

Fluoride and Chromium Removal from Contaminated Water  
Using Activated Alum Based Water Treatment Sludge as an Adsorbent



By: Dema Teklu

A Thesis Submitted to the Department of Applied Chemistry  
School of Applied Natural Science

In Partial Fulfillment of the Requirements for the Degree of  
Master of Science in Chemistry (Industrial Chemistry)

Office of Graduate Studies  
Adama Science and Technology University

January, 2020  
Adama, Ethiopia

FLUORIDE AND CHROMIUM REMOVAL FROM CONTAMINATED  
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SLUDGE AS AN ADSORBENT

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## DECLARATION

I hereby declare that the thesis entitled “Flouride and Chromium Removal Using Activated Alum Based Water Treatment Sludge as an Adsorbent” been carried out by me under the supervision of Dr.Eshetu Bekele and Prof.Neraj Gupta,during the year 2019/2020 as part of Master of Science Program in Industrial Chemistry.I further declare that this work has been submitted to any other Universities or institution for the award of any degree.All quotations and their sources are specially acknowledged by means of eferences.

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This M.Sc thesis has been submitted for examination with our approval as thesis advisors.

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Date of Submission -----/-----/-----

## **DEDICATION**

This M.Sc thesis is dedicated to my beloved families, especially to my Mother Wube Kebede, my Father Teklu Leta and to my Sister Aster Teklu, whose advice, support, prayers and love helped me all along the right way made me who I am today. They will always be in my heart forever.

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## LIST OF ABBREVIATIONS

AA	Activated Alumina
Al-WTS	Alum Based Water Treatment Sludge
APHA	American Public Health Association
ASTM	Active Standard Test Methods
AWWA	American Water Work Association
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DP	Diphenyl Carbizide
EC	Electrical Conductivity
EPA	Environmental Protection Agency
GAC	Granular Activated Carbon
HAL-WTS	Hydrochloric Acid Digested, Alum Based Water Treatment Sludge
IUPAC	International Union of Pure and Applied Chemistry
MOCA	Manganese Oxide-Coated Alumina
OSHO	Oromia Self Health Organization
PAC	Powdered Activated Carbon
RSM	Response Surface Methodology
SAL-WTS	Sun Dried Alum Based Water Treatment Sludge
SEM	Scanning Electron Microscope
SS	Suspended Solids
TAL-WTS	Thermally Treated Alum Based Water Treatment Sludge
TISAB	Total Ionic Strength Adjustment Buffer
TISAB	Total Ionic Strength Adjustment Buffer
TOC	Total organic carbon
TP	Total Phosphorous
TSS	Total Suspended Solid
UNESCO	United Nations Educational, Scientific and Cultural Organization
UV-Vis	Ultraviolet Spectrophotometer spectroscopy
WTS	Water Treatment Sludge
XRD	Energy Dispersive X-ray Diffraction

## ABSTRACT

*Chromium and Fluorine are among the prioritized contaminants of water which are causes for disease if taken above recommended levels. Hence their removal by implementing a cost effective, locally accessible, not time consuming and environmentally friendly technology has been widely studied by many scholars. The objective of this study was to use Activated Alum sludge from the water treatment plant as an adsorbent for the removal of chromium from chromium contaminated tannery wastewater and Fluoride from Fluoride riche well water at optimized value of pH, contact time, adsorbent dose and initial concentration. To improve the adsorption ability, the original alum water treated sludge; the sample was treated thermal at different temperature, digested with hydrochloric acid alone and/or acid digestion followed by thermal treatment. Hydrochloric acid treatment improved the adsorption efficiency of the sludge on the fluoride and Chromium in water significantly, with maximum adsorption efficiency of 92% and 83.802%, respectively. The effects of experimental parameters such as, pH of initial concentration of Chromium and Fluoride solutions, contact time, dosage of adsorbent and initial concentration of chromium and fluoride in the solutions were thoroughly investigated. Those showed that 95.5% removal efficiency observed at pH 2, 1.5h contact time and 20g/L of adsorbent dose for fluoride removal. Highest removal efficiency of chromium, 91.04% were observed at pH 4, 2.5h contact time and 20g/L of adsorbent dose. With this optimum condition kinetics and isotherm of the adsorption process were analyzed using different models. The result revealed that kinetics of the process fitted well the pseudo-second order kinetic model and from the tested isotherm models the Freundlich model was found to be the best fit. Moreover, SEM images and XRD patterns of the adsorbent were recorded to get a better insight into the adsorption process. In general activation of Alum based water treatment sludge improved its potential to be used as an alternative low cost adsorbent for the removal of chromium and Fluoride from contaminated water.*

**Keywords:** *Drinking water, wastewater treatment, Adsorption, Alum based water treatment sludge, Activation, Fluoride; Chromium, Isotherm and Kinetics*

# 1. INTRODUCTION

## 1.1. Background of the Study

Water contamination is a common problem to all over the world and higher levels of contaminants in the environment and drinking water are a cause of serious health effects and environmental concern (Farwell and Nieuwen., 2003). The types and concentrations of natural contaminants depend on the nature of the geological materials through which the groundwater flows and quality of the recharge water. Groundwater moving through sedimentary rocks and soils may pick up a wide range of compounds, such as Magnesium, Calcium, Chloride, Arsenate, Fluoride, Nitrate, and Iron; thus, affect the quality of groundwater depends on their types and concentrations. Moreover, naturally occurring elements present at unacceptable levels can contaminate water (Rukah *et al.*, 2004). Other contaminants are man-made such as by-products of industry, and agriculture, including heavy metals, hazardous chemicals, and oxygen demanding pollutants, dyes and nutrients.

Fluorine and Chromium are among the contaminants of water frequently occurred in most ground and surface water at higher level and causes serious health effects and deteriorate the quality of the environment (EPA, 2006). Chromium occurs naturally in the ground and is often used in electroplating of metals and leather industries. As a result; it gets into water from runoff from old mining operations and improper waste disposal from these industries (Ray *et al.*, 2009). Sources of Fluoride may be geological or anthropogenic. Weathering of Fluoride-bearing minerals (Fluorite, Fluorspar Cryolite, Fluor apatite, Ralstonite and others) on the earth's crust often lead to higher fluoride levels in groundwater. Their effects are especially harmful to children and the elderly people. Fluoride is known to cause dental and skeletal fluorosis. It is also associated with Alzheimer's disease and other forms of dementia (EPA US., 2009A). Effective treatment and removal of these toxic contaminants from the drinking and waste waters has been the concern of different scholars in the area.

Many methods are being discovered and used to remove Chromium and Fluorine from the environment, such as chemical precipitation, ion-exchange, Reduction, adsorption, membrane filtration, and electrochemical treatment technologies. However, most of these techniques have drawbacks. For instance chemical precipitation and reduction methods of contaminant removal

require large amounts of chemicals; it is quite expensive and led to excessive toxic sludge production (Kurniawan, and Babe., 2006). Ion exchange is a suitable technique to remove heavy metals from the waste water. This process reduces the amount of waste for disposal and cost of operation is generally lower. However, the effectiveness of this method is highly dependent on the pH of water (Rengaraj *et al.*, 2003). Application of Electro-chemical treatment methods for the removal of a broad spectrum of heavy metals such as  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Ag^+$  and Cr requires relatively large capital investment and the expensive electricity supply (Fu and Wang., 2011). Membrane technology is also one of water pollutant treatment method. A semi permeable membrane is used for the removal of water impurities. It has an ability to remove almost all kinds of contaminates like  $Cl^-$ ,  $NO_3^-$ ,  $F^-$ ,  $SO_4^{2-}$ ,  $Pb^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ , organics as well as microorganisms. But, Membrane technology may become clogged after prolonged use and, hence, requires periodical replacement of the membrane (Charcosset *et al.*, 2009). Whereas adsorption is widely recognized that, it is an ideal and appropriate technique compared to other techniques, for small community water source de-contamination (Foo and Hameed., 2010).

Adsorption can be defined as enrichment of material or increase in the density of the fluid in the vicinity of an interface (Rouquerol and Sing., 1999). In this process certain components of the solution are transferred to active sites of the adsorbent. There are two kinds of forces which help the adsorption process to take place. These forces are physical and chemical. If the adsorption takes place because of the physical forces the process is known to be physisorption, in this case the force that retains adsorbate and adsorbent is Vander Walls forces and this phenomena is reversible. However, chemisorptions takes place through the chemical interaction of adsorbate and adsorbent molecules and the process is irreversible (Yadla *et al.*, 2012). This method has been widely used for the removal of many contaminants from wastewater.

Removal of chromium and fluorine from contaminated water using adsorption is one of the most promising areas in the treatment of wastewater. Since it is simple, economically viable, technically feasible and socially acceptable (Foo and Hameed., 2010)

Many adsorbents have been used for de fluoridation and hexavalent chromium removal, including activated carbon, bone charcoal, tricalcium phosphate, synthetic ion exchangers, activated alumina, alum, and lime (Sujana, and Asian., 1997). In recent years, considerable attention has been devoted to the study of different types of low-cost materials such as tree bark,

wood charcoal, saw dust, weeds, and other waste materials for adsorption of some toxic elements (Arulanantham, and Balasubramanian., 1992). However, there is also a need to find locally available media with high fluoride and chromium adsorption capacity as an alternative method for safe and easy use both at household and small community levels.

Alum-based water treatment sludge is a material deposited in waste disposal areas in many parts of the world (Babatunde and Zhao., 2007). Indeed, Alum is the most widely used coagulant in drinking water treatment. Once the alum dissolves,  $Al^{3+}$  exists in solution as aluminum hexa hydronium ion  $(Al(H_2O)_6)^{3+}$ . These ions can sequentially dissociate as pH increases, leaving OH to form species such as  $[Al(H_2O)_5OH]^{2+}$  and  $[Al(H_2O)_4(OH)_2]^+$ . These positively charged species polymerize to form positively charged polynuclear complexes, which form a gel-like substance that adsorbs and coagulates colloidal materials such as soluble organic matter and fine soil particles. During flocculation, sedimentation and filtration, colloids in the raw water remain entrapped in, or adsorbed to, the Al gel and after dewatering the water treatment sludge is transferred to disposal sites. Beneficial use of this material would reduce both the cost and need for disposal. Research has shown that water treatment sludge can be used as an effective adsorbent for phosphate (Babatunde and Zhao., 2007) but little research has centered on its use as a heavy metal adsorbent.

The present study was intended to remove Fluoride ion and Hexavalent Chromium from contaminated water using Alum-based water treatment sludge (Al-WTS) as a low cost adsorbent. The effect of operating parameters like, initial pH, contact time, adsorbent dose and initial contaminant concentration studies were investigated in batch adsorption techniques and the equilibrium effective conditions for these parameters were evaluated. Study of adsorption isotherms and kinetics were carried out and best fitting models for the adsorption process were suggested. These fundamental data will be useful for further applications in the treatment of practical waste or process effluents.

## **1.2. Statement of the Problem**

Water is a media for the metabolic activities of living organisms; it is possible to say that most living organisms cannot survive without it. Living organisms not only require water, it should also be free of any contaminants (Pickering *et al.*, 1997) but there are different natural and

anthropogenic contaminants that affect the purity of water. For instance, higher level of fluoride naturally found in ground water is serious problem in Ethiopia, specifically in Rift valley regions of the country (Kloos and Tekle-Haimanot., 1999). Extensive use and subsequent release of chromium by different industries such as electroplating, steel production, wood preservation and leather tanning has been also a cause of river pollution or detection of high level of chromium in river water of Ethiopia. Chromium exists as two stable oxidation states, Cr (III) and Cr (VI). Cr (III), which is often used in tanning of leather, is considered as an essential element for living organisms but can be toxic in large doses (Kimbrough *et al.*, 1999).

These contaminants must be removed from water because of their toxic nature for human health. To date there have been only a few field trials of fluoride and chromium mitigation systems in Ethiopia. The tested methods have low acceptability by the local community due to complexity in operation and maintenance, cost, environmental and socio-cultural reasons which seriously affect sustainability.

Thus, there is a pressing need for high performance, and sustainable water treatment technologies for chrome and fluoride removal—the subject of this research. Sustainability requires technical efficiency, local availability, economic and social viability, and simplicity of operation and maintenance. While motivated by challenges in rural villages of Ethiopia, research results will also benefit those living in rural communities of other East African countries impacted by fluoride and Chromium.

So far various water treatment techniques have been used to remove heavy metals from industrial wastewater and Fluorine from drinking water. Water treatment through adsorption is one treatment technique used. Different adsorbent have been used to remove chromium and fluorine from wastewater and drinking water too. But those adsorbent which have high removal capacity, low cost and easy accessibility are no question in being a choice for industrial wastewater treatment process. This research is intended to use low cost adsorbent called Alum water treatment sludge (Al-WTS) for removal of Fluorine and Hexavalent chromium.

Al-WTS which is a byproduct of water treatment plants using Alum as a coagulant can be easily available from local water treatment plants without any charge. Annually about 80,000 tons of the alum sludge waste is produced from water treatment plants (Owaid *et al.*, 2013). Al-WTS

from most of the Water Treatment Plants in Ethiopia is being discharged into nearby drains, which ultimately meet the water source on downstream side of intake. The simple method of final disposal, although a less expensive, is not a proper solution due to the possibility of contamination of water bodies and soil from the chemical products used in the treatment. The management of this sludge has become important environmental issue due to stringent of environmental regulation and increasing public awareness (Nair and Ahammed, 2013). Reuse of the sludge as adsorbents; building, construction and cementitious materials; and land improvement additives such as structural soil improver have been reported (Babatunde and Zhao., 2007). But, still there is a need for reuse of Al-WTS. Therefore to best of my knowledge, the planned research will be to synthesis Fluoride and Chromium adsorbent material from this Al-WTS.

### **1.3. Scope of the Study**

This study has been supported by different types of literatures and laboratory works. However, the findings of the research are limited to prepare and characterization of Alum based water treatment sludge (Al-WTS) as adsorbant. The results were also specific to remove Flouride ion and Hexavalent Chromium ion from contaminated water by adsorption mechanism.

### **1.4. Objective of the study**

#### **1.4.1. General Objective**

The general objective of this study is to evaluate the removal efficiency of Chromium and Fluoride ion from contaminated water using low cost alum based water treatment sludge, as an adsorbent.

#### **1.4.2. Specific Objectives**

- Preparation of Alum based water plant sludge as adsorbent and to characterize it with proximate analysis, Morphological analysis and Crystalline structure
- Investigating the removal efficiency of treated WTS with respect to Chromium and Fluoride ion from contaminated water at optimized condition
- To study effects of different variables on adsorption of Fluoride and Chromium
- Study the equilibrium adsorption isotherm and kinetics

## 2. LITERATURE REVIEW

### 2.1. Water Contamination

Availability of fresh water, the nature's gift controls the major part of the world economy. The adequate supplies of water are necessary for agriculture, human consumption, industry as well as recreation. Ironically, sometimes, natural or added contaminations rob us of the gift and making us confront a lot more challenging world. It is a well-known fact that fresh water is an important necessity for our health. With the advancement of technology and industrial growth, fresh water resources all over the world are threatened. One-sixth of the world population suffers from the freshwater unavailability situation (Elimelech,*et al.*,2006). It is seen that developed countries suffer most from chemical discharge problems, whereas developing countries from agricultural sources. Contaminated water causes problems to health and leads to waterborne diseases which can be prevented by taking measures even at the household level. Providing safe water for all is a challenging task. Continued research efforts in this area for more than few decades result in many processes/technologies (Shannon,and Mayes., 2008).

Water contaminants can be geological or anthropogenic or man-made (Farwell and Nieuwen., 2003). Higher levels of contaminants in drinking water are seldom to cause acute health effects. The natural occurring elements present at unacceptable levels can contaminate water. Groundwater moving through sedimentary rock sand soils may pick up a wide range of compounds, such as magnesium, calcium, and chloride, arsenate, fluoride, nitrate, and iron; thus, the effect of these natural contaminations depends on their types and concentrations (Rukah and Alsokhny., 2004). Man-made by-products of industry, and agriculture, including heavy metals like mercury, copper, chromium, lead, and hazardous chemicals, dyes and compounds like insecticides and fertilizers. Improper storing or disposing of household chemicals such as paints, synthetic detergents, solvents, oils, medicines, disinfectants, pool chemicals, pesticides, batteries, gasoline and diesel fuel can lead to also water contamination (Kass *et al.* ,2005). According to UN report 2003 very day 2 million tons of sewage, industrial and agricultural waste are discharged into the worlds water (United Nations World Water Assessment Programme, 2003).

### **2.1.1. Chromium in water**

Chromium is an odorless and tasteless metallic element with an atomic number of 24 and atomic weight of 51.996. The element chromium can exist in six valiancy states: 0, II, III, IV, V and VI, which represent the number of bonds an atom is capable of making. Metallic chromium Cr (0) does not occur naturally in the environment and Cr (II) is unstable and converted quickly to Cr (III). Cr (IV) and Cr (V) are also unstable and occur briefly as intermediates of conversions between Cr (III) and Cr (VI). Cr (III) and Cr (VI) are the environmentally important chromium species. Chromium is most commonly found in nature as Cr (III), which is the most stable species. Most Cr (III) compounds are insoluble in water and Cr (III) is considered to be an essential trace element for human diets, although ingestion of large amounts can cause toxic effects. The second most common and stable form of chromium in the environment is Cr (VI) compounds which are more toxic than Cr (III) due to their high water solubility and mobility (Zayed *et al.*, 2003).

