

IMPACT OF METALLURGICAL INDUSTRIES ON WATER

By

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DECLARATION

I hereby declare that the dissertation submitted for the Degree:Magister Technologiae in the Department of Chemistry at Vaal University of Technology, Vanderbijlpark.is my own original work and has not been submitted before for any degree or examination to any other University. I further declare that all sources cited are indicated and acknowledged by means of a comprehensive list of references.

Simon Sello Matsie July 2012

Signed_____

DEDICATION

I dedicate this work to my wife Mamosa and children Tiisetso, Katleho, Malebina and Lethabo for allowing me time to complete this project.

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PRESENTATIONS AND PUBLICATIONS

The work presented in this dissertation has been published and presented at conferences.

40th South African Chemical Institute (SACI) National Convention and Federation of Chemical Societies, University of Witwatersrand, Gauteng South Africa, January 2011.

4th SEANAC conference held at the Joachim Chissano International Conference centre ,Maputo, Mozambique, July 2012.

Publication submitted

Matsie, S.S., Naidoo, E.B., (2012) Biosorption capacity of the Eucalyptus Myrtaceae in the removal of heavy metals from waste water.

ABSTRACT

The increase in industrial activities has contributed towards an increase in environmental pollution problems. Many ecosystems have deteriorated as a result of an accumulation of pollutants including heavy metals contained in effluents discharged from various industrial processes. Legislative standards require that pollutant levels be controlled to fall within set limits. The World Health Organisation (WHO) states that the following metals: aluminium, chromium, manganese, iron, cobalt, nickel, copper, cadmium, mercury and lead are a concern.

The research has focussed on the removal of heavy metals from industrial waste water. This was achieved by investigating, characterising and quantifying pollutants within a metallurgical industry environment resulting from applied operations technology and then looking into abatement measures that can be put in place. The study was done and conclusions are discussed below.

Analysis of samples indicated the presence of heavy metals with varying concentrations at different sampling points. D1 borehole is found to have higher chromium levels because ferrochrome was once stored in that catchment area. The dam and road bridge sites manganese content is higher due to suspended particulates settling on the ground and being washed down by water streams . Raw materials from mines contain heavy metals which are transferred to water systems during handling.

In this research the toxic metal ion biosorption on an inexpensive and efficient biosorbent from agricultural waste materials has been investigated as replacement strategy for existing conventional systems.

The study was conducted by using eucalyptus leaves powder for sequestering heavy metal ions from waste water. The metal uptake from an aqueous solution is facilitated by functional groups in the ligno-cellulosic material Many solids are capable of adsorbing ions and molecules from solutions. The removal of heavy

V

metals from aqueous solution using eucalyptus leaves has been investigated under different experimental conditions viz. initial metal concentration and adsorbent mass.

Results obtained indicated a decrease in metal concentration due to biosorption of a known elemental concentration per known volume by a known mass of sorbent over a specific time. Sorption is found to be dependent upon contact time, initial concentration, sorbent dose of small quantities of wastewaters containing heavy metals.

In the event of high levels of heavy metal being experienced, ground eucalyptus leaves can be used for heavy metal recovery from wastewater. A procedure covering the sorbent mass required per average specific pollutant concentration over a specific time frame can be compiled to optimise sorption. The advantage of biosorption compared to conventional treatment methods are low cost, high efficiency, minimisation of chemical and biological sludge as well as the regeneration of biosorbents and a possibility of metal recovery.

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LIST OF ABBREVIATIONS

- ICP Inductively Coupled Plasma UV-VIS Ultraviolet Visible spectroscopy WHO World Health Organisation PCB Polychlorinated biphenyl CFC Chlorofluorocarbons HCFC Hydrochlorofluorocarbons ΡM Particulate matter VOC Volatile Organic Compounds NMVOC Non Methane Volatile Organic Compounds International Standards Organisation for the environment ISO 14001 POP Persistent Organic Pollutants USEPA United State Environmental Protection Agency DE Diesel exhaust CWA Clean Water Act NPS Non Point Source DNAPL Dense Non Aqueous Phase Liquids
- EDC Endocrine Disrupting Chemicals

UNFCCC	United Nations Framework Convention on Climate Change
COP	Congress Of the Parties
CERLA	Comprehensive Environmental Response Compensation and Liability
	Act
RCRA	Resource Conservation and Recovery Act
EU	Europe
NL	Netherlands
SA	South Africa
D1	Borehole
XRF	X Ray Fluoresence
HC FeMn	High Carbon Ferro Manganese
MC FeMn	Medium Carbon Ferro Manganese
SiMn	Silico Manganese
HCS	High Carbon Slag
H Trench	Hymat trench
MS	Molten slag
SMS	Silico Manganese Slag

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CHAPTER ONE

INTRODUCTION AND PROBLEM STATEMENT

1.1 Background

Water pollution is a major problem in the global context. It has been suggested that it is the leading cause of deaths and diseases [2,9].

The industrial activities of man has intensified environmental pollution problems. A number of ecosystems have deteriorated as a result of the accumulation of many pollutants, particularly heavy metals which are introduced into the air, water and soil. [9]. Various industries discharge effluents containing heavy metals from their processes into natural systems. These water borne pollutants pose a threat to human health and other life forms on earth due to their toxicity and bio accumulation tendency [1, 6, 7]. Extinction of bison and alligator in aquatic systems as well as an annual decrease in wetlands indicates the posed health threat [9].

Although industrial chemicals are essential to support modern society, growth in the number and quantity of chemicals during recent decades has been extraordinary resulting in an increase in quantity and complexity of hazardous waste materials [3, 8]

Hence, management of water quality is one of the most critical environmental health challenges facing both the developed and developing world [10]. In this context metallurgical industries contribute to the discharge of heavy metals, therefore monitoring and control is essential.

1.2 Metallurgical Industries

Metallurgical industries are vast depending on the operations e.g. steel, stainless steel, ferroalloys, base metals, platinum group metals, gold, foundries, coal, diamonds, petrochemical, cement and lime glass, ceramic ,pulp and others [4]. The metallurgical industry can be divided into primary and secondary metal production operations [11]. Primary refers to the production of metal from ore whereas secondary refers to production of alloys from ingots and to recovery of metal from scrap and salvage.

The primary metals industry includes both ferrous and nonferrous operations. These processes are characterised by emission of large quantities of sulphur oxides and particulate matter. Secondary metallurgical processes are characterised by emission of particulates in the form of metallic fumes, smoke and dust [5]. Particulates and sulphur oxides ultimately settle on the ground, transported by water particles or wind and join terrestrial water cycles.

The metallurgical industry being studied is a ferroalloy industry in which both primary and secondary operations are involved.

The generalised reactions can be illustrated as follows:

 $FeO + C - (700 \ ^{\circ}C) \rightarrow Fe + CO$ (1)

 $MnO + C - (1400 \ ^{0}C) \rightarrow Mn + CO$ (2)

 $SiO_2 + C - (1600 \ ^{\circ}C) \rightarrow Si + CO_2$ (3)

The above reactions are arranged in order of increasing energy input required . As the furnace heats up and melts the furnace contents, Fe will be formed first followed by Mn and Si respectively. By manipulating the proportions of SiO₂, MnO and FeO in the furnace (through the selection of different amounts of ore and quartz), the desired

Si, Mn and Fe content in the product can be achieved. Al₂O₃, MgO and CaO can also be reduced to Al, Mg and Ca respectively. This requires more energy and occurs at higher temperatures than the reduction of SiO₂. Generally the furnaces will be operated so that these reactions do not occur, hence Al₂O₃, MgO and CaO and other unreduced material will form material called slag.

1.3 Problem statement

Delivery and handling of raw materials (manganese ores and sinter products, quartzite, coal, coke, lime and dolomite) to the industry site by road and rail trucks contributes to generation of diesel fumes and diesel could also leak on soil. During rainy days these pollutants are washed into the river water or river bodies.

The raw materials stored in stockpiles lead to contamination of run-off water by hazardous substances (including phenols from coal stockpiles and heavy metal ions from ores) leading to both surface and groundwater contamination with toxic compounds.

The effluents generated from production process water circuits may also contain high levels of dissolved solids some of which may be harmful to the environment.

Some of these recyclable materials are legally defined internationally as wastes. However, if they exhibit any hazard characteristic, they are regulated equivalently to hazardous wastes destined for final disposal [5].

1.4 Objectives

The objectives of this research were to:

Characterise some pollutants that might be present in water in a metallurgical industry using techniques such as ICP and UV-VIS spectroscopy.

- Establish the trends in the distribution of these compounds over the industry and establish the transport and fate of these pollutants in the environment.
- **4** Establish the possible environmental impact associated with the pollutants.
- 4 Investigate possible abatement measures that can be put in place.

1.5 Value and outcome of the research

This research will contribute to the development of mitigation strategies for the environmental pollution. The strategies developed will in turn also help in terms of a cleaner and healthier environment conducive to all living organisms, as required by the WHO (World Health Organisation).

- Masters degree
- Publications
- Conference attendance

1.6 Outline of the dissertation

This research is outlined as follows:

Chapter one : This chapter provides an insight into the research project that was done. The problem statement as well as the objective are presented in this chapter.

Chapter two : In this chapter a review of literature pertaining to industrial air and water pollution impact ,as well as legislation is presented.

Chapter three : All analytical methods and experimental procedures that were used in this research project are discussed in this chapter.

Chapter four : Results obtained from this study will be presented and discussed in this chapter.

Chapter five : Based on results obtained with respect to the initial objectives, conclusions are drawn and recommendations are made in this chapter.

References

[1] Garg,U.K.,Kaur, M.P.,Garg ,V.K.,Sud, D. 2007.Removal of hexavalent chromium from aqueous solution by agricultural waste biomass.Journal of hazardous materials , 140 :60-68

[2] Ghodbane, I., Hamdaoui ,O. 2008.Removal of mercury(II) from aqueous media using eucalyptus bark: Kinetic and equilibrium studies .Journal of Hazardous Materials, 160, (2-3):301-309,December 30.

[3] Howard ,K.W.F. 2007.Urban ground water, meeting the challenge. London: Taylor and Francis Group.

[4] Industrial Metallurgy Reg. ISSN 1024-316X :30-32, June 2011.

[5] Industrial Metallurgy Reg. ISSN 2024-316X:6, September 2011.

[6] Kelland, M. A. 2009.Production chemicals for oil and gas industry, Boca Raton: CRC Press.

[7] Manahan ,S.E. 2011. Water Chemistry: green science and technology of nature's most renewable resource .USA:Taylor and Francis Group.

[8] Sodhi ,G.S., 2009.Fundamental concepts of environmental chemistry. New Delhi: Narosa.

[9] Spellman Frank R., 2008. The science of water: concepts and applications, 2nd ed, Boca Raton:CRC Press .

[10] The Water Wheel ISSN 0258-2244,10 (3):16-21 May/June 2011.

[11] www.mhmhd.com/metallurgical -industry.>.Accessed:04/11/2011.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Pollution is the release of harmful environmental contaminants as a result of a wide range of human activities. It is an unwelcome concentration of substances that are beyond the environment's capacity to handle and adversely affects human health or the quality of life, bio systems, the environment, structures, equipment, recreational opportunities, aesthetics or natural beauty. A pollutant is a substance present in greater than natural concentration as a result of human activity that has a net detrimental effect upon its environment [15].

These substances are detrimental to people and other living things. In an undisturbed ecosystem, all substances are processed through an intricate network of biogeochemical cycles, such as the nitrogen and carbon cycles. During theses cycles, substances are taken up by plants, move through the food chain to larger and more complex organisms, and when the latter die, are decomposed(broken down) into simpler forms to be used again when they are taken up by plants. Biodegradable substances are those that can be broken down by the environment's biological systems.

Pollution occurs when the environment becomes overloaded beyond the capacity of these normal processing systems. Examples include:

• An excess of normally helpful substances, such as the nutrients nitrogen and phosphorus.

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- An excess of substances that are harmless, and perhaps even in tiny amounts, but toxic in higher concentrations. Copper, for example, is necessary in small amounts for healthy plant growth, but becomes a pollutant if it occurs in greater quantities.
- Synthetic (man made) compounds that are poisonous in the environment, often even in trace amounts, such as DDT (1,1,1-trichloro-2,2-bis (pchlorophenyl ethane, (p-CIC₆H₄)₂CHCCl₃).
- , Dioxin, PCBs (Poly chlorinated biphenyls) and organochlorines.
- Substances that in any amount, are not biodegradable, such as plastics and highly persistent chemicals like DDT and other organochlorines. Some pollutants kill living organisms outright, other sub-lethal pollutants do not kill, but may cause long-term biological damage, interfere with organism' reproductive cycle, or make them more vulnerable to disease.
- Heavy elements such as mercury and arsenic.

Pollutants such as oil, detergents, nitrogen and phosphates from fertilizers as well as lead and mercury from mining industries can have a tremendous impact on the ecosystem, especially if the water gets polluted. In a lake, for example, it can introduce disorders on the ecological balance by stimulating plant growth and causing the death of fish due to suffocation from lack of oxygen. The oxygen cycle will cease, and the polluted water will also affect the animals dependent on the lake water [18].

The Vaal Triangle in the southern part of Johannesburg is home to a number of heavy industries, which are sources of high levels of environmental pollution (air, water and soil). The problem of pollution in this region requires an integrated approach embracing all stakeholders' needs to be developed so as to come up with sound policies and techniques that are going to bring about a change for the better regarding the pollution within the region.

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The diversity of industries within the Vaal triangle results in a large range of pollutants being emitted into the environment. Metallurgical industries are situated in this area and need to meet the requirements set out for the control of pollution.

2.2. Air Pollution

Air pollution is the introduction into the atmosphere, of chemicals, particulate matter, or biological materials that cause harm or discomfort to humans or other living organisms, or damage the natural environment [20].

2.2.1 Types of air pollutants

Air pollutants may be natural or man-made (anthropogenic [9].

(a) Natural sources

This type of pollution occurs naturally without any input from man and can be noted as:

- Dust from natural sources such as large areas of land with little or no vegetation.
- Methane emitted from digestion of food by animals, for example cattle

Radon gas from radioactive decay within the earth's crust. Radon is a colourless, odourless, naturally occurring, radioactive noble gas that is formed from the decay of radium. Radon is considered a health hazard and as a gas from natural sources can accumulate in buildings, especially in confined areas such as the basement and it is the second most frequent cause of lung cancer after cigarette smoking [16].

• Smoke and carbon monoxide from wildfires.

• Volcanic activity, which produce sulphur, chlorine and ash particulates.

(b) Anthropogenic sources

Anthropogenic sources result from human activities mostly related to burning of different kinds of fuels and include the following:

- Stationery sources include smoke stacks of power plants, manufacturing facilities (factories) and waste incinerators, as well as furnaces and other types of fuel burning heating devices.
- Mobile sources include motor vehicles, marine vessels, aircrafts and the effect of sounds.
- Chemicals, dust and controlled burn practices in agriculture and forestry management. Controlled or prescribed burning is a technique sometimes used in forest management, farming, prairie restoration or greenhouse gas abatement. Fire is a natural part of both forest and grassland ecology, and controlled fire can be a tool for foresters. Controlled burning stimulates the germination of some desirable forest trees, thus renewing the forest.
- Fumes from paint, hair spray, varnish, aerosol sprays and other solvents.
- Waste deposition in landfills, which generates methane. Methane is non toxic but highly flammable and may form explosive mixtures with air. Methane is also an asphyxiant and may displace oxygen in an enclosed space. Asphyxiation (suffocation) may result if the oxygen level is reduced to below 19.5% by displacement.
- Military activities such as nuclear weapons, toxic gases, germ warfare and rocketry [25].

