ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING
ENVIRONMENTAL ENGINEERING STREAM

CHROME REMOVAL FROM WASTEWATER USING WATER TREATMENT PLANT SLUDGE AS AN ADSORBENT

By,
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A Thesis submitted to Addis Ababa University, Institute of Technology, School of Chemical and Bioengineering, in partial fulfillment for the requirement of Masters Science Degree in Environmental Engineering

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Declaration

I the undersigned declare that this Thesis is my original work and has not been presented for any degree in any university and all the resource of materials used for the Thesis have been duly acknowledged

Wegene Deriba _____

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List of abbreviations

Al-WTS	Alum Based Water Treatment Sludge
BOD	Biological Oxygen Demand
CCD	Central Composite Design
COD	Chemical Oxygen Demand
DOE	Design of Expert
RSM	Response Surface Methodology
SS	Suspended Solids
SEM	Scanning Electron Microscope
TN	Total Nitrogen
TOC	Total organic carbon
TP	Total Phosphorous
TSS	Total Suspended Solid
WTS	Water Treatment Sludge

Abstract

Industries produces large amount of waste and the effluent of these wastes are often hazardous in polluting the environment and affecting human health. Tanneries are among industries which release large amount of waste which contains hazardous heavy metals such as chromium. Hexavalent chromium in the environment is often harmful and it should be treated before releasing to the environment. Chromium carcinogenicity to humans and other living organisms has promulgated extensive research on its treatment technologies with varying levels of success.

The present study deals with removal of Cr(VI) by alum based water treatment sludge (Al-WTS) through batch and fixed bed column study. Response surface methodology (RSM) was applied in batch wise experiment for designing and analysis of experiment. Cr(VI) concentration and pH increase, is shown to decrease chrome removal percent, while adsorbent dose and shaking time increase, is shown to increase chrome removal. Factor interaction terms: Cr(VI) concentration with pH shows that maximum chrome removal 95.62.1% was obtained at Cr(VI) concentration of 2.4mg/l and pH 2.45, while interaction of Cr(VI) concentration and adsorbent dose shows, 97.06% chrome removal was obtained at chrome concentration of 3.3mg/L and adsorbent dose of 6.3g. Interaction of pH and adsorbent dose also shows that maximum chrome removal 92.2 was obtained at pH 2.44 and adsorbent dose of 6.17g. Theoretical Langmuir, Freundlich isotherms are subjected to adsorption data to estimate adsorption capacity. The results gained from this study were well described by the theoretical Langmuir and maximum adsorptive capacity of 33.33mg/g was obtained.

The removal of Cr(VI) by Al-WTS was also investigated in a fixed bed column study. Experiments were conducted to study the effect of bed depth (10–30cm), flowrate (5–15mL/min) and initial concentration (10-30mg/L). The column data was fitted by BDST, Thomas and Yoon-Nelson models. Adsorption capacity increases with increase in initial Cr(VI) concentration and bed depth. Thomas model well fits the experiment and gives high adsorptive capacity of 14.8mg/L. Al-WTS was used for the Cr(VI) removal from tannery wastewater in fixed bed column study and showed a high potential for the wastewater treatment.

Key words: ***Alum based water treatment sludge, batch adsorption, response surface methodology, Cr(VI), fixed bed column***

1. Introduction

1.1 Background

Growing awareness of the risks posed by heavy metals in the environment has recently been driving the search for sustainable technologies for treatment of contaminated sites. Soils, groundwater, sediments and rivers at many locations have been exposed to intense pollution from industrial activities. Whilst the industry has improved practices over time, the accumulated pollutants persist in the affected areas, posing local and peripheral environmental risks. The redistribution of heavy metals can adversely affect water resources and endanger the health of surrounding ecosystems and human populations. So, cost effective and ecological remediation of these sites is essential. The application of sorbents with high affinity for heavy metals, and in particular those derived from low cost waste materials, is a promising and attractive remediation route (Chiang, Santos et al. 2012).