#### **Sources of hexavalent Chromium**

Chromium can present in air, water and soil in varying concentrations. Chromium is found in the environment mainly because of some natural processes and human activities. The concentrations of chromium are generally low when it occurs naturally, but its concentrations tend to be rather high in contaminated areas around industries where chromium and its compounds are used. The main sources of Cr (VI) are tannery, electroplating, paint, ink, dye, and from Aluminum manufacturing industries. The wastewater of the tanning process is an important source adding Chrome pollutant to the environment.

#### **Health effects of chromium**

Human exposure pathways to chromium are inhalation, ingestion and skin contact. Cr (III) and Cr (VI) are known to accumulate in animal and human tissues. Excretion from the body is very slow, with elevated chromium concentrations observed in human tissues even decades after exposure cease. Observed toxic effects of chromium compounds to humans include developmental issues, damage to skin, respiratory, reproductive and digestive systems and cancer.

Cr (VI) is much more toxic than Cr (III) because of its greater ability to enter cells and its strong oxidation potential. Once inside cells, Cr (VI) is reduced and produces free radicals, Cr (V), Cr (IV) and eventually Cr (III), which are believed to be responsible for toxic and carcinogenic effects (Dhal and Pandey., 2013).

### **2.1.2. Occurrence of fluoride in groundwater**

Fluorine is the most reactive and the most electronegative non-metal and therefore almost never occurs in nature in its elemental state. It is the 13th most abundant element in the earth's crust (Koritnig, S., 1951). It occurs in a combined form as fluorides in rocks and soil in a wide variety of minerals such as Fluorspar (fluorite) ( $\text{CaF}_2$ ), Cryolite ( $\text{Na}_3\text{AlF}_6$ ), Apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) and Topaz  $\text{Al}_2\text{SiO}_4(\text{FOH})_2$  (WHO, 1994).

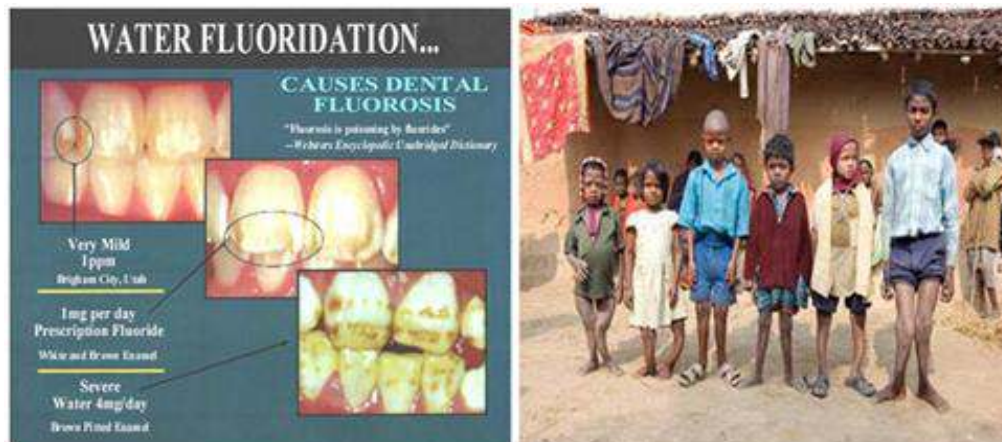
Traces of Fluoride are present in many natural waters, and higher concentrations often associated with ground waters. The release of Fluoride to groundwater is dependent on chemical and physical processes that take place between the groundwater and its geological environment. Fluorite ( $\text{CaF}_2$ ) is the predominant mineral that controls the dissolved Fluoride concentration in the groundwater (Edmunds *et al.*, 2005). Thus Fluoride-rich ground waters are often associated with low calcium concentrations associated with rocks with low calcium content, or high pH conditions where sodium bicarbonate dominates the groundwater composition and calcium precipitates as calcite ( $\text{CaCO}_3$ ). Apart from the groundwater chemistry, hydrological properties (e.g., residence time) as well as climatic conditions (e.g. evapo-transpiration, precipitation) and soil conditions (e.g., pH, soil type) have an influence on Fluoride concentration (Ayoob *et al.*, 2008). The links between high Fluoride and both high alkalinity ( $\text{HCO}_3^-$ ) and increased temperature are quite strong in the Ethiopian ground waters. These parameters can therefore be used as potential indicators of groundwater-Fluoride problems in areas of exploration for new groundwater sources.

Drinking water is often the main source of fluoride intake by humans, especially in areas where fluoride concentrations in groundwater and/or surface water are high (Kloos and Tekle-Haimanot., 1999). In some areas, foodstuffs (tea in particular can contain high fluoride concentrations, 0.1 mg/g) (Zerabruk *et al.*, 2010) and indoor air pollution due to the burning of coal may make significant contributions to the daily intake of fluoride (Nielsen *et al.*, 2002).

On a local scale anthropogenic activities, such as the application of phosphate-containing fertilizers or Aluminum smelting, may introduce considerable amounts of fluoride into the environment (Saxena *et al.*, 2003).

### Health effects of fluoride

The effects of fluoride upon human health have been studied since the early 20th century. Both the benefits of minimal exposure and the risks of high fluoride doses have been established (Hichour and Persin., 2000). A higher daily dose has been linked to permanent dental and skeletal fluorosis (Mahramanlioglu *et al.*, 2002). It is estimated that more than 200 million people worldwide (UNESCO) rely on drinking water with Fluoride concentrations exceeding the present WHO guideline of 1.5 mg/L (WHO, 2004). The incidence of fluorosis has been reported in some parts of Ethiopia, where fluoride concentrations in drinking water exceed the WHO guideline value of 1.5 mg/L (Kloos and Tekle-Haimanot., 1999). Many water sources in Ethiopia contain Fluoride in elevated concentrations up to 26 mg/L. According to estimates of the Ethiopian Ministry of Water Resources, more than 11 million people in the Ethiopian Rift Valley rely on drinking water contaminated by Fluoride. Over 40% of deep and shallow wells are contaminated and over 80% of children suffer from different degrees of dental fluorosis and skeletal fluorosis is increasing, mainly among older people (Kloos and Tekle-Haimanot., 1999)



**Figure 1: Effect of Excess Amount of Fluoride Intake on Human Health.**

## Distribution of fluoride in the world

High Fluoride concentrations can be found in many parts of the world, particularly in some parts of India, China, Central and East Africa and South America (Amini *et al.*, 2008). The most well-known and documented area associated with volcanic activity follows the East African Rift system from the Jordan valley down through Eritrea, Ethiopia, Uganda, Kenya and Tanzania. Many of the lakes of the Rift Valley system, especially the soda lakes, have extremely high Fluoride concentrations; 1,640 mg/L and 2,800 mg/L, respectively, in the Kenyan Lakes Elmentaita and Nakuru (Nair and Gitonga., 1984), and up to 690 mg/L in the Tanzanian Momella soda lakes. Of the total 1438 water samples tested in Ethiopia, 24.2% had Fluoride concentrations above the 1.5 mg/L. Regionally; by far the highest Fluoride levels were recorded in the Ethiopian Rift Valley, where 41.2% of all samples exceeded the 1.5 mg/L level. The highest Fluoride concentrations were recorded for Ethiopian Rift Valley lakes Shala (264.0 mg/L) and Abijata (202.4 mg/L) and the lowest in Lake Tana (1.0 mg/L). The fluoride distribution in rivers, wells and springs are summarized in the following Table.

**Table 1:** Fluoride concentrations in and outside Rift Valley (Kloos and Tekle-Haimanot., 1999)

F(mg/L)	Outside Rift Valley				Within Rift Valley			
	Deep Well		Shallow Wells		Deep Wells		Shallow wells	
	No of Samples	%	No. of Samples	%	No. of Samples	%	No. of Samples	%
<1.0	225	86.5	169	92.3	192	37.9	90	55.6
1.0-1.5	25	9.6	4	22	61	12.1	28	17.3
1.51-3.0	9	3.5	10	55	93	18.4	19	11.7
3.1-7.0	1	0.4	-	-	102	20.2	15	9.3
7.1-13.0	-	-	-	-	53	10.5	7	4.3
>13.0	-	-	-	-	5	1.0	3	1.9
Total	260	100	183	100	506	100	162	100

## **2.2. Removal Methods of Water Contaminants**

### **2.2.1. Chemical precipitation**

Chemical precipitation is the method, in which dissolved and suspended metal ions are transformed to the insoluble solid through a chemical reaction. Usually a precipitating agent accelerates this conversion from metal ions into insoluble solid. The commonly used precipitation agents are lime and magnesia. This technique has been proven as an effective way to remediate heavy metals including chromium from wastewater. It is a simple, inexpensive, convenient, and safe method. However, this technique requires large amounts of chemicals, and excessive toxic sludge is produced.

Sludge filtration and disposal increase the overall cost of the Process. Sometimes metal precipitation is slow, and aggregation of metal precipitates take place (Kurniawan and Babel., 2006).

### **2.2.2 Reduction**

Reduction is a treatment process in which the higher valance state of metal ion is converted or reduced to the lower valance state using reducing agents. This technique offers several advantages such as recovery of metals from contaminated wastewaters; recycle of treated water and short treatment times. However, the disadvantages include additional chemicals requirement, and hazardous sludge formation. It is also quite expensive (Kurniawan and Babel., 2006)

### **2.2.3 Ion exchange**

Ion exchange is a suitable technique to remove heavy metals from the wastewater and this technique has also been applied as a remediation measure for Cr (VI). Various ion exchange resins are commercially available which can effectively remove Cr (VI) below the standard limit of Cr (VI) (0.1 mg/L) in wastewater. This process reduces the amount of waste for disposal and the cost of operation is generally lower. However, limitation of this method is that efficiency dependent on the pH of water (Rengaraj *et al.*, 2003).

#### **2.2.4 Membrane separation**

Membrane separation methods like Electro dialysis, Nano-filtration, Ultra Filtration, and Reverse Osmosis (Fu and Wang., 2011) have received considerable attention for the treatment of inorganic effluent, since they are capable of removing not only suspended solid and organic compounds but also inorganic contaminants such as heavy metals. Although it can be applied in occasions to low metal ion concentrations, for example, the removal efficiencies of Co(II) and Ni(II) were 90 % and 69 %, at initial metal concentrations of 0.84 and 11.72 mg/L/, respectively.

The main disadvantages of these processes are inadequate selectivity, high energy consumption, and immature technologies, which limit the popularization of this technology ( Tzanetakis *et al.*, 2003)

#### **2.2.5. Adsorption**

Adsorption is the process in which different molecules, ions and atoms of a liquid or gas get attached to the surface. Adsorbate is attached in the form of a film on the surface of the adsorbent. This process is different from absorption since in absorption, the substrate which is usually in the form of fluid percolates into the absorbent (Ramakrishna *et al.*, 2013). Thus adsorption includes the whole matter whereas adsorption is only effective on surfaces. But both the terms are included in a single term called “sorption”, and the reverse of “sorption” is called “desorption”. Adsorption is proving to be a better and more efficient method of waste water treatment in recent years. It is the process of formation of a layer of solid or gas on the substrate. Thus in the process of adsorption, the substance gets separated from fluid phase and gets accumulated on the solid phase substrate (Abbas *et al.*, 2013).

It is a well-known equilibrium separation process and an effective method for water decontamination application. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. The process is influenced by many physicochemical factors such as sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time (Ramakrishna *et al.*, 2013).

Most of the solid adsorbents of great industrial applications possess a complex porous structure that consists of pores of different sizes and shapes. In terms of the adsorption science, total porosity is usually classified into three groups. According to international union of pure and applied chemistry (IUPAC) recommendation, the micro-pores are defined as pores of a width (<2nm), mesopores are pores of a width (2-50nm), but macro-pores represent pores of a width (>50nm) (Hasan *et al.*, 2008).

However, the importance of porous structure on adsorption of many contaminants in aqueous solution is not well understood. As to physic sorption on porous materials, it's generally accepted that adsorption mechanism and process may be significantly different as a consequence of porous structure. Further, a powder is easily recognized as a mass of small dry particles, but the precise definition is inevitably somewhat arbitrary. The term fine powder is also used in an imprecise manner, but it seems reasonable to apply it to a material consisting of particles less than about 1µm. The unit mass of a fine powder contains a large number of small particles and exhibits an appreciable surface area (Serin and Selen., 2012).

In addition to the performance, a number of other factors greatly influence the choice and viability of waste materials as adsorbents, for example the cost of processing materials, Wastewater selectivity and regeneration of materials. Cost is a very important factor when considering materials for use as adsorbents. It is generally recognized that a material can be deemed low-cost if it requires little processing, is abundant in nature, or is a byproduct or waste material from another industry (Eng-Cheong *et al.*, 2011).

#### **2.2.5.1 Commonly used adsorbents**

Currently, there are different kinds of adsorbents available for wastewater treatment. A number of researchers have used different types of adsorbents to examine their efficiency towards several heavy metals. Form this we can mention the most commonly used once such as activated carbons, low cost materials, and others.

##### **Activated Alumina**

Activated alumina consists mainly of aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) spherical beads, highly porous and exhibits tremendous surface area. The surface area of activated alumina is 345–415 m<sup>2</sup>/g. It does

not shrink, swell, soften or disintegrate when immersed in water. It can exist in three forms, viz. activated alumina sorbent, activated alumina desiccant and activated alumina catalyst carrier. The granulated alumina has the internal active surface of the alumina. In this process, contaminated water is passed through a cartridge or canister of activated alumina. The contaminant adsorbs on the alumina (Chen and Snoeyink., 1987)

As the physical adsorption has a particular limit, the cartridge of activated alumina must be replaced periodically. Activated alumina is effective in removing  $\text{As}^{5+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ , and  $\text{F}^-$  from water. But the method is not very much capable of reducing levels of other contaminants of health concern. It needs another support.

### **Activated carbon**

The most commonly used adsorbent is activated carbon a substance which is quite similar to common charcoal. Actually, the active carbon is much more efficient because of its high porous character. The high porous character is generated by treating carbon to steam and high temperature ( $1300^\circ\text{C}$ ) with or without oxygen in the presence of inorganic salts (physical method).

The carbon may be of petroleum coke, bituminous coal, lignite, wood products, and coconut/peanut shells. At high temperature, parts of carbon are oxidized in  $\text{CO}_2$  and steam. The gases are evacuated and micro fractures and pores are generated in the carbon structure. It dramatically increases the carbon surface area, making a useful material for the removal of contaminant (Yang *et al.*, 2003). In some cases, the carbonaceous matter may be treated with a chemical activating agent such as phosphoric acid, zinc chloride and the mixture carbonized at an elevated temperature, followed by the removal of activating agent by water washing or chemical method.

Active carbon uses the physical adsorption process, whereby Vander Waals attractive forces pull the solute contamination out of the solution and onto its surface. The efficiency of the adsorption depends on the nature of the carbon particle and pore size, surface area, density and hardness as well as the nature of the contaminants (concentration, hydrophobicity, polarity and solubility of the contaminant and contaminant attraction to the carbon There are two different forms of

activated carbon in common use, granular activated carbon (GAC) and powdered activated carbon (PAC). Physically, the two differ as their names suggested by particle size and diameter. The reusability of the carbon is done primarily with the GAC as PAC particles are too small to be reactivated.

Activated charcoal is effective for trapping carbon based impurities (volatile organic chemicals), chlorine (including cancer-causing by-product trihalomethanes) as well as colors and odors. The limitation of is in GAC scheduled filter replacements, it is important to eliminate the possibility of ‘channeling’ which reduces the contact between the contaminant and the carbon. Therefore, it reduces efficiency, and the accumulation of bacteria in the filter.

#### **2.2.5.2 Low cost adsorbents**

Different review articles describe a number of low cost adsorbents regarding their availability in the environment. Relatively high cost of preparing activated carbon forces us to search for other materials which are low cost and effective. Now days, there are study results available on research carried out on the treatment of heavy metals of different sources using agricultural wastes, industrial byproducts and natural substances as adsorbents (Bhatnagar and Minoch., 2006)..

##### **Industrial wastes as low cost adsorbent**

Widespread industrial activities generate huge amount of solid waste materials as by-products. One of the beneficial uses of these wastes is to convert them as inexpensive adsorbents for water treatment. Various industrial wastes have been examined with or without modification for fluoride removal from water. The ability of fly ash (a thermal power plant waste) to remove fluoride from water and wastewaters was studied (Chaturvedi *et al.*, 1990) and found the removal of fluoride was favorable at low concentration, high temperature and acidic pH. The Langmuir maximum adsorption capacity of fly ash for fluoride ranged from 20.0 to 20.3 mg/g.

The industrial waste residue, generated during the manufacture of aluminum sulfate (alum) from kaolin by the sulphuric acid process was used as defluoridating media (Nigussie and Chandravanshi. *et al.*, 2007). The percentage of fluoride removal remained nearly constant within the pH range of 3–8, with further increase in the solution pH.

The fluoride removal efficiency decreased and the declining trend became significant at pH values >10. The presence of positively charged and neutral sites at the surface of the adsorbent in the pH range up to 8 was mentioned as the reason for better fluoride removal in that range. The adsorbent fluoride removal efficiency was affected significantly by bicarbonate ion concentrations and little or no effect by other anions such as phosphates, chlorides, sulfates and nitrates.