2.2.2 Classification of air pollutants

Pollutants are classified as either primary or secondary. Primary pollutants are substances usually emitted directly from a process, such as ash from a volcanic eruption, the carbon monoxide gas from a motor vehicle exhaust or sulphur dioxide from factories.

(a) Primary pollutants

The following are some major primary pollutants produced by human activity:

Ammonia (NH₃)

Ammonia is a compound, emitted from agricultural processes. It is also normally encountered as a gas with a characteristic pungent odour. Ammonia contributes to the nutritional needs of terrestrial organisms by serving as a precursor to foodstuffs and fertilizers. It is also a building block for the synthesis of many pharmaceuticals. Although it is widely used, ammonia is both caustic and hazardous.

Carbon dioxide (CO₂)

Carbon dioxide is a greenhouse gas (a gas that creates a condition in the upper atmosphere causing a trapping of heat and leading to increased lower atmosphere (troposphere) temperatures) emitted from combustion [8] but is also a gas vital to living organisms. It is a natural gas in the atmosphere.

Carbon monoxide (CO)

Carbon monoxide is a colourless odourless, non irritating but very poisonous gas. It is a product of incomplete combustion of fuel such as natural gas(methane), coal or wood. Vehicular exhaust is a major cause of carbon monoxide. *Chlorofluorocarbons(CFC's)*

Chlorofluorocarbons contribute towards depletion of the ozone layer. These chemicals are currently banned from use. According to [1], many industries are aware of the spectre of global and local legislation governing hydrochlorofluorocarbons (HCFC's) but in the current economic downturn, many are delaying making vital decisions on whether to change to new blends or go down the recycling path.. There are thousands of HCFC's in installations across South Africa, which could prove a real headache in terms of risking threats to business continuity and spiraling costs, if these users fail to decide on the way forward now or pay dearly later.

The HCFC R22 has been the refrigerant of choice for commercial and industrial refrigeration for more than 40 years, but it has been found that releases of R22, such as those from leaks, contribute to ozone depletion.

R22 is also a greenhouse gas and its manufacture results in a by-product called HCFC23 that contributes significantly to global warming.

At the moment South Africa consumes more than 4000 tonnes of HCFC's annually, the highest consumer in Africa. They are mainly used in the refrigeration, air-conditioning,foam-blowing,mining and aerosol industries. These industries invested heavily on HCFC's technology since moving away from CFC's and when South Africa was denied usage of these substances.[1].

Nitrogen oxides (NO_X)

Nitrogen dioxides (NO₂) are emitted from high temperature combustion. It can be seen as a brown haze dome above an industry or a plume downwind of cities. It is one of the most prominent air pollutants with a characteristic sharp , biting odour.

Odours

Odours come from garbage, sewage and industrial processes.

Particulate matter

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Particulate matter(PM) comprises particulates or fine particles which are tiny particles of solid or liquid suspended in a gas. In contrast, aerosols refer to particles and the gas together. Sources of particulate matter can be man made or natural.

Natural particulates originate from volcanoes, dust storms, forest and grassland fires, living vegetation and sea spray. Human activities such as burning of fossil fuels in vehicles, power plants and various industrial processes also generate significant amounts of aerosols. Anthropogenic (made by human activities) aerosols account for about 10 percent of the total amount of aerosols in the atmosphere.

Increased levels of particulates in the air are linked to health hazards such as heart disease, altered lung function and lung cancer.[16].

Radioactive pollutants

Radioactive pollutants are produced by nuclear explosions, war explosives, and natural processes such as the radioactive decay of Radon (Rn)

Sulphur oxides (SO_X)

Sulphur oxides(SO_X), especially sulphur dioxide (SO_2), is produced by volcanoes in various industrial processes. Since coal and petroleum also contain sulphur compounds their combustion generates sulphur dioxide. Further oxidation of SO_2 , usually in the presence of a catalyst such as NO₂, forms H₂SO₄.

 $SO_2 + \frac{1}{2}O_2 + H_2O \xrightarrow{NO_2} H_2SO_4$

Toxic metals

Cadmium (Cd) Copper (Cu), Lead (Pb) and Mercury (Hg)

Volatile Organic Compounds (VOC)

Volatile Organic Compounds (VOC) are important outdoor air pollutants and are often divided into separate categories of methane(CH_4) and non-methane (NMVOC's).

Methane is an extremely efficient greenhouse gas which contributes to enhanced global warming. Other hydrocarbon VOC's are also significant greenhouse gases via their role in creating ozone and in prolonging the life of methane in the atmosphere, but the effect varies depending on local air quality.

Within the NMVOC's, the aromatic compounds benzene(ArH),toluene (ArCH₃) and xylene (Ar(CH₃)₂) are suspected carcinogens and may lead to leukemia through prolonged exposure. 1,3-butadiene (C₄H₆)is another dangerous compound which is often associated with industrial uses.

(b) Secondary pollutants

Secondary pollutants form in the air when primary pollutants react or interact. One example of a secondary pollutant is ground level ozone, that make up photochemical smog. However, some pollutants may be both primary and secondary i.e. they are both emitted directly and formed from other primary pollutants. According to the Environmental Science Engineering Program at the Harvard School of Public Health, about 4 percent of deaths in the United States can be attributed to air pollution.

Notable Secondary pollutants

 Particulate matter are formed from gaseous primary pollutants and compounds in photochemical smog. Smog (derived from smoke and fog) is a kind of air pollution that results from burning of large amounts of coal in an area, and is caused by a mixture of smoke and sulphur dioxide. Modern smog from vehicular and industrial emissions that are acted upon in the atmosphere by sunlight, form secondary pollutants that also combine with the primary emissions to form photochemical smog.

- Ground level ozone (O₃) is formed from NO_X and VOC's .Ozone is a key component of the troposphere (the lowermost atmospheric layer). It is also an important constituent of certain regions of the stratosphere (the earth atmosphere between about ten and sixty kilometers above the surface of the earth) commonly known as the Ozone layer. At abnormally high concentrations brought about by human activities (largely the combustion of fossil fuel), it is a pollutant and a constituent of smog.
- Peroxyacetyl nitrate (PAN), similarly formed from NOx and VOC's,

(c) Minor air pollutants

- A large number of minor hazardous air pollutants are also present. Some of these are regulated in USA under the Clean Air Act and in Europe under the Air Framework Directive. In South Africa the Green Gain Consulting Company has developed a turnkey environmental legal compliance system called Digilex which regulates the environmental (ISO 14001) legal compliance.
- A variety of persistent organic pollutants, which can attach to particulate matter exist.

Persistent organic pollutants (POP'S) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. As a result they have been observed to persist in the environment, to be capable of longrange transport. They bioaccumulate in human and animal tissue, biomagnify in food chains, and have potential significant impacts on human health and the environment.

2.2.3 Sources of air pollution

Sources of air pollution refer to various locations, factors which are responsible for the releasing of pollutants in the atmosphere. Sources can be classified into two major categories which are:

Emission factors

Air pollutant emission factors are representative values that attempt to relate the quality of a pollutant released to the ambient air with an activity associated with the release of pollutant. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance or duration of the activity emitting the pollutant (gram of particulate emitted per kilogram of coal burned). Such factors facilitate estimation of emissions from various sources of air pollution.

In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages.

The United States Environmental Protection Agency (USEPA) has published a compilation of air pollutant emission factors for a multitude of industrial sources[2]. The United Kingdom, Australia, Canada and many other countries have published similar compilations, as well as the European Environment Agency [4,6,7,17,19].

Indoor air quality (IAQ)

A lack of ventilation indoors concentrates air pollution where people often spend the majority of their time. Radon (Rn) gas, a carcinogen (causing cancer), is exuded from the Earth in certain locations and trapped inside houses. Building materials including carpeting and plywood emit formaldehyde(H_2CO) gas [16].

Paint and solvents give off volatile organic compounds (VOC's) as they dry. Lead paint can degenerate into dust and be inhaled. Intentional air pollution is introduced with the use of air fresheners, incense, and other scented items. Controlled wood fires in stoves and fireplaces can add significant amounts of smoke particulates into the air.

Indoor pollution fatalities may be caused by using pesticides and other chemical sprays indoors without proper ventilation.
Carbon monoxide (CO) poisoning and fatalities are often caused by faulty vents and chimneys, or by the burning of charcoal indoors. Chronic carbon monoxide poisoning can be a result of poorly adjusted pilot lights. Traps are built into all domestic plumbing to keep sewer gas, hydrogen sulphide, out of interiors. Clothing emits tetrachloroethylene (CCl₂CCl₂), or other dry cleaning fluids, for days after cleaning.

The extensive use of asbestos (soft fibrous mineral substance) in industrial and domestic environments in the past (though its use has now been banned in many countries) has left a potentially very dangerous material in many localities.

Asbestosis is a chronic inflammatory medical condition affecting the tissue of the lungs. It occurs after long-term heavy exposure to asbestos from asbestos containing materials in structures. Sufferers have severe dyspnea (shortness of breath) and are at an increased risk regarding several different types of lung cancer.

Biological sources of air pollution are also found indoors, as gases and airborne particulates. Pets produce dander, people produce dust from minute skin flakes and decomposed hair, dust mites in bedding, carpeting and furniture produce enzymes and micrometre-sized faecal droppings, inhabitants emit methane, mould forms in walls and generates mycotoxins and spores, air conditioning systems can incubate Legionnaires' disease and mould, and houseplants, soil and surrounding gardens can produce pollen, dust and mould. Indoors, the lack of air circulation allows these airborne pollutants to accumulate more than would otherwise occur in nature.

2.2.4 Health effects

The World Health Organisation (WHO) states that 2.4 million people die each year from causes directly attributable to air pollution, with 1.5 million of these deaths attributable to indoor air pollution[10]. Epidemiological studies suggest that more than 500,000 Americans die each year from cardio pulmonary diseases linked to breathing fine particle air pollution.

A study by the University of Birmingham has shown a strong correlation between pneumonia related deaths and air pollution from motor vehicles. Worldwide more

deaths per year are linked to air pollution than to automobile accidents. Direct causes of air pollution related deaths include aggravated asthma, bronchitis, emphysema, lung and heart diseases, and respiratory allergies.

The USEPA (United States Environmental Protection Agency) estimates that a proposed set of changes in diesel engine technology (Tier 2) could result in 12,000 fewer premature mortalities, 15,000 fewer heart attacks, 6,000 fewer emergency room visits by children with asthma, and 8,900 fewer respiratory related hospital admissions each year in the United States.

The worst short term civilian pollution crisis in India was the 1984 (Bhopal Disaster). Industrial vapours that leaked from the Union Carbide Factory, belonging to the Union Carbide, Inc., U.S.A., killed more than 2,000 people outright and injured anywhere from 150,000 to 600,000. About 6,000 others died later from injuries.

The United Kingdom suffered its worst air pollution event when the December 4 Great Smog of 1952 formed over London. In six days more than 4,000 died , and a further 8,000 died within the following months.

An accidental leak of anthrax spores from a biological warfare laboratory in the former USSR in 1979 near Sverdlovsk is believed to have been the cause of hundreds of civilian deaths, The worst single incident of air pollution to occur in the United States of America occurred in Donora, Pennsylvania in late October , 1948 when 20 people died and 7, 000 were injured .Health effects caused by air pollution may range from subtle biochemical and physiological changes to difficulty in breathing, wheezing, coughing and aggravation of existing respiratory and cardiac conditions. The human health effects of poor air quality are far reaching , but principally affect the the body's respiratory system and the cardiovascular system. Individual reactions to air pollutants depend on the type of pollutant a person is exposed to , the degree of exposure, the individual's health status and the genetics.

A new economic study of health impacts and associated costs of air pollution in Los Angeles Basin and San Joaquin Valley of Southern California shows that more than

3800 people die prematurely (approximately 14 years earlier than normal) each year because air pollution levels violate federal standards.

The number of annual premature deaths is considerably higher than the fatalities related to automobile collisions in the same area, which averages fewer than 2,000 per year.

Diesel exhaust (DE) is a major contributor to combustion derived particulate matter air pollution. In several human experimental studies, using a well validated exposure chamber setup, DE has been linked to acute vascular dysfunction and increased thrombus formation. This serves as a plausible mechanistic link between the previously described association between particulate matter air pollution and increased cardiovascular morbidity and mortality.

2.3 Water pollution

Water pollution is the contamination of water bodies such as lakes, rivers, oceans and groundwater.[15,18]. All water pollution affects organisms and plants that live in these water bodies and in almost all cases the effect is damaging not only to individual species and populations but also to the natural biological communities. This occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful constituents.

Water pollution is a major problem in the global context. It has been suggested that it is the leading cause of deaths and diseases and that it accounts for deaths of more than 14,000 people daily. An estimated 700 million Indians have access to proper toilets, and 1,000 Indian children die of diarrhoeal sickness every day Some 90% of China's cities suffer from some degree of water pollution[33], and nearly 500 million people lack access to safe drinking water. In addition to acute problems of water pollution in developing countries, industrialized countries continue to struggle with pollution problems as well [18]. In the most recent national report on water quality in the United

States, 45 percent of assessed stream miles, 47 percent of assessed lake acres, and 32 percent of bay and estuarine square miles were classified as polluted.

Precipitation (e.g. rain, snow, hail) represents an effective removal mechanism of atmospheric pollutants. These pollutants end up joining the water system.

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, like serving as drinking water, and undergoes a marked shift in its ability to support its constituent biotic communities, such as fish. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water. Water pollution has many causes and characteristics.

2.3.1 Water pollution categories

Surface water and ground water have been studied and managed as separate sources, although they are interrelated. Sources of surface water pollution are generally grouped into two categories based on their origin. The two categories are point source pollution and non point source pollution.

(a) Point source pollution

Point source pollution refers to contaminants that enter a waterway through a discrete conveyance, such as a pipe or ditch. Examples of sources in this category include discharges from a sewage treatment plant, a factory, or a city storm drain. The U.S. Clean Water Act (CWA) defines point source for regulatory enforcement purposes. The CWA definition of point source was amended in 1987 to include municipal storm sewer system, as well as industrial storm water, such as from construction sites.

(b)Non point source pollution

Non point source (NPS) pollution refers to diffuse contamination that does not originate from a single discrete source. NPS pollution is often an accumulative effect of small amounts of contaminants gathered from a large area.

The leaching out of nitrogen compounds from agricultural land which has been fertilized is a typical example. Nutrient runoff in stormwater from "sheet flow" over an agricultural field or a forest are also cited as examples of NPS pollution.

Contaminated storm water washed off parking lots, roads and highways, called urban runoff, is sometimes included under the category of NPS pollution. However, this runoff is typically channeled into storm drain system and discharged through pipes to local surface waters, and is a point source. However where such water is not channeled and drains directly to ground it is a non point source.

2.3.2 Ground water pollution

Interaction between groundwater and surface water are complex. Consequently, groundwater pollution, sometimes referred to as groundwater contamination, is not as easily classified as surface water pollution. By its true nature, groundwater aquifers are susceptible to contamination from sources that may not directly affect surface water bodies, and the distinction of point vs. non-point source may be irrelevant. A spill of chemical contamination on soil, located away from a surface water body, may not necessarily create point source or non-point source pollution, but nonetheless may contaminate the aquifer below. Analysis of groundwater contamination may focus on soil characteristics and hydrology, as well as the nature of the contaminant itself.

2.3.3 Causes of pollution in water

Specific contaminants leading to pollution in water included a wide spectrum of chemicals, pathogens and physical or sensory changes such as elevated temperatures and discolouration [18]. While many of the chemical substances that are regulated may be naturally occurring (calcium, iron, manganese, sodium) etc., the concentration is often the key in determining what is a natural component of water,

and what is a contaminant. More than two-thirds of elements in the periodic table are metals. Some are major environmental pollutants because of their widespread use.

