Treatment of Acid Mine Drainage Using Constructed Wetland and UV/TiO2

# **Photocatalysis**

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# Declaration

I, <u>Tumelo Wordsworth Poloko Seadira</u> declare that this is my own work. It is being submitted for the degree of Master's of Technology at the Vaal University of Technology, Vanderbijlpark. It has not been submitted before for any degree or examination in any other university and all sources of the material used for this MTech project have been duly acknowledged.

Signature of Candidate

Date

#### Abstract

Acid mine drainage (AMD) is a serious problem associated with mining activities, and it has the potential to contaminate surface and ground water. The aim of this study was to evaluate the performance of constructed wetland and photocatalysis in treating AMD. Three identical unvegetated upflow constructed wetlands packed with natural zeolite (clinoptilolite) and coarse silica sand were made of a cylindrical plastic pipe, and the slurry photocatalyst was prepared using quartz material. A hydro-alcohol thermal method was used to prepare an anatase core-void-shell TiO<sub>2</sub> photocatalyst.

The results showed that the three unvegetated upflow constructed wetlands (CW) had relatively similar percentage removal of heavy metals despite their varying concentrations within the AMD. The removals were: Fe (86.54 - 90.4%); Cr (56.2 - 64.5%); Mg (56.2 - 67.88%); Ca (77.1 - 100%); and 100% removal was achieved for Be, Zn, Co, Ni, and Mn. The removal of sulphate was also 30%. Heavy metals concentration in CW packing material was significantly higher in the outlet of the constructed wetlands than in the inlet. The adsorption isotherms revealed that the experimental data fitted the Langmuir Isotherms better, which suggested a monolayer coverage of heavy metals on the surface of the adsorbents; thermodynamic studies showed that the nature of adsorption taking place was physical; the kinetics models showed that the adsorption was first order reaction. A higher photocatalytic reduction (62%) of Cr(VI) was obtained at pH 2, 30 mg/l Cr(VI) initial concentration, and three hours of irradiation time. It was also found that the presence of Fe(III) enhanced the reduction of Cr(VI). The core-void-shell TiO<sub>2</sub> photocatalyst showed a better activity than the commercial P25 Degussa for the reduction of Cr(VI) to Cr(III). The kinetic studies showed that the reduction of Cr(VI) was first order reaction. Photocatalytic reduction of Cr(VI) in real AMD sample was achieved only for the Douglas North Discharge (DND) sample (68%), and the Fe(III) reduction was found to be 83%. Therefore it was concluded that the combination of constructed wetland and UV/ TiO<sub>2</sub> photocatalysis employing anatase core-void-shell TiO<sub>2</sub> as a photocatalyst has a potential to reduce the toxicity of Cr(VI)-laden acid mine drainage.

## Publication related to this work

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# **Chapter 1**

### 1. Introduction

Wastewater containing high concentration of heavy metal and acidic nature is known as acid mine drainage (AMD). It is generated when sulphide minerals such as pyrite are oxidized by atmospheric oxygen and ground/surface water (Holmstrom, 2000). The oxidation of pyrite releases dissolved ferrous ion and acidity into the water, which in turn releases high concentrations of other heavy metals such as Fe, Mn, and Zn, and lower concentrations of Cu and Cd. However, the concentrations of heavy metals in AMD vary because of the different minerals mined (Akcil & Koldas, 2006). Frequently, the most important sites for the creation of AMD are the discharge from open pits, expulsion from underground mining shafts, as well as ore stockpiles (Mandres *et al.*, 2009). Most water or wastewater that spews from these mines is essentially a toxic end-product of underground mining activities. Moreover, because the formation of AMD is affected by mineralogy as well as other variables, the formation of AMD will differ from one area to another, which renders the predictive capacity with regard to its formation - as well as occurrence - both highly expensive but also of ambiguous reliability (US EPA 1993). The extreme pH and high ionic content are responsible for highly toxic wastewater, and its handling requires expensive storage, remediation and disposal techniques.

AMD can be neutralized using chemicals like lime, calcium carbonate, hydrated lime, caustic soda, and soda ash which often results in the production of voluminous sludge (solids in this sludge comprise 5%). This sludge disposal represents a further environmental problem and additional cost (Fiset *et al.*, 2003). Thus, the high cost of conventional clean up technologies has caused economic pressure and motivated engineers to search for creative, cost-effective and environmentally sound ways to treat AMD. In the past decades, therefore research efforts have been directed towards wetlands as an alternative low cost means of removing heavy metals from AMD besides domestic, commercial and industrial waste water (Matagi *et al.*, 1998). Both natural and artificially constructed wetlands can be efficient treatment technologies with minimum inputs, low investment costs, low operating costs and no external energy input (Woulds & Ngwenya, 2004).

Constructed wetlands are engineered systems that have been designed to employ natural processes including vegetation, soil, and microbial activity to treat contaminated water. Constructed wetlands possess the merits of low-cost and low-maintenance, and are capable of removing various pollutants

including heavy metals, nutrients, organic matters, and micro-pollutants (Keffala & Ghrabi, 2005). In addition, constructed wetlands have been used recently for treating various wastewater types including point source domestic sewage, acid mine drainage, agricultural wastewater, landfill leachate, and non-point source storm water runoff (Rousseau *et al.*, 2008). Constructed wetlands consist of properly designed basins that contain water, a substrate, and, most commonly, vascular plants (emergent macrophytes such as planting cattail and planting reed). These components can be manipulated in constructing a wetland. Other important components of wetlands, such as the communities of microbes and aquatic invertebrates, develop naturally.

The presence of toxic species such as hexavalent chromium in AMD however, poses a major threat to the environment even at low concentrations. The chromium removal treatment includes precipitation, ion exchange, photocatalysis, reverse osmosis, and adsorption process (Lin *et al.* 1993). Most of these methods require high capital and recurring expenditure and consequently they are not suitable for small-scale industries (Lee *et al.*, 2006).

Among all the aforementioned methods, photocatalysis is a highly effective and cheap process than the other methods. Photocatalysis is one of the potential techniques to either oxidize or reduce hazardous pollutants such as hexavalent chromium. This process use semiconductors such as TiO<sub>2</sub>, SnO<sub>2</sub>, WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, and CdSe (Kanki *et al.*, 2004). TiO<sub>2</sub> has received the most interest because of its photocatalytic activity, low cost (Watts *et al.*, 1995), low toxicity, and high stability to light illumination (Kaneko & Okura, 2002). Titania dioxide, TiO<sub>2</sub> illuminated with UV light has highly reductive electrons (Kanki *et al.*, 2004). The reduction converts a variety of inorganic compounds, such as dichromate (Cr<sub>2</sub>O<sub>7</sub> <sup>2–</sup>), to less hazardous substances (reduces Cr(VI) to Cr(III)), which is easier to dispose of or recycle (Sabate *et al.*, 1992).

# 1.1. Problem Statement

The formation of AMD in mining activities is very problematic and it poses threats of potentially contaminating ground/surface water. When AMD is discharged untreated, it can pollute receiving water streams and aquifers, and the resulting overall effect on streams and waterways can be dramatic. Acid Mine Drainage is currently affecting the residents of some parts of Johannesburg as well as Carolina (Mpumalanga) by contaminating their drinking water. Treatment technologies such as addition of alkaline substances like sodium hydroxide and limestone, remediate already generated AMD by adjusting its pH from acidic to basic, and decrease the concentration of heavy metals and sulphate by precipitation and co-precipitation. The main problem with the chemical

treatment methods is the high cost involved and high sludge volume. For this reason, the employment of constructed wetlands to remediate AMD can be an alternative process to chemical processes. A drawback of these systems is their relatively high demand for land, which poses a challenge especially in urban areas. Therefore to reduce the demand for land highly effective adsorbents with high adsorbent efficiencies are required. Natural zeolite (clinoptilolite) is selected as the most effective adsorbents because it is low-cost and easily accessible. One of the major problems associated with the use of constructed wetlands in treating AMD is the suppressed growth of plants in low pH of AMD and the accumulation of salts. The presence of toxic species such as hexavalent chromium in AMD however, poses a major threat to the environment even at low concentrations. Photocatalysis is one of the potential techniques to either oxidize or reduce hazardous pollutants such as hexavalent chromium. The drawback of photocatalysis with TiO<sub>2</sub> suspension is the difficult and costly separation step after treatment (Chen *et al.*, 2000; Dijkstra *et al.*, 2002).

# 1.2. Objectives

The aim of this study is to treat AMD and assess the feasibility of using constructed wetland (CW) containing natural zeolite and UV/TiO<sub>2</sub> photocatalysis.

The specific objectives of this study are as follows:

# Constructed wetland:

- i. to design and commission a laboratory-scale wetland to be used for treating AMD
- ii. to analyze the morphology of the CW packing material
- iii. to determine the effect of pH on adsorption efficiencies of CW packing material
- iv. to determine the best operating hydraulic retention time (HRT) of acid mine drainage in constructed wetland.
- v. to analyze the accumulation and removal of heavy metals in the CW sediments
- vi. to analyze the adsorption isotherms, thermodynamics, and reaction kinetics

#### Photocatalysis:

- i. to synthesize and analyze the morphology of the synthesized core-void-shell TiO<sub>2</sub> photocatalyst
- ii. to determine the best operating parameters such as initial concentration (Co), pH, hydraulic retention time (HRT), and the catalyst loading for Cr(VI) reduction
- iii. to analyze the reaction kinetics of Cr (VI) reduction

# 1.3. Justification

With the increasing amounts of AMD discharging from open mine pits into the surface water bodies, there is a need to improve low cost wastewater treatment techniques to handle these wastes. Improving the efficiency of constructed wetlands and  $UV/TiO_2$  processes will ensure efficient treatment of toxic heavy metals which are potential environment pollutants, and also relieve the water stress that the country is currently experiencing.

# Chapter 2

## 2. Theory and Literature Review

#### 2.1. Acid Mine Drainage

Acid mine drainage is associated with mining of minerals such as gold, copper, nickel and coal. The acidity of this mine water is accelerated by naturally occurring bacteria which oxidizes sulphidebearing-minerals such as pyrite (equation 1), in underground water from deserted mines, or mine tailings and mineral rock heaps (Jarvis & Younger, 1999; Younger et al., 2002).

Trivalent iron,  $Fe^{3+}$  (2) is produced when divalent iron  $Fe^{2+}$  present in ground water is released during the oxidation of pyrite. Trivalent iron resulting from oxidation therefore precipitates as ferric oxyhydroxides (3)

$$2FeS_{2(s)} + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{-2} + 4H^+$$
(1)

$$4Fe^{2+}O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$
(2)

$$Fe^{3+} + 3H_2O \rightarrow Fe (OH)_{3(s)} + 3H^+$$
(3)

Although equation (3) represents the formation of proton acidity, bi-modal pH distribution has been exhibited by different mine discharge sources (Kirby & Cravotta, 2005). There are several factors that determine the rate of acid AMD production (USEPA). The most important factors that influence AMD generation are oxygen content; oxygen in water phase;  $Fe^{3+}$  chemical activity; surface area exposed to metal sulphide; chemical activation energy needed to generate acidity; and bacterial activity (Younger, 1995; Akcil & Koldas, 2006). Factors such as extremely low pH, dissolved salts, and heavy metals found in AMD are harmful on to the aquatic environment (Kelly, 1988; Ye *et al.*, 2001; Espana *et al.*, 2005). According to Akcil & Koldas (2006), high chemical rates of reaction and high temperature due to exothermic oxidation reaction influence sulphide generation, which in turn influences the acidic strength of the AMD.

Some of the harmful effects of AMD on the environment include the disappearance of all aquatic life, the coating of river bottoms with layers of rust-like particles, and the decrease in pH of the water and streams. Therefore, it is therefore essential that methods are in place to treat mine drainage to limit its negative effect on the environment (Kontopoulos *et al.*, 1996). As this

underground polluted water rises to the surface, it becomes a part of the drinking water that is utilized by both the urban as well as agrarian population (Taylor, 2010).

This is further supported by studies which indicated that approximately 80% of South Africa's water will be undrinkable by 2015 as a result of severe over-pollution with no remedy being present to reverse this trend once it comes into place (Water Sense, 2010). Moreover, the intake of this water is highly hazardous to human health as a result of the presence of heavy metals in the water (Zeelie, 2010). Currently, AMD not only poses a hazard to South Africa's water supplies, but also to its major industrial centres. A typical AMD characteristics from the Department of Water Affairs are given in Table 1.

Table 1. Composition of acid mine drainage (AMD), in relation to the DWA target water quality for irrigation and domestic usage (*Kumar* et al., 2008)

Parameter		DWA* g	uidelines		
	AMD	Irrigation	Domestic		
pН	2.7	6.5-8.4	6 - 9		
$SO_4^{2-}(mg/l)$	18 889	-	0 - 200		
Al (mg/l)	13.8	5	0 - 0.15		
Fe (mg/l)	3523	5	0 - 0.15		
Ca (mg/l)	497	-	0 - 32		
Na (mg/l)	76.8	70	0 - 100		
K (mg/l)	20.5	-	0 - 50		
Mg (mg/l)	294	-	0 - 30		
B (mg/l)	1.1	0.5	-		
$Zn (\mu g/l)$	4911	1000	0 - 3000		
Cu (µg/l)	320	200	0 - 1000		
Pb ( $\mu$ g/l)	33.6	200	0 - 10		
Mo (g/l)	20	10	-		
Co (µg/l)	640	50	-		
Ni (µg/l)	922	200	-		

\*Department of Water Affairs, Pretoria. -, no data available for either irrigation or for domestic use.

Among the various heavy metals, the potential sources of chromium include mining and steel alloys (Pradhan *et al.*, 1999). Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI). The behaviour of chromium species strongly depends on its oxidation state. Cr(VI) is mobile and highly toxic, whereas Cr(III) is mostly immobile and environmentally friendly. Chromium is vital to human life: a dose of 0.1-0.3 ppm per day is required for normal development and this amount comes from various foods and drinks. Cr(III) plays an essential role in plant and

animal metabolism, while Cr(VI) is directly toxic to humans, animals and plants (Francoise *et al*,. 1991).

#### 2.2. Constructed Wetlands

Constructed wetlands are employed mostly as tertiary treatment technologies when treating AMD because of their low cost effectiveness, great performance record when designed in accordance with customary guidelines; their ability to handle flow rates changes to large storage; and their addition to ecological remediation. Constructed wetlands constitute complex systems where the biological, chemical and physical processes interact and cause the removal of many contaminants from water. Effluent treatment is performed by techniques such as adsorption, precipitation and co-precipitation to the bottom sediment, and uptake by plants (Ye *et al.*, 2001).

#### 2.2.1. Types of Constructed Wetlands

## 2.2.1.1. Surface-flow system

The surface flow (SF) also known as free water surface (FWS) wetland typically consists of a shallow basin or channels with some type of barrier to prevent seepage, soil or any other media to support the roots of the emergent vegetation, and water at a relatively shallow depth flowing through the substrate at low velocities in a slow moving manner (Figure 1). Surface flow treatment wetlands mimic the hydrologic regime of natural wetlands, where water flows over the soil surface from an inlet point to an outlet point or, in few cases, is totally lost to evapotranspiration and infiltration within the wetland (Knight *et al.*, 1999; Scholz *et al.*, 2007). The wetland is flooded from the top and water flows horizontally on top of the wetland soil, infiltrates the soil or is evaporated as the water surface is exposed to the atmosphere (US EPA, 1993). The influent enters the wetland at the bottom and flows to the top of the ground surface where it is discharged. The first full-scale surface flow constructed wetland (CW) was built in The Netherlands to treat wastewaters from a camping site during the period 1967–1969 (Vymazal, 2005). Reed & Brown (1992) characterize this type of wetland as most closely mimicking natural marshes.