The pressure to adopt cleaner technologies normally emanates from environmental imperatives such as the need to meet specific discharge norms, reduce treatment costs or comply with occupational safety and health standards. The typical primary targets are: lower water consumption, improved uptake of chemicals, better quality/re-usability of solid waste, and reduced content of specific pollutants such as heavy metals and electrolytes. The spread of cleaner technologies and processes has been neither spontaneous nor extensive. For all the claims about favorable cost-benefit ratios or environmental benefits to be derived from many of these technologies, tanners are not quick in adopting them, be it due to inertia, higher costs or the limitations mentioned earlier (UNEP).

Confronted with increasing legal and social pressures, no tanner can afford the luxury of not being familiar with the main issues and principles of environmental protection pertaining to tannery operations. Obviously, pollution prevention, the persistent promotion of cleaner leather processing, which ultimately leads to lower treatment costs, remains the supreme priority. By applying industrially proven low-waste advanced methods such as the use of salt free preserved raw hides and skins, hair-save liming, low-ammonia or ammonia-free deliming and bating, advanced chrome management systems, etc., it is possible to decrease significantly the pollution load, namely: COD and BOD5 by more than 30%, sulphides by 80-90%, ammonia nitrogen by 80%, total nitrogen by 50%, chlorides by 70%, sulphates by 65%, and chromium by up to 90%. Yet, despite all preventive measures, there is still a considerable amount of pollution load to be dealt with by end-of-pipe methods (Buljan, Kral et al. 2011)

1.2 Problem statement

Rapid population growth, urbanization and industrial development have been adversely degrading the environment by their effect through loss of biodiversity and pollution from wastes.

Industrialization, like other activities that impact on the environment, often results in pollution and degradation. It carries inevitable costs and problems in terms of pollution of air, water resources and general degradation of natural environment. Industrial waste is the most common point source of water pollution in present day and it increases yearly due to the fact that industries are increasing because most countries are getting industrialized. In Ethiopia too, industries are increasing in number, turning out wastes which are peculiar in terms of type, volume and pollution strength depending on the type of industry, raw materials used and process and technological variations applied to the process (Zinabu and Zerihun 2002).

Growing attention is being directed towards environmental and health hazards caused by accumulation of heavy metals in aqueous environments. Extensive use of chromium in industries such as electroplating, steel production, wood preservation and leather tanning can result in release of chromium containing effluents to the environment. 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. By contrast, Cr(VI) is highly toxic, mutagenic and potentially carcinogenic to living organisms. Accumulation of Cr(VI) in aqueous waste streams is therefore of great concern. Chromium carcinogenicity to humans and other living organisms has promulgated extensive research on its treatment technologies with varying levels of success; generally, the most efficient methods come with a significantly higher cost burden (Kimbrough, Cohen et al. 1999).

The main strategies used to remove chrome are: (a) reduction of Cr(VI) to Cr(III) with subsequent immobilization as hydroxide, (b) membrane filtration and (c) adsorption onto various materials. A number of specialized processes have been developed for the removal of metals from waste discharges. These unit operations include: chemical precipitation, coagulation/flocculation, ion exchange/solvent extraction, cementation, complexation, electrochemical operations, biological operations, adsorption, evaporation, filtration, and membrane processes. More over tanning industries also follow one of the above industrial waste water treatment for is effluent treatment. Obviously effluent treatment cost and the technology used has its own impact on the treatment quality (Peters, Ku et al. 2008).

Aluminium based water treatment sludge (Al-WTS), commonly referred to as alum sludge is a byproduct derived from the purification processes of drinking water treatment plants when Aluminium salts are used as coagulant. It is the most widely generated drinking water treatment residual worldwide since Al-salts are the most widely used primary coagulant for water purification. Accordingly, alum sludge consists of various impurities in the raw water (e.g., colour, turbidity, hardness and varied concentrations of organics and microorganisms) and coagulant products and residues. The chemical composition of water treatment sludges gives it a highly reactive surface and a strong affinity sorption of heavy metals (Babatunde and Zhao 2007).