Thirteen metals are classified by USEPA as priority pollutants, aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, swelenium, silver and zinc. The mobility of eight metals in soil viz. arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver is measured as recommended by the Resource Conservation and Recovery Act to determine the characteristic of toxic waste [16].

Oxygen-depleting substances may be natural materials, such as plant matter (e.g leaves and grass) as well as man-made chemicals. Other natural and anthropogenic substances may cause turbidity which blocks light and disrupts plant growth, clogs the gills of some fish species.

A number of chemical substances are toxic. Pathogens can produce waterborne diseases in either human or animal hosts. Alterations of water's physical chemistry include change in pH, electrical conductivity, temperature and eutrophication (an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases in the primary productivity of the ecosystem). Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia and severe reduction in water quality, fish, and other animal population may occur.

(a) Pathogens

Coliform bacteria are commonly used bacterial indicator of water pollution, although not an actual cause of disesase. Other microorganisms sometimes found in surface waters which have human health problems include:

- Burcholderia pseudomallei
- Cryptosporidium parvun
- Giardial lamblia
- Salmonella
- Novovirus and other viruses

• Parasitic worms(helminthes

High levels of pathogens may result from inadequately treated sewage discharges. This can be caused by a sewage plant designed with less than secondary treatment (more typical in less developed countries). In developed countries, older cities with aging infrastructure may have leaky sewage collection systems (valves, pipes, pumps), which can cause sanitary sewer overflows. Some cities also have combined sewers, which may discharge untreated sewage during rain storms. Pathogen discharges may also be caused by poorly-managed livestock operations.

(b) Chemical and other contaminants

Contaminants may include organic and inorganic substances.

- (i) Organic water pollutants
 - Detergents
 - Disinfection by-products found in chemically disinfected drinking water, such as chloroform
 - Food processing waste, which can include oxygen-demanding substances, fats and grease
 - Insecticides and herbicides, a huge range of organohalides and other chemical compounds
 - Petroleum hydrocarbons, gasoline, diesel fuels, jet fuel and fuel oil and lubricants such as motor oils, and fuel combustion by-products. Tree and bush debris from logging operations
 - Volatile organic compounds (VOC's), such as industrial solvents.

Chlorinated solvents, which are dense non aqueous phase liquids (DNAPL's), may fall to the bottom of reservoirs ,since they don't mix well with water and are denser.

Various chemical compounds found in personal hygiene and cosmetic products.

(ii) Inorganic water pollutants

- Acidity caused by industrial discharges such as sulphur dioxide from power plants
- Ammonia from food processing waste
- Chemical waste as industrial by-products [12], Fertilizers containing nutrients, nitrates and phosphates, which are found in storm water run off from agriculture, as well as commercial and residential us.
- Heavy metals from motor vehicles, via urban storm water runoff. and acid mine drainage
- Silt (sediment) in run off from construction sites, logging, slash and burn practices or land clearing sites.
- (iii) Macroscopic pollution

Large visible items polluting the water may be termed "flotsam "in an urban storm water context, or marine debris when found on open seas, and can include such items as:

- Trash (paper, plastic, or food waste) discarded by people on the ground, and washed by rainfall into storm drains and eventually discharged into surface waters
- Nurdles, small ubiquitous waterborne plastic pellets
- Shipwrecks and large derelict ships
- (iv) Thermal pollution

Thermal pollution is the rise and fall in the temperature of a natural body of water caused by human influence. A common cause of thermal pollution is the use of water as a coolant by power plants and industrial manufacturers. Elevated water temperatures decrease oxygen levels, which kill fish, and affects ecosystem composition, such as invasion by new thermophylic species. Urban runoff may also elevate temperature in surface waters.

Thermal pollution can also be caused by the release of very cold water from the base of reservoirs into warmer rivers.

2.3.4 Transport and chemical reactions of water pollutants

Most water pollutants are eventually carried by rivers into the oceans. [18]. In some areas of the world the influence can be traced hundreds kilometers from the mouth by studies using hydrology transport models. Advanced computer models have been used in many locations worldwide to examine the fate of pollutants in aquatic systems. Indicator filter feeding species such as copepods have also been used to study pollutants fate in the New York Bight, for example. The highest toxin loads are not directly at the mouth of the Hudson River, but 100 kilometres south, since several days are required for incorporation into planktonic tissue.

The Hudson discharge flows south along the coast due to coriolis force. Further South then are areas of oxygen depletion, caused by chemicals using up oxygen and by algal blooms, caused by excess nutrients from algal cell death and decomposition. Fish and shellfish kills have been reported, because toxins climb the food chain after small fish consume copepods, then large fish eat smaller fish, etc. Each successive step up the food chain causes a stepwise concentration of pollutants such as heavy metals (e..g mercury) and persistent organic pollutants such as DDT. This is known biomagnifications, which occasionally as is used interchangeably with bioaccumulation.

Large gyres (vortices) in the oceans trap floating plastic debris. The North Pacific Gyre for example has collected the so-called "Great Pacific Garbage Patch" that is now estimated at 100 times the size of Texas .Many of these long-lasting pieces wind up in the stomachs of marine birds and animals. The result is obstruction of digestive pathways which leads to reduced appetite or even starvation.

Many chemicals undergo reactive decay or chemical change especially over long periods of time in groundwater reservoirs. A noteworthy class of such chemicals is the chlorinated hydrocarbons such as trichloroethylene (used in industrial metal degreasing and electronics manufacturing) and tetrachloroethylene used in the dry cleaning industry. Both of these chemicals, which are carcinogens themselves,

undergo partial decomposition reactions, leading to new hazardous chemicals (including dichloroethylene and vinyl chloride).

Groundwater pollution is much more difficult to abate than surface pollution because groundwater can move great distances through unseen aquifers. Non-porous aquifers such as clays partially purify water of bacteria by simple filtration (adsorption and absorption), dilution, and, in some cases, chemical reactions and biological activity. However, in some cases the pollutants merely transform to soil contaminants. Groundwater that moves through cracks and carverns is not filtered and can be transported as easily as surface water. In fact, this can be aggravated by the human tendency to use natural sinkholes as dumps in areas of karst topographry.

There are a variety of secondary effects stemming not from the original pollutant, but a derivative condition. An example is silt-bearing surface runoff, which can inhibit the penetration of sunlight through the water column, hampering photosynthesis in aquatic plants

2.3.5 Wastes and pollutants in soil

Large quantities of waste products are deposited into the soil. Much of the sulphur dioxide emitted in the burning of sulphur- containing fuels end up as soil sulphate [15]. Atmospheric nitrogen oxides are converted to nitrates in the atmosphere, and the nitrates eventually are deposited on soil. Soil sorbs NO and NO₂, and these gases are oxidised to nitrates in the soil. Carbon monoxide is converted to CO₂ and possibly to biomass by soil bacteria and fungi. Particulate lead from automobile exhausts is found at elevated levels along heavily travelled highways. Elevated levels of lead from lead mines and smelters are found on soil near such facilities.

2.3.6 Natural water pollution

Man-made pollution and poor water quality is a major environmental concern, but there are many natural processes influencing water quality. Recharge from infiltration by rivers to the upper part of the aquifer as well as lateral recharge from the mountain area lead to water pollution.[5] Natural water- rock interaction as well as the following

- Lithology and structural geology (karst, joints, faults) of country rocks,
- Fe and metal rich gravel beds, sediments and soils.
- Evaporite sediments and occluded brines mixing of prestine waters with marine and intrusive, trapped connate Chlorides and sulphate brines.
- Concentration by evaporation.

2.3.7 Anthropogenic water pollution

Anthropogenic water pollution is brought about by many different human activities taking place on a daily basis. Sources include industry, agriculture, power generation(coal, oil or gas power station), mining and waste dumps.

Types of water quality problems facing South Africa [4] are:

- U = Urban/Industrial effluent pathogens and organics
- T = Acidic atmospheric deposits
- G = Ground water contamination fluoride and/ or nitrates
- A = Agricultural chemicals
- E = Excessive sediment
- M =Metals (mining and industry)
- R =Radioactivity
- S =Salinity

Currently, waterborne toxic chemicals pose the greatest threat to the safety of water supplies in industrialized nations [15]. This is particularly true of ground water in the U.S.

There are many possible sources of chemical contamination including wastes from industrial chemical production, metal plating operations, and pesticides runoff from agricultural lands. Some specific pollutants include industrial chemicals such as chlorinated hydrocarbons; heavy metals, including cadmium, lead, mercury, saline water, bacteria, particularly coliforms, and general municipal and industrial wastes.

Since World War II there has been a tremendous growth in the manufacture and use of synthetic chemicals [15]. Many of the chemicals have contaminated water supplies. Two examples are insecticides and herbicides runoff from agricultural land and industrial discharge into surface waters. There is also a threat to groundwater from waste chemical dumps and landfills, storage lagoons, treating ponds, and other facilities. Water pollution should clearly be a point of concern to all citizens. It is essential to understand the sources, interactions, and effects of water pollutants to the environment.

Mercury is typically released into the environment through coal combustion, waste incineration, base metal smelting, gold and cement production [23]. Mercury is released into the environment at the coal fired power stations in South Africa and end up in the water ecosystems through wet and dry deposition. According to Dr Somerset [2] ,mercury emissions remain a concern due to biomagnifications in aquatic. food chains, while some concentrations may be perceived to being relatively low. Inorganic mercury can be transformed under specific conditions into a more toxic organic form, called methyl mercury that is able to bioaccumulate in the food chain, ending up in fish consumed by humans. The result can be that people eating methyl mercury contaminated fish on a regular basis experiencing symptoms of mercury poisoning.

The degradation of the countries underground resources(aquifers) by dense nonaqueous phase liquids (DNAPLs) is currently becoming a concern.

DNAPLs are chemicals or mixtures of chemicals that are heavier than water, and are only slightly soluble in water. This means that when they are released into the environment in sufficient quantities, they can move through soils and groundwater until they encounter an impermeable layer that will impede further mass vertical movement and allow the liquid to pool or move along the dip of an impermeable layer or within a fracture [23].

Contamination by DNAPLs is a world wide phenomenon, but to date there has been limited awareness and understanding of the problem locally. There are thousands of potential sites in South Africa as elsewhere in the world, where DNAPLs may have been released to the sub surface in varying quantities. Examples that can be cited are: chlorinated solvents e.g. degreasers and dry cleaning fluids, creosote, coal tar, and poly chlorinated biphenyls, as found in dielectric oils. Because of their low solubility, DNAPLs often persist for several decades in the subsurface.

In addition, some DNAPLs are highly toxic at even very low concentrations and can thus pose unacceptable health risk to both humans and the environment. It is also reported that DNAPLs are not often released into the environment as pure chemicals but rather as solvents that contain varying amounts of other contaminants. These other components can significantly influence the overall properties of the DNAPL, and both aid detection and complicate remediation. DNAPLs trapped in the subsurface act as continuing sources of dissolved contaminants to groundwater. Their removal from aquifers is very difficult and costly. As a result these chemicals have been classified as high priority pollutants in several countries, including South Africa.

Top ten sources of possible DNAPLs ground water contamination are:

- Automotive manufacturing
- Production of agricultural chemicals(fertilizers, herbicides, pesticides)
- Metallurgical processes
- Metal(predominantly gold) and coal mining
- Petrol service stations(underground storage tanks)
- Wood processing and preserving

- Manufacturing- chemicals
- Workshops(mechanical and electrical)
- Storm water / sewer

Mining and metallurgical industries devastate both terrestrial and aquatic environments in Poland. Large quantities of wastes produced are deposited on land or in aquatic systems. The major effects are due to pollution of air, soil, river water, and ground water with heavy metals.

Pollutants are grouped according to the main ecosystem they affect. One pollutant can affect more than one ecosystem.

2.4 General Impacts of Pollutants

2.4.1 Air impact

Sulphur dioxide (SO2)

Sulphur dioxide result from the burning of coal and it's inhalation causes respiratory problems. Upon further oxidation and reaction with water, acid rain is formed: SO₂ + $\frac{1}{2}$ O₂ + H₂O -> H₂SO₄

Nitrogen oxides (NOx)

Nitrogen oxides result from vehicle emissions. They combine to form photochemical smog and it's inhalation causes respiratory problems.

Volatile hydrocarbons (-CH-)

Volatile hydrocarbons result from vehicle emissions. They combine to form photochemical smog and it's inhalation causes respiratory problems.

Carbon monoxide (CO)

Carbon monoxide result from vehicle emissions and it's inhalation restricts oxygen uptake, causes drowsiness, headaches and death

Carbon dioxide (CO2)

Carbon dioxide source includes burning of coal .It contributes towards global warming and climate change [8].

Chloro Fluoro Carbons(CFCs)

Chloro Fluoro Carbons(CFCs) result from aerosols, refrigeration, air conditioning and foam-blowing industries. They destroy ozone layer.

Methane

Methane result from feedlots rubbish dumps. It contributes towards Global warming

Noise

Noise result from industry and traffic .It affects hearing ability.

Asbestos dust

Asbestos dust result from construction, mining and industry. It causes asbestosis and mesothelioma.

2.4.2 Fresh water impact

Sewage

Sewage problems result from inadequate sanitation .The result of inadequate sanitation leads to the presence of pathogens that cause diseases such as gastroenteritis, typhoid, and cholera. Nutrients cause eutrophication.

Fertilizers

Fertilizers are used in agriculture for soil fertilization processes. Fertilizers cause eutrophication .

Silt

Silt is used in agriculture, construction and mining. Silt smothers aquatic organisms, and affects light penetration.

Pesticides

Pesticides are used in agriculture and health services. Pesticides are toxic, interfere with breeding of mammals and birds .

Toxic metals

Toxic metals result from industry and are health and life threatening

Salinisation

Salinisation result from industry, agriculture and landfill .Salinisation causes reduced crop yields, scale and corrosion in domestic and industrial water systems

2.4.3 Marine impact

Sewage

Sewage problems result from inadequate sanitation .The result of inadequate sanitation leads to the presence of pathogens that cause diseases such as gastroenteritis ,typhoid, and cholera. Nutrients cause eutrophication (an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases in the primary productivity of the ecosystem).

Fertilizers

Fertilizers are used in agriculture for soil fertilization processes . Fertilizers cause eutrophication .

Oil spills

Oil spills result primarily from motor industries and can smother marine plants and animals.

Plastics

A large range of plastics goods contain pthalates that are meant to add flexibility to the structures. The phthalates are endocrine disrupting chemicals (EDC's).

The World Health Organisation (WHO),[24] reports that the EDC's health effects witnessed in wild life species vary from subtle changes in the physiology and sexual behaviour of species to permanently altered sexual differentiation.

The EDC's has been shown to adversely impact the reproductive and immune function in Baltic seals, resulting in marked population decline.

Pesticides

Pesticides are used in agriculture and health services. Eggshell thinning and altered gonadal development have been observed in birds of prey exposed to pesticides such as DDT [24].

2.4.4 Land impact

Solid waste

Solid waste is classified as hazardous (radio active pesticides, medical, poisons), and non-hazardous (domestic, urban, mining industrial, scrap metal). Hazardous waste is health and life threatening whereas non-hazardous waste disposal takes up much space

2.5 Health impacts of pollutants

Manganese

Manganese can enter the body by inhalation and ingestion and causes a disease known as manganism. Manganism is a Parkinson-like disease that supposedly results from absorption of toxic levels of manganese and such exposure can cause an irreversible damage to the central nervous system. Some of the symptoms of this disease are: muscle stiffness and soreness, fatigue and weakness, speech disturbances, loss of coordination, abnormal walk, tremors, leg cramps and weakness, fixed facial expression, impotence, difficulty in breathing, difficulty in swallowing, slow and clumsy movements, stooped posture and mental and emotional disturbance.