Tchobanoglous & Burton (1991) observed that facultative ponds are useful for pre-treatment of primary effluent or certain industrial wastes. The removal mechanisms that take place at the bottom regions of wetlands are similar to the ones taking place in the bottom regions of the lagoon, with a microbial region subjugated by bacteria (Kadlec, 2001). Anaerobic microbial activity in wetlands is an effective treatment process in these bottom regions due to the absence of light and oxygen.

However, surface-flow systems do not behave the same as facultative ponds at regions close to the surface. This is attributed to the macrophytes that shade and cool the water surface, which in turn suppress the algae growth and decreasing the rate of dissolved oxygen production (Kadlec, 2001). In addition, surface-flow systems produce high carbon content than facultive lagoons. This is attributed to a high carbon content production supplemented by the degradation resistance and low rates of organic carbon decomposition in poor oxygenated regions (Kadlec, 2001). This difference in biogeochemical cycles occurring in wetlands and lagoons or ponds shows that wetlands cannot be regarded as lagoons or ponds.



Figure 1. Typical configuration of a surface flow wetland system (Kadlec and Knight, 1996)

# 2.2.1.2. Sub-Surface-Flow

Subsurface Flow (SSF) wetlands are constructed generally with a porous material such as soil, sand, or gravel for a substrate. These type of wetlands are also known as reed beds, rock-reed wetlands, gravel beds, vegetated submerged beds, and the root method. Reed beds and rock-reed wetlands use sand, gravel, or rock as substrates, while the root method uses soil. Subsurface flow constructed wetlands first emerged as a wastewater treatment technology in Western Europe based on research by Seidel (1966) commencing in the 1960s, and by Kikuth (1977) in the late 1970s and early 1980s. They are designed so that water flows below ground surface through the substrate (ITRC, 2003). In subsurface flow wetlands, the wastewater flows through a constructed media bed planted with wetland plants (US EPA, 1993).

In these wetlands, wastewater streams are treated as they are fed slowly and flow beneath the ground surface, and pass through the roots-shoot-region of the macrophytes until they exit the system as effluents. Cooper (1993) reported that the depth of flow for in this type of wetlands normally ranges from 0.3 to 0.6 meters. The wetland depth is low since the roots and stems become smaller and fragile at high depths, and the efficiency of the treatment region becomes low when the depth of the wetland is less than 0.3 meters. According to Cooper (1993), constructed wetlands packed with gravel with uniform range of 3 mm to 10 mm have shown great treatment performance.

The beds of constructed wetlands normally are sealed on all sides with either clay or a plastic liner/membrane to prevent leakage. As the wastewater flows through the constructed wetland bed, it passes through different anoxic, aerobic, and anaerobic conditions, and the presence of macrophytes provides hydraulic pathway for wastewater (Cooper, 1993).

A SSF wetland combines aerobic, anoxic and anaerobic zones. Water purification, achieved through microbiological, physical a chemical processes, mainly takes place in the aerobic zone, which is situated in the rhizosphere. SSF wetlands have the primary benefit that water is not exposed during the treatment process, minimizing energy losses through evaporation and convection. This makes the SSF system more suitable for winter application (Wallace *et al.*, 2000). There are two basic types of SSF wetlands: horizontal flow (HF) and vertical flow (VF). Both allow water to flow through permeable, root-laced media, but some vertical flow systems combine an organic substrate with the permeable media. Large populations of bacteria and beneficial fungi live in the beds as biofilm attached to the media surfaces.

VF systems have removal mechanisms similar to those of HF systems but with completely different hydraulics. The advantages of SSF systems include increased treatment efficiencies, fewer pest problems, reduced risk of exposing humans or wildlife to toxics, decreased waterfowl use (advantageous near certain facilities such as airports), and increased accessibility for upkeep (no standing water). Subsurface-flow systems have the advantage of requiring less land area for water treatment, but are not generally as suitable for wildlife habitat as are surface-flow constructed wetlands. The substrate provides more surface area for bacterial biofilm growth over SF wetland, so increased treatment effectiveness may require smaller land areas. Saving land area is important at many installations and translates into reduced capital cost for projects requiring a land purchase. SSF wetlands are also better suited for cold weather climates since the earth insulates them more. Finally, many industrial waste streams, such as landfill leachate, can be treated in reed-bed systems with minimal ecological risk since an exposure pathway to hazardous substances does not exist for wildlife and most organisms (ITRC, 2003).

# 2.2.1.3. Horizontal-flow System

Horizontal flow (HF) systems (Figure 2) are designed in such a way that water flows in a horizontal direction with the inlet at one end and the outlet at the opposite end. The first full-scale horizontal flow system was built in 1974 in Othfresen in Germany (Vymazal, 2005). Vymazal (2005) reported that the early horizontal flow systems used predominantly heavy soils, often with high content of

clay. These systems had a very high treatment effect but because of low hydraulic permeability, clogging occurred shortly and the systems resembled more or less surface flow systems. Kikuth (1977) proposed the use of cohesive soils instead of sand or gravel; the vegetation of preference was Phragmites and the design flow path was horizontal through the soil media. The original concept as developed by Seidel included a series of beds composed of sand or gravel supporting emergent aquatic vegetation such as cattails (typha), bulrush (scirpus), and reeds (phragmites), with phragmites being the most commonly used.



Figure 2. Schematic representation of a standard planted constructed wetland with horizontal sub-surface flow (Vymazal, 2001). 1: inflow; 2: distribution zone filled with large stones; 3: impermeable layer; 4: aggregates (e.g. gravel, sand and crushed stones); 5: macrophytes; 6: outlet collector; 7: collection zone filled with large stones; 8: water level; 9: outflow.

#### 2.2.1.4. Vertical-flow System

Vertical-subsurface flow constructed wetlands (VFCWs) are attracting more and more attention due to their excellent oxygen transfer capacity and steadily high nutrient removal efficiency (Prochaska & Zouboulis, 2006). In fact, two kinds of the most frequent VFCWs, vertical upflow (VUF) and vertical downflow (VDF) CWs are able to provide both aerobic and anaerobic conditions at the same time. Vertical flow wetlands (Figure 3) originally developed by Seidel (1966) are above ground constructions either built of impermeable materials or lined with synthetic or clay materials to prevent seepage to the groundwater. In vertical subsurface flow system, the surface of the wetland floods to a depth of several centimeters then slowly percolates downwards through the granular media undergoing filtration and coming into contact with the dense microbial populations on the surface of the media particles and macrophytes roots. Vertical flow wetlands can be saturated with water or dried, thus enabling oxygen to be regenerated in all areas of the wetland which are usually flooded and anaerobic. Vertical flow systems are becoming more popular than the horizontal flow systems. The reason for growing interest in using vertical flow systems are (i) they

have much greater oxygen transfer capacity resulting in good nitrification, (ii) they are considerably smaller (1-2  $m^2/pe$ ) (pe means person equivalent (equal to one person living continuously in catchment area for wetland treatment)) than the HF system which need 5-10  $m^2/pe$  for secondary treatment, (iii) they can efficiently remove BOD5, COD and bacteria (Cooper, 1999, USEPA, 2000). In comparison, HF systems have tendency to become oxygen limited because wetland macrophytes have low oxygen rates. Therefore, the macrophytes cannot nitrify to high levels because of the difference low oxygen rate supply and the wastewater requirements (Kadlec, 2001).



Figure 3. Schematic representation of a standard planted constructed wetland with a vertical flow (Cooper et al., 1996)

#### 2.2.1.5. Up-flow Vertical System

Up-flow vertical constructed wetlands (Figure 4) are a new idea and their performance has only been studied in smaller scales. In addition, there is no literature available regarding their long termperformance (Kadlec, 2001). In these systems, the bed is packed with gravel with of a small diameter over a rock layer. The wastewater is fed at the bottom of the bed and flows vertically upwards through the bed until it reaches the outlet. The up-flow vertical constructed wetland have more equal root distribution and water-filter media contact and fewer problems of bad odour since they do not have a free water surface (Haberl *et al.*, 1995; Cooper, 1999). The up-flow vertical constructed wetlands were developed with the aim to treat wastewaters with high ammonia levels, higher than those in municipal wastewaters. A version of up-flow vertical constructed wetland is flooded with water to minimise oxygen transport into the body of the wetland and is used to create anaerobic, reducing conditions for sulphur management purposes and metals immobilisation. It can also be used for biosolids and sludge dewatering (Kadlec & Wallace, 2008).



Figure 4. Schematic representation of an up-flow vertical constructed wetland (Ong et al., 2009)

The vertically percolating water creates unsaturated, highly oxidised conditions. Consequentially high redox conditions favour aerobic processes with high biological BOD removal and nitrification and low denitrification compared to free water surface and horizontal subsurface flow (Li *et al.*, 2008). High nutrient content and oxygen rate both promote microbial growth with maximum density and activity in the first 5-10 cm of the filter material (Faulwetter *et al.*, 2009).

# 2.2.1.6. Un-vegetated Up-flow Vertical System

Since the major problem associated with the use of constructed wetlands in treating AMD is the suppressed growth of plants, un-planted up-flow vertical constructed wetlands were employed in this study to treat AMD. Unlike an adsorption column/bed where adsorption is the only removal mechanism that takes place, the un-vegetated up-flow vertical wetland employs other mechanism apart from adsorption such as precipitation, co-precipitation, and settling and sedimentation due to longer hydraulic retention time (HRT) involved (Figure 5). Plant contribution to oxygenation is considered negligible since the concentration is already very high. Plants are known to stabilize

substrates and limit channelized flow. However, in the case of un-vegetated constructed wetland, during the initial operation, any erosion and the channelling that develops should be eliminated by raking the substrate and filling by hand until thoroughly compacted.



Figure 5. Schematic representation of an un-vegetated up-flow vertical constructed wetland (Kamarudzaman *et al.*, 2011)

The length and depth of the wetland among other factors influence redox conditions in this type of CW. Oxidised and reduced zones are present, but overall the reduced environment prevails (Headley *et al.*, 2005). Redox potential increases with length due to progressive pollution degradation and mechanical filtration, and it decreases with depth, namely higher potential close to surface zone (5-20 cm) is a result of passive oxygen diffusion and plant oxygen release (Faulwetter *et al.*, 2009). However since there is vertical mixing of water present in the matrix, depth variation is not always present. The vertical redox profile varies with the CW length, being more pronounced at the outlet compared to the inlet. Shallower (0.27-0.5 m) CWs reportedly have higher redox potentials compared to deeper ones (0.5-1m) and so are more efficient in chemical oxygen demand (COD), biological oxygen demand (BOD), ammonium (NH<sub>3</sub>) and phosphorus (P) removal (Headley *et al.*, 2005). Therefore, the height of the up-flow vertical wetland must be kept low to avoid high pressure drop causing relatively high pumping costs (Kunii & Levenspiel, 1969).

Un-vegetated constructed wetlands have been used in many studies as control in order to investigate the metal up-take efficiency of macrophytes in constructed wetlands. Studies reported that macrophytes have a minor contribution in the remediation of metals, while other studies reported that macrophytes act as temporary storage of sites for the duration of the growing season, which could imply negative effects on water quality during plant senescence (St-Cyr Coats *et al.*, 1994; Mitsch and Wise, 1998; Sobolewski, 1999).

Yadav *et al.*, 2010 employed the up-flow vertical constructed wetland to remove chromium and nickel from aqueous solution. The maximum removal of chromium and nickel achieved was 98.3 and 62.2 %, respectively at initial concentrations of 10 mg/L and at a hydraulic retention time of 48 hrs. The lowest chromium and nickel removal achieved was 75.1 and 75.2%, respectively at initial concentration of 20 mg/L. The adsorption capacities of the filter media varied between 7 and 128 mg/kg for chromium and 10 and 89 mg/kg for nickel with varying initial concentration. Kamarudzaman *et al.*, 2011 also employed the up-flow constructed wetland to remove heavy metals from landfill leachate. The study revealed that there were slender differences in the removal efficiencies of heavy metals in the planted system and un-planted systems for a longer treatment period (99.2 and 91.5 %, respectively).

The unvegetated up-flow vertical constructed wetlands used in this study were very small compared to large-scale systems used in industry. However, previous findings based on similar column experiments proved that the results obtained were applicable in field scale and thus have been fully accepted by the scientific community (Omari *et al.*, 2003, Scholz, 2004).

## 2.2.2. Role of Fill Material in Constructed Wetlands

Soils consist of unconsolidated natural material that supports or is capable of supporting plant life. The upper limit contains air, and the lower limit is either bedrock or limit of biological activity (ITRC, 2003). Soils generally are divided into two different types - mineral and organic. Soils can be further categorized based on the amount of moisture present. Under wetland conditions, soils are considered hydric, which implies that it is saturated sufficiently during the growing season to develop anaerobic conditions in the upper portion of the soil. Hydric soils are developed under conditions sufficiently met to support vegetation typical to wet areas (hydrophytic vegetation). The physical and chemical characteristics of soils and other substrates are altered when they are flooded. In a saturated substrate, water replaces the atmospheric gases in the pore spaces and microbial metabolism consumes the available oxygen. Since oxygen is consumed more rapidly than it can be replaced by diffusion from the atmosphere, substrates become anoxic (without oxygen) (US EPA 2000). A mixture of sand and gravel is recommended to improve hydraulic condition and the removal of contaminants (IWA specialist group, 2000; Stottmeister *et al.*, 2003; Collins *et al.*, 2005). For vertical flow constructed wetland, a relatively small range of effective grain size of 0.06

to 0.1 mm was evaluated, while that for horizontal-flow system was found to be higher at 0.1 mm (Stottmeister *et al.*, 2003). The soil matrix has a decisive influence on the hydraulic processes (Stottmeister *et al.*, 2003).

A number of specialty media have been studied to access the possibility of increasing the adsorption capacity of filter media with different substrates. However, there has been contradictory view about the function of costly filter media in the treatment process of constructed wetlands. A study carried out by Scholz and Xu (2002) demonstrated that there was no additional benefit in using expensive adsorption media like granular activated carbon to enhance filtration performance of constructed wetlands. Wetland researchers have started to use industrial by-products like alum sludge (waterworks sludge), light weight aggregates and waste materials from industries, as well as natural materials with higher adsorption capacities (Zhu *et al.*, 2002; Babatunde & Zhao, 2007).

#### 2.2.3. Macrophytes in Wetlands

Most macrophytes play a role in maintaining oxidizing conditions by shoot-to-root oxygen transport (Armstrong, 1978). Such conditions promote the formation of iron oxides, hydroxides and oxyhydroxides, such as the iron-plaques, and consequently result in metal removal by adsorption and co-precipitation. Macrophytes, such as phragmites australis, promote sedimentation of suspended solids and prevent erosion by decreasing water flow rates by increasing the length per surface area of the hydraulic pathways through the system (Lee & Scholz, 2007). Despite the importance of macrophytes for contaminant removal, sediment is the main pollutant storage compartment (Maine *et al.*, 2009).

The performance of metals uptake by macrophytes in wetlands has been proven contradictory. Some authors have reported that macrophytes are effective for the removal of heavy metals by plant uptake (Mitsch & Wise, 1998; Sobolewski, 1999), while others have reported conflicting results (Fritioff & Greger, 2006; Vardanyan & Ingole, 2006). Furthermore, macrophytes are regarded as temporary storage medium for metal removal during the blooming season, and this can result in a poor effect on improving the quality of water as the plants grow old (St-Cyr Coats *et al.*, 1994). Fritioff & Greger (2007) reported opposite results in their study. They found that some macrophytes contained high concentrations of heavy metals in dead tissues. This was attributed to insignificant leakage of heavy metals when the plant decomposed and lack of organic matter in dead plant tissue.