The removal of fluoride from aqueous solution using the original and HCl-activated red mud (an aluminum industry waste) has also been studied (Cengeloglu *et al.*, 2002). The fluoride adsorption capacity of the activated form was found to be higher than that of the original form. The maximum removal of fluoride ion was obtained at pH 5.5. It was found that the required time for adsorption equilibrium of fluoride ions was 2 h. The removal of fluoride ion using red mud was explained on the basis of the chemical nature and specific interaction with metal oxide surfaces, and the results were interpreted in terms of pH variations. The Langmuir maximum adsorption capacity of activated red mud for fluoride was calculated to be 6.3 mg/g. Thus, using industrial waste materials for removal of fluoride and Chromium from water is promising because of their low cost and high fluoride uptake capacity. However, the applicability of those adsorbents in the field is not reported.

**Table 2: Adsorption of chromium by different low cost adsorbents**

Material Used	Types of heavy metal removed	Efficiency	References
Clay	Cr (VI),PbII)	55 and58.16.mg/g respectively	Višekruna <i>et al.</i> , 2011
Clarified Sludge	Cr (VI),	26.31 mg/g	Bhattacharya <i>et al.</i> , 2008
Saw dust	Cr (VI),	39.7mg/g	Sharma andForster.1994.
Fertilizer industry waste	Cr (VI),	15.24 mg/g	Gupta <i>et al.</i> , 2010
Wheat bran	Cr (VI),	310.58 mg/g	Singh <i>et al.</i> , 2009
Sugarcane bagasse	Cr (VI),	92.2%	Garg <i>et al.</i> , 2009

### **2.2.5.3 Factors influencing adsorption process**

#### **Contact time**

Contact time is one of determinant factor in adsorption process. Every waste treatment options should be effective economically (Tangjuank and Udeye., 2009). In order to see the rate and effectiveness of any wastewater treatment process it is very important to study the effect of time. The time of contact between the adsorbate and adsorbent is the determinant factor of the kinetics and equilibrium of the adsorption process. Therefore, studying the effect of contact time on adsorption experiment is very important for its practical applications (Iscen, *et al.*, 2007).

#### **pH**

pH of the solution is another factor of the determinant environmental factors in adsorption process. It affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during adsorption process (Gill and Aslam., 2014). Adsorption of chromium is highly influenced by the pH of the solution according to many studies on chromium removal efficiency which decreased with an increase in pH for hexavalent chromium (Pandey *et al.*, 2010).

#### **Dose of adsorbent**

When the amount of adsorbent is increased more active sites will be available to which more amounts of metal pollutants can be attached (Semerjian *et al.*, 2010). However, further increase in the amount of adsorbent will have a negative effect on the adsorption process. This means either the metal adsorption decreases or it becomes steady because the active site for adsorption is blocked by a screening effect (Hammami, *et al.*, 2007).

#### **Initial contaminant concentration**

The initial concentration of contaminant is important in adsorption, since a given mass of sorbent material can only adsorb a fixed amount of ions. Normally, removal capacity of adsorbant will decrease with increase in initial contaminant concentration. This is because for a given mass of adsorbent material; the amount of ions that can be adsorbed is fixed.

The higher the concentration of the contaminant, the smaller the volume it can remove. At a low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial concentration increases, the active sites required for adsorption of the ions will be lacking. But the actual amount of contaminants adsorbed per unit mass of adsorbent increased with increase in contaminant concentration. This may be due to the high driving force for mass transfer at a high initial ion concentration (Ramesh,*et al.*, 2013). .

### **Effect of temperature**

Normally, increasing the temperature leads to a decrease in adsorption due to the adsorbed molecules having greater energies and therefore becoming more likely to release from the surface of the adsorbent. The reason for the fall in the adsorption capacity at elevated temperatures may be that at higher temperatures a part of the dye leaves the solid phase and re-enters the liquid phase (Mafra and Ferreira., 2013).

### **2.2.6. Mechanism of adsorption**

Among the unit operations in waste water treatment, adsorption occupies an important position since it is an efficient and economically feasible process for treatment of wastewater containing dissolved pollutants (Aseel and Kadim., 2010). In the adsorption process, molecules are extracted from one phase (liquid phase) and concentrated at the surface of a second phase (solid phase, adsorbent) which occurs due to an attractive force existing between the adsorbent surface and the adsorbate molecules. Therefore, it is a removal process where certain molecules are bound to an adsorbent particle surface by either chemical or physical attraction. The adsorption process consists of three consecutive steps (Muhi Mohammed., 2011).Substances adsorb to the exterior of the adsorbent, Substances move into the adsorbent pores and finally Substances adsorb to the interior walls of the adsorbent.

While adsorption is the phenomenon of accumulation of a large number of molecular species at the surface of solid or liquid phase in comparison to the bulk. These phenomena can be classified into two types depending on the nature of the bonding between the molecules of the adsorbate and the surface of adsorbent, namely chemisorption and physisorption.

Both types take place when the molecules in the liquid phase (sorbet) become attached to the surface of the solid phase (adsorbent) as a result of the attractive forces at the adsorbent surface overcoming the kinetic energy of the adsorbate molecules (Semerjian *et al.*, 2010).

### **Physisorption**

Physisorption or physical adsorption occurs when, as a result of energy difference and / or electrical attractive forces (weak Van der Waals forces), adsorbate molecules become physically fastened to the adsorbent surface. Physisorption takes place with the formation of single or multiple layers of adsorbate on the adsorbent surface and is characterized by low activation energy (enthalpy) of adsorption.

### **Chemisorptions**

Chemisorptions or chemical adsorption occurs when a chemical reaction occurs between the adsorbed molecules and the adsorbent. Chemisorptions takes place with the formation of a single layer of adsorbate attached to the adsorbent surface by chemical bonds. This type of interaction is strong with a covalent bond between adsorbate and the surface of the adsorbent is characterized by a high enthalpy of adsorption (Beyene *et al.*, 2014).

#### **2.2.7. Adsorption isotherm**

An adsorption isotherm models are used to describe the phenomenon governing the retention (or release) or agility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH (Foo and Hameed., 2010).

#### **Langmuir adsorption isotherm**

This model is used to describe the formation of monolayer adsorbate on the outer surface of the adsorbent. It is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane.

It also describes that different adsorbent sites has equal probability for the adsorbate which refers that only one molecule can attach to the active site (Kumar and Kirthika., 2009). The equation for Langmuir Adsorption Isotherm can be described as:

$$\frac{1}{q_e} = \left( \frac{1}{C_e} \times \frac{1}{K_L q_{max}} \right) + \frac{1}{q_{max}} \dots\dots\dots 1$$

Where,  $C_e$  = the equilibrium concentration of chromium in the solution (mg/L)  $q_e$  = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).  $q_{max}$  = maximum monolayer coverage capacity (mg/g)  $K_L$  = Langmuir isotherm constant (L/mg).

**Freundlich adsorption isotherm**

It is one of the oldest models which is extensively used, it was developed by Freundlich in 1932 (Cooney *et al.*, 1998). The Freundlich Isotherm is an empirical equation employed to describe heterogeneous systems. In this model it is described that during the adsorption process different sites of the adsorbent are involved with several adsorption energy (Kumar and Kirthika., 2009).

$$q_e = K_f C_e^{1/n} \dots\dots\dots 2$$

In which  $q_e$  is the amount of adsorbate per unit weight of adsorbent in equilibrium with a solution concentration  $C_e$  in mg/L. Where,  $K_f$  and  $1/n$  are Freundlich constants and the characteristics of the system.

**2.2.8. Adsorption kinetics**

In order to determine the rate limiting step during the adsorption process different kinetic models have been used to analyze the experimental data. These models include first-order, pseudo-second-order and intra-particle diffusion.

**Pseudo first order model**

First order model which is believed to be the earliest model, was developed by Lagragren in 1898 (Qiu *et al.*, 2009). To describe the kinetic process of liquid-solid phase adsorption he presented first order model as:-

$$\frac{dq_t}{dt} = k_{p1}(q_e - q_t) \dots \dots \dots 3$$

Where  $q_e$  and  $q_t$ (mg/g) are the adsorption capacities at equilibrium and time  $t$ (min), respectively.  $k_{p1}$  (min<sup>-1</sup>) is the pseudo first order rate constant for the kinetic model.

Integration of the equation with the boundary conditions of  $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$ , gives,

$$\ln \frac{q_e}{q_e - q_t} = k_{p1}t \dots \dots \dots 4$$

That can be rearranged to:-

$$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303}t \dots \dots \dots 5$$

**Pseudo-second-order model**

For adsorption process pseudo-second order model is used in different literatures in order to describe the adsorption isotherm (Ho and McKay, 1998). Most of the time this equation is used when the first-order model fails and the equation for this model is written as:-

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \dots \dots \dots 6$$

Integrating the equation for the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \dots \dots \dots 7$$

$q_e$  is the amount of ions sorbed at equilibrium, mg/ g ;  $k$  is the equilibrium rate constant of pseudo-second order sorption, g /mg min

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \dots \dots \dots 8$$

And

$$h = kq_e^2 \dots \dots \dots 9$$

Where,  $h$  is the initial sorption rate, mg/g min

**Intra-particle diffusion model**

The case of intra-particle diffusion model it is assumed that an uptake of metal ions from the solution by an adsorbent varies almost proportionally with the square root of t (i.e.  $t^{0.5}$ ) rather than t, nearly linear variation of the quantity is sorbet with  $t^{0.5}$  and is predicted for a large initial fraction of reactions controlled by rates of intra-particle diffusion (Ho and McKay., 1998). An equation for this model can be written as:-

$$qt = K_i \sqrt{t} \dots\dots\dots 10$$

Where, qt is metal uptake at time t and  $k_i$  is the intra-particle diffusion rate constant  $Mg\ g^{-1}\ min^{0.5}$ .

### 2.3. Aluminum-Based Water Treatment Sludge (‘Al-WTS’)

Aluminum-coagulated water treatment sludge (‘Al-WTS’) is an inescapable by-product obtained as a result of water treatment processes, such as coagulation, flocculation, clarification and filtration using aluminum sulfate as the primary coagulant (Zhao *et al.*, 2011). Al-salts are the most commonly used primary coagulating agents by water industries across the world for water treatment processes due to their effectiveness and low costs (Gebbie *et al.*, 2001). Therefore, Al-WTS is the most extensive byproduct generated by the water industries globally.

Water treatment processes generate large volumes of Al-WTS around the world where the immediate attention must be directed for economically sustainable and environment friendly management of alum sludge. Sludge production from drinking water treatment process generally estimated to be 1–3% by volume of the raw water use through the treatment process (Blakemore *et al.*, 1998). In addition, the solids content of thickened sludge is typically 2–4%, and mechanically dewatered sludge (via centrifuge) varied between 17% and 23% solids (Maiden *et al.*, 2015).

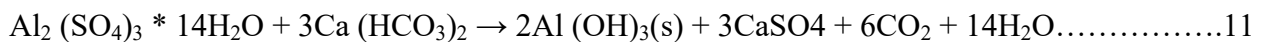
Annually about 80,000 tons of the AL-WTS waste is produced from water treatment plants (Shannon *et al.*, 2008). Therefore, there is an identified need to examine potential options for recycling and reuse of alum sludge and to quantify the potential cost savings and benefits of alternatives. Stockpiling, disposal into sewers and landfill have been the most widely adopted conventional practices (Ippolito *et al.*, 2011; Elliott and Dempsey., 1991) in many countries for decades, however financial and environmental costs of these practices are escalating and forcing the industry to develop alternative management strategies such as recycling, reuse and resource recovery. In the meantime, practicability, long term viability and sustainability of some of those

options have been questioned (Kolarik and Priestley, 1995); therefore, there is a clear need for investigating and evaluation of commercially viable better management options for alum sludge reuse particularly where this material can effectively be utilized in substantial quantities easing the pressure on water treatment industry.

### 2.3.1. Composition and characteristics of Al-WTS

Alum salts using in water purification is technically an aluminium sulphate with general composition of  $Al_2 (SO_4)_3 \cdot 14H_2O$ . When alum salts added to raw turbid water sources during drinking water purification process, aluminium ions are hydrolyzed into aluminium hydroxide which is a precipitate (Bugbee and Frink., 1985). Organic matter and other water insoluble impurities in the raw water can be absorbed by aluminium hydroxide precipitates after the flocculation–clarification process during drinking water treatment process.

Al-WTS is principally formed as gelatinous amorphous structures and consists of organic and suspended matter, inorganic matter, various microbial consortia, coagulant products and chemical substances (Boaventura *et al.*, 2000). As an example, Equation 11 depicts the formation process of amorphous  $Al (OH)_3$  after addition of alum to raw turbid water where it reacts with bicarbonate (Ippolito *et al.*, 2011).



pH of Al-WTS varied in the range of 5.12–8.0 and it is within the typical range of 5.0–8.0 which is satisfactory for plant growth (Bohn *et al.*, 1985). The range of electrical conductivity (EC) of Al-WTS (0.36–1.66 dS  $m^{-1}$ ) is well below the critical value recommended (4.0 dS  $m^{-1}$ ) for salt-sensitive crops in agriculture (Brady and Weil., 2002).

It contains significant amount of carbon and organic matter which can augment soil physico-chemical properties. Total C, N and P values found in alum sludge varied in the ranges of 127–188, 4.0–4.8 and 3.13–3.5 g  $kg^{-1}$ , respectively. The Principal metallic constituent is aluminium which ranged from 27–153 g  $kg^{-1}$ .

Al-WTS generates hardly any environmental hazards in comparison to sewage sludge originated from wastewater treatment plants because it is comparatively clean with respect to heavy metals

and other hazardous organic compounds. The toxicity characteristic leaching procedure (TCLP) guidelines (USEPA, 1993) guidelines are widely used to differentiate municipal and industrial solid waste as hazardous or nonhazardous for the purpose of landfilling. Heavy metal levels measured in Al-WTS reported in the literature were significantly lower than that of the regulatory levels for the TCLP and consistent with other nonhazardous wastes. In addition, detrimental pathogen levels in the alum sludge are generally significantly lower compared to the sewage sludge (Elliott and Dempsey, 1991).

Al-WTS were found to exhibit amorphous nature. X-ray diffraction (XRD) analysis of the sludge showed no sharp characteristic diffraction peaks, indicating poorly ordered particles, having no distinct shape or form and suggesting that the crystalline  $\text{Al}(\text{OH})_3$  phase is absent within it, although pure aluminium hydroxide exhibited a regular crystalline structure (Yang *et al.*, 2006a,b). Even the aged sludge exhibited similar XRD characteristics as that of fresh sludge indicating that the crystallization did not occur during the ageing process. XRD pattern illustrates the amorphous structure of alum sludge, however silica ( $\text{SiO}_2$ ) was the major crystalline solids identified in numerous XRD analyses (Yang *et al.*, 2008).

Ippolito studied Al-WTR using X-ray diffraction (XRD) analysis but did not observe the presence of crystalline Al mineral phases. He also used XRD analysis, verifying quartz, feldspar, Calcite, illite/smectite, and kaolinite, but no crystalline  $\text{Al}(\text{OH})_3$  phase in Al-WTR, suggesting that an amorphous Al form was present (Ippolito and Barbarick., 2011).

Al-WTS have shown, via scanning electron microscopy (SEM), to be of various shapes and sizes and are highly porous (Ippolito and Barbarick., 2011). Using SEM, Yang compared dewatered Al-WTS to pure aluminum hydroxide and noted that the Al-WTS was virtually amorphous, having no distinct shape or form, in contrast to pure aluminum hydroxide, which exhibited a regular crystalline structure (Yang and Zhao., 2006). Ippolito and Makris used SEM to identify elements present in the sludge. They noted the presence of Ca and Al in Al-WTS, and verified the presence of Al, Fe, P, Si, Ca, and Na in Al- and Fe-WTS. These reports imply that WTS are composed of a heterogeneous mixture of inorganic elements (Makris *et al.*, 2006).

Makris also reported that the total micro pore volumes for Al and Fe WTS were 0.042 and 0.012 cm<sup>3</sup>/g respectively. The amorphous and porous nature of Al and Fe hydroxides makes the sludge, an adsorption site for majority of anions (Makris *et al.*, 2005)

### **2.3.2. Utilization of Al-WTS in different areas**

Large quantity of aluminum- laden sludge is produced from various waterworks worldwide. Al-WTS contains 39% aluminum by weight after coagulation. Free and complexed aluminum species are toxic to aquatic life, and it has environmental (Wang *et al.*, 1998). So the water treatment sludge must be handled in accordance with environmental regulations in force particularly in this era when emphasis is on green technology. According to environmental protection regulations, it is required to minimize the quantity of wastes produced or where possible, the wastes should be re-used or recovered as a raw material for various applications.

Different categories of Al-WTS reuse were identified during literature searches. The first one is the reuse of sludge as building and construction materials such as Brick making and manufacture of cement and cementitious material (Goldbold and Graham., 2003). The other one is land application of Al-WTS for different purposes involving, the controlled spreading of the sludge onto or into the surface layer of soil to stabilize, degrade, and immobilize the sludge constituents, those applications can be as soil buffer, agricultural soil improvement and as nutrient reduction in laden soils and runoffs (Elliott., 1990, Elliott., 2002, De Wolfe *et al.*, 2006).

