and Cr onto the soil surface representing an agricultural soil impacted by mining activities was studied, using a continuous flow fixed-bed column script. The results indicated that initial concentration of the elements will have an effect on the adsorption of Cd and Cu. The breakthrough curves obtained indicated that at higher initial concentrations, the adsorption sites on the soil will be covered by the elements faster than at low concentrations. Therefore, the mobilisation of these elements to ground water will increase with increasing concentration. The adsorption of Cr onto the soil was not favoured and this could be due to the oxidation of Cr³⁺ to the more soluble Cr⁶⁺. The dominant Cr⁶⁺ species formed were HCrO₄⁻ and Cr₂O₇²⁻ which, mobilised to ground water. However, the results

were inconclusive and further interrogation of the script is required to determine the course of oxidation of Cr^{3+} species. There was no significant difference on the adsorption of Cd and Cu with changing bed depth because the mineral surface had high adsorption sites that have high affinity for Cd and Cu as was confirmed with ANOVA (results shown in the appendix section). The adsorption of Cr also showed no significant difference with bed depth. The adsorption of Cd and Cr onto the soil surface was not affected by pH. But the adsorption capacities of Cu were affected by changing pH. Basic pH decreased the adsorption of Cu due to the formation of $\text{Cu}(\text{OH})_2$ which were also large in size thus prevented further adsorption of Cu due to the lack of adsorption sites that would otherwise be available at lower pH values since there would be smaller Cu species. This phenomenon was also observed in batch studies.

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CHAPTER 8

General conclusions and future recommendations

This chapter focuses on the general conclusions of the study.

GENERAL CONCLUSIONS

Analytical experiments and geochemical modelling were used to understand the distribution and behaviour of Cd, Cu and Cr in the agricultural soil at different conditions simulating the natural environment. The variables used in the study are well known to affect the fate of elements in soils.

The agricultural soil was highly composed of SiO_2 and Al_2O_3 minerals which were responsible for the adsorption capacities observed in analytical experiments. The N-H and O-H peaks observed in FTIR could imply the presence of amine-containing groups and humic substances, respectively which are known to adsorb elements. Freundlich isotherm described the adsorption data better for Cd, Cu and Cr, which indicated the heterogeneous nature of the soil with the possibility of multilayer adsorption of the elements onto the soil. The energy of adsorption was greater than 8 kJ mol^{-1} for all the elements, indicating that the adsorption was favoured in the absence of complexing agents and competing ions. Pseudo second-order described the kinetic data better indicating that chemisorption was the rate controlling mechanism.

The soil was generally effective in adsorbing and retaining the elements. However, the retention was highly dependent on elemental speciation and prevailing conditions such as pH as well as the presence of competing ions, plants exudates and fertilisers. Such conditions could have implications on groundwater.

The change in pH did not have a significant effect on the adsorption of Cd, thus, Cd element will be adsorbed by the soil despite the soil or solution pH conditions. However, the adsorption capacities of Cu and Cr decreased at alkaline pH values. The decrease was attributed to the species dominating at those pH values. In the presence of competing ions, the adsorption of soft Lewis acid Cd, decreased, but that of borderline and hard Lewis acids, Cu and Cr, respectively were hardly affected. This was attributed to the availability of hard Lewis bases on the surface of the soil which favoured the adsorption of hard Lewis acids.

The presence of fertilisers (ammonium nitrate and ammonium phosphate) and calcium chloride did not significantly affect the adsorption of Cu and Cr but, the

adsorption capacity of Cd decreased with increasing concentration of ammonium nitrate and calcium chloride. Thus, the mobility of Cd in the soil will be enhanced and that can increase the groundwater pollution and this was attributed to the affected solubility and speciation of Cd. In the presence of calcium chloride, CdCl^+ species were dominant and since they were large in size they occupied more space on the mineral surface, preventing further adsorption of other species. The dominant Cd species in the presence of ammonium nitrate was CdNO_3^+ as determined by PHREEQC which were also large in size. Therefore, the concentration of Cd in groundwater should be highly considered in areas where agriculture and mining activities take place.