Al-WTS is an easily available by-product in towns, cities and metropolis regions worldwide that utilize surface waters as a drinking water source. And since Al-WTS is derived from residual of treatment of raw water which contains mainly turbidity, colour, suspended clays and humic substances, it is unlikely to contain a substantial quantity of toxic substances. More over it is a low cost material that can simply released as a byproduct from water treatment plants. Knowledge of its physicochemical characteristics and chromium adsorption capacity would be very useful for practical guidance in utilizing it as chromium adsorbent from industrial wastewater. Al-WTS can be obtained free of charge from drinking water treatment plants, and they have been successfully used to reduce soluble phosphorus, selenite, selenate, arsenite, arsenate, and perchlorate as well as the cations Pb(II), and Hg(II) (Ippolito, Barbarick et al. 2011).

1.3 Objective

1.3.1 General objective

The general objective of this study is to remove chromium from wastewater using low cost alum based water treatment plant sludge, as an adsorbent.

1.3.2 Specific objective

- ✓ To characterize locally available alum based water treatment sludge
- ✓ To evaluate chrome adsorption efficiency of alum based water treatment sludge, via batch adsorption study.
- ✓ To evaluate chrome adsorption capacity of alum based water treatment sludge through fixed bed column study.

1.4 Significance of the study

So far various wastewater treatment techniques have been used to remove heavy metals from industrial wastewater. Wastewater treatment through adsorption is one treatment technique used. Different adsorbent have been used to remove chromium from wastewater 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 water treatment sludge (WTS) for removal of chromium. WTS which is a byproduct of water treatment plants can be easily available from local water treatment plants without any charge. Knowing its chrome removal capacity and its application can be beneficial, because:

- It's a low cost adsorbent which can be easily available without charge.
- Its application in industrial wastewater treatment can be a choice and at the same time reduce its accumulation in the environment, because
- The sludge is simply discharged into the nearby environment from local water treatment plant from which sample of WTS in these study has been taken.
- Re-usability of these by product is a win-win technique too.

2. Literature review

2.1 Environmental problem associated with industrial wastewater discharge

Growing attention is being directed towards environmental and health hazards caused by accumulation of heavy metals in aqueous environment. Rapid population growth, urbanization and industrial development have been adversely degrading human environment by their effect through loss of biodiversity and pollution from wastes. Industrialization, like other activities that impact on the environment, often results in pollution and degradation. It carries inevitable costs and problems in terms of pollution of air, water resources and general degradation of the natural environment. Industrial waste is the most common point source of water pollution in the present day and it increases yearly due to the fact that industries are increasing because most countries are getting industrialized (Ogedengbe and Akinbile 2004).

Industrial effluents which discharged from textile and tannery contains a higher amount of metals especially chromium, copper and cadmium. These effluents released on the land as well as dumped into surface water which ultimately leaches to ground water and lead to contamination due to accumulation of toxic metallic components and resulted in a series of well documented problems in living things because they cannot be completely degraded. Hence, industrial effluents offer a wide scope of environmental problems and health hazards are becoming more complex and critical not only in developing countries but also in developed countries (Malarkodi, Krishnasamy et al. 2007).

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals through wastewaters are directly or indirectly discharged into the environment, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium (Fenglian and Qi 2011).

Essentially it is now recognized that direct contact with some industrial chemicals can potentially cause disability, illness (toxigenic/carcinogenic) and death in humans. Minor exposures can cause the buildup of toxic levels within humans. Solvents from degreasing and finishing are a source of exposure through vapors. Human health can also be affected by toxic hazards through the unskilled and unprotected handling of pesticides, tanning chemicals and treated hides and skins (Mwinyihija, Meharg et al. 2005).

Tanning industry as an agro based sector is by far the largest source of hazardous wastes. Previous research has related leather tanning and finishing, as one of the main industries

producing hazardous wastes and pollution (Khwaja 1998). It is unfortunate that there are no reliable estimates of the quantity and types of hazardous waste generated in most developing countries. This therefore warrants an immediate inventory on matters of waste generation and methods currently in place to manage such wastes. Approximately 10-15% of the wastes produced by industry overall are likely to be hazardous, increasing at a rate of 2-5% per year (Chaaban 2001).