Since it has been proved that grazing animals can be harmed by high-shoot-concentration, it is important to have more literature regarding the plant-roots-and-shoot metal concentration (Stoltz and Greger, 2002). In this study, no plants were vegetated in the construction wetlands since the heavy metal uptake by plants was negligible, and also because they pose potential harm for grazing animals.

#### 2.2.4. Microorganisms in Wetlands

Microorganisms provide a measurable amount of heavy metal uptake and storage; their metabolic processes play the most significant role in removal of heavy metals (Russell *et al.*, 2003; Hallberg & Johnson, 2005).

Sobolweski (1999) reported that removal of metals by microorganism to non-mobile forms can be achieved in wetlands. Heavy metals such as Cr and Fe are retained by microorganisms through accelerated biological processes. Several authors also reported effective removal of Cr from 39.9% to 85 % reduction to immobilized form by bacterial process (Adriano 2001; Nelson *et al.* 2002). The iron and sulphate reduction by microbial activity takes place naturally in sediments which promotes heavy metals removal by increasing the pH which leads to metals hydroxides and sulphides precipitates (Kalin, 2001; Russell *et al.*, 2003) as given in equation 4:

$$2CH_2O + SO^{2-}_4 \longrightarrow 2HCO_3 + S^{2-} + 2H^+$$
(4)

#### where: CH<sub>2</sub>O represents organic matter.

The dissolved sulphide ion precipitates metals as sulphides, reversing the reactions that occurred to produce AMD, such as:

$$Zn^{2+} + S^{2-} \longrightarrow ZnS$$
(5)

## 2.2.5. Hydraulic Retention Time

Hydraulic Retention Time (HRT) is one of the most crucial factors in designing and operating a constructed wetland and variable in determining the efficiency of settling solids, biochemical processes, and plant uptake (Kedlec & Knight, 1996). In some instances, nominal HRT is not necessarily indicative of the actual HRT because it is based on the assumption that the entire volume of water in the wetland is involved in the flow (Kadlec & Knight, 1996). This can generate

considerable errors in wetland HRT estimations when a relatively large volume of water remains stagnant without taking part in the flow movement. Under these circumstances, the actual HRT will tend to be shorter than the nominal HRT. One of the design consideration options could be the estimations of HRT with the assumption that the hydrodynamic processes occur under steady-state flow conditions. Existing wetlands are designed with a wide range of HRT, generally ranging from 2 to 20 days. However, wetlands with longer HRT will result in an increase of dissolved organic carbon leached from plant derived material (Pinney *et al.*, 2000). It is suggested that wetlands should have a minimum retention time of at least 10-15 hours to achieve a high level of removal efficiency (Ellis *et al.*, 2003). However, hydrodynamics (fluid dynamics) controls the retention time of a wetland and thus the time available for water quality enhancement to take place.

# 2.3. Heavy Metal Removal Mechanisms in Wetlands

## 2.3.1. Adsorption

In sediments heavy metals are adsorbed to the soil particles by electrostatic attraction or cation exchange (Patrick & Verloo 1998). Cation exchange is a phenomenon whereby positively charged ions physically attach to the surfaces of adsorbing soils and organic matter by Van der Waals forces. Once the heavy metals are adsorbed on the soils and organic matter, they remain as metals atoms. The metals species in wetland land may alter as the conditions of sediment change with time (Batty *et al.*, 2002; Wiebner *et al.*, 2005). Trace metals such as Zn, Fe, and Ni in acid mine drainage and metallurgical wastewater exist as cations. The adsorption capacity of soils for removal of heavy metals generally increases with different soils.

#### 2.3.2. Precipitation and Co-Precipitation

The most important adsorptive mechanisms in wetlands for heavy metals removal are precipitation and co-precipitation. Precipitation of metals hydroxides and sulphides take place under reducing environment. However, the undissolved cations precipitates limit the bioavailability of cations in wetlands. In wetlands co-precipitation of heavy metals takes place with secondary minerals. Coprecipitation of Ni, Mn, and Zn takes place in Fe oxides; Fe, Ni, Zn co-precipitate in Mn oxides; Fe, Ni, and Co co-precipitate in Ca carbonates; Ni, Co, Cr, Zn, Mn, Fe co-precipitate in soils minerals (Stumm & Morgan, 1981; Noller *et al.*, 1994). Since oxiferric hydroxide surface charge is negative in acidic environment and positive in basic conditions, the removal of oxyanions such as chromate, iron co-precipitations must take place under an acidic environment (Brix, 1993).

#### 2.3.3. Metal Carbonates

Metals may also form metal carbonates. Carbonates are less stable than sulphides; however they can contribute to initial trapping of metals (Sheoran & Sheoran, 2006). Carbonate precipitation is especially effective for the removal of Pb and Ni (Lin, 1995). According to Maine *et al.*, (2009) for the incoming wastewater composition containing high pH, carbonate and calcium concentrations favoures the metal retention in the sediment. Calcium carbonate precipitation represents an important pathway governed by the incoming water pH, and metals are adsorbed to carbonates.

#### 2.3.4. Metal Sulphides

The growth of sulphate reducing bacteria in anaerobic environment is achieved by using appropriate substrate in wetlands. Since AMD is sulphates rich, these bacterial are able to produce hydrogen sulphide. Hydrogen sulphide then reacts with most heavy metals to form extremely insoluble metal sulphides (Stumm & Morgan, 1981):

$$2CH_2O + SO^{2-}_4 \longrightarrow H_2S + 2HCO_2 \tag{6}$$

where CH<sub>2</sub>O represents organic matter.

Bacterial sulfate reduction results in the precipitation of dissolved metals as metal sulfide solids:

$$M^{2+} + H_2S + 2HCO_3 \longrightarrow MS + 2H_2O + 2CO_3$$
(7)

where M represents metals. For Fe, pyrite formation is also possible:

$$Fe^{2+} + H_2S + S_0 \longrightarrow FeS_2 + 2H^+$$
(8)

Water quality improves when the mineral acidity decreases as a result of metal sulphides precipitation in an organic substrate without increasing proton acidity. The H<sub>2</sub>S dissociation (into  $2H^+$  and S<sub>2</sub>) releases protons, which are neutralized by HCO<sub>3</sub> released through the reduction of sulphates. The sulphate reduction acid mine drainage treatment is strongly influenced by the wetland substrate (Groudev *et al.*, 1999; Gibert *et al.*, 2004).

Several authors have reported on the sulphide minerals in constructed wetland sediments (Schiffer 1989; Sobolewski, 1999; DeBusk & DeBusk, 2000). ITRC, 2003 reported that heavy Zn reacts with hydrogen sulphide to form insoluble zinc sulphides. Collins et al. (2004) achieved the highest metal removal of 99- 99% Al, Fe and Zn to be 93–99%. Zinc and Cu were completely removed due to the formation of sulphide. Mungur et al. (1997) employed a laboratory scale constructed wetland to treat Cu and Zn. The highest metal removal was achieved Cu (82 - 92%), Pb (76 - 9%), and Zn (83 - 90%). Hawkins et al., (1997) Contradictory results were reported. The highest metal removal achieved in their study was Cu (33%), Pb (79%), Zn (85%). The removal of heavy metals in constructed wetlands by cation exchange onto the soils and organic matter is an important process during the early days after commissioning of the constructed wetland, and sulphide precipitation is the dominant process for heavy metals removal in constructed wetland over time (Machemer and Wildeman, 1992; Murray-Gulde et al. 2005).

#### 2.3.5. Settling and Sedimentation

The removal of heavy metals in acid mine drainage by settling and sedimentation in constructed wetlands is achieved with association of particulate matter (ITRC, 2003). Different alteration of heavy metals may occur in wetlands regardless whether the water is still or flowing (Johnston, 1993; Matagi *et al.*, 1998). Heavy metals can be removed from the wastewater to the soils or organic matter. Heavy metals can be removed efficiently and retained from AMD by constructed wetlands. When the water is still, the particles which are denser than the water will settle out. The effective removal of suspended solids is relative to the length of wetland and settling velocity of the particle (Johnston, 1993). The particles less dense or lighter than water can only settle out after flock-formation has occurred. In wetlands, flocks tend to settle faster than separate particles. Flocks can also settle with heavy metals and other suspended solids.

Flocculation in wetlands is affected by conditions such as alkaline conditions, strength of ions, and concentration of particles in suspension and algal (Matagi et al., 1998). Sedimentation in natural and constructed wetlands has been regarded for a long time as an important removal mechanism of heavy metals. However, for sedimentation to occur, mechanism such as precipitation and co-precipitation must take place first.

#### 2.4. Constructed Wetlands Performance

The performance of wetlands over long period of time has been reported by several authors (Beining and Otte, 1996; Heal and Salt, 1999; Woulds and Ngwenya, 2004). The performance of natural wetland unattended for more than a century treating Pb and Zn mine drainage was studied by Beining and Otte (1996). The effectiveness of wetlands treating acid mine discharge critically depends in the growth and sustained performance of appropriate microbes in compost-based wetlands. Therefore, the compost-based wetlands effectiveness for AMD significantly differs.

The performance of typha latiflolia compost wetland treating pyrite mine discharge was evaluated by Heal and Salt (1999). They reported removal efficiency of 20 - 40% for Fe, Mn, and Al under acidic conditions with the removal rate of 0.8 grams per square meter per day. These poor results were attributed to slow rates of metals oxidation and precipitation under extremely low pH. Woulds and Ngwenya (2004) later assessed the same compost wetland performance focusing on the sulphate bacterial reduction, however they also reported similar poor treatment of heavy metals removal due to high concentrations and acidic pH. At pH of 4-6, the removal efficiency of compost wetlands have been reported to be excellent. It has been reported that wetlands treating AMD treated Fe (55 – 92%), and below detection for Cr, Cd, and Zn. Therefore the performance of wetlands for heavy metals removal is rather unpredictable.

Since the macrophytes in the constructed wetlands act only as temporary metal storage and pose a health risk to the grazing animals, it was proposed in this study that a natural zeolite be employed as a low cost and effective adsorbent in the un-vegetated constructed wetland in order to improve the performance efficiency of the wetland.

#### 2.5. Application of Natural Zeolite in the Constructed Wetland

In order to improve CW performance, natural zeolites have been proposed to be utilized in CWs. The use of natural zeolites in environmental applications is increasing due to their properties and significant worldwide occurrence. Use of natural zeolites is attractive from the economic point of view, due to their availability in many countries and their relative low cost (Pansini, 1996). Clinoptilolite is the most common and abundant natural zeolite, because of its worldwide spread and its large deposits. It has high content in silicon, and its chemical formula depends on its composition and origin. The particle size varies between 25 and 100 nm, while its pores can reach 500 nm (Kowalczyk *et al.*, 2006). Despite the great interest in ion exchange with natural zeolite, there is very little literature published on the influence of competing cations on the removal of

certain heavy metals from mixed solutions by natural zeolite. The primary application of clinoptilolite have to do with its use as a substrate inside the wetlands (Sakadevan & Bavor, 1998).

Although the performance of the constructed wetland might be improved by employment of low cost effective adsorbents, the total removal of heavy metals such as hexavalent chromium achievement cannot be guaranteed. Therefore it is proposed that photocatalysis be employed to reduce toxic hexavalent chromium present in the constructed wetland acid mine drainage effluent in to less toxic trivalent chromium.

## 2.6. Photocatalysis

Photocatalysis involves capturing of photons by a semiconductor such as titanium dioxide (TiO<sub>2</sub>), resulting in the creation of electrons and positive holes and subsequent redox reactions. More specifically, the void energy region where no electron states can exist in a semiconductor is called the band gap. The band gap also refers to the energy difference between the top of the filled valence band and the bottom of the vacant conduction band (Linsebigler *et al.*, 1995). When a semiconductor is exposed to photon, the electron present in the valence band gap energy of the conduction band provided the photon energy (hv) equals or exceeds the band gap energy of the semiconductor/photocatalyst. As the result, an electron vacancy or a positive charge called a hole ( $h^+$ ) is generated in the valence band (Kabra *et al.*, 2004).

Ultimately, the process creates a reaction between the activated electrons or the generated holes and the chemicals adsorbed on the surface of the semiconductor. Generally, the hole oxidizes water to hydroxyl radicals which subsequently initiate a chain of reactions leading to the oxidation of organics. Similarly, the electron can be donated to an electron acceptor such as a metal ion (with a reduction potential more positive than the band gap of the photocatalyst). This metal ion can be reduced to its lower valence states and deposited on the surface of the photocatalyst/semiconductor (Kabra *et al.* 2004). The recombination of the electron and the hole must be prevented as much as possible to increase the photocatalytic reaction efficiency. Among the semiconductors capable of photocatalysis, titanium dioxide (TiO<sub>2</sub>) is the most widely used because it is photostable, chemically stable, photoactive, relatively inexpensive, and non-toxic.

# 2.6.1. Mechanism of UV Photocatalysis

The mechanism of UV photocatalysis involves the generation of valence band (VB) holes ( $h^+_{VB}$ ) and conduction band (CB) electrons ( $e^-_{CB}$ ), when a semiconductor photocatalyst absorbs light

photon of energy greater than or equal to its band gap ( $hv \ge EBG$ ). The holes mediate the oxidation of organic compounds by the formation of hydroxyl radicals, and the electrons mediate reduction and oxidation reactions by the formation of superoxide radicals. A pictorial representation of the mechanism of TiO<sub>2</sub> photocatalysis is shown in Figure 6. The following steps provide a detailed mechanism of photocatalytic degradation of organic compounds, which is well documented (Bhatkhande *et al.*, 2001; Kabra *et al.*, 2004). While TiO<sub>2</sub> has been used as the semiconductor photocatalyst for the sake of representation, most of the following reactions are applicable for other semiconductor photocatalysts as well.