The effect of concentration of fertilisers, pH and initial concentration of elements under study affected the adsorption of Cd. Concentration of fertilisers and pH did not show any significant effect on the adsorption of Cu and Cr. Thus, the application of fertilisers into the soil will prevent the adsorption of Cd and probably other elements of a similar nature and this will have implications on groundwater contamination.

The effect of fertilisers was in the order: calcium chloride >>> ammonium nitrate > ammonium phosphate for Cd, ammonium phosphate > ammonium nitrate \approx calcium chloride for Cu and ammonium phosphate > ammonium nitrate \approx calcium chloride for Cr.

This study demonstrated that the presence of plant exudates such as acetic acid (AA), citric acid (CA), oxalic acid (OA) and EDTA decreased the adsorption capacities of Cd, Cu and Cr. The sequence followed in terms of the effect of EDTA and LMWOA with different concentrations of the elements is: AA < OA < CA < EDTA for Cd; AA < CA < OA < EDTA for Cu and AA < OA < CA < EDTA for Cr. When there are similar concentrations of EDTA and low molecular weight organic acids (LMWOA) in the soil, EDTA will have more effect in increasing the mobility of elements in the soil. The adsorption of the elements was observed to increase with increasing concentration of the elements in the presence of plant exudates but the increase was less than when there were no exudates and this can be attributed to the complexed species formed between the analytes and

complexing agents as was observed in PHREEQC. The adsorption of Cd and Cu decreased as the concentration of the exudates increased due to more negative species or complexes forming which were not favourable for adsorption onto the soil surface. Some of the elements which were already in the soil were desorbed by OA and EDTA. Therefore the presence of OA and EDTA will not only complex the elements entering the soil but will also dislocate those that are already in the soil from their conventional adsorption sites.

PHREEQC can determine the speciation of elements at specific conditions. It is thus, an important tool to use when trying to understand the processes that occur in the natural environment. The results obtained from continuous flow fixed-bed column indicated that initial concentration of the elements will have an effect on the adsorption of Cd and Cu as was also shown in batch studies. The higher concentration of these elements led to high adsorption onto the soil surface groups hence more adsorption sites were occupied at lower pore volumes than at low concentrations as confirmed by the breakthrough curves obtained. The Cr^{3+} species were oxidized to Cr^{6+} , leading to the formation of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ which were not favourable for adsorption. This observation of oxidation within the column is not conclusive at this stage and would require further interrogation, especially by changing the solution compositions in the simulation script as the solution traverses the soil profile. Changing the bed depth of the soil from 5 to 10 cm did not have a significant effect on the adsorption of the elements as was confirmed with ANOVA. This can be attributed to the surface of the soil which had adsorption sites that had high affinity for Cd^{2+} and Cu^{2+} . The changing pH did not have significant effect on the adsorption of Cd and Cr onto the soil surface. But the formation of $\text{Cu}(\text{OH})_2$ at pH 7 and 9 decreased the ability of the adsorption sites to hold Cu.

Modelling has proven to be a reliable tool in understanding the behaviour of elements at different conditions, which would be difficult to deduce from just the analytical experiments. The study has shown that the speciation of the elements can affect the degree of adsorption onto the mineral surface. PHREEQC modelling has shown that the speciation of the elements change in the presence of

fertilisers, exudates and pH hence the trends that were followed in analytical experiments. Without modelling, it would have been difficult to explain the changes that occurred in adsorption. For example, many studies have shown that increasing pH leads to increasing adsorption of elements due to the increasing negative character of the adsorbent but, it was found that the adsorption of Cd was not affected by pH. Modelling was able to account for this observation as it showed that the speciation of Cd hardly changes with pH.

The results obtained from column studies correlated with those from the experimental studies, confirming the reliability and usefulness of modelling. The modelling in column studies showed that more than 2000 shifts are required for the elements to reach breakthrough which, would have been challenging to conduct using analytical experiments. Thus, when necessary information is obtained, time and resources could be saved by using modelling to determine processes occurring in the environment. Therefore, modelling can be very useful in environmental assessment as it can accurately determine the behaviour of elements in soils as in this study. The transport and speciation of elements through the soil profile could not have been known without modelling hence, it will be a useful tool when determining the processes that occur in the natural environment that would otherwise be difficult to determine and estimate with analytical experiments. This study therefore, gave background to the wider application of geochemical modelling in agricultural soils. Furthermore, geochemical modelling can be used to determine the risk assessment measure in different types of soils.

