Addis Ababa University
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ETHIOPIAN INSTITUTE OF WATER RESOURCES

Potentials of Local Rock Substrate and Plant Species for an Integrated Treatment of Chromium (Cr) Containing Tannery Wastewater Using Constructed Wetland Systems (CWSs), Bahir Dar, Ethiopia

By Agegnehu Alemu Wondimagegn

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Advisors: Prof. Brook Lemma
Dr. Nigus Gabbiye (Asso. Professor)

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This is to certify that the thesis presented By **Agegnehu Alemu Wondimagegn** Entitled **"Potentials of Local Rock Substrate and Plant Species for an Integrated Treatment of Chromium Containing Tannery Wastewater Using Constructed Wetland Systems, Bahir Dar, Ethiopia"** is submitted in partial fulfillment of the requirements for the degree of doctor of philosophy in water and health specialization water and wastewater treatment complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

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Declaration

I, the undersigned, declare that this thesis is my original work and has not been presented for a degree in any other university, and that all sources of materials used for the thesis have been duly acknowledged.

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Nomenclature

Symbols and Abbreviations

Symbols

A	Surface area (m^2)
b	The Langmuir constant (L mg^{-1})
C	The intercept (mg g^{-1}) of Weber and Morris model
C_A	Metal concentration in the above ground tissue (mg kg^{-1}) of DW
C_e	The equilibrium concentration (mg L^{-1})
C_O	Initial Cr concentration in solution (mg L^{-1})
C_P	metal concentration in the whole plant (mg kg^{-1})
Cr	Chromium
C_t	Concentration of Cr in solution at time t (mg L^{-1})
C_u	Metal concentration in the underground tissue (mg kg^{-1}) of DW
C_W	Metal concentration in the wastewater (mg L^{-1})
D	depth of the bed (m)
K_F	The Freundlich constant (mg^{1-n} .L^n g^{-1})
k_1	The rate constant of the pseudo-first-order kinetic equation (min^{-1})
k_2	The rate constant of pseudo-second-order kinetic equation (kg $mg^{-1}min^{-1}$)
k_{id}	The intraparticle diffusion rate constant (mg $g^{-1}min^{-0.5}$)
L	bed length (m)
m	Weight of adsorbent (g)
N	porosity of bed medium (as a fraction)
n^{-1}	The heterogeneity of the sorption sites
pH_i	Initial pH
pH_f	final pH

Q	flow rate (m^3 d^{-1})
S	Standard deviation
q_e	Amounts of Cr (VI) adsorbed at equilibrium (mg kg^{-1})
q_{max}	The maximum adsorption capacity (mg kg^{-1})
q_t	Amount of Cr sorbed at time t *(*mg kg^{-1})
R	Adsorbed amount at time t (%)
R_L	separation factor
t	time (min)
T°	Temperature (^{o}C)
T_{max}	The daily maximum temperature (^{o}C
T_{mm}	The mean maximum temperature (^{o}C)
V	Initial volume of the aqueous phase in contact with the adsorbent (L)
W	bed width (m)

Abbreviations

APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
BDH	British Drug Houses
BOD_5	5-day Biological Oxygen Demand
COD	Chemical Oxygen Demand
CSA	Central Statistical Agency
CWS	Constructed Wetland System
CWU	Constructed Wetland Unit
CW	Constructed wetland
DW	Dry weight
EC	Electrical Conductivity (µs cm^{-1})
EDS	Energy Dispersive X-Ray Spectroscopy
EIA	Ethiopian Investment Agency
EEPA	Ethiopian Environmental Protection Agency

EPTI	Environmental Technology Program for Industry
ET	Evapotranspiration (mm day^{-1})
FT-IR	Fourier Transform Infrared Spectroscopy
FWS	Free Water Surface
HDPE	High Density polyethylene
HF	Horizontal Flow
HLR	Hydraulic Loading Rate (m d^{-1})
HRT	Hydraulic Retention Time
HSSF	Horizontal subsurface flow
IARC	International Agency for Research on Cancer
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IPPC	Integrated Pollution Prevention and Control
IULTCS	International Union of Leather Technologists and Chemists Societies.
JCPDS	Joint Committee for Powder Diffraction Standards
MDL	Method detection limits
pHpzc	pH of point zero charge
SBR	Sequential Batch Reactor
SEM	Scanning Electron Microscopy
SSF	Subsurface Flow
TDS	Total Dissolved Solid (mg L^{-1})
TSS	Total Suspended Solid
TP	Total phosphorus (mg L^{-1})
UNEP	United Nations Environment Program
UNIDO	United Nations Industrial Development Organization
USDA-NRCS	United States Department of Agriculture-Natural Resources Conservation Service
USEPA	United States Environmental Protection Agency
VB	Vesicular Basalt
VSSF	Vertical Subsurface Flow
WHO	World Health Organization
XRD	X-ray Diffraction

Abstract

Chromium is one of the most important chemical substances widely applicable in various industrial processes both in elemental and compound forms. In developing countries like Ethiopia, industries, like tanneries discharge a large quantity of chromium with little treatment to the environment. Chromium occurs in the environment in two most common oxidation states, Cr (III) and Cr (VI), which have quite different chemical properties. Cr (VI) is extremely toxic compared to Cr (III) and can cause carcinogenic, teratogenic and mutagenic effects according to different studies.

In this study, vesicular basalt volcanic rock was obtained in the North West Ethiopia and its applications for adsorption of Cr (VI) and Cr (III) from aqueous solution were investigated. Different physical and chemical properties of the powdered rock was studied using Fourier transform infrared spectroscopy (FT-IR), Powder X-ray diffraction(XRD) and scanning electron microscopy (SEM). A series of batch experiments were carried out to study the effect of various experimental parameters (pH, ionic strength and contact time) on Cr (VI) and Cr (III) adsorption. The concentrations of Cr (III) and Cr (VI) were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and UV-Vis spectroscopy with 1, 5-diphenyl carbazide respectively.

Instrumental investigations of vesicular basalt rock indicated mineral compositions such as plagioclase, pyroxene, olivine, silica, hematite, magnetite and goethite. The major elemental compositions by weight were 48.46 % Oxygen, 17.37 % Silicon and 9.55 % aluminium. Other elements such as iron (Fe), calcium (Ca), sodium (Na), potassium (K) and magnesium (Mg) are also identified in the sample.

Batch adsorption experiments of Cr (VI) from aqueous solution onto the vesicular basalt rock indicated that the removal efficiency of Cr (VI) decreased with increasing pH and ionic strength. The maximum adsorption capacity was 79.20 mg kg^{-1} at pH of 2, initial concentration of 5.0 mg L^{-1} and adsorbent dosage of 50 g L^{-1}. In individual adsorption tests, Pseudo-second-order kinetic and Freundlich isotherm models could better describe Cr (VI) adsorption on the vesicular basalt.

Adsorption studies of Cr (III) onto the VB surface were highly dependent on pH. The maximum adsorption capacity was 0.976 mg g^{-1} at pH 6, initial concentration of 100 mg L^{-1} and adsorbent dosage of 50 g L^{-1}. Kinetic experiments indicated that the pseudo-second-order model displayed the best correlation with adsorption kinetic data. The adsorption mechanism of Cr (III) onto the surface of the vesicular basalt involved film diffusion and intraparticle diffusion during the reaction. Equilibrium studies indicated that Langmuir Isotherm model was found to be in better correlation with experimental data.

Adsorption studies of both Cr (VI) and Cr (III) indicated that vesicular basalt, which is abundantly available and low cost, has the potential to remove Cr (VI) and Cr (III) from polluted water.

Tannery wastewater is composed of a complex mixture of chromium and other organic and inorganic components from various processes that can critically pollute water bodies, if discharged without treatment. In this study, local emergent plant species were used in a HSSF constructed wetland system filled with vesicular basalt to investigate the removal efficiency of chromium containing tannery wastewater. Four pilot units were vegetated with *P.purpureum*, *T. domingensis*, *C. latifolius and E. pyramidalis*, and a fifth unit was left as an unvegetated (control). The HSSF constructed wetland system was effective in removing Cr, COD and BOD from the inflow tannery wastewater. Its removal efficiency reached up to 99.38 %, 84.03 % and 80.32% for Cr, COD and BOD_5 respectively in the 6 days of HRT. The removal efficiency of TSS, TP and NO_3^- obtained to a maximum of 70.59 %, 62.32% and 71.23 % respectively. The reduction of TDS, EC and Cl^- in the outlet reached up to a maximum 40.62 %, 34.52% and 25.09 % , respectively.

All the plant species used for removal of Cr (III) indicated BCF > 1 and TF < 1. These plants might not be adequate for phytoextraction, since most of the Cr (III) is accumulated in the roots, not in the harvestable parts of plants. Though *P. purpureum* showed low TF, it might be used to accumulate Cr (III) in its rhizomes, because of its rapid growth and biomass production. The removal of Cr (III) from the inflow tannery wastewater was high during operation, but no significant differences in performance were observed between the vegetated and the control

units. This might be precipitation of Cr (III) (hydroxides, sulphides, sulphates, and carbonates), and adsorption onto the surface of vesicular basalt bed in the 6 days of retention time.

Key words: Adsorption, Bioconcentration factor, Chromium (III), Chromium (VI), Constructed wetland, Tannery wastewater, Translocation factor, Vesicular Basalt

1.0 Introduction

1.1 Background of the Study

Ethiopia is a rapidly developing country with increasing population number and committed to industrialization, agriculture and tourism to create wealth and alleviate poverty (UNIDO, 2012). These development efforts are not exactly coupled with compatible environmental protection protocols, as a result of which the environment, especially water bodies are increasingly becoming polluted from both point and non-point sources (Girma, 2004). Urban settlements and industrial expansions constitute the largest source of wastewater discharges. Industries discharge a variety of wastes some of which are toxic to human beings and the general environment. According to EEPA (2003) report 90% of the industries found in Addis Ababa discharge their wastes without any form of treatment into sewage systems, nearby water bodies and open lands. The report also showed that leather industries and textile factories discharge their effluents in a similar way and they are the most polluting industries which happen to be critical environmental concerns in the country.

Industrial wastes are generated from different processes and the amount and toxicity of waste released varies with its own specific industrial processes. In tanning industry the processing of raw animal skins into commercial products requires many chemicals at various stages that include chromium salts. These chemicals in tannery effluents cause the highest toxic intensity per unit of output (Khan, 2001). Leta *et al.* (2003) reported that composite tanneries in Mojo region, wastewater samples possessed of total Cr (12 - 64 mg L^{-1}), BOD_5 (1900 - 4800 mg L^{-1}), COD (7900 - 15200 mg L^{-1}) and sulfide (325 - 930 mg L^{-1}). Another study in Modjo tanneries showed average concentration of total chromium 40 mg L^{-1}, COD composition between 2202 - 8100 mg $L^{-1}$and BOD_5 650 - 1950 mg L^{-1} (Tadesse and Seyoum, 2015). These values were all beyond the standard of surface water discharge limits set by WHO (1998), which is 1 mg/L.

Chromium occurs in the environment commonly as Cr (III) and Cr (VI) oxidation states, which have quite different chemical properties. Cr (VI) can be transformed to Cr (III) and vice versa

depending on pH, the presence of oxidizing and reducing compounds, redox potential, the kinetics of the redox reactions, and the total chromium concentration in soil, water and atmospheric systems (Wittbrodt and Palmer, 1995; Deng and Stone, 1996; Bokare and Choi, 2011).

Cr (III) is considered to be an essential trace element in animal and human nutrition, mainly for proper functioning, control of glucose and lipid metabolism (Langard and Norseth, 1986; Anderson 1989). But when present in excess, it has a potential of soil, surface and ground water contamination under specific conditions. Higher concentrations of Cr (III) mainly affects respiratory and immunological systems and likely to produce genotoxic DNA effects in the cell nucleus (ATSDR, 2012).

The chrome salt used in leather processing is in Cr (III) form, but there is a possible conversion to a more toxic Cr (VI) form in the tannery effluent(Kimbrough *et al.,* 1999). Cr (VI) is a powerful oxidant and many of its compounds are highly soluble in water that makes it easily bioavailable (Kotaś & Stasicka (2000). Cr (VI) is the most toxic and its effects are carcinogenic (IARC, *1990;* Cheng and Dixon, 1998; Rowbotham *et al.,* 2000); mutagenic (McCarroll *et al.,* 2010); and teratogenic (Qureshi & Shakoori, 1998) to humans and animals. Other most sensitive non-cancer effects of Cr (VI) compounds are severe respiratory (nasal and lung irritations), gastrointestinal (irritation, ulcer of the stomach and small intestine), haematological (microcytic, hypochromic anaemia), liver, kidney and reproductive organs damage and malfunctions such as decrease in sperm counts in males (Guertin *et al.*,2016 ; ATSDR, 2012).

There are various conventional methods for the treatment of Cr, such as chemical precipitation (Park *et al.,* 2008) adsorption and filtration (Babel & Kurniawan, 2003), ion exchange (Petruzzelli *et al.,* 1995; Rengaraj *et al.,* 2001), Electrocoagulation (Gao *et al.,* 2005), membrane separation (Kozlowski & Walkowiak, 2002) and electrodialysis (Ge *et al.,* 2016). These treatment techniques have shown performances up to 99% removal of chromium from the spent liquor of tannery effluent (Kornaros and Lyberatos, 2006). However, the methods are either expensive, energy intensive, complicated and /or produce secondary pollution and are often not

considered cost effective for small sized tannery industries (USEPA, 1997). These challenges make them not applicable for developing countries around the world.

In comparison adsorption method is simple to operate, solves the challenge of sludge disposal, and it is an effective method for the removal of Cr (VI) and other heavy metals from aqueous solutions. However, extra care and handling procedures are required for the proper management of the used adsorbents and recovery of heavy metals. Some studies have revealed that adsorbents like activated carbon are effective in removing a wide range of contaminants from water and wastewater, but they are not cost effective (Babel & Kurniawan, 2004; Li *et al.,* 2007; Owalude & Tella, 2016). In view of its high cost there is continuing search for low cost potential adsorbents for the removal of Cr and other heavy metals from water and wastewater. An adsorbent is considered as a low cost if it requires little processing, abundant in nature and is a by-product or waste material resulting from an industry (Bailey *et al.,* 1999). Several low cost adsorbents including clays (Kyziol-Komosinska *et al.,* 2014; Erdem *et al.,* 2004; Sprynskyy *et al.,* 2006; Sdiri *et al.,* 2011), industrial by-products (Mohan & Singh, 2002 ;Khan *et al.,* 2009) agricultural wastes (Ajmal *et al.,* 2003; Kadirvelu *et al.,* 2003), biomass (Moussavi & Barikbin, , 2010), and polymeric materials (Wang *et al.,* 2015), and vesicular volcanic rocks (Alemayehu *et al.,* 2011; Kyziol-Komosińska *et al.,* 2014) have been investigated for Cr (VI) removal.

Vesicular basalt rocks have unique properties as described below that deserve further investigation. Vesicular basalt is a volcanic rock formed by rapid cooling of lava on the earth's surface. Pumice and scoria are the most abundant vesicular basalt rock types. Pumice is a white or grey finely porous rock frothy with air bubbles and rich in silica (felsic) whereas Scoria is texturally macro-vesicular and more dense than pumice, silica-deficient (mafic) rock owning different colours ranging from red to black depending on its mineral composition (Carlson *et al.,* 2008; Mboya *et al.,* 2017).Vesicular basalt is abundant in many parts of the world such as Western Europe, Central America, Western South America, Western and Northern part of the Pacific belt (Soubrand-Colin *et al.,* 2005), Saudi Arabia (Moufti *et al.,* 2000), Central Africa (Benedetti *et al.,* 2003) and East Africa (Tadesse *et al.,* 2003). Its abundance, variation in the chemical composition and variation of surface nature depending on the source composition and

type of eruption of the magma received considerable interest to assess the ability of locally available vesicular basalt for the removal of Cr (VI) and Cr (III) from wastewater.

Currently, CW treatment for industrial wastewaters is attracting the public attention, due to its appropriate technology with low cost and easy maintenance**.** Moreover, this method is environmentally sound and economically feasible. A constructed wetland system (CWS) consists of a properly designed basin that contains water, a substrate and plants, which may be manipulated to some extent to provide an adequate performance and treatment efficiency (USEPA, 1995). CWS are highly complex systems that separate and transform contaminants by physical, chemical, and biological mechanisms that may occur simultaneously or sequentially as the wastewater flows through them (USEPA, 2000). The process of metal removal in wetlands include sedimentation, filtration, adsorption, complexation, precipitation, cation exchange, plant uptake and microbially-mediated reactions especially oxidation (Watson *et al.,* 1989; Dunbabin and Bowmer, 1992; Kadlec and Knight, 1996).

Heavy metals are effectively removed in CWS by a combination of physico-chemical and biological processes (Dunbabin and Bowmer, 1992; Kadlec and Knight, 1996). Despite a lot of recent research efforts, the understanding of the complex removal processes of pollutants in CWS, how they interact with each other and which the major influencing factors are still rather incomplete. A reason for this is that CWS depend on the interaction of many different components, including the substrate, sediment, vegetation and water column (Stottmeister *et al*., 2003). Natural biogeochemical processes can be involved in the removal of heavy metals from the wastewater in CWs. The way in which a wetland is constructed largely determines how wastewater treatment occurs and which mechanisms are effectively operating in that specific physical condition (Kosolapov *et al*., 2006).

The selection of plants is an important issue in CWS, as they must survive the potential toxic effects of the wastewater and its variability. *Phragmites australis* (common Red), *Typha latifolia,* bulrushes (*Scipus* spp.) and reed canarygrass (*Phalaris arundinacea*) have been used for both domestic and industrial wastewater treatment are widely used wetland plant species in a CWS (Bastviken, 2005; Vymazal and Kropfelova , 2005). Recent studies have shown that some

wetland plant species such as *Typha domingensis*, *Phragmites karka* (Reeds) , *Phragmites australis*, *Arundo donax* , *Sarcocornia fruticosa* have the potential to withstand the saline chrome containing tannery effluent and phytoremediate chromium after secondary treatment in a constructed wetland system at a pilot scale (Tadese & Seyoum, 2015; Calheiros *et al* ., 2012; Saeed *et al.*, 2012).

There has been some recent work that has attempted to investigate the influence of two different substrates gravel and granite in the removal of chromium from tannery effluent. This was operated in a simple gravity-flow horizontal subsurface flow unit vegetated with *Typha latifolia* operated after conventional primary treatment supplemented with chemicals. Both rock types were efficient at retaining chromium, with 57-83% and 67-77% efficiencies in the first run for the gravel and granitic rocks, respectively (Dotro *et al.*, 2012).

1.2 Statement of the Problem

Tannery industries are one of the most chemical intensive processes to convert animal skins and hides into leather products. In different unit operations numerous types of toxic chemicals such as chromium are released into the environment that can critically affect the health of biological systems.

In Ethiopia, the numbers of tannery industries are increasing due to availability of raw materials, namely, animal skins and hides. These industries release large quantities of toxic tannery effluents into the environment with little or no treatment. Bahir Dar Tannery is one of these industries which discharges its wastewater into the nearby water bodies and/or open fields with little or no treatment at all**.** As a result, pollution of the environment is intensifying in the area. This may contribute to pollution of the nearby fresh water bodies of Abbay River and Lake Tana which are the homes of many Flora and Fauna, including fishes that are consumed by a very high population in Bahir Dar and elsewhere in the country. The existing conventional treatment methods are not feasible. It is therefore eminent to develop an environmentally benign, low cost treatment options to ensure the reduction of the toxic chromium bearing tannery effluent.

This study therefore focuses on the evaluation of the adsorption potentials of Cr (VI) and Cr (III) from aqueous solutions using locally available vesicular basalt volcanic rock types in the lab scale and use it as a supporting medium for the pilot scale wetland plant growth. The selected local wetland plant species were vegetated and their potentials of chromium biosorption were investigated. Moreover, the integrated removal of chromium and other organic and inorganic compositions of the tannery wastewater were studied in a HSSF constructed wetland system.

1.3 Significance of the Study

The significance of this study is to reduce the high concentration of toxic chromium containing tannery effluent which is one of the top pollutants of the environment with locally available high sorbent rocks and plant species in a HSSF constructed wetland system in environmentally friendly way with low cost and energy consumption.

The study will help tannery industries to raise their interest to use the low cost constructed wetland system on a large scale and reduce the chromium containing effluent discharge to the open lands or water bodies that critically affect the human health and the environment as a whole.

This study will help as an input to different bodies such as governmental organizations, non-governmental organizations, policy makers, researchers, etc. involved in the protection of the health of people, livestock and generally the environment from heavy metal contaminations such as chromium.

1.4 Objectives of the Research

1.4.1 General Objective

- ✓ To investigate the potential of local rock substrate and plant species for an integrated treatment of Cr containing tannery wastewater in CWS.

1.4.2 Specific Objective

- ✓ To characterize the compositions of the VB rock using spectroscopic techniques.
- ✓ To investigate the adsorption behaviour of Cr (VI) and Cr (III) on the rock surface at different operating conditions (such as pH, initial concentration of Cr and contact time).
- ✓ To characterize the compositions of the Bahir Dar Tannery effluent and evaluate the wetland plants tolerance to the toxic chromium containing wastewater.
- ✓ To construct a pilot scale HSSF wetland unit by integrating the VB and local plant species
- ✓ To investigate the biosorption potential of chromium by the wetland plant species in the HSSF constructed wetland system.
- ✓ To evaluate the potential of an integrated pilot scale constructed wetland units for the removal of efficiency of Cr and other pollutants from tannery effluent.

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2.0 Literature Review

2.1 Leather Industries in Ethiopia

Ethiopia has a long tradition in processing and export of leather and leather products. However, the modern leather goods industry dates back to the time when the modern tanning industry was established in the mid 1920s (EIA, 2008). According to CSA (2011) report the country is one of the richest countries of Africa in livestock resource; having 53.4 million cattle, 25.5 million sheep and 22.7 million goats. It is estimated that the country can collect 3.7 million cattle hides, 8.4 million sheep and 7.7 million goat skins per year. The availability of raw materials (skins and hides) in the country illustrates the potentials of Ethiopia to establish leather industries to export finished leather products, create jobs and earn sizable international revenues. The manufacturing sector showed an average growth performance of 10% between the years 2004/05-2010/11(UNIDO, 2012) to which the leather industries contribute substantially.

According to UNIDO (2012) report, in Ethiopia currently there are 26 tannery industries in operation (**Table 2.1**). Ethiopia Tannery with 12,000 sheep and goat skin and 1,200 cowhide soaking capacity and Ethio-Leather with 15,500 sheep and goat skin and 1,050 cowhides soaking capacity are the two largest industries.

Table 2. 1 Tannery industries in Ethiopia (UNIDO, 2012).

No	Name of factory	Location	Soaking capacity per day	
			Sheep and goat skin	Cow hides
1	Ethiopia Tannery	Mojo	12,000	1200
2	Kolba Tannery	Mojo	8,000	500
3	Gelan Tannery	Mojo	3,000	0
4	Mesako Global Tannery	Mojo	3,000	0
5	East Africa Tannery	Mojo	8,000	0
6	Modjo Tannery	Mojo	8,000	500
7	Friendship Tannery	Mojo	10,000	1,000

8	Farida Tannery	Mojo	7,000	0
9	Vasen United Tannery	Mojo	5,000	0
10	Bale Tannery	Debre zeit	2,000	400
11	Hora Tannery	Debre zeit	7,000	0
12	Ethio Leather Industry	Addis Ababa	15,500	1050
13	Dire Tannery	Addis Ababa	6000	600
14	Walia Tannery	Addis Ababa	5000	1000
15	Batu Factory	Addis Ababa	8000	1000
16	Addis Ababa tannery	Addis Ababa	2400	1200
17	Christal Tannery	Addis Ababa	1750	100
18	China Africa Tannery	Sululata	10,000	0
19	Debre Berhan Tannery	Debre Berhan	6,000	0
20	Hafde Tannery	Sebeta	6,000	250
21	Blue Nile Tannery	Sebeta	3,500	0
22	Kombolcha Tannery	Kombolcha	6,000	0
23	Mersa Tannery	Mersa	6,500	325
24	Sheba Tannery	Wukro	6,000	600
25	Bahir Dar Tannery	Bahir Dar	4,000	0
26	Habesah Tannery	Bahir Dar	4,000	0
	Total		163,650	9725

Most of the leather industries discharge their wastewater directly into the surrounding surface water and/ or open land without any treatment (EEPA, 2003). As a consequence, the burdens of environmental pollution are increasing with poor government intervention policies. The effluent from industries to the surrounding water bodies affects the water quality and causes reduction and death of aquatic fauna and flora (Seyoum *et al.*, *2003*).

Davimpex Enterprises Bahir Dar Tannery Plc was established in 1998 and produces various types of leather from sheep and goat skins .It has a soaking capacity of about 4000 sheep and goat skins per day (UNIDO, 2012). In the processing of skins in to leather; numerous chemicals are used in different unit processes to produce a high quality of leather. Chrome is one of the

chemicals added in the tanning process. Finally, the industry discharges the toxic wastewater with little treatment to open land and water bodies.

2.2 The Chemistry of Chromium in the Environment

The name chromium is related to many different characteristic colours of its compounds (Greek word chroma meaning colour) (Motzer *et al.*, 2005). Chromium (Cr) is a Group VID transition metal element with atomic number of 24 and an atomic mass of 52.00 amu. The unique properties chromium are associated with its partially occupied d orbitals and the potential for several different oxidation states, which can range from -2 to +6. The most common forms of chromium in the environment are chromium (III) and chromium (VI), Except for the rarely, naturally-found, elemental Cr with an oxidation number of zero, Cr (0), other oxidation states of Cr are unstable and therefore, are not found in the natural environment.

Chromium (III) is the most stable form of chromium in the environment and it can be produced by different physical and chemical processes such as hydrolysis, complexation, redox reactions and adsorption (Stollenwerk and Grove, 1985). Cr (III) in the presence of H_2O or OH^- without complexing agents, it can produce hexa-aquachromium (III) and its hydrolysis product (Rai *et al.*, 1989).

$$Cr(H_2O)_6^{3+} + H_2O \rightleftharpoons Cr(OH)(H_2O)_5^{2+} + H_3O^+ \qquad pka = 3.85 \qquad (1)$$

$$Cr(OH)(H_2O)_5^{2+} + H_2O \rightleftharpoons Cr(OH)_2(H_2O)_4^{+} + H_3O^+ \qquad pka=10.06 \qquad (2)$$

$$Cr(OH)_2(H_2O)_4^{+} + H_2O \rightleftharpoons Cr(OH)_3 + H_3O^+ \qquad pka =18.70 \qquad (3)$$

Cr^{3+} is a hard acid which exhibits a strong tendency to form hexacoordinate octahedral complexes with a variety of ligands such as water, ammonia, urea, ethylenediamine, and other organic ligands containing oxygen, nitrogen or sulphur donor atoms (Nakayama *et al.*, 1981; Salem *et al.*, 1989). The complexation of Cr^{3+} by ligands other than OH^- increases its solubility when the ligands are in form of discrete molecules or ions.

Chromium (VI) exists in aqueous solutions as chromate (CrO_4^{-2}), hydrogen chromate or bichromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{-2}$).The existence of these ions depend on pH and the concentration of Cr (VI) ions. These oxyanions with hexavalent chromium will be reduced to trivalent forms by electron donors such as organic matter or reduced inorganic matter in the environment (Stollenwerk and Grove, 1985).

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^- \qquad \log K = 6.03 - 6.55 \qquad (4)$$

$$2CrO_4^{2-} + H^+ \rightleftharpoons Cr_2O_7^{2-} \qquad \log K = 13.99 - 14.77 \qquad (5)$$

$$2HCrO_4^- \rightleftharpoons 2Cr_2O_7^{2-} + H_2O \qquad \log K = 1.60 - 2.16 \qquad (6)$$

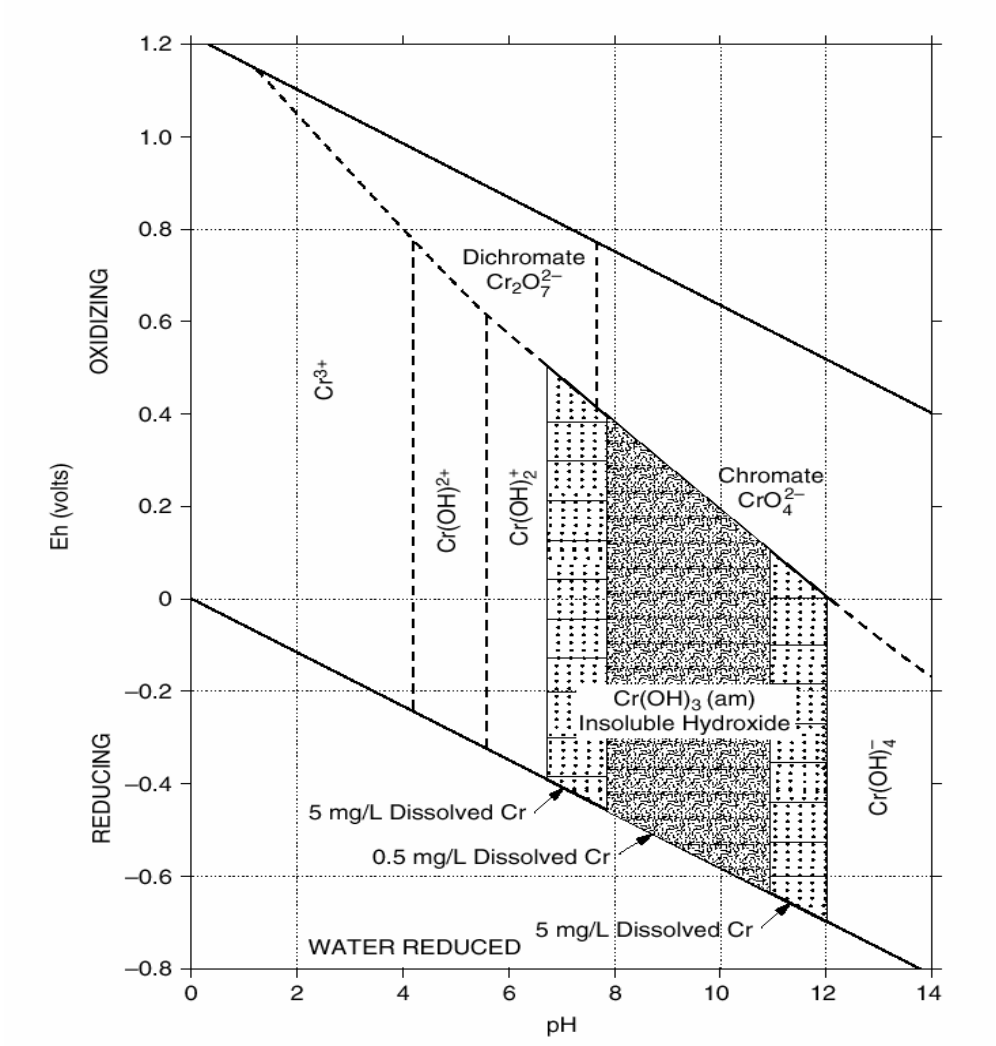


Fig. 2.1 Eh-pH diagram for the chromium–oxygen–water system (Hem, 1989).