Charge carrier generation:

$TiO_2 + hv$ $hv > EBG$ $h^+v_B + e^-c_B$	(9)
Charge carrier trapping:	
$Ti^{IV} - OH^- + h^+_{VB} \longrightarrow Ti^{IV} - OH^{\bullet}$	(10)
Surface trap:	
$Ti^{IV} - OH^- + e^{CB} \iff Ti^{III} - OH^-$	
(11)	
Deep trap: $Ti^{IV} + e^{CB} \longrightarrow Ti^{III}$	(12)
Electron-hole recombination:	
Free electron with a trapped hole:	
$Ti^{IV} - OH^{\bullet} + e^{-}_{CB} \longrightarrow Ti^{IV}OH^{-}$	(13)
Free hole with a trapped electron:	
$Ti^{III} + h^+_{VB} \longrightarrow Ti^{IV}$	(14)
Free hole with a free electron:	
$h^+_{VB} + e^{CB} \longrightarrow heat.$	(15)
Generation of hydroxyl radicals in the aqueous medium:	
hole pathway:	
$Ti^{IV} - H_2O + h^+_{VB} \longrightarrow Ti^{IV} - OH^+ + H^+$ .	(16)
Electron pathway:	
$Ti^{III} + O_2  \longleftarrow  Ti^{III} - O_2^- \bullet$	(17)
$Ti^{IV} - O^{-}_{2} + 2H^{+} + e^{-}_{CB} \iff Ti^{IV} - H_2O_2$	(18)
$Ti^{IV} - O^{-\bullet}_2 + H^+ \longleftarrow Ti^{IV} - HO^{\bullet}_2$	(19)
$Ti^{IV} - 2HO_2 \cdot \longrightarrow Ti^{IV} - H_2O_2 + O_2$	(20)
$Ti^{IV} - H_2O_2 + e^{CB} \longrightarrow Ti^{IV} - OH^{\bullet} + OH^-$	(21)
$Ti^{IV} - H_2O_2 + O^{-\bullet}_2 \longrightarrow Ti^{IV} - OH^{\bullet} + OH^{-} + O_2.$	(22)

Adsorption–Desorption of a reductant (any organic substrate S):

$$Ti^{IV} + S \iff Ti^{IV} - S$$
(23)  

$$Ti^{IV} - OH^{\bullet} + S \iff Ti^{IV} - OH^{\bullet} - S.$$
(24)  
Adsorption-Desorption of an oxidant (eg. metal ion):  

$$Ti^{IV} + Mn^{+} \longrightarrow Ti^{IV} - Mn^{+}.$$
(25)  
Photooxidation of a reductant:  
Direct hole attack:  

$$Ti^{IV} - S + Ti^{IV} (h^{+}_{VB}) \longrightarrow Ti^{IV} + Ti^{IV} - I \longrightarrow CO_{2} + H_{2}O.$$
(26)  
Photoreduction of a metal ion:  

$$Ti^{IV} - Mn^{+} + me^{-} \longrightarrow Ti^{IV} - M^{(n-m)+}.$$
(27)

In all the above reactions, Ti<sup>IV</sup> denotes the four coordinated surface functionality of TiO<sub>2</sub> or the "active site". Hoffmann et al., (1995) have found by laser flash photolysis studies that the characteristic time scale for the generation of charge carriers is of the order of femto seconds (fs). The charge carriers thus generated gets trapped to the  $TiO_2$  surface, which occurs over a time scale of tens of nano seconds (ns). Reaction (10) represents the trapping of the holes by the surface hydroxyl groups present in TiO<sub>2</sub>, and reactions (11) and (12) represent the reversible trapping of the electrons in the surface of TiO<sub>2</sub> (shallow traps), and the irreversible trapping or relaxation of the electrons to the bottom of the CB (deep traps), respectively. Reactions (13) - (15) represent the electron-hole recombination reaction, which occurs at surface states of the TiO<sub>2</sub>, or in the bulk medium due to the delocalization of the electrons and holes. This is one of the detrimental reactions in photocatalysis as this affects the interfacial charge transfer processes and hence the quantum efficiency of the photoprocess. Reaction (16) represents the generation of hydroxyl radicals (OH) by the reaction of surface adsorbed water molecules with the holes, and reactions (17) - (22) shows the formation of superoxide  $(O^{-2})$ , hydroperoxy (HOO<sup>•</sup>) and hydroxyl species through the electron pathway. All the above radical species are referred to as the "active species". When the reactions are carried out in non-aqueous (organic) medium, the surface bound hydroxyl species present in the semiconductor plays a major role (reaction (10)), and the contribution of reactions (16) - (22) for the overall oxidation of the substrate is negligible.

Once the active species are generated, the reactants are adsorbed onto the surface of the photocatalyst (reactions (23) - (25)). This is followed by the oxidation of the reductant and the concomitant reduction of the oxidant by the attack of the hydroxyl radicals and CB electrons, respectively (reaction (26)). Metal ions are reduced to their thermodynamically stable oxidations

states by the CB electrons (reaction (27)). Similarly, when organic compounds are present in the system, they degrade through the formation of intermediates (I), which transform finally to  $CO_2$  and  $H_2O$ . Therefore, the overall photocatalysis reaction can be depicted as follows, wherein, the oxidants are reduced and the reductants are oxidized by the action of UV radiation on the semiconductor photocatalyst

$$(Ox_1)_{ads} + (Red_2)_{ads} \xrightarrow{hv/TiO2} Red_1 + Ox_2$$
(28)

#### 2.6.2. Photocatalyst

A photocatalyst is defined as a substance that is activated by the absorption of a photon and helps to accelerate a reaction, without being consumed. The Titanium dioxide  $TiO_2$  owing to its special properties is the most frequently used photocatalyst in water and air purification processes. It shows the highest photocatalytic activity and resistance to so-called anodic photo corrosion. However, the present drawbacks for  $TiO_2$  photocatalysis in the treatment of wastewater include: (1) the difficulty of separating the fine semiconductor photocatalyst from treated water; (2) the rapid unfavourable charge carrier recombination reaction in  $TiO_2$  compared with the redox reactions resulting in low quantum yield; and (3) the high band gap energy which limits its application from using solar energy (Figure 6).



Figure 6. Mechanism of photocatalysis in the presence of UV irradiation
## 2.7. Titanium Dioxide (TiO<sub>2</sub>) Nano Materials

Titanium dioxide (TiO<sub>2</sub>) with anatase crystal structure is used as a photocatalyst in a wide variety of applications because of its superior material and economic properties (Linsebigler *et al*, 1995; Fujishima *et al.*, 2002). Since the structure and the crystalline state strongly affect the photocatalytic activity and selectivity, proper control of the morphology of nanostructured TiO<sub>2</sub> materials plays an important role (Zhang *et al.*, 2002; Cozzoli *et al.*, 2003). A considerable variety of nanostructured TiO<sub>2</sub> materials with different morphologies have been successfully synthesized, including nanowires, nanorods, nanotubes, nanowhiskers, microspheres, foams and films (Nakashima & Kimizuka, 2003). Among various morphologies, the design and fabrication of spherical materials with hollow interiors have attracted considerable attention recently because of their potential applications as low density capsules for controlled release of drugs, dyes and inks, development of artificial cells, protection of proteins, enzymes, and especially as photocatalysts as well for supports as catalysts (Yang *et al.*, 2003). Both the excellent photocatalytic ability of these hollow spheres photocatalyst and its much easier separation from the reaction mixture make them a promising candidate in further fundamental studies and industrial applications.

### 2.8. Core-Void-Shell Ti<sub>2</sub>O Synthesis

In recent years, a great number of processes have been developed to synthesize hollow spheres with a desired property profile. These processes can be classified into nozzle-reactor systems (spray processes) and template sacrificial methods. An overview on the methods and the processes leading to the formation of hollow spheres is given in Figure 7.



Figure 7. Different synthesis routes for hollow spheres (Roy et al., 2005)

In the nozzle-reactor systems, the solid formation occurs as a result of the reaction of the dissolved wall material with a second component in the gas flow. After the formation of the droplets the wall formation occurs by vaporization of the solvent or by chemical reaction of the wall material with a second component in the surrounding gas phase (Bruinsma *et al.*, 1997; Roy *et al.*, 2005). The first is used in spray drying and spray pyrolysis while the latter is used in reactive spry drying. In spray drying and spray pyrolysis the solubility of the wall material is exceeded due to the vaporization of the solvent and the material is precipitated or crystallized in the droplet. In spray pyrolysis in contrast to spray drying the temperature of the gas is much higher so that after precipitation of the wall material all the organics are burned and pure inorganic spheres remain.

Major advantages of the nozzle processes are the high throughput combined with the low costs of the processes. However, on the other hand there are also limitations of the processes. One disadvantage is that there is only a limited number of wall materials which can be prepared as solution or colloidal dispersion, preferably in water to avoid safety issues related to organic solvents. Another point is that the size of the hollow spheres is based on the droplet distribution generated by the nozzle and thus very broad particle size distributions are generated. Although smaller size distributions or even unimodal sizes of particles can be generated when capillaries instead of nozzles are used in consequence this leads to low throughputs due to the formation of the discrete particles (Roy *et al.*, 2005).

In the template sacrificial methods the formation of hollow spheres occurs in a liquid medium in which soft templates (droplets, gas bubbles or vesicles) or hard templates (particles) are coated with the desired wall material. In a second step after separating the particles from the solution the template material is removed by drying or extraction in case of the soft templates and by calcination or chemical etching in case of the solid cores leaving back shell of the wall material. Although template methods are arguably the most effective and certainly the most common means of synthesizing hollow inorganic spheres on the micro and nano scales, some inherent disadvantages have proven very difficult to overcome. For example, in most hard template-based methods, removal of the template by either thermal or chemical means is very complicated and energy consuming. In soft template-based methods, the morphology and monodispersity of the hollow spheres are very difficult to control (Strohm & Lobmann, 2004). Therefore, a template-free method for direct synthesis of core-void-shell photocatalyst is preferred in practical applications due to the ease of handling and scaling up (Liu *et al.*, 2009).

### 2.9. Template Free Method

In the present study, anatase core-void-shell TiO<sub>2</sub> was synthesized by hydro-alcohol thermal method which has been applied to synthesize nanosized materials already (Chen *et al.*, 1995; Kominami *et al.*, 1998), since products prepared by this method have well-crystalline phase, which benefits to thermal stability of the nanosized materials (Zhu *et al.*, 2004). Hydro-alcohol thermal synthesis normally is conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature or pressure with the reaction in aqueous solutions. The temperature can be elevated above the boiling point of water, reaching the pressure of vapour saturation. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced. It is a method that is widely used for the production of small particles in the ceramics industry. TiO<sub>2</sub> nanoparticles can be obtained by hydrothermal treatment of peptized precipitates of a titanium precursor with water (Luo *et al.*, 2013).

The basic principle of the hydro-alcohol thermal process is that the larger crystals grow from those of smaller size, which have higher solubility than the larger ones. Within a colloidal aggregate, smaller, less crystallized, or less dense crystallites will dissolve into the liquid phase as a nutrient supply for the growth of larger, better crystallized, or denser ones. When the crystals grow in

solution, the concentration of growth units varies across the mother solution, due to the size difference of resultant nanocrystals (Yan *et al.*, 2007; Xu *et al.*, 2008). With the driving force of the minimization of surface energy, metastable nanoparticle aggregates occur first due to the reduction of supersaturation in solution. Once the particles with different sizes are attached to each other, the large particles begin to grow, drawing from smaller ones. Voids gradually form and grow in the cores of large aggregates, and the shell thickness increases owing to the outward diffusion of solutes through the permeable shell (Liu *et al.*, 2009).

## Chapter 3

### **3.** Methodology

Constructed wetlands and photocatalysis processes were employed to treat acid mine drainage. Three identical unvegetated upflow constructed wetlands were employed as a pre-treatment process and photocatalysis as a post-treatment. Natural zeolite (clinoptilolite) and coarse silica sand were employed as CW packing materials. Core-void-shell TiO<sub>2</sub> photocatalyst was prepared from the hydro-alcohol thermal method. Both the CW packing material and photocatalyst morphologies were characterized. Batch studies were conducted to determine the effect of operating parameters on the treatment efficiencies of both processes. All the experiments were carried out at Mintek, RSA.

### 3.1. Constructed Wetland

Three identical laboratory scale unvegetated up-flow vertical constructed wetlands were constructed using cylindrical plastic pipes of internal diameter and the length of 14 cm and 50 cm respectively (Yadav *et al.*, 2010; Kamarudzaman *et al.*, 2011). An impermeable film was placed at the bottom and sides of the columns. Each CW was divided into two compartments. Three CW were layered with sand (5-8 mm) in the first compartment and clinoptilolite (2-5 mm) in the second compartment as a main adsorbent (Figure 8). This kind of configuration was chosen in order to maximise the removal efficiency of the constructed wetlands based on the efficient wetting of packing materials. Also, the wetlands were well compacted in order to avoid channelling. The wetlands were constructed at Mintek, RSA.



Figure 8. Constructed Wetland setup: (1) AMD influent; (2) Peristaltic pump; (3) ball valve; (4) coarse silica sand bed; (5) clinoptilolite bed; (6) ball valve; (7) AMD effluent

### 3.1.1. Materials

The AMD samples were collected in August 2013 at Mpumalanga, South Africa. The surface water sample was taken from an open pit in the mining area at different depth levels. Three 100 L polypropylene drums were used to store the samples (collected from three locations), which is in accordance with the commonly accepted sampling procedures (Hermond & Fechner-Levy, 2000). Filtration of the sample was carried out in the laboratory using a portable vacuum filter and a 0.45  $\mu$ m Millipore filter. A 250 ml of each sample was taken for characterization of toxic heavy metals and sulphates, and the rest of the sample was stored in a cool place.

### 3.1.2. Experimental Procedure

Three un-vegetated constructed wetlands were packed with sand (h = 23 cm) in the first compartment and natural zeolite (h = 23 cm) in the second compartment. The influent was pumped into the wetlands using a peristaltic pump through a PVC tube to produce a laminar flow, and hydraulic retention time (HRT) was carefully determined. The wastewater samples (250 ml) were collected at the inlet and outlet of each CW for a month. To determine the total concentration of the heavy metals and sulphate, concentrations in the wastewater, the atomic absorption spectrometer and ion chromatograph were employed. Samples (100 g each) were taken at the inlet and the outlet at the end of the experiment for analysis. The pH measurements were taken at the inlet, and outlet using a pH meter. The substrates samples were dried in an oven until constant weights were reached and ground using mortar and pestle. Subsequently, they were sieved through a 53 µm sieve and then wet digested in concentrated HNO<sub>3</sub> for 24 hours to obtain the total fraction, and atomic absorption spectrophotometer was used to analyse the metal concentrations in sediments.

#### 3.2. Photocatalysis

The anatase core-void-shell  $TiO_2$  photocatalyst was synthesized and its performance was compared to that of P25  $TiO_2$  for photocatalytic reduction of Cr(VI) present in the CW effluent. All experiments were conducted at Mintek, RSA.

### 3.2.1. Photocatalytic Reactor

A laboratory scale slurry photocatalytic recycle reactor with an inner diameter of 40 mm and height of 340 mm was fabricated using a quartz material. The reactor contained an inlet on one end and an outlet on the other end (both with inlet diameters of 25 mm), and it was operated as a recycle reactor. The reactor was placed inside a shading box with 12 UV lamps (8W x 4; 6W x 4; 4W x 4W) installed on the inside walls (see Appendix B). The lamps were mounted 1 - 2 cm apart from each other, and the distance between the lamps and the reactor was 4 cm. A peristaltic pump was employed to circulate the wastewater inside the reactor (Figure 9).



Figure 9. Slurry photocatalytic reactor: (1) Constructed wetland effluent; (2) Peristaltic pump; (3) Photocatalytic reactor; (4) Shading box; (5) UV lamps

### 3.2.2. Synthesis of Core-Void-Shell TiO<sub>2</sub> Photocatalyst

A TiO<sub>2</sub> core-void-shell catalyst was synthesized from the hydro-alcohol thermal method in which 17 g of ammonium sulphate,  $(NH_4)_2SO_4$  and urea, 138 g of  $CO(NH_2)_2$  were dissolved in 75 ml of deionized water. A 17 g of titania butoxide dissolved in 67 ml of ethanol was added to the above mixture. After stirring for 2 hrs, the mixture was heated to 95°C for 4 hrs, and then allowed to cool to ambient temperature. The resulting slurry was filtered and washed twice with distilled water, and subsequently washed three times with absolute ethanol. The precipitates were dried overnight at 120°C, followed by calcination in flowing air at 500°C for 4 hrs to get an accurate phase transition.