Arsenic

Arsenic is a metalloid which forms a number of toxic compounds. The toxic +3 oxide, As₂O₃, is absorbed through the lungs and intestines. Biochemically, arsenic acts to coagulate proteins, forms complexes with coenzymes, and inhibits the production of adenosine triphosphate(ATP) in essential metabolic processes involving the utilization of energy.(Manahan- Environmental chemistry)

Cyanide

Hydrogen cyanide and cyanide salts (which contain CN⁻ ion) are rapidly acting poisons; a dose of 60-90mg is sufficient to kill a human. Metabolically, cyanide bonds to iron (III) in iron-containing ferricytochrome oxidase enzyme., preventing its reduction to iron(II) inn the oxidative phosphorylation process by which the body utilizes O2. This prevents oxygen utilization in cells , so that metabolic processes cease.

Mercury

Elemental mercury vapor can enter the body through inhalation and be carried by the bloodstream to the brain where it penetrates the blood- brain barrier. It disrupts metabolic processes in the brain causing tremor and psychopathological symptoms such as shyness, insomnia, depression, and irritability .Divalent ionic mercury,Hg^{2+,}damages the kidney. Organometallic mercury compounds such as dimethylmercury, Hg(CH₃)₂, are also very toxic.

Lead

It is widely distributed as metallic lead, inorganic compounds and compounds, has a number of toxic effects, including inhibition of the synthesis of hemoglobin. It also affects the central and peripheral nervous system and kidneys.

Chromium

Cr(VI) is present as the chromate (CrO_4^{2-1} or dichromate(Cr_2O7^{2-1}) anion depending on pH and concentration. Cr (VI) anions are less likely to be adsorbed onto solid surfaces than Cr(III). Most solids in soils carry negative charges that inhibit Cr(VI) adsorption. Clays interact little with Cr(VI) because of the similar charges carried by the anion and clay in the common pH range of the soil and groundwater.

The only common soil solid that adsorbs Cr (VI) is iron oxyhydroxide. Generally, a major portion of Cr(VI) and other anions adsorbed in soils can be attributed to the

presence of iron oxyhydroxide. The quantity of Cr(VI) adsorbed onto the iron solids increases with decreasing pH [21].

Chromium can exist as either trivalent or hexavalent compounds in raw waste water streams [21]. Chromium that passes through the POTW (Public Owned Treatment Works) is discharged to ambient surface water. Chromium is toxic to aquatic organisms at levels observed in POTW effluents.

Trivalent chromium significantly impaired the reproduction of Daphnia magna(water fleas) at levels of 0.3 to 0.5 mg/l. [21]. Hexavalent chromium retards growth of chinook salmon at 0.0002 mg/l. Hexavalent chromium is also corrosive and a potent human skin sensitizer and causes cancer [8].

Phenol

A certain amount of phenol (Ar-OH), as well as the cresols (CH₃-Ar-OH, ortho, meta or para) is obtained from coal tar. The larger portion of coal that is mined today is converted into coke, which is needed for the smelting of iron to steel. When coal is heated in the absence of air, it is partly broken down into simpler, volatile compounds which are driven out leaving behind a residue called coke. The volatile materials consist of coal gas and a liquid known as coal tar. From coal tar there are obtained a number of aromatic compounds.

Phenol is a protoplasmic poison that damages all kinds of cells and is alleged to have caused "an astonishing number of poisonings" since it came into general use. The acute toxicological effects of phenol are largely upon the central nervous system and death can occur as soon as half an hour upon exposure. Acute poisoning by phenol can cause severe gastrointestinal disturbances, kidney malfunction, circulatory system failure, lung edema and convulsions. Fatal doses of phenol may be absorbed by the skin. Key organs damaged by chronic phenol exposure include the spleen, pancreas and kidneys and the disruption of endocrine function in fishes, wildlife and humans [16]. The toxic effect of substituted phenols i.e nonyl- and octyl phenols as

well as their mono-,di-,and triethoxylates, resemble those of the unsubstituted phenol. Phenols are endocrine disrupting chemicals(EDC's).

2.6. Air quality legislation

2.6.1 National air quality legislation

Section 24 of the Bill of Rights in the Constitution of the Republic of South Africa guarantees environmental rights for the people of South Africa (Act 108, 1996). Section 24 states that:

"Everyone has the right-

- a. to an environment that is not harmful to their health or well-being; and
- b. to have the environment protected for the benefit of present and future generations, through reasonable legislative and other measures that
 - i. prevent pollution and ecological degradation;
 - ii. promote conservation; and
 - iii. secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development."(Act 108, 1996, Section 24)

In order to give people this constitutional right, legislation must be in place to control pollution and waste effectively. The legislation in place for the control of air pollution is the National Environmental Management: Air Quality Act No.39 Of 2004 (AQA) which was drawn up in September 2004.

2.6.2 International legislation

Aside from local legislation there are international laws that South Africa must comply with, with regard to the control of air pollution. International agreements pertaining to air quality include:

- United Nations Framework Convention on Climate Change (UNFCCC): "The UNFCCC emanated from the Rio Earth Summit in 1992 and represents a global agreement to reduce the emissions of greenhouse gases (particularly carbon dioxide, methane and nitrous oxide) to prevent a major impact on global climate change. This convention was ratified by South Africa in August 1997.
- "Emanating from the UNFCCC is the Kyoto Protocol, which was adopted at the third session of the Conference of the Parties to the UNFCCC in Kyoto, Japan, on 11 December 1997. The Kyoto Protocol sets legally-binding greenhouse gas emission objectives for industrialized countries. These countries should, as a whole, achieve at least a 5% reduction in emissions from 1990 levels over the 2008-2012 period. The Protocol stipulates areas for action, and sets up a number of mechanisms for international cooperation, such as emissions trading.
- Montreal Protocol on Substances that Deplete the Ozone Layer (1987): According to DEAT(Department of Environmental Affairs and Tourism) 2000 South Africa's accession to the Montreal Protocol on substances that deplete the ozone layer was approved on 15 January 1990. The Montreal Protocol controls the use of ozone-depleting substances (chemicals), as well as the import of such chemicals. The Department of Environmental Affairs and Tourism authorises permits for chemicals that may be brought into the country through the Department of Trade and Industry. The import of chlorofluorocarbons (CFCs) into South Africa is banned. The strategic goal is to protect the ozone layer by restricting and controlling the use of ozone-depleting substances and phasing out and replacing ozone-depleting substances with ozone-friendly substances (DEAT, 2000).
- The seventeenth congress of parties (COP17) regarding climate change .The United Nations Climate Change Conference Durban 2011, delivered a breakthrough on the international community's response to climate change [13].

 The parties decided to adopt a universal legal agreement on climate change not later than 2015.

The key to good air quality is being able to monitor and measure the air pollutants that are emitted from industries and also identify whose pollution it is. The legislation currently in existence in South Africa will allow this to be achieved since it has set benchmarks against which government and industry can be called to account. Although environmental legislation is generally welcomed by the broader community since everyone wants a cleaner, safer environment, there is still some resistance from industrialists since there is concern over the economic viability of the legislation. However a truly competitive industry is more likely to take up new environmental legislation as a challenge and respond with innovation instead of fighting against it.

2.7 Management of water quality and pollution

Management of water quality is one of the most critical environmental health challenges facing both the developed and developing world. Water quality is affected by economic activities which introduce pollutants into the environment. These water-borne pollutants pose a threat to human health and other life forms on earth.

2.7.1 Water quality legislation

The National Water Act 36 of 1998 stipulates that the National Government has public trusteeship of the nation's water resource.

2.7.2 National regulation

Regulation 704 of the water act (Act 36 of 1998) stipulates that water used at the mines and some industries must be contained for reuse with minimal amount of treatment with an objective to save tapping more fresh water [22].

2.7.3 Water pollution prevention act

Local Government (Water Pollution) Act 1977 and Amendment Act 1990

This is the principal legal framework relating to Water Pollution. These Acts make provision for the protection of watercourses by:

- Prohibiting the entry of polluting matters to waters
- Outlining statutory requirements relating to the licensing of discharges to waters and sewers
- Outlining water quality standards and water quality management plans
- Outlining nutrient management plans and agricultural by-laws
- Detailing civil liability relating to water pollution

Acting through the minister ensure that water is protected, used, developed, conserved, managed and controlled in a sustainable and equitable manner for the benefit of all persons.(ISSN 0378-4738: Water S.A Vol .30. No. 5 Special edition)

2.7.4 International legislation

Governments in a number of nations have passed legislation to deal with hazardous substances and wastes. In the U.S. such legislation has included the following:

- Toxic substance Control Act of 1976
- Resource Conservation and Recovery Act (RCRA) of 1976(amended and reauthorized by the Hazardous and Solid Wastes Amendments Act(HSWA) of 1984
- Comprehensive Environmental Response, Compensation, and Liability Act(CERCLA) of 1980.

RCRA legislation charged the U.S. Environmental Protection Agency (EPA) with protecting human health and the environment from improper management and disposal of hazardous wastes by issuing and enforcing regulations pertaining to such wastes. RCRA requires that hazardous wastes and their characteristics be listed and controlled from the time of their origin until their proper disposal and destruction.

2.7.5 Route of entry

There exist different types of water quality problems, spread over different regions, in South Africa [3]. The types of water quality problems encountered are urban due to industrial effluents including pathogens and organics, acidic atmospheric deposits, groundwater contamination with fluorides and nitrates, agricultural chemicals, excessive sediments, metals from mining and industries, radioactivity and salinity. Water being a basic human need is needed for drinking, washing and cooking. Through these processes pollutants enters the human body.

South African Drinking Water Standards

The main aim of treating drinking water is to produce water that is safe (without pathogenic micro organisms and toxic compounds), attractive (free from colour, taste and odour) and to avoid accumulation of solids, corrosion and after-growth of bacteria in the distribution pipeline.

Drinking water standards should be set up appropriately taking into account national, regional and local situations. The monitoring and enforcement of these standards differ across the world. In most parts of the world the monitoring is done by water suppliers while the data is audited by public health authorities or regulatory authorities responsible for environmental health. The standards often provide a basis for judging the safety of drinking water. It is not practical to set standards for every contaminant that could reach drinking water. However, water suppliers should always be up to date about emerging pollutants in water supply lines and the take appropriate action regarding reducing the pollutants' concentration to safe levels or completely remove them. (The Water Wheel January/February 2008)

Tables 2.1(a) and 2.1(b) below compare the health chemical parameters (inorganic and organic) for drinking water standards between the World Health

Organisation (WHO), Europe(EU), the Netherlands(NL) and South Africa (SA) .Table 2.1 (c) indicates the Vaal Barrage reservoir water quality guidelines.

Determinant	Unit	WHO	EU	NL	SA
		Max Limit	Max Limit	Max Limit	Max Limit
Aluminium	ppm	0.200	0.200	0.200	0.300
Ammonia	ppm	No guideline	0.500	0.200	1.000
Antimony	ppm	0.005	0.005	0.005	0.010
Arsenic	ppm	0.010	0.010	0.010	0.010
Bromate	ppm	No guideline	0.010	0.001*	No guideline
Chromium	ppm	0.050	0.050	0.050	0.100
Copper	ppm	2	2	2	1
Iron	ppm	0.300	0.200	0.200	0.200
Lead	ppm	0.010	0.010	0.010	0.020
Manganese	ppm	0.500	0.050	0.050	0.100
Mercury	ppm	0.001	0.001	0.001	0.001
Nickel	ppm	0.020	0.020	0.020	0.150
Sodium	ppm	200	200	150	200
Zinc	ppm	3	No guideline	3	5
Chloride	ppm	250	250	150	200
Cyanide	ppm	0.070	0.050	0.050	0.050
Fluoride	ppm	1.5	1.5	1.1	1.0
Sulphate	ppm	500	250	150	400
Selenium	ppm	0.010	0.010	0.010	0.020
Nitrate	ppm	50 (as total N)	50	50	10 (as total N)
Nitrite	ppm	50 (as total N)	0.5	0.1	10 (as total N)

Table 2.1(a): Health Related Chemical Parameters(Inorganic)

Table 2.1 (b): Health Related Chemical Parameters(Organic)

Determinant	Unit	WHO	EU	NL	SA
		Max Limit	Max Limit	Max Limit	Max Limit
Polychlorinated	ppm	-	0.0001	0.0001	No
Aromatic					guideline
Hydrocarbons(
PAH) sum					
Trihalomethanes	ppm	-	0.110	0.025	0.200
(sum)					
Polychlorinated	ppm	-	No guideline	0.0001	No
biphenyls –PCB					guideline
(individual)					
Polychlorinated	ppm	-	No guideline	0.0005	No
biphenyls –PCB					guideline
(sum)					
Pesticides(ppm	-	0.0001	0.0001	No
individual)					guideline
Pesticides(sum)	ppm	-	0.0005	0.0005	No
					guideline
Tetraethene and	ppm	-	0.020	0.020	No
trichloroethene					guideline
(sum)					
	ppm	-	0.0005	0.0005	No
Vinyl chloride					guideline
Dissolved	ppm	-	*	*	10
organic carbon (
DOC)					
Total organic		-	No guideline	No	No
carbon				guideline	guideline-

Table 2.1 (c) Vaal Barrage Water quality guidelines

Variable	Unit	Catchment	Manageme	Interim	Unaccept
		Background	nt Target	Target	able
Physical					
Conductiv	mS/m	<18	18-30	30-70	>70
ity					
Dissolved	%	*	>6	5.0-6.0	<5.0
Oxygen					
рН	рН	7.0-8.4	6.5-8.5	6.0-9.0	<6.0->9.0
	units				
Organic					
Atrazine	nnh	<5	5-10	10-20	>20
COD		<10	10-20	20-30	>30
Phenols		*	<0.01	0.01-0.1	>0.1
	ppin		<0.01	0.01-0.1	20.1
		Micro E	lomonts		
Antimony			-5	E 10	> 10
Anumony			<0	5-10	>10
Arsenic	ррр	NV	<10	10-20	>20
Cadmium	ppb	*	<3	3-5	>5
Chromini	ppb	*	<30	30-50	>50
m(Total)					
Cobalt	ppb	*	<50	50-100	>100
Cyanide	ppb	NV	<5	5-10	>10
(Free)					
Lead	ppb	<10	10-30	30-50	>50
Mercury	ppb	NV	<1	1-2	>2
Nickel	ppb	*	<50	50-100	>100
Selenium	ppb	<10	10-20	20-30	>30
Vanadium	ppb	<50	50-100	100-200	>200
Zinc	ppb	<50	50-100	100-200	>200

Macro Elements					
Aluminium	ppm	NV	<0.3	0.3-0.5	>0.5
Ammonia	ppm	*	<0.5	0.5-1.0	>1.0
Boron	ppm	NV	<0.3	0.3-0.5	>0.5
Calcium	ppm	<15	15-70	70-150	>150
Chloride	ppm	<5	5-50	50-75	>75
Copper	ppm	<0;05	0.05-1	1-2	>2
Fluoride	ppm	<0.19	0.19-0.7	0.7-1	>1
Iron	ppm	NV	<0.5	0.5-1	>1
Magnesium	ppm	<8	8-30	30-70	>70
Manganese	e ppm	*	<0.15	0.15-0.2	>2
Nitrate	ppm	<0.5	0.5-3	3-6	>6
Phosphate	ppm	NV	<0.03	0.03-0.05	>0.05
(Ortho)					
Potassium	ppm	<5	5-15	15-25	>25
Sodium	ppm	<15	15-50	50-100	>100
Sulphate	ppm	<20	20-100	100-200	>200
	1	Bacteria a	nd Protozoa		I
Cryptospori	di Organ	i 0	0	0	1
um	sms/				
	101				
Cyano	Count	S *	<10 000	10 000-	>20 000
Bacteria	/100m	I		20 000	
Faecal	Count	S *	<126	126-1000	>1000
Coliforms	/100m	I			
Giardia	Organ	i 0	0	0	1
	sms/10	D			
	I				
Biological					

Chlorophylla	ppb	<5	5-15	15-30	>30
Daphnia	%	100	90-100	80-90	<80
(Acute	Surviv				
toxicity)	al				

*No abnormal changes.