The aqueous solubility of Cr (III) is a function of the pH of the water. Under neutral to basic pH, Cr (III) will precipitate and conversely under acidic pH it will tend to solubilize. The forms of Cr (VI) chromate and dichromate are extremely soluble under all pH conditions, but they can precipitate with divalent cations (Kimbrough *et al.,* 1999). The recommended limit for Cr total concentration in water is 50 μg L^{-1} (WHO, 2008).

2.3 Sources of Chromium Contamination in the Environment

Chromium is a naturally occurring element present in the earth's crust in the form of compounds or as ions in water and is a common contaminant in surface water and groundwater (Bartlett and James, 1988). Chromium is also released to the environment from anthropogenic sources and it is the major contributors of chromium contamination in the environment (ATSDR, 2008). Cr can enter the atmosphere as a result of fossil fuel burning, steel production, stainless steel welding, and Cr manufacturing, whereas, discharges to water and soil can result from industrial processes such as electroplating, tanning, water treatment, or disposal of coal ash (USEPA, 1995). Cr (III) occurs naturally in compounds, which exhibit a wide range of colours, structure, and chemical properties and used in many industries. However, Cr (VI) compounds are produced industrially essentially by heating Cr (III) compounds (Bartlett and James 1988). Most of the chromium released in water will be deposited in the sediments (ATSDR, 2012).

2.3.1 Chrome Tanning

Chrome salt is an important chemical used in the process of converting raw animal hides in to leather. Pickle Chrome tanning is one of the most polluting processes in leather industry .The problem with this method is that all the chemicals are dissolved in the water, but not all are absorbed by the hide. This means that the effluent from the tanning process itself contains a lot of Cr (III) and chlorides in the resulting wastewaters. Specifically, 70% of total chrome and 20% of chlorides are discharged during this process (IULTCS, 2004).At present nearly 90% of all leather produced is tanned using Cr salts (Stein and Schwedt, 1994). This is because chrome tanning is quick , easy to produce, stain & water resistant, soft and supple to the touch, cheap to

buy and has a high degree of thermal resistance as compared to vegetable tanning (Hafez *et al.*, 2002).

2.4 Impact of Chromium Containing Tannery Effluents on the Environment

The processing of hides and skins into leather is a complex procedure that requires a precise combination of many chemical and mechanical operations. During this process, the leather is made resistant to biological decays by stabilizing the collagen structure of the hide, using natural or synthetic chemicals (UNEP, 1991). The tanning process can be broadly divided into three stages: pre-tanning (Beamhouse operation); the tanning process; and post-tanning (the finishing operation). Finishing includes mechanical processes to shape and smoothen the leather and chemical treatments to colour, lubricate, soften and apply a surface finish to the leather.

In the tanning processes various types of chemicals used include lime, common salt, sodium carbonate, sodium bi-carbonate, chrome sulphate, sodium sulphate, vegetable oils, fat liquors and dyes. Moreover other chemicals such as zinc chloride, formaldehyde and mercuric chloride are used as disinfectants, sodium chloride in curing purposes and sodium fluoride to prevent putrefaction, calcium oxide for liming, ammonium chloride, sodium sulphate, borax and hydrochloric acid for deliming. Hence, the tannery effluent is characterized by high Cr concentration; high BOD, COD, pH, and high dissolved solids and strong colour (Krishanamoorthi *et al.,* 2009). The discharge of various combined chemicals from tanneries pollute water bodies, soil and the air and seriously affect the environment as shown in **Fig.2.2** below.

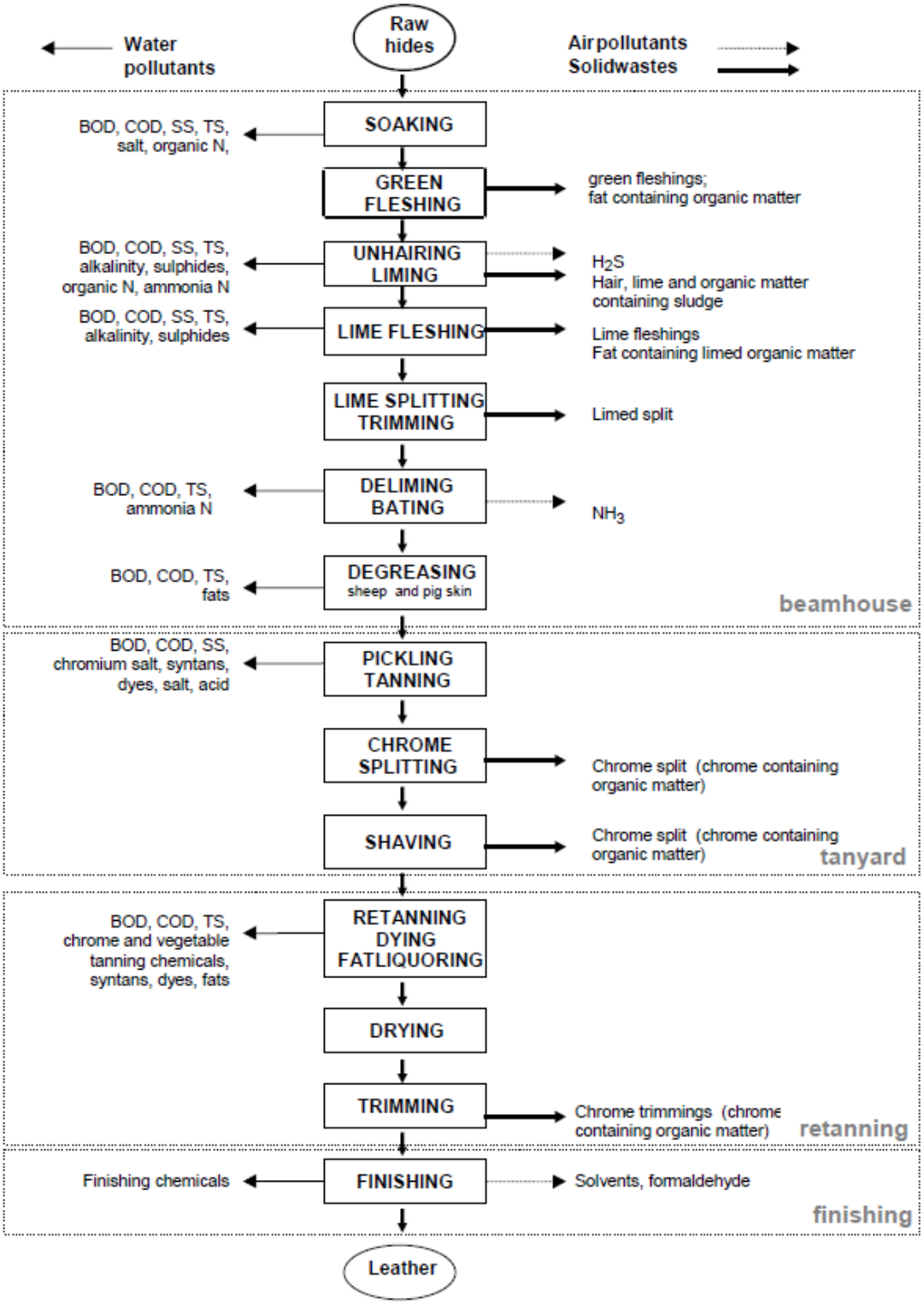


Fig. 2.2 Schematic of tanning process, indicating waste stream (UNEP, 1991)

In chrome tanning industries, Cr (III) in the effluents is the most expected form but with Redox reactions occurring in the sludge, an increase in the hexavalent form can occur. Again Cr (VI) can be reduced to chromium (III) under suitable conditions in the wastewater, if an appropriate reducing agent is available such organic matter, hydrogen sulphide, sulfur, iron sulphide, ammonium, and nitrate (Kimbrough *et al.*, 1999). High content of organic matter originating from hide/skin material processing is effective in forming soluble Cr (III) complexes (Stein and Schwedt, 1994; Walsh and O'Haloran, 1996).

2.5. Toxic Effects of Chromium

Major factors governing the toxicity of chromium compounds are its oxidation state and solubility (ATSDR, 2008). Cr (VI) compounds, which are powerful oxidizing agents and thus tend to be irritating and corrosive, appear to be much more toxic systemically than Cr (III) compounds, given similar amounts and solubilities. The variation in toxicity may be related to the ease to pass through cell membranes and its subsequent intracellular reduction to reactive intermediates. Cr (VI) enters cells by facilitated uptake, whereas Cr (III) crosses cell membranes by simple diffusion; thus, cellular uptake of Cr (VI) is more effective than the uptake of Cr (III) (ATSDR, 2012). Furthermore, in biological systems, reduction of Cr (VI) to Cr (III) results in the generation of free radicals, which can form complexes with intracellular targets.

In humans and animals, Cr (III) is an essential nutrient that plays a role in glucose, fat, and protein metabolism by potentiating the action of insulin (Anderson, 1981). Although Cr (III) has been reported to be an essential nutrient, exposure to high levels via inhalation (air), ingestion (water, food), or dermal contact may cause some adverse health effects targeted at the respiratory (following inhalation exposure) and immunological systems (ATSDR, 2012). Adverse health effects associated with Cr (VI) exposure include occupational asthma, eye irritation and damage, perforated eardrums, respiratory irritation, kidney damage, liver damage, pulmonary congestion and edema, upper abdominal pain, nose irritation and damage, respiratory cancer, skin irritation, and erosion and discoloration of the teeth, allergic contact dermatitis, gastrointestinal (irritation, ulceration of the stomach and small intestine), hematological (microcytic, hypochromic anaemia)

, and reproductive (effects on male reproductive organs, including decreased sperm count and histopathological change to the epididymis) (ATSDR, 2008; ATSDR, 2012).

2.6 Treatment Methods of Chromium in Tannery Effluents

Treatment of tannery effluent is a challenge because it is a mixture of biogenic matter of hides, inorganic chemicals and a large variety of organic pollutant with large molecular weights and complex structures (Genschow *et al.,* 1996). Tanneries are typically characterized as pollution intensive industrial complexes which generate widely varying high-strength toxic wastewaters per unit output (Khan *et al.,* 1999). During the tanning process at least about 300 kg chemicals are added per ton of hides (Verheijen *et al.,* 1996). Tannery wastewaters are variable due to the different procedures used for hide preparation, tanning and finishing. These procedures are dictated by the kind of raw hides employed and the required characteristics of the finished product.

The chemistry and geochemistry of chromium helps to understand the occurrence of Cr in nature .The oxidation states of Cr has a significant effect on the transport and fate of Cr and on the type and cost of treatment required to reduce Cr concentrations. There are different methods used to reduce potentially harmful substances before effluents are released to the environment. The effluent treatment varies among tanneries but generally consists of a selection of the following processes: mechanical treatment, physico-chemical treatment and biological treatments (IPPC, 2003; US EPA, 2004)

2.6.1 Mechanical Treatment

The mechanical treatments include operations for a first treatment of the raw effluent. The solid and organic content in the untreated wastewater and subsequently the loads introduced in the biological stage can be reduced through primary sludge separation. Pre-treatment includes screening to remove coarse material such as pieces of skin and leather fibres, which would otherwise block pipes and pumps. The materials removed are compacted and become easy to handle. These wastes that make up the gross suspended solids, including hair and gross fats

which are not in emulsion that make up to 30 - 40 % of the raw waste stream that can be removed by properly designed screen (IPPC, 2003).

2. 6. 2 Physico-chemical Treatment System

Physico-chemical treatment of tannery effluents consist of coagulation, flocculation, sedimentation, filtration, air stripping, chemical precipitation, adsorption, ion exchange, electrochemical (electro-oxidation), and chemical oxidation (Ramesh *et al.*, 2007; Kyung-Sok *et al.*, 2004; USEPA, 2004; UNEP, 2004; Linda & Peter, 1999*).*

Conventional treatment methods for the removal of chromium from tannery effluents are simple in principle. However, they are expensive requiring high operating and maintenance cost, and consumption of chemicals. They may also produce harmful secondary products such as chrome-bearing solid wastes. Using precipitation method there is 99% Cr removal, 85-90% BOD_5 removal and 60 - 70% removal of COD can be achieved (Kornaros and Lyberatos, 2006).

2.6.2.1 Adsorption

Adsorption is a process in which substances dissolved in fluid phase are accumulated onto the surface of a solid through chemical or physical forces (Mohan *et al.*, 2008). This process can remove the contaminating metals from water and wastewater. The solid material onto which accumulation of the pollutant or contaminant takes place is called the adsorbent. The removal efficiency of adsorbents depends on pH, influent concentration; contact time and sorbent dosages (Ajouyed *et al.*, 2011). There are different types of adsorbents available which can be used for the removal of chromium in water and wastewater. The common adsorbents are synthetic polymeric sorbents, natural and synthetic zeolites, fiber and Lignite, industrial wastes or by-products, agricultural by-products, bio-sorbents, activated carbon, clay minerals and oxides such as kaolinite, and bauxite (Mohan & Pittman, 2006).

Natural clay minerals have the characteristics of adsorption and cation exchange capabilities which play a significant role by taking up all kinds of pollutants toxic to human and wildlife in the environment (Ajouyed *et al.*, 2011). The application of clay minerals differ widely based on

their cation exchange capacity, swelling capacity, high specific surface area, and consequential strong adsorption capacity(Xi *et al* .,2010). Adsorptions of heavy metals on clays mainly depend on their mineral compositions and external conditions (Yu *et al.*, 2008). According to Khan and Singh (2010), an Indian clay adsorbent removed 87 % Cr (VI) with initial concentration of 30 mg L^{-1} at pH 2.5. Kaolinite and Illite clays absorbed Cr (VI) a maximum of 0.047 and 0.033 Mg g^{-1} respectively at a pH of 2-4, which best fits the Freundlich Model (Ajouyed *et al.*, 2011). The adsorption of Cr (VI) on laterite removed about 80%, the reaction was fast and reached equilibrium within two hours. The optimal adsorption of Cr (VI) on the laterite soil was 250 µg mL^{-1} at a pH of 2-5 (Yu *et al.*, 2009). Other studies on adsorption capacity of Cr (VI) on different adsorbents and reaction parameters are shown in **Table 2.2** below.

Table 2. 2 Adsorption capacity of Cr (VI) on different adsorbents

Adsorbent	T (oc)	pH	Adsorbent dose (g L^{-1})	Cr (VI) conc. (mg L^{-1})	Adsorption capacity (mg g^{-1})	Reference
kaolinite	30	4.6	2.0	50.0	6.10	(Bhattacharyya & Gupta, 2006)
Bentonite	40	2	50	0.5-50.0	0.57	(Khan and Khan, 1995)
Turkish clay	20	1	10	250.0	3.61	(Akar *et al.,* 2009)
pumice	24.5	2.0	100.0	10.0	0.046	(Alemayehu *et al.,* 2011)
Scoria	24.5	2	100.0	10.0	0.027	(Alemayehu *et al.,* 2011)
Sawdust	30	2	16	100.0	15.82	(Dakiky et al., 2002)
Activated alumina	25	2	10	10.0	7.44	(Mor *et al.,* 2007)
Activated charcoal	25	4	10	10.0	12.87	(Mor *et al.,* 2007)
palygorskite clay	25	7.0	2	100.0	58.50	(Haghseresht *et al.,*1998)
Akadama clay	25	2	5	50	4.29	(Zhao *et al.,* 2013)

Cr (III) is the primary form of Cr that is retained by adsorption and it behaves like a positively charged ion when adsorbing onto surfaces (Motzer *et al.*, 2005). As pH increases, surfaces get deprotonated, increasing the attraction between Cr (III) and the surface. Adsorption of Cr (III) is therefore enhanced as pH increases. If the adsorbent has a high organic content, adsorption is also enhanced, as more sites are available for sorption to occur. Trivalent chromium readily substitutes Fe^{3+} in minerals, and co-precipitates with Fe^{3+} as insoluble $Fe(OH)_3$ at high pH values (Hawley *et al.*, 2004). In contrast, Cr (VI) is usually mobile, its adsorption decreases with increasing pH.

It is reported that indigenous China Clay adsorbent removed 80.3 % Cd ions at pH 6.5 (Sharma, 2008) and local illitic clay in Jebel Tejra (Tunisia), North Africa, showed an adsorption capacity of 35.70 mg g^{-1} for Cr (III) and 52.5 mg g^{-1} for Cd (II) in a synthetic aqueous solution (Ghorbel-Abid *et al.*, 2010) . Brazilian vermiculite was used for the removal of specific toxic metal ions such as zinc, cadmium, chromium and manganese from aqueous solutions. The adsorption efficiency of the clay was 39.05 mg g^{-1} Cr, 63.28 mg g^{-1} Cd, 41.77 mg g^{-1} Zn (II) and 31.53mg g^{-1} Mn (II) (da Fonseca *et al.*, 2006). Moreover, various studies of adsorption capacity of Cr (III) on different adsorbents at various reaction conditions such as T (^{o}c), pH, adsorbent dose and initial concentration are shown in **Table 2.3** below.

Table 2. 3 Adsorption capacity of Cr (III) on various adsorbents and operating parameters

Adsorbent	**T (^{o}c)**	**pH**	**Adsorbent dose (g L^{-1})**	**Cr (III) conc. (mg L^{-1})**	**Adsorption capacity (mg g^{-1})**	**Reference**
China bentonite	20	7	20	100	4.68	(Chen *et al.*, 2012)
Brazilian scolecite	25	6	10	50	3	(Dal Bosco *et al.,* 2005)
powdered marble	25	5	12	3210	262	(Elabbas *et al.,* 2016)
Celtek clay	20	6	2	4	21.55	(Sarl *et al.,* 2007)
Kaolin	25	6	25	300	0.898	(Liu *et al.*, 2016)
natural sepiolite	20	3	25	100	0.5341	(Kocaoba, 2009)

Activated carbon	25	5	3	20	23.04	(Leyva-Ramos *et al.,* 1995)
Rice hull ash	30.0	4.1	20	350	15.66	(Wang & Lin, 2008)
Tunisian smectite	25	-	10	20	15.47	(Ghrab *et al.,* 2018)
Illite	-	2	4	0.5	0.033	(Ajouyed *et al.,* 2011)

Adsorption kinetics models

The study of adsorption dynamics describes the solute uptake rate and this rate controls the habitation time of adsorbate uptake at the solid–solution interface. In addition, sorption kinetics shows a large dependence on the physical and/or chemical characteristics of the adsorbent material (Tan & Hameed, 2017). There are three steps in an adsorption process (Largitte & Pasquier, 2016). First, the external mass transfer of the adsorbate from the bulk solution to the external surface of the adsorbent, followed by the internal diffusion of the adsorbate to the sorption sites and finally the sorption itself. The prediction of the adsorption kinetics is an important step for the design of an adsorption system. The adsorption rate constants and the order of adsorption rate kinetics are important physico-chemical parameters to evaluate the basic qualities of the good adsorbent. The Pseudo-first-order and the pseudo second-order equation are the most widely used kinetic models to describe the adsorption of a solute from a liquid solution as shown **Table 2.4** below.

Table 2. 4 Empirical adsorption kinetic models

Kinetic Model	**Equation**	**Reference**	**Equation no**
Pseudo-first-order	$\frac{dq_t}{dt} = K_1(q_e - q_t)$	(Lagergren, 1898)	(2.1)
Pseudo-second-order	$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2$	(Ho *et al.,* 2000)	(2.2)

Adsorption mechanism

The adsorption of metal ions onto an adsorbent is a solid–liquid adsorption process which is characterized by film diffusion (external diffusion), intraparticle diffusion (internal diffusion), or

both (Kiruba *et al.*, 2014). The kinetic models only show us whether adsorption process follows pseudo-first-order or pseudo-second-order kinetics. In order to find the adsorption mechanism and rate controlling steps in the removal of metal ions by adsorbent, important models such as Weber and Morris intraparticle diffusion model and Boyd kinetic model are used.

The Weber and Morris model investigates whether intraparticle diffusion was the only rate-controlling mechanism in the adsorption process (Weber and Morris, 1963) and is expressed as:

$$q_t = k_{id} t^{1/2} + C \tag{2.3}$$

The plot of q_t versus $t^{1/2}$ is linear and passes through origin; intra-particle diffusion is the only rate-limiting step. Otherwise, the rate-limiting step is governed by both adsorption and intra-particle diffusion.

The Boyd model determines whether the actual slowest step in the adsorption process is film diffusion or pore diffusion. The Boyd model equations (Boyd *et al.*, 1947) are given in equation (4) and (5) below:

$$\mathrm{F} = 1 - \frac{6}{\pi^2}\exp(-\mathrm{Bt}) \tag{2.4}$$

$$\mathrm{F} = \frac{\mathrm{q_t}}{\mathrm{q_e}} \tag{2.5}$$

Where F is the function of the solute sorbed at different time t. Bt is the mathematical function of F. Bt is calculated by transforming and then integrating Equation (2.4) and (2.5) as follows (Reichenberg, 1953):

$$\text{For F value} < 0.85, \quad \mathrm{Bt} = 2\pi - \frac{\pi^2 \mathrm{F}}{3} - 2\pi\left(1 - \frac{\pi \mathrm{F}}{3}\right)^{1/2} \tag{2.6}$$

$$\text{F value} > 0.85, \quad \mathrm{Bt} = -0.4977 - \ln(1 - \mathrm{F}) \tag{2.7}$$

The Boyd linear plot Bt versus t passes through the origin, it indicates that particle diffusion is the actual slowest step in the adsorption of adsorbate ions onto the adsorbent. But, if the plot does not pass via origin, the adsorption process is controlled by film diffusion.

Adsorption Isotherm

The principle of the adsorption isotherms relates the adsorbate concentration in the bulk and the adsorbed amount at the interface (Eastoe and Dalton, 2000). The adsorption isotherms of adsorbate onto the adsorbents will be evaluated by plotting the equilibrium sorption data using the Langmuir and Freundlich models (**Table 2.5**). The assumptions of the Langmuir model are such that sorption of sorbate occurs in monolayer on a homogeneous sorbent surface, and sorbate species do not interact with each other. However, the Freundlich isotherm model works based on the assumption that the sorption of adsorbate occurs in multilayer on heterogeneous adsorbent surfaces since the active sites of sorbent have heterogeneous surface energy (Eastoe and Dalton, 2000; Hameed *et al.,* 2008). Adsorption isotherm is characterized by certain constants, which express the surface properties, the affinity of the adsorbent, and also can be used to find the adsorption capacity of adsorbent.

Table 2. 5 Freundlich and Langmuir isotherm Models

Isotherm	**Equation**	**Reference**	**Equation no**
Langmuir isotherm	$Q_e = \frac{q_{max} b C_e}{1 + b C_e}$	(Langmuir,1918)	(2.8)
Freundlich isotherm	$Q_{e\,=} K_F (C_e)^{1/n}$	(Freundlich,1906)	(2.9)

The kinetic studies showed that the adsorption of Pb^{2+} ions onto different weathered basalt rock followed to the pseudo-second-order model and the adsorption isotherm data were fitted well to the Langmuir model with the maximum adsorption capacities between 15.92 and 23.31 mg g^{-1} (Ammar *et al.*, 2016). A study on adsorption kinetics of total Cr onto pumice and scoria vesicular basalt rocks indicated a good fit with pseudo-second-order kinetics and isotherm studies

indicated that data fit well to the Langmuir model with maximum adsorption 0.071 g kg^{-1} for pumice and 0.016 g kg^{-1} for scoria from tannery wastewater (Aregu *et al.,* 2018). Alemayehu *et al.* (2011) also reported that kinetic studies of adsorption of Cr (VI) onto pumice and scoria in a synthetic solution, kinetic data fitted well with pseudo-second-order reaction rate model and the equilibrium data followed the Langmuir and Freundlich isotherm models.

2.6.3. Microbiological Treatment Systems

The microbiological treatment of wastewater is based on the consumption of organic matter by microorganisms which include bacteria, viruses, algae and protozoa. In this system the stabilization of waste is done by decomposing in to harmless inorganic solids by aerobic, facultative or anaerobic (or some combination thereof) processes (USEPA, 2004; UNIDO, 2011). In aerobic process, the decomposition rate is more rapid than anaerobic process and it is not accompanied by unpleasant odours, where as in anaerobic process longer detention period is required and gives unpleasant odours.

Microbiological treatment systems can be classified into fixed film or attached growth system and suspended growth systems.

2.6.3.1 Fixed Film or Attached Growth System

In attached growth or fixed film systems, the microorganisms responsible for the conversion of organic matter that are attached to an inert packing material (Spellman, 2003). Trickling filters and biological towers are examples of systems that contain biomass adsorbed to rocks or plastics.

Trickling filters consist of fixed media such as rocks or plastic materials over which wastewater is sprayed and trickled down over the attached biomass or slime layer, so as to remove the waste through sorption and biodegradation (EPTI, 1998). Continuous flow provides the needed contact between the microbes and the organics (Peter, 2005; Thomas, 2005). Using a trickling filter a removal 85 - 90% for BOD and 60-70% for COD can be achieved (Kornaros and Lyberatos, 2006). Aslam *et al.* (2017) also indicate that trickling filters system using cotton sticks as filter

media for municipal wastewater removal efficiency about 69-78 % BOD_5, 65-80 % COD, 38-56 % TSS and 20-36 % TDS (Aslam *et al.*, 2017).

Rotating biological contactor is an attached system where biomass is attached to a series of thin, plastic wheels that rotate the biomass in and out of the wastewater. This coating of microorganisms is able to trap and consume BOD and ammonia in the wastewater (Spellman, 2003). An operation in a leather and fur wastewater treatment plant with BOD and COD loading of the influent to the rotating biological contactor (RBC) were 15 to 20 $g/m^{2}{\cdot}d$ and 50 to 65 $g/m^{2}{\cdot}d$ respectively. The removal efficiency of BOD_5, COD, suspended solids (SS), S^{2-}, and Cr^{3+} were 87.8, 77.4, 84.8, 93.6, and 81.0%, respectively (Zao-yan & Zhen-san, 1990). The performance of RBCs depends upon several design parameters such as rotational speed, organic and hydraulic loading rates, hydraulic retention time , rotating biological contactor media, staging, temperature, wastewater and biofilm characteristics, dissolved oxygen (DO) levels, effluent and solids recirculation and medium submergence (Cortez *et al.*, 2008).

2.6.3.2 Suspended Growth Systems

Suspended-growth systems are biological treatment processes based on the growth and retention of a suspension of microorganisms which convert biodegradable, organic wastewater constituents and certain inorganic fractions into new cell mass and byproducts. Activated sludge is the most widely used biological treatment process for both domestic and industrial wastewater (Metcalf & Eddy, 2003). The activated sludge process is a biological process in which the activity of a microbial species community under controlled operating conditions permits the biodegradation of organic matter and nutrients from wastewater.

Microbial treatment of wastewater is more favourable and cost effective as compared to other physicochemical methods. Various microorganisms are capable of reducing the content of pollutants significantly by utilizing them as energy and nutrient source in the presence or absence of oxygen (Eddy, 1979). Combined physicochemical pretreatment and aerobic treatment of tannery wastewater reduces chemical oxygen demand (COD) by 60-80% and biological oxygen demand (BOD) by 95% (Sastry, 1986).

2.6.4 Phytoremediation

Phytoremediation is the use of vegetation for *in situ* treatment of contaminated soils, sediments, and water by breaking down, or degrading organic pollutants or contain and stabilise metal contaminants by acting as filters or traps (Schnoor, 1997). Treating metal contaminants at sites contaminated with metals, plants are used to either stabilise or remove the metals from the soil and groundwater through three mechanisms: phytoextraction, rhizofiltration, and phytostabilisation. Phytoextraction, also called phytoaccumulation, refers to the uptake and translocation of metal contaminants by plant roots into the above ground portions of the plants. Some plants are hyperaccumulators; unusually absorb large amounts of metals in comparison to other plants. One or a combination of these plants is selected and planted at a particular site based on the type of metals present and other site conditions (Glass,1999; US EPA,1997).

Plants hold Cr by converting it to the less mobile Cr (III) (phytostabilization) and simultaneously reduce its toxicity (USEPA, 1997). Phytoaccumulation, one of the most common forms of Cr (VI) phytoremediation, consists of the uptake of the Cr from the soil to the plant roots and ultimately into the above ground parts of the plants. High Cr accumulating plants have the risk of generating hazardous plant waste and/or passing Cr along in the food chain. Some plants can accumulate very large amounts of a specific metal, such as Cr.