### 3.2.3. Experimental Procedure

The photocatalytic reduction of Cr(VI) was carried out in the TiO<sub>2</sub> suspension under UV irradiation (Figure 10). The reaction suspensions were prepared by adding 2 g of the photocatalyst to 250 ml of aqueous Cr(VI) solution with initial concentration of 30 mg/L. Prior to the photo-reduction, the suspension was magnetically stirred in the dark for 1 hour to establish the adsorption/desorption equilibrium condition. After one hour of dark adsorption, the aqueous suspension containing Cr(VI) and the photocatalyst was then irradiated by the UV with constant stirring using 125W high pressure UVC light. Photocatalytic reduction experiments were run for 5 hrs with samples taken in 60 min intervals, and immediately centrifuged for 10 min, followed by filtering through a 0.45  $\mu$ m Millipore filter to remove any traces of solid particles. Subsequently, the Cr(VI) content was analyzed qualitatively by measuring the absorption band at 360 nm using the Hitachi-U-200 UV-vis spectrophotometer (Colon *et al.*, 2002; Rengaraj *et al.*, 2007). After obtaining the best operating parameters, real acid mine drainage samples were treated using a slurry photocatalytic reactor. Samples were taken at time intervals during the photocatalysis treatment. The reduction of Cr(VI) in the wastewater was determined by employing UV-vis spectrophotometer.



Figure 10. Batch experiment set-up for photocatalytic reduction of Cr(VI). 1- UVC bulb; 2- Glass beaker with Cr(VI) solution with TiO<sub>2</sub> suspension; 3-Stirrer bar; 4-Magnetic stirrer

## 3.3. Experimental Design

#### 3.3.1. CW treatment

A one-factor-at-time experimental design was employed for this experiment. HRT and initial concentration are the parameters that were under investigation. Table 2 shows the variation of the parameters under investigation.

Table 2. Variation of parameters for CW treatment

Parameters	Variation
HRT (days)	3 - 5
Cr(VI) mg/l	200-1000

This type of experimental design was chosen because the real wastewater was employed and the treatment process is based on the manipulation of the natural process in order to observe whether the desired goals (specific objectives) can be achieved. Therefore three constructed wetlands containing natural zeolite were fed with acid mine drainage of different Cr(VI) concentrations and operated at different hydraulic retention time. This arrangement assisted in identifying the optimum initial Cr(VI) concentration and hydraulic retention time at which the performance of CWs was best.

### 3.3.2. Photocatalysis:

One-factor-at-time experimental design was employed for this experiment. The initial concentration Co, pH, HRT, and catalyst loading are the parameters that were under investigation. Table 3 shows the variation of the parameters under investigation.

Parameters	Variation	
Cr (VI) mg/l	30 - 50	
pH	2 - 10	
HRT (hrs)	1 - 5	
Catalyst loading (g)	1-5	

Table 3. Variation of parameters for photocatalysis

### 3.4. Data Analysis

The percentage removal (R<sub>0</sub>) of metals from water passing through the wetlands was calculated as:

$$R_{o} = \underline{[Me]_{in} - [Me]_{out}} \times 100$$

$$[Me]_{in}$$
(29)

where [Me]<sub>in</sub> refers to the metal concentration in water flowing into the wetlands and [Me]<sub>out</sub> refers to the metal concentration in water flowing out of the wetlands.

The percentage reduction of (R<sub>o</sub>) of Cr(VI) photocatalytic reduction was calculated as:

$$R_{o} = \frac{C_{o} - C}{C_{o}} \times 100 \tag{30}$$

where  $C_0$  is the initial concentration of metals in the wastewater, and C is the final concentration of metals in the wastewater.

### 3.5. Characterization and Analytical Techniques

Characterization was done using, Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry (SEM-EDX), Transmission Electron Microscopy (TEM), X-ray powder Diffraction spectroscopy (XRD), Brunauer–Emmett–Teller surface area analysis (BET). Atomic Absorption Spectrophotometer (AAS), UV-*vis* Spectrophotometer, and Direct Reading Spectrophotometer were used to analyse the concentrations of heavy metals and sulphates present in the acid mine drainage.

The SEM-EDX analysis for the constructed wetland packing material and photocatalyst were obtained using FEI NOVA NANOSEM 200. The samples were deposited on a sample holder with a piece of adhesive carbon tape in order to make them conductive, and then inserted in the SEM.

TEM images of the synthesized photocatalyst were obtained using the LEO 912 OMEGA TEM, operating at 120 kV, and a Proscan CCD camera and image analysis was done using the Soft Image System (SIS) software. The sample was firstly prepared by depositing it in the copper grid and coated with carbon. Then it was inserted in the TEM for analysis.

The crystalline phases of the TiO<sub>2</sub> photocatalyst were analyzed by XRD (Bruker AXS D8 advance). XRD patterns of both photocatalyst ( $2\theta$  ranges from 20 to 70°) were recorded at room temperature with scanning speed of 2° min<sup>-1</sup> using Co K  $\alpha$  radiation ( $\lambda = 1.8$  nm) from a 40 kV X-ray source and diffracted beam monochromator, operated at 35 mA. The samples were deposited into sample holder, and then placed on the sample collector.

Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to obtain the BET surface areas of the constructed wetland packing material and the synthesized photocatalyst. The Surface Area values were measured via low-temperature (LN<sub>2</sub> temperature) isothermal adsorptiondesorption of N<sub>2</sub>. Before the SSA measurements, 0.1g of the sample material was evacuated at 623 K for 3 hr in order to remove water,  $CO_2$  and hydrocarbons from the pores inside the sample. After the degassing is completed, the net mass loss of the sample was measured for the Surface Area calculations.

Atomic Absorption Spectrophotometer (210VGP) was employed to analyse the concentration of the heavy metals present in the acid mine drainage. The spectrophotometer was firstly calibrated using appropriate standards solution. The samples were diluted up to low concentrations before they were analysed.

HACH DR/2000 Direct Reading Spectrophotometer (Method 680) was used to determine the sulphate concentrations at 450 nm. The sulphate reagent powder pillow was added to the diluted sample. After 5 min the cuvette was inserted into the spectrophotometer, and the concentration was measured in mg/L.

Hitachi-U-200 UV-vis spectrophotometer was used to measure the absorbance of Cr(VI) at 360 nm (Colon *et al.*, 2002; Rengaraj *et al.*, 2007) and Fe (III) at 260 nm (Penich & Raut, 2006). Samples were transferred directly to a 1cm path-length quarts cell, and inserted into the UV-vis spectrophotometer for absorbance measurements.

# Chapter 4

## 4. Results and Discussion

## 4.1. Constructed Wetland Packing Material Characterization

Morphological observation of clinoptilolite and silica were performed using a scanning electron microscopy (SEM). The analysis showed the surface of the adsorbents was rough and porous, and the structure was compact and presented clearly alveolate holes. Figure 11 shows the SEM analysis of clinoptilolite, and silica respectively.



Figure 11. SEM Images of (a) Clinoptilolite, (b) Silica

The energy-dispersive x-ray spectroscopy (EDX) analysis was performed for clinoptilolite and silica respectively. A chemical analysis of the adsorbents obtained at 90 nm magnification is presented in Table 4. This study showed that the natural zeolite contained a complement of exchangeable sodium, potassium, and calcium which can be replaced with heavy metals. The adsorption capabilities of zeolite result from a net negative charge on the structure of fine-grain silicate minerals. This negative charge is neutralized by the adsorption of positively charged species, giving clinoptilolite the ability to attract and hold cations such as heavy metals. The large surface area of clinoptilolite also contributes to the high adsorption capacity (Cadena *et al.*, 1990). Silica chemical analysis showed that it contains no exchangeable ions (such as sodium, potassium, calcium) for cation exchange process to take place. Therefore the large surface area of silica is what contributes to high adsorption capacity. Table 5 shows the BET surface area and distribution of pore width of the constructed wetland packing materials.

Clinoptilolite(wt.%)	Silica sand(wt.%)
47.83	54.51
7.23	0.72
38.77	44.77
1.65	-
0.91	-
1.56	-
1.66	-
0.39	-
	Clinoptilolite(wt.%) 47.83 7.23 38.77 1.65 0.91 1.56 1.66 0.39

Table 4. CW packing materials EDX analysis

Table 5. BET surface area of CW packing material

	Clinoptilolite	Coarse Sand
Surface area $(m^2/g)$	36.7	351
Average pore (nm)	7.3	48
Particle size (mm)	2 - 5	5 - 8

### 4.1.2. Photocatalyst Characterization

### 4.1.2.1. XRD Analysis

XRD was used to investigate the crystal structure of TiO<sub>2</sub>, which depends on the calcinations temperature. The as-prepared sample appeared to be amorphous since no peaks could be identified (Figure 12(a)). Figure 12(b) shows the XRD patterns of core-void-shell calcined in air at 500 °C for 4hrs. The peaks were identified at 29.5°, 44.2°, 56.5°, 63.6°, 65°, 74°, 82°, and 84° which suggested that the sample was 100% anatase phase by employing the phase representation method (search/match from the EVA library database). Guo *et al.*, (2013) reported peaks similar to the ones found in this study.



Figure 12. XRD characterization of core void-shell TiO<sub>2</sub>: (a) as-prepared; (b) calcined in air at 500 °C for 4hrs.

### 4.1.2.2. BET Surface Area Analysis

The specific surface areas of P25, as-prepared core-void-shell TiO<sub>2</sub> and calcined samples were measured using the BET method of N<sub>2</sub> adsorption and desorption at 75 K. The BET surface areas of both the as-prepared sample, calcined sample, and the P25 Degussa were 513, 73, and 49 m<sup>2</sup>/g respectively. These results revealed that the synthesized core-void-shell TiO<sub>2</sub> particles had a greater surface area than the commercial P25 Degussa. Liu *et al.*, (2009) reported a surface area of the as-prepared core-void-shell TiO<sub>2</sub> synthesized via flame combustion method, and the BET surface area was 39.218 m<sup>2</sup>/g, which is much smaller compared to that of core-void-shell TiO<sub>2</sub> synthesized by hydro-alcohol thermal method in this study.

The Nitrogen adsorption/desorption isotherms and the pore size distribution of the obtained corevoid-shell TiO<sub>2</sub> particles aggregates are shown in Figure 13. The isotherms in Figure 13(a) exhibited similar shape of type I according to the BDDT classification without any obvious hysteresis loop (Sing *et al.*, 1985). This type of isotherm is associated with microporous powders with uniform distribution of pores 2 nm or less in diameter. These high values of adsorbed volumes are attributed to the amorphous titania as shown in XRD analysis. The type IV-like isotherms with inflection of nitrogen-adsorbed volume at  $P/P_o = 0.45$  indicated the presence of the well-developed mesoporosity in the microspheric samples, Figure 13 (b). The shape of the hysteresis loops is type H3, associated with narrow slit-like pores. The pore size distribution data indicated that the average pore diameters of the sample ranged between 2.5 - 4.5 nm. The single-point total volume of pores at  $P/P_o = 0.987$  was 0.0956 cm<sup>3</sup>/g.



Figure 13. Nitrogen adsorption/desorption isotherms of core-void-shell TiO<sub>2</sub>: (a) as-prepared sample, (b) calcined photocatalyst and the corresponding pore size distribution (inset)

## 4.1.2.3. SEM Analysis

The SEM images of the as-prepared and calcined samples (Figure 14) show that the titania powders consists of spherical structured particles. The diameter of a single dispersed microspheres for the asprepared sample was mostly within  $0.6 - 2 \mu m$ . After calcination, the diameter of a single dispersed microspheres ranged within  $0.5 - 1.7 \mu m$ , which implied that the core-void-shell TiO<sub>2</sub> particles are thermally stable. Further observation indicated that the TiO<sub>2</sub> spheres were connected to each other to form multimers. This formation of multimers may occur because of the existence of the Ti-OH group on the surface of the spheres (Yu *et al.*, 2007).



Figure 14. SEM micrographs of core-void-shell TiO2: (a) as-prepared; (b) calcined at 500°C for 4 hrs

### 4.1.2.4. TEM Analysis

Figure 15 (a) and (b) shows the TEM images of the as-prepared and calcined core-void-shell samples. The images suggested that indeed the core-void-shell TiO<sub>2</sub> particles were achieved; also the structural morphology did not change after calcination which implied that the particles were thermally stable at high temperatures. Xu et al., (2008) reported that the presence of ethanol as a co-solvent and the use of ammonium sulphate as a dispersing agent are essential for the final formation of spherical titania particles with well-developed mesoporosity and hollow interiors. During the precipitation process, ammonium sulphate behaves as an electrolyte and thus modifying the Zeta ( $\zeta$ ) potential of spherical polycondensed titania species generated at the initial stage of the hydrolysis reaction. The hollow interiors are therefore created due to the subsequent precipitation of the titania species onto the ammonium sulphate stabilized spherical titania in the reaction systems. Bakardjieva *et al.*, (2005) also reported that the urea precipitation method leads to colloid anatase particles assembled into rather big (about 1–2µm) porous spherical hollow clusters. These reports are supported by the findings of this study.



Figure 15. TEM images of (a) as-prepared core-void-shell, (b) calcined core-void-shell in air at 500°C for 4 hrs

### 4.2. Acid Mine Drainage Treatment in Constructed Wetland

Batch studies were done in order to investigate the effect of pH on the adsorption efficiencies of the constructed wetland packing material. Two grams of both clinoptilolite and silica sand were mixed with 250 ml of Fe(II) solution and placed in a magnetic stirrer. The adsorption isotherms, thermodynamics, and kinetics were also investigated.

### 4.2.1. Effect of pH on Adsorption Efficiency of the CW Packing Materials

Figure 16 shows the effect of pH on the adsorption of Fe(II) by clinoptilolite, and silica. The pH ranged was from 3 to 5, and each experiment was run for three hours. The maximum Fe(II) adsorption at pH of 3 was 70.4%, and 71.7% for clinoptilolite, and silica respectively. At the pH of 5, the maximum Fe(II) adsorption efficiency was 86.47%, 74.2% for clinoptilolite, and silica respectively. The effect of pH can be explained considering the surface charge on the adsorbent material. When pH was low, hydrogen ion with high concentration was predominant in adsorption onto the adsorbent. The adsorbent surface was positively charged, which prevented Fe(II) adsorption. When pH was elevated, the positive charge on the material surface became weak and the adsorption efficiency also increased. The above fact related to the effect of pH on adsorption is also supported by several studies (Akil *et al.*, 2004; Munther, 2004).

Adsorption of  $SO_4^{2-}$  ions was also investigated at the end of the experimental runs. The maximum  $SO_4^{2-}$  adsorption at pH of 3 was 56.7%, and 50% for clinoptilolite, and silica respectively. At the pH of 5 the maximum  $SO_4^{2-}$  adsorption was 50%, and 41.7% for clinoptilolite, and silica respectively. These findings implied that an increase in pH adjustment resulted in an insignificant

change in  $SO_4^{2-}$ , therefore for the rest of the study, pH adjustments were not done. Again, since constructed wetlands operates at longer hydraulic retention time (1-7 days), it is believed that the remaining Fe(II) concentration would be removed by other processes such as precipitation/co-precipitation, and sedimentation that take place in the constructed wetland (Murray-Gulde *et al.*, 2005).



Figure 16(a). Adsorption of Fe(II) by clinoptilolite, and silica: pH 3, , 60°C, C<sub>0</sub> 62 mg/L, contact time 3 h.



Figure 16(b). Adsorption of Fe(II) by clinoptilolite, and silica: pH 5, 60°C, C<sub>0</sub> 62 mg/L, contact time 3 h.