Organic compounds have now become a threat to human health. Although they are often

present in very low concentrations in drinking water, they can still have serious health implications.

The guideline values given in Tables 2.1 (a) and 2.1 (b) represent an upper limit of the concentration of individual chemical species that does not exceed tolerable risk to the health of the consumer over a lifetime of consumption. Some chemical contaminants, such as lead and fluoride, may cause ill health effects to water consumers when they are exceeded.

The Vaal Barrage reservoir situated at the Vaal river bank in Vanderbijlpark in the Vaal triangle area also controls its water quality systems as shown in Table 2.1(c).

2.7.5 Sample preservation

In order to combat compounds dissociation and reaction with container walls, water samples are preserved in dedicated containers and at controlled temperature for a pecific time frame to ensure reliable analysis. Table 2.2 illustrates storage conditions of water samples.

Table 2.2: Preservation of samples for analysis

Parameter Name	Container Preservation		Maximum
			holding time
Alkalinity	Polyethylene or	Cool, 4°C	14 days
	glass		
Ammonia	Polyethylene or	Cool, 4°C, H ₂ SO ₄ to	28 days
	glass	pH<2	
Chemical oxygen	Polyethylene or	Cool, 4°C, H ₂ SO ₄ to	28 days
demand	glass	pH<2	
Chloride	Polyethylene or	None required	28 days
	glass		
Conductivity	Polyethylene or	Cool, 4°C	24 hours
	glass		
Fluoride	Polyethylene or	None required	28 days
	glass		
Hardness	Polyethylene or	HNO ₃ to pH<2, H ₂ SO ₄	6 months
	glass	to pH<2	
Hydrogen ion (pH)	Polyethylene or	None required	Analyse
	glass		immediately
Chromium VI	Polyethylene or	Cool 4°C	24 hours
	glass		
Nitrate	Polyethylene or	Cool 4°C	48 hours
	glass		
Phenols	Glass only	Cool, 4°C, H ₂ SO ₄ to	28 days
		pH<2	
Turbidity	Polyethylene or	Cool, 4°C	48 hours
	glass		

2.8 Metallurgical Industries

Metallurgy is the domain of material science that studies the physical and chemical behavior of metallic elements, their inter metallic compounds and their compounds, which are called alloys. It is also the technology of metals; the way in which science is applied to their practical use.

It is the process of extraction of metals or alloys from ores in a metallurgical furnace at temperatures ranging from 200 $^{\circ}$ C to 2000 $^{\circ}$ C [26].

Metallurgical industries around the globe are classified according to the main product as follows [11].

- Steel
- Stainless steel
- Ferro alloys
- Base metals
- Platinum group metals
- Gold
- Foundaries
- Coal
- Diamonds Petrochemical
- Cement and lime
- Glass
- Ceramic and pulp.

Different kinds of furnaces are used for extractive metallurgy in metallurgical industries and are classified as follows:

- The basic oxygen furnace.
- The electric arc furnace

2.8.1 The basic oxygen furnace

This process is rapidly becoming the main producer of steel. A cylindrical furnace which can be rotated into horizontal or vertical positions is used(Fig.2.1).

The furnace is charged with molten cast iron and up to 30 per cent scrap, whilst in a tilted position. It is then moved into a vertical position and a high speed jet of oxygen is directed on to the surface of the charge through a water cooled lance. Some of the carbon in the charge is converted into gaseous oxides which escape from the furnace through a hood. Other impurities also form oxides and these react with added lime to form slag. After the 'blow' the furnace is tipped into a horizontal position so that the molten steel can be run off through the tap-hole. It is then inverted to pour away the slag. A large furnace can make 350 tons of steel in 40 minutes.



Fig.2.1 Basic oxygen furnace

2.8.2 The electric arc furnace

This furnace consists of a cylindrical vessel with a removable lid carrying three graphite electrodes which can be lowered into the vessel when the lid is in place. The charge is made up entirely of scrap steel and it is heated by forming arcs between the ends of the electrodes and the surface of the charge. Lime, fluorspar and iron oxide are added to form a slag with the impurities and to give a steel of

the required composition. The slag is raked or poured from the surface and the steel is run out through the tapping spout by tilting the furnace. A typical furnace can make 150 tons of steel in 4 hours, and the process can be closely controlled due to the absence of oxidizing gases. High quality steels can be made.



Fig. 2.2 Electric arc furnace

 The Ferroalloys division of the Union Carbide Corporation has operated covered furnaces with mix seals around the electrodes since the 1930's; in this design a major part of the furnace gas is withdrawn and scrubbed before combustion. With the advent of strict regulations, the emission control performance was often no longer sufficient for those products subject to " blows" or slag "boils" and those with a steel scrap charge requiring more difficult and can lead to gas and fume escape.

2.8.3 Abatement of open furnace operations pollution

A significant aspect of fume collection from open furnace is capture of the fume containing gases. To a first approximation the capital and energy requirements of the control system are proportional to the volumetric flow of gas, so that minimization of gas flow volume, consistent with satisfactory limitation of emissions, has been emphasized

The metallurgical industry's key commitment is towards sustainable development .The core reason for this is to ensure that the community in which it operates is free from the health impacts of the pollution generated from its operations. Legislation provides the standards by which the industry can ensure that they are abiding by their commitment to the sustainable development.

2.8.4 Objective

In order to ensure conformance to legislation the steps below will be followed:

- 1. Characterise pollutants that might be present in soil and water in a Metallurgical industry.
- 2. Establish the trends in the distribution of these compounds.
- 3. Establish the transport and fate of these pollutants in the environment.
- 4. Establish the possible environmental impact associated with the pollutants.
- 5. Propose pollution impact combating measures.

2.9 References

[1] Analytical Reporter Africa, 5, 2009

[2] AP 42, I (<u>http://www.epa.gov/ttn/chief/ap42/index.html</u>).>Accessed:15/01/2011.

[3] Ashton P.J; Facing up to the water crisis in South Africa- The need for innovative solutions. Seminar 2007.

[4] Australian National Pollutant Inventory Emission Estimation Technique Manuals (<u>http://www.npi.gov.au/hanbooks/approved</u>)>Accessed:16/12/2010

[5] Brenner J: Environmental Testing.Seminar 2007.

[6] European environment Agency's 2005 emission Inventory Guidebook (<u>http://reports.eea.eu.int/EMEPCORINAIR4/en</u>)>Accessed:14/01/2011.

[7] Canadian GHGHG Inventory Methodologies (<u>http://www.ec.gc.ca/pdb/ghg/guidance/calcu pro e.cfm</u>)>Accessed :16/01/2011.

[8] Chemical and Engineering News, January 3, 2011:10-16.

[9] EPA: Air Pollutants (<u>http://www.epa.gov/ebtpages/airpollutants.html</u>)>Accessed: 22/01/2011.

[10] Estimated deaths & DALYs attributable to selected environmental risk factors, by WHO Member State, 2002

(<u>http://www.who.int/entity/quantifyingehimpactscountryprofilesbd.xls</u>)>Accessed: 25/01/2011.

[11] Industrial Metallurgy, Reg ISSN 1024 316X ,Jun 2011 :14-32.

[12] Financial Mail ,October 22, 2010 :6.
[13] <u>http://www.cop17-cmp7durban.com</u> >Accessed 14/02/2012.

[14] Industrial Metallurgy Reg. ISSN 1024-316X , September 2011:6-25.

[15] Manahan, S.E. 2011.Water Chemistry: green science and technology of nature's most renewable resource .USA .: Taylor and Francis Group.

[16] Patnaik, P. Hanbook of environmental analysis.2010. 2nd ed,USA: Taylor and Francis Group.

[17] Revised 1996 IPCC Guidelines For National Greenhouse Gas Inventories (referencemanual)(<u>http://www.ipcc-nggip.iges.or.jp/public/gl/invs6.htm</u>> Accessed:01/02/2011 .

[18] Spellman Frank R., The science of water:concepts and applications, 2008. 2nd ed, Boca Raton: CRC Press.

[19] United Kingdom's emission factor database (http://www.naei.org.uk/emissions/index.php)>Accessed:20 /02/2011.

[20 Vallero, D.A. 2008. Fundamentals of air pollution.Amsterdam;Boston:Elsevier.

[21] Wang Lawrence K. Shammas Nazih K.,Hung Yung-Tse. 2009. Waste treatment in the metal manufacturing, forming, coating, and finishing industries. Boca Raton:CRC Press.

[22] Water Wheel ISSN 0258-2244 Sept/ Oct 2009, 8(5).

[23] Water Wheel ISSN 0258-2244 July/ Aug 2009,8 (4).

[24]. Water Wheel ISSN 0258-2244 March/April 2008, 7 (2) .

[25] Yadav, M.S. 2007. Nuclear energy and power: environmental impacts and other effects. New Delhi:SBS Publishers and Distributers.

[26] www.mhmhd.com/metallurgical -industry >Accessed:25/11/2011.

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CHAPTER 3

EXPERIMENTAL

3.1 Introduction

Raw materials are mined from different parts of the globe, transported to production sites and utilised as starting reagents in production. The starting reagents contain other elements and compounds, some of which may interfere with production reactions during the manufacturing process. It is therefore essential that the purity and assay of raw materials be determined. The assay will also indicate possible pollutants resulting from handling and reactions during production.

Hence this research is aimed at investigating the contribution of the metallurgical industry operations to water with a view to introduce procedures for the removal of heavy metals

In order to achieve objectives outlined, pollution levels within the metallurgical industry will be compared against international standards. The principal legal framework relating to water pollution (Local Government, Water Pollution, Act 1977 and Amendment Act 1990) make provision for the protection of watercourses by:

- Prohibiting the entry of polluting matters to waters
- Outlining statutory requirements relating to the licensing of discharges to waters and sewers
- Outlining water quality standards and water quality management plans
- Outlining nutrient management plans and agricultural by-laws
- Detailing civil liability relating to water pollution

3.2 Study area, sampling sites and types of samples

Solid samples and water samples were collected for analysis .

3.2.1 Metallic and non metallic solid samples collected from storage sites were raw materials, final products and by-products. Raw materials were manganese ore and coal while final products were high carbon ferromanganese, medium carbon ferromanganese as well as silicon manganese and by-products were high carbon ferromanganese slag, molten slag as well as silicon manganese slag.

3.2.2 Water samples were taken from the D1 borehole, the main and hymat trenches, the amcor dam and the spring as well as the the road bridge and the fourie spruit.

3.3 Sample collection

Raw materials, final products and by-products were taken from bunkers and heaps and water samples were taken from boreholes, dams, trenches and streams over a period (2008-2010)..

3.3.1 Collection of samples

3.3.1 (a)Solid samples

A heap was subdivided into four quarters for sampling purposes. A sampling rope, with eight knots separated by thirty centimetres, was placed vertically every two meters and a piece of solid was handpicked at each knot. The sample was placed into a sampling bag.

3.3.1(b) Water samples

Water samples were collected from boreholes, streams and dams. For the sampling of boreholes, a sampling bailer was immersed into the borehole to scoop a sample and transferred into a plastic bottle. A sample scoop was used for collection of samples from streams and dams and transferred into a plastic bottle.

3.3.2 Preparation of samples

3.3.2.1 For the preparation of solid samples, the sample was crushed to 12 mm diameter and then milled down to down to 75 μ m and pressed for the XRF (X-Ray Fluorescence) analysis.

3.3.2.2 For the preparation of water samples aliquots were pipetted into 15 ml plastic test tubes for aspirating into the ICP (fig 2),and for pH determination aliquots were transferred into 50 ml plastic bottles while separating funnels were used for phenol determination aliquots. Samples, if not analysed immediately after collecting, were preserved in dedicated containers as shown in the table 1.

3.3.2.3 Heavy metal concentrations can be reduced further by adsorption using agricultural waste materials.

Many solids are capable of adsorbing ions and molecules from solutions [1]. Adsorption by solids is dependent upon the temperature, the nature of the adsorbent and the adsorbate and on the concentration of the adsorbate.

Adsorption from dilute solution may be represented by the Freundlich empirical equation : $x/m = kc^{1/n}$, where x is the amount of solute(moles) adsorbed by m grammes of sorbent when the equilibrium concentration in solution is c/mol dm⁻³,k and n are constants (n>1).

The adsorbent (eucalyptus leaves dried at 90°C in an oven overnight), for 12 hrs, was grounded to a fine powder using the mortar and pestel and then screened over a one millimetre sieve. Two grams of powder was weighed out into a 50 ml plastic reaction bottle and 25 ml aliquot of sample of known metal concentration was transferred into the 50 ml plastic reaction bottle. The sample was stirred moderately at room temperature (22°C), and the start and stop time noted and then filtered and filtrate collect into a test tube for analysis.

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3.4. Experimental Set up

Instrumentation

The following instruments were used

XRF Spectrometer

The XRF was used to analyse solid raw materials and final products for metals and their oxides to indicate the other source of pollutants before processing

The XRF technique is a rapid and non destructive technique with analysis time of ninety seconds

Leco carbon & sulphur analyser

The Leco was used to determine total carbon and sulphur in the solid raw materials and final products. It is a rapid combustion technique for analyzing solid samples

Inductive Coupled Plasma (ICP)

The ICP was used to determine to trace elements in liquid samples. It will be mostly used because it is applicable over a wide range of elements to be analysed

Spectrophotometer (uv-vis)

The uv-vis spectrophotometer was used for analysis of those elements absorbing electromagnetic radiation at specific wavelengths within the uv-vis range

<u>pH meter</u>

The pH meter was used to determine the pH range of the working solutions and in adjusting solutions to desired pH ranges

3.4.1 Optimisation of the XRF Spectrometer

Analytical conditions

Parameter	Setting 1	Setting 2	Setting 3
Counting time/sec	20	15	25
X-Ray tube voltage	40	50	60
/Kv			
X-Ray tube	40	50	60
current/mA			

Optimum conditions are : Time 15 sec, Voltage 50 Kv and Current 50 Ma

3.4.2 Optimisation of the Leco carbon and sulphur analyser

Analytical conditions

Parameter	Setting 1	Setting 2	Setting 3
Oven current/mA	40	48	60
Grid current /mA	1.1	1.21	1.5
Carbon detector	8.0	8.68	9.0
current/Ma			
Sulphur detector	8.0	8.43	9.0
current/mA			

Optimum conditions are: Oven current 48 mA, Grid current 1.21 mA, Carbon detector current 8.68 mA and Sulphur detector current 8.43 mA in the parameter sequence

3.4.3 Optimisation of the ICP (Inductively Coupled Plasma)



Fig. 3.1: ICP spectrometer

Analytical conditions

Parameter	Setting 1	Setting 2	Setting 3	
Gas flow / Imin ⁻¹	10	15	20	
Auxiliary /Imin ⁻¹	0.1	0.2	0.3	
Nebuliser/ Imin ⁻¹	0.5	0.8	1.0	
RF power/ watt	1000	1300	1500	
Pump /mlmin ⁻¹	1.0	1.5	2.0	
Plasma initial purge	40	45	50	
/sec				

Optimum conditions are: Gas flow 15 Imin⁻¹, Auxiliary gas flow 0.2 Imin⁻¹, Nebuliser flow 0.8 Imin⁻¹, RF power 1300 watt, Pump 1.5 mlmin⁻¹ and Plasma purge 45 sec in the parameter sequence.