Rhizofiltration phytoremediation method refers to the uptake of Cr from wastewater by plant roots (Mesjasz-Przybylowicz *et al.,* 2004). Terrestrial plants with long fibrous roots and high surface areas are typically used because sorption onto the surface of roots provides an additional uptake mechanism .Studies showed that some selected free floating aquatic plants such as Alfalfa shoots took up 7.7 mg chromium per gram of biomass and water hyacinth (*Eichhornia crassipes*) accumulated 6 mg g^{-1} Cr (dry weight) was observed in the plant's roots (Dushenkov *et al.,* 1995; Cervantes *et al.,* 2001).

As shown above, chromium is accumulated in different parts of plants such as roots, stems, leaves and seed. The majority of Cr is accumulated in the roots; hence small amounts of Cr are translocated to leaves (Tiwari *et al.*, 2013).

The heavy metal ions can be stored in the roots or translocated to the aboveground biomass primarily through xylem vessels and mostly deposited in the vacuoles (Denton, 2007; Jabeen *et al.*, 2009).Sequestration of heavy metals in the vacuole is one of the ways to remove heavy metal ions and reduce interactions with cellular metabolic processes (Sheoran *et al.*, 2011). Sequestration of metal ions in plant tissues and metal tolerance are important requirements for metal accumulations in the phytoremediation process (Tong *et al.*, 2004).

The efficiency of any plant species for the phytoremediation of heavy metals is evaluated by calculating bioconcentration factor (BCF) and translocation factor (TF) (Pandey, 2012). The BCF of heavy metals (L kg^{-1}) is calculated as follows (Soda *et al.*, 2012):

$$BCF = \frac{C_P}{C_W} \tag{2.10}$$

Translocation factor (TF) provides an index of the plant ability to transfer metal from underground tissue to aboveground tissue, and is calculated by the following equation (Soda *et al.*, 2012):

$$TF = \frac{C_A}{C_U} \tag{2.11}$$

The accumulation of heavy metals in some plants has been reported as shown in **Table 2.6** below. The extent of accumulation of heavy metals is dependent on plant species, pH, organic matter content, cation exchange capacity and type of heavy metal (Barman *et al.*, 2001; Spinoza-Quinones *et al.*, 2005).

Table 2. 6 Heavy metal uptake potential by different plant species

Plant species	Heavy metal	Meta conc. Water/soil	Bioaccumulation (mg kg^{-1})			TF	BCF	Reference
			Root	Stem	Leave			
T. domingensis	Total Cr	23.8 mg kg^{-1}	5.88 ± 1.02	-	1.24 ± 0.2	0.29	0.15	Bonanno & Cirelli, 2017
P. purpureum	Cr (VI)	20 mg L^{-1}	925.0	1.995	6.404	-	-	Mant *et al.,* 2005
A. acuminata spp.acuminata	Pb	196.7 mg kg^{-1}	111	-	-	1.30	1.37	Escobar & Dussán , 2016
A. acuminata ssp. acuminata	Cr	63.3 mg kg^{-1}	105	-	-	5.07	1.49	Escobar & Dussán , 2016
Z. mays	Cr (VI)	40 mg kg^{-1}	33.9	29.1	6.1	0.37	0.39	Gheju *et al.,* 2009
S. vulgaris	Cr (III)	60 µmol L^{-1}	-	-	-	0.02-0.04	2.6-10	Pradas-del-Real *et al.,* 2013
S. vulgaris	Cr (VI)	60 µmol L^{-1}	374 - 481	-	-	0.018 -0.03	13-31	Pradas-del-Real et al., 2013
A. wilkesiana	Pb	-	42.76	46.44	36.88	2.21	7.79	Iya *et al.,* 2018
A. saxatile	Cd	292 mg kg-1	124	92.7	-	0.75	0.37	Palutoglu *et al*., 2018

2.6.5. The Use of CWs for Wastewater Treatment

Constructed wetlands are artificial wastewater treatment systems consisting of shallow (usually less than 1 m deep) ponds or channels which have been planted with wetland plants on impervious clay or synthetic liners, and engineered structures to control the flow direction, liquid detention time and water level (USEPA, 2000). Pollutants in a constructed wetland system are removed by complex physical, chemical, and biological interactions between wastewater, wetland media, microorganisms, and plants as shown in **fig. 2.3 and Table 2.7** below. Microbial activities have been considered to be the primary mechanism for removing most pollutants including organic carbon and nitrogen (Kadlec and Knight, 1996).

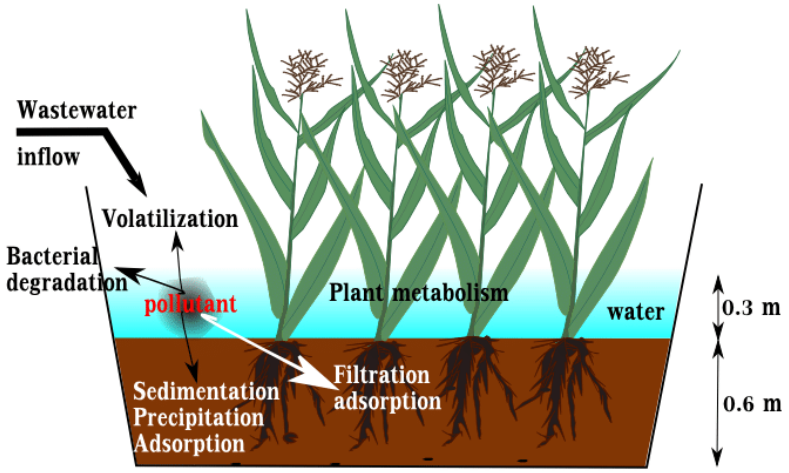


Fig.2.3 Pollutant removal mechanism (Truijen & van der Heijden, 2013)

Table 2. 7 Pollutant Removal Mechanisms in Constructed Wetlands (Cooper *et al.*, 1996)

Wastewater Constituents	**Removal Mechanism**
Suspended Solids	▪ Sedimentation ▪ Filtration
Soluble organics	▪ Aerobic microbial ▪ Degradation ▪ Anaerobic microbial degradation
Phosphorous	▪ Matrix sorption ▪ Plant uptake

Nitrogen	▪ Ammonification followed by microbial nitrification ▪ Denitrification ▪ Plant uptake ▪ Matrix adsorption ▪ Ammonia volatilization
Metals	▪ Adsorption and cation exchange ▪ Complexation ▪ Precipitation ▪ Plant uptake ▪ Microbial Oxidation /reduction
Pathogens	▪ Sedimentation ▪ Filtration ▪ Natural die- off ▪ Predation ▪ Excretion of antibiotics from roots of macrophytes

Studies about wetlands for wastewater treatment were started during the early 1952 at the Max Planck Institute in Germany (Seidel, 1965), and in the United States increased dramatically in scope during the 1970's. As a result, the use of wetlands for water and wastewater treatment has gained considerable popularity worldwide (Kyambadde, 2005). The constructed wetlands are new green technologies, which have been recognized and accepted as a creative, cost-effective and environmental friendly system when compared to the expensive conventional treatment systems (USEPA, 1993).

Recently, CW have been widely used for treating a variety of wastewaters from different sectors. Thus, extensive research and practical applications are being gained in order to operate the CW systems effectively. The use of constructed wetland to capture industrial pollutants is increasingly utilized and these represent promising alternative methods to treat the various types of industrial wastewaters using the new technology of constructed wetlands (Kadlec and Knight, 1996).

There are different types of CWs including, surface flow wetlands, subsurface flow wetlands, and hybrid systems that incorporate surface and subsurface flow wetlands. Constructed wetland systems can also be combined with conventional treatment technologies for effective treatment of wastewater released from different sectors. (USEPA, 2000).

Constructed wetlands are built with a much greater degree of control, to gain higher treatment efficiency using a well-defined composition of substrate, type of vegetation and flow pattern. In addition, constructed wetlands offer several additional advantages compared to natural wetlands including site selection, flexibility in sizing and most importantly, control over the hydraulic pathways and retention time (USEPA, 1993). Depending on the flow pattern constructed wetlands systems can be classified in to three as free water surface flow and subsurface flow (horizontal and vertical) (Haberl, 1999).

2.6.5.1 Free Water Surface (FWS) Wetlands

FWS wetlands closely resemble natural wetlands in appearance because they contain aquatic plants that are free floating or rooted in a soil layer at the bottom of wetlands. In this type of CWS the water flows horizontally through the leaves and stems of the plants, above the substrate. The near-surface layer of water is aerobic while the deeper waters and the substrate are usually anaerobic (USDA-NRCS, 1995).

Free water wetlands can further be sub-classified according to the dominant type of macrophytes growing in the system. This type of wetland systems can be a floating macrophyte system, e.g. *Nymphae* spp. (water lily), and species which are free floating on water surface , e.g. *Eichhornia crassipes* (water hyacinth); a submerged macrophyte system *e.g*. *Myriophyllum aquaticum* (parrot feather) and a rooted emergent macrophyte system (Plants grow at well above the water level, producing aerial stems and an extensive root and rhizome system. e. g. *Phragmites australis* (common reed), *Thypha* spp. (USDA-NRCS, 1995; USEPA, 2000).

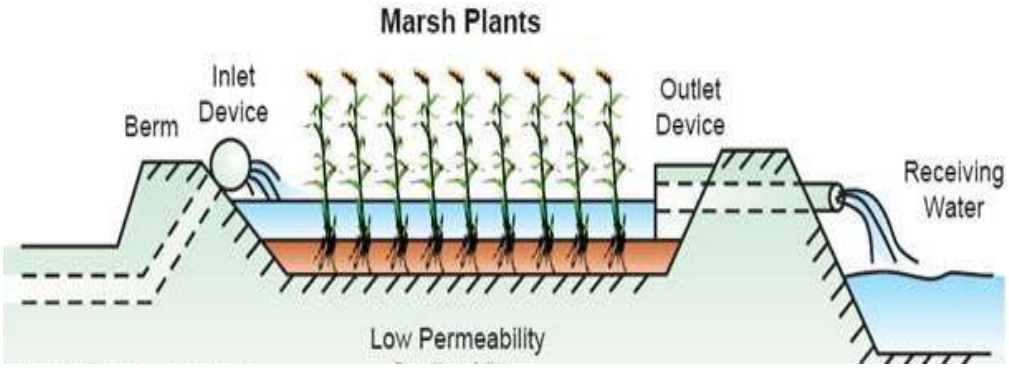


Fig. 2.4 Section view of a typical FWS wetland (Extracted from Kadlec and Knight, 1996).

2.6.5. 2 Subsurface Flow (SSF) Constructed Wetlands

SSF constructed wetlands do not resemble natural wetlands because they do not have standing waters. They are constructed with a substrate (usually small rocks, gravel, sand or soil) which are planted with aquatic plants, and the wastewater flows beneath the surface of the support matrix but in contact with the plants roots (USDA-NRCS, 1995). SSF systems must be planted with emergent macrophytes that can be sub-classified according to their water flow patterns as horizontal subsurface flow systems, vertical subsurface flow systems (upstream or downstream characteristics) and hybrid systems (Cooper *et al.*, 1996)

Horizontal Subsurface flow (HSSF)

In HSSF constructed wetlands, wastewater flow is first led into wetland by inlet and then is in contact with three different zones which are aerobic, anoxic and anaerobic zones from top to bottom (Vymazal, 2011), Since HSSF constructed wetlands is sealed by gravel in order to control outflow and prevent offensive odours, the aerobic zone is thinner than that of FWS constructed wetlands and occurs around plant roots where plant uptake and aerobic bio-degradation are carried out. During the passage of wastewater through the rhizosphere, the wastewater is cleaned by microbiological degradation and by physical and chemical processes (Cooper *et al.* 1996). HSSF wetland can effectively remove the organic pollutants (TSS, BOD_5 and COD) from the wastewater. Due to the limited oxygen transfer inside the wetland, the removal of nutrients (especially nitrogen) is limited; however, HF wetlands remove the nitrates in the wastewater.

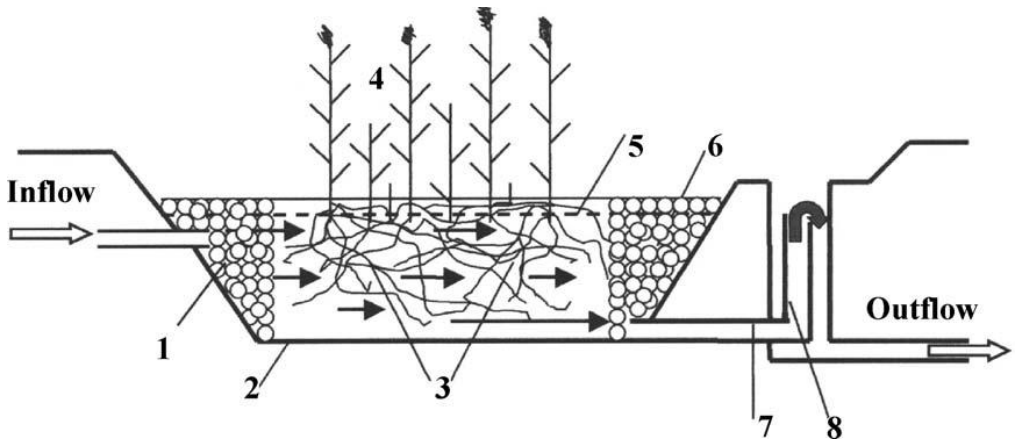


Fig. 2.5 Schematic representation of a HSSF constructed wetland system. (1- distribution zone filled with rocks; 2-impermeable liner; 3- filtration medium (gravel, crushed rock); 4- vegetation; 5- water level in the bed; 6- collection zone filled rocks;7- collection drainage pipe; 8-outlet structure for maintaining of water level in the bed (Vymazal, 2001)).

Most HSSF wetlands in Europe provide a bed depth of 60 cm (Cooper *et al.*, 1996). In the United States, HSSF wetlands have commonly been designed with beds 30 cm to 45 cm deep (Steiner and Watson, 1993). An experimental study carried out in Spain showed that shallow horizontal flow wetlands with an average depth of 27 cm were more effective than deep horizontal flow wetlands with an average water depth of 50 cm. (Garcia *et al.*, 2004).

Media selection plays an important role in designing of a constructed wetland. It functions as: rooting material for vegetation, help to evenly distribute/collect flow at inlet/outlet, provide surface area for microbial growth, and filter and trap particles (UN-HABITAT, 2008). It is reported that the diameter of media used in horizontal flow wetlands varies from 0.2 mm to 30 mm (USEPA, 1993; Normungsinstitut, 2005).It is recommended that the media in the inlet and outlet zones should be between 40 and 80 mm in diameter to minimize clogging and in the treatment zone, with different sized media in the range of 10 to 60 mm (USEPA, 2000). Before filling substrates, the partitioning of inlet/outlet zones must be done. Outlet arrangements should be addressed properly while filling the substrates. The substrate should be sieved and washed before filling the designed substrate sizes in the inlet/outlet zones and treatment zone (UN-HABITAT, 2008).

According to USEPA (1993) report SSF constructed wetlands have several advantages over the FWS type. Since water surface is maintained below the media surface there is little risk of odour, exposure and insect vectors. Besides the media in SSF constructed wetlands, provides greater available surface area for treatment and the treatment may be faster, the bed offer greater thermal protection in cold climates and uses small areas as compared to FWS types.

Calheiros *et al.* (2007) investigated the survival and potential of bisorption of five different types of plant species grown in subsurface horizontal flow constructed wetlands units receiving tannery wastewater. The vegetated plants were *Canna indica, Typha latifolia, Phragmites australis, Stenotaphrum secundatum* and *Iris pseudacorus*, and a sixth unit was left as an unvegetated control. The COD and BOD_5 reduced significantly under two different hydraulic loading rates of 3 and 6 cm d^{-1}. *Phragmites australis* and *Typha latifolia* were the only plants that were able to establish successfully. Tadese and Seyoum (2015) reported the treatment of Modjo tannery effluent in a HSSF constructed wetland system using four different plant species: *C. alternifolius, T. domingensis, P. Karka* and *B. aethiopium*, showed high treatment performance of Cr, COD and BOD_5 under a 5 day hydraulic retention time. *P. karaka* and *B. aethiopium* were the plants that established successfully and showed higher BOD_5, COD and nutrient removal.

Vertical Subsurface Flow (VSSF)

VSSF constructed wetland comprises of a flat bed of sand/gravel topped up with sand/gravel and vegetation .Wastewater is fed from the top and then gradually percolates down through the bed and is collected by a drainage network at the base.

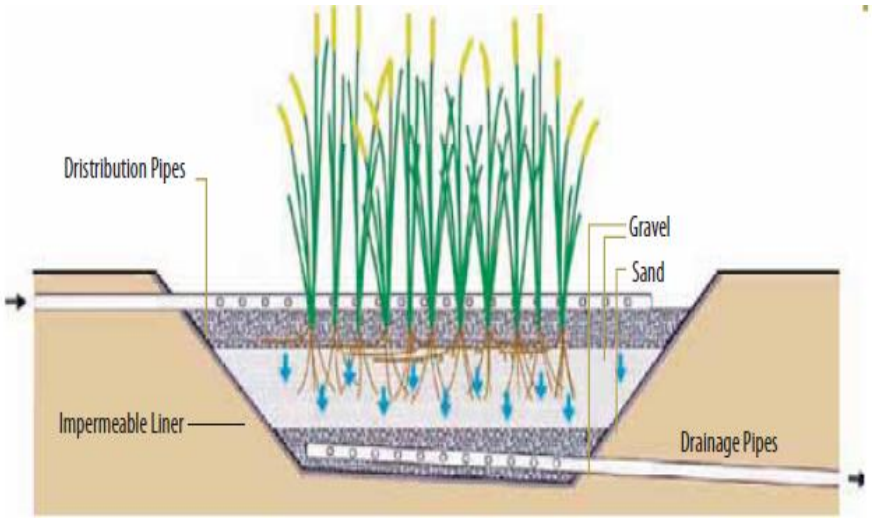


Fig. 2.6 Schematic cross- section of a vertical flow constructed wetland (Morel & Diener, 2006)

Vertical flow wetlands are fed intermittently in a large batch flooding the surface. The liquid gradually drains down through the bed and is collected by a drainage network at the base. The bed drains completely free and it allows air to refill the bed. The wastewater traps the air and leads to good oxygen transfer and hence the ability to nitrify. Brix (1997) showed that the oxygen transfer through plants (common reed species) has a potential oxygen transfer of 2 g O_2 m^{-2} d^{-1} to the root zone, which mainly is utilized by the roots and rhizomes themselves. Vertical flow systems are very important due to greater oxygen transfer capacity resulting in good nitrification; considerably smaller than HF system and can efficiently remove BOD_5, COD and pathogens.

Vertical flow systems have larger depths compared to horizontal flow systems. Most vertical flow systems in the UK are built 50 – 80 cm depths (Cooper *et al.*, 1996); while in Denkark a a minimum depth of 100 cm is recommended (Brix & Arias, 2005)). In a subtropical climate, it is possible to increase the applied loading rates above guidelines issued in Central Europe and achieve nitrification in vertical flow system. The average results by vertical beds of 75 cm depth showed better performance in comparison with vertical beds of 45 cm depth (Philippi *et al.*, 2004).

There is no uniform standard substrate design for the construction of vertical flow wetland. Various literature reports that the effective grain size of the particles used in constructed

wetlands should be between 0.2 and 1.2 mm (Brix & Arias, 2005). Compared to the gravel, the sands show a relatively more rapid reduction in their permeability due to effects of sediment accumulation at the surface of the sands.

Hybrid Constructed Wetland

A hybrid system is the combined use of HSSF and VSSF constructed wetland systems to improve the treatment efficiency by complementing the limitations of any one of the two systems (UN-HABITAT, 2008). HSSF wetlands are recognized for their better removal of BOD_5 and TSS, while they have limited oxygen transfer capacity. On the other hand, VSSF wetlands have a much greater oxygen transfer capacity and considerably less area requirement, but they are less efficient solid removers and they are likely to show clogging problems if the media selection is not correct (USEPA, 1993). As a result, there has been a growing interest of developing combined (hybrid) wetlands. Depending on the purpose, hybrid wetlands could be either horizontal flow wetland followed by vertical flow wetland or vertical flow wetland followed by horizontal flow wetland.

Table 2. 8 Treatment of tannery wastewater containing Cr in a constructed wetland system at different operating Conditions

CW type	**CW area (m^2)**	**HRT (days)**	**Porous media**	**Inlet conc. ($mg\ L^{-1}$)**	**Plant used**	**% removal**	**Reference**
HSSF	378	5-11	gravel	0.2	*P. australis*	43-55	Kucuk *et al.,* 2003
FWS	450	2	sediment	22-31	*Typhs spp., S. americanus*	58	Aguilar *et al.,* 2008
HSSF	0.31	1	gravel	5	*Typha spp.*	90-99	Dotro *et al.,* 2011a
HSSF	0.45	1.8	Pumice + limestone	303-420	*P.mauritianus*	99.83	Kaseva and Mbuligwe, 2010
HSSF	4.5	5,2.4	Granite	1.1, 0.08-5.9	*T. latifolia*	50-95	Dotro *et al.*, 2012
HSSF	450	4	Gravel	10-35	*P. karka*	97.3	Alemu *et al.,*2018
HSSF	15	1.5	Gravel	2	*T. latifolia*	93	Gikas *et al.*, 2013

3.0 Materials and Methods

3.1 Description of the Study Site

The rock samples used for adsorption experiments and as a substrate in the constructed wetland units were collected around Bahir Dar City (North West of Ethiopia) close to Lake Tana and around the outlet of Abbay (Blue Nile) River. Its geographical location is at about 11°36′00″ N latitude and 37°24′00″ E longitude at an elevation of 1,800 m, where apparently all the hills of the area are mainly composed of volcanic rocks.

The pilot constructed wetland units for the treatment of Cr and other pollutants were established at Davimpex Enterprise Bahir Dar Tannery PLC, Bahir Dar, as shown in **Fig.3.1**. The experimental set ups were constructed close to the equalization pond of the tannery wastewater. The wastewater was pumped from the equalization pond to 2000 L HDPE storage tank to irrigate the vegetated plants in the experimental the constructed wetland units.

The climate of Bahir Dar city is typical of semi-arid regions close to the Equator; including a high daily temperature variation between day time extremes of 30 °C to night low temperature of 6°C (Vijverberg *et al.,* 2009). Bahir Dar has a maximum rainfall during summer from June to September. It has high temperature and little rainfall during the winter.

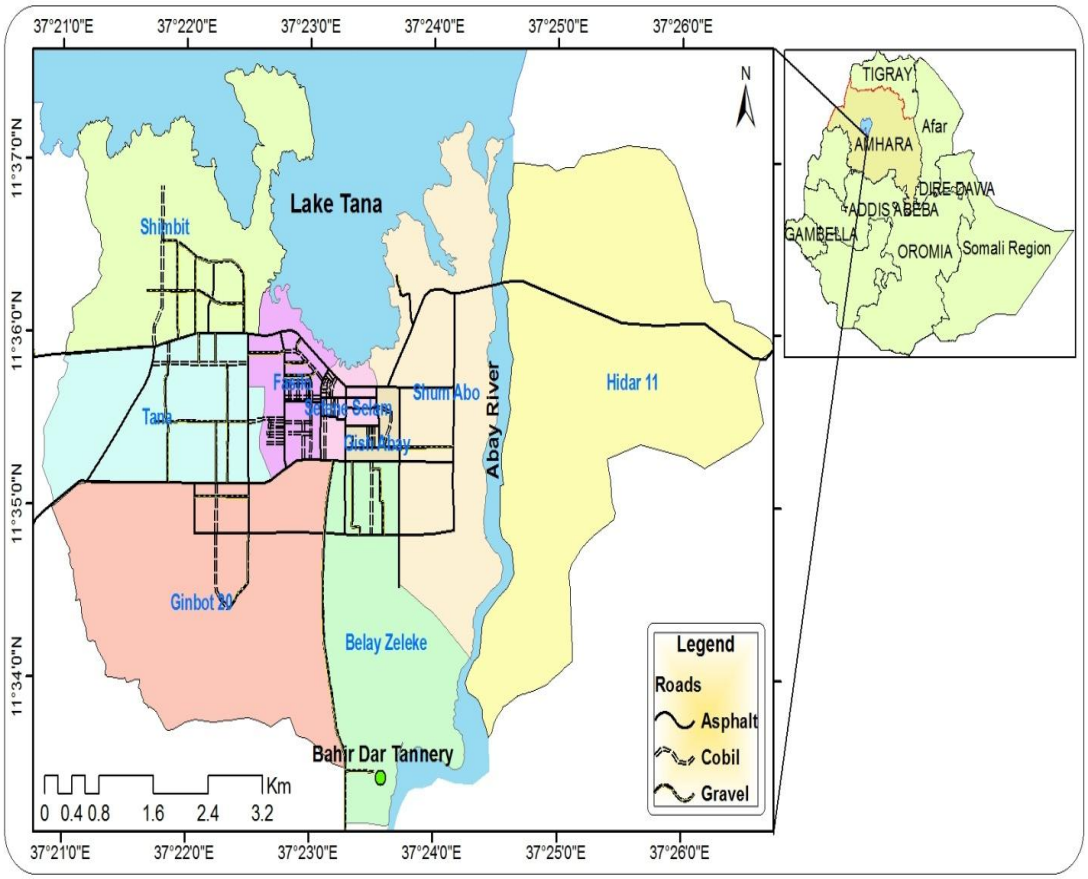


Fig.3. 1 Map of study area (Bahir Dar Tannery)

3.2 Reagents and Standard Solutions

The reagents potassium dichromate (≥ 99 % purity), diphenylcarbazide solution: was prepared by dissolving 250 mg 1, 5-diphenylcarbazide (98 %) in 50 mL acetone (assay ≥ 99.5 %) following the standard procedures described in APHA (1998). All the reagents were obtained from Fisher Scientific. Nitric acid (assay 68-70%) and potassium nitrate (99.0-100% assay), chromium chloride hexahydrate **(**$CrCl_3.6H_2O$) (≥ 99 % purity), hydrochloric acid (36.5-38%) and potassium nitrate (99.0-100% assay) were purchased from BDH laboratory supplies. Sodium hydroxide pellets, (extra pure 98 %) was purchased from Research Lab Fine Chemical Industries and ultra pure water (conductivity =0.05 µs cm^{-1}), was obtained from Evoqua Water Technologies. All the reagents were of analytical grades. Stock standard solution of chromium metal (1000µg mL^{-1}, Buck Scientific Puro-Graphic tm, USA), prepared as nitrates in 2% HNO_3,

and was used as calibration standards for determination of chromium concentration using ICP-OES (**Appendix A.2**).

3.3 Experimental Set Up and Description

There are three parts in this study: part I and part II are lab-scale determinations of Cr (VI) and Cr (III) adsorption from aqueous solution based on batch system with locally available vesicular basalt rock substrates and part III is pilot-scale application of the substrate in CWS for the treatment of chromium containing wastewater. In part III, wastewater from Bahir Dar Tannery was used as a feed for the pilot plant.

3.3.1 Lab Scale Batch Adsorption Experiment of Cr with Local Rock Substrates

3.3.1.1 Selection and Preparation of Local Adsorbent Rock Substrates

The selection of local adsorbents was based on their abundance in the area and potential to adsorb chromium from aqueous solutions. Around the study area, near the outlet of Abbay River, black hard rock types with and without vesicles are abundantly available. In addition red vesicular types are also found around the mountains. Rock samples from these sites were collected and taken to Bahir Dar University Geology Department for identification. The rocks were identified to be basalt rock types and this was further confirmed by lab analysis. In preliminary verification experiments, the locally available black and red basalt rocks were tested for adsorption of Cr. Based on our studies, the vesicular types showed better adsorption than the non-vesicular one because of its high surface area of contact with the adsorbate material (Akratos and Tsihrintzis, 2007; Alemayehu & Lennartz, 2009). The black vesicular basalt showed better performance than the red type and hence all the study was conducted using this rock type. For further adsorption studies, the vesicular basalt rock was crushed using Geocrusher and sieved to decipher particle sizes ranging between 90 to 500 μm. This was then washed with ultra-pure water and dried in an oven at 105 ^{o}C overnight. It was cooled down to room temperature and made the crushed, sieved, cleaned and dried basalt ready for the batch adsorption experiments (**Appendix A. 3 & 4**).

3.3.1.2 Characterization of Vesicular Basalt Rock

Perkin Elmer Spectrum 65 Spectrometer (USA) was used to record the IR spectra in the mid infrared region (4000-400 cm^{-1}) with a spectral resolution of 2 cm^{-1} using a pressed KBr pellet technique. The pellet was prepared by mixing approximately 1.0 % VB with 250 mg KBr and then finely pulverized and put into a pellet forming die. The minerals in the VB were identified by using a Bruker D2-phaser diffractometer using Cu Kα radiation of wavelength, λ=1.54056 Å, with variable slits at 45 kV/40 mA. Scanning between 10 and 75(2θ) at a scanning rate of 2^{o} min^{-1} in steps of 0.02^{o}. The morphological investigation and elemental identification of the VB was carried out using scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS), JEOL, JSM-6500F (Japan) at an accelerating voltage of 15 kV and a beam current of 1-3 nA.

3.3.1.3 Determination of pH of Point Zero Charge (pHpzc)

The pHpzc of the VB samples was determined by batch equilibration technique (Lazarevic *et al.*, 2007). 5 g of VB was added to a series of six flasks that contain each 100 mL of 0.01mol L^{-1} KNO_3 as a background electrolyte. The initial pH values were adjusted in the pH range of 2-11 using 0.1M of HNO_3 or NaOH. Equilibration was carried out by shaking for 12 hours using Heidolph Unimax 2010 shaker at the speed of 250 rpm at room temperature. Ultimately the dispersions were filtered and the final pH (pH_f) of the solution was determined. The pHpzc was found from a plot pH_f vs. pH_i . This procedure was repeated at various concentrations of 0.05 and 0.1 mol L^{-1} KNO_3 solutions.