Al-WTS also reused as a co-conditioner in sewage sludge conditioning and dewatering process (Babatunde and Zhao, 2007). Moreover, it is documented that alum sludge can be utilized as a coagulant to remove oil and grease (Jangkorn *et al.*, 2011) chemical oxygen demand (COD) (Guan *et al.*, 2005) and suspended solids (SS) (Leader *et al.*, 2005) from wastewater.

### **2.3.3. Al-WTS as an adsorbent**

Al-WTS is considered as one of the major adsorbent for pollutant removal from wastewater treatment plants and it can eliminate a wide range of heavy metals from the wastewater by augmenting adsorption and chemical precipitation (Dayton., 2003 and Gibbons., 2009). The amorphous nature of the hydroxyl-Al present and its high surface area are the main parameters responsible for the elevated metal adsorption capacities (Zhou *et al.*, 2011). These adsorption

properties of the alum sludge can be used to remove heavy metal pollutants such as Hg (Ippolito *et al.*, 2009b), Pb (Zhou and Haynes, 2011a,b), Se (Ippolito *et al.*, 2009b), As (Mudhoo *et al.*, 2011) and Cu (Nagatenah *et al.*, 2010).

### 2.3.3.1. Al-WTS as a phosphorous adsorbent

Several extensive research studies (Gibbons and Gagnon, 2011; Huang and Chiswell, 2000; Babatunde and Zhao, 2010; Mortula and Gagnon, 2007) have been conducted on the possible utilization of alum sludge as an adsorbent for phosphorus removal in wastewaters.

The coagulant property of the Al-WTS can be utilized to eliminate pollutants from the wastewater treatment process and alum sludge can be used to remove P up to 94% (Horth *et al.*, 1994). It has been reported that the P-adsorption capacity is largely dependent upon the pH of the P-containing solution where adsorption being enhanced in the acidic region

It is highlighted the insignificant competitive effect of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  (which are typical anions found in wastewaters) on phosphorous adsorption onto the Al-WTS surface. (Yang *et al.*, 2006b). It was proposed that phosphate adsorption onto the sludge is through a kind of inner-sphere complex reaction, which occurs when phosphate replaces the functional groups on the surface of Al-WTS and becomes bound to the surface. Consequently phosphate adsorption with aluminum ions through a precipitation process is described by Equation 12 and the major adsorption mechanism is ligand exchange.



The phosphorous adsorption capacity described in different literatures assured that pH plays a key role in the phosphorus adsorption capacity. However, considerable research on phosphorus adsorption by the sludge with respect to the influence of solution pH, characteristics of the sludge, and the effect of phosphorus speciation, alum sludge dosage and other process variables should be investigated and understood as a guide to further extending its utilization. It is reported that oven dried alum sludge is a low cost and reliable technological solution for P removal for small and medium-sized municipalities (Mortula and Gagnon., 2007).

It is reported that P in wastewater in the range of 597–675 mg P L<sup>-1</sup> to 0.14–3.20 mg P L<sup>-1</sup> can easily be removed by alum sludge application (Yang *et al.*, 2009). 85% of phosphorus removal can be achieved by adding oven dried alum sludge to wastewater (Mohammed and Rashid, 2012). Experimentally P adsorption capacity is identified to be 0.7–3.5 mg P (g sludge)<sup>-1</sup> depending on pH of the phosphorus solutions (Yang *et al.*, 2006a).

It was also reported that Al-WTS discharged to a sewer in a treatment plant has proven completely successful phosphate removal up to 94%, at a dose ratio of 0.3–1 corresponding to about 3.5 mmole L<sup>-1</sup> of Al (Horth *et al.*, 1994).

The maximum adsorption capacities of alum sludge were varied in the range of 0.7–3.5 mg P g<sup>-1</sup> where the pH of the synthetic P solution was varied from 9.0 to 4.3. Studies conducted by Yang *et al.*, 2006a,b) indicated that alum sludge is suitable for use as an adsorbent for removal of phosphate from wastewater.

### **2.3.3.2 Al-WTS as per chlorate (ClO<sub>4</sub><sup>-</sup>) adsorbent.**

It is well known that perchlorate (ClO<sub>4</sub><sup>-</sup>) in human body interacts and decreases iodine uptake into the thyroid gland, with changes in thyroid hormone secretion potentially resulting in hypothyroidism (USEPA, 2008). Irreversible changes, particularly in the brain, are associated with hormone insufficiencies during human development (Chan *et al.*, 2000).

Makris *et al.* (2006a) reported that alum sludge may be a promising adsorbent for perchlorate removal in contaminated ecosystems. In a research study, Makris *et al.* (2006a,b) found that greatest amount of ClO<sub>4</sub><sup>-</sup> (65%) was removed and its removal efficiency has increased up to 76% after 24 h. It is further reported that per chlorate did not desorbs from alum sludge, which suggested stable immobilization process for per chlorate in the wastewater.

### **2.3.3.3 Al-WTS as textile dye adsorbent.**

Textile industry is considered as one of the most polluting sectors in terms of effluent composition and volume of discharge. Textile dyes are gradually promising as anthropogenic organic substances that pose severe environment hazards (Yadav *et al.*, 1998). Textile dye disposal into inland water streams can be toxic to aquatic ecosystems because of they may be

mutagenic or carcinogenic and subsequently can cause severe damage to human and other livestock. Even the existence of very low concentrations of dyes (less than  $1 \text{ mg L}^{-1}$ ) in the effluent is considered detrimental and required to be removed before the wastewater can be discharged into the inland water bodies (Vandevivere *et al.*, 1998).

It is reported that the Al-WTS can be used to remove the hydrophobic dye from the textile wastewater at the removal efficiency of 88%. The sludge utilization for the removal of hydrophilic dyes is not recommended because the high solubility characteristics of hydrophilic dyes can create deterioration in the water quality during recycling (Chu *et al.*, 2000).



### **3. MATERIALS AND METHODS**

#### **3.1. Apparatus and Equipments**

The apparatus and equipments used during this research work are: XRD (Shimadzu, XRD-7000S South Korea,) UV Vis-spectrophotometer ((JASCO T 80+ UV-Vis spectrophotometer) SEM (Inspect F50 made in Japan), Fluoride Ion selective Electrode(Metrohm 826 pH mobile made in Germany),Digital electronic balance(FA2104,made in China),Muffle Furnace(Ambassador F-07,Made in India) pH/conductivity meter(AD8000,Made in Romania),Oven, glass-filters, beakers, Vacuum Filter Pump(PDF 2-25,India) Magnetic stirrer(JHMS-6293), filter paper(What man 125mm), mortar and pestle, glass rod, Gravimeter Sieves, Pipettes, spatulas, Erlenmeyer flask, volumetric flask, different types of beakers, and sample collection materials(buckets, glass bottles and plastic bottles).The pictures of materials used in the analysis procedure are described in the annex.

#### **3.2 Chemicals and Reagents**

All the reagents and chemicals used in this study were analytical grade. The supplier of all chemicals was Fine Chemical Supplier except TISAB from OSHO, Diphenyl Carbizide from Modjo Tannery and De ionized water from AMASSC quality control laboratory.

De ionized water (40L) for reagent preparation and to rinse equipments, sodium Fluoride (5gm) for stock solution preparation, 37% v/v Hydrochloric Acid(25 ml) and Sodium Hydro Oxide pellet (4gm) for pH adjustment, TISAB (500ml) for Fluoride content determination using FISE,98% v/v Sulphuric Acid(500 ml) for reagent preparation to Uv- Vis determination and to wash sample taking bottles , Potassium Dichromate(5gm) for stock solution preparation, Diphenyl Carbizide(100gm) and Acetone (100ml) for UV-Vis Determination of Chromium.

#### **3.3. Sample Collection and Preparation**

##### **3.3.1. Waste Water Sample Collection and Preparation**

The composite wastewater sample was obtained from Haudaochen Leather Production industry located in Modjo town and the fluoride attacked water was taken from deep well found around Methehara, which is located in the Rift valley region of the country.

Samples were collected from each sampling site with a total sample volume of 2 L each using glass bottles during the month of December. Effluent samples from Haudaochen Leather production industry were collected when it was pumped into the factory oxidation pond located near the factory.

Bottles used for collecting waste water samples were previously washed carefully with detergent and 1M H<sub>2</sub>SO<sub>4</sub> and rinsed by water samples at the point of collection. Care was taken not to introduce errors during sampling and storage where contamination resulting from improperly cleaned sampling devices and sample containers. Loss of metals or precipitation in sample containers was avoided by acidifying the sample properly using HNO<sub>3</sub> to pH < 2.

Sample Preservation is made by adding 1.5 ml of concentrated HNO<sub>3</sub> per liter of sample. Storage and transportation of samples were performed in manners that maintain sample quality. Transportation arrangement was maintain proper storage conditions and provide for effective sample pickup and delivery to the Analytical laboratory and refrigerated at 4°C. Prior to treatment, the samples were warmed to room temperature (21 to 25°C). The wastewater samples collected were filtered using filter paper (what man 125 mm) before each adsorption analysis. Sample collection, preservation and storage were performed according to standard procedures recommended by USEPA guide to drinking water Sample collection.

### **3.3.2. Preparation of standard stock Solutions and working solutions**

Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) standard stock solution was used as the source for chromium working solutions for optimization Process. A standard stock solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (1000ppm) was prepared by dissolving 2.835 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 1000 ml of distilled H<sub>2</sub>O. Standard working solutions of Cr (VI) with different concentrations were prepared by pipetting 2,4,6,8 ml of 1000 ppm K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution into different 1000 mL volumetric flasks and deionized water was added up to 1000ml.

Fluoride stock solution (1000mg/L) was prepared by dissolving 2.21g anhydrous sodium fluoride in 1L deionized water. Standards F<sup>-</sup> samples at a required concentration were prepared using appropriate dilution of the stock solution.

Standard working solutions of fluoride with different concentrations were prepared by pipetting 2,4,6,8 ml of 1000 ppm NaF solution into different 1000 mL volumetric flasks and deionized water was added up to 1000ml.

The pH of the solution was adjusted by adding 0.1 mol/L HCl or NaOH solution. The pH values were periodically measured and readjusted until they were constant.

### **3.3.3. Collection and Pretreatment of Adsorbent**

Al-WTS was taken from Awash Melkassa Chemical Factory located at Awash Melkassa, 17km from Adama from OB-50 raw water treatment plant. This is. Freshly generated three batches of drained Water treatment sludge was collected with 20L buckets. The liquid sludge was settled for 24hrs to separate the liquid part from the sludge and filtered using filter cloth. The filtered sludge was air dried in a clean yard. The dried sample was then crushed and sieved with 0.2 mm particle size using gravimetric sieve and stored for further use and characterization.



**Figure 2: Sun dried Al-WTS (SAI-WTS)**

The prepared adsorbent was characterized for basic physical parameters such as pH, moisture content, Volatile mater, ash content, loss on ignition Bulk density, Particle density and porosity. An ASTM (D1102-56) standard procedure was followed to determine the physical parameters of the adsorbent. The procedures of physical parameters determination are described below

**PH**

The sun dried WTS grounded and sieved (< 1mm).PH of the sample will be determined in a 1;1 WTS to distilled water accordingly, 50gm of WTS sample will be weighed and transferred into a 250 mL beaker and 50 ml of distilled water was added then it was stirred Samples were allowed to stabilize and then pH was measured using an electronic pH meter (Multi 3620 IDS).

**Moisture content**

A crucible was taken and weighed. 2g of sample was added in the crucible and weighed. It was kept in hot air oven at 105°C for 24h. It was taken out and kept in the desiccators. Then the weight was measured and the moisture content is calculated as:

$$M=100X \frac{B\_F}{B\_G} \dots\dots\dots Eq.14$$

Where, M = moisture content (%), B= mass of crucible plus sample (4.6278), F = mass of crucible plus dried sample (4.5157), G = mass of empty crucible (2.6059g). Accordingly, moisture content is calculated to be 5.54%.

**Ash content**

2 g of sample was taken in crucible and weighed. The sample was kept in a muffle furnace for 2h at a temperature of 550°C. Then, it was taken out and kept in desiccators for half an hour to cool down. Then, again the weight was measured and ash content was calculated as:

$$M=100X \frac{F\_G}{B\_G} \dots\dots\dots Eq.15$$

Where, A = Ash content, B= Mass of crucible plus sample (39.25g), F= mass of crucible plus ash sample (after heating) 38.82g, G = mass of empty crucible (37.23g). So, ash content is calculated to be 78.71%.

**Volatile Matter**

A crucible was taken and weighed. 2g of sample was added in the crucible and weighed. It was kept in the muffle furnace at a temperature of 650°C for 10 minutes. Then it was taken out and

kept in the desiccators for half an hour to cool down. The weight of the sample in crucible was measured again. Percent volatile matter was then calculated as,

$$V=100 \times \frac{100(B-F) - M*(B-G)}{(B-G)*(100-M)} \dots\dots\dots \text{Eq.16}$$

Where, V= volatile matter (%), B= mass of crucible plus sample (39.33), F=mass of crucible plus ash sample (38.95g), G = mass of empty crucible (37.23), M=5.54%. So as Eq. (7), percent volatile matter was found to be 13.29%.

**Bulk density**

The sample was dried to constant weight for 24 hours in hot air oven at 105°C.50gm of the dried sample was transferred to 100ml graduated cylinder carefully using funnel. Then, the cylinder was tapped four times to settle the sludge. The volume was read and the bulk density was calculated as;

$$B = D/P \dots\dots\dots \text{Eq.17}$$

Where, B = Bulk density (gm/cm<sup>3</sup>), D = Mass of dry sample (50gm), P =Volume of packed sample (78cm<sup>3</sup>).So, bulk density is calculated to be 0.64.

**Particle Density**

60ml distilled water was measured and transferred to 100ml Cylinder.50gm of dried sample was weighed and transferred into the cylinder with water, Then, it was stirred to remove trapped air. The volume was read and the particle density was calculated as;

$$P =D/S \dots\dots\dots \text{Eq.18}$$

Where, P =Particle density (gm/cm<sup>3</sup>), D = Mass of dry sample (50gm), S=Volume of sample (23cm<sup>3</sup>).so, particle density is calculated to be 2.17.

### **Porosity**

Porosity is the fraction of the total powder volume that is taken up by the pore. The porosity of the sludge powder was determined based on the particle density and bulk density of the sludge. The porosity for the sludge powder was obtained from bulk and particle density using equation 19:

$$P = 1 - (BD/PD) \dots\dots\dots Eq.19$$

Where, P=Porosity(%), Bd=Bulk density(0.64 gm/cm<sup>3</sup>), Pd=Particle density(2.17 gm/cm<sup>3</sup>), So porosity is calculated to be 70.55%.

### **3.4. Treatment of Adsorbent**

The prepared adsorbent (SAI-WTS) was treated with three different methods. Because chemical and physical treatment improves the surface area of the adsorbent by creating more surface binding sites with the ions (Anteneh Mesfin.,2009). The sun dried adsorbent was treated thermally at three different temperatures or digested with hydrochloric acid or a combination of the two, in which, a portion of the dried acid digested sludge was again treated with three different temperatures: at low temperature (400°C), mild temperature (600°C) and High temperature (800°C) using muffle furnace to prepare a sample so called thermally treated alum water treated sludge(TAI-WTS). Then the treated sludge was cooled in desiccators for further use.

To get the hydrochloric acid acidified alum water treated sludge(HAI-WTS), the sun dried Water treated sludge(SAL-WTS) was water-washed twice, and then digested with 5% hydrochloric acid for 24 h, and the supernatant was filtered off using vacuum pump and Whatman filter paper(125mm). The sludge was washed with deionized water for 3 to 5 times until it was neutral and was dried at oven following the procedure from the research work of Ying Li, Shengke Yang and Qianli Jiang(Ying Li, Shengke Yang and Qianli Jiang,2018). A portion of dried acid digested sample was treated thermally at 400°C, 600°C and 800°C to get Hydrochloric Acid and thermally treated alum based water treated sludge(HAI-WTS).

### 3.5 Characterization

#### 3.5.1 Crystalline structure Analysis

XRD is a powerful and routine technique for determining the crystal structure of materials (Murray *et al.*, 1995). The XRD analysis was done for the sun dried adsorbent, and the treated adsorbents at ASTU research laboratory of Material science and engineering department using x-ray diffractometer (XRD-7000S South Korea). XRD spectrum was recorded from  $10^{\circ}$  to  $80^{\circ}$  with  $2\theta$  angles operated at 40 kV and 30 mA.

The raw alum was used to differentiate whether the basic peaks of the treated adsorbents loss their structure and mineral content due to treatment or not. The XRD analysis result were considered to select potential adsorbents for further optimization study by comparing the result with the peaks of original Alum sample.

For the XRD characterization, approximately 2g of samples were prepared, grounded and filled in the sample holder and mounted on X-ray diffractometre.

#### 3.5.2 Morphological analysis

SEM is a powerful and popular technique for imaging the surface morphology of almost any material with a resolution down about 1  $\mu$ m (Hanada *et al.*, 2018). It provides high resolution image of the sample by rastering a focused electron beam across the surface and detecting secondary or backscattered electron signal (Pusit *et al.*, 2009)

### 3.6. Optimization and adsorbent selection

Based on the XRD result of the adsorbents t four best adsorbent which do not loss their crystalline structure due to treatment were selected for the adsorption experiment. This was done by making all the parameters constant for Cr (VI) and F<sup>-</sup> (at pH=2, Adsorbent Dose 2g/L, Initial adsorbet concentration 2mg/l). The optimization of pH, initial concentration of adsorbetes, adsorbent dosage and contact time was carried out by varying one parameter at a time while other factors were kept constant at a shaker speed of 150 rpm and room temperature. Accordingly, the pH values of 2, 4, 6 and 8 with increments of 1 were used for both Cr (VI) and F<sup>-</sup> analysis. These pH ranges were maintained by adding either solution of HCl or NaOH. Adsorbent dosage of 5,

10, 15, and 20 g/L were used to study the effect of adsorbent dosage on removal efficiency of the Al-WTS. The optimum contact time for the process was identified by conducting the experiment under 1, 1.5, 2, 2.5 hrs. of contacts of adsorbent and the adsorbent.