3.5. Methodology

3.5.1 Analysis of the solid samples

(i) Calibration of the XRF spectrometer

A certified powder standard was pelletized on a press and an analytical programme with known analyte values was created on the XRF. The pelletized standard was run on the XRF, the instrument calibrated and solid pressed samples were analysed.

(ii) Calibration of the Leco

An analytical program for carbon and sulphur were created on the Leco and a certified powder standard values were fed into the software. 0.2 gram of the standard was weighed out into a ceramic crucible, subjected to combustion and the instrument calibrated. Solid powder samples were analysed on the Leco for carbon and sulphur.

3.5.2 Analysis of the liquid samples

(i) Calibration of the ICP

An analytical program for selected analytes was drawn on the instrument software. A certified liquid standard value for each element was fed in, the multielemental standard was aspirated and the calibration carried out, Samples were then analysed.

(ii) Calibration of the pH meter

Buffer solutions pH 4 ,7 and 10 were used. Calibration was done with buffer pH 4 and buffer pH 10 whereas buffer pH 7 was used to verify the calibration. Sample pH values were determined by the pH meter.

(iii) Phenol and Cr⁶⁺ were determined using the uv-vis spectrophotometer.

References

[1] Laidler,K.J.,Meisner,J.H.,1995. Physical Chemistry. 2nd ed. New Jersey: Houghton Mifflin Company.

[2] Patnaik, P. 2010.Handbook of Environmental Analysis. 2nd ed.USA: Taylor and Francis Group.

[3] Wang, L. K., Shamas, N. K., Hung Yung-Tse. 2009. Waste Treatment In The Metal Manufacturing, Forming, Coating, And Finishing Industries. New York: Taylor and Francis Group.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Raw material results

From the plot on Fig.4.1 it could be seen that the manganese was the main component in the mined manganese ore as desired by production, but other elements of concern such as Ca, Mg, Si, Al, Fe, Al and P were also present. A low phosphorus content was ideal in that the element tends to poison the reduction process with a resultant low quality yield of the final product.

Table 4.1	:	Manganese ore analys	sis	by	/ XRF
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Date	Mn%	Fe%	SiO ₂ %	CaO%	MgO%	Al ₂ O ₃ %	P%
2010/02/01	45.61	10.94	4.35	9.4	0.79	0.293	0.028
2010/04/01	36.82	5.47	4.62	14.22	3.134	0.267	0.0154
2010/06/01	32.29	7.73	6.28	15.39	2.25	0.31	0.04

From the plot on Fig.4.2 carbon was the main component in the coal assay. A high fixed carbon was ideal for reduction purposes. Reduction of ores' best efficiency is achieved as a result of high carbon content. Low volatiles and ash were essential in ensuring a high carbon content of the reductant. Coal is used as a reducing agent in the production of alloys from ores. A generalised reduction reaction can be presented as : $Mn_xO_y + C \rightarrow x Mn + CO_{xy}$.

The furnace off gas(CO) was captured not to escape into the atmosphere but be used in electricity generation.



Fig.4. 1 :Plot of manganese ore analysis

Table 4.2 : Coal analysis by heating

Date	Volatiles	Ash	Fixed Carbon		
	%	%	%		
Average	1.62	15.5	82.9		



Fig.4.2: Plot of coal analysis

4.2 Final products

From the plot on Fig.4.3 it could be seen that the Mn yield was high. An alloy with a high Mn is suitable for use in steel industries .Naturally occurring metals can be improved for specific purposes by melting them together to form steel. The manganese alloy product was used in low alloy steels (steels which contain between 1% and 5 % of another metal)

Manganese steel is used to make rifle barrels because it is able to withstand high energy impact battering. This alloy is also used to make the dipper teeth of power shovels employed in rock and earth moving machinery.

Table 4.3 Average alloy analysis by XRF

	Mn %	Fe%	Si %	P%	S%	Al%	С
Average	77.21	15.07	0.040	0.062	0.0040	0.0070	7.0



Fig.4.3: Plot of average alloy analysis

From the plot on Fig.4.3 results showed completion of reaction for the extraction of Mn and Fe at set operating conditions, and raw material ratios, which were aimed at avoiding the reduction of SiO_2 , CaO, MgO and Al_2O_3 to undesirable levels in the final

product. Reduction of SiO₂ CaO, MgO and Al₂O₃required higher temperatures, and a different ore to reductant ratio condition.

4.3. By Products (Slags)

Table 4.4: High Carbon FeMn slags (HCS), MC FeMn slag (MS) and Silicon Manganese Slag (SMS), by XRF

	MnO%	FeO %	SiO ₂ %	CaO %	MgO %	Al ₂ O ₃ %
HCS	24.05	0.081	31.43	30.47	7.71	3.50
MS	18.50	0.100	28.40	36.30	8.20	6.50
SMS	17.00	0.160	44.10	19.80	5.30	9.10



Fig.4. 4: Plot of different slag results

From the plot on Fig. 4.4, the concentrations of the different constituent compounds vary as a result of production raw material ratios used with a view to obtain a specific product.

4.4 Water Analysis

The plot on Table 4.5 summed up results of selected rainwater pollutants taken during different seasons over a period of three years. Given that rain water is drinkable, analysis gave an indication of anthropogenic impact into natural systems (Table 2.1). Rainwater washed air borne pollutants in the environment and analysis therefore indicate pollutant levels in the environment. This was shown by periodically higher manganese and lead. Possible sources of phenol were airborne carbonaceous particles and coal used as reductants in production.

Anthropogenic (man-made) pollution and poor water quality is a major environmental concern. Anthropogenic water pollution is brought about by many different human activities taking place on a daily basis. Sources include industry, agriculture, power generation (coal, oil or gas power station), mining and waste dumps.

Table 4.5 : Average environment (Rain Water) by ICP, UV-Vis spectrophotometer and pH meter over the period 2008-2010

			UV-Vis	UV-Vis			
	ICP	ICP	Cr(VI)	Phenols	ICP		ICP
	Mn ppm	Cr ppm	ppm	ppm	Pb ppm	pН	B ppm
Autumn	1.023	1.055	0.490	0.132	0.51	6.9	1.04
Winter	1.005	1.05	0.48	0.135	0.01	7.1	1.03
Spring	0.955	1.05	0.5	0.175	0.005	7.2	1.03
Summer	0.985	1.02	0.51	0.199	1.00	6.8	1.02



Fig.4.5: Plot of rain water results

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From the plot on fig.4.6, the average phenol value was less than 0.1 ppm. Extremely low levels of phenols are desirable due to health risks associated with the compound. Sources of phenols in trench water arise from carbonaceous elements in production. Coal and coke are sources of carbonaceous elements. Phenols are endocrine disrupting chemicals (EDC's) and chemicals in these products have the ability to mimic the functioning of steroid hormones in human bodies. EDCs can disrupt the normal functioning of the endocrine system in humans. Main trench water originates from production and immediate environment and is directed to the dam.

 Table 4.6: Average main trench water results over the period 2008-2010

	UV-Vis Phenols ppm	рН
Autumn	0.081	9.2
Winter	0.103	9.0
Spring	0.080	8.7
Summer	0.088	8.7



Fig.4.6: Plot of Main trench water results

From the plot on Fig.4.7, average phenol results were less than 0.2 ppm. Phenols originate from coke and coal used as reducing agents in production. Hymat trench water originates from production and immediate environment and is directed to the dam.

Research has shown that EDC's have had an impact on infertility levels in some communities, the occurrence of certain type of cancers as well as hormone related bodily changes such as hermaphroditism (The Water Wheel ISSN 0258-2244, May/June 2011)

Table4.7: Average hymat trench water results over the period 2008-2010

	UV-Vis	рН
	Phenol	
	ppm	
Autumn	0.147	8.2
Winter	0.015	8.4
Spring	0.215	8.5
Summer	0.202	8.6



Fig.4.7: Plot of Hymat trench water results

From the plot of Fig 4.8, results fall below 1 ppm. Runoff water from within the industry and the surroundings collect in the dam. Dam water is pumped up to the different plant for cooling purposes. The water recycles back to the dam via the different trenches. This is an equivalent of a closed system. All process waters were monitored on a frequent basis.

	1						
	ICP	ICP	UV-Vis	ICP	ICP	рΗ	ICP
	Mn	Cr	Cr(VI)	Phenol	Pb		В
	ppm	ppm	ppm	ppm	ppm		ppm
Autumn	0.603	0.043	0.003	0.019	0.007	8.6	0.97
Winter	0.273	0.025	0.005	0.050	0.009	9.7	*
Spring	0.750	0.055	0.000	0.019	0.007	9.5	*
Summer	0.605	0.000	0.006	0.032	0.005	9.1	*

Table 48: Average dam water results over the period 2008-2010.



Fig.4.8: Plot of dam water results

From the plot on Fig.4.9, metal results fall below 1 ppm and the pH fall within the 6.5-8.5 range. The Mn levels and pH are of concern primarily due to airborne particles settling on the ground and being swept into streams by water. Fourie spruit water is channelled to guide water from neighbouring regions such as the municipality sewerage area, to the road bridge and then out of the industry.

	ICP	ICP	UV-Vis		ICP
	Mn	Cr	Cr(VI)	pН	B ppm
	ppm	ppm	ppm		
Autumn	0.970	0.027	0.009	7.8	*
Winter	0.763	0.040	0.004	7.9	*
Spring	0.570	0.055	0.005	7.8	*
Summer	0.760	0.000	0.013	7.7	*

 Table 4.9: Average bridge water results over the period 2008-2010



Fig.4.9: Plot of bridge water results

From the plot on Fig.4.10, metal results fall below 1ppm and the pH fall within the 6.5-8.5 range. Road bridge water comprises water cascading down from upper regions surrounding the industry, through the industry as well as contributions from the neighbouring environment, such as the maize fields in the region. Air borne particles settling on the ground are swept with the waters. Table 4.10: Fourie Spruit water results over the period 2008-2010

	ICP	
	Mn ppm	рН
Autumn	0.283	7.5
Winter	0.207	7.5
Spring	0.163	7.5
Summer	0.124	7.7



Fig.4. 10: Plot of spruit water results

From the plot on Fig.4.11 low levels of pollutants are indicated The fountain is situated outside the production perimeter. A low water permeable layer (acquiclude) underlies a higher water permeable layer (acquifer) as the ground water flows in a

downward slope. Once the downward percolation of water is blocked, a seep or spring(fountain) is formed. This is indicated by a slow flow of water emerging from the ground. Analysis are aimed at verifying pollutant levels that might have percolated downward and emerge at a remote site

Table4.11 : Average fountain (Eye) water results over the period 2008-2010

	ICP	ICP	UV-Vis	UV-Vis	ICP		ICP
	Mn	Cr	Cr(VI)	Phenol	Pb	pН	В
	ppm	ppm	ppm	ppm	ppm		ppm
Autumn 2008-							
2010	0.00	0.00	0.012	0.003	0.010	7.2	0.505
Winter 2008-2010	0.00	0.00	0.005	0.005	0.003	7.3	0.505
Spring 2008-2010	0.00	0.00	0.020	0.006	0.000	7.2	0.550
Summer 2008-							
2010	0.00	0.00	0.005	0.002	0.020	7.3	0.655



Fig. 4.11: Plot of fountain water results

Table 4.12 : Average Borehole (D1) water results over the period 2008-2010

	ICP	ICP	UV-Vis	UV-Vis	ICP		ICP
	Mn	Cr	Cr(VI)	Phenol	Pb	pН	В
	ppm	ppm	ppm	ppm	ppm		ppm
Autumn	0.011	0.420	0.430	0.126	0.010	8.2	0.74
Winter	0.023	0.420	0.408	0.015	0.014	8.2	0.68
Spring	0.005	0.470	0.420	0.216	0.005	8.3	0.63
Summer	0.011	0.735	0.405	0.166	0.008	8.4	0.67



Fig.4 12 : Plot of borehole water analysis

From the plot on Fig.4 12 results of compounds and elements fall below 1ppm.

Boreholes were drilled on selective spots in and around the premises. On each of the spots two holes were bored close to each other but up to different depths. The reason for this is to monitor possible pollution at different ground levels. It will provide a good indication of contaminants filtrating through the different ground levels.

Table 4.13 : Mn data (ppm) for different sample points results over the period 2008-2010

	Amcor	Road	Fourie	D1	Spring
	Dam	Bridge	Spruit		
Autumn	0.603	0.970	0.200	0.020	0.000
Winter	0.273	0.870	0.200	0.023	0.003
Spring	0.650	0.570	0.120	0.005	0.000
Summer	0.605	0.760	0.230	0.011	0.000



Fig. 4.13: Plot of manganese content for different sample points

From the plot on Fig.4.13 ,Mn values vary at different sampling points as a result of sources of origin. Cooling water from production is directed into the dam by means of trenches. Airborne dust settling on the ground is swept by water into the dam. The bridge source of Mn levels is due to the airborne dust settling on the ground and then swept away by water.

Table4.14 : Phenol Data (ppm) for different sample points results over the period 2008-2010

	Amcor	D1	Spring	Main	
	dam		(Eye)	trench	Hymat trench
Autumn	0.018	0.126	0.003	0.058	0.147
Winter	0.050	0.017	0.002	0.089	0.015
Spring	0.015	0.215	0.012	0.080	0.215
Summer	0.035	0.165	0.002	0.083	0.202



Fig.4.14: Plot of phenol content over different sample points

From the plot on Fig.4.14 the D1 and the Hymat trench indicate levels between 0.2 and 0.25 ppm. There are two large reservoirs of organic material, coal, petroleum, and aromatic compounds are obtained from both reservoirs. Aromatic compounds are separated as such from coal tar and are synthesized from the alkanes of petroleum. By far the larger portion of coal that is mined today is converted into coke which is needed for smelting (extraction of metals from ores). When coal is heated in the absence of air, it is partly broken down into simpler volatile compounds which are

driven out, the residue is coke. The volatiles consist of coal gas and a liquid known as coal tar, from coal tar by distillation a number of aromatic compounds are obtained e.g benzene ,toluene, xylene, phenol, cresol, and naphthalene. Higher phenol levels in the D1 borehole is attributed to underground percolation as well as long term down seeping. Higher phenols in the Hymat trench water is attributed to washing of airborne particles dissolving in rain water.

Higher levels during the spring season is attributed to concentration as a result of less solvent(water) due to preceding dry seasons.

		Road	Fourie	D1		М	Н	Rain
	Am dam	Bridge	Spruit		Spring	Trench	trench	Water
Autumn	8.6	7.8	7.5	8.2	7.2	9.2	8.2	6.9
Winter	9.7	7.9	7.5	8.3	7.3	9.0	8.4	7.0
Spring	9.5	7.8	7.5	8.3	7.2	8.7	8.5	7.2
Summer	9.1	7.7	7.3	8.4	7.3	8.7	8.6	7.1

Table 4.15 : pH Data for different sample points results over the period 2008-2010



Fig.4.15 Plot of pH over different sample points

From the plot on Fig.4 15, it is indicated that pH values vary as a result of dissolved salts and chemicals present in the water body at various sampling points.