3.3.1.4 Adsorption Studies

For adsorption studies of Cr (VI), a stock solution of 1000 mg L^{-1} Cr (VI) was prepared by dissolving 2.8289 g of potassium dichromate ($K_2Cr_2O_7$) using ultra pure water. Standard solutions for adsorption experiments were prepared by a series of dilution of the stock solution using ultra pure water. The ionic strength of the solution was attuned to 0.01, 0.05 and 0.1 M using KNO_3 as background electrolyte. The pH of the solution was adjusted in the range of 2-11 using 0.1 mol L^{-1} NaOH and HNO_3. 5 g of VB was mixed with 100 mL of solution containing 5 mg L^{-1} Cr (VI) in a 250 mL polypropylene Erlenmeyer flask to the point of equilibrium (9 hours)

without further control of pH. Control (only the test substance without adsorbent) and blank (only the adsorbent without the test substance) experiments have been carried out for each set of experiment. The flasks were tightly wrapped with polyethylene parafilm to avoid pH changes during experiments due to CO_2 escape. The reactions were taking place at 25± 0.5 ^oC with continuous stirring at 300 rpm.

After the end of each adsorption process, it was allowed to settle for 5 minutes. Subsequently the final pH was measured. The pH changes in the experiments were observed up to a maximum value of 1. 10 mL of the supernatant sample was centrifuged and filtered through Whatman filter (pore size 2.5 μm) and the concentration of Cr (VI) was determined using UV-Vis spectrophotometer (Perkin Elmer Lambda 35, USA) by using diphenylcarbazide at maximum absorption of 540 nm (APHA,1998) based on instruments listed in **Appendix A.5**. Each experiment was conducted in triplicate and data represent the mean value. Before each measurement, the instruments were calibrated with standard solutions (**Appendix A. 1**).

For adsorption studies of Cr (III), a stock solution of 1000 mg L^{-1} Cr (III) was prepared from chromium chloride hexahydrate ($CrCl_3.6H_2O$). Standard solutions of varying concentrations for adsorption experiments were prepared by a series of dilution of the stock solutions using ultra pure water. The ionic strength of the solution was attuned to 0.01, 0.05 and 0.1 mol L^{-1} using KNO_3 as background electrolyte. The pH of the solution was adjusted in the range of 2-7 using 0.1mol L^{-1} NaOH and HCl. 5 g of VB was mixed with 100 mL solution containing a concentration of 100 mg L^{-1} of Cr (III) in a 250 mL polypropylene Erlenmeyer flask to the point of equilibrium (8 hours) without further control of pH. Control (only the test substance without adsorbent) and blank (only the adsorbent without the test substance) experiments had been carried out for each set of experiments. The flasks were tightly wrapped with polyethylene parafilm to avoid pH changes during experiments due to CO_2 escape. The reactions were taking place at 25± 0.5 ^oC with continuous stirring at 300 rpm.

After the adsorption process was over, it was allowed to settle for 5 minutes. Subsequently the final pH was measured. The pH changes in the experiments were observed up to a maximum of 0.35 pH. 10 mL of the supernatant sample was centrifuged and filtered through Whatman filter (pore size 2.5 μm) and the concentration of Cr (III) was determined using ICP-OES.

The amount of Cr (VI) and Cr (III) adsorbed at time t, q_t, and the absorbed percentage were determined using equation (3.1) and (3.2), respectively (Lo *et al.*, 2004).

$$q_t = \frac{(C_o - C_t) \times V}{m} \tag{3.1}$$

$$R(\%) = \frac{(C_o - C_t)}{C_o} \times 100 \tag{3.2}$$

3.3.1.5 Adsorption Kinetics

The adsorption kinetic experiments for adsorption of Cr (VI) were carried out in 500 mL flask containing 5 g of VB and 350 mL solutions with initial concentrations of 0.1, 1 and 5 mg L^{-1} Cr (VI) at an optimum pH and contact time between 0 to 720 min.

The adsorption kinetic experiments for adsorption of Cr (III) were carried out in 500 mL flask containing 5 g of VB and 350 mL solutions with initial concentrations of 20, 60 and 100 mg L^{-1} Cr (III) at an optimum pH and contact time between 0 to 540 min

The reactors agitation speed, temperature and volume of the sample taken and analysis were identical to the description given above in adsorption studies.

The adsorption kinetics of Cr (VI) and Cr (III) onto the VB, experimental data were modelled by linear fitting pseudo-first order (3.3) (Lagergren, 1898) and pseudo-second-order adsorption kinetic equations (3.4) (Ho *et al.*, 2000*).*

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3.3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad (3.4)$$

3.3.1.6 Adsorption Isotherms

For adsorption isotherm studies of Cr (VI), a series of 250 mL Erlenmeyer flasks were filled with 100 mL Cr (VI) solution of varying concentrations (0.1, 1 and 5 mg L^{-1}), maintained at 25 ± 0.5 ^{o}C, reaction time of 540 min and optimum pH of 2. Then 5 g VB was added into each flask and agitated to equilibrium adsorption time.

The adsorption isotherm studies for Cr (III), followed the same procedure as Cr (VI), but varied concentrations (20, 60 and 100 mg L^{-1}), maintained at 25 ± 0.5 ^{o}C, reaction time of 540 min and optimum pH of 6. Then 5 g VB was added into each flask.

After adsorption equilibrium time, the concentrations of Cr (VI) and Cr (III) were determined following the above procedures in adsorption studies. At the end of the experiments, two most commonly used isotherm adsorption models, the Langmuir and Freundlich, were used to describe the obtained equilibrium data. The linear equations of Langmuir (3.5) and Freundlich (3.6) adsorption models were expressed as follows (Betancur *et al.*, 2009):

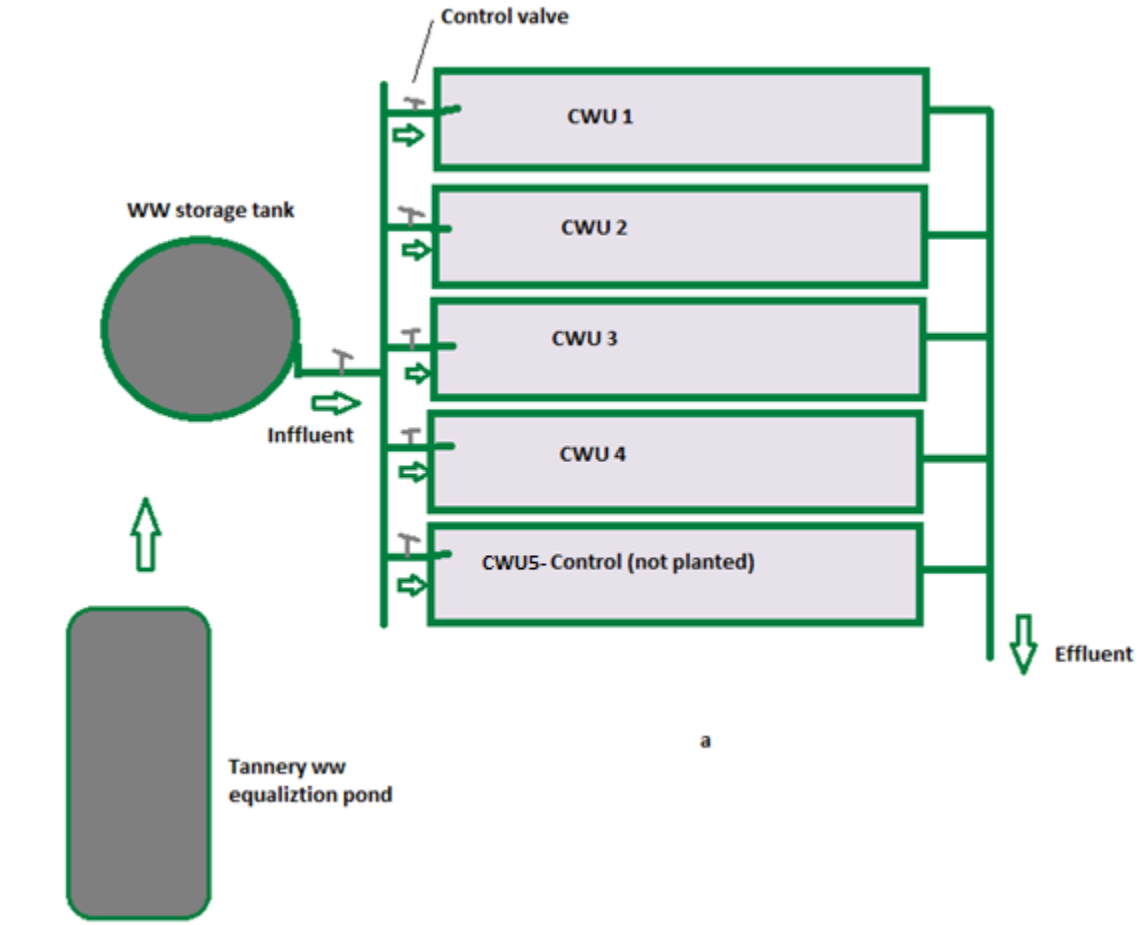
$$\frac{C_e}{q_e} = \frac{1}{b\, q_{max}} + \frac{C_e}{q_{max}} \quad (3.5)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3.6)$$

3.3.2 Pilot Scale Treatment of Cr Containing Tannery Wastewater Using HSSF CWS

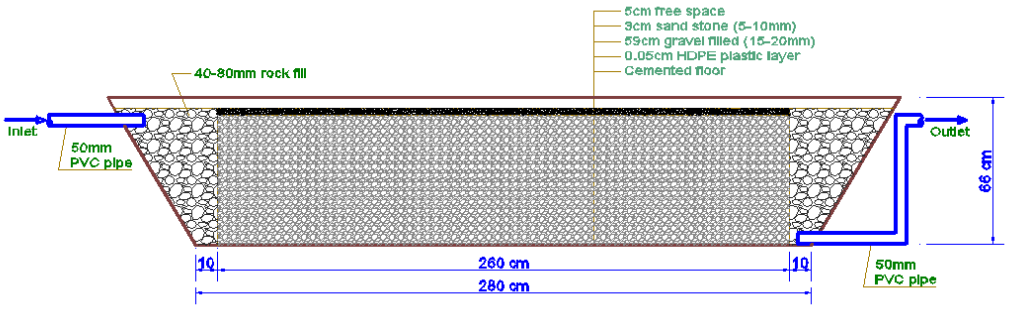
3.3.2.1 Design of CWUs

Five parallel constructed wetland subsurface flow units, each with a length of 2.8 m, width of 0.80 m and height 0.62m having a volume of 1.39 m^3, were constructed (**Fig. 3.2 (**a**)**). The aspect ratio (Length to width) of the bed was 3.5:1 and bed slope 1% (US EPA, 1993). The base floor and the internal walls of each unit were cemented and covered with 0.5 mm thickness HDPE geomembrane plastic to prevent interaction with the bed and prevent water leakage. The inlet and outlet zones of the constructed wetland units were filled with 40 - 80 mm diameter rock to minimize clogging and facilitate water distribution. After this, constructed units were filled upto 0.59 m depth with 15-20 mm VB followed by 0.03 m height with 5-10 mm rock to support the wetland plant growth. Above this surface, 0.05 m depth was left unfilled to prevent overflowing of the wastewater as shown in **Fig. 3.2 (b)** and **Appendix B.1 (a) & (b)**. The selection of media size is based on different literatures (Vymazal, 1997; US EPA, 1988; UN-HABITAT, 2008). The porosity of the gravel bed was determined in the lab and it was about 38%. Feeding of wastewater to the five pilot CWUs was made through a HDPE pipe with flow control valve and HRT of 6 days. A HRT of 6-7 days has been reported to be optimal for the treatment of primary and secondary wastewater for temperatures above 15 ^oC (Crites, 1988; Akratos and Tsihrintzis, 2007). The level of wastewater was about 3 cm below the surface of the CWUs.



a

CWU denotes constructed wetland unit



b

Fig.3. 2 pilot scale CWUs experimental lay out plan (a), components of each unit in a CWU (b).

The inflow and outflow rates of the wastewater were adjusted using a stopwatch and measuring cylinder. The wastewater hydraulic retention time (HRT) was calculated based on Darcy's law (USEPA, 1993).

$$HRT = \frac{L.W.D.n}{Q} \tag{3.7}$$

Hydraulic Loading Rates of pollutants from the tannery wastewater, HLR (m d^{-1}) applied to each of the constructed wetland units were determined using the equation:

$$HLR = \frac{Q}{A} \tag{3.8}$$

3.3.2.2 Selection of Wetland Plants, Vegetation and Adaptation to Wastewater

The selection of plants was based on their local availability, ability to withstand high saline conditions and emergent type of plant species were taken into consideration. Moreover the selected plant species growing around the tannery effluents gave some hints for the ability of these species to survive in the toxic tannery wastewater discharged onto them. Consequently, four local plant species were selected for this study. The plants were also found around the wastewater stream to Abbay River. But the plant species to be transplanted to the constructed beds were collected far from the wastewater discharge areas, around the upstream of Abbay River and Lake Tana. This was done in order to avoid accumulation Cr from the tannery effluent during growth. The vegetation of the bed units were performed based on the suggestions of USEPA (1993). It was planted by hand with initial spacing 0.3 - 0.6 m and root/rhizome material was placed in the gravel, at a depth equal to the operational water level. An individual root/rhizome material with a growing shoot at least 0.2 m (8 in) in length was planted. A few dead plants were replaced by new ones during adaptation periods.

The four plant specimens were taken to Addis Ababa University, National Herbarium, to be identified. The scientific names of the plants were *Pennisetum purpureum*, *Typha domingensis*, *Cyprus latifolius and Echinochloa pyramidalis*.

The vegetated plants on the constructed bed were fed with tap water until it was completely reinstated. The plants were fed with dilute tannery wastewater from lower to higher concentrations to improve the resilience of these plants to the stress of the toxic tannery effluent. (**Appendix B.1(c)**). According to Davis (1995), Irrigation of the wastewater concentration will be increased gradually in order to reduce the sudden shock and provide adaptation periods for the constructed wetland plants.

Before the wastewater was supplied to the wetland units, it was preliminarily characterized by taking samples from the sedimentation pond. The analysis indicated pH 9.2, total chromium 42.6 mg L^{-1}, EC 6860 (µs cm^{-1}) , total dissolved solid 6333 mg L^{-1}, chloride 4150.55 mg L^{-1} and COD 4388.6 mg L^{-1}.

The high pH, total dissolved solids and organic loadings might be a challenge for the growth and treatment of the tannery wastewater. Thus, it was adapted by feeding the plants to different proportions of tannery wastewater with tap water as shown in **Table 3.1**. Up to the 4^{th} run the plants overcome the shock of the diluted toxic tannery wastewater, though some drying of leaves and a few dying plants observed. The plants resumed with increasing propagation. The 5^{th} run was almost 1:1 proportion considering evapo-transpiration. This treatment continued for longer periods to examine the adaptation of the selected plants in this proportion. In the early stages, drying of leaves and complete dying of some individual plants were observed. This shock was common for all plants but increased for *P. purpureum* and *E. pyramidalis.* After two months, the remaining plants regained and continued propagation. Since the factory effluent does not come with consistent levels of contaminant concentrations, there were still some individual plants that came under shock due to the variable nature of tannery wastewater. Therefore, supplying 100 % of the wastewater may not allow the plants re-establish well and treat the wastewater. Though the characteristic of the wastewater was not uniform, 1: 1.67 ratio continued throughout the study period in the pilot scale constructed wetland units.

Table 3. 1 Adaptation of plant species on the constructed bed to the toxic tannery effluent

Feeding Phases	Dilution ratio	Duration
1st run	100% Tape water	2 week
2nd run	1:20	2 week
3rd run	1:8	2 week
4th run	1:4	6 weeks
5th run	1:1.67	Up to 12 weeks

The dilution ratio is wastewater to tap water

3.3.2.3 Estimation of Evapotranspiration (ET) of the CWUs

Enku-Melesse method (Enku & Melesse, 2014) was used to estimate evapotranspiration in the Abbay Basin, which showed small difference, compared to the FAO-56 Penman-Monteith a global standard method, but it requires numerous weather data for the estimation ET. To estimate ET for constructed wetland units, five year maximum daily temperature data (January, 2013 to December, 2017) of Bahir Dar City were used. The equation (Enku-Melesse, 2014) is as follows:

$$\mathrm{ET} = \frac{(T_{max})^n}{k} \tag{3.9}$$

Where n = 2.5; k is the coefficient, which can be calibrated for local conditions. The coefficient, k, could be approximated as:

$k = 48 * T_{mm} - 330$ for combined wet and dry conditions.

3.3.2.4 Characterization of Tannery Effluent

The tannery effluent was collected from industry and characterized for its physical and chemical properties of the waste before it was used for irrigation of the constructed wetland unit. The basic parameters used for characterization include temperature, pH, EC, TDS, TSS, Cr (VI), Cr (total), Cl^-, BOD_5, COD, NO_3^- and TP based on standard methods (APHA,1998).

3.3.2.5 Wastewater Sampling and Analysis

Wastewater samples were collected for three consecutive months at an interval of two weeks during the study period. The samples were collected from the inlet (storage tank) and from the outlet of constructed wetland units (CWU1, CWU2, CWU3, CWU4, and CWU5) using HDP plastic bottles, which were cleaned by soaking them in 10% nitric acid overnight followed by rinsing with distilled water. Wastewater parameters T^o and pH were analysed at the sampling site. For other parameters, samples were transported to Bahir Dar University Chemistry Laboratory. The preservation and measurement for each parameter was performed using the standard procedures set in APHA (1998) : total Cr (digestion using concentrated nitric acid followed by ICP-OES analysis), Cr (VI)- diphenyl carbazide method, pH (Potentiometric Method) i.e. using pH meter, chemical oxygen demand (COD; closed reflux, titrimetric method), biochemical oxygen demand (BOD_5; 5-day BOD test), total suspended solids (TSS); chloride (argentometric titration method), NO_3^- (Palintest Nitratest method, using 8000 photometer), total phosphorus (Digestion followed by Ascorbic acid method), TDS, T° and electrical conductivity (EC) was measured using conductivity meter.

Cr total concentration in the wastewater after digestion was calculated using the following formula (APHA, 1998):

$$Total\ Cr\ (\ mg\ L^{-1}) = A\ \times \frac{B}{C} \tag{3.10}$$

Where A is concentration of Cr in the digested solution (mg L^{-1}); B is final volume of the digested solution (mL) and C is the sample size (mL).

3.3.2.6 Analysis of Plant Tissue

The plant tissues were washed properly with ultrapure water to remove debris and other materials attached to them before analysis. The cleaned plant tissues were cut into small pieces and dried in air for a week and finally kept in an oven at 105 ^oC overnight. The dried roots, stems and leaves of each wetland plants were separately ground into fine powder using mortar and pistil that were cleaned using standard methods mentioned above for glassware. The ground

samples were sieved using 250 µm mesh to make it uniform size throughout. Then 1g of each ground plant parts was digested with a mixture 69% HNO_3 and 30% H_2O_2 (6: 2) at the temperature of 95-100 ^oC in a flask on hot plate. The flask was covered with a watch glass during digestion. The heating process continued until the appearance of clear solution, which indicated complete digestion. The digest was cooled and filtered through a Whatman filter paper (grade 42). Finally, it was diluted up to 50 mL volumetric flask with ultrapure water (Kassaye *et al.*, 2017). The total Cr in the digested plant samples was analyzed using ICP-OES (Optima 8000 ICP-OES, Perkin Elmer). The wave length (λ) selected for Cr analysis was 267.716 nm (**Appendix B. 4 (a)-(e)**).

Cr concentration in the plant tissue on a dry weight (DW) base was calculated using the following formula (APHA, 1998):

$$Cr\ (mg\ kg^{-1}) = A\ \times \frac{B}{C} \tag{3.11}$$

Where A is concentration of Cr in digested solution (mg L^{-1}), B is final volume of digested solution (mL) and C is sample size (kg).

3.4 Detection Limits

Method detection limits (MDL) were calculated as three times the standard deviation of the ultra pure water (blanks) (n=7).This approach for MDL determination represents the lower limit of qualitative analysis. For all elements

$$MDL = 3S \tag{3.12}$$

The analysis the blank samples indicated that detection limits of total Cr in the ICP - OES was 1.6 µg L^{-1}.

3.5 Percent of Recovery

Recovery can be defined as the fraction of the analyte determined after addition of a known amount of the analyte to a sample. The concentration of both Cr (VI) and Cr (III) were determined for the spiked and unspiked portion of samples. The % recovery was calculated as (APHA,1998) :

$$\%\ Recovery = \frac{Spiked - Unspiked}{conc.of\ analyte\ added\ to\ the\ spike} * 100 \qquad (3.13)$$

The percent of recovery of Cr (III) in the plant tissue was 94.26%. If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judged-out of control, and the source of the problem should be identified and resolved before continuing analyses (USEPA, 1994. For all experiments and instrumental analysis, blanks were run and corrections applied.

3.6 Statistical Data Analysis

The collected data were analyzed using Origin lab software and Microsoft Excel. One-way ANOVA at 95% confidence interval ($p < 0.05$) was used to determine if there was statistically significant difference in mean removal efficiencies of Cr and other pollutants between the pilot constructed wetland units. Multiple comparisons were performed using Tukey's HSD tests. Statistical analyses were performed using SPSS Statistics 24.0

4.0 Results and Discussion

4.1 Adsorbent Characterization

Instrumental techniques including FT-IR spectroscopy, Powder X-ray diffraction (XRD), SEM, and EDS have been employed to characterize the vesicular basalt adsorbent used in this study.

4.1.1 FT-IR Analysis

The FT-IR spectroscopic measurement of the VB volcanic rock is shown in **Fig. 4.1(a)**. The band in the region 3000-3700 cm^{-1}, maximum peak at 3430 cm^{-1} was due to -OH symmetric stretching vibration and in the region 1600 -1700 cm^{-1} a maximum peak at 1634 cm^{-1} was fundamental bending vibrations of H-OH (Ohlin *et al.,* 2013; Kyziol-Komosinska *et al.,* 2014).The spectral features displayed in the reststrahlen band region (1200-800 cm^{-1}) revealed more overlap and are comparable to mineral features in the range of silica polymerization such as plagioclase, pyroxene and olivine. Such mineral composition is typical for basaltic rocks (Morgan-Sagastume & Noyola, 2008; Kwon *et al.,* 2010). In this region silicon absorption features moved to lower wave numbers owing to changes in the Si-O-Si stretching vibrations as a function of decreasing Si-O polymerization (Walter & Salisbury, 1989; Preston *et al.,* 2011; Rajesh *et al.,* 2013). The FT-IR spectra showed absorption bands at 766 cm^{-1}, 535 cm^{-1} and 584 cm^{-1} due to O-Si-O bending of silicates, Fe-O bending of hematite and magnetite respectively (Seetha & Velraj, 2016). In the range of 400-500 cm^{-1} (**Fig. 4.1(b**)) numerous vibration bands were produced at 420, 428, 456, 470 and 480 which are the characteristics of the deformation vibration of Si-O (Saikia *et al.,* 2003; Maia *et al.,* 2014).

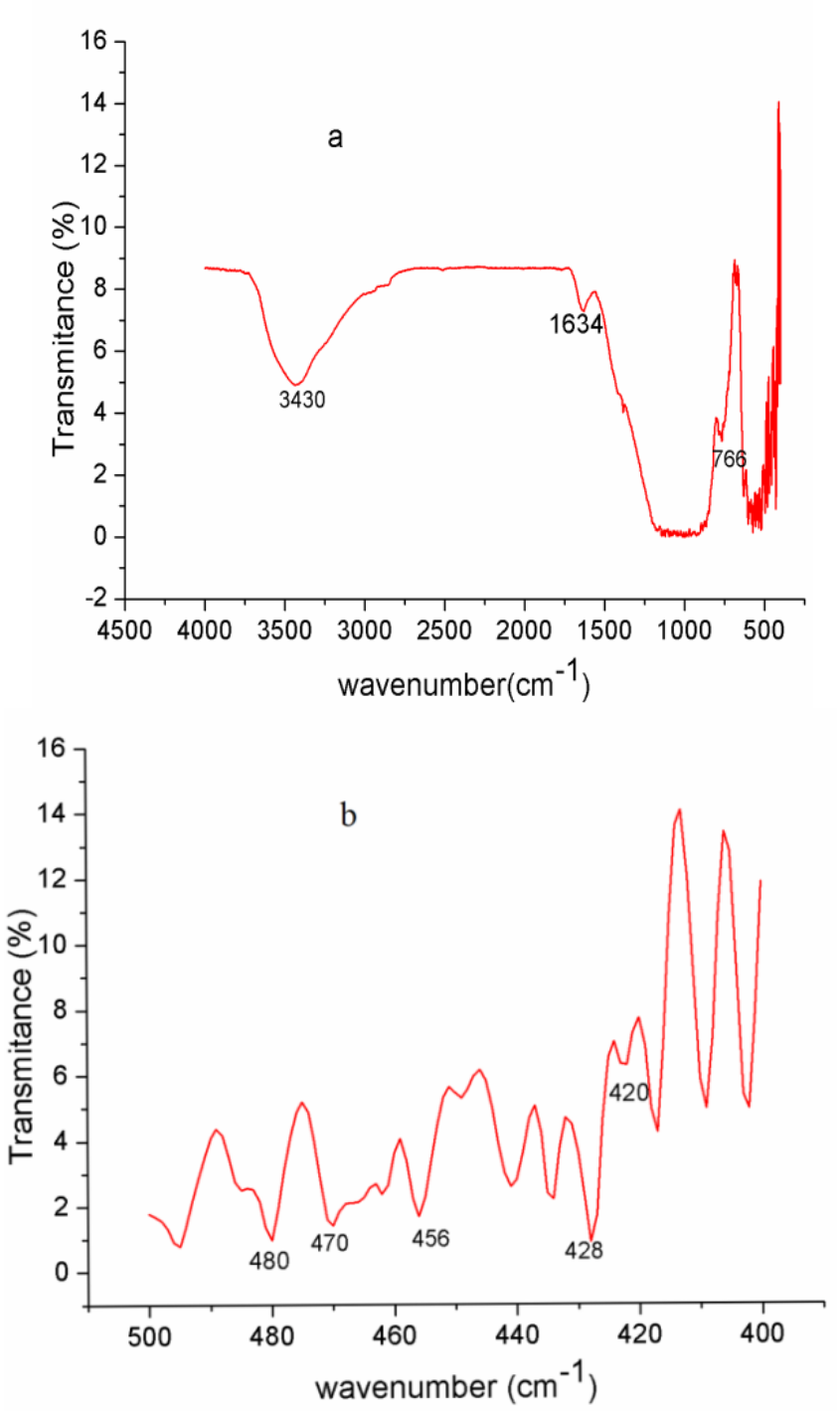


Fig.4. 1 Infrared spectrum of powdered VB sample between wavenumber ranges 4000-400 cm^{-1} (a); Zoom in of FT-IR spectrum of (a) between wavenumber ranges 500 -400 cm^{-1} (b).

4.1.2 XRD Analysis

Identification of minerals in the VB was carried out based on the XRD patterns given by the Joint Committee for Powder Diffraction Standards (JCPDS) patterns of inorganic compounds. The X-ray diffractogram of powdered VB and its analysis is shown in **Fig. 4.2**. The diffractogram analyses of powdered VB revealed the presence of plagioclase, pyroxene (augite), quartz, olivine, goethite, hematite and magnetite, which is in agreement with other studies (de Jesus Filho *et al.*, 1995; Lalla *et al.*, 2016; Mendes *et al.*, 2016). As can be seen from XRD spectrum, plagioclase is the most abundant mineral followed by Pyroxene (augite) and quartz. Moreover, the diffractogram revealed the presence of olivine, goethite, hematite and magnetite in the analyzed sample (Costa *et al.*, 1999; Parthasarathy *et al.*, 2001; Lalla *et al.*, 2015; Hadnott *et al.*, 2017). In general, the minerals identified from the VB were in agreement with the FT-IR analyses verifying the principal minerals identified.

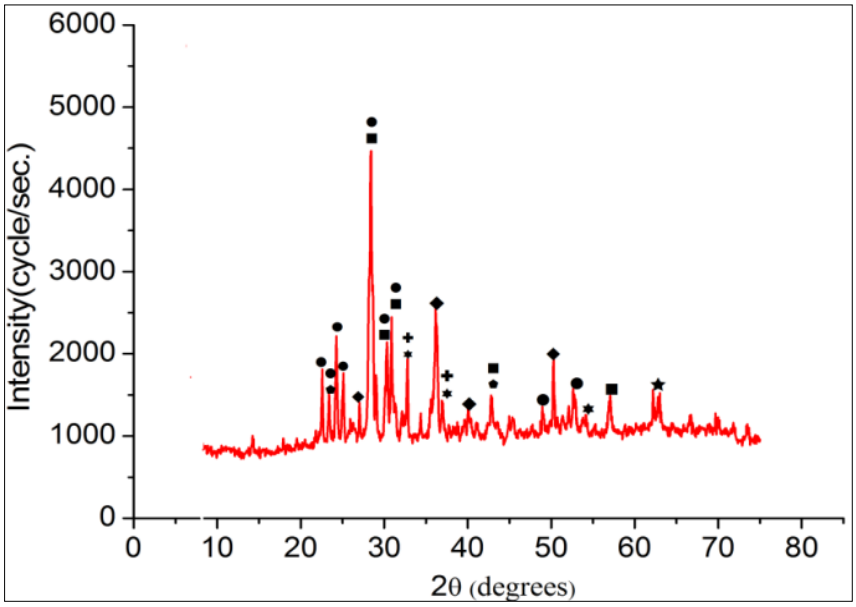


Fig.4. 2X-ray diffractogram of powdered vesicular basalt sample. Mineral assignment: (●) Plagioclase, (■) Pyroxene, (⬟) Olivine, (◆) Quartz, (✚) Hematite, (✸) Goethite and (★) magnetite.