Four samples in the concentration range of 2 to 8 mg/L with increments of 2 mg/L were considered for the sake of determining the effect of initial concentration of Cr (VI) and F<sup>-</sup> on the removal efficiency of AL-WTS. The experiments were carried out in triplicate and the average results were used for calculations.

### **3.6.1. Batch adsorption experiment**

UV-Spectrophotometer was used to determine the concentration of Cr (VI) and Fluoride ion Selective electrode (FISE) to determine the concentration of F<sup>-</sup> were used because of its availability and reliability of the result.

All adsorption experiments were carried out in batch mode because of its simplicity and reliability (Curkovic *et al.*, 2001:3437). The batch adsorption experiments were done according to the procedures adopted from the research work of Abraham Abraham Aynekugnem *et al.*, 2015

The test was done by taking weighed dosage 5, 10, 15 and 20 gm of the adsorbent in 1L of adsorbates and at pH of 2, 4, 6 and 8 and 1L of 2, 4, 6 and 8 mg/l initial concentration of Chromium and Fluoride solutions with the contact time 60, 90, 120 and 150 min. The pH of solution was adjusted by adding 0.1M HCl and 0.1M NaOH solution until pH reach to desired pH. The solutions were shaken at room temperature (25°C) with a shaker speed of 150 rpm for about the desired time. The samples were then filtered (gravitational filtration) using a Whatman filter paper (125 mm) and the filtrate was analyzed for the residual Cr(VI) and F<sup>-</sup> concentration in the solution. Equilibrium of this experiment was studied using Langmuir, and Freundlich, isotherm models. The kinetics was also studied by Pseudo- first order and Pseudo-second order models. Satisfactory conformity between experimental data and the model-predicted values was expressed by the correlation coefficient ( $R^2$ ).

Adsorption efficiency in percent and milligram of Cr and F<sup>-</sup> adsorbed per gram of adsorbent were calculated using the equations 17 and 18 respectively. Finally, average of the triplicate results was presented.

$$\% R = \frac{C_o - C_f}{C_f} \dots\dots\dots \text{Eq. 12}$$

Where %R is percent removal C<sub>o</sub> is initial concentration and C<sub>f</sub> concentration after adsorption

$$q = \frac{(C_o - C_f)V}{m} \dots\dots\dots \text{Eq.13}$$

Where q is metal removal in mg/g, c<sub>o</sub> is initial concentration, c<sub>f</sub> concentration after adsorption, m is adsorbent mass in gram and v is volume of contaminated water used during the experiment

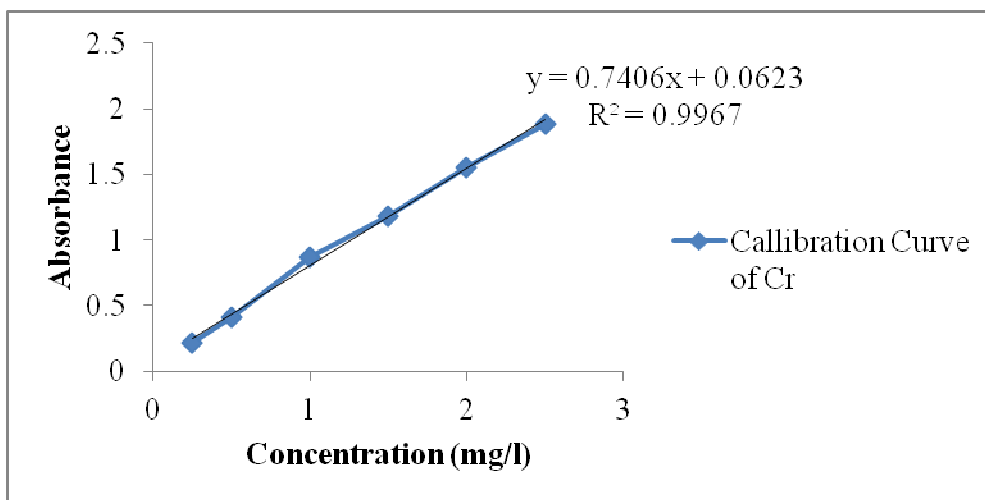
**3.6.2 Chromium analysis**

Cr (VI) analysis was carried out in accordance to DiphenylCarbizide method (APHA, AWWA et al.1998).To determine residual chromium for the treated samples, A drop of diphenyl carbazide(DPC) solution was added prior to measurement. After a time of 5 to 10 min for full color development, the adsorbent was isolated by filtration. The filtrate was then analyzed for chromium.

The 1.5-DPC (0.5%) solution was prepared by dissolving 250mg 1.5-DPC in 50 ml acetone. The analyte solutions' containing Cr (VI) ions was taken into 50 mL standard flasks. To each flask, 2 mL of 3M H<sub>2</sub>SO<sub>4</sub> and 1 mL DPC were added and diluted up to the mark and mixed well. The mixtures were allowed to stand for 5 to 10 minutes for full red brownish color development.

The concentration of Cr (VI) ions was determined by the color intensity of complex formed using UV spectrophotometer at 540 nm. Each batch experiment was carried out in duplicate. For the determination of residual concentration of Cr (VI) ions from each batch adsorption experiment, a linear calibration graph (Figure 1) was generated over the range 0.25 mg/L to 2 mg/l of Cr (VI) ions on a UV-Vis spectrophotometer with 1 cm quartz cells at a wavelength of 540 nm. Linear calibration curve of this data was served as the basis for determining the chromium concentration variation as a result of the hexavalent chromium adsorption process during the experimental

work. As shown on Fig the experimental data was fitted by straight line with a high regression coefficient value  $R^2=0.996$ .



**Figure 3:** Calibration line for determination of Cr (VI) in the form of a complex with 1, 5-diphenylcarbazine

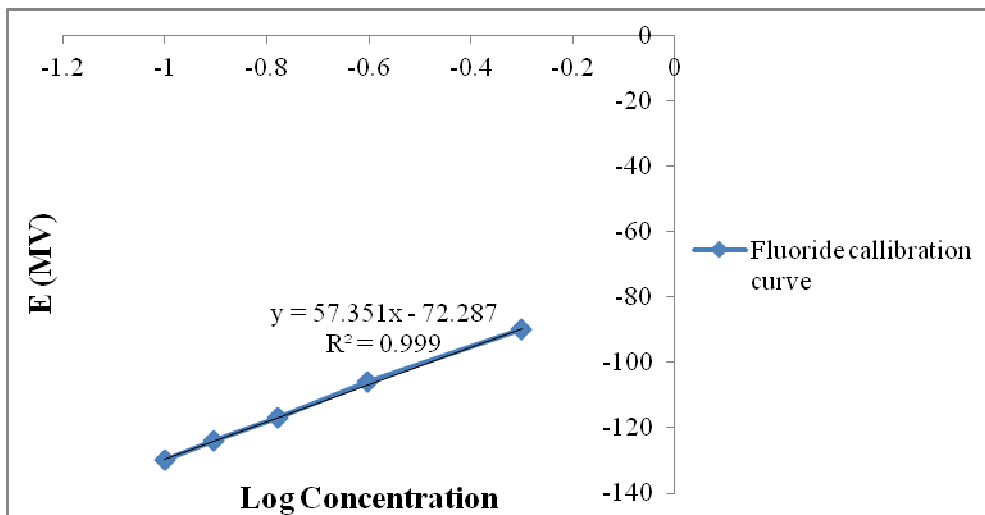
### 3.6.3 Fluoride determination.

Fluoride determination was carried out in accordance to the method used in OSHO fluoride removal center working manual. The total ionic strength adjustment buffer (TISAB) was prepared following the procedure developed by Agarwal. Accordingly 57 mL of glacial acetic acid, 58 g of NaCl, 7 g of sodium citrate, and 2 g of EDTA were added to 500 mL of double distilled water and allowed to dissolve, and then, the pH was adjusted to 5.3 with 6 M NaOH. Finally, the solution was adjusted up to 1,000 mL in a volumetric flask with double distilled water.

Five standard solutions 2, 4, 6, 8 and 10 mg/L were prepared from the stock solution (1000 mg/L of fluoride prepared by dissolving Anhydrous sodium fluoride (2.210 gm) in double distilled water (fluoride free) and then diluted to 1 L by serial dilution. Calibration graph was plotted as potential versus the logarithm of concentration of fluoride ion. The slope and intercept were used to convert the experimentally obtained potential into concentration of fluoride.

The liquid-phase fluoride concentration was measured by taking 15 mL of distilled water, 20 mL of sample and 3ml total ionic strength adjustment buffer (TISAB) in a 100-mL volumetric flask,

and the mixture was stirred uniformly using magnetic stirrer. The same amount of sample was used throughout the experiment. Then Potential was measured in mV of the Fluoride ISE.



**Figure 4: Calibration line for determination of F-**

### 3.7. Experiments for Adsorption Isotherms

The adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. The purpose of an adsorption isotherm is to relate the adsorbate concentration in the bulk solution to the amount adsorbed at the solid/solution interface (Subasri *et al.*, 2015). The adsorption isotherms were analyzed using the Langmuir and Freundlich isotherm models. To study the adsorption isotherms the optimum conditions which were found from previous optimization experiments was applied only by varying adsorbent dose. Data for plotting isotherm were obtained by mixing a constant fluoride and chromium ion concentration of 2-8 mg/L and 0.5-8 mg/L respectively with adsorbent dosages of 5 g/L. The mixture was agitated at optimum time to ensure the equilibrium, and residual fluoride and chromium were determined after filtration.

Based on the data generated, adsorption isotherms were plotted. Regression methods are generally used to determine the coefficients of the isotherm equations.

### **3.8. Experiments for Adsorption Kinetics**

Kinetic models were used to investigate the controlling mechanism of sorption process such as chemical reaction, diffusion control and mass transfer (Meena Soni *et al.*, 2012). It is very important to know the rate at which the process takes place and the factors that control the rate of the process, for this purpose kinetics of the process was evaluated.

These experiments were conducted for the optimum contact time by setting chromium and fluoride concentration of 2 mg/L and 6 mg/L, pH of 4 for Cr and pH of 2 for F<sup>-</sup>, adsorbent dosage of 5g/L and agitation speed constant. Then samples were withdrawn in every 30 minute interval in the time frame of 60 to 150 minutes for determination of residual chromium and fluoride concentration in the solution. Then data from the experiment was introduced into pseudo-first order models and pseudo-second order models

### **3.9. Data Analyses**

Batch adsorption experiment and the analysis of variables were presented using tables, and graphs. Microsoft excel was used for data analysis.

### **3.10. Data Quality Assurance**

The quality of data is very important for the validity of the adsorption experiment. For this reason, preliminary test was carried out on the adsorbent to identify the adsorption performance of the adsorbents ratio used for adsorption study.

In waste water sampling, every attempt was made to minimize changes in the chemistry of the samples. To assist in maintaining the natural chemistry of the samples, preservation methods such as pH control, refrigeration and protecting from light was performed. Sampling Equipments were cleaned before sampling and at the end of sampling, sampling equipment labeled referring to the sampling point and date of sampling. Deionized water is used for rinsing and solution preparation.

Before starting adsorbent preparation and sludge collection the liquid Alum water treated sludge which leaves the treatment plant in each batch was checked for its pH value whether it was valuable for adsorption process or not by referring different literatures. The sludge sampling

equipment (Plastic Bucket) was cleaned properly using detergent and Sulphuric acid then rinsed with deionized water. After adsorbent preparation the adsorbents were put in tightly closed plastic bag for further analysis at room temperature, in a place which was free from any contamination

Accuracy and precision of methods used in the analysis of samples, including measurements. Quality control and quality assurance procedures used to ensure the validity of the result. For example, use of blank samples, record keeping and data validation

## 4. RESULT AND DISSCUSION

### 4.1. Characterization

#### 4.1.1 Physical characteristics

The prepared adsorbent was characterized for basic physical parameters using tije following procedures. Table 3 shows the pH, moisture content, ash content, Volatile matter, Bulk density, Particle density and the porosity value of alum sludge.

**Table 3:** Physical characteristics of the dry alum sludge

Contents	Value
pH	7.6
Moisture Content (%)	5.54 ± 0.5
Ash Value (%)	78.71 ± 0.3
Volatile Matter	13.29 ± 0.01
Bulk Density (g/cm <sup>3</sup> )	0.64 ± 0.1
Particle Density (g/cm <sup>3</sup> )	2.17 ± 0.1
Porosity (%)	70.55 ± 0.1

#### pH

As shown on table 3, the Al-WTS has a residual pH of 7.6, compared with pH range of 5.1–8.0 for water treatment residuals reported by Dayton and Basta, 2001. The main concern about pH effect is on Aluminum toxicity due to the quantity of Aluminum present in Al-WTS. However, given the nearly neutral pH of Al-WTS, it is expected that this will pose no problem. It is well known that Aluminum speciation is highly pH dependent, with soluble species present in higher concentrations at pH levels less than 6 (Dayton *et al.*, 2001).

### **Moisture content**

Measuring the moisture content of the adsorbent is one of the important features in order to know the adsorbent quality. The above table shows that the moisture content of powder Alum sludge was found to be 5.54% in this study. This is lower as compared to other adsorbents such as activated carbon from coffee husk where the moisture content was 19% (Dessalew Berihun., 2013).

The lower the moisture content, the higher its adsorption efficiency since water molecules can have the potential effect in the pores of an adsorbent through filling the adsorbent binding site before it contact with the solution. Therefore, adsorption efficiency decreased with an increase in moisture content of an adsorbent (Silgado *et al.*, 2014).

### **Ash value**

Ash is defined as the quantity of mineral matter which, after application of the described working methods, remains as incombustible of tested substance (Cauvain and Young., 2009). It can influence the adsorptive capacity of the adsorbents as it is linked directly to the pore structure even if the effect is negative (Anisuzzaman *et al.*, 2015). In this study the Ash value of Alum Sludge was 78.87% which was less than compared with a study for Characterization of WTS conducted by; Ahmad and Alam., 2015

### **Bulk density**

In order to design an adsorption treatment pilot plant or tower systems some physical parameters of the adsorbent should be taken into consideration such as particle size and bulk density in which adsorption rate of activated carbon depends and also during wastewater treatment process the residence time of the wastewater in the column containing granular activated carbon is affected by the bulk density (Aidan *et al*, 2012). In this study it was found that the bulk density of Alum Sudge was 1.55 g/cm<sup>3</sup> and the particle density was 0.64.

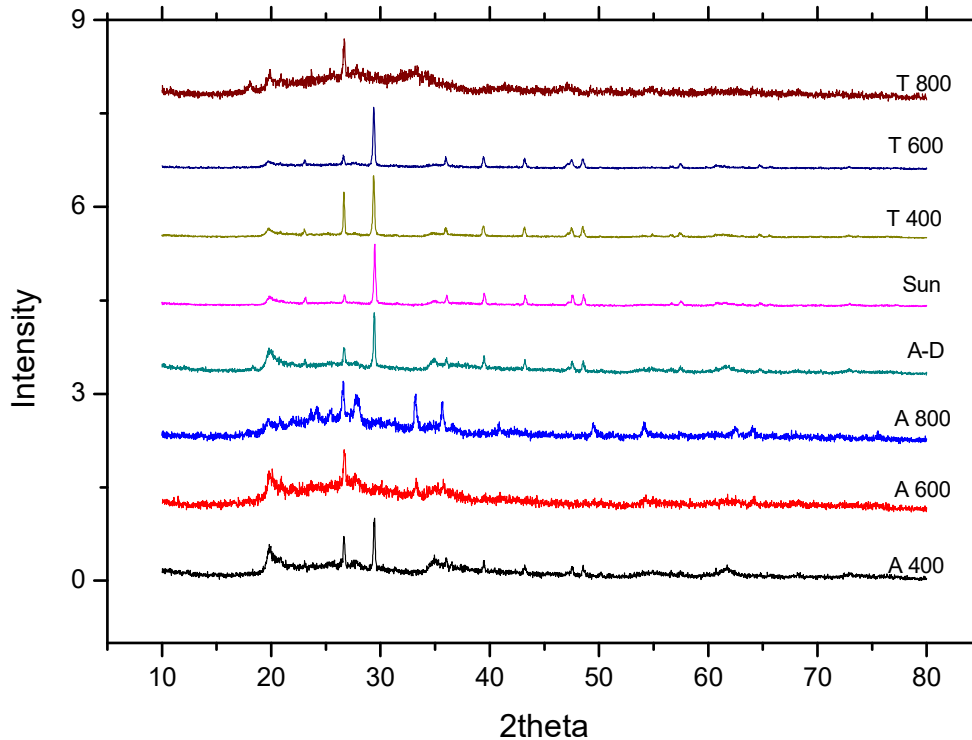
### **Porosity**

As shown on table 3, water treated Alum sludge was found to have 74.9% of porosity. According to Malik *et al.* (2006) for activated carbon there is a direct relation between porosity and adsorptive property. An increase in porosity means the adsorbent has relatively large potential of adsorbing the adsorbate.