Moreover, there is very little information on hazardous waste production, waste disposal and management practices in most developing countries. The major public concern over tanneries has traditionally been about odors and water pollution from untreated discharges. Important pollutants associated with the tanning industry include chlorides, tannins, chromium, sulphate and sulphides as addition to trace organic chemicals and increasing use of synthetic chemicals such as pesticides, dyes and finishing agents, as well as from the use of newer processing chemical solvents. These substances are frequently toxic and persistent, and affect both human health and the environment (Buljan, Kral et al. 2011).

It is critical to note that to-date many diverse environmental impacts of tanneries have made them subject to complex pollution control policies in many countries. For example, factory sites, lagoons, storage areas and temporary waste dumps are known to pollute the underlying soil especially so when appropriate management practices are not put in place. This impact has been recognized to debilitate structures and interrupt agro-based activities like farming and animal husbandry as well as potentially degrade ground water systems (Mwinyihija, Meharg et al. 2005). Consequently when the deposition of solids is considered, it becomes apparent that raw unsettled tannery wastewaters can cause encrustation of calcium carbonate and serious corrosion of metals as well as concrete sewers due to H_2S biological oxidation to H_2SO_4 (Balusubramanian and Pugalenthi 2000). Thus high pollutant loads, involving chromium, sulphates, chlorides etc could easily interfere with key biological processes used in sewage treatment plants.

In Ethiopia, industries are increasing in number turning out wastes which are peculiar in terms of type, volume and pollution strength depending on the type of industry, raw materials used and process and technological variations applied to the process. As compared to other industries, leather tanning is one of the most polluting activities as it consumes huge amount of water in several stages, generating an enormous sum of liquid effluents which are hazardous for the environment to which they are discharged. Tannery wastewater is highly polluted in terms of biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), Nitrogen, conductivity, sulphate, sulphide and chromium and in most developing countries tannery effluents are discharged directly into sewers or water bodies without treatment (Favazzi 2002). In Ethiopia also, industries turnout wastes directly into the nearby water bodies. This makes industrial and chemical pollution to become major problem in the country and one of the great environmental concerns (Zinabu and Zerihun 2002).

2.2 Chromium in aqueous environment

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 and Terry 2003).

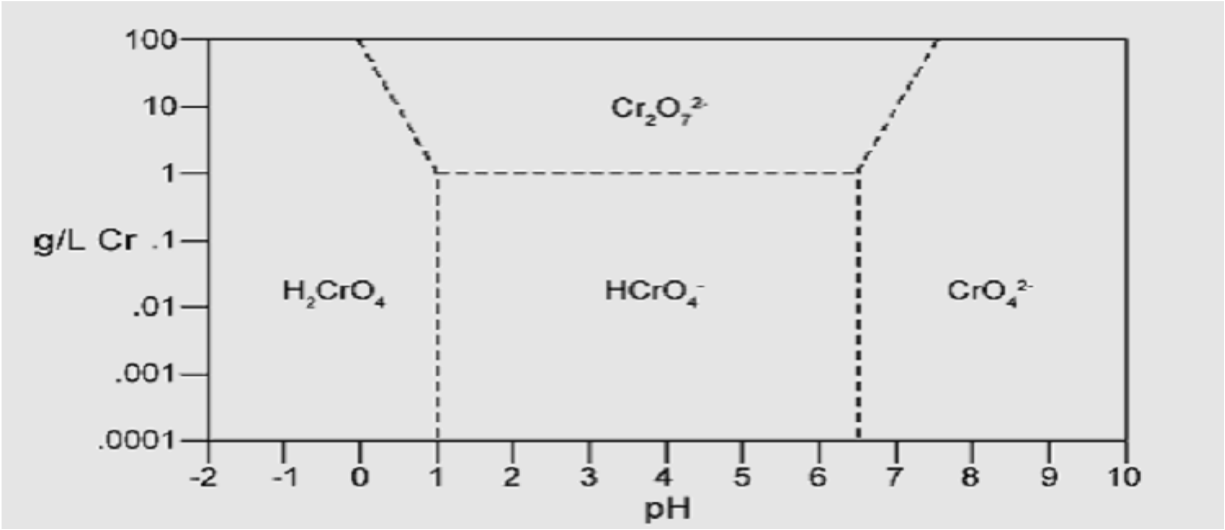

Figure 1: Speciation diagram of Cr(VI)
Source; Mohan, D. Singh, K. Singh, V 2005.