4.1.3 SEM/EDS Analysis

The SEM image and EDS analysis of the VB are provided in **Fig. 4.3 (a)** and **4.3 (b)** below. The SEM micrographs showed homogeneous and corrugated morphology consisting of grey, light grey and white platelets of different sizes. The SEM micrographs indicate feldspars (plagioclase) with uniform grey part; light grey is the silica and white platelets are Fe-bearing aluminosilicate which is in agreement with the literature of these minerals that has been identified by direct comparison to their SEM micrographs (Gonzalez *et al.,* 2003 ; Michalski *et al.,* 2006). The elemental composition in **Table 4.1** (left) indicated that the dominant elements in the VB are oxygen (O) and silicon (Si) whose percentage compositions by weight are 48.46 and 17.37 % respectively. Other elements aluminium (Al), iron (Fe), calcium (Ca), sodium (Na), potassium (K) and magnesium (Mg) are also identified in the sample.

To confirm the VB in the removal of Cr (VI), SEM-EDS analysis of the exhausted adsorbent was done (**Fig. 4.3 (c)** and **4.3 (d))**. Though it is difficult to get information about the adsorption of Cr (VI) using SEM image, from the EDS spectrum, the Cr peak is observed clearly of 4.95 % (**Table 4.1** (right)). The presence of this peak after adsorption process confirms that the VB has the capability to adsorb Cr (VI) from aqueous solution.

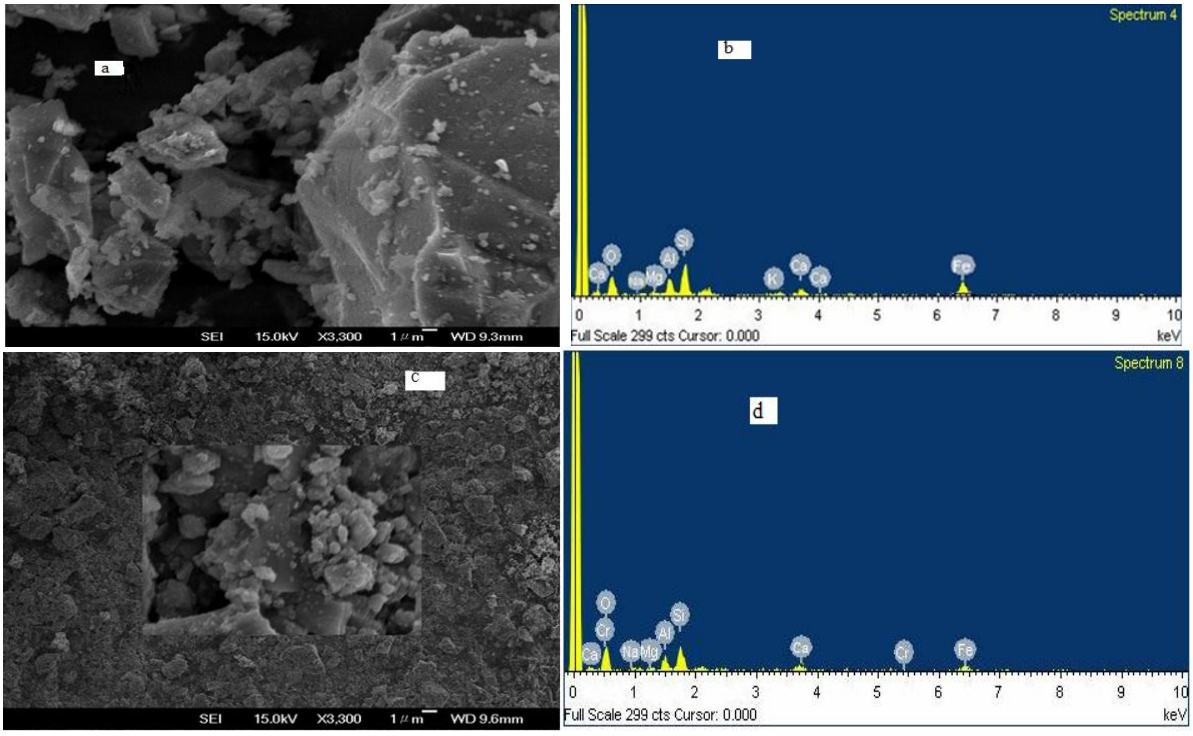


Fig.4. 3 SEM image and EDS spectra of VB (a) and (b) before adsorption; SEM image and EDS spectra of VB (c) and (d) after Cr (VI) adsorption.

Table 4.1 Elemental composition of the VB before adsorption (left) and after adsorption (right)

Element	Weight %	Atomic %
O K	48.46	63.42
Mg K	0.87	0.70
Al K	9.55	6.95
Si K	17.37	14.62
Ca K	8.80	4.31
FeK	8.83	3.93
NaK	4.87	5.27
K K	1.25	0.80
Totals	100.00	100.00

Element	Weight %	Atomic %
O K	46.41	54.63
Mg K	0.85	0.76
Al K	9.52	7.91
Si K	17.25	14.17
Ca K	7.90	5.08
FeK	8.64	6.83
NaK	4.46	7.50
Cr K	4.97	3.12
Totals	100.00	100.00

4.2 Evaluation of Cr (VI) Removal from Aqueous Solution Using VB

4.2.1 Effect of pH and Ionic Strength

Effect of pH and ionic strength were investigated for the adsorption of Cr (VI) on vesicular basalt surface, as shown in **Fig. 4.4 (a)**. Maximum removal of Cr (VI) was observed at acidic pH ranges with 81.19 % removal at pH 2. As the pH of the solution increased, the percentage of removal of Cr (VI) decreased and its adsorption capacity reached under 10 %. pH affected adsorption capacity of a system due to its influence on the surface properties of VB and the ionic forms of chromium in solution. In acidic condition $HCrO_4^-$ exist with higher domination, whereas the dominant species changed to CrO_4^{2-} when pH > 6 (Oliveira *et al.,* 2008). The pHpzc of the VB at different concentrations of KNO_3 was found to be 7.6 (**Fig. 4.4 (b**)). After equilibration, the change in the pH_f was observed at lower pH_i (2-5) and higher pH_i (8-11) values. But in the pH_i range of 6-8, there was no significant change in the pH_f .This implies that in this pH_i ranges the pHpzc is almost independent of ionic strength of KNO_3 solution. According to Sheng *et al.* (2012), a solid surface is positively charged at pH< pHpzc and negatively charged at pH > pHpzc. In this study at pH < 5, the surface of the VB was highly protonated with positive charges, which facilitated the adsorption of $HCrO_4^-$ species, resulting in high adsorption efficiencies (Chen *et al.,* 2014). When the pH > 7. 6, the surface of the VB developed less positively charged ions, which would reduce the electrostatic attractions between the VB surface and negatively charged species, lowering the adsorption efficiencies. Also, the competition of OH^- for the limited adsorption sites became more serious with increasing solution pH. Thus, pH 2 was taken as an optimal condition in this work. Therefore all other adsorption experiments were conducted at pH 2 to ensure for maximum removal of Cr (VI) onto the VB.

Ionic strength is another factor that affects adsorption of a system. Figure 4a shows adsorption of Cr (VI) onto VB using different ionic strength (0, 0.01, 0.05 and 0.1 mol L^{-1}) as a function of pH (2-11). The percentage of removal of Cr (VI) decreased with increasing of ionic strength in aqueous solutions. The removal of Cr (VI) decreased in the range of 1.28 - 4.47 % on the basis of stated ionic strength and pH ranges. This is presumed to be due to (1) competition of NO_3^- with $HCrO_4^-$or CrO_4^{2-} with the surface of VB; (2) effect of increased ionic strength on the transformation of Cr (VI) from aqueous solutions to the VB surfaces, and (3) with increasing

ionic strengths 0 to 0.1 mol L^{-1}, the electrostatic repulsions would be reduced lowering the available active sites on VB surface (Strawn & Sparks, 1999).

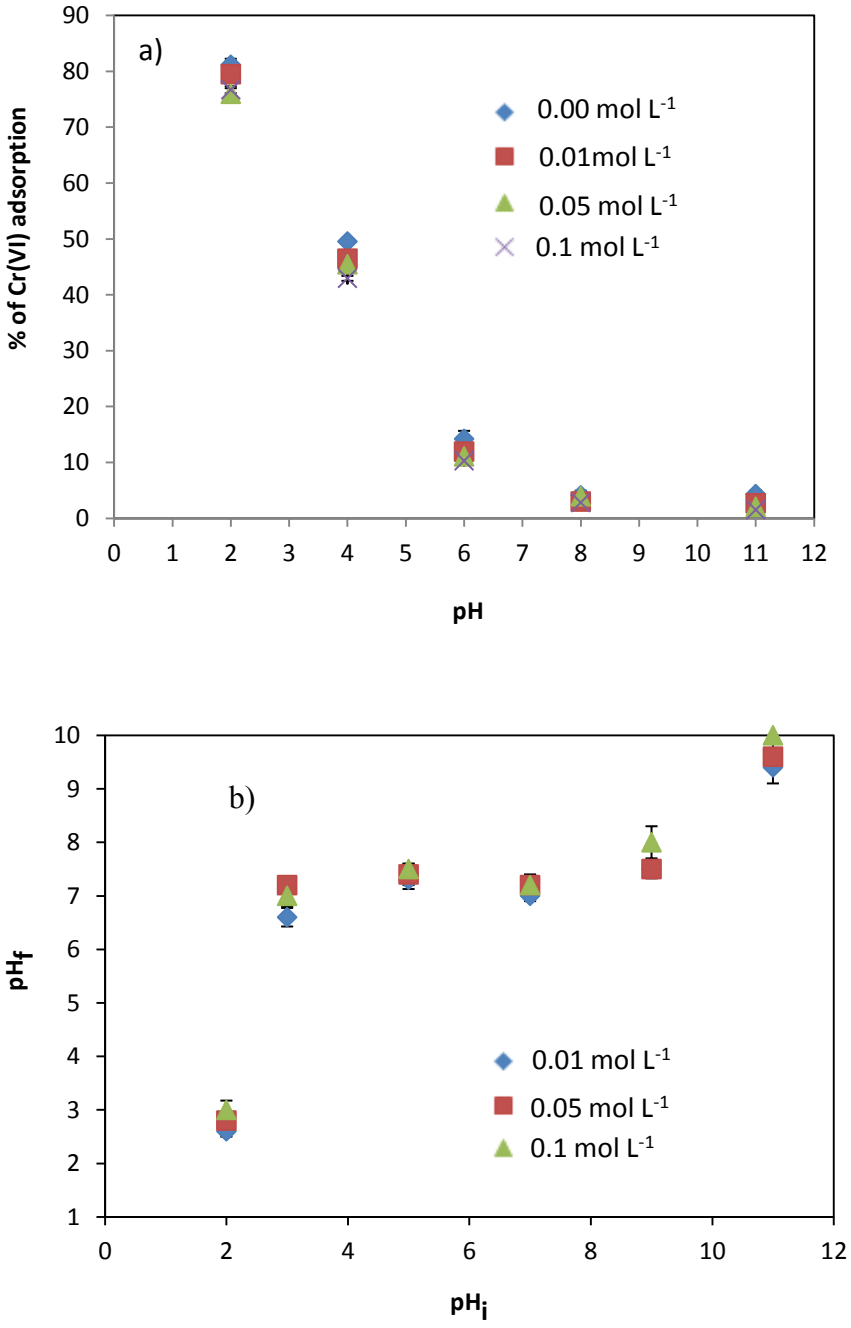


Fig.4. 4 (a) Effect of pH and ionic strength for Cr (VI) adsorption onto the VB (dose 50 g L^{-1}; Cr (VI) conc. 5 mg L^{-1}: temperature 25 ± 0.5 ^{o}C); (b) pH_f Vs. pH_i of the VB suspension with different concentrations of KNO_3 as a background electrolyte.

4.2.2 Effect of Contact Time

The kinetic studies obtained for the adsorption of Cr (VI) from aqueous solutions onto VB surface are shown in **Fig. 4.5**. The time required to reach equilibrium for initial concentrations of 0.1 mg L^{-1}, 1 mg L^{-1} and 5 mg L^{-1} were 180, 360 and 540 min, respectively. For lower initial concentrations (0.1 mg L^{-1}), the adsorption process took place very quickly, with a maximum adsorption of 1.93 mg kg^{-1}. For higher initial concentration of 5 mg L^{-1}, the maximum adsorption of VB at equilibrium was79.20 mg kg^{-1}. This is in agreement with other adsorption studies of Cr (VI) from aqueous solution onto a solid surface (Rodrigues *et al.*, 2010; Khan & Singh, 2010).

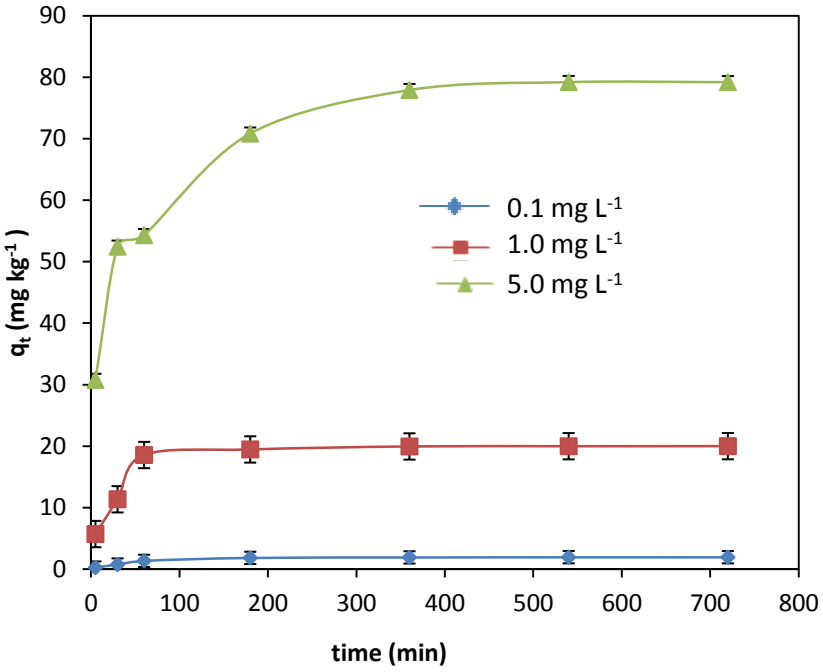


Fig.4. 5 Effect of contact time on adsorption of different concentrations of Cr (VI) ions (0.1, 1.0, and 5.0 mg L^{-1}) on VB. (Adsorbent dose 50 g L^{-1}, solution pH 2.0 and reaction temperature 25 ± 0.5 ^{o}C).

4.2.2.1 Adsorption Kinetics

In order to study the adsorption kinetics, the pseudo-first- order and pseudo-second-order models were used to model the kinetics of Cr (VI) adsorption onto VB. A comparison of the results with the correlation coefficients is shown in **Table 4.2**. The correlation coefficients for the first-order kinetic model obtained at the studied concentrations (0.1, 1 and 5 mg L^{-1}) were low. The q_e values from the graph of pseudo-first-order equation (**Fig. 4.6 (a**)) showed significant variation from experimental q_e values. Thus this kinetic model might not be sufficient to describe the mechanism of Cr (VI)-VB interactions.

The plot of $t\ {q_t}^{-1}$ versus t (**Fig. 4.6 (b**)) produces very good straight lines for different initial Cr (VI) concentrations. The correlation coefficients (R^2) for the second-order kinetic equation were ≥ 0.99 for all concentrations. The calculated q_e values also agreed well with the experimental data. These indicate that the pseudo-second- order kinetic model is suitable for describing the adsorption kinetics of Cr (VI) on VB.

Table 4. 2 Kinetic parameters for Cr (VI) adsorption onto VB

$C_o(mgL^{-1})$	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	q_e $mg\ kg^{-1})$	R^2	k_2 $(kg\ mg^{-1}min^{-1})$	q_e $(mg\ kg^{-1})$	R^2
5	0.01	1.14	0.938	0.001	83.33	0.999
1	0.02	9.53	0.923	0.01	20.41	0.999
0.1	0.01	49.89	0.989	0.34	2.09	0.997

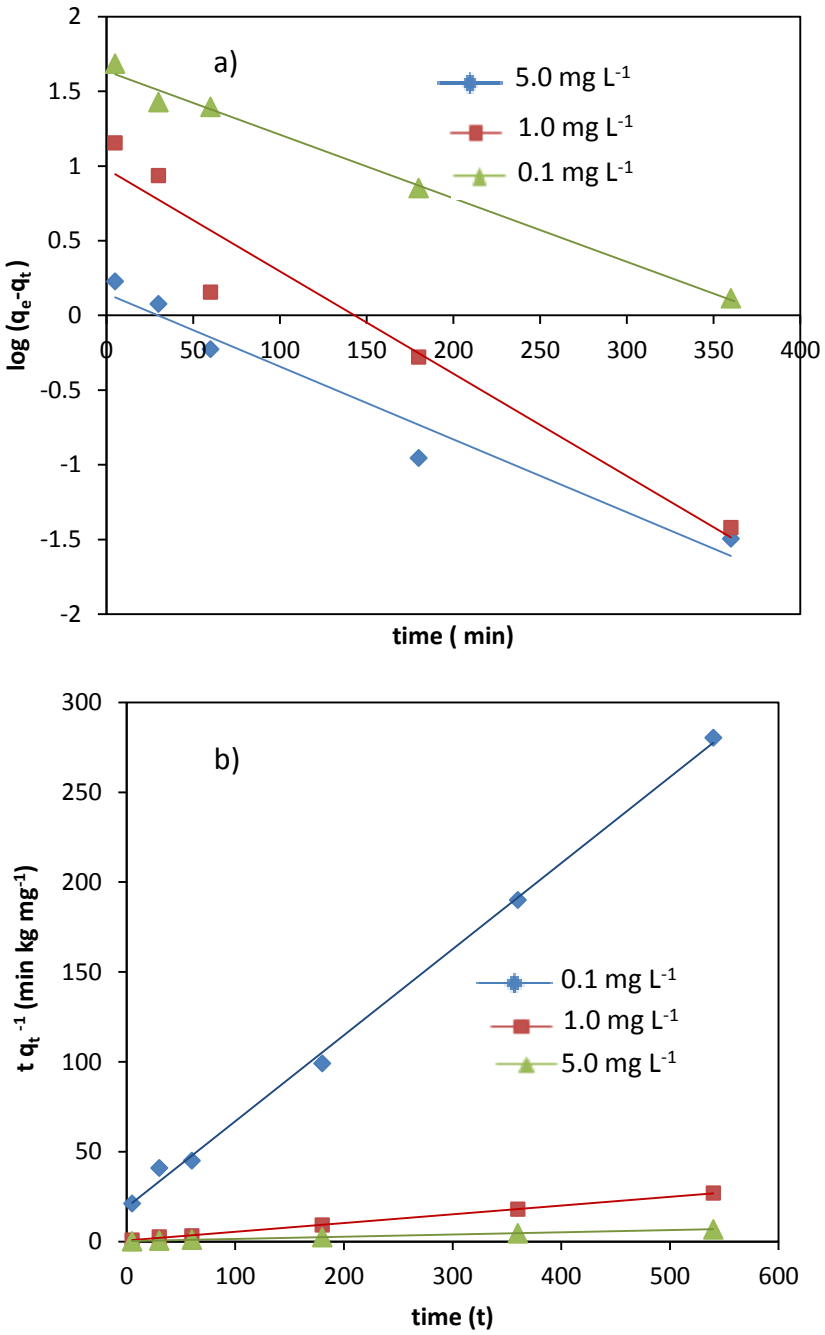


Fig.4. 6 Kinetics for the adsorption of Cr (VI) onto VB: Pseudo-first-order (a); pseudo-second-order (b). [(initial concentration (0.1, 1 and 5 mg L^{-1}), solution pH 2, adsorbent dosage 50 mg L^{-1}, temperature 25± 0.5 ^{o}C)]

4.2.2.2 Adsorption mechanism

To study the adsorption mechanism, the kinetic data of adsorption are fitted into intra-particle diffusion and Boyd model equations as shown **Fig.4.7** (a) and (b) respectively.

The intraparticle diffusion Model

In this study, the intraparticle diffusion rate constant (K_{id}), C and R^2 values were estimated from the linear plot of q_t versus $t^{1/2}$ (**Table 4.3**). The intra-particle diffusion becomes the only rate-limiting step if the plot line passes via origin (Weber and Morris, 1963). The linear plot for different concentration of Cr (VI) in a wide range of contact time did not pass through the origin (**Fig. 4.7**(a)). This indicated that intraparticle diffusion was not the only rate determining step during the adsorption process. The intraparticle diffusion rate constant (k_{id}) increased with increasing initial concentration of Cr (VI) in the solution. This might be due to formation of higher concentration gradient from increased initial concentrations that will ultimately cause faster diffusion and adsorption (Nethaji *et al.*, 2013).

The Boyd's model

The Boyd model was also used to further investigate the adsorption of Cr (VI) onto the VB. This model was employed to distinguish between sorption controlled by film diffusion or particle diffusion. The Boyd linear plot (Bt versus t) of the experimental data did not pass through the origin (**Fig.** 4.7 (b)). This indicated that the adsorption process was controlled by film diffusion. R^2 values were between 0.86 to 0.99 (**Table 4.3**). This might be due to the electrostatic interaction between Cr (VI) and the VB surface. Thus the adsorption of Cr (VI) onto VB was controlled by both film diffusion and intraparticle diffusion. This is in agreement with the study of Alemayehu *et al.* (2011).

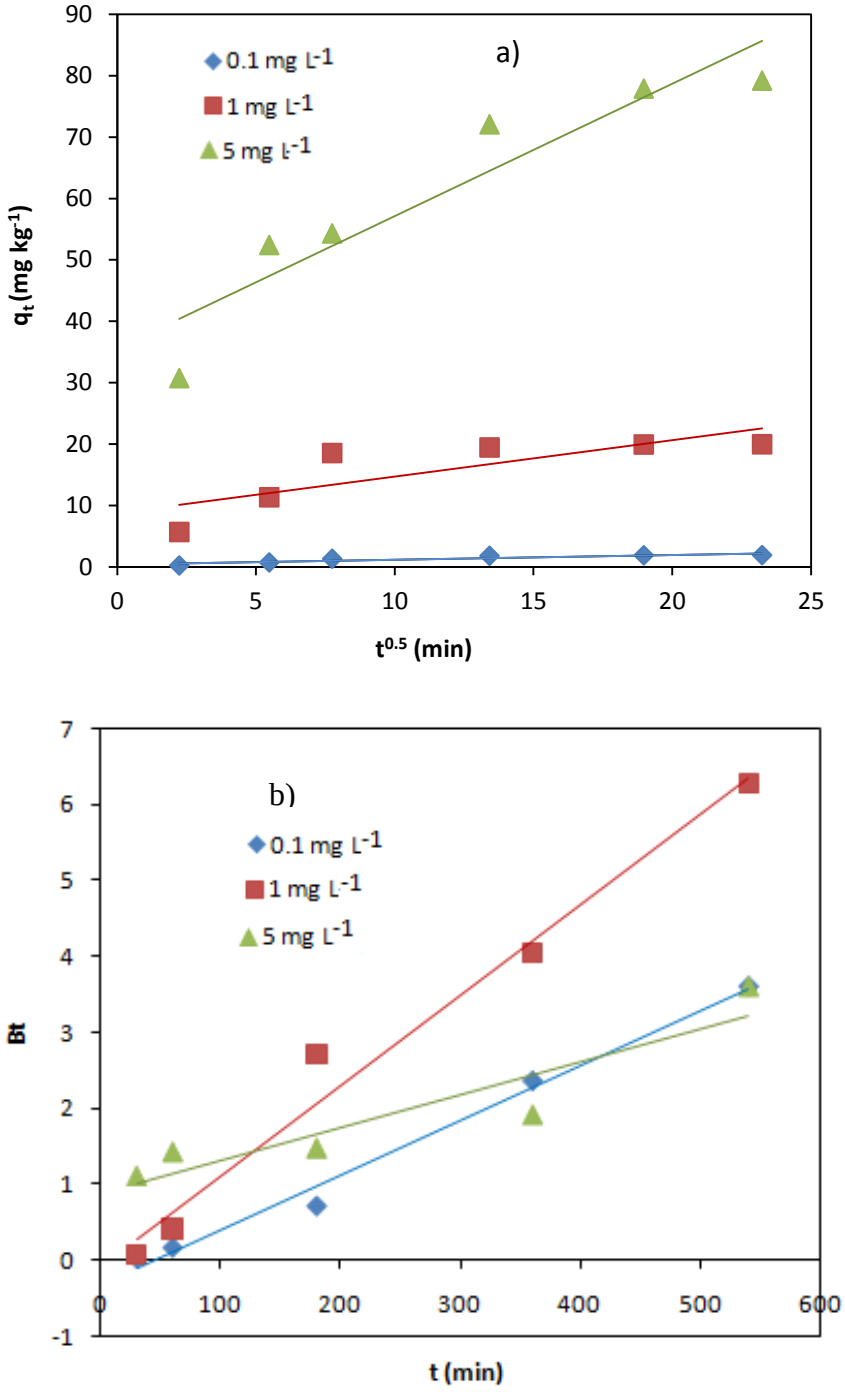


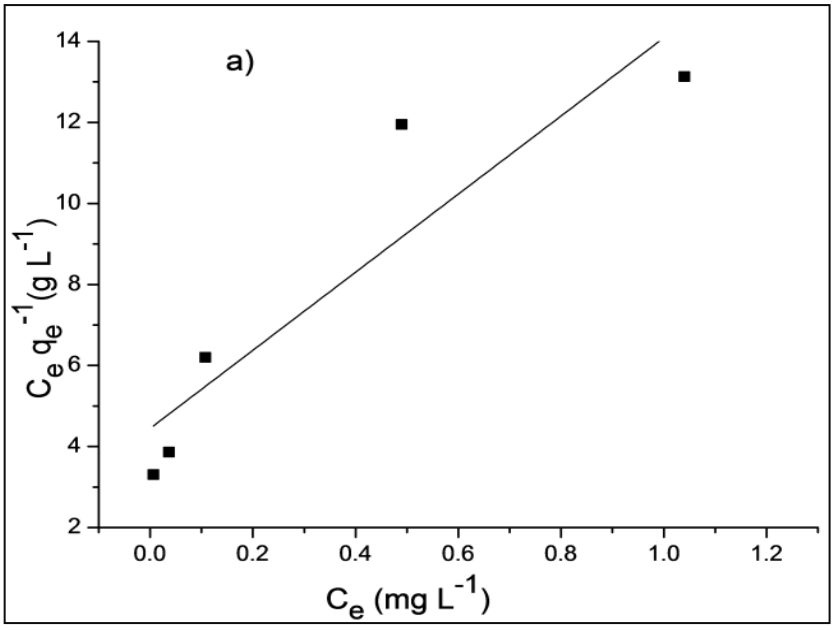
Fig.4. 7 Linear plots of Intraparticle Diffusion (a) and Boyd (b) models for adsorption mechanism of Cr (VI) onto the VB rock.

Table 4. 3 Adsorption mechanism models for the adsorption of Cr (VI) onto the VB

$C_o(mg\ L^{-1})$	Intraparticle diffusion Model			Boyd model
	k_{id}(mg g^{-1} min$^{-0.5}$)	C	R^2	R^2
0.1	0.08	0.40	0.818	0.990
1	0.77	5.92	0.729	0.979
5	2.16	35.55	0.873	0.860

4.2.3 Adsorption Isotherm Studies

The interactive behaviour between adsorbate and adsorbent was described using Langmuir and Freundlich equilibrium adsorption models. The linear plots of Langmuir and Freundlich isotherm equations are displayed in **Fig. 4.8 (a)** & **(b),** respectively. Moreover, adsorption constants and correlation coefficients are shown in **Table 4.4**. The correlation coefficients (R^2) obtained from these equations, were used as the fitting criteria to find out these models. It was found that the plots were well fitted with Freundlich isothermal adsorption models (R^2 = 0.96). The slope (1/n) was 0.783 kg L^{-1} which is in the range of 0 and 1. This indicates that adsorption conditions were favourable and chemisorptive type of sorption was taking place rather than physical adsorption between aqueous Cr (VI) solution and VB surface (Haghseresht & Lu, 1998).