RECOMMENDATIONS FOR FUTURE WORK

- There is a need to study other elements that result from platinum mining activities such as Ruthenium, Rhodium, Osmium, Iridium, and Platinum and determine their behaviour in the agricultural soil.
- The effect of other constantly used fertilisers such as ammonium sulphate, urea and potassium nitrate should be considered.
- To carry out studies of adsorption dependency on the mass transfer not only at room temperature as industrial wastewaters are discharged at various temperatures.
- Freundlich, Langmuir and Dubinin-Radushkevich isotherms should be used to determine the type of adsorption that occurs in the presence of plants exudates and fertilisers.
- There is a need to carry out column studies to determine the effect of fertilisers and plants exudates on the adsorption of elements.
- Different environmental conditions such as temperature, oxidation-reduction potential and rain water should be considered in PHREEQC in order to get a better representation of the real environment.

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Appendix

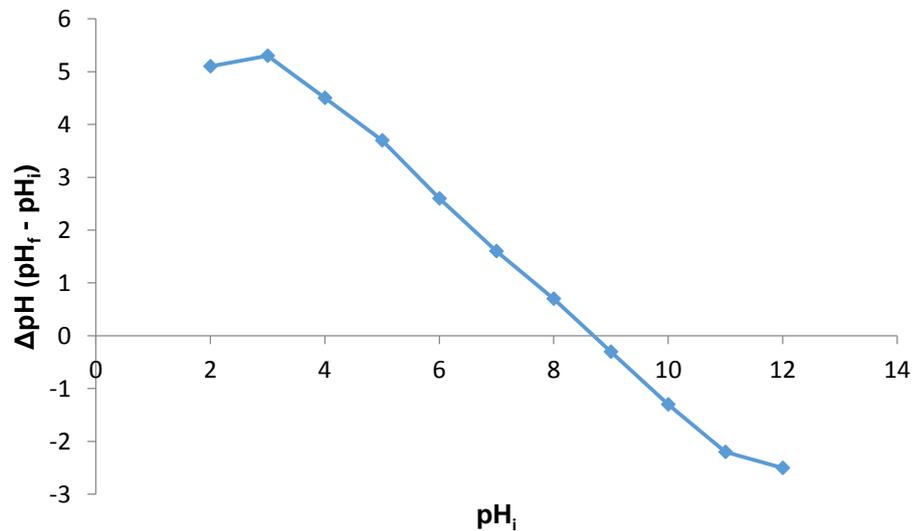


Figure A1 The graph of the point of zero charge (PZC) of an agricultural soil

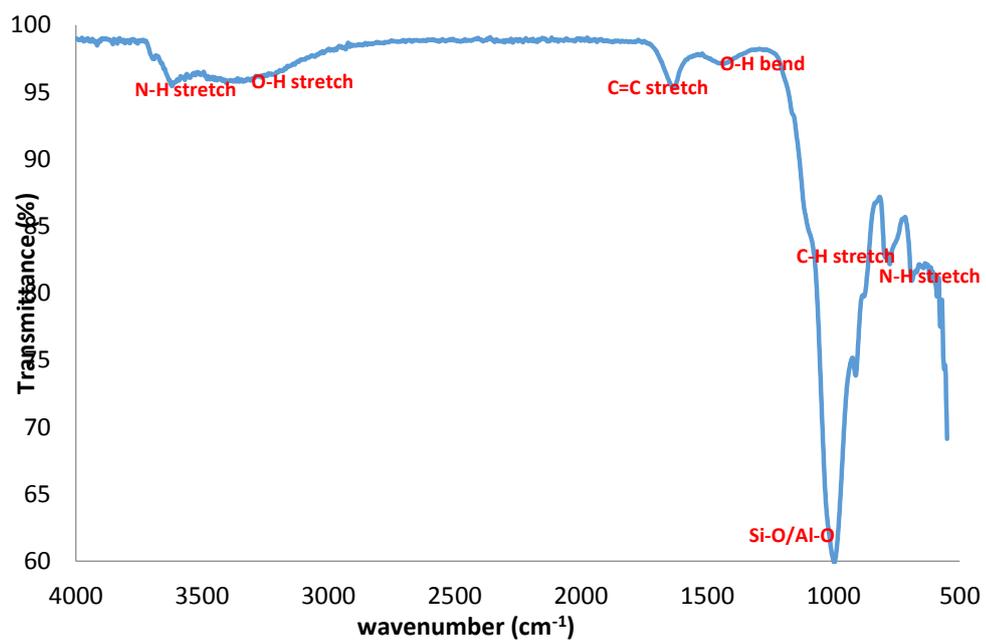


Figure A2 FTIR graph of an agricultural soil

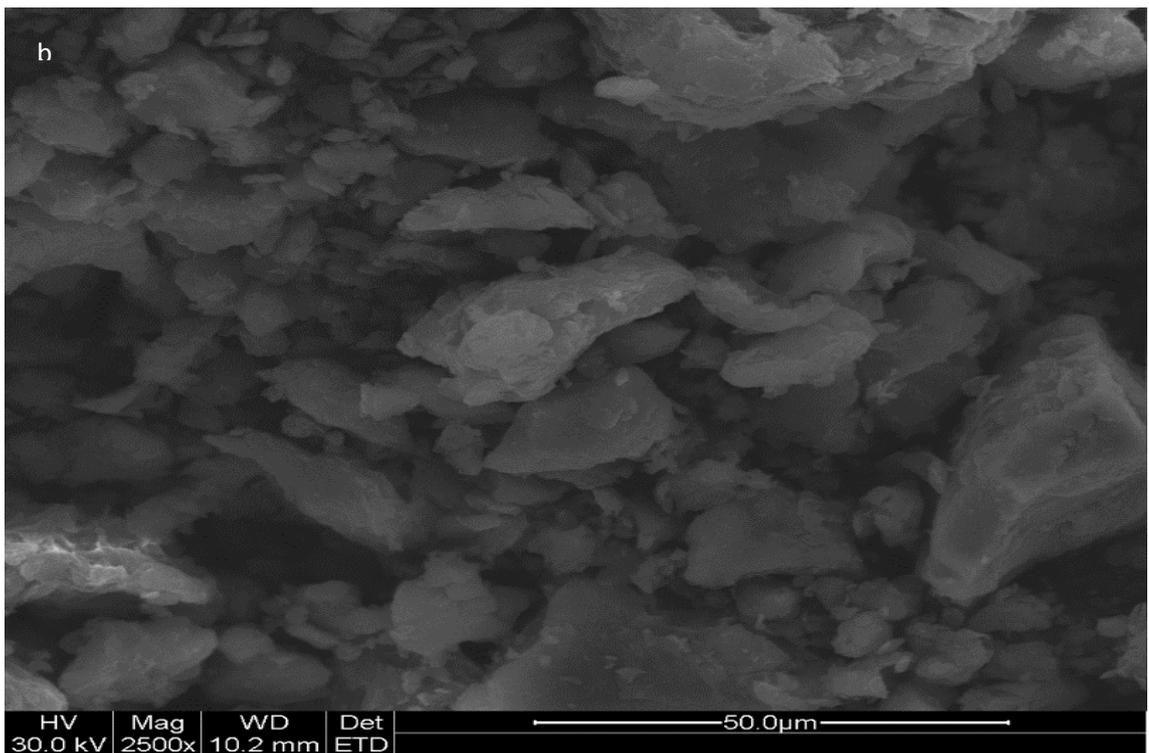
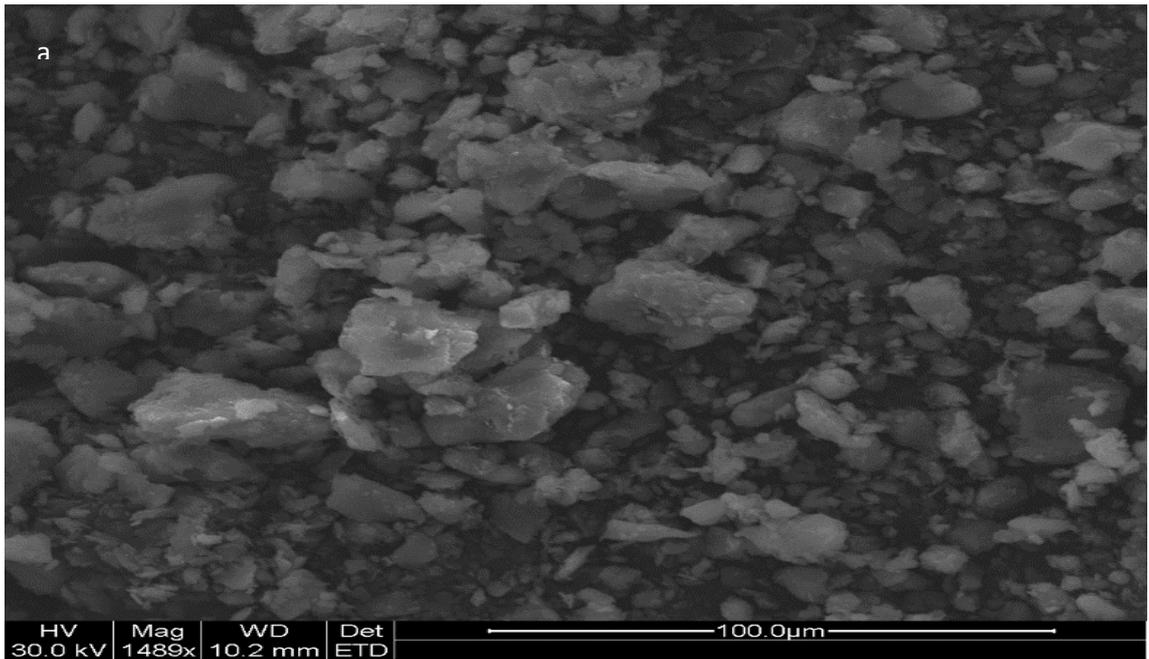