Cr(III) is the most thermodynamically stable oxidation state under reducing conditions. Cr(VI) can remain stable for significant periods of time. Hexavalent chromium exists primarily as salts of chromic acid (H_2CrO_4), hydrogen chromate ion ($HCrO_4-$) and chromate ion (CrO_4^{2-}). Depending on the pH, H_2CrO_4 predominates at pH less than 1.0, $HCrO_4^-$ at pH between 1.0 and 6.0, and CrO_4^{2-} at pH above 6.0. The dichromate ion ($Cr_2O_7^2$) forms when the concentration of chromium exceeds approximately 1g/L (Mohan, Singh et al. 2005).

2.3 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. Hafez et.al., 2002 and Fabiani et.al., 2002 reported that the Cr(VI) ion concentration in the tanning wastewater varies from 2500 to 8000 and 1300 to 2500 ppm, as total chromium respectively (Fabiani, Ruscio et al. 1997, Hafez, El-Manharawy et al. 2002).

2.4 Health impacts 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 ceased. 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, Thatoi et al. 2013).

2.5 Chromium Removal Technologies

Chromium contamination is common all over the world. For water resources, the impact of this contamination is severe. Hence, it is desirable to remove chromium from the contaminated water. Many treatment processes have been developed to remove chromium from wastewater

2.5.1 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, Chan et al. 2006).

2.5.2 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 (Martinez and Rodriguez 2007).

2.5.3 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, Joo et al. 2003).

2.5.4 Adsorption

The adsorption technique has several benefits. It is effective and economical. It can remove the contaminating metals as well as recovery and recycle of sorbet metals from sorbent. It has evolved as the suitable alternative for those metal ions that cannot be removed easily by other techniques. The removal efficiency is excellent for this process and depends on pH, adsorbate concentration, and adsorbent dosages (Mohan, Singh et al. 2008).

Adsorption is the process through which a substance originally present in one phase is removed from that phase by accumulation at the interface between that phase and a separate solid phase. The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid (Mohan, Singh et al. 2008).

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements be they ionic, covalent or metallic of the constituent atoms of the material are filled. But atoms on the clean surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available.

Adsorption can result either from the universal van der Waals interactions (physisorption) or it can have the character of a chemical process(chemisorptions). Contrary to physisorption, chemisorptions occurs only as a monolayer. Physorption is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance. Chemisorptions

occur usually at temperatures much higher than the critical temperature (Ferrari, Kaufmann et al. 2010).

According to Mohan & Pittman, 2006 (Mohan, Pittman et al. 2006), the sorption of Cr(VI) is governed by four consecutive steps; 1) Transport of Cr(VI) in the bulk solution; 2) Diffusion across the liquid film boundary surrounding the sorbent particles; 3) Intra particle diffusion in the liquid contained in the pores and in the sorbent along the pore walls; 4) Sorption and desorption within the particle and on the external surface. The sorption mechanism of hexavalent chromium can be described by four different ways which are:1) anionic sorption, 2) sorption-coupled reduction, 3) anionic and cationic sorption and 4) reduction and anionic sorption. In anionic sorption, negatively charged chromium species CrO_4^{2-} and $Cr_2O_7^{2-}$ bind to positively charged functional groups on the surface of sorbents electrostatic attraction and surface complexation provide the binding phenomenon between the opposite charge.

In the anionic sorption mechanism, the sorption of Cr(VI) is increased at low pH whereas at high pH Cr(VI) sorption decreases