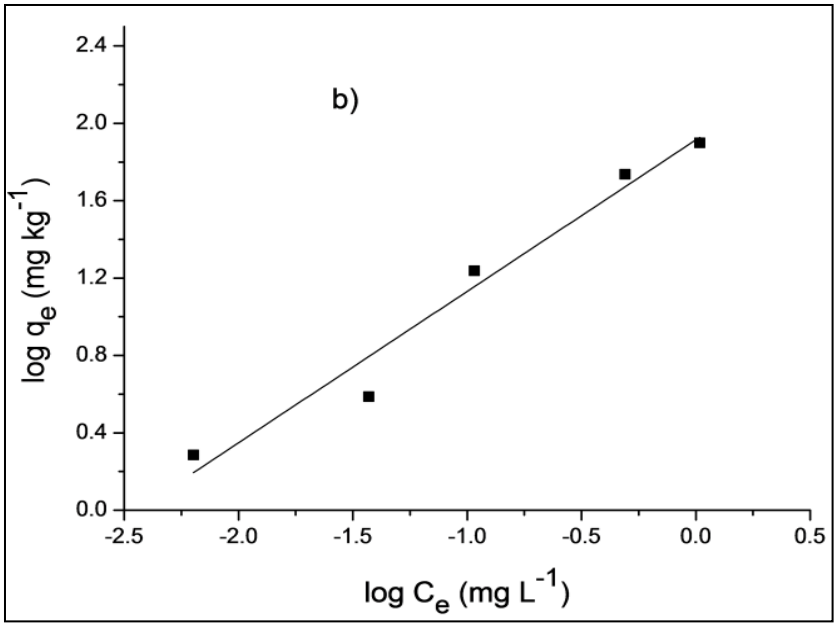


Fig.4. 8 The fitting of Langmuir (a) and Freundlich (b) isotherms of Cr (VI) adsorption of onto VB volcanic rock, pH 2, dose 50 g L^{-1}

One of the essential characteristics of the Langmuir equation could be expressed by dimensionless constant called equilibrium parameter, R_L (Hall *et al.* 1996):

$$R_L = \frac{1}{1 + bC_o} \tag{4.1}$$

The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The calculated R_L value was 0.085, which indicated that the sorption of Cr (VI) ion on VB is favorable.

Table 4. 4 Langmuir and Freundlich isotherms constants for the adsorption of Cr (VI) onto VB

Langmuir model			**Freundlich Model**		
q_{max} (mg kg^{-1})	b(L mg^{-1})	R^2	K_f (L kg^{-1})	1/n	R^2
104.00	2.16	0.803	6.07	0.78	0.96

The adsorption capacity of the VB for the removal of Cr (VI) was compared with other adsorbents reported in literature. The values of adsorption capacities with their experimental settings are presented in **Table 4.5**. The VB indicated good adsorption potential for Cr (VI) in aqueous solution. Based on its large availability, preparation process and general cost, it might hold superiority compared with other adsorbents and could be ideal to reduce Cr (VI) contaminated water from industries or other sources.

Table 4. 5 Comparison of adsorption capacity Cr (VI) onto VB with other adsorbents

Adsorbents	**pH**	**Particle size (µm)**	**Adsorbe ($g\ L^{-1}$)**	**Metal conc. ($mg\ L^{-1}$)**	**Adsorption capacity ($mg\ kg^{-1}$)**	**Reference**
Clay(treated)	*2.50*	*75.00*	20.00	10.00	200.00	(Khan & Singh, 2010)
palygorskite clay	7.00	-	2.00	100.00	58480.00	(Haghseresht *et al.,*1998)
kaolinite	4.60	-	2.00	50.00	6100.00	(Bhattacharyya & Gupta, 2006)
Volcanic pumice	2.00	75.0-425.0	100.00	10.00	46.10	(Alemayehu *et al.,* 2011)
Riverbed sand	2.50	-	20.00	7.84	150.00	(Sharma & Weng, 2007)
VB	2.00	90.0-500.0	50.00	5.00	79.20	This study

4.3 Removal of Cr (III) from Aqueous Solution Using VB Rock

4.3.1 SEM/EDS analysis of VB after adsorption of Cr (III)

The SEM/EDS analysis was used to confirm the adsorption of Cr (III) onto the surface of the VB after the reaction was over (**Fig. 4.9 (a) and (b**)). Even though difficult to identify Cr adsorbed on the SEM image, the EDS analysis showed 2.97 % by weight Cr in the exhausted VB **(Table 4.6).** This confirms the adsorption of Cr (III) onto the surface of the VB during the reaction.

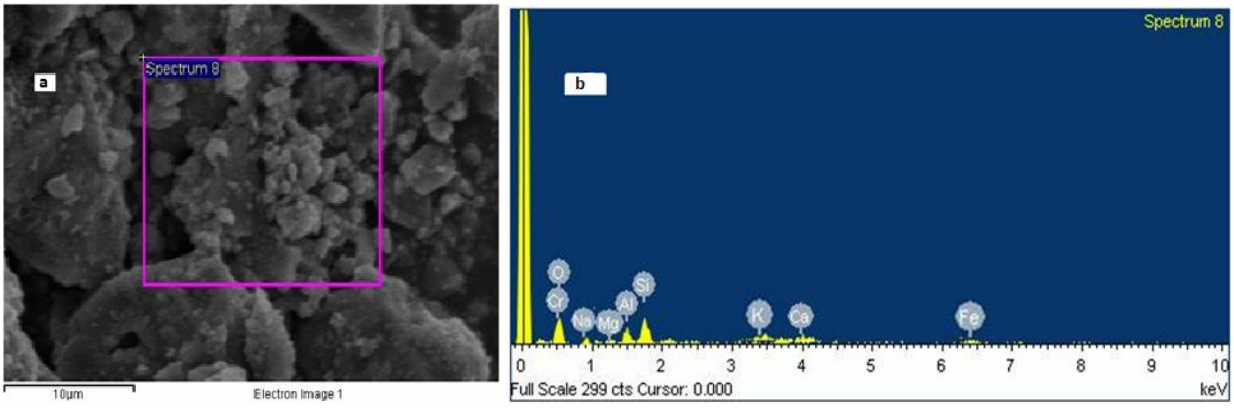


Fig.4. 9 SEM image (a) and EDS spectra (b) of VB after adsorption of Cr (III).

Table 4. 6 Elemental analysis of the VB after adsorption using EDS spectroscopy

Element	Weight %	Atomic %
O K	48.46	63.42
Si K	17.37	14.62
Al K	9.55	6.95
Mg K	0.87	0.70
Ca K	8.8	4.31
Fe K	8.83	3.93
Na K	2.64	3.17
K K	0.51	0.60

Cr K	2.97	2.30
Total	100	100

4.3.2 Effect of pH and Ionic Strength

The influence of pH and ionic strength for the adsorption of Cr (III) on the VB surface were investigated as shown in **Fig. 4.10 (a)**, which shows that adsorption of Cr (III) increased with increasing pH. At pH 2 the removal efficiency of Cr (III) was very low (0.036-2.03%). The adsorption was increased sharply to 40.93 - 46.43 % at pH 4. Meanwhile the maximum adsorption observed was 54.67% at pH 6. To explain the effect of pH for adsorption of Cr (III) on the VB surface, it is essential to understand the speciation of Cr (III) in aqueous solution. According to Rai *et al.* (1987), Cr (III) exists in aqueous solutions as hexa-aquachromium (3+) and its hydrolysis products as shown reaction (1), (2) and (3).

The occurrences of these species of chromium (III) complex are pH dependent. According to the Cr(III) speciation diagram, the predominant Cr(III) species in a water solution were hexa-aquachromium at pH 2 ; $Cr(OH)^{2+}$ at pH 4(60%); $Cr(OH)^{2+}$ at pH 5 (70%); and $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$; and $Cr_3(OH)_4^{5+}$ approximately 40%, 35%, 25% respectively at pH 6 (Leyva-Ramos *et al.* 1995; Kotas & Stasicka, 2000). This means that the Cr (III) was adsorbed on the VB as Cr $(OH)^{2+}$, Cr $(OH)_2^{+}$; or $Cr_3(OH)_4^{5+}$ species.

The pHpzc value for the VB was 7.6 (**Fig. 4.10 (b**)). At the pHpzc, the surface of the VB has all its charges balanced. The surface of VB is negatively charged above the value of pHpzc, while the surface of the VB is positively charged below the value of the pHpzc (Sheng *et al*. 2012). The smallest adsorption capacity occurred at pH 2 because of the strong electrostatic repulsion of highly protonated ions of the solution with positively charged surface of the VB. An increase in the adsorption of Cr (III) in the pH range of 2-6 might be due to reduction of repulsion of cations of Cr (III) complexes in the solution with positively charged VB surface. Above pH value of 6.4, Cr (III) precipitates as Cr $(OH)_3$ (Liu *et al.*, 2016). All other adsorption experiments were conducted at pH 6, for maximum adsorption of Cr (III) onto the VB.

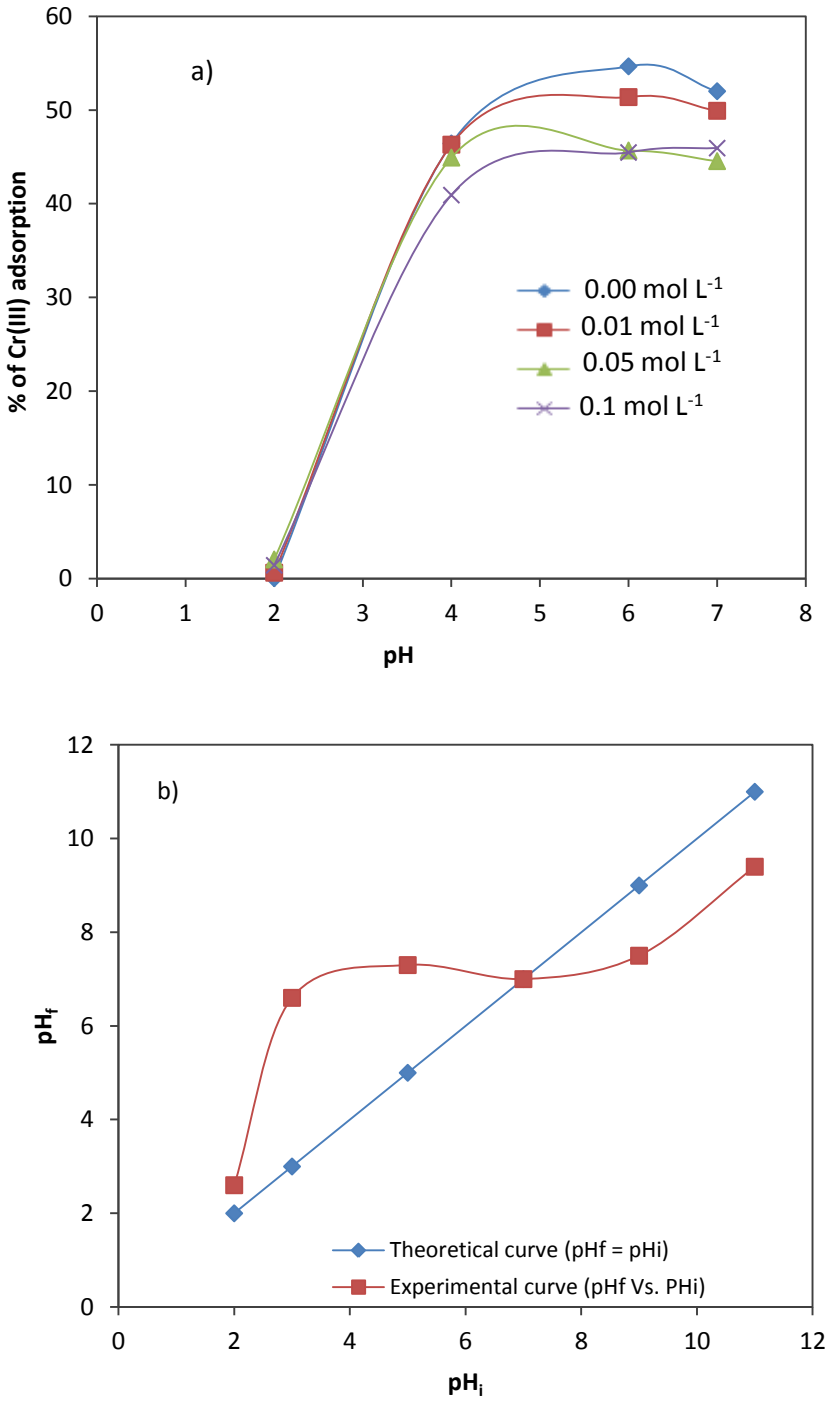


Fig.4. 10 Effect of pH and ionic strength for Cr (III) adsorption onto the VB (dose 50 g L^{-1}; Cr (III) conc. 100 mg L^{-1} ; temperature 25 ± 0.5 ^{o}C) a) ; Determination of pHpzc of Crushed VB in 0.01 mol L^{-1} KNO_3 solution b)

Ionic strength, like pH also affects adsorption of a system. **Fig. 4.10 (a)** showed the removal of Cr (III) at different ionic strength (0, 0.01, 0.05 and 0.1 M) as a function of pH (2-7) onto VB. The percentage of removal of Cr (III) decreased with increasing of ionic strength of aqueous solutions. The removal of Cr (III) decreased in between 1.99-9.195 % in the stated ionic strength and pH ranges. This might be due to competition of K^+ with Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^+$, or $Cr_3(OH)_4^{5+}$ with the surface of VB. Effect of increased ionic strength on the activity coefficient of Cr (III) limits transformation of Cr (III) from aqueous solutions to the adsorbent surfaces and with increasing ionic strengths, the electrostatic repulsions would be reduced with increasing ionic strength lowering the available active sites on VB surface (Strawn & Sparks 1999).

4.3.3 Effect of Contact Time

The adsorption of Cr (III) onto the VB is examined at different contact time intervals using 20, 60, and 100 mg L^{-1} initial concentrations as shown in **Fig. 4.11**. It is observed that a rapid uptake was experienced in the first 60 min but slowed down noticeably as reaction approached to equilibrium after 480 min. The fast removal in the first 60 min might be due to availability of vacant sites at the VB surface (Pathania *et al*. 2017). For lower 20 mg L^{-1} and higher 100 mg L^{-1} initial concentrations, the maximum adsorption capacity onto the VB surface reached up to 0.360 and 0.976 mg g^{-1} respectively. The considerable uptake at higher initial concentration is a consequence of larger concentration gradient between the bulk solution and sorbent phase. This is in agreement with other adsorption studies of Cr from aqueous solution onto a solid surface (Rodrigues *et al*. 2010; Mthombeni *et al.* 2015).

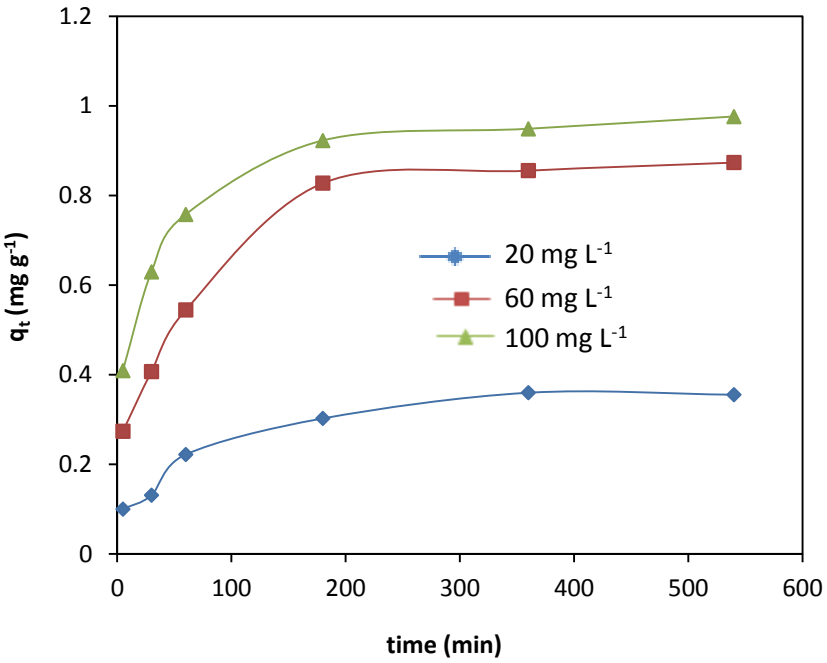


Fig.4. 11 Effect of contact time on adsorption of different concentrations of Cr (III) ions (20, 60 and 100 mg L^{-1}) on VB. (Adsorbent dose 50 g L^{-1}, solution pH 6 and reaction temperature 25 ± 0.5 ^{o}C).

4.3.3.1 Adsorption Kinetics

In order to study the adsorption processes such as mass transfer and chemical reaction, the pseudo-first order and pseudo-second order kinetic models were applied to model the kinetics of Cr (III) adsorption onto VB. A comparison of the results with the correlation coefficients is shown in **Fig. 4.12 (a)** and **Table 4.7**. The R^2 for the pseudo-first order kinetic model for initial concentrations (20, 60, and 100 mg L^{-1}) are high. But, large differences are observed between the theoretical and experimental equilibrium adsorption capacities (q_e). This indicates that pseudo-first order model is not appropriate for the adsorption of Cr (III) by VB.

The pseudo-second-order kinetic linear plot (**Fig. 4.12 (b**)) gives very good straight lines for different initial Cr (III) concentrations. The correlation coefficients (R^2) were ≥ 0.99 for all concentrations (**Table 4.7**). The calculated q_e values also agreed well with the experimental data. These indicate that the pseudo-second-order kinetic model is suitable for describing the adsorption kinetics of Cr (III) onto the VB surface.

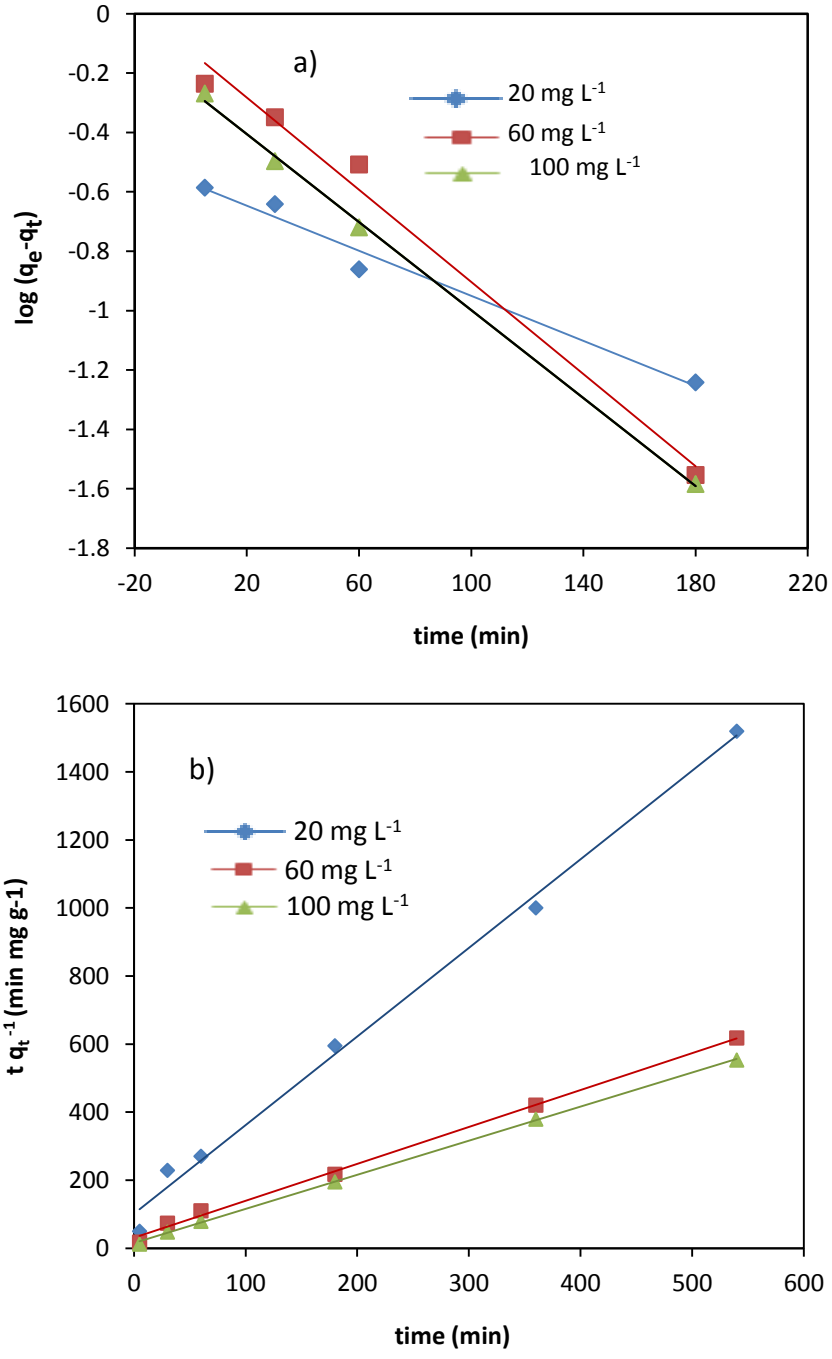


Fig.4. 12 Adsorption kinetics: pseudo-first-order kinetic linear plot (a) and pseudo-second-order kinetic linear plot (b) for adsorption of Cr (III) onto VB { initial concentration (20, 60, and 100 mg L^{-1}), solution pH 6 ,adsorbent dosage 50 g L^{-1} , temperature 25 ± 0.5 ^{o}C)}.

Table 4. 7 Kinetic parameters for Cr (III) adsorption onto VB

$C_o(mgL^{-1})$	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	q_e *(mg g-1)*	R^2	k_2 (min^{-1})	q_e *(mg g-1)*	R^2
20	0.009	0.269	0.967	0.067	0.384	0.993
60	0.020	0.746	0.982	0.039	0.921	0.997
100	0.017	0.553	0.998	0.068	0.997	0.999

4.3.3.2 Adsorption mechanism

The adsorption mechanism of Cr (III) onto the VB was investigated using intraparticle diffusion and Boyd models. The linear plots of intraparticle diffusion model, K_{id}, C and R^2 values were calculated from the linear plot of q_t versus $t^{1/2}$ (**Table 4.8)**. The linear plot for different concentration of Cr (III) in a wide range of contact time did not pass through the origin (**Fig. 4.13** (a)). This indicated that intraparticle diffusion was not the only rate determining step during the adsorption process. The k_{id} increased with increasing initial concentration of Cr (III) in the solution. This might be due to formation of higher concentration gradient from increased initial concentrations that will ultimately cause faster diffusion and adsorption (Nethaji *et al.,* 2013).

The adsorption mechanism of Cr (III) onto the VB was further investigated by Boyd model. The Boyd linear plot (Bt versus t) of the experimental data did not pass through the origin, which indicated that adsorption process was controlled by film diffusion (**Fig. 4.13** (b)). This might be due to the electrostatic interaction between Cr (III) and the VB surface. The R^2 values were between 0.928 to 0.971 (**Table 4.8**). From the results observed, it was indicated that the adsorption of Cr (III) ions onto the VB was controlled by film and/or intraparticle diffusion. This is in agreement with the study of Alemayehu *et al.* (2011).

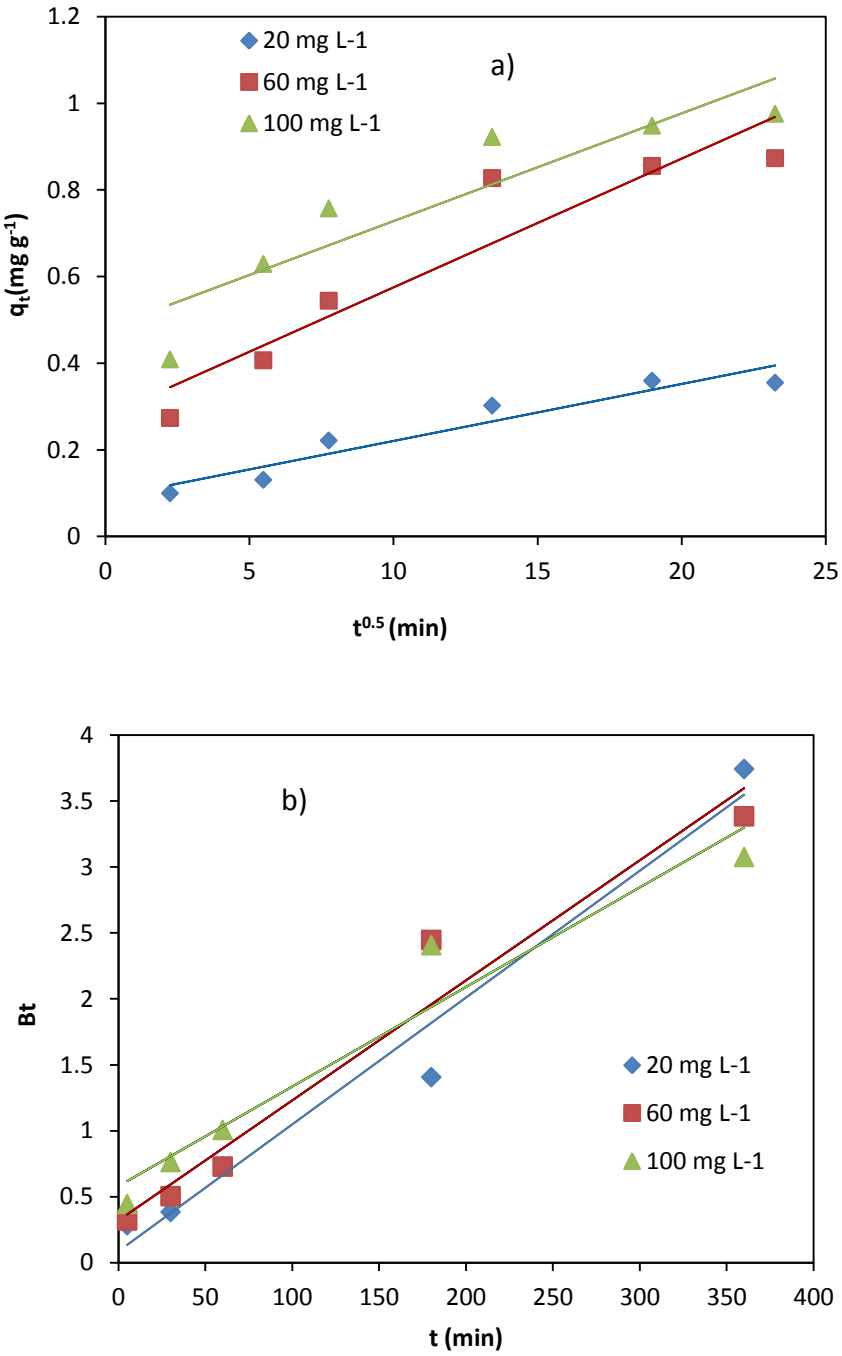


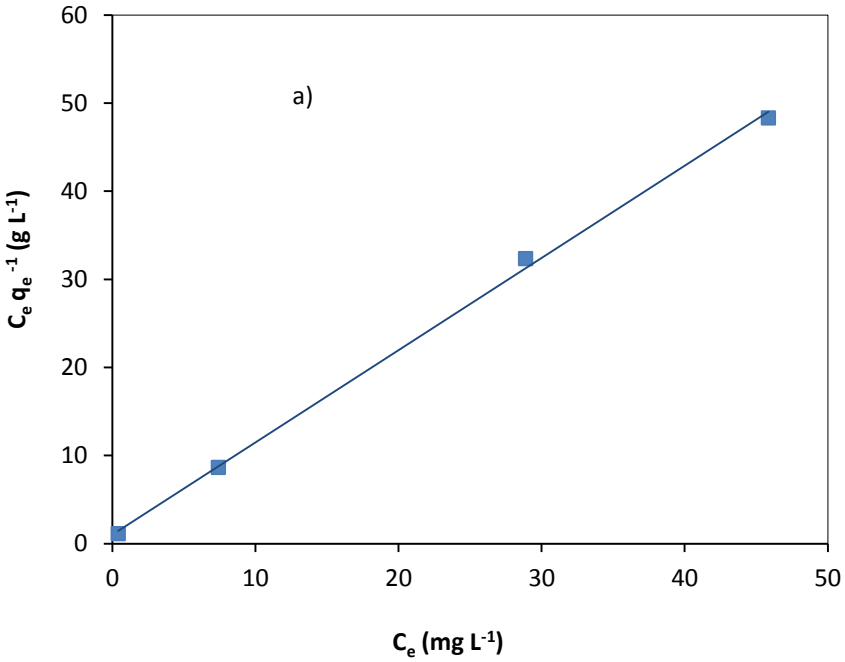
Fig.4. 13 Linear plots of Intraparticle Diffusion (a) and Boyd (b) models for adsorption mechanism of Cr (III) onto the VB rock.

Table 4. 8 Adsorption mechanism models for the adsorption of Cr (III) onto the VB

C_o (mg L^{-1})	Intraparticle diffusion model			Boyd model
	k_{id} (mg $g^{-1}min^{-0.5}$)	C	R^2	R^2
20	0.013	0.269	0.912	0.971
60	0.024	0.746	0.881	0.947
100	0.029	0.553	0.83	0.928

4.3.4 Adsorption Isotherm Studies

The adsorption capacity of Cr (III) onto the VB at equilibrium was evaluated using the linear Langmuir and Freundlich isotherm models (Gupta & Rastogi, 2008). The linear plots of Langmuir equation $C_e\, q_e^{-1}$ versus C_e and Freundlich equation $\log q_e$ versus $\log C_e$ are indicated in **Fig. 4.14 (a)** & **4.14 (b)**, respectively. The adsorption isotherms and equilibrium data fittings are shown in **Table 4.9**. According to the correlation coefficient (R^2), the equilibrium data are better described by the Langmuir isotherm. The maximum adsorption capacity of Cr (III) on the surface of the VB was 0.872 mg g^{-1}.