Table 4.16:Cr ⁶⁺ Data (ppm) for different sample points results over the period 2008-2010

		Road	D1	Spring	
	Amcor dam	bridge	borehole	(Eye)	Rain Water
Autumn	0.003	0.009	0.43	0.012	0.510
Winter	0.005	0.004	0.41	0.012	0.485
Spring	0.000	0.005	0.42	0.010	0.500
Summer	0.009	0.013	0.41	0.000	0.510



Fig. 4.16 Plot of Cr⁶⁺ over different sample points

The low Cr⁶⁺ levels in samples are attributable to higher pH values. For the D1 the higher values are attributable to gravity percolation and acidity, while with rainwater it is a result of suspended particulates.

Table4.17: Cr Data (ppm) for different sample points over the period 2008-2010

	Amcor	Road	D1		
	dam	Bridge		Spring	Rain Water
Autumn	0.043	0.027	0.420	0.000	1.075
Winter	0.017	0.040	0.420	0.000	1.050
Spring	0.055	0.055	0.470	0.000	1.050
Summer	0.000	0.000	0.735	0.000	1.020



Fig. 4.17 : Plot of Cr levels over different sample point

From the plot on Fig. 4.17 the D1 borehole indicates a chromium level of between 0.4 and 0.8 ppm It is believed that total Cr at the borehole (D1) results from ferrochrome slag once stored in the region. Rain water wash particulates from the environment, hence higher Cr.

	Dam	D1	Spring	Rain Water
Autumn	0.007	0.010	0.010	0.010
Winter	0.009	0.014	0.007	0.010
Spring	0.020	0.005	0.020	0.010
Summer	0.007	0.015	0.015	0.010

Table 4.18: Pb Data (ppm) for different sample points over the period 2008-2010



Fig.4.18: Plot of Pb over different sample points

From the plot on Fig. 18, Pb levels show to be highest during spring. This can be attributed to concentration as a result of lowered volume of solvent (water). Rainy seasons are summer and autumn, there is very little rain during winter and spring.

Lead (Pb) is widely distributed as metallic lead, inorganic compounds and organometallic compounds. It posseses a number of toxic effects, including inhibition of the synthesis of haemoglobin. It also affects the central and peripheral nervous system and kidneys. The South African limit in drinking water is 0.02 ppm, and the average result is within the limit.

4.5 Theoretical Discussion

Drinking water standards are a useful indication of potential risk relating to pollutants. SANS241 and DAWF (1996), South African Water Quality Guidelines are essentially the same.

Tables 2.1 (a),(b) and (c) indicate control limits set out by different controlling bodies. From the tables it comes out that each controlling body has its own standards. Looking at Mn for example it is found that EU and NL are tightest at 0.05 ppm, with SA at 0.1 ppm and the WHO at 0.5 ppm while the Vaal Barrage is at 0.2 ppm. For copper it can be seen that SA is the tightest at 1 ppm, while the other bodies are at 2 ppm. The Vaal Barrage is also at 2 ppm maximum. In general, it comes out that NL has the tightest control limits.

Comparison of pollutant levels indicates that concentrations generally fall within limits set by SA (South Africa), WHO (World Health Organisation) and the EU (European Union).

The research have shown that the company has strict occupational exposure limits to various substances that are relevant to different sites (road bridge), table. However, heavy metal concentrations can be reduced further by adsorption using agricultural waste materials. This is illustrated in appendix 2.

Appendix 2

Adsorption of metals by the eucalyptus

Table 4.6(a): Metal concentrations before and after 10 hrs sorption with 2 gram powder (synthetic water sample with different concentrations)

Element	Initial	Final	Adsorb	Initial	Final	Adsorb	Initial	Final	Adsorb
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mn	0.24	*	0	1	*	0	2	*	0
Fe	0.24	0	0.24	1	0	1	2	0	2
Со	0.24	0	0.24	1	0.4	0.6	2	1.0	1
Ni	0.24	0	0.24	1	0.5	0.5	2	1.0	1
Cu	0.24	0	0.24	1	0.3	0.7	2	0.5	1.5
Zn	0.24	0	0.24	1	0.6	0.4	2	1.1	0.9
Cd	0.24	0	0.24	1	0	1	2	0	2
Sn	0.24	0.1	0.23	1	0.1	0.9	2	0.3	1.7
Cr	0.24	0	0.24	1	0.2	0.8	2	0.6	1.4
Hg	0.24	0	0.24	1	0	1	2	0	2
Ti	0.24	0	0.24	1	0	1	2	0.8	1.2
Pb	0.24	0	0.24	1	0	1	2	0.9	1.1

From Table 4.6(a), different initial concentrations for the elements:, 0.24 ppm,1 ppm and 2 ppm were selected for adsorption. The adsorbed amounts indicate that reaction took place with the exception on manganese. Due to competitive adsorption other elements present in the matrix occupy sites that the manganese would occupy, hence manganese remains high.

From Table 4.6(b) a real sample was analysed as is after sampling and results are labelled initial concentrations. The sample was then spiked with 1 ppm sothat the new concentration would be 1 ppm higher than the initial concentration. Samples were then subjected to adsorption .Results indicated in the last column are for amounts

adsorbed, indicating that competitive adsorption did take place and manganese was not adsorbred as a result.

Table 4.6(b): Bridge water metal concentrations before and after 6 hrs sorption with 2 gram powder

Element	Initial	Initial	I ppm spiked	Adsorbed
	concentration	concentration	remaining	concentration
	ppm	plus 1 ppm	ppm	ppm
		spiked		
		ppm		
Mn	0.044	1.044	*	0
Fe	0	1	0	1
Со	0.005	1.005	0.415	0.59
Ni	0	1	0.511	0.489
Cu	0.004	1.004	0.503	0.502
Zn	0.006	1.006	0.802	0.204
Cd	0.005	1.005	0.158	0.847
Sn	0.005	1.005	0.281	0.724
Cr	0	1	0.517	0.483
Hg	0	1	0.224	0.776
Ti	0	1	0	1
Pb	0	1	0	1

Table 4.6 (c): Adsorbed dam water metal concentrations after 6 hrs sorption with 2 gram powder

Element	Initial con	Sorption	Adsorbed	1 ppm	Initial	Adsorbed
	w/o	over 6 hrs	conc	spike then	before	conc
	sorption		ppm	sorption	spiked	ppm
	ppm			over 6 hrs	ppm	
Fe	0	0	0	0	1	1
Со	0.006	0.003	0.003	0.4131	1.006	0.581
Ni	0	0	0	0.511	1	0.489
Cu	0.004	0	0.004	0.303	1.004	0.693
Zn	0.006	0	0.006	0.802	1.006	0.192
Cd	0.003	0.001	0.002	0.138	1.003	0.859
Sn	0.005	0	0.005	0.261	1.005	0.734
Cr	0	0	0	0.317	1	0.683
Hg	0	0	0	0.228	1	0.772
Ti	0.001	0	0.001	0.001	1.001	0.998
Pb	0	0	0	0	1	1

From Table 4.6(c) a real sample was analysed as is after sampling and then subjected to adsorption, results are labelled initial concentrations and adsorbed concentration. The sample was then spiked with 1 ppm so that the new concentration would be 1 ppm higher than the initial concentration. Samples were then subjected to adsorption .Results indicated that competitive adsorption did take place.

Table 4.6 (d): Sorption over 25.5 hrs on 21 ppm original concentration 1g ground leaf (adsorbent)

Element	Original ppm	Adsorbed ppm
Fe	21	8
Со	21	3
Ni	21	4
Cu	21	1
Zn	21	1
Sn	21	1
Cr	21	3

From Table 4.6 (d), a synthetic sample of 21 ppm was adsorbed for a contact time of 25 hrs. Results indicate that adsorption did indeed take place.

Table 4.6(e) : Sorption over 52 hrs, 2g ground leaf (adsorbent)

Element	Original (ppm)	Adsorbed (ppm)
Fe	21	6
Со	21	4
Ni	21	4
Cu	21	1
Zn	21	3
Sn	21	17
Cr	21	3
Ti	21	21

From Table 4.6 (e), it is clearly indicated that adsorption took place, in which case Ti and Sn were adsorbed the most.

Element	Original	Adsorbed	Original	Adsorbed	Origional	Adsorbed
Fe	2	2	4	4	8	8
Со	2	2	4	3.5	8	3
Ni	2	0.3	4	2.4	8	2
Cu	2	2	4	4	8	4
Zn	2	2	4	4	8	4
Cd	2	1.9	4	3.7	8	4.8
Sn	2	2	4	4	8	8
Cr	2	2	4	4	8	3
Hg	2	1.6	4	3.3	8	4.8
Ti	2	2	4	4	8	8
Pb	2	0.7	4	2.5	8	6.3

Table 4.6 (f): 2g ground leaf (adsorbent) over 25 hrs

From Table 4.6 (f), it is indicated that adsorption took place, in which case Ti and Sn were adsorbed the most.

Element	0rig 21(ppm)	Adsorbed (ppm)
Fe	21	13
Со	21	11
Ni	21	11
Cu	21	9
Zn	21	8
Cd	21	10
Sn	21	17
Cr	21	10
Hg	21	9
Ti	21	20
Pb	21	15
Hg	21	10

Table 4.6 (g): Sorption over 123 hrs with 2g ground leaf (adsorbent)
From Table 4.6(g), a 21 ppm sample was allowed to adsorb for 123 hours to ensure that equilibrium was reached. Adsorption took place competitively for the different metals.

	Original	Adsorbed	Original	Adsorbed	Original	Adsorbed
Element	ppm	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Fe	1	1	2	2	4	4
Со	1	0.7	2	1.4	4	1.9
Ni	1	0.6	2	1.3	4	2.1
Cu	1	0.8	2	1.7	4	2.9
Zn	1	0.6	2	1.3	4	1.5
Cd	1	1	2	1.7	4	2.3
Sn	1	0.9	2	1.8	4	3.5
Cr	1	0.7	2	1.5	4	2.5
Hg	1	0.7	2	1.4	4	2.4
Ti	1	1	2	1.9	4	3
Pb	1	1	2	0.4	4	2.3

Table 4.6 (h): Sorption over 22 hrs, 2g ground leaf (adsorbent)

From table 4.6 (h): different concentrations: 1ppm, 2 ppm,4 ppm were allowed to adsorb for 22 hrs .Results indicate that adsorption did take place.

Chromium adsorption tests for Freundlich and Langmuir equations

Table 4.6(i):x/m against c where x is the amount of solute adsorbed by m grammes of adsorbent at the equilibrium concentration c.

x/m	0.35	1.25	5.3	18.5
С	1.3	1.5	10.4	47



Fig. 4.19: Plot of x/m vs c

Table 4.6(j):	log(x/m)	against	log c
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log(x/m)	-0.82	-0.6	-0.12	0.72
log c	-0.52	-0.30	0.18	1.02



log c

Fig .4.20: Plot of log (x/m) vs log c



Fig. 4.21 : Plot of c/(x/m) vs c

The eucalyptus leaf powder was found to selectively adsorb heavy metal onto its reactive sites at a pH of 3 and temperature of 296K. Of the selected metals Mn was found to adsorb the least in the presence of the others in the multielement mixture. This can be ascribed to competitive adsorption in which case other metal ions occupy the site that Mn would occupy. Freundlich and Langmuir adsorption isotherms show a direct proportion of amount and concentration at equilibrium for Cr as shown in Figures.4.19 to 4.21.

Biosorption is a relatively new process that has shown significant contribution for the removal of metal contaminants from aqueous effluents. In this research the toxic metal ion biosorption on an inexpensive and efficient biosorbent from agricultural waste materials (eucalyptus leaves) has been investigated as replacement strategy for existing conventional systems. The functional groups present in agricultural waste biomass viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino and sulphydryl have affinity for heavy metal ions to form metal complexes and chelates.

Ground eucalyptus leaves have been used successfully in the removal of heavy metals from waste water.

Appendix 1

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Table 4.1(a): Manganese ores analysis by XRF

Date	Mn	Fe	SiO ₂	CaO	MgO	Al ₂ O ₃	Р
	%	%	%	%	%	%	%
Average	38.24	8.05	5.08	13.0	6.17	0.29	0.028



Fig. 4.1 (a): Plot of manganese ore analysis

Table 4.2 (a): HC FeMn analysis by XRF

Mn %	Fe%	Si %	P%	S%	AI%	С
73.94	16.03	6.26	0.079	0.010	0.0075	3.27



Fig. 4.2 (a): Plot of HC FeMn analysis by XRF

Table 4.3	(a)	: MC	FeMn	anal	ysis	by	XRF
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Date	Mn %	Fe%	Si %	P%	S%	Al%	С
	78.58	19.01	0.491	0.1012	0.014	0.0071	1.58



Fig 4.3(a) Plot of MC FeMn analysis by XRF

Table 4.4	(a): S	SiMn	analy	/sis	by	XRF
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Date	Mn %	Fe%	Si %	P%	S%	Al%	С
Ave	66.04	14.01	18.26	0.0745	0.0125	0.0084	1.284



Fig 4.4 (a): Plot of SiMn analysis by XRF

Table 4.5 (a): High Carbon FeMn slags (HCS), MC FeMn slag (MS) and Silicon Manganese Slag (SMS), by XRF

	MnO%	FeO %	SiO ₂ %	CaO %	MgO %	Al ₂ O ₃ %
HCS	24.05	0.081	31.43	30.47	7.71	3.50



Fig 4.5 (a) : Plot of High Carbon FeMn slags(HCS) by XRF

Table 4.7(a):MC FeMn slag(Molten slag) by XRF





Fig 4.7(a):Plot of MC FeMn slag(Molten slag) by XRF

Date	MnO%	FeO %	SiO ₂ %	CaO %	MgO %	Al ₂ O ₃ %
Average	17.00	0.160	44.10	19.80	5.30	9.10

Table 4.8 (a) : Silicon Manganese Slag (SMS) by XRF



Fig 4.8(a): Plot of Silicon Manganese Slag (SMS) by XRF

Water Analysis

Table 4. 9 (a): Environment (Rain Water) by ICP, UV-Vis spectrophotometer and pH meter

						рΗ	В
			Cr(VI)	Phenols	Pb		рр
	Mn ppm	Cr ppm	ppm	ppm	ppm		m
Autumn						7.0	*
2008	1.010	*	*	0.091	*		
Winter						7.1	*
2008	0.970	*	*	0.099	*		
Spring						7.2	*
2008	0.940	*	*	1.000	0.000		
Summer						7.0	*
2008	0.990	*	*	0.099	0.000		
Autumn						7.1	1.0
2009	1.020	1.020	*	0.115	0.010		5
Winter						7.1	1.0
2009	1.040	1.050	0.480	0.171	0.010		3
Spring						7.1	1.0
2009	0.970	1.050	0.500	0.175	0.010		3
Summer						6.6	1.0
2009	0.980	1.020	0.510	0.199	1.00		2
Autumn				0.191	1.01	6.7	1.0
2010	1,04	1.09	0.49				3

	Phenols ppm	рН
Autumn 2008	0.08	9.6
Winter 2008	0.14	9.3
Spring 2008	0.10	9.1
Summer 2008	0.08	8.8
Autumn 2009	0.07	9.1
Winter 2009	0.07	8.7
Spring 2009	0.06	8.3
Summer 2009	0.096	8.6
Autumn 2010	0.094	9.0
Winter 2010	0.098	9.0