#### 4.1.2. Results for Crystalline structure of Adsorbents

The XRD patterns of SAl-WTS (Sun), HAl-WTS (A-D), TAl-WTS at 400°C (T 400), 600°C (T 600) and 800°C (T 800°C) and HTAl-WTS at 400°C (A 400), 600°C (A 600) and 800°C (A 800°C) are shown in Figure 2. The patterns reveal that the A 400, A-D, Sun dried and T 400 sludges have well-defined crystalline structures as indicated by the presence of sharp peaks. The similarity of the XRD patterns of those alum water treated sludge indicates that treating of sludge with Hydrochloric acid and at that particular temperature does not significantly disrupt the structure of the sludge. These sludges have also similar XRD patterns and peaks with original Alum which was reported by Yang and Dayong., 2018.

The acid digested sample contains predominantly sharp peaks at 19.78°, 19.9°, 20°, 25°, 25°.62°, 26.72°, 35.72° and 43.28° whereas the sun dried sample contains 20.02°, 20.32°, 29.44°, 29.46°, 29.48°, and 39.52°. Thermally treated sample at 400 °C contains also at 19.72°, 19.78°, 20.44°, 25.58°, 26.6°, and 35.98° and 39.4°. The acid digested and thermally treated sample at 400 °C contains sharp peaks at 20.14°, 20.18°, 20.3°, 25.46°, 26.7°, 34.66° and 39.44°. Predominant sharp peaks are observed for acid digested and sun dried samples .The observation in the XRD pattern helps to identify the potential adsorbent among the different treatments for further adsorption studies.

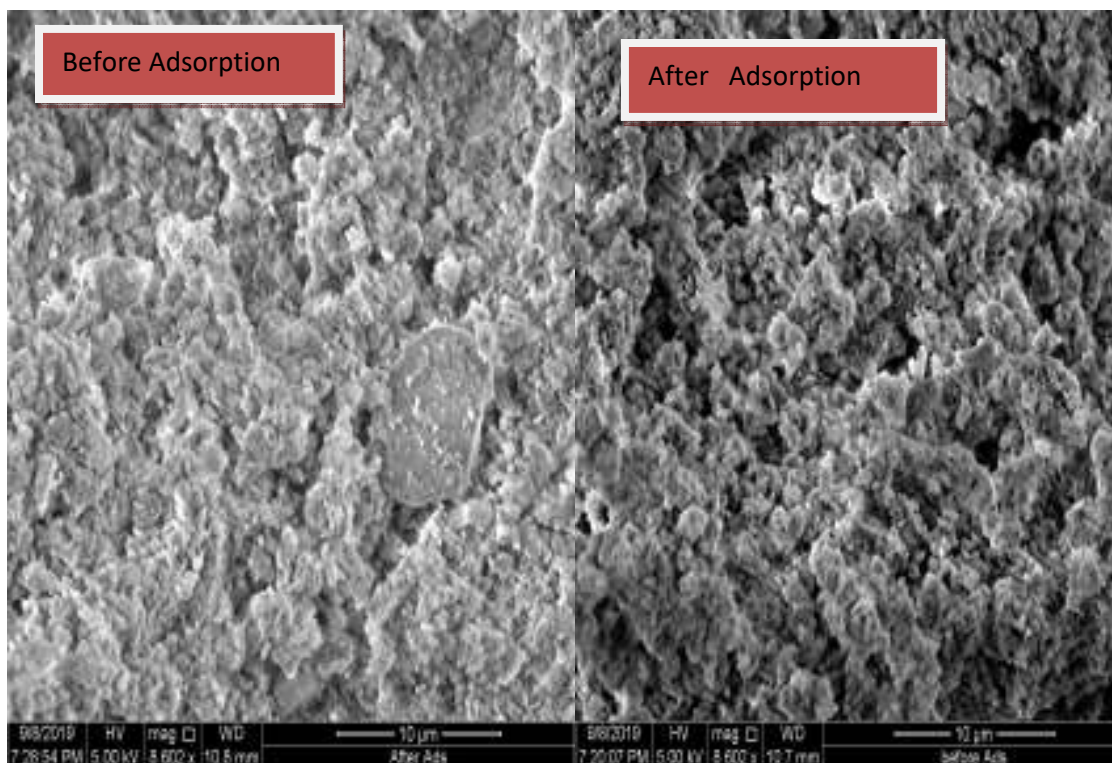


**Figure 5** The XRD patterns of differently treated Alum water treated sludge; Sun dried alum water treated sludge (SAI-WTS), Hydrochloric acid digested alum water treated sludge (HAI-WTS), thermally treated (TAI-WTS), and Hydrochloric acid digestion followed by thermal treatment (HTAI-WTS)

#### 4.1.3. Result for Morphological analysis

The SEM images of water treatment Alum Sludge before and after adsorption are shown in Figure 6. The SEM observation was done after and before the adsorption process. The observed SEM micrograph of the sample is prepared by treating the sun dried samples by hydrochloric acid which is the best adsorbent among the treated sludges before and after adsorption process. Figure 6 also shows that there is no morphological change after adsorption. The SEM image shows that both samples have similar surface morphology which was heterogeneous mixtures with irregular packed of flake like particles shape. Similar observations have been reported by Fungaro and Silva (Fungaro et al., 2014).

The micrographs also clearly show that the surface of the both sludges before and after adsorption were rough and porous, therefore they are good candidates as adsorbents.



**Figure 6: SEM image of HAI-WTS before and after adsorption**

## **4.2. Adsorption Studies**

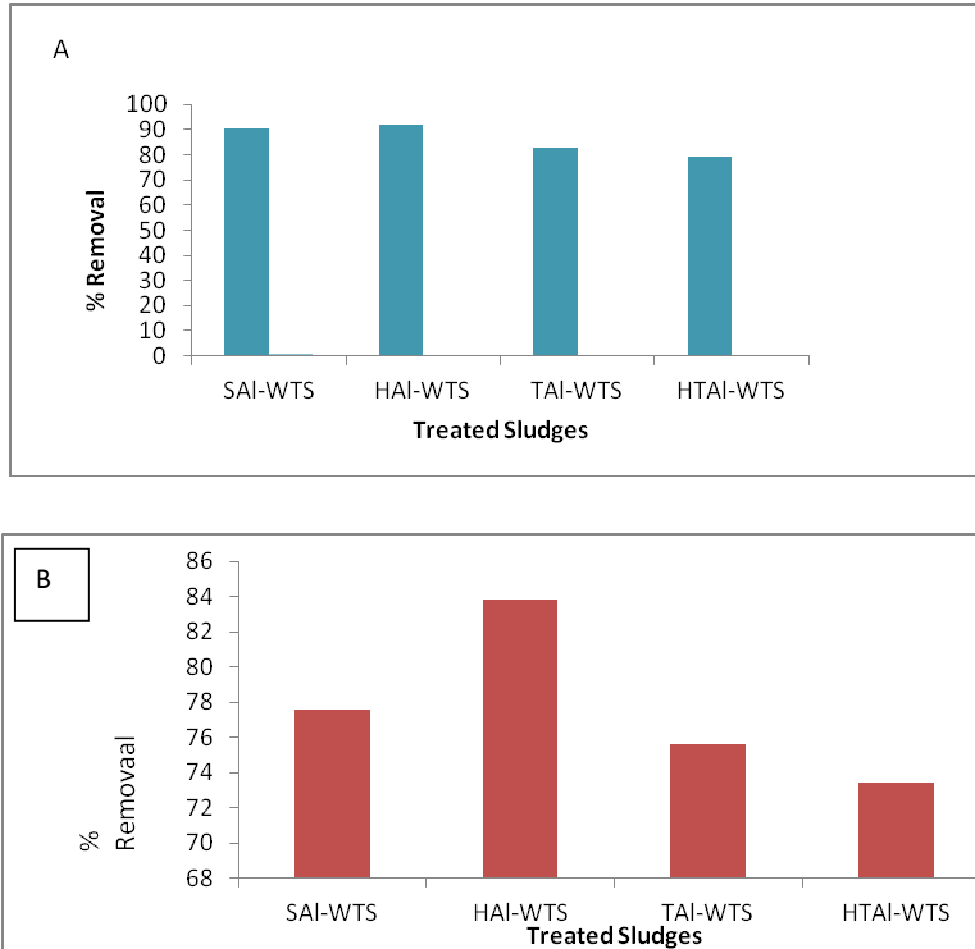
### **4.2.1. Optimization Response**

#### **4.2.1.1 Effects of treated Sludge on fluoride removal**

Effects of differently treated sludge on the removal of Fluoride and Chromium were shown in Figure 7A and 7B, respectively. As shown in Fig.7, the removal efficiency of the adsorbent were in the order of HAI-WTS > SAI-WTS > TAI-WTS >HTAI-WTS.92%, 90%, 83%, and 79.5%, for HAI-WTS,SAI-WTS,TAI-WTS and HTAI-WTS respectively for fluoride removal. The highest removal efficiency of fluoride (92%) was obtained using acid digested water treated alum sludge.

Chromium removal experiment results that the removal efficiency of the sludges were 83.802%, 77.586%, 75.588%, and 73.442% for HAI-WTS, SAI-WTS, TAI-WTS and HTAI-WTS respectively. The highest removal efficiency of Chromium (83.802%) was obtained using acid digested water treated alum sludge.

For both contaminant adsorption process the acid digested sludge had high removal capacity than others. This indicates that acid digestion can improve the SAI-WTS removal efficiency; while thermal treatment decreases the efficiency of adsorption.



**Figure 7:** A) Fluoride removal efficiency of differently treated Alum water treated sludge; B) Chromium removal efficiency of differently treated Alum water treated sludge;

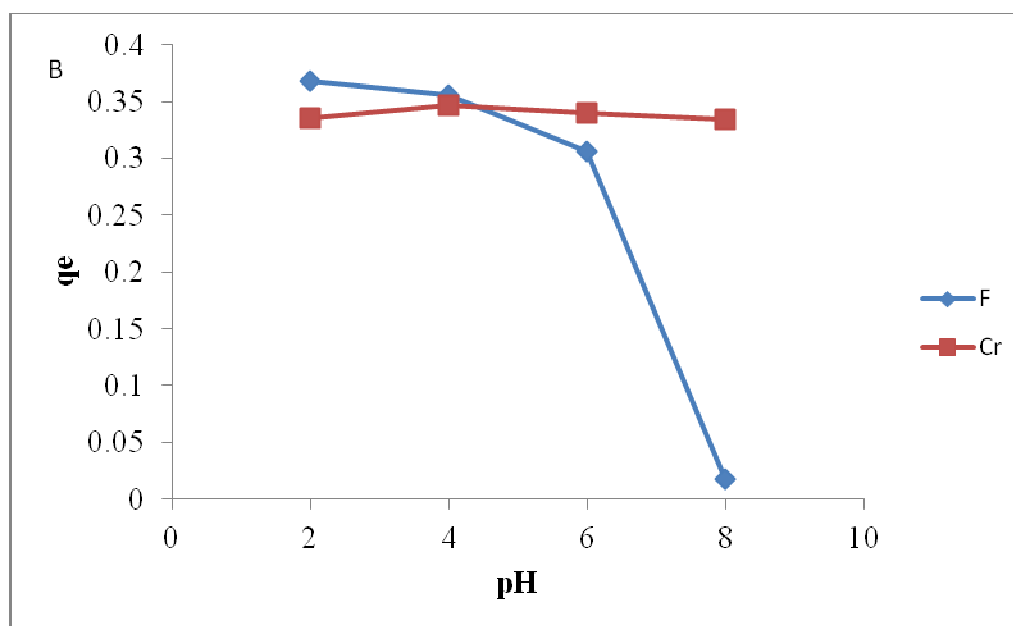
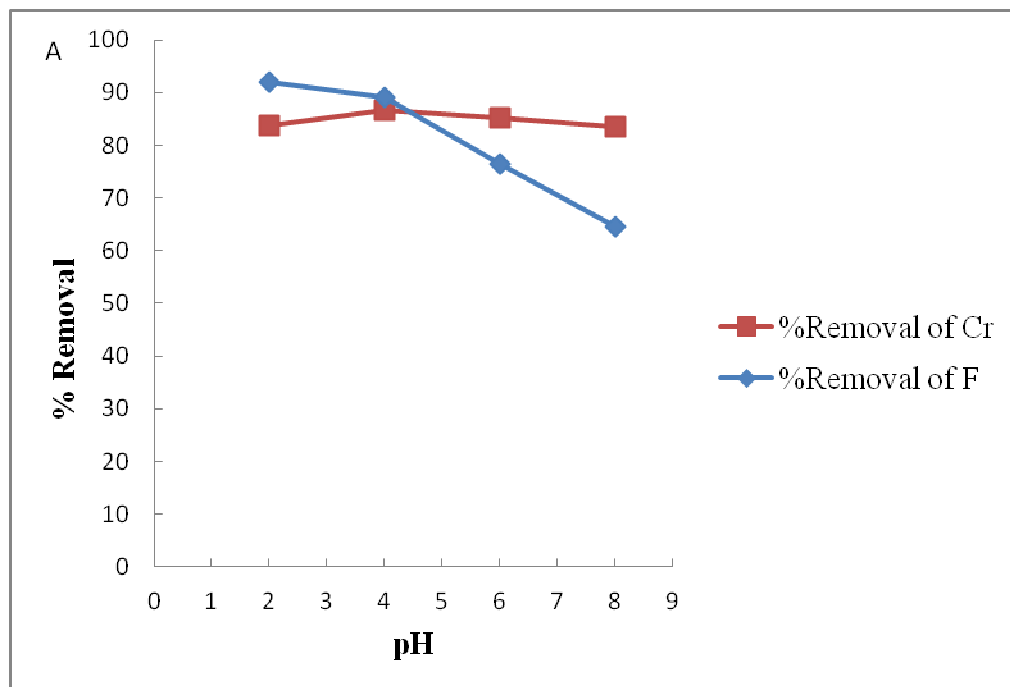
#### 4.2.1.2 Effects of pH

The pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecules. This can be most probably due to its influence on the surface properties of the adsorbent and ionization or dissociation of the adsorbate molecule (Santhi and Smitha., 2010).

The effect of pH on the removal of Cr (VI) and Fluoride ion was studied by changing pH values in the range, 2 to 8. From the adsorption study acidic pH was favorable for both ions adsorption by the adsorbent.

This is due to the fact that low pH value leads to an increase in  $H^+$  ion concentration in the system and the surface of Adsorbent may acquires positive charge by absorbing  $H^+$  ions. As the sludge is positively charged at low pH value, a strong electrostatic attraction appears between the negatively charged anionic adsorbate and the sludge leads to maximum adsorption of the contaminants. On the other hand, increase in pH value led to increase in the number of negatively charged sites on the adsorbent. The negatively charged surface on Alum sludge doesn't favor the sorption of anionic ions due to electrostatic repulsion appears between the negatively charged anionic molecules and the adsorbent surface leads to minimum adsorption of the contaminant. Based on the result high removal efficiency of 86.614% was achieved at pH 4.0 for Cr (IV) and 92% at pH 2 for Fluoride ion.

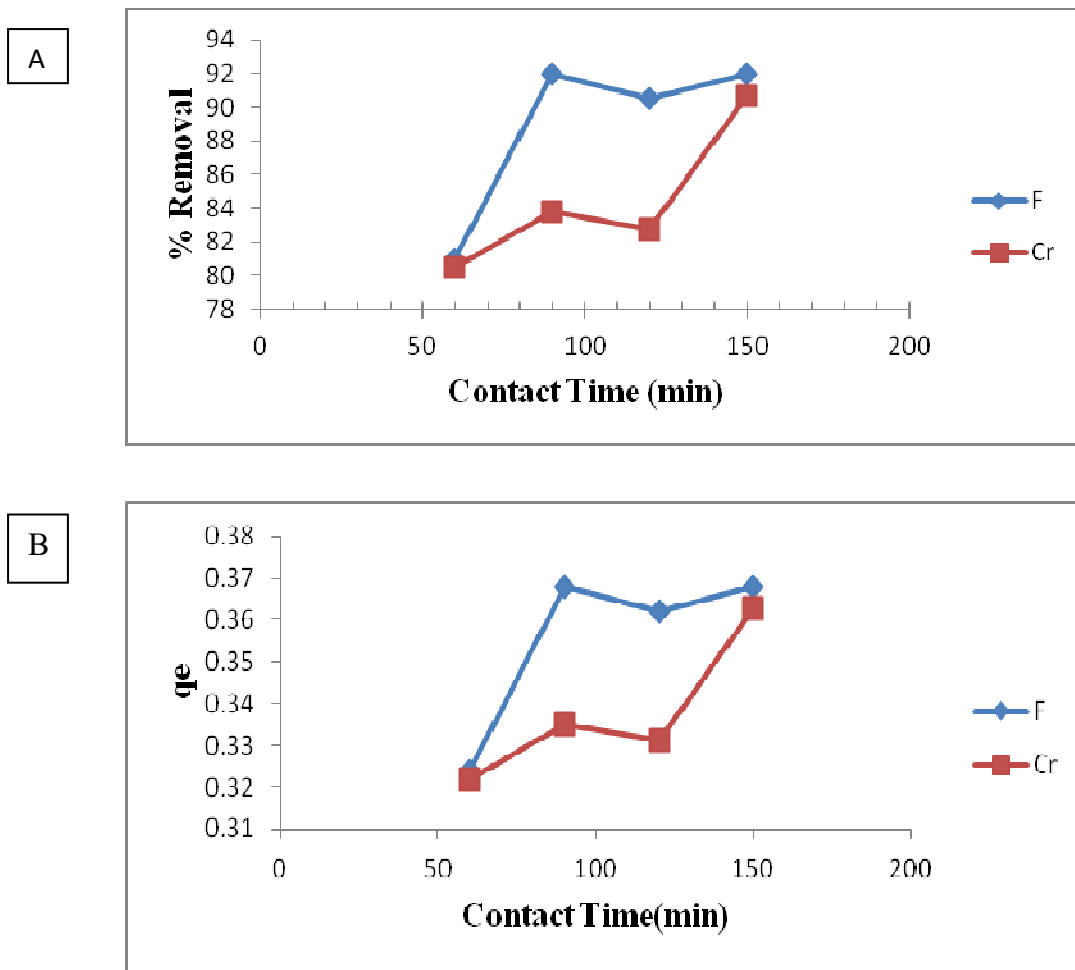
The stability of Cr (VI) is dependent on the pH of the system. Cr (VI) in aqueous solution can present in different ionic forms, which are closely related to the pH of the solution. It was determined that at pH 4, removal efficiency increases. This is due to the Cr (VI) found in aqueous solution in  $HCrO_4^-$  form. Increasing the pH will shift the concentration of  $HCrO_4^-$  to other forms,  $Cr_2O_4^{2-}$  and  $Cr_2O_7^{2-}$ . The maximum percent removal of Cr (VI) was obtained at pH 4. Maximum adsorption at pH 4.0 indicates that it is the  $HCrO_4^-$  form of Cr (VI) which is the predominant species and adsorbed preferentially on Al-WTS (Cimino *et al.*, 2000). Figure 8 is evident that, percentage removal of the fluoride significantly decreased from 92 % to 49.5% as the solution initial pH increases from 2.0 to 8.so pH value of contaminants influence the adsorption process.