A control experiment was conducted to investigate whether the removal of Fe was due to adsorption or precipitation in the form of metal hydroxide. The control experiment was conducted by varying the pH of synthetic Fe solution without an absorbent. The experiment was carried out for 3 hrs and the resulting precipitates were filtered from the solution and analysed for Fe. From the results, it was observed that significant Fe precipitation occurred at pH 6, and complete precipitation occurred at pH 7 – 10 (Table 6). These findings are in agreement with the other authors reported on (Rose & Waite, 2003; Mohapatra *et al.*, 2010). Furthermore, this results show that the removal of Fe was attributed to adsorption onto both clinoptilolite and coarse silica sand.

pH	Fe(II) Precipitation(%)
3	0
4	3
5	7
6	95
7	100
8	100
9	100

Table 6. Fe precipitation with varying pH

#### 4.2.2. Adsorption Isotherms and Reaction Kinetics Studies

The adsorption isotherms, thermodynamic, and reaction kinetics studies of the packing material where studied under the treatment time of 5 days using simulated AMD (Table 7). The simulated acid mine drainage (1 L) was mixed with 50 g of clinoptilolite and coarse silica sand in separate flasks. The flasks were allowed to stand for 5 days at room temperature. Water samples were taken on daily basis and filtration of the sample was carried out in the laboratory using a portable vacuum filter and a 0.45  $\mu$ m Millipore filter.

Table 7. Simulat	ted Acid mine Drainage	
pН	3	
SO <sub>4</sub> (mg/l)	1730	
Fe (mg/l)	100	
Cr (mg/l)	30	+600

In this study, the adsorption isotherms were studied for Fe and Cr adsorption on clinoptilolite and coarse silica sand. The data obtained was fitted to the Langmuir adsorption isotherm (Figure 17) which is the most popular and is a two-parameter equation described as:

$$Ce/qe = 1/q_m b + Ce/q_m \tag{31}$$

Where constants b and  $q_m$  relate to the energy of adsorption and adsorption capacity and their values are obtained from the slope and intercept of the plot of Ce/qe versus Ce as shown in Figure 4 for temperature 288K. The linear nature of the plot shows that the adsorption follows the Langmuir isotherm. The value of b, which is a measure of heat of adsorption, is utilized to calculate dimensionless separation parameter  $R_L$  (Weber & Chakraborti, 1974). The adsorption data obtained are also fitted to the Freundlich isotherm (Figure 17) which is the earliest known relationship described by the following equation:

$$\log qe = \log K + 1/n \log Ce$$
(32)

where K and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity respectively. The slope (1/n) and intercept (K) of a log-log plot of qe versus Ce are determined. The Freundlich exponent 1/n gives an indication of the favourability of adsorption conditions. The value of 1/n < 1 represents a favourable adsorption conditions.

The results of both regressed isotherms are tabulated in Table 8. The Correlation coefficient ( $R^2$ ) shows that the Langmuir model is better than the Freundlich model in simulation of the adsorption of the isotherm. The agreement of the Langmuir model with the experimental results suggests that a monolayer coverage of Fe and Cr on the outer surface of the adsorbents. Weber & Chakarborti (1974) expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor  $R_L$ , which is defined as:

$$R_L = 1/(1 + bCo)$$
 (33)

where b is the Langmuir constant and C<sub>0</sub> is the initial concentrations of Fe and Cr. According to McKay *et al.*, (1982) R<sub>L</sub> values between 0 and 1 indicate favourable adsorption. The data obtained represent favourable adsorption in the case of adsorption of Fe and Cr ions ( $R_L = 0.021 - 0.084$ ).

This may be attributed to the fact the zeolites in general are weakly acidic in nature and sodiumform exchangers are selective for hydrogen, which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions (Leinonen & Lehto, 2001), making metal hydroxide precipitation feasible.



Figure 17 (a). Adsorption Isotherms of clinoptilolite Treating: Langmuir Isotherms (a)-(b), Freundlich Isotherms (c)-(d).

The Freundlich adsorption capacity K followed the trend Fe > Cr for clinoptilolite, and Cr > Fe for coarse silica sand. The value of 1/n < 1 represents a favourable adsorption conditions, as new sites could be available and the adsorption capacity would be increased. In this study, 1/n > 1 for both Cr and Fe on both clinoptilolite and silica sand, which was an indication of weak adsorption bonds. This indicated that the capacity of the adsorbent decreased because of its saturation (Alemayehu & Lennarts, 2009).





Figure 17(b). Adsorption Isotherms of coarse silica sand Treating: Langmuir Isotherms (a)-(b), Freundlich Isotherms (c)-(d).

Table 8.	Isotherms	parameters	for	Fe and	Cr	adsor	ption	at 1	bН	3
					_				~	-

		Langmui	r		Freundlich	
	<b>R</b> <sup>2</sup>	$Q_m (mg/g)$	b (L/mg)	$\mathbb{R}^2$	log K (mg/g)	1/n
<b>Clinoptilolite:</b>						
Fe	0.9665	812	0.46586	0.728	0.4421	1.208
Cr	0.905	387	0.26605	0.7304	0.168	3.487
<b>Coarse Silica</b>						
Sand:						
Fe	0.9531	635	0.36053	0.7548	0.06365	1.08436
Cr	0.9258	225	0.831255	0.7325	0.255	1.06407

Desorption tests were performed in plastic bottles with 50 ml of concentrated HNO<sub>3</sub>. Flasks were kept overnight, after which the solutions were filtered and analysed for Fe and Cr. The concentration of metal desorbed from the surface of the adsorbent ( $q_{des}$ , mg/g) was calculated as

$$\mathbf{q}_{\rm des} = \mathbf{C}_{\rm des} \ge \mathbf{V}/\mathbf{M} \tag{34}$$

where  $C_{des}$  is the metal concentration in the solution at the end of the desorption experiment (mg/L), V the volume and M is the mass of the adsorbent. The maximum desorption of Fe and Cr achieve on from clinoptilolite were 26% and 18% respectively; and from the coarse silica sand, the maximum desorption of Fe and Cr achieved were 34% and 18% respectively. The poor desorption of Fe and Cr is contradictory to the nature of adsorption which was suggested by the Langmuir isotherm. It is generally known that the Langmuir is based on the basic assumption of mono-layer coverage (Jenne, 1998), therefore desorption of metals which underwent physical adsorption onto

the surface of the adsorbent (Gong et al., 2005). The poor desorption maybe attributed to the adsorptive precipitation of heavy metals taking place on the surface of the adsorbents (Stumm & Morgan, 1981; Leinonen & Lehto, 2001).

### 4.2.3. Thermodynamic Parameters

The thermodynamic equilibrium constant ( $K_C$ ) was obtained by calculating the apparent equilibrium constant  $K'_C$  at different initial concentrations of Fe and Cr, and extrapolating to Zero (Bhattacharya *et al.*, 2006). The experiments were carried out at the temperatures of 298.15 K, 301.15 K, and 303.15 K.

$$K'c = Ca/Ce$$
(35)

where Ca is the concentration of Fe and Cr adsorbed on the of adsorbents at equilibrium in mg/L and Ce is the equilibrium concentration of Fe and Cr (II) in solution in mg/L. The thermodynamic constants, Gibb's free energy ( $\Delta G^{\circ}$ ), enthalpy change ( $\Delta H^{\circ}$ ) and entropy change ( $\Delta S^{\circ}$ ) are calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The Gibb's free energy change of the process is related to equilibrium constant (Kc) by:

$$\Delta G^0 = - RT \ln K_C \tag{36}$$

The Gibb's free energy change is related to the enthalpy change ( $\Delta H^{\circ}$ ) and entropy change ( $\Delta S^{\circ}$ ) as:

$$\ln K_{\rm C} = \Delta S^0 / R - \Delta H^0 / RT \tag{37}$$

The thermodynamic parameters as calculated are reported in Table 9. The negative value of  $\Delta H^0$  indicates exothermic nature of adsorption. The enthalpy change due to chemisorption takes value between 40 – 120 kJ/mol, which is larger than that due to physisorption (Alkan *et al.*, 2004). Therefore, the low value of heat obtained in this study indicated that adsorption is likely due to physisorption precipitation taking place on the surface of the adsorbent. The negative value of the free energy change ( $\Delta G^0$ ) is an indication of a spontaneous process whereby no energy input from

outside system is required. The negative value of entropy ( $\Delta S^0$ ) shows a decreased disorder at the solid/liquid interface during Fe and Cr adsorption.

Table 9. Thermodynamic parameters of Fe and Cr at 298K						
Packing Material	$\Delta G^{0}(kJ/mol)$	ΔH <sup>o</sup> (kJ/mol)	ΔS° (kJ/mol)			
Clinoptilolite:						
Fe	-3.248	-30.86	-94.78			
Cr	-6.319	-21.71	-96.32			
Coarse Silica Sand:						
Fe	-4.153	-33.97	-74.158			
Cr	-8.063	-16.32	-105.38			

Table 9 Thermodynamic parameters of Fe and Cr at 298K

### 4.2.4. Kinetic Modelling of Clinoptilolite and Coarse Silica Sand Treating Simulated AMD

The first order equation was applied in the analysis of kinetic data. The linear form of the first order equation (Panday et al., 2009) is given below:

$$-\ln \left( C_t / C_0 \right) = K_1 t \tag{38}$$

where  $C_t$  (mg/l) is the concentration of Fe and Cr in solution at a given time t,  $C_0$  (mg/l) is the initial Fe and Cr ion concentration in solution,  $K_1(min^{-1})$  is the first order rate constant of adsorption. The applicability of this equation was tested by a linear plot of  $-\ln(C_t/C_0)$  against t, illustrated in Figure 18. The first order kinetic parameters are presented in Table 10.

The second order equation was also used to analyse kinetic parameters (Panday et al., 2009), this equation in its linear form is given below:

$$(1/C_{t}-1/C_{o}) = K_{2}t$$
(39)

where  $K_2$  (Lmg<sup>-1</sup>min<sup>-1</sup>) is the second order rate constant for the adsorption process. This isotherm was tested by a linear plot of  $(1/C_t-1/C_o)$  versus t, shown in Figure 18. The rate equation K<sub>2</sub> was obtained from the slope of the plot. The value of  $K_2$  and the regression  $R^2$  are presented in Table 10.

Figure 18 shows the fitted results of first order and second order kinetic models based on the experimental adsorption data of Fe and Cr. The value of the linear regression coefficient  $(R^2)$  obtained suggested the applicability of the first order equation in the description of the kinetics of sorption. From the  $R^2$  obtained from the first order kinetic plots is greater than 0.9 compared to the second order kinetic plots, which indicated a good fit to the experimental data of both Fe and Cr. Therefore, it ca be concluded that the first order correlated the experimental data quite well, which is different from the second order kinetic models.



Figure 18 (a). First order kinetic plots for Fe and Cr on, (a)-(b) clinoptilolite; (c)-(d) coarse silica sand.



<sup>0</sup>Figure 18 (b).<sub>1</sub>Second order kingtic plots for Fe and Cr on (a)-(b) Clinoptilolite; (c)-(d) Coarse Silica Sand. 5 HRT (day) HRT (day)

	First Order Kinetics		Second Ord	er Kinetics
Clinoptilolite	$\mathbb{R}^2$	Kv (h <sup>-1</sup> )	$\mathbb{R}^2$	Kv (h <sup>-1</sup> )
Fe	0.9757	0.8846	0.2649	0.129
Cr	0.9792	0.2054	0.927	0.1297
Silica Sand	$\mathbb{R}^2$	Kv (h <sup>-1</sup> )	$\mathbb{R}^2$	Kv (h <sup>-1</sup> )
Fe	0.9896	1.09447	0.0521	0.1054
Cr	0.964	0.219	0.926	0.134

Table 10. The kinetic parameters of Fe and Cr adsorption

A mass balance analysis for heavy metals precipitation within individual systems of clinoptilolite and silica sand was established on the following equation (Sekomo *et al.*, 2009):

Influent = Effluent + Precipitation/co-precipitation + Adsorption(40)

From this equation, the removal of heavy metal was achieved by adsorption and sulphide precipitation onto the CW packing material. Since precipitation is known to be the most important mechanism for heavy metals removal; it was assumed that the difference of heavy metals in the influent and effluent plus adsorption would represent the fraction of heavy metals precipitated; another assumption was that the heavy metals desorbed from the adsorbents was equal to the amount of heavy metals adsorbed onto the surface of the same adsorbents. The mass balance

analysis showed that metals were mainly removed by accumulation in sediments, possibly as sulphides precipitates for clinoptilolite and silica sand systems (Table 11), additional heavy metals removal was attributed to adsorption. Sokomo *et al.*, (2011) also reported that the removal of heavy metals in CW was mainly due to sulphide precipitation while using volcanic rock as CW packing material.

	Influent	Effluent	Accumulation	Adsorption	Precipitation	Removal %
Clinoptilolite:						
Fe (mg/L)	80	2	78	20.8	59.2	98
Cr (mg/L)	30	6	24	5.4	24.6	80
Coarse sand:						
Fe (mg/L)	80	4	76	27.2	52.8	96
Cr (mg/L)	30	10	20	5.4	24.6	67

Table 11. Mass balance analysis

### 4.2.5. Acid Mine Drainage Characterization

According to characterization conducted in this study, samples from ground water in the mining area typically show high concentration of sulphates, low pH and elevated metal concentrations (Table 12), confirming previously reported results (Jones *et al.*, 1988; Naicker *et al.*, 2003; Winde & Sandham, 2004). Acid mine drainage samples were characterized for toxic heavy metals and sulphates. High sulphate and iron content are a result of pyrite oxidation during the formation of AMD. The pH ranged from 2.55 - 2.7. Other metals such as Al, Ca, Mg, and Si were present in the mine drainage in large quantities, while Li, Be, Zn, Co and Mn were present in low quantities. No traces of Cr, V, Pb, Cu, Cd, Sn, and Ag were detected during characterization. Therefore, all the water samples were spiked with varying concentrations of Cr(VI) in order to simulate Cr(VI)-laden-acid-mine-drainage.

	Middelburg Steam					
	Douglas North Discharge	Coke and Coal	T&DB Decant			
	(DND)	(SSC)	(TDB)			
pH	2.7	2.65	2.55			
SO <sub>4</sub> (mg/l)	2690	3595	6055			
Fe (mg/l)	280.815	148.483	20.776			
Al (mg/l)	246	143.333	9.95			
Ca (mg/l)	80.188	389.986	450.245			
Li (mg/l)	0.413	4.157	3.99			
Be (mg/l)	0.063	0.082	0.05			
Mg (mg/l)	46	216	211			
Si (mg/l)	80.182	38.711	50.482			
Zn (mg/l)	5.7	8.6	1.55			
Cu (mg/l)	< 0.05	< 0.05	< 0.05			
Pb (mg/l)	< 0.05	< 0.05	< 0.05			
V(mg/l)	< 0.05	< 0.05	< 0.05			
Co (mg/l)	1.729	2.727	0.559			
Ni (mg/l)	2.6	3.187	0.867			
Mn (mg/l)	6.095	35.852	11.771			
Cd (mg/l)	< 0.05	< 0.05	< 0.05			
Sn (mg/l)	< 0.05	< 0.05	< 0.05			
Ti (mg/l)	< 0.05	< 0.05	< 0.05			
Cr (mg/l)	+200	+600	+1000			
Ag (mg/l)	< 0.05	< 0.05	< 0.05			

Table 12. Acid Mine Drainage Characterization

\*+, concentration was below detection, therefore spiked into the wastewater.

#### 4.2.6. Acid Mine Drainage Treatment in Constructed Wetlands

All three constructed wetlands were fed with acid mine drainage wastewater sampled at different points. The first constructed wetland was fed with the sample taken from Douglas North Discharge (DND); the second wetland was fed with the Middelburg Steam Coke and Coal (SCC); and the third wetland with the sample from T&DB Decant (TDB). Samples of effluent wastewater were taken manually for heavy metal and sulphates determination during treatment. The effect of hydraulic retention time on the efficient removal of heavy metals and sulphates was investigated. However, the redox potential was not monitored in this study; this parameter might be useful to explain the metal behaviour in the wetland sediment. Nevertheless, the pH and oxidizing conditions favoured partitioning of soluble metals to the solid phase, by precipitation and sorption to solids matter (Pontier *et al.*, 2004). The results for the removal of heavy metals and sulphates for three pilot-scale wetland systems are shown in Figure 19.