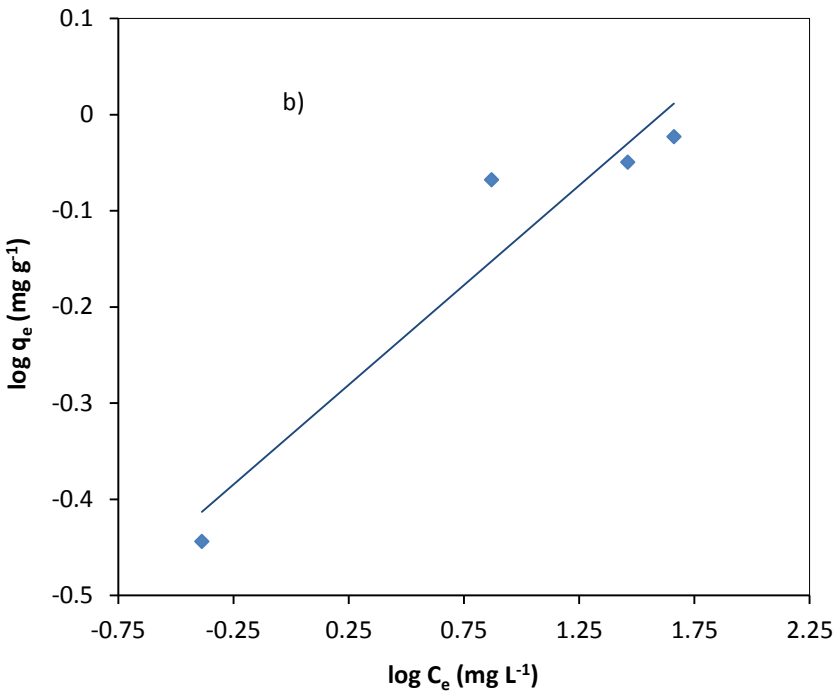


Fig.4. 14 The fitting of Langmuir (a) and Freundlich (b) isotherms of Cr (III) adsorption onto VB volcanic rock, pH 6, dose 50 g L^{-1}

The essential features of the Langmuir adsorption isotherm parameter, which can be used to predict the interaction or affinity of adsorbent and adsorbate known as equilibrium parameter or separation factor (R_L) was determined (Hall *et al.* 1996). The calculated R_L value for Cr (III) ion adsorption onto VB was 0.01. This value shows that the adsorption process is favourable.

Table 4. 9 Langmuir and Freundlich isotherm parameters for adsorption of Cr (III) onto VB

Langmuir model			**Freundlich Model**		
q_{max} (mg g^{-1})	b(L mg^{-1})	R^2	K_f (L kg^{-1})	1/n	R^2
0.872	1.04	0.998	2.153	0.207	0.878

The potential of adsorption of Cr (III) by VB was compared with other adsorbents reported in the literature. The values of adsorption capacities are presented in **Table 4.10** with their experimental settings. Experimental studies containing Cr (III) aqueous solutions showed good

adsorption potential of Cr (III) onto the surface of VB. Based on its abundant availability, ease of preparation, environmental friendly use and general cost, it might be preferred compared with other adsorbents and could be ideal to reduce Cr (III) contaminated water and wastewater from industries or other sources.

Table 4. 10 Comparison of adsorption capacity Cr (III) onto VB with other adsorbents

Adsorbents	***pH***	***Particle size(μm)***	***Adsorbent dose(g L^{-1})***	***Metal conc. (mg L^{-1})***	***Adsorption capacity(mg g^{-1})***	***Reference***
Bentonite	2	-	50	50	0.57	(Khan *et al.* 1995)
Bentonite	7	Up to 160	20	100	4.64	(Chen *et al*. 2012)
kaolinite	2	-	25	100	1.92	(Koppelman *et al*.,1980)
Natural Scolecite	6	< 200	10	50	3.00	(Bosco *et al.* 2005)
Kaolin	4.5	-	25	300	0.898	(Liu *et al*. 2016)
VB	6	90-500	50	100	0.997	This study

4.3.5 Adsorbent Cost

The average cost of VB in the year 2017 was about US \$14 ton^{-1} around Bahir Dar City (Ethiopia). This cost includes all expenses like transportation, electrical power for crushing, human labour, etc. In **Table 4.11** below the estimated cost of other adsorbents are compared with the naturally available VB. This price is very low and it is promising for the treatment of Cr (VI) containing wastewater for low income countries.

Table 4. 11 Estimated cost of VB and other adsorbents reported in literature

Adsorbents	***Price (US \$ ton^{-1})***	***Reference***
Natural Zeolite	840.34	(Salam *et al.,* 2011)
Fly ash	490.20	(Salam *et al.,* 2011)
Commercial activated carbon	20000.00	(Atun *et al.,* 2003)

Diatomite (for adsorbent)	92.00	(Crangle, 2012)
Perlite	< 1500.00	(Mathialagan & Viraraghavan, 2002)
Commercial activated carbon	3300.00	(Toles *et al.,* 2000)
VB	16.00	This study

4.4 Removal of Cr Containing Tannery Wastewater Using CWS

4.4.1 Tannery Wastewater Characterization

Bahir Dar Tannery produces crust and finished leather for export to the global market. In the tanning process, the industry uses chromium (III) salts and other chemicals for high quality leather production. The wastewater generated from different unit processes passes through a screen and collected in a large rectangular pond of length 18 m, width 9 m and depth 3 m (volume =486 m^3). Wastewater from the tanning industry was characterized by high organic and inorganic loadings due to the processes used to turn raw hide or skin into leather.

The diluted tannery wastewater was collected in a thick plastic equalization tank with capacity of 2000 liters to feed the wetland units. The average compositions of the inflow and outflow (after treatment) were characterized as shown in **Table 4.12** below.

Table 4. 12 Average composition of the inflow and outflow concentration (minimum - maximum) ranges of the pilot CWUs (n=6)

Parameters	Influent conc. (mg L^{-1})	Effluent concentration (mg L^{-1}) for each wetland unit				
		CWU1	CWU2	CWU3	CWU4	CWU5
Cr total (mg L^{-1})	11.728 ± 7.00	0.073 ± 0.07	0.122 ± 0.125	0.093 ± 0.109	0.194 ± 0.139	0.315 ± 0.243
(range)	(4.27-20.48)	(0.012-0.146)	(0.011-0.266)	(0.014-0.248)	(0.032-0.318)	(0.044-0.586)
Cr(VI)- (mg L^{-1})	0.019 ± 0.007	0.028 ± 0.011	0.022 ± 0.008	0.023 ± 0.007	0.022 ± 0.005	0.029 ± 0.017
(range)	(0.014-0.029)	(0.021-0.045)	(0.016-0.033)	(0.011-0.027)	(0.015-0.026)	(0.005-0.041)
BOD5 (mg L^{-1})	163.90 ±94.26	32.25 ± 22.40	38.05 ± 25.34	34.40 ± 20.97	37.04 ± 19.87	42.29 ± 23.43
(range)	(53.75-299.20)	(11.00-62.2)	(15.00-75.20)	(12.50-60.20)	(20.40-68.00)	(20.61-72.94)
COD (mg L^{-1})	1185.5± 596.08	189.36 ± 111.09	222.84 ± 148.60	203.2 ± 144.53	225. 28 ± 121.33	251.55 ± 123.27
(range)	(297.024-1976)	(106.2-400.39)	(70.8-456.74)	(65.1-451.17)	(70.80-441.17)	(139.50-425.61)
Cl- (mg L^{-1})	1115.99 ± 416.22	835.95 ± 447.42	913.83 ± 474.53	891.52 ± 476.01	901.23 ± 484.78	903.70 ± 495.34
(range)	(417.87-1649.49)	(259.39-1378.59)	(359.89-1459.54)	(305.89-1479.51)	(318.9-1379.45)	(257.43-1569.74)
TP (mg L^{-1})	3.74 ± 0.50	1.478 ± 0.384	1.54± 0.389	1.41± 0. 483	1.572 ± 0.680	1.597 ± 0.575

(range)	(2.99-4.77)	(0.945-1.935)	(0.745-1.981)	(0.773-1.994)	(0.538-2.216)	(0.58-2.203)
TSS (mg L^{-1})	427.83 ± 305.90	128.00 ± 80.90	140.5 ± 85.64	125.83 ± 77.42	129. 33 ± 80.58	138.00 ± 85.32
(Range)	(36-859)	(15-207)	(25-230)	(24-211)	(22-235)	(8-354)
EC (ms cm^{-1})	4.933 ± 1.788	4.134 ±1.281	4.328 ±1.617	3.881 ±1.517	4.174 ± 1.843	3.235 ± 1.08
(range)	(2.17-6.85)	(1.893-5.481)	(1.987-6.29)	(1.78-5.71)	(1.739-6.35)	(1.3-4.25)
pH	7.2 ± 0.269	7.457± 0.403	7.287 ± 0.402	7.255 ± 0.434	7.215 ± 0.384	7.675 ± 0.257
(range)	(6.92-7.71)	(6.9-8.06)	(6.82-7.91)	(6.84-7.97)	(6.73-7.82)	(7.4-8.06)
NO_3^--N (mg L^{-1})	29.61 ± 7.91	8.87 ± 6.94	8.52 ± 3.72	8.92 ± 3.91	10.33 ± 7.33	10.87 ± 6.25
(range)	(19.48 - 42.52)	(2.3-12.48)	(4.92-12.04)	(3.10-13.36)	(2.30-20.18)	(2.78-17.86)
TDS (mg L^{-1})	3033.5 ± 975.06	2615 ± 828.13	2704 ± 940.25	2411 ±976.74	2524.33 ± 1257.87	1801.25 ±512.43
(range)	(1411-4158)	(1220-3563)	(1248-4089)	(1162-3574)	(1073-4021)	(872.5-2410)
T^0 (^oC)	22.21 ± 0.86	20.45 ± 1.04	20.55 ± 1.07	20.48 ± 0.90	20.52 ± 0.98	20.2 ± 0.55

Data collected from October to December 2017 (n = 6)

The constructed wetland units worked with an average hydraulic loading rate of 0.0357 m d^{-1} (3.57 cm d^{-1}), increased by 0.57 cm d^{-1} to the HLR used by Calheiros *et al.* (2007). The inflow compositions of the tannery wastewater into the pilot wetland units, indicated variability of the wastewater during the study time (**Fig. 4.15**). This might be due to variations in the type of chemicals used at different unit operations in the tanning process. The concentration of total Cr in the wastewater was found in the range of 4.27 to 20.48 mg $L^{-1}$with an average value of 11.73 ± 7.00 mg L^{-1}. The concentration of Cr (VI) in the inflow wastewater was also determined. It was found in the range of 0.014 to 0.029 mg L^{-1} with an average concentration of 0.019 ± 0.007 mg L^{-1}. The variation of inflow COD concentration ranged from 297.02 to 1976 mg L^{-1} with an average concentration of 1185.5 ± 596.08 mg L^{-1}. The average influent loading rate of COD was 423.39 kg d^{-1} ha^{-1}. The influent concentration of BOD_5 ranged from 53.75 to 299.2 mg L^{-1} with an average loading rate of 58.53 kg d^{-1} ha^{-1}.The inflow wastewater was also composed of an average total suspended solid (TSS) of 427.83 ± 305.90 mg L^{-1} in the range of 36 to 859 mg L^{-1}.

The pH of inflow wastewater from the tank was in the range of 6.92 to7.71 with an average value 7.2 ± 0.27 during the operation period. This was a good pH range for the plants to grow well and microorganisms to degrade the input wastewater to it. The average temperature of the inflow

tannery wastewater was 22.21 ± 0.86 ^{o}C .The inflow wastewater was also composed of high salinity with an electrical conductivity between 2.17-6.85 ms cm^{-1}, total dissolved solid concentrations of 1411-4158 mg L^{-1} and chloride (Cl^{-}) concentration of 417.87-1649.49 mg L^{-1}

The wastewater composition of tanning industries varied in their physico-chemical properties. Tadese & Seyoum (2015) reported the average concentrations of Mojo tannery effluent as Cr 40 ± 27 mg L^{-1}, COD 4434 ± 1846 mg L^{-1}, BOD_5 1054 ± 448 mg L^{-1}, S^{2-} 152.9 ± 3.3 mg L^{-1} and Aregu *et al.*(2018) reported the concentrations of Dire Tannery effluent as pH 9.1 ± 3.1, total Cr 35.7 ± 8.6 mg L^{-1}, COD 12913 ± 6874.7 mg L^{-1}, BOD_5 1081 ± 159.55 mg L^{-1} ,TSS 2426 ± 515.2 mg L^{-1} and S^{2-} 417 ± 130.7 mg L^{-1}. Mandal *et al.*(2010) also reported the wastewater produced from leather industries in the area Tangra, Tiljala and Topsia of Kolkata, India as total Cr 258 mg L^{-1}, COD 2533 mg L^{-1} , BOD_5 977 mg L^{-1}, TSS 1244 mg L^{-1},TDS 21620 mg L^{-1}, Cl^{-} 6528 mg L^{-1}, S^{2-} 860 mg L^{-1} and EC 20.042 ms cm^{-1}. All the above three studies indicated wide differences in their compositions of tannery wastewater. The variations might be due to the type of hides used, differences in the unit processes, and capacity of producing finished leather and amount /type of chemicals used.

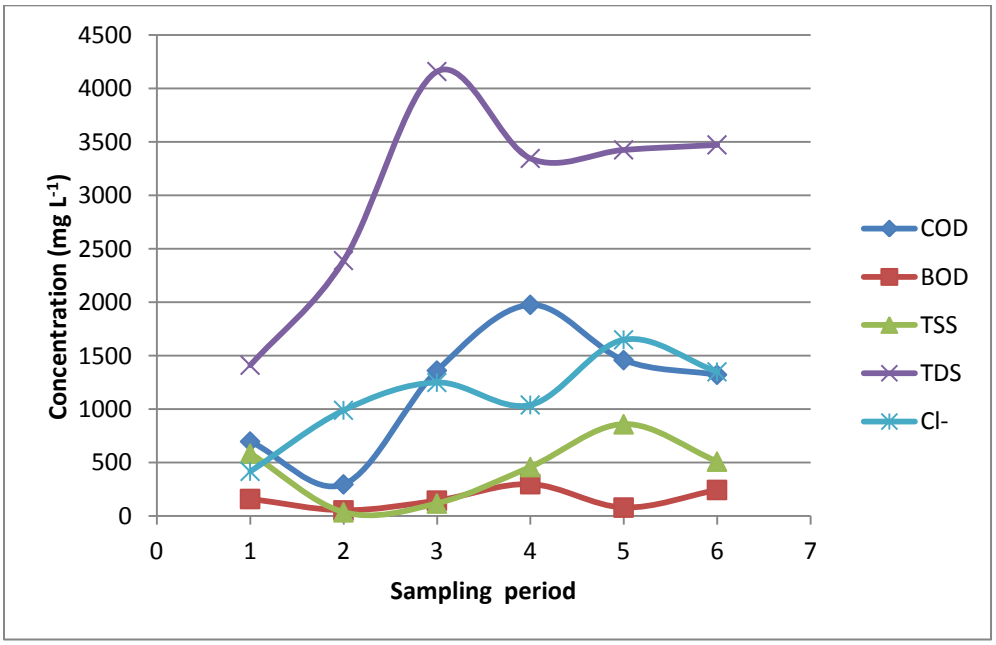


Fig.4. 15 Variations in the compositions of an inflow tannery wastewater supplied to the HSSF constructed wetland units during the operation period (n=6)

4.4.2 Plant Growth in the Pilot Constructed Wetland Units

The growth of vegetated plants on the HSSF constructed beds were monitored before and during experimental period. The plants were adapted to the toxic wastewater by supplying it step by step, i.e. from lower to higher preferred concentrations (**Appendix B.2**). The vegetated plants were well adapted to the feed wastewater. Though there were some observable changes of the plant leaves to yellow, drying and dropping leaves and dying of a few plants, there was good growth and propagations. There was appearance of some weeds in all of the four wetland units except the control. The weeds were removed by a continuous follow up almost every day. A few numbers of trees of *P. purpureum* were infested by pests during two weeks of experimental period and disappeared without any treatment to it.

P. purpureum vegetated on bed 1(CWU1) and *T. domingensis* on bed 2 (CWU2) reached maximum heights of 4.5 m and 3.2 m, respectively. *C. latifolius* vegetated on bed 3 (CWU3) and *E. pyramidalis* on bed 4 (CWU4) are relatively short with a maximum height of 1.53 and 1.60 m respectively. After the experiment the wetland plants were dug up and their roots were examined (**Appendix B.3**). *P. purpureum* has dense, fine compacted roots that hold the gravel and dye tightly. The roots reached a maximum length of 32 cm length. The *T. domingensis* has a thicker root with a maximum root length of 28 cm. *C. latifolius* has less thicker roots compared to *T. domingensis*. It produced long roots of about 48 cm and expanded roots that can hold the gravel and the wastewater tightly. The root length of *E. pyramidalis* reached to a maximum of 37 cm, which was longer than the first two plants vegetated on the constructed wetland bed. The root is thinner and fiberous in nature.

In general, the plants in this operation conditions indicated a continuous healthy growth, which is an important factor in the choice of plants for phytoremediation. The plants will take up more Cr to a higher extent as far as the plants can grow and tolerate the concentration of the metal in the media (Mant *et al.*, 2006).

4.4.3 Removal Efficiency of Cr in the Pilot CWUs

The inflow and outflow concentrations of total Cr in the constructed wetland units are shown in **Table 4.12**. Total Cr removal efficiencies at different constructed wetland units indicated between 97.32-99.38% for an inflow concentrations in the range of 4.27-20.48 mg L^{-1} (**Fig. 4. 16**). CWU1 (*P. purpureum) and CWU3 (C. latifolius*) removed 99.38% and 99.21 % total Cr respectively. Relatively lower removal of total Cr was observed for CWU5 (control) with an average removal efficiency of 97.32 % as compared to all vegetated constructed wetland units. This might be due to the development of root system in vegetated units that can provide surface area for biofilm development, chemical precipitation and metal binding (Papaevangelou *et al.*, 2017) .This study was in agreement with the findings of the removal efficiency of chromium by some selected wetland plants from Modjo Tannery wastewater in HSSF constructed wetland system. The study indicated that 97.7-99.3% total Cr removal for planted wetland units and 97.4 % for the control unit (Tadese and Seyoum, 2015).

All the HSSF constructed units show efficient removal of total Cr. This might be associated with microbial populations, media type and pH of the wastewater. Dotro *et al. (*2011) reported that the sorption sites of the biological flocs were occupied by Cr (III) from tannery wastewater in a constructed wetland system. Studies also indicated biosorption of Cr (III) onto industrial biomass at an optimum pH of 5-6 (sekhar *et al.,* 1998). Cr (III) can form complexes with a variety of ligands in the tannery wastewater such as water, ammonia, and other organic ligands containing oxygen, nitrogen or sulphur donor atoms (Nakayama *et al.,* 1981; Salem *et al.,* 1989). The complexation of Cr^{3+} increases its solubility and may facilitate its removal related to sorption by the biomass growing in the media of the constructed wetland unit. In addition the vesicular basalt used as a supporting media for wetland plants adsorbs Cr (III) onto its surface as indicated in the lab studies. The other potential removal of Cr (III) from the tannery wastewater in the HSSF constructed wetland unit could be precipitation of Cr (III) with hydroxides, sulfides, sulphates and carbonates obtained from chemicals used in the tanning process (USEPA, 2000). The sulfides and sulphates can be obtained from the decay of animal hides and skins in oxic and anoxic conditions that can further precipitate Cr (III) in the pilot units (Mitsch and Gosselink, 1993).

The pilot scale HSSF vegetated units indicated increased total Cr removal efficiencies compared to the control (unvegetated) unit. This could be related to the effect of plants in the treatment system. Zhang *et al*. (2010) reported the role of plants in Cr removal processes, such as supply of surface area for microbial growth; provide an impact on metal mobility and toxicity through root exudates release, entrapment and accumulation of Cr in the parts of plants such as root, shoot and leaf. Statistically one-way ANOVA did not indicate any significant differences ($P > 0.05$) for mean removal efficiencies of total Cr between the HSSF constructed wetland (vegetated) and the control (unvegetated) units. This might be precipitation of Cr (III) in the alkaline condition in the six days of retention time in the bed (Campanella, 1996). The outlet concentrations of Cr after the constructed wetland units were below the permissible limit (2 mg L^{-1}) set for tanning and leather finishing industries discharge to water bodies (EEPA, 2003). Cr concentrations in the outflow wastewater samples were also significantly lower ($P < 0.05$) than the in inflow of the constructed wetland units. This indicated that the constructed units removed Cr effectively from the tannery wastewater.

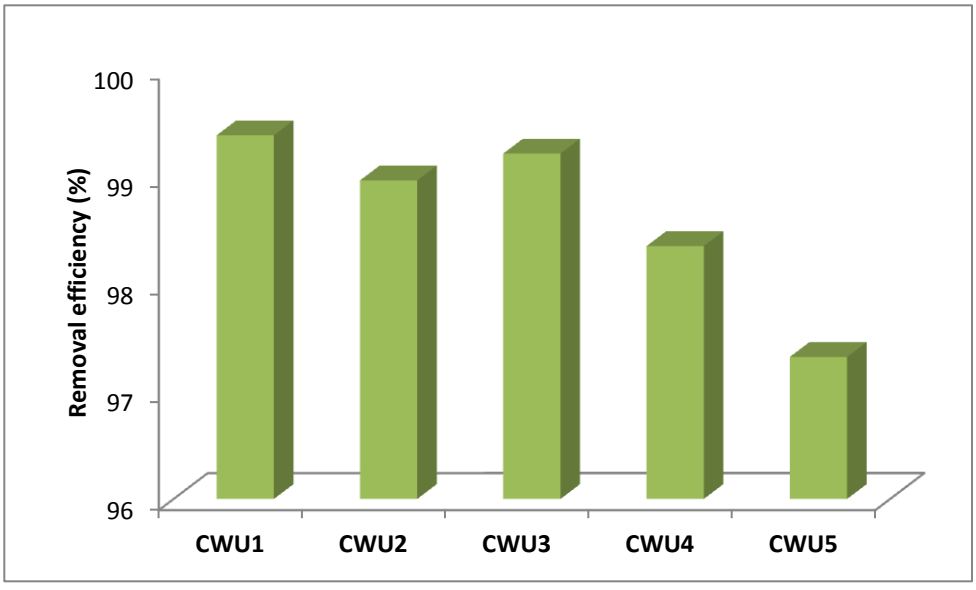


Fig.4. 16 Average removal efficiency (%) of total Cr in the constructed wetland units. n=6 , CWU1- *P. purpureum*, CWU2- *T. domingensis*, CWU3- *C. latifolius*, CWU4- *E. pyramidalis and* CWU5- Control (Unvegetated)

The Cr (VI) concentrations in the inflow tannery wastewater samples were in the range of 0.014-0.029 mg L^{-1}. Analysis of Cr (VI) in the outflow wastewater indicated in the range of 0.005-0.041mg L^{-1}. This range in the outlet showed a slight decrease and increase in the lower and upper boundaries from the initial inflow concentrations respectively. The reduction of Cr (VI) might be adsorption by the gravel used as a supporting media for the plant growth and sorption of (VI) by plant roots in the constructed wetland system (Augustynowicz *et al.*, 2010). The increase in the Cr (VI) range might be conversion of Cr (III) to Cr (VI) by microorganisms and various chemical reactions taking place in constructed wetland unit. Homa *et al*. (2016) reported an average concentration of 0.332 ± 0.007 mg L^{-1} Cr (VI) in tannery effluent generated from Ethiopia Tannery Share Company. Apte *et al. (*2006) also reported up to 17 % conversion of Cr (III) to Cr (VI) in sludge under aerobic conditions by 30 days. In general the concentrations of Cr (VI) in the outlet samples were less than the permissible discharge limit set for tanneries (0.1 mg L^{-1}) to water bodies (EEPA, 2003).

4.4.4 Chromium Accumulation in the Plant Parts

The accumulation of total Cr in different parts of plants (roots, stems and leaves) in the pilot scale HSSF constructed wetland units is shown in **Table 4.13**. *P. purpureum* accumulated an average of 193.75 ± 35.09 mg kg^{-1} total Cr in its root, which was the highest, compared to the other vegetated wetland units. *C. latifolius* and *T. domingensis* accumulated an average 123.75 ± 23.07 and 82.75 ± 14.39 mg kg^{-1} total Cr in their roots respectively. The lowest concentration of total Cr (25.5 ± 9.19 mg kg^{-1}) accumulated in the root of *E. pyramidalis*.

The maximum concentration of total Cr (21.5 ± 1.80 mg kg^{-1}) was found in the leaves of *C. latifolius*. The leaves of *P. purpureum and E. pyramidalis* accumulated an average of 20.00 ± 1.87 and 16.5 ± 1.38 mg kg^{-1} total Cr, respectively. The stems accumulated lowest concentrations as compared to the other parts of the plants used in this study. The maximum amount of Cr accumulated in the stem of *P. purpureum* was 12.25 ± 1.77 mg kg^{-1}.

The root parts accumulated the highest concentration of total Cr from the tannery wastewater.

In the total Cr partitioning in plants, *T. domingensis* and *P. purpureum accumulated* 88.27 and 85.73% total Cr in their roots respectively (**Fig. 4.17**). The highest concentration of total Cr (33.5%) accumulated in the leaves of *E. pyramidalis* compared to the other three plant species. Generally the accumulation of total Cr in the plant parts was in an increasing order of stems < leaves < roots. This is in agreement with other studies that plants accumulate metals mainly in their roots followed by leaves and then by the stems of plant parts (Ranieri *et al*., 2013; Sultana *et al.*, 2015; Papaevangelou *et al.*, 2016).

Table 4. 13 Average total chromium concentration (mg kg^{-1}) DW plant parts of the constructed wetland units (n=3).

Wetland plant species	**Plant parts**		
	Root	**Stem**	**leave**
P. purpureum	193.75 ± 35.09	12.25 ± 1.77	20 .00 ± 1.87
T. domingensis	82.75 ± 14.39	-	10 ± 1.53
C. latifolius	123.75 ± 23.07	8.75 ± 0.56	21.5 ± 1.80
E. pyramidalis	25.5 ± 9.19	7.25 ± 0.88	16.5 ± 1.38

DW- Dry weight

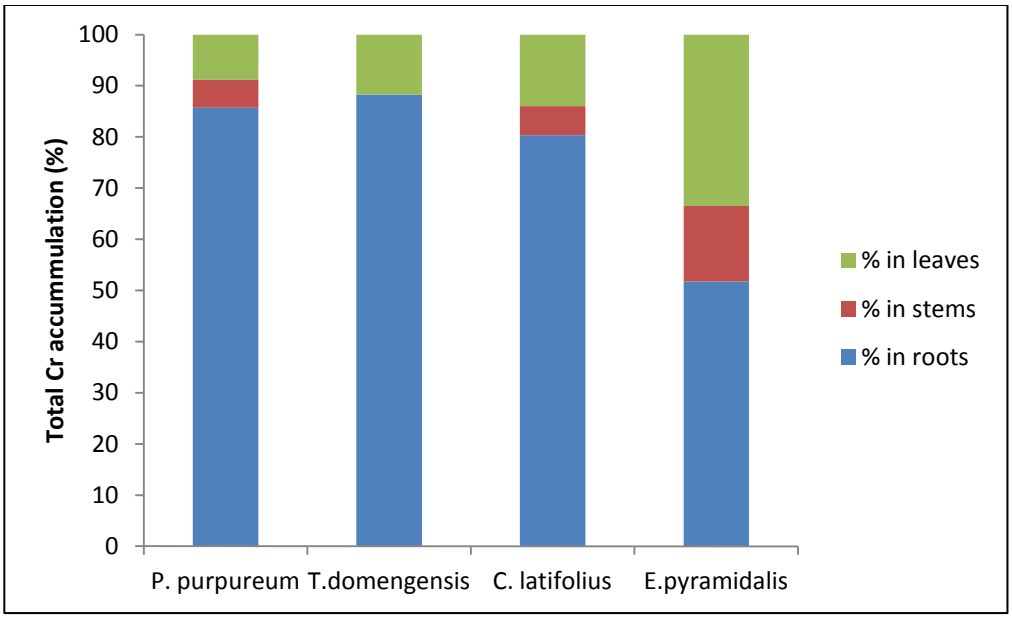


Fig.4. 17 Total Cr partitioning in plants

4.4.4.1 Bioconcentration (BCF) and Translocations Factors (TF)

The calculated BCF and TF values help to evaluate and select plants for the purpose phytoremediation (Wu *et al.*, 2011). BCF and TF were determined for the plant species used in the pilot units for the treatment of chromium containing tannery wastewater (**Table 4.14**). In this study *C. latifolius* and *P. purpureum* showed BCF of 7.90 and 5.71 respectively. The lowest BCF was observed for *T. domengenesis* (2.09) compared to the other three plant species. Plants with a bioaconcentration factor greater than 1, sometimes reaching as high as 50-100 are considered as hyperaccumulators (Cluis, 2004). Therefore, the selected plants have good potential to remove highly concentrated Cr in tannery wastewater. The higher BCF of the selected plants indicate immobilization of Cr ions in the vacuoles of the root cells (Shanker *et al*. 2005). This helps to reduce the mobility and bioavailability of Cr in the environment. Plants can immobilize heavy metals in soils through sorption by roots, precipitation, complexation or metal valence reduction in rhizosphere (Ghosh and Singh, 2005; Wuana and Okieimen, 2011).

The TF of Cr in the study plants indicated the highest (0.45) for *E. pyramidalis* and the lowest

(0.08) for *P. purpureum* (**Table 4.14**). TF > 1, when there is high translocation of heavy metals from the root to the aerial parts of the plants. According to Badr (2012), high TF (root to shoot) of heavy metals indicated phytoextraction of heavy metals. The TF of Cr in the study plants had values < 1. The degree of translocation of contaminants from the root to the shoots is dependent on the plant species, contaminant type, and environmental conditions (Weis and Weis, 2004). According to Sinha *et al*. (2002) partitioning of Cr in a plant is a mechanism to manage concentrated toxic ions in the roots to prevent toxic effects on the leaves, the site of photosynthesis, and other metabolic activities. Moreover, Cr (III) is not an essential element for the plants, accordingly the plants did not develop specific mechanisms to translocate Cr (III) from root to shoot (Shanker *et al.,* 2005; Augustynowicz *et al.,* 2010).