**Figure 8:** Effects of initial pH on F and Cr (VI) adsorption onto Hal-WTS (A) Removal efficiency (%) (B) Adsorbent capacity (mg/g).

#### 4.2.1.3 Effects of Contact Time

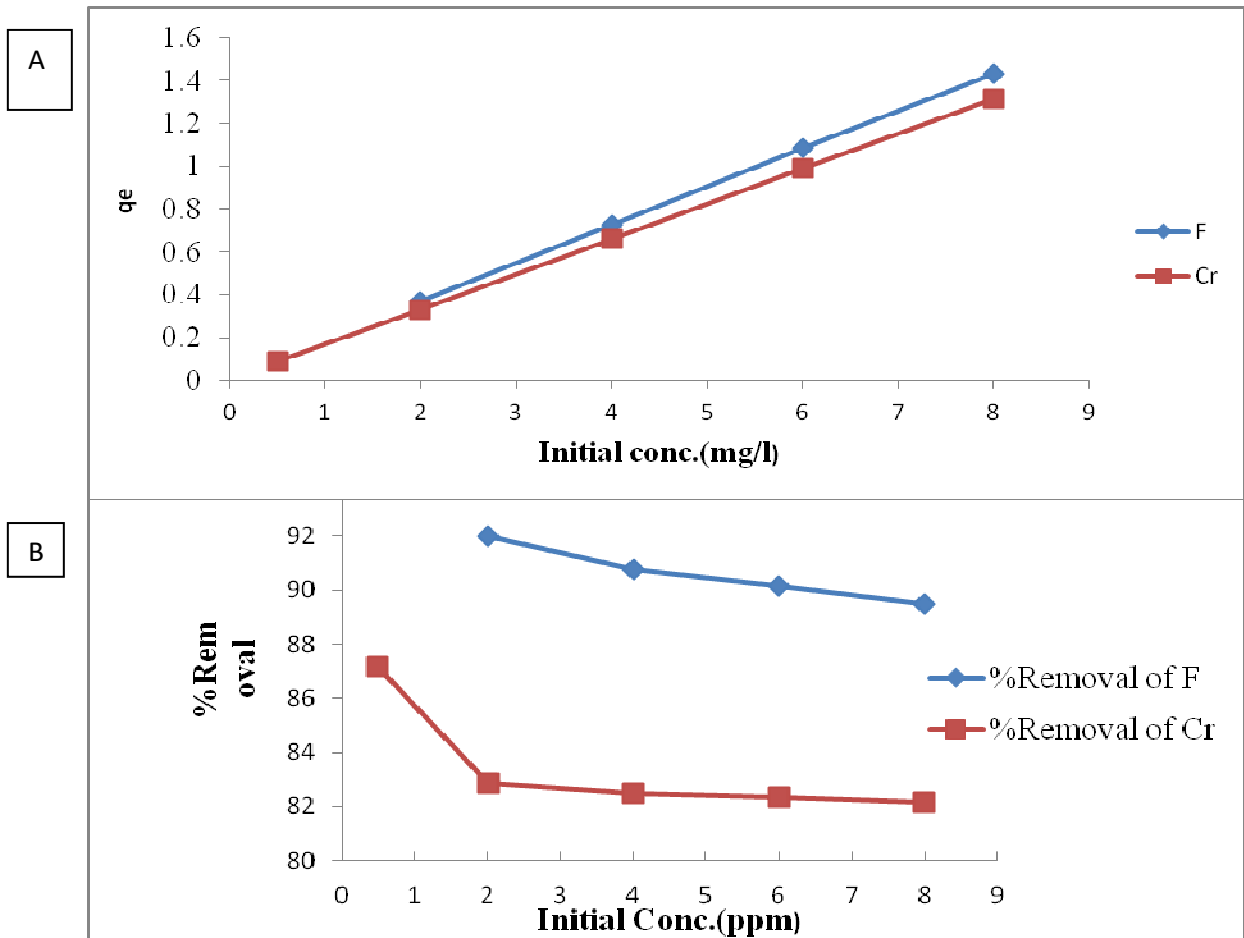
To see the effect of contact time on adsorption efficiency and to find the optimum contact time between the adsorbate and adsorbent the experiment was conducted in the time range of 60-150 minutes with 30 minute interval. From the analysis contact time had no significant effect on the adsorption process. Higher removal efficiency for Fluoride was found at 90 min and 120 min. so for the optimum value 90 minute is preferred since it is economical. For Cr (VI), removal high efficiency was at 150 minute contact time, it has 90.86% removal efficiency.



**Figure 9:** Effects of contact time on F and Cr (VI) adsorption onto HAl-WTS (A) Removal efficiency (%) (B) Adsorbent capacity (mg/g) [At initial concentration 2mg/L, adsorbent dose 5g/L and pH 2]

#### 4.2.1.4. Effect of initial Concentration

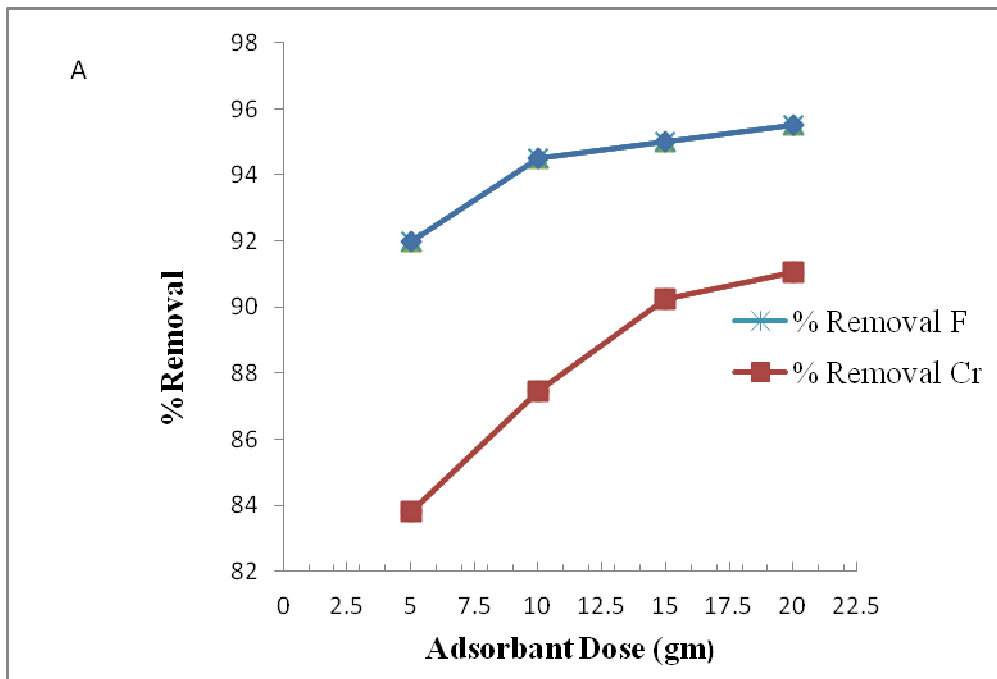
Effect of concentration was studied by varying the Cr (VI) concentration from 0.5-8mg/L and for Fluoride from 2-8mg/L. The percentage removal decreases with increasing initial concentration; this is due to the fact that the adsorbent has a definite capacity and can adsorb only a maximum specific amount. Therefore additional adsorbate does not get adsorbed and hence the percentage removal decreases (Farnam *et al.*, 2015). Changing concentration from 0.5mg/L to 8mg/L of Cr (VI) can decrease removal percentage from 87.156 to 82.137%. Changing concentration from 2- 8 mg/L decrease the removal efficiency from 92 to 89.5%. Adsorbent capacity of the sludge increases with increasing initial concentration of contaminants.

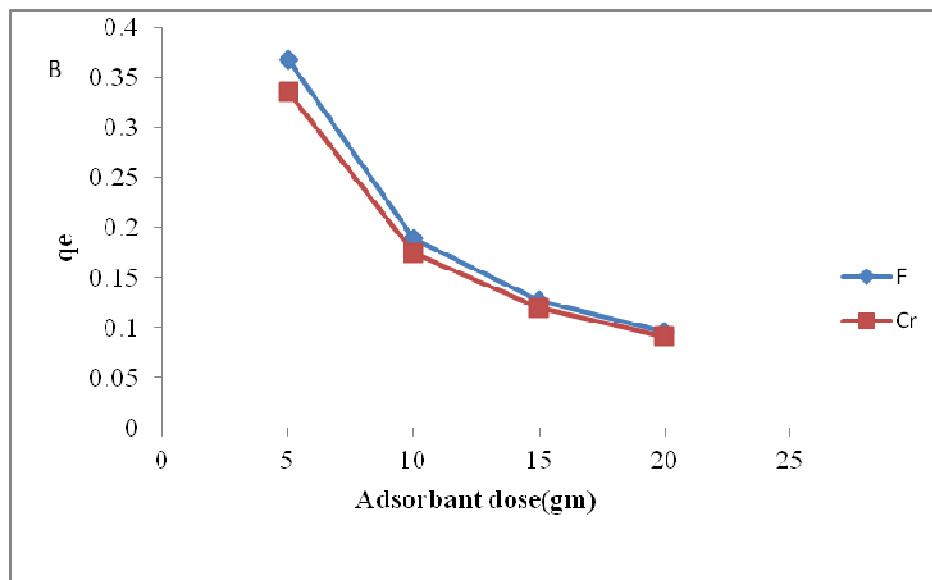


**Figure10:** Effects of initial contaminant concentration on F and Cr (VI) adsorption onto HAL-WTS (A) Removal efficiency (%) (B) Adsorbent capacity (mg/g) [At pH 2 for F and pH 4 for Cr(VI),dose 5g/L and contact time 90 min for F and 150 min for Cr (vi)]

#### 4.2.1.5. Adsorbent dose

Adsorbent dosage is an important parameter, because this determines the capacity of an adsorbent for a given initial concentration, separation cost and consequently the overall water treatment cost (Ouazene and Sahmoune., 2010). The effect of adsorbent dose on chrome and fluoride removal was studied by varying adsorbent dose from 5 to 20g and it was seen that removal efficiency increases with increasing adsorbent dose. The change in adsorbent dose from 5g to 20g can increase removal from 92% to 95.5% for Fluoride removal and 83.802% to 91.0392% for chromium removal by keeping other factors at the center. This trend was due to increase in surface area and adsorption sites available for adsorption. As shown in figure 12, the adsorption capacity of adsorbents was found to decrease with increasing adsorbent dosage as the number of adsorption sites per unit mass decreases





**Figure 11:** Effects of adsorbent dose on F and Cr (VI) adsorption HAl-WTS (A) Removal efficiency (%) (B) Adsorbent capacity (mg/g)[At pH 2 for F and pH 4 for Cr (VI), initial conc.2mg/L for both and contact time 90 min for F and 150 min for Cr (VI)]

#### 4.2.2. Adsorption isotherm results

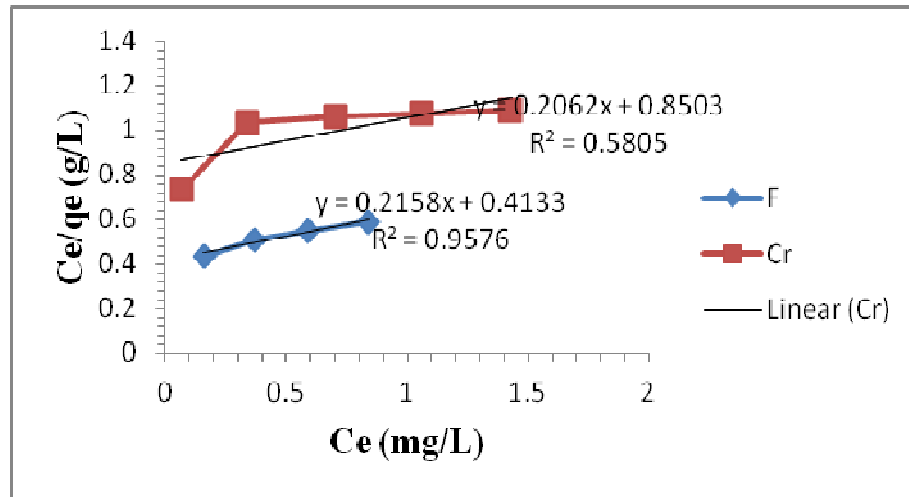
The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Adsorption isotherm is important from both a theoretical and a practical point of view. In order to optimize the design of an adsorption system to remove the contaminant, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental adsorption data. These data provide information about the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the system concentrations (Said and Mansour., 2012).

The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich isotherm (Seeds and Sepehr., 2011). These two most common isotherm equations have been tested in the present study to analyze equilibrium data of solute between adsorbent and adsorbate. The parameters obtained from these different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

## Langmuir Isotherm model

The Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface (Langmuir *et al*, 1916). The experimental data were analyzed according to the linear form of the Langmuir isotherm equation 1. The linear plots of  $C_e/q_e$  versus  $C_e$  suggest that Langmuir isotherms for the removal of Fluoride and hexavalent Chromium onto alum based AWS was not applicable. The values of  $q_m$  and  $k_L$  of linear expression of Langmuir adsorption isotherm was calculated from the slopes and intercept of the linear plot of  $C_e/q_e$  versus  $C_e$  and shown in Figure.12.

The inadequacy of the linear form of Langmuir isotherm model to H AL-AWS was also proved by the low correlation coefficients  $R^2 = 0.957$  for  $F^-$  and  $R^2 = 0.580$  for Cr (VI), which are very low compared to the correlation factor of Freundlich isotherm model figure 13. This suggests that the Langmuir isotherm was not a good model of the adsorption system.



**Figure 12:** Langmuir isotherm model for Fluoride and Cr(VI) adsorption on AL-AWS at constant adsorbent dose (5gm/l), pH optimum (2 for  $F^-$  and 4 for Cr(VI), contact time (90 min, for  $F^-$  and 150 for Cr(VI)) shaker speed 150 rpm, room temperature and concentration 2-8 mg/l within 2mg/l intervals.

**Table 4:** Summary table for the line fit graph of Langmuir Isotherm model

	Fluoride	Hexavalent Chromium
R <sup>2</sup>	0.957	0.580
Equation	$1/q_e = 0.215(1/c_e) + 0.413$	$1/q_e = 0.206(1/c_e) + 0.850$
K <sub>L</sub>	1.92	4.13
q <sub>max</sub>	2.42	1.176

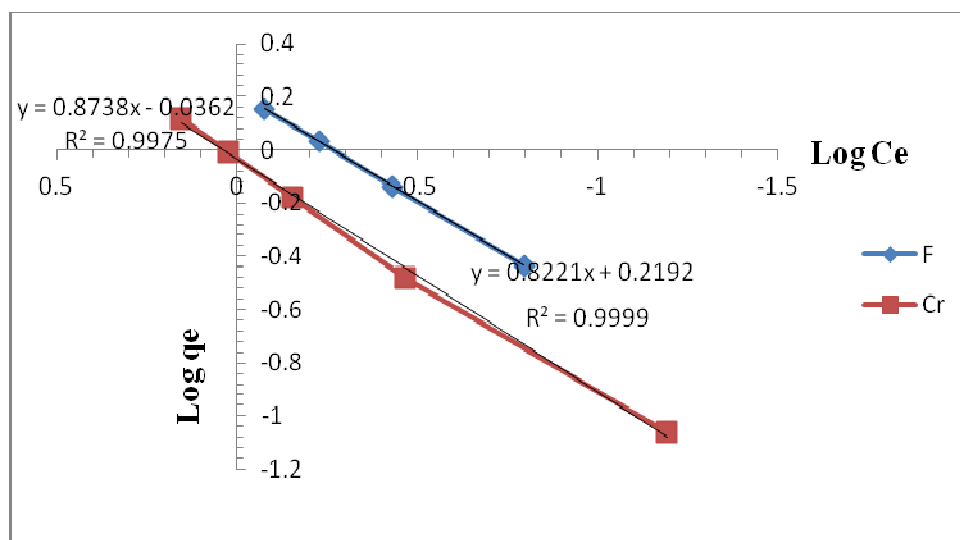
### Freundlich isotherm model

While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on adsorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites (Freundlich *et al*, 1906).