Table 4.10 (a): M Trench by ICP, UV-Vis spectrophotometer and pH meter



Fig. 4. 10 (a): Plot of M trench analysis

	Phenols ppm	рН
Autumn 2008	0.31	8.2
Winter 2008	0.02	8.5
Spring 2008	0.41	8.6
Summer 2008	0.320	8.5
Autumn 2009	0.06	8.2
Winter 2009	0.02	8.3
Spring 2009	0.02	8.4
Summer 2009	0.083	8.6
Autumn 2010	0.072	8.3
Winter 2010	0.005	8.4

Table 4.11 (a): H.Trench by ICP, UV-Vis spectrophotometer and pH meter



Fig. 4.11(a): Plot of H.Trench analysis

			Cr(VI)	Phenols		рН
	Mn ppm	Cr ppm	ppm	ppm	Pb ppm	
Autumn 2008	0.270	0.130	0.000	0.013	0	7.9
Winter 2008	0.150	0.040	0.000	0.022	0	10.5
Spring 2008	0.270	0.100	0.000	0.023	0	10.6
Summer 2008	0.290	0.000	0.010	0.008	0.000	9.4
Autumn 2009	0.960	0.000	0.010	0.011	0.010	8.7
Winter 2009	0.220	0.010	0.010	0.020	0.010	9.4
Spring 2009	1.230	0.010	0.000	0.014	0.020	8.4
Summer 2009	0.920	0.000	0.008	0.056	0.014	8.7
Autumn 2010	0.58	0.00	0.000	0.034	0.003	9.2
Winter 2010	0.45	0.000	0.006	0.109	0.007	9.2

Table 4.12(a): Dam by ICP, UV-Vis spectrophotometer and pH meter



Fig 4.12 (a): Plot of Dam

	Mn	Cr		pН
	ppm	ppm	Cr(VI) ppm	
Autumn 2008	0.890	0.080	0.000	7.6
Winter 2008	0.700	0.120	0.000	7.9
Spring 2008	0.790	0.110	0.000	7.7
Summer 2008	0.790	0.000	0.010	7.7
Autumn 2009	0.990	0.000	0.020	7.9
Winter 2009	1.040	0.000	0.010	7.8
Spring 2009	0.350	0.000	0.010	7.8
Summer 2009	0.730	0.000	0.015	7.7
Autumn 2010	1.030	0.000	0.007	7.8
Winter 2010	0.550	0.000	0.003	7.9

Table 4.13 (a): Road Bridge water by ICP, UV-Vis spectrophotometer and pH meter



Fig. 4.13(a): Plot of Road Bridge water analysis

	Mn	рН
	ppm	
Autumn 2008	0.260	7.6
Winter 2008	0.140	7.7
Spring 2008	0.240	7.4
Summer 2008	0.230	7.3
Autumn 2009	0.170	7.6
Winter 2009	0.230	7.3
Spring 2009	0.000	7.5
Summer 2009	0.018	7.3
Autumn 2010	0.420	7.4
Winter 2010	0.250	7.5

Table 4.14 (a) Spruit water by ICP, UV-Vis spectrophotometer and pH meter



Fig 4.14 (a) Plot of Spruit water

	Mn	Cr	Cr(VI)	Phenols	Pb	pН	В
	ppm	ppm	ppm	ppm	ppm		ppm
Autumn		0.00	0.00		0.00		0.00
2008	0.00			0.002		7.2	
Winter		0.00	0.00		0.00		0.00
2008	0.00			0.004		7.1	
Spring		0.00	0.00		0.00		
2008	0.00			0.019		7.1	0.00
Summer					0.00		
2008	0.00	0.00	0.01	0.003		7.1	0.77
Autumn					0.00		
2009	0.00	0.00	0.01	0.003		7.2	0.64
Winter					0.00		
2009	0.00	0.00	0.01	0.010		7.4	0.59
Spring					0.00		
2009	0.00	0.00	0.02	0.00		7.3	0.55
Summer							
2009	0.00	0.00	0.00	0.00	0.02	7.4	0.54
Autumn				0.005	0.01	7.2	0.39
2010	0.00	0.00	0.013				
Winter				0.00	0.003	7.3	0.42
2010	0.00	0.00	0.00				

Table 4.15 (a): Fountain (Eye) water by ICP, UV-Vis spectrophotometer and pH meter



Fig 4.15(a): Plot of Fountain (Eye) water analysis

Table 4.16(a): Borenole (D1) water results from 2008 -201	(a): Borehole (D1) water results from	2008 -2010
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	Mn	Cr	Cr(VI)	Phenols	Pb	pН	В
	ppm	ppm	ppm	ppm	ppm		ppm
Autumn							
2008	0.030	0.000	0.410	0.310	0.000	8.3	0.000
Winter -	0.000	0.000	0.470	0.020	0.000	8.3	0.000
Spring -	0.000	0.000	0.300	0.410	0.000	8.4	0.00
Summer-	0.010	0.960	0.370	0.320	0.000	8.4	0.680
Autumn							
2009	0.000	0.570	0.610	0.060	0.010	8.3	0.770
Winter -	0.040	0.600	0.510	0.015	0.010	8.3	2.940
Spring -	0.010	0.470	0.540	0.021	0.010	8.2	0.630
Summer -	0.012	0.510	0.44	0.011	0.016	8.4	0.66
Autumn				0.007	0.010	8.1	0.71
2010	0.03	0.27	0.27				
Winter -	0.028	0.24	0.243	0.010	0.018	8.2	0.68



Fig 4.16(a): Borehole (D1) water results

Table 4.17(a): Mn Data(ppm) for different sample points

	Dam	Bridge	Spruit	D1	Spring
	ppm	ppm	ppm	ppm	ppm
Autumn 2008	0.27	0.89	0.26	0.03	0.00
Winter 2008	0.15	0.70	0.14	0.00	0.01
Spring 2008	0.27	0.79	0.24	0.00	0.00
Summer 2008	0.29	0.79	0.23	0.01	0.00
Autumn 2009	0.96	0.99	0.17	0.00	0.00
Winter 2009	0.22	1.04	0.23	0.04	0.00
Spring 2009	1.23	0.35	0.00	0.01	0.00
Summer 2009	0.920	0.73	0.23	0.012	0.00
Autumn 2010	0.58	1.03	0.17	0.030	0.00
Winter 2010	0.450	0.55	0.23	0.028	0.00



Fig. 4.17 (a): Plot of Mn levels over different sampling points

	Dam	D1		М	Н	
	ppm	ppm	Spring	Trench	Trench	Rain Water
			ppm	ppm	ppm	ppm
Autumn 2008	0.01	0.31	0.002	0.08	0.31	0.09
Winter 2008	0.02	0.02	0.000	0.14	0.02	0.10
Spring 2008	0.02	0.41	0.023	0.10	0.41	1.00
Summer 2008	0.01	0.32	0.003	0.07	0.32	0.10
Autumn 2009	0.01	0.06	0.003	0.00	0.06	0.12
Winter 2009	0.02	0.02	0.003	0.03	0.02	0.17
Spring 2009	0.01	0.02	0.000	0.06	0.02	0.18
Summer 2009	0.06	0.0097	0.000	0.096	0.083	0.20
Autumn 2010	0.034	0.007	0.005	0.094	0.072	0.199
Winter 2010	0.109	0.010	0.000	0.098	0.005	0.191

Table 4.18(a): Phenol Data (ppm) for different sample points



Fig. 4.18(a): Plot of phenol levels over different sample points

	Amcor	Road	Fourie	D1		Main	Hymat	Rain
	dam	Bridge	Spruit		Spring	Trench	trench	Water
Autumn								
2008	7.90	7.60	7.60	8.30	7.20	9.60	8.2	7.00
Winter -	10.50	7.90	7.70	8.30	7.20	9.30	8.50	7.10
Spring -	10.60	7.70	7.40	8.40	7.10	9.10	8.60	7.20
Summer	9.40	7.70	7.30	8.40	7.10	8.80	8.50	7.00
Autumn								
2009	8.70	7.90	7.60	8.30	7.20	9.10	8.20	7.10
Winter -	9.40	7.80	7.30	8.30	7.30	8.70	8.30	7.10
Spring -	8.40	7.80	7.50	8.20	7.20	8.30	8.40	7.10
Summer -	8.70	7.7	7.3	8.4	7.4	8.6	8.6	7.1
Autumn								
2010	9.2	7.8	7.4	8.1	7.2	9.0	8.3	6.6
Winter -	9.2	7.9	7.5	8.2	7.3	9.0	8.4	6.7

Table 4.19 (a) :pH data for different sample points over the period 2008-2010



Fig. 4.19(a): Plot of pH levels over different sample points

	Amcor	Road	D1		Rain
	dam	Bridge		Spring	Water
Autumn 2008	0.00	0.00	0.41	0.00	0.00
Winter 2008	0.00	0.00	0.47	0.00	0.00
Spring 2008	0.00	0.00	0.30	0.00	0.00
Summer 2008	0.01	0.01	0.37	0.00	0.00
Autumn 2009	0.01	0.02	0.61	0.01	0.00
Winter 2009	0.01	0.01	0.51	0.01	0.48
Spring 2009	0.00	0.01	0.54	0.01	0.50
Summer 2009	0.008	0.015	0.44	0.000	0.51
Autumn 2010	0.000	0.007	0.27	0.013	0.51
Winter 2010	0.006	0.003	0.243	0.000	0.49

Table 4.20 (a) :Cr ⁶⁺ Data(ppm) for different sample points



Fig 4.20 (a) Plot of Cr⁶⁺ levels over different sampling points

	Amcor	Road	D1		
	dam	Bridge		Spring	Rain Water
Autumn 2008	0.13	0.08	0.00	0.00	0.00
Winter 2008	0.04	0.12	0.00	0.00	0.00
Spring 2008	0.10	0.11	0.00	0.00	0.00
Summer 2008	0.00	0.00	0.96	0.00	0.00
Autumn 2009	0.00	0.00	0.57	0.00	1.02
Winter 2009	0.01	0.00	0.60	0.00	1.05
Spring 2009	0.01	0.00	0.47	0.00	1.05
Summer 2009	0.00	0.00	0.51	0.00	1.02
Autumn 2010	0.00	0.00	0.27	0.00	1.09
Winter 2010	0.00	0.00	0.24	0.00	0.00

Table 4.21 (a) :Cr Data (ppm) for different sample points



Fig.4. 21(a): Plot of Cr over different sample points

Table 4.22((a)	: Pb	Data ('nna	h) for	different	samr	ole i	ooints
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	Amcor dam	D1	Spring	Rain Water
Autumn 2008	0.00	0.00	0.00	0.00
Winter 2008	0.00	0.00	0.00	0.00
Spring 2008	0.00	0.00	0.00	0.00
Summer 2008	0.00	0.00	0.01	0.00
Autumn 2009	0.01	0.01	0.01	0.01
Winter 2009	0.01	0.01	0.01	0.01
Spring 2009	0.02	0.01	0.02	0.01
Summer 2009	0.014	0.016	0.02	0.01
Autumn 2010	0.003	0.010	0.01	1.01
Winter 2010	0.007	0.018	0.003	0.00



Fig. 4. 22(a): Plot of Pb over different sample point.

References

[1] Garg,U.K.,Kaur, M.P.,Garg ,V.K.,Sud, D. 2007.Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. Journal of hazardous materials , 140 :60-68.

[2] Laidler,K.J.,Meisner,J.H.,1995. Physical Chemistry. 2nd ed. New Jersey: Houghton Mifflin Company.

[3] Patnaik, P. Hanbook of environmental analysis.2010. 2nd ed,USA: Taylor and Francis Group.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Analysis of samples indicated the presence of heavy metals with varying concentrations at different sample points. The D1 borehole is found to have higher chromium levels because ferrochrome was once stored in that catchment area .The dam and road bridge manganese content is higher due to suspended particulates settling on the ground and being washed down by water streams. Raw materials from mines contain heavy metals which are transferred to water systems during handling.

The research has focussed on the removal of heavy metals from industrial waste water. This was achieved by investigating, characterising and quantifying pollutants within a metallurgical industry environment resulting from applied operations technology and then looking into abatement measures that can be put in place. The study was done and conclusions are discussed below.

Strong chelating agents methods are effective for removing metals from contaminated waters yet they are either expensive or time consuming and have their inherent limitations [1]. The need for economical and effective methods of removing heavy metals from wastewater has resulted in the search for unconventional materials that may be useful in reducing the levels of accumulation of heavy metals in the environment.

Biosorption is a relatively new process that has shown significant contribution for the removal of contaminants from aqueous effluents. In this research the toxic metal ion biosorption on an inexpensive and efficient biosorbent from agricultural waste

materials has been investigated as replacement strategy for existing conventional systems [4].

The study was conducted by using eucalyptus leaves powder for sequestering heavy metal ions from waste water. The metal uptake from an aqueous solution is facilitated by functional groups in the ligno-cellulosic material [3]. Many solids are capable of adsorbing ions and molecules from solutions [2]. The removal of heavy metals from aqueous solution using eucalyptus leaves has been investigated under different experimental conditions viz. initial metal concentration and adsorbent mass..

Results obtained indicated a decrease in metal concentration due to biosorption of a known elemental concentration per known volume by a known mass of sorbent over a specific time. Sorption is found to be dependent upon contact time, initial concentration, sorbent dose of small quantities of wastewaters containing heavy metals.

Differential adsorption shows a competitive pattern where Mn is adsorbed the least, from the list of selected heavy metals. The general pattern is of the following order: Ti>Sn> Fe>Co>Ni> Cu>Zn>Cd>Cr>Hg>Pb >Mn.

Agricultural waste materials containing lignin and cellulose are an abundant source for significant metal biosorption, highly efficient, low cost and renewable source of biomass.

They can be exploited for heavy metal remediation. These biosorbents can be modified for better efficiency and multiple reuses to enhance their applicability at industrial scale.

In the event of high levels of heavy metal being experienced, ground eucalyptus leaves can be used for heavy metal recovery from wastewater. A procedure covering the sorbent mass required per average specific pollutant concentration over a specific time frame can be compiled to optimise sorption. The advantage of biosorption compared to conventional treatment methods are low cost, high efficiency,

minimisation of chemical and biological sludge as well as the regeneration of biosorbents and a possibility of metal recovery.

Use of biosorbents is relatively cheap or of no cost, easily available, renewable and show high affinity for heavy metals. Literature also reveals that in some cases the modification of the adsorbent increases the metal sequestration efficiency [1,4].

5.2 Recommendations

The company has mechanisms to remove heavy metals from water. Comparison of pollutant levels indicates that concentrations fall within limits set by SA (South Africa), WHO (World Health Organisation) and the EU (European Union).

However, heavy metal concentrations can be reduced further by adsorption using agricultural waste materials, having properties including being highly efficient, low cost and renewable source of biomass.

Further studies should be done to explore the possibility of optimising recovery of heavy metals from wastewater using eucalyptus leaf powder. This can be achieved for example, by modification of the adsorbent through addition of reactive functional groups and optimising the mass of eucalyptus leaves per volume of wastewater to complete adsorption over a specific time.

References

 [1] Akporhonor, E. E., Egwaikhide, P.A., 2007. Removal of selected metal ions from aqueous solution by adsorption onto chemically modified maize cobs.
Scientific Research and Essay, 2 (4) 132-134.

[2]. Laidler,K.J.,Meisner,J.H.,1995. Physical Chemistry. ^{2nd} ed. New Jersey: Houghton Mifflin Company.

[3] Marshall W.E., Wartelle L.H., Boler D.E., Johns M.M., 1999. Bioresource Technology 69: 263-268.

[4] Sud Dhiraj, Mahajan Garima,Kaur M.P., 2008. Agricultural waste material as potential. adsorbent for sequestering heavy metal ions from aqueous solutions – A review. Bioresource Technology, 99 : 6017-6027.