Table 4. 14 Chromium Translocation Factor (TF) and Bioconcentration factor (BCF) for the wetland unit species

plant species	BCF	TF
P. purpureum	5.71	0.08
T. domingensis	2.09	0.13
C. latifolius	7.90	0.12
E. pyramidalis	4.44	0.47

All the plant species indicated TF < 1 and BCF > 1. The plant species are proposed to be efficient for Cr accumulation in their rhizomes (Hesami *et al.,* 2018). Especially *P. purpureum is* preferred over the other three plant species for use in the treatment system, because of its greater accumulation, growth rate and biomass production, that contributes for higher removal of Cr in it.

4.4.4.2 The Fate of Plants Used for Phytoremediation of Cr

The treatment of Cr using phytoremediation is a recent concern because the system is simple and environmentally friendly. But the challenge is proper management of the plants used in

constructed wetlands for the treatment of Cr. One of the alternatives is to use the biomass as a potential source of bioenergy. Biofuels are environmentally safe with respect to carbon dioxide emissions. Long term effects associated with the gradual accumulation of Cr in the environment are not acceptable. As a result, the sludge with elevated total contents of the metal will generally need to be disposed in a controlled and confined manner (Vervaeke *et al.*, 2006). The other alternative is incineration (smelting) of used plants and recovery of Cr or dispose the ash safely in specialized dumps (Jadia and Fulekar, 2009; Sheoran *et al.*, 2010; Ali *et al.*, 2013). Incineration (smelting is feasible, economically acceptable and environmentally sound (Sas-Nowosielska *et al.*, 2004).

4.4.5 Removal Efficiency of COD, BOD_5 and TSS

The removal efficiency of the pilot constructed wetland units was determined from the characteristics of the wastewater collected from the inflow and outflow of each pilot wetland units shown in **Table 4.12**. The organic matter removal efficiency of COD, BOD_5 and TSS is shown **Fig. 4.18** below.

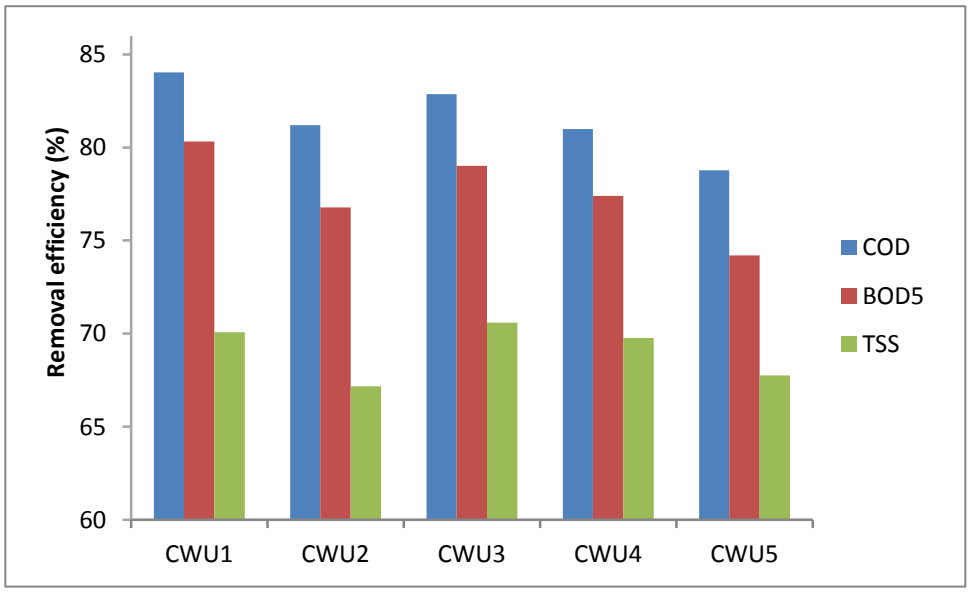


Fig.4. 18 Removal efficiency of COD, BOD_5 and TSS (%) on the average inlet and outlet concentrations of tannery wastewater in the pilot HSSF constructed wetland units. n=6 , CWU1- *P. purpureum*, CWU2- *T. domingensis*, CWU3- *C. latifolius*, CWU4- *E. pyramidalis*

and CWU5- Control (unvegetated)

COD removal efficiencies of the pilot constructed wetland units varied in the range of 78.78 - 84.03 % during experimental period. The maximum removal efficiency of COD (84.03 %) was observed for the HSSF wetland unit vegetated with *P. purpureum* (CWU1). It was followed by *C. latifolius* vegetated wetland unit (CWU3) with an average COD removal efficiency of 82.86%. Wetland units vegetated with *T. domingensis* (CWU2) and *E. pyramidalis* (CWU4) showed 81.02 and 80.99 % COD removal efficiencies, respectively. The control (unvegetated) removed 78.78 % of COD, which was relatively low as compared to vegetated units. According to single factor ANOVA, there were no statistical significant differences ($p > 0.05$) between the constructed wetland units in the removal efficiency of COD.

The average removal efficiencies of BOD_5 in the outlet of constructed wetland units varied in the range of 74.20-80.32% during treatment operations. The maximum removal efficiency (80.32 %) was observed by *P. purpureum* vegetated wetland unit (CWU1). *C. latifolius (CWU3)* also showed high removal efficiency (79.01 %) of BOD_5 close to pilot CWU1. While, *E. pyramidalis* (CWU4) and *T. domingensis* (CWU2) showed a removal efficiency of (77.4 %) and (76.78%) respectively. The lower removal efficiency of BOD_5 was observed in the control (74.2%) compared to all wetland units. No significant differences were seen in BOD_5 removal among each wetland units and the control.

According to Calheiros *et al.(*2007), HSF constructed wetland units vegetated with different plants, an average inflow COD of 1966 - 2093 mg/L , removal efficiency of the pilot units varied between 41- 67 % for HLR of 3 cm/d and 54-73% for HLR 6 cm/d, respectively. Moreover, the pilot units with an average inflow BOD_5 concentrations in the range 875- 898 mg/L removed 41-55% for HLR of 3 cm/d, and 41-58 % for an HLR of 6 cm/d respectively. Calheiros *et al. (*2012) also reported maximum 80 % COD and 90 % BOD_5 removal efficiencies for a conventionally treated tannery wastewater of inlet concentration of 68-425 mg/L COD and 16-220 mg/L BOD_5 respectively using three horizontal subsurface flow wetland units in series. The system was operated on a HLR of 60 mm/d and a hydraulic

retention time (HRT) of 2 days). Alemu *et al.* (2016) also reported 90 % COD and 91.4 % BOD_5 removal efficiencies with an average inflow concentration of 1,134 ± 269 mg L^{-1} and 523±219 mg L^{-1} respectively. This was obtained after an integrated two phase anaerobic and aerobic SBR followed by a horizontal subsurface flow wetland system on a 5 day HRT. In this study the observed treatment efficiencies for organic matter were inspiring compared with the above integrated multistage studies .This might be due to the optimum conditions produced by dilution, such as increased DO, reduced organic and inorganic loadings and inlet pH in the range of 7-8, which produced an optimum condition for microbial degradation of the waste, nutrient transformation and plant uptake. More over the long period of HRT (6 days), would facilitate sedimentation, filtration, precipitation and adsorption (Kadlec and knight, 1996; Vymazal, 2011).

The removal efficiency of TSS in the pilot wetland units with an average inflow concentration in the range of 36-859 mg L^{-1} was determined. It was observed that a maximum of 70.59 % TSS was removed in a wetland bed vegetated with *C. latifolius* (CWU3). The removal efficiency of *P. Purpureum* containing bed (CWU1) showed 70.08 % TSS, which was comparable to *C. latifolius* vegetated bed (CWU3). The control showed a removal efficiency of 67.75% TSS. TSS removal did not differ significantly ($p > 0.05$) between the vegetated and the control (unvegetated) units. This indicates the role of gravel in the filtration of suspended matter and the long hydraulic residence time (6 days) for sedimentation of suspended materials during operation. Moreover the colloidal particles that are not removed by pretreatment are removed by settlement and filtration in the first few meters away from the inlet zone (Cooper *et al.*, 1996; Vymazal *et al.*, 1998). Colloidal solids might be removed by bacterial growth that could decay & settle it. Moreover collisions of colloids with solids (gravel, plant roots, suspended solids, etc.) could favour adsorption (Stowell *et al.*, 1981).

This study was supported by Calheiros *et al.*(2007) that TSS removal efficiencies varied between 48-92% for 3 cm d^{-1} and 62-77% for 6 cm d^{-1} HLRs for horizontal subsurface flow wetland system vegetated with different plants with an inflow concentration ranged between 33 -125 mg L^{-1} TSS. In another study Calheiros *et al.* (2012) reported the removal efficiency of TSS did not differ significantly between the Arundo and the Sarcocornia-planted beds.

Billore *et al*. (1999) also reported 78 % removal of TSS for the treatment of domestic wastewater based on a sub-surface horizontal flow CW vegetated with indigenous *P. karka.*

The accumulation of suspended solids in the porous beds is a major threat for good performance of HSSF systems as the solids may clogg the bed. Therefore, the effective pretreatment is necessary for HSSF treatment systems.

4.4.6 Removal Efficiency of TDS, EC and Cl^-

The removal efficiency of TDS in the pilot constructed wetland units indicated 10.86 - 40.62 % for an inflow tannery wastewater varying in the range of 1411-4158 mg L^{-1} (**Table 4.12**). The EC was also removed between 12.26-34.52 % for an inflow concentration in the range of 2.17-6.85 ms cm^{-1}. The chloride (Cl^-) concentrations were also decreased 18.11- 25.09 % at the outlet for an inlet concentration in the range of 417.87-1649.49 mg L^{-1}. Calheiros *et al.* (2008) reported 10.29-14.54 % reduction of EC from 4.74–10.05 ms cm^{-1} inlet tannery wastewater in the pilot units. Calheiros *et al.* (2012) also reported a decrease of 3.70-12.96 % Cl^- from a tannery wastewater inlet varying between 2.2-6.6 g L^{-1}. Furthermore the Cl^- concentration in the outlet reduced from 3.85-15.39 % from the inlet in the range of 4.2-12.3 g/L. Alemu *et al*.(2016) reported a reduction of 69.27 - 72.8 % EC and 23.40 - 41.18 % Cl^- with an average influent concentration 8.2 ± 0.53 ms cm^{-1} and 765 ± 132 mg L^{-1} respectively.

4.4.7 Removal Efficiency of TP and NO_3^-

The TP concentration in the inlet varied between 2.99 - 4.50 mg L^{-1} (**Table 4.12**). The outlet concentration in the pilot HSSF constructed wetland units varied in the range of 0.58 - 2.22 mg L^{-1}. CWU3 vegetated with *C. latifolius* indicated 62.32% removal of TP as compared to the other units. It was followed by CWU1 (*P. purpureum)* with a removal efficiency of 60.48 %. The unvegetated unit removed 57.32%. The one way ANOVA indicated that there was no significant difference in the removing of TP between the vegetated and unvegetated units. This was supported by Keizer-Vlek *et al*. (2014) that there was no significance difference in the removal of TP for vegetated and unvegetated units. Studies indicated that the major

phosphorus removal processes include sorption, precipitation and plant uptake (Vymazal, 2007). Plants uptake low concentration of phosphorus, unless high sorption media are used in the constructed wetland unit (Arias and Brix, 2005; Akratos and Tsihrintzis, 2007). The vesicular basalt rock used in this study, characterized for its composition of Fe and Al on the surfaces might promote both the adsorption and precipitation of phosphates in the pilot constructed wetland units (Kadlec and Knight, 1996; Arias *et al.,* 2001). Calhereious *et al.* (2012) reported 40-93 % removal of TP in HSSF constructed wetland system planted with *Arundo donax* and *Sarcocornia fruticosa.*

The NO_3^--N inflow wastewater concentration varied between 19.48 and 42.52 mg L^{-1}. The average removal efficiency in the constructed wetland units varied in the range between 63.28 and 71.23 %. NO_3^--N concentrations in the outflow decreased on average up to 71.23 % high in CWU2 (*T. domingensis*). CWU1 (*P. purpureum),* decreased NO_3^--N in the outflow as high as 70.05 % from the inflow concentration. While unvegetated unit (CWU5) reduced the inflow NO_3^--N concentration by 63.28 % in the outflow of the HSF constructed system. No significant differences have been observed in the vegetated and unvegetated units in the removal of NO_3^--N from the wastewater. The main nitrogen removing mechanisms in constructed wetlands include microbial interactions with nitrogen, sedimentation, chemical adsorption, and plant uptake (Khatiwada and Polprasert, 1999). A study on the fate of ^{15}N-nitrate in the riparian of wetland soil microcosms indicated 24-26 % immobilized in the soil, 11-15 % assimilated in the plant and 61-63 % was lost through denitrification (Matheson *et al.,* 2002). Denitrification is most important processes in which nitrate is converted into free nitrogen (N_2) through intermediates NO_2-, NO and N_2O (Jetten *et al.,* 1997; Vymazal, 2007). There are different environmental factors that influence denitrification such as pH value, temperature, the absence of O_2, redox potential, substrate type, and presence of denitrifiers, organic matter and nitrate concentration (Focht & Verstraete, 1977; Vymazal, 1995). Studies indicated that the optimum pH for removal of NO_3^--N ranged between pH 6 and 8 and an increase in temperature with lower bound 5 ^oC and upper bound 70 ^oC (Bremner and Shaw, 1958; Keeney *et al.,* 1979; Paul and Clark, 1996, Beutel *et al.,* 2009). Belmont *et al.* (2004) reported 76.7 % NO_3^--N removal in a HSSF constructed wetland vegetated with Cattail and an average inflow concentration of 28.4 ± 7.3 mg L^{-1}. Alemu *et al.* (2016) also reported

66.3% removal of NO_3^--N with an influent concentration of 87.2 ± 26 mg L^{-1} in a HSSF constructed wetland system.

Both TP and NO_3^- removal in the HSSF constructed wetland units were lower when compared with that of the provisional maximum discharge limit set by EEPA (2003) for tannery industry, which are 10 mg L^{-1} and 20 mg L^{-1} or > 80 % removal for TP and NO_3^- respectively. This indicates that the dilution of tannery wastewater can help to reach effluent discharge limit in areas where there is sufficient water.

5. Conclusions and Recommendations

5.1. Conclusions

In this study, VB was characterized using FT-IR, XRD and SEM-EDS spectroscopic techniques. The instrumental analysis indicated that plagioclase, pyroxene, silica, olivine, goethite, hematite and magnetite were the main components of VB. The VB rocks were tested for the removal of Cr (VI) and Cr (III) from aqueous solutions. The adsorption potential of Cr (VI) and Cr (III) onto the VB were investigated using batch technique under different experimental parameters including pH, ionic strength, contact time and initial concentrations.

The percentages of adsorption Cr (VI) were higher at low pH but decreased with increasing pH. At pH 2 the maximum Cr (VI) adsorbed onto the vesicular basalt volcanic rock was 81.19 %. The ionic strength reduced Cr (VI) adsorption on VB volcanic rocks to a certain extent. Kinetic studies indicated that the time required to reach adsorption equilibrium depends on the initial Cr (VI) concentrations; lower initial concentration reaches equilibrium faster than the other higher initial concentrations. The maximum adsorption capacity of Cr (VI) at equilibrium was 79.20 mg kg^{-1} at a dose of 50 g L^{-1} with initial Cr (VI) concentration of 5 mg L^{-1} at optimum pH of 2.0.It was found that the pseudo-second-order kinetic model could be used to describe the individual adsorption of Cr (VI) on VB. The adsorption isotherm data were fitted well with the Freundlich model slope (1/n) 0.78 kg L^{-1} indicating that the VB surface was heterogeneous and favourable for adsorption.

In the adsorption process of Cr (III) onto the VB surface, the pH of the medium was found to be the controlling factor. The percentage of adsorption of Cr (III) increased with increasing pH. At pH 6 the maximum Cr (III) adsorbed onto the VB surface was 54.67 %. The influence of ionic strength was investigated and showed reduction in the adsorption of Cr (III) onto the surface of the VB. kinetic studies showed that equilibrium adsorption time was dependent on the initial concentration of Cr (III) in the solution. The adsorption of Cr (III) onto VB followed the Pseudo-second-order kinetics. The experimental data fit well with Langmuir isotherm model.

This study indicates that VB has the potential to be used as an alternative adsorbent material for the removal of Cr (VI) and Cr (III) ions from aqueous solutions due to its abundance, simple preparation of adsorbent material (low cost) and environmental friendly nature.

The VB was used as a supporting media for the vegetated plant species on the pilot scale constructed bed units. The potential of different plant species for the removal of Cr (III), organic and inorganic matters from tannery wastewater were investigated using HSSF constructed wetland system. The plant species were well adapted and propagated compensating the variable tannery effluent supplied to them. Though *P. purpureum* was susceptible to the change in the wastewater concentrations, it was also strong to overcome the problem and grow faster. The HSSF constructed wetland system was effective in removing Cr, COD and BOD_5 from the inflow tannery wastewater. Its removal efficiency reached up to 99.38 %, 84.03 % and 80.32% for Cr, COD and BOD respectively. It can fulfill the interim discharge limit of tanneries set by EEPA (2003).

All the plants used in this study for removal of Cr (III) indicated BCF > 1 and TF < 1. These plants might not be adequate for phytoextraction, since most of the Cr (III) is accumulated in the roots, not in the harvestable parts of plants. Though *P. purpureum* showed low TF, it might be used to accumulate Cr (III) in its rhizomes, because of its rapid growth and biomass production. The lower difference obtained in the performance of the vegetated and unvegetated HSSF constructed wetland units in the removal of Cr (III) might be precipitation of Cr (III) (hydroxides, sulphides, sulphates, and carbonates) and adsorption onto the surface of vesicular basalt bed in the 6 days of retention time. In areas where adequate water resource is available, the primary tannery wastewater has to be diluted to reduce the high alkaline/acidic pH, salt, Cr (III), organic and inorganic loadings. This reduces the shock that appears on the plants and produce good condition for plants to grow well and establish a continuous system that can increase the removal efficiency of Cr (III) and other organic and inorganic chemicals in the wastewater

This study helps to reduce the risk of Cr pollution and other pollutants in the environment from the expanding tanning industries in Ethiopia with safe, low cost and environmentally friendly way by integrating VB rock with local plant species in a HSSF constructed wetland system. This method may be preferred to the existing conventional methods that require high investment for the treatment of wastewater and can produce other extra burdens on the environment.

5.2. Recommendations

- ✓ Further study has to be done on the phytoremediation potential of Cr (III) using P. *purpureum*, T. *domingensis*, C. *latifolius* and E. *pyramidalis* from tannery wastewater based on different hydraulic retention times.
- ✓ The potentials of the integrated treatment system should further be extended into the feasibility studies of such CWS for use in an industrial level, the space that would be necessary to put up these structures, management of the same system with the appropriate safety measures
- ✓ The study indicates the potential the integrated system to be used as a secondary treatment, therefore it is necessary to check their full potential in areas where there is primary treatment
- ✓ Further studies have to be done on the management of used plants in the constructed wetland system and recovery of the VB in the bed for continuous use within the system.
- ✓ Further studies on adsorption of PO_4^{3-} onto the VB have to be done.
- ✓ Microbial dynamics and their potential of treatment in HSF constructed wetland unit has to be studied

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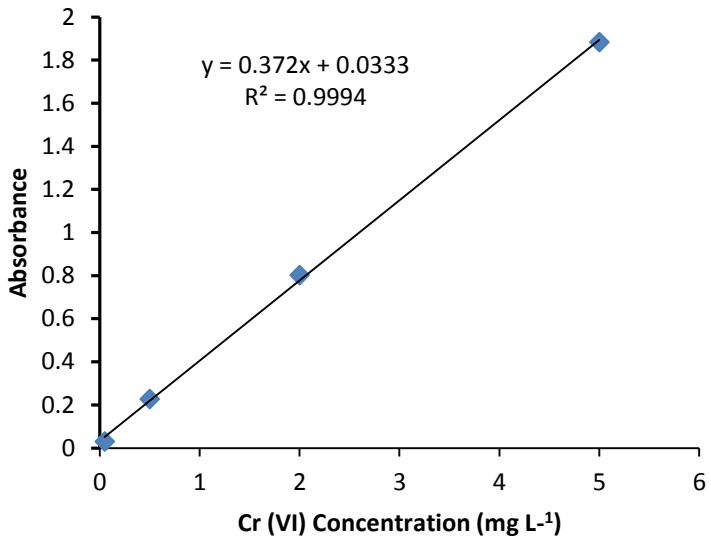
Appendix

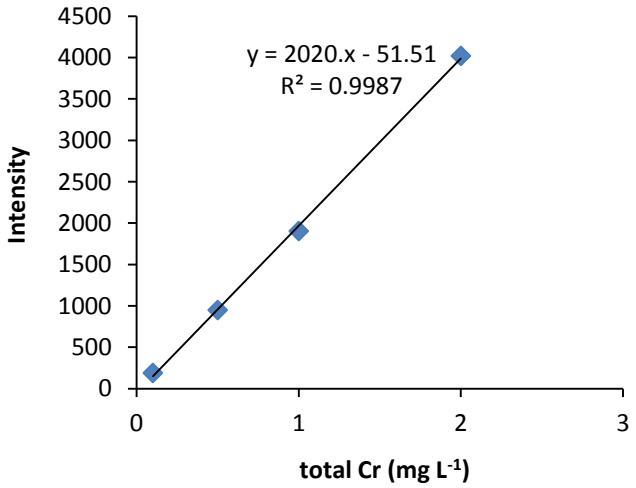
Appendix A: Adsorbent preparation, Adsorption process, and analysis of Cr.

Cr (VI) -mg L^{-1}	Absorbance
0.05	0.03
0.5	0.227
2	0.802
5	1.883

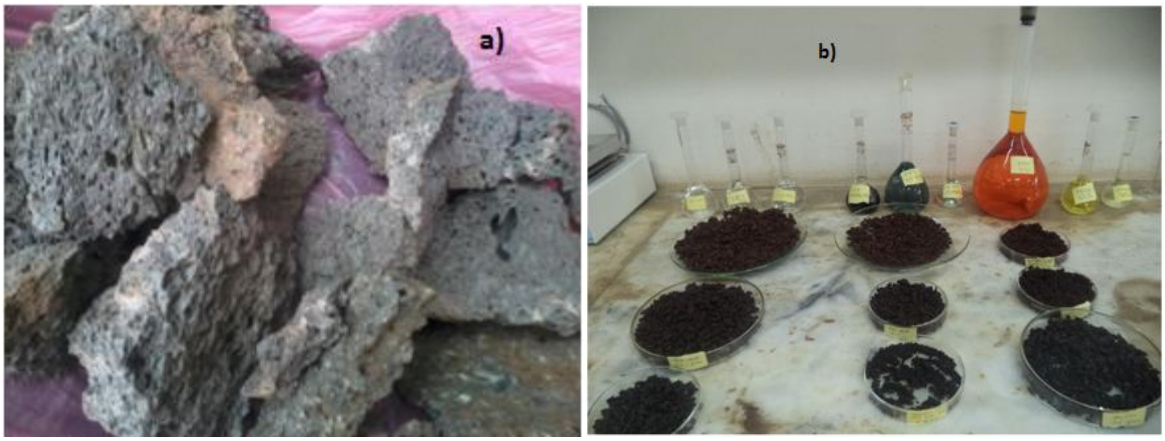


Appendix A. 1: Calibration curve for Cr (VI) determination using 1, 5- diphenyl carbazide UV-Vis spectroscopy

total Cr (mg L^{-1})	Intensity
0.1	190.51
0.5	950.76
1	1905.45
2	4021.85



Appendix A. 2 : calibration curve for total Cr standard solution using ICP-OES



Appendix A.3: VB rock (a); prepared VB rock for experiment, 1000 mg L^{-1} Cr (III) and Cr (VI) stock solutions (b).

Appendix A.4: Adsorption process and determining Cr (VI) using diphenylcarbzide method

d)

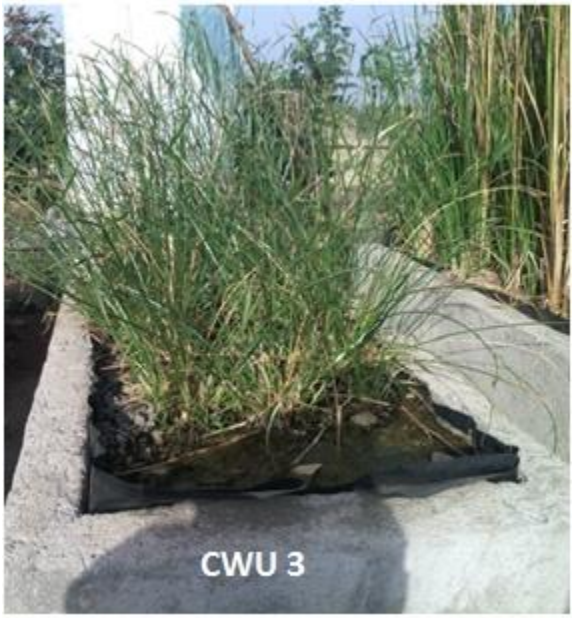
Appendix A.5**:** Hach portable pH meter (a), Perkin Elmer Lambda bio+ photometer (b) , Perkin Elmer Lambda 35 UV-Vis spectrophotometer (c) and FT-IR Perkin Elmer Spectrum 65 Spectrometer (d)used in this study.

Appendix B: Constructed wetland units

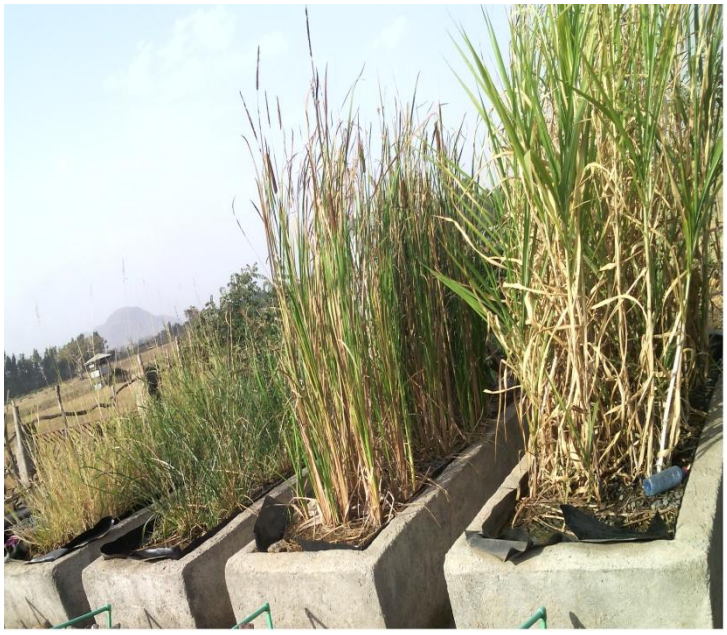
Appendix B.1 HSSF constructed wetland units(a), a CWU with cemented floor and inner walls (b), CWU filled with VB rock and vegetated with local plant species(C).


CWU 1


CWU 2


CWU 3


CWU 4



Appendix B.2: The pilot scale HSSF constructed wetland units established for the treatment of tannery wastewater

Appendix B.3: the nature of plant roots used in the treatment of tannery wastewater in a CWUs.


a)


b)


C)


d)

Appendix B.4: samples collected from different parts of plants from the CWUs (a); grinding of plant samples (b); storage of grinded samples in a plastic bag (c); sample digestion (d); prepared sample for measurement (e); and Perkin Elmer ICP-OES 8000 series.

Publications-Abstracts

1.

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Removal of chromium (VI) from aqueous solution using vesicular basalt: A potential low cost wastewater treatment system

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Abstract

In this study, vesicular basalt volcanic rock was taken and its application for adsorption of chromium (VI) from aqueous solution was investigated. Different physical and chemical properties of the powdered rock was studied using Fourier transform infrared spectroscopy (FT-IR), Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). A series of batch experiments were carried out to study the effect of various experimental parameters (pH, ionic strength and contact time) on chromium (VI) adsorption. It was found that the removal efficiency of chromium (VI) decreased with increasing pH and ionic strength. The adsorption process was optimal at pH 2. The maximum adsorption capacity was 79.20 mg kg^{-1} at an initial concentration of 5.0 mg L^{-1} and adsorbent dosage of 50 g L^{-1}. In individual adsorption tests, Pseudo-second-order kinetic and Freundlich isotherm models could better describe chromium (VI) adsorption on the vesicular basalt. This study indicated that vesicular basalt, which is inexpensive, has the potential to remove chromium (VI) from polluted water.

Keyword: Environmental science

2.

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Adsorption of chromium (III) from aqueous solution using vesicular basalt rock

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Additional information is available at the end of the article

Abstract: Chromium (III) is one of the chemicals widely used in various industrial processes. The wastewater containing Chromium (III) can be interconverted to Cr (VI) in the environment, which is one of the most toxic chemicals to biological systems. This paper investigates the removal of chromium (III) from aqueous solutions by adsorption process using abundant vesicular basalt available around Abbay River in Ethiopia. The batch adsorption method has been employed to evaluate the effect of various experimental parameters (pH, ionic strength, initial concentration and contact time) on Cr (III) adsorption. The adsorption process was highly dependent on pH. The maximum adsorption capacity was 0.976 mg g^{-1} at pH 6, initial concentration of 100 mg L^{-1} and adsorbent dosage of 50 g L^{-1}. Kinetic experiments indicated that the pseudo-second-order model displayed the best correlation with adsorption kinetic data. The adsorption mechanism of Cr (III) onto the surface of the vesicular basalt involved film diffusion and/or intraparticle diffusion during the reaction. Equilibrium studies indicated that the Langmuir Isotherm model was found to be in better correlation with experimental data. This study indicated that vesicular basalt rock owned good potential for the treatment of Cr (III) containing polluted water.