The effect of hydraulic retention time (HRT) was investigated between 3 - 5 days. Metal concentrations were significantly lower in the outlet than in the inlet. After three days, the highest

metal average metal retention was attained by Fe (68.86%), Ca (69.35%), Cr (63%), Al (47.97%), Mg (33.5%), Si (26.42%) and 100% removal was achieved for Be, Zn, Co, Ni, and Mn. After five days, the highest metal average metal retention was attained by Fe (100%), Ca (79.69%), Cr (68%), Al (22.15%), Mg (51.1%), Si (36.39%) and 100% removal was achieved for Be, Zn, Co, Ni, and Mn. The sulphate removal after three days was 34.9%, and after five days it 21.9%. Therefore, hydraulic retention time of 5 days was chosen as the best operating parameter for all three constructed wetlands. Once the best operating HRT was determined, the experiments were conducted for 20 days to study the treatment performance over a long period.

During the experiment, removal efficiencies of heavy metals and sulphates fluctuated. The concentration of some heavy metals in the outlet of the wetlands decreased, while for some, the concentration of the heavy metals increased. At the end of the experiment, the highest average metal removal was attained by Fe (90.39%), Cr (64.5%), Mg (67.88%); 100% removal was achieved for Ca, Be, Zn, Co, Ni, and Mn; however, Al and Si concentration increased by 17.9% and 2.7% respectively in the first constructed wetland. For the second constructed wetland, the highest average metal retention was attained by Fe (86.45%), Cr (56.17%), Mg (67.1%); 100% removal was achieved for Ca, Be, Zn, Co, Ni, and Mn; however, Al and Si concentration increased by 17.48% and 2.7% respectively. For the third constructed wetland, the highest average metal retention was attained by Fe (83.62%), Cr (56.4%), Mg (64.23%); 100% removal was achieved for Ca, Be, Zn, Co, Ni, and Mn; however, Al and Si concentration increased by 14.6% and 2.7% respectively. The sulphates reduction in all constructed wetlands was 30%. These results were remarkable considering the ability of the constructed wetlands to treat Cr(VI)-laden AMD with high strength by 56.4% compared to 60.4% treatment efficiency achieved by CW treating AMD with lowest Cr(VI) concentration in this study.



Figure 19. Heavy metals and sulphate removal during treatment AMD treatment with constructed wetlands. (a) DND, (b) SSC, (c) TDB

As mentioned earlier, the efficient reduction of the metals and sulphate contents was due to adsorption, precipitation/co-precipitation, and sedimentation. The adsorption capacity by cation exchange or non-specific adsorption depends upon the physico-chemical environment of the medium, the properties of the metals concerned and the concentration and properties of other metals and soluble ligands present (Matagi et al., 1998). More than 50% of the heavy metals can be adsorbed easily onto particulate matter in the wetland and thus be removed from the water component by sedimentation (Muller, 1988).

In wetlands, heavy metals such as Fe, Al, and Mn are removed through hydrolysis and oxidation to form insoluble compounds. This results in different oxyhydroxides, hydroxides, and oxides formation (Brix, 1993; Batty *et al.*, 2002). The removal of Fe is depends on the pH, redox potential, and different anions present in the wastewater (ITRC, 2013). The removal of Fe(III) can be

achieved in mildly acidic environment and longer HRT. Trivalent iron, Fe (III) can precipitate to form oxides, hydroxides, and oxyhydroxides which in turn can co-precipitate other metals. Soluble divalent, Fe(II) iron is a significant bioavailable form of Fe because it can oxidized to Fe(III) with hydroxyl ions ingesting under aerobic conditions (Robbins & Norden, 1994). The maximum Fe removal of 99.99% was achieved by SIMCO wetlands after more than 7 years of operation (Stark *et al.*, 1994).

Hedin *et al.*, (1994) reported that precipitation of Al into Al hydroxides can be achieved at pH close to 5. Stumm & Morgan (1981) reported that Mn removal is problematic since the oxidation of Mn occurs under basic environment. Zinc is removed by forming insoluble species with sulphide and carbonate. It is also be removed by co-precipitation with Mn and Fe oxides (Stumm & Morgan, 1981; Noller *et al.*, 1994). Chromium is present as Cr(VI), which is relatively mobile and after release into the pore, it migrates downward into the reducing zone and precipitates as Cr(OH)<sub>3</sub> (Shaw *et al.*, 1990). The hydrolysed form of Cr(VI) is readily absorbed by hydrous Fe and Mn oxides (Davis *et al.*, 1996).

Sulphate adsorption was also expected based on the preliminary studies of the effect of pH on the adsorption capacities of the adsorbents. Swedlund & Webster (2001) found that at pH 4 and below, nearly 40% of SO<sub>4</sub> present is adsorbed onto the Fe oxyhydroxides and oxy-hydroxysulphates. These finding are relatively similar to the ones found in this study. Although the ability of clinoptilolite based constructed wetland has demonstrated the ability to reduce sulphate concentration, literature relating to sulphate reduction could not be found. Further work is required to determine the mechanism of sulphate reduction, be it chemical, biochemical, physical or a combination thereof.

#### 4.2.7. Metals and Sulphur Concentrations in Sediments

The metals and sulphur concentrations in sediments were obtained by concentrated HNO<sub>3</sub> extraction at the end of the experiment. However, it seems that the acid extraction was achieved for Fe (0.576 - 0.8 %), Ca (0.39 - 0.81), and Mg (0.115 - 0.53 %) since the rest of the metals concentration were below detection when analysed using AAS. Oduoza & Miaphen (1993) assessed the suitability of various methods in the extraction of trace metals and pollutants in aquatic sediments. They reported that the extraction efficiency depends on the decomposition procedure, and that certain metals are recovered better by one method as compared to the other. They further proposed that factors that affect the extraction efficiency are losses due to volatilisation depending

on the drastic conditions of the decomposition procedure, the metal that is subsequently to be determined, and optimal digestion time in acids. These factors could be the possible reason why some of the metals were below detection limit. Another reason might be that the heavy metals underwent precipitation and co-precipitation, a phenomenon supported by several authors (Murray-Gulde *et al.*, 2005; Sekomo *et al.*, 2009). Therefore, XRF was employed to analyse the concentrations of the rest of the metals that were below detection during AAS analysis. Metal concentrations were significantly higher in the wetlands outlet than in the inlet, except for Ni, Be, and Li that were below detection in all samples (Table 13). It should be noted that prior to the analysis, it was difficult to separate the white-yellowish precipitates from the sediments, therefore the heavy metals and sulphur contents were analysed from a sample made up of sediments and precipitates.

The concentration of sulphur in all core samples indicated that it is transported from bottom sediment layers to the sediment-water interface (Wijsman *et al.*, 1999). This also suggests that there is enrichment of sulphur below the suboxic/anoxic interface, indicating that sufficient oxidants must be present to generate sulphides; and are namely metal oxides, which interact with sulphur species to form sulphides (Aller & Rude, 1988). The significant relationship of sulphur with trace metals shows that these trace metals are precipitated as metal sulphides and are also responsible for the fixation of trace metals in core sediments (Astrom, 1998).

	Douglas North		Middelburg Steam			
	Discharge (DND)		Coke and Coal (SSC)		T&DB Decant	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
pН	2.7	2.85	2.65	2.8	2.55	2.85
S (mg/l)	2237	7328	2210	1010	5080	1040
Fe (mg/l)	2440	7776	2082	1080	5793	9888
Al (mg/l)	15	591	14	571	16	561
Ca (mg/l)	288	7512	124	7887	1874	7272
Mn (mg/l)	103	149	128	182	210	183
Cr (mg/l)	256	172	378	490	185	562
Mg (mg/l)	5	53	<5	49	<5	41
Zn (mg/l)	<5	59	<5	66	<5	60
Co (mg/l)	<5	1.9	<5	2.6	<5	2.3
Ni (mg/l)	<5	<5	<5	<5	<5	<5
Li (mg/l)	<5	<5	<5	<5	<5	<5
Be (mg/l)	<5	<5	<5	<5	<5	<5

Table 13. Metals concentration in sediments

# 4.2.8. Kinetic Modelling Of Constructed Wetlands Treating AMD Samples With Different Fe And Cr Concentrations

The first order dynamic model, which was used to predict the removal efficiencies of the pollutants treated by CWs, should be used in the design of the CWs (Kadlec 1995; Kadlec & Knight, 1996; Rousseau et al., 2004). Though the parameter and the calculation of the equation are simple, first order dynamic model has some limitations. However it is still an appropriate equation for describing the removal mechanism of the CWs treating pollutants. In the present study, the first order model with two parameters was used to describe the removal mechanism of the different CWs. If steady and plug flow conditions are assumed, pseudo first order dynamic model can be used to describe the reduction of pollutants. The equation can be written as:

$$\ln\left(C/C_{o}\right) = -k_{v}t\tag{41}$$

where C is the concentration of the quantity concerned (mg/L), t is the hydraulic resident time (h), and  $k_v$  is volumetric rate constant (h<sup>-1</sup>).

The rate constant always has two ways of expressions,  $k_v$  and k. Literature is available on  $k_v$  with subsurface flow constructed wetland and k with surface flow constructed wetland (Simi & Mitchell, 1999). Removal rate constant represents the removal ability of the CWs. In theory, the removal rate constant relates to temperature, medium and pollutants. Therefore, in this study the temperature was kept at room temperature and the removal efficiencies Fe and Cr were analysed. In order to compare the removal ability of up-flow constructed wetlands, the volumetric rate constant,  $k_v$  was determined.

The heavy metal removal was investigated as a function of hydraulic retention time and data were fitted to a pseudo first-order reaction model as reported by various authors who have worked on heavy metals removal using constructed wetland (Kadlec & Knight, 1996; Rousseau *et al.*, 2004).

Figure 20 shows the first order plots of constructed wetlands treating AMD samples from different locations with different concentrations. From the figures, it is evident that the data follow the linear shape predicted by Equation (39), and the  $k_v$  values and the correlation coefficients where calculated and the results are listed on Table 14.



Figure 20(a). First-order model fitting plot of unvegetated up-flow constructed wetland treating DND AMD: (a) Fe; (b) Cr



Figure 20(b). First-order model fitting plot of unvegetated up-flow constructed wetland treating SSC AMD: (c) Fe; (d)

Cr



Figure 20(c). First-order model fitting plot of unvegetated up-flow constructed wetland treating TDB AMD: (e) Fe; (f) Cr

The removal efficiencies for Fe are higher than the efficiencies for Cr in all constructed wetlands. These results well agree with the results of (Walker & Hurl, 2002). The constructed wetlands had different rate constants because of the different heavy metals concentration in AMD. The results showed that the constructed wetlands treating DND and TDB AMD samples did not have significant differences in the volumetric rate constant in respect to Fe and Cr. However, the volumetric rate constants (with respect to Fe and Cr) of the constructed wetland treating SSC AMD sample were significantly different. It is indicated that the CWs had better purification effect on Fe than that on Cr in all AMD samples. Also, all three constructed wetlands proved to have the relative same satisfactory removal efficiencies for chromium despite the varying initial concentrations of chromium in all AMD samples.

Table 14.	Rate cons	tant and c	correlation	coefficient	values

	DND		SSC		TDB	
HeavyMetal	$\mathbb{R}^2$	Kv (h <sup>-1</sup> )	$\mathbb{R}^2$	Kv (h <sup>-1</sup> )	$\mathbb{R}^2$	Kv (h <sup>-1</sup> )
Fe	0.9489	0.2147	0.9048	0.20145	0.9318	0.1453
Cr	0.914	0.2404	0.9046	0.09016	0.9146	0.1145
# 4.3. UV/TiO<sub>2</sub> Photocatalysis

# Photocatalytic Activity

The best operating parameters for photocatalytic reduction study were determined by using P25 Degussa as a photocatalyst by batch studies using synthetic wastewater. Once determined, the synthesized anatase core-void-shell  $TiO_2$  was employed as a photocatalyst in order to compare its photocatalytic activity with that of P25 Degussa. After one hour of dark adsorption, 23% of Cr(VI) was achieved, therefore one hour of dark adsorption was performed throughout the experimental study.

# 4.3.1. Effect of pH

The effect of pH on the photocatalytic reduction of Cr(VI) is one of the important parameters. A series of experiments were conducted at different pH values ranging from 2 to 10, containing 30 mg/L Cr(VI) and 2 g of photocatalyst in order to investigate photocatalytic reactions of Cr(VI). Under illumination with the UV lamp, the Cr(VI) solution gradually lost its original deep yellow colour, which indicated that Cr(VI) was indeed reduced to Cr(III). The effect of pH on photocatalytic reduction efficiency of Cr(VI) is shown in Figure 21. The maximum Cr(VI) reduction was obtained at pH of 2 (62%) after three hours of UV irradiation. The effect of pH can be explained by considering the surface charge on the catalyst. Generally, the hydroxyl groups on the surface of TiO<sub>2</sub> are considered as the Cr(VI) adsorption sites (Oosawa *et al.*, 1998). At pH of 2.5, Cr(VI) exists in the solution as HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (Ku & Jung, 2001).

Furthermore, the surface of the catalyst is positively charged at pH 2.5 as  $pH_{zpc}$  of TiO<sub>2</sub> was reported to be 6.15 (Ku & Jung, 2001), which suggests that Cr(VI) species are adsorbed on the surface of the catalyst via electrostatic interaction. The surface of TiO<sub>2</sub> has been reported to have a large surface proton exchange capacity. The photon-generated electrons can be captured by the adsorbed H<sup>+</sup> to form H<sub>ads</sub>, which is able to reduce Cr(VI) to Cr(III). At high pH, the surface of the catalyst has a net negative charge due to the significant fraction of surface sites present as TiO<sup>-</sup>. Therefore the adsorption of Cr(VI) onto the TiO<sub>2</sub> surface becomes slow, resulting in a decrease in reduction to Cr(III). It has also been reported that TiO<sub>2</sub> may deactivate at pH > 4.5 (Weng *et al.*, 1997), therefore pH 2 was chosen for further studies.



Figure 21. Effect of pH on Cr(VI) photocatalytic reduction:  $C_o = 30 \text{ mg/L}$ ; contact time of 5 hrs, and photocatalyst loading of 2 g

### 4.3.2. Effect of Initial Concentration (Co)

The photocatalytic reduction efficiency of Cr (VI) is affected by the initial metal ion concentration, with decreasing percentage reduction as concentration increases from 30 - 50 mg/L (Figure 22). The effect of initial concentration on photocatalytic reduction can be explained as follows: as initial Cr(VI) concentrations increases, more metal ions are adsorbed on the surface of the photocatalyst. Therefore, the photo-generated electrons required for the removal of Cr(VI) also increased and hence, the available electrons were inadequate for pollutant removal at higher concentrations. Moreover, with the increase in the Cr(VI) concentration, less photons reach the photocatalyst surface (light screening effect), resulting in slower production of the photogenerated pair hole/electron. Consequently, the photocatalytic activity decreased, since fewer available electrons were available to reduce more Cr(VI) ions (Wang *et al.*, 2004). It was observed also that the photocatalytic reduction was most efficient for an irradiation time of 3hrs. After 3hrs of irradiation, higher percentage reduction could not be achieved suggesting that equilibrium was reached, the subsequent decrease in reduction may be attributed to desorption of Cr(VI) from the surface of the photocatalyst. Therefore pH 2 and C\_0 = 30 mg/L were taken for further studies.