Figure A3 SEM diagrams at 1489 (a) and 2500 (b) magnifications

Table A1 Concentration of elements in the agricultural soil

Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	U
(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
18.98	94.37	1307.09	37.69	164.56	25.25	41.31	9.14	16.07	61.85	12.5	161.18	5.99	153.99	11.51	1.81	d.l.

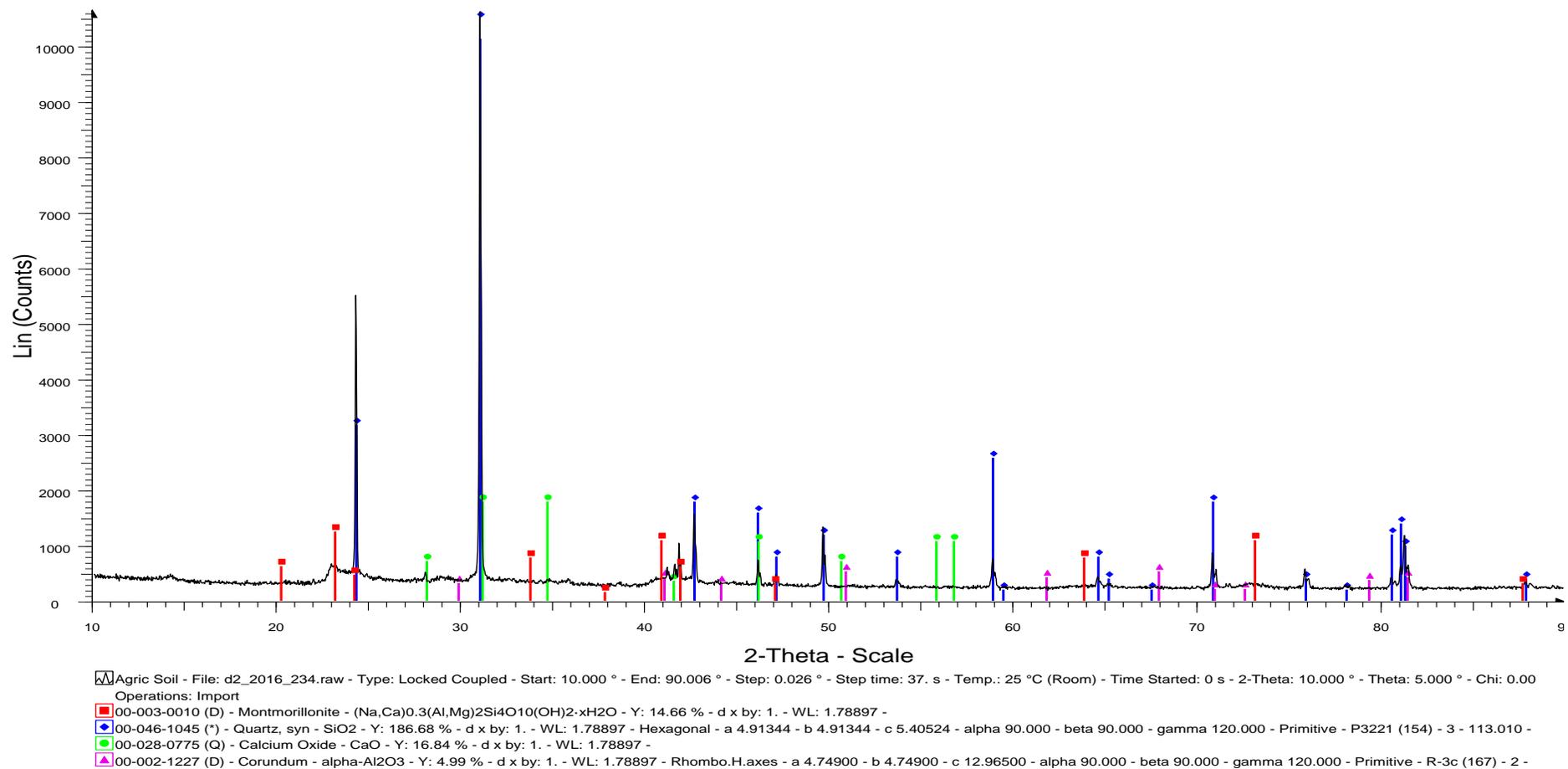


Figure A4 PXRD pattern of an agricultural soil

Table A2 ANOVA results from column studies comparing bed depth for Cu

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	471	6563.508	13.93526	688.4276
Column 2	484	7262.604	15.00538	981.0632

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	273.3548	1	273.3548	0.32669	0.56775	3.851235
Within Groups	797414.5	953	836.7413			
Total	797687.9	954				

Table A3 ANOVA results from column studies comparing bed depth for Cd

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	699	981,1841	1,403697	32,46922
Column 2	718	629,5711	0,87684	19,33297

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	98,31439	1	98,31439	3,808731	0,051183	3,848039
Within Groups	36525,25	1415	25,8129			