The Freundlich equation is purely empirical based on adsorption on heterogeneous surface and is commonly given by non-linear equation on equation 2. K<sub>f</sub> and 1/n can be obtained from the intercept and slope of the linear plot of log q<sub>e</sub> versus Log C<sub>e</sub>.

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data. The Freundlich plots between log q<sub>e</sub> versus log C<sub>e</sub> for the adsorption of Fluoride and hexavalent chromium are drawn in Fig.13 and Table 5. It was found that for both contaminants the correlation coefficient values R<sup>2</sup>>0.99. This suggests that the Freundlich isotherm provides a good model of the F and Cr (VI) adsorption system.

K<sub>f</sub> and 1/n were 1.656 and 0.822 for Fluoride and 0.920 and 0.873 for Hexavalent Chromium, respectively. The slope ranges between 0 and 1 and it is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below 1 implies chemisorptions process where 1/n above 1 is an indicative of cooperative adsorption.



**Figure 13:** Freundlich isotherm model for Fluoride and Cr(VI) adsorption on HAL-AWS at constant adsorbent dose (5gm/l), pH optimum (2 for F<sup>-</sup> and 4 for Cr(VI)), contact time (90 min, for F<sup>-</sup> and 150 for Cr(VI)) shaker speed 150 rpm, room temperature and concentration 2-8 mg/l within 2mg/l intervals.

**Table 5:** Summary table for the line fit graph of Freundlich Isotherm model

	Fluoride	Hexavalent Chromium
R <sup>2</sup>	0.999	0.997
Equation	Log qe=0.822Logc <sub>e</sub> +0.219	Log qe=0.873Logc <sub>e</sub> -0.036
1/n	0.822	0.873
K <sub>f</sub>	1.656	0.920

#### 4.2.3. Adsorption kinetics Result

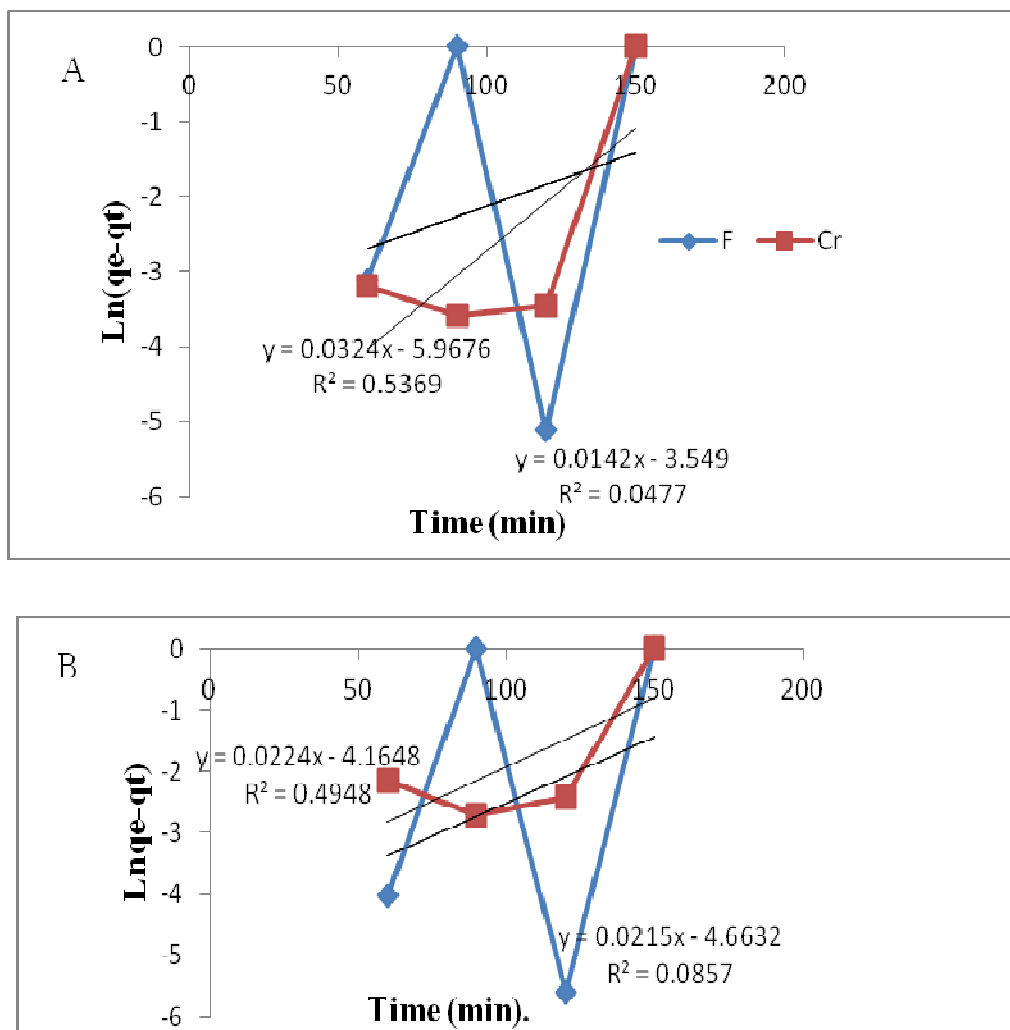
Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes (Santhi and Smitha., 2010) Thus, the kinetics of Fluoride and Hexavalent chromium adsorption onto Al-AWTS was analyzed using pseudo-first-order and pseudo-second-order kinetic models.

The kinetic study was done using two different initial concentrations, 2 mg/l and 6 mg/l. The conformity between experimental data and the model-predicted values was expressed by the

correlation coefficients. The relative higher value is the more applicable model to the kinetic study.

### Pseudo-first order kinetics

The pseudo-first-order rate expression based on solid capacity is generally expressed on section 2.2.8, equation 3-5. In order to obtain the rate constants, the values of  $\ln(q_e - q_t)$  were linearly correlated with  $t$  from which predicted  $q_e$  from the slope and intercept of the plot, respectively and the results were presented as in Figure 13.



**Figure 14:** Pseudo 1<sup>st</sup> order kinetics (a) at 2 mg/l for all (b) at 6 mg/l for all adsorbent

The sorption kinetics of Cr and F removal using AL-AWTS (Figure 14) was not predicted by pseudo-first order kinetics model because the correlation factor was very low and also, calculated

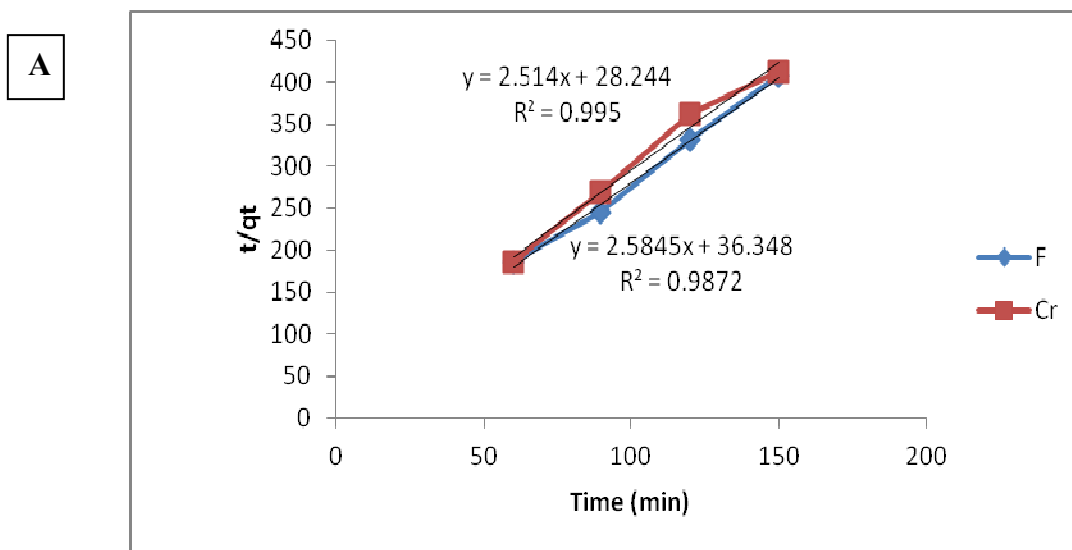
and experimental metal removal were not close to each other as it can be seen from the Table 6. The rate constant and  $q_e(\text{cal})$  was calculated from the slope and intercepts of the graph  $\log(q_e - qt)$  vs. time.

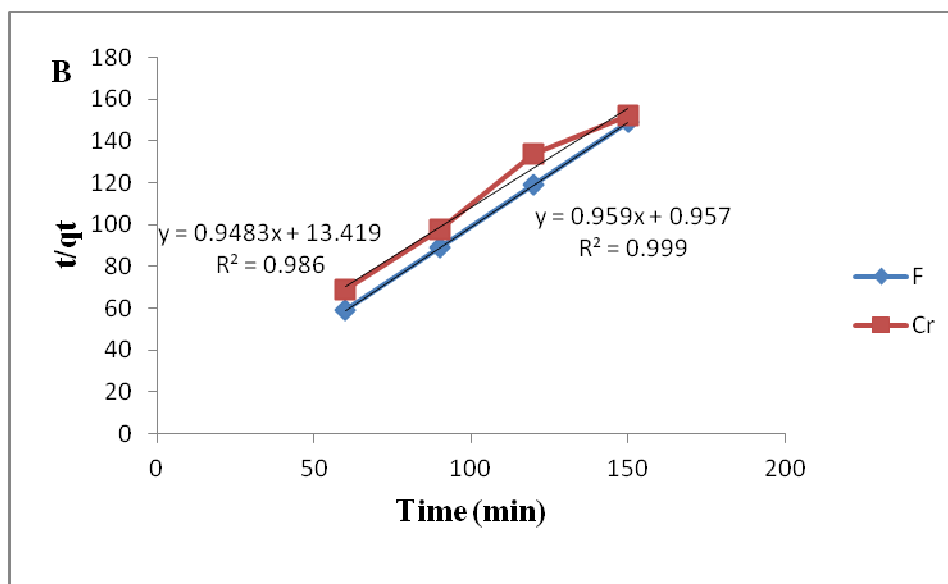
**Table 6:** Results of line fit model of pseudo - first order kinetic

Contaminant	Concentration (mg/l)	$Q_e \text{ exp}$ (mg/l)	$R^2$	K	$q_e$ (mg/l)
Fluoride	2	0.368	0.536	0.032	0.000282
	6	1.082	0.377	0.377	2.82488
Chromium	2	0.362736	0.047	0.014	1.08E-06
	6	0.988	0.494	0.494	0.383354

**Pseudo- second order kinetic model**

The data obtained from kinetic experiment was further fitted to pseudo-second order kinetic model (Figure 15). Calculated equilibrium adsorption capacity  $q_e(\text{cal})$ , pseudo-second order rate constant and the initial adsorption rate were obtained from the model. The experimental equilibrium adsorption capacity and the calculated capacity are close to each other as can be seen from Table 7 with the  $R^2$  value of 0.9997. The rate expression was used to describe chemisorptions involving valiancy forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange.





**Figure 15** Pseudo<sup>2<sup>nd</sup></sup> order kinetics (a) 2 mg/l (b) 6 mg/l concentration.

**Table 7:** Results of line fit model of pseudo – second order kinetic.

Contaminant	Concentration (mg/l)	Qe exp (mg/l)	R <sup>2</sup>	K	qe (mg/l)
Fluoride	2	0.368	0.995	0.223	0.3977
	6	1.082	0.999	0.961	1.042
Chromium	2	0.362736	0.987	0.183	0.387
	6	0.988	0.986	7.0*10 <sup>-5</sup>	1.054

### 4.3. Treatment of Contaminated water sample

Table 8 shows the removal efficiency HAL-WTS for contaminated real water samples that were collected from Haudaochen Leather Production (Chromium contaminated water) and from deep well around Methehara (fluoride attacked water). The adsorbent removed Hexavalent Chromium ion from the chromium contaminated water with an efficiency of 69.06% while it removes fluoride ion from Fluoride attacked water 87.34%.

The contaminated water samples were first determined for their initial concentration. (Hexavalent Chromium content in 0.362ppm and Fluoride concentration 3.32ppm). Both water

samples were above permissible level. Then, the samples were treated at room temperature and shaker speed of 150 rpm with HAL-WTS using the optimized values of other parameters ( adsorbent dose 5gm/l, pH 2 for F<sup>-</sup> and 4 for Cr(VI), contact time 90 min,for F<sup>-</sup> and 150 for Cr(VI))

HAL-WTS effectively removed the contaminants as it can be seen on Table 8. But the percentage removal of real water samples were low compared to standard solutions (used for optimization process).This is because of the real water samples have different ions which may affect the adsorption of the adsorbent.

**Table 8:** Real contaminant water samples data

Contaminated water samples	Contaminant Concentration Before Adsorption (ppm)	Adsorbant(HAL-WTS) dose(gm/L)	pH	Contact Hr(min)	Concentration after adsorption (ppm)	% Removal
Fluoride attacked water	3.32	5	2	90	0.42	87.34
Chromium attacked water	0.362	5	4	150	0.112	69.06

## 5. CONCLUSION AND RECOMMENDATION

### 5.1. Conclusion

The study examined removal of Fluoride and Hexavalent Chromium ions from fluoride attacked Well water and chromium rich tannery waste water by using low cost, environmental friendly and locally available prepared adsorbent, Alum sludge from water treatment plant. To enhance the adsorption ability of the raw sludge, it was activated using hydrochloric acid digestion, thermal treatment (at 400, 600 and 800°C) and hydrochloric acid digestion followed by thermal treatment (at 400, 600 and 800°C). XRD analysis of the differently treated Al-WTS indicates that the SAl-WTS, HAl-WTS, TAl-WTS (400°C) and HTAl-WTS (at 400°C) had well defined crystalline structure and appearance of sharp peaks. But, predominant sharp peaks were observed for acid digested sample and also during adsorption study; it has gained best efficiency 92% and 83.802% among other activated Al-WTS for removing fluoride and chromium ions from contaminants.

Different experimental conditions such as contact time, pH, initial adsorbate concentration and adsorbent dose; to get optimum values of the mentioned parameters for the adsorption process were investigated. It was shown that the change in those parameters affect the adsorption process. The differential parameters of the process such as, pH, dose of adsorbent and equilibrium time were optimized at 2, 20 gm/l and 90 min, for fluoride and 4, 20gm/l and 150 min for chromium respectively. The adsorption of the ions was heavily dependent on these parameters of the waste water. Fluoride removal efficiency of HAl-WTS was 95.5% and chromium removal of 91.04% was achieved at optimum studied condition. The data from kinetic experiments was found to fit well with pseudo-second order kinetic model with high  $R^2$  value of 0.9997 than pseudo-first order kinetic model which indicates the presence of chemisorption. Adsorption process of this research is well described by Freundlich model than the Langmuir model. Batch adsorption studies were used for the experimental optimization analysis, equilibrium and kinetic study using standard reagents. Potassium dichromate ( $K_2Cr_2O_7$ ) and sodium fluoride (NaF) standard solution were used as the source for chromium and fluoride working solution respectively for experimental study.

Chromium and fluoride contaminated water samples that were collected from tannery chromium rich waste water and fluoride attacked well water were treated using HAL-WTS with optimized parameters. The adsorbent removed Hexavalent Chromium ion from the chromium contaminated water with an efficiency of 69.06% while it removes fluoride ion from Fluoride attacked water 87.34%. SEM analysis for HAL-WTS micrographs before and after the adsorption process shows that both have similar surface morphology which was rough, porous and heterogeneous mixtures with irregular packed of flake like particles shape. These and the above results indicate that acid treated alum based water treatment sludge can be used for the removal of chromium and fluoride from wastewater.

## **5.2. Recommendation**

From the result of the study the following recommendation has been forwarded. As a byproduct of water treatment plant, AL-WTS is low cost, environmental friendly and easily available resource to be used as an adsorbent for chromium and fluoride removal from wastewater and it should not be simply discarded to the environment.

Further studies should be carried out to enhance the adsorption ability of Al-WTS treating with different types cost effective acids. From the experimental result and different literatures, WTS has shown high affinity for anions. So other researches should also be conducted to evaluate the applicability of Al-WTS for different ions sorption from industrial wastewater too.

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## Appendix

### Appendix1. Picture of instruments used for the research work



Vacuum pump

SEM

Uv-Vis spectrometer

FISE

### Appendix 2. Picture of Chromium attacked Tannery water before adsorption



### Appendix 3. Steps for adsorbent preparation



Settling



Dewatering



Sun drying



Adsorbent



Sieving



Crushing

Sun Dried