Figure 22. Effect of  $C_0$  on Cr(VI) photocatalytic reduction: pH 2; contact time of 5 hrs, and photocatalyst loading of 2 g

# 4.3.3. Effect of Fe(III) on Cr(VI) Reduction

The presence of Fe(III) was investigated by preparing synthetic wastewater containing 30 mg/L Cr(VI) and 30 mg/L Fe(III), and the pH was adjusted to pH of 2 using sulfuric acid. From Figure 23 it can be observed that the photocatalytic reduction of Cr(VI) was enhanced after one hour in the presence of Fe(III). Chen & Ray (2012) reported that the preferential reduction of Fe(III) to Fe(II) over Hg(II) to Hg occurs due to strong adsorption of Fe(III) over Hg(II) on P25 TiO<sub>2</sub> photocatalyst. Wang *et al.*, (2004) also demonstrated that this mechanism is operative for Cr(VI) reduction. They suggested that the Fe(II) generated by photocatalytic reduction of Fe(III) on the surface of TiO<sub>2</sub> may be consumed by the thermal reduction of Cr(VI) in the bulk solution. Furthermore, they also proposed that the photocatalytic reduction Cr(VI) in the presence of Fe(III) occurs via two pathways:

(a) by the surface reaction :

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$$
 (42)

and (b) by the following redox reactions:

$$Fe^{3+} + e^{-} \xrightarrow{\text{TiO2, } UV} Fe^{2+}$$
(43)

$$3Fe^{2+} + Cr^{6+} \xrightarrow{UV} 3Fe^{3+} + Cr^{3+}$$
 (44)

The homogeneous reaction between Fe(II) and Cr(VI) under the UV illumination demonstrated that the Cr(VI) decreased with illumination time. In this study, the photocatalytic reduction of Cr(VI) increased from 62% to 77% in the presence of Fe (III). Therefore UV/ TiO<sub>2</sub> photocatalysis employing anatase core-void-shell TiO<sub>2</sub> as a photocatalyst has a potential to reduce the toxicity of

AMD by reducing toxic metal such as Cr(VI) into their less toxic states since Fe(III) is normally present in large quantity in Acid Mine Drainage.



Figure 23. Effect of Fe(III) on Cr(VI) photocatalytic reduction: Fe(III) = 30 mg/L, Cr(VI) = 30 mg/L, pH 2; contact time of 5 hrs, and photocatalyst loading of 2 g

# 4.3.4. Effect of Photocatalyst Loading

Figure 24 shows the effect of photocatalyst loading on the photocatalytic reduction of Cr(VI). The photocatalyst variation was 2, 4, 6, and 10 g per 350 ml. Initially the reduction of Cr(VI) was similar in all four cases but as time proceeded, the reduction slowed down. For the same initial feed concentration different catalyst loading gave different results. As expected increase in catalyst amount slightly increased reduction. This suggests that after particular amount of catalyst loading, the reduction slightly change or even stay constant with time. The catalyst loading that gave a higher Cr(VI) reduction was 6 g (73%), but the percentage reduction was 9% greater than that achieved with the loading of 2 g (62%). However, considering the cost of the catalyst, it is economical to use the catalyst loading of 2g since 100% of Cr(VI) reduction was not achieved with increase in catalyst loading. Therefore in this study, 2 g of the photocatalyst loading was chosen as the best loading for Cr(VI) reduction.



Figure 24. Effect of photocatalyst loading on Cr(VI) photocatalytic reduction: Cr(VI) = 30 mg/L; pH 2 and contact time of 5 hrs

### 4.3.5. Photocatalytic Activity of P25 Degussa and Synthesized Core-Void-Shell TiO<sub>2</sub>

Figure 25 shows the photocatalytic activities of both the P25 Degussa and synthesized Core-Void-Shell TiO<sub>2</sub> photocatalyst for reduction of Cr(VI). It was observed that the synthesized Core-Void-Shell displayed a higher photocatalytic activity than the commercial P25 Degussa. High reduction (93%) of Cr(VI) was obtained after 2 hrs of treatment in the presence of synthesized Core-Void-Shell photocatalyst, and only 56% reduction in the presence of P25 Degussa photocatalyst. The higher photocatalytic activity of synthesized core-void-shell TiO<sub>2</sub> can be attributed to three parameters namely the crystallite phase, surface area, and the structure of the photocatalyst. Firstly, it was reported that the anatase phase of TiO<sub>2</sub> shows a better photocatalytic activity than the rutile one (Xu et al., 2008). This is supported by the crystallite phase of the synthesized core-void-shell TiO<sub>2</sub> which was found to be 100% anatase by the XRD analysis, P25 Degussa was found to be 80% anatase and 20% rutile). Secondly, the large surface area renders TiO<sub>2</sub> a high photocatalytic activity; thirdly, the core-void-shell structure of TiO<sub>2</sub> makes multiple reflections of UV light within the hollow chamber, allowing more efficient use of the light source (Guo et al., 2013). The BET surface analysis revealed that the synthesized core-void-shell TiO<sub>2</sub> had a higher surface area than the commercial P25 Degussa. These three reasons contribute greatly to the improved photocatalytic activity.



 $\label{eq:Figure 25. Photocatalytic activity of P25 Degussa an synthesized Core-Void-Shell TiO_2 photocatalysts: Cr(VI) = 30 \\ mg/L, pH 2; contact time of 5 hrs, and photocatalyst loading of 2 g$ 

# 4.3.6. EDX Analysis

The energy-dispersive x-ray spectroscopy (EDX) analysis was conducted for both P25 Degussa and core-void-shell TiO<sub>2</sub> photocatalysts after the photocatalytic reduction of Cr(VI). The EDX revealed that the synthesized core-void-shell TiO<sub>2</sub> adsorbed more Cr(VI) content than the P25 Degussa, a phenomenon which might enhanced the photocatalytic activity of the photocatalyst (Figure 26). The Cr(VI) on the synthesized core-void-shell TiO<sub>2</sub> and P25 Degussa was found to be 0.99 %wt and 0.21 %wt respectively.



Figure 26. EDX spectrum of, (a) P25 Degussa; (b) synthesized Core-Void-Shell TiO<sub>2</sub> photocatalysts after Cr(VI) photocatalytic reduction

### 4.3.7. Kinetic Parameters of Cr(VI) Photocatalytic Reduction Using Core-void-shell TiO<sub>2</sub>

In this study, kinetic experiments were performed to study the photocatalytic reduction of Cr(VI) using core-void-shell TiO<sub>2</sub>. The dependence of the reduction rate on the influencing factors (e.g., catalyst dose, pH and initial Cr(VI) concentration were investigated and gotten from the corresponding kinetic data. The kinetic models of the photocatalytic reduction process are essential to the optimization of experimental conditions and subsequently, to the design of large-scale photocatalytic reactors. Several kinetic models have been developed and most of them can not completely account for all possible factors affecting the reduction rate. The Langmuir–Hinshelwood model has been widely used to formulate the rate equations for the photocatalytic reaction:

$$\ln \left[ Cr(VI)_0 / Cr(VI) \right] = k_{red}t \tag{45}$$

where  $Cr(VI)_0$  is the initial Cr(VI) concentration, Cr(VI) is the Cr(VI) concentration at time t,  $k_{red}$  is the photocatalytic reduction rate constant, and t is the contact time. For a surface-catalyzed reaction, chemisorption is of interest. Langmuir developed the adsorption isotherm that leads to a unimolecular layer of adsorbed molecules (Tanaka *et al.*, 2000; Yang *et al.*, 2001). Figure 27 shows the kinetics of photocatalytic reduction of Cr(VI) for an initial concentration of 20 mg/L under optimized conditions. The results show that the photocatalytic reduction of Cr(VI) can be described by the first order kinetic model,  $ln (C_0/C) = kt$ , where  $C_0$  is the initial concentration and C is the concentration at any time, t. The kinetic parameter of the first order and second order are listed in Table 15.



Figure 27. Kinetic plots for Cr(VI) photocatalytic reduction using core-void-shell TiO<sub>2</sub>, (a) First order kinetics plot (b) Second order kinetics plot

First Order Kinetics		Second Order Kinetics	
R <sup>2</sup>	Kv (h <sup>-1</sup> )	$\mathbb{R}^2$	Kv (h <sup>-1</sup> )
0.9827	1.4135	0.70202	0.07937

Table 15. Kinetic parameters of Cr(VI) photocatalytic reduction using Core-void shell TiO<sub>2</sub>

### 4.3.8. Photocatalytic Reduction of Constructed Wetlands Effluent

Table 16 shows the characterization of the constructed wetland effluents. The constructed wetland effluents were treated photocatalytically using a slurry photocatalytic recycle reactor for Cr(VI) reduction. The synthesized TiO<sub>2</sub> core-shell was employed as a photocatalyst and HRT of experiment was 3 hrs and the recycle rate was kept constant at 400 ml/min. After 3 hrs, the samples were analyzed for Cr(VI) and Fe(III) reduction using a UV-vis spectrophotometer, The spent catalyst was rinsed with deionized water and dried overnight at 120 °C, then re-used again.

	Middelburg Steam				
	Douglas North Discharge	Coke and Coal	T&DB Decant		
	(DND)	(SSC)	(TDB)		
pН	2.4	2.5	2.5		
SO <sub>4</sub> (mg/l)	2710	2710	2940		
Fe (mg/l)	28	38	46		
Al (mg/l)	290	289	282		
Ca (mg/l)	<2	47	62		
Mg (mg/l)	79	81	88		
Si (mg/l)	83	83	79		
Cr (mg/l)	72	263	436		

Table 16. Constructed wetland Effluents Characterization

Photocatalytic reduction of Cr(VI) was achieved only for the DND sample (68%), and the Fe(III) reduction was found to be 83% (Figure 28). The reason why photocatalytic reduction of Cr(VI) was not achieved in SCC and TDB samples may be attributed to the accumulation of Cr(VI) on the active sides of the catalyst, resulting in the light screening-effect and absence of photogenerated pair hole/electron production. Furthermore, the presence of Aluminium, Calcium, Magnesium, and Silicon might have impacted negatively on the overall photocatalytic reduction of Cr(VI) by also accumulating on the active side of the catalyst although they cannot be reduced. Photocatalytic reduction (54%) of Cr(VI) in the DND sample was also achieved using a spent catalyst. The achievement of Cr(VI) in the DND is attributed to the low concentration of Cr(VI); the presence of Fe(III); and the structural morphology of the catalyst.



Figure 28. Photocatalytic reduction of Cr(VI) in real AMD sample using both fresh and spent catalyst

# Chapter 5

# 5. Conclusion and Recommendations

The performance of the unvegetated upflow constructed wetland and UV photocatalytic reduction in the AMD treatment was investigated. The aim of this study was to employ the constructed wetland as a pre-treatment stage to reduce the concentration of toxic heavy metals such as Cr(VI)and Fe in AMD, and subsequently reduce toxic Cr(VI) present in the constructed wetland effluent by  $UV/TiO_2$  photocatalysis. In this study, unvegetated upflow constructed wetland and slurry photocatalytic reactor were designed and commissioned. An anatase core-void-shell  $TiO_2$  was prepared and employed to photocatalytically reduce toxic Cr(VI). Batch studies were conducted to investigate the effect of operating parameters on both processes. Finally, the performance of slurry photocatalytic reactor treating constructed wetland effluents was evaluated.

### 5.1. Conclusions

# 5.1.1. Design of Unvegetated Upflow Constructed Wetland and Slurry Photocatalytic Reactor

Unvegetated upflow constructed wetland and slurry photocatalytic reactor were designed and commissioned. However, it was found that the configuration of the photocatalytic reactor would make it difficult to maintain because the removal of the reactor from the shading box would require careful handling and consequently be costly.

# 5.1.2. CW Packing Material and Prepared Core-Void-Shell TiO<sub>2</sub> Characterization

Characterization showed that the constructed wetland packing material had high surface area, high porosity, and exchangeable ions, this can effectively adsorb heavy metals. The EDX analysis revealed that clinoptilolite (natural zeolite) contained a complement of exchangeable sodium, potassium, and calcium which can be replaced with heavy metals. Silica sand analysis showed that it contained no exchangeable ions for cation exchange process to take place. A core-void-shell TiO<sub>2</sub> was prepared using hydro-alcohol thermal method. The XRD showed that the TiO<sub>2</sub> powder was 100% anatase; SEM analysis showed that the TiO<sub>2</sub> nanoparticles were spherical; TEM analysis showed that the TiO<sub>2</sub> nanoparticles were hollow; BET analysis revealed that the TiO<sub>2</sub> nanoparticles had high surface area and were mesoporous.

#### 5.1.3. Acid Mine Drainage Treatment in CW

The effect of pH on the adsorption efficiencies of CW packing material was determined in batch studies using synthetic Fe wastewater, and the pH was ranged between 3 –5. It was found that increasing the pH slightly increased the adsorption efficiencies of the packing material. The HTR was investigated between 3- 5 days, and the hydraulic retention time of 5 days was more efficient than that of 3 days. The metals ions in CW packing materials were extracted with acid at the end of the experiment for analysis. The results showed that the heavy metals and sulphur were well retained within the constructed wetlands as sediments. Therefore, the application of unvegetated constructed wetland has a potential for practical applications to circumstances where harsh conditions do not allow vegetation to grow.

#### 5.1.4. UV/TiO<sub>2</sub> Photocatalytic Reduction of Cr(VI)

The effect of operating parameters on the photocatalytic reduction of Cr(VI) was investigated. High photocatalytic reduction of Cr(VI) was achieved under acidic environment (pH 3). The presence of Fe(III) enhanced the reduction of Cr(VI). An increase in photocatalyst loading slightly increased the reduction of Cr(VI). The reduction (54%) of Cr(VI) in constructed wetland effluent (DND sample) was achieved by using a slurry photocatalytic reactor under the best operating parameters obtained from batch reactors. This can be attributed to the accumulation of irreducible species such as Al, Ca, Ma, and Si on the active sides of the photocatalyst.

### 5.2. Recommendations

The constructed wetland employed in this study was a laboratory scale which yielded satisfactorily results, however it is still uncertain whether this technology can be commissioned on a larger scale. Therefore, it is recommended that the CW be up-scaled in order to investigate the effect of the size of the wetland on the treatment of AMD. It was observed that maintenance of the photocatalytic reactor employed in this study could be costly and time consuming; it is recommended that an annular photocatalytic reactor be employed because of its ease of operation and low cost maintenance. In addition, the life time of the prepared core-void-shell photocatalyst should be studied in order to determine after how many experimental runs before it deactivates. Lastly, it is

recommended that nanofiltration membrane stage (to remove Al, Ca, Ma, and Si ions) be employed before the constructed wetland effluents can be treated photocatalytically.

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# Appendix A: Images of Acid Mine Drainage sampling locations



Figure A1. Douglas North Discharge (DND)



Figure A2. Middleburg Steam and Coal (SCC)



Figure A3. T&DB Decant



Figure A4. Sampling location map





Tumelo Seadira	Photocata	lytic reactor			
Email: tumelose@mintek.co.za	Material : Quartz glass, Polyvinyl Chloride (PVC)				
Tel: 011 709 4182		DWG NO: 1	REV		
	Scale 1:1	ALL UNITS IN CM	SHEET 1 OF 1		

Figure B1. Slurry Photocatalytic Reactor



(a) Side view

Figure B2. Slurry Photocatalytic Reactor inside a shading box with 12 UVC bulbs (All units in cm).