Total	36623,56	1416				
Total	3,7E+10	2134				

<pre> TITLE Cd adsorption SOLUTION 0 Units mg/L pH 5 pe 4 temp 25 Cd 100 N(5) 110.3 SOLUTION 1-10 temp 25 pH 7 pe 4 Units mmol/kgw density 1 -water 1 #kg Na 1 K 0.2 EXCHANGE 1-10 -equilibrate solution 1 X 0.516 USE exchange none TRANSPORT -cells 10 -shifts 3000 -lengths 0.0001 -time 30 -dispersivities -print_cells 10 END a </pre>	<pre> TITLE Cu adsorption SOLUTION 0 Units mg/L pH 5 pe 4 temp 25 Cu(2) 100 N(5) 195 SOLUTION 1-10 temp 25 pH 7 pe 4 Units mmol/kgw density 1 -water 1 #kg Na 1 K 0.2 EXCHANGE 1-10 -equilibrate solution 1 X 0.516 USE exchange none TRANSPORT -cells 10 -shifts 2700 -lengths 0.0001 -time 30 -dispersivities -print_cells 10 END b </pre>	<pre> TITLE Cr adsorption SOLUTION 0 Units mg/L pH 5 pe 4 temp 25 Cr(3) 100 N(5) 357.7 SOLUTION 1-10 temp 25 pH 7 pe 4 Units mmol/kgw density 1 -water 1 #kg Na 1 K 0.2 EXCHANGE 1-10 -equilibrate solution 1 X 0.516 USE exchange none TRANSPORT -cells 10 -shifts 2500 -lengths 0.0001 -time 30 -dispersivities -print_cells 10 END c </pre>
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Figure A5 PHREEQC scripts for Cd, Cu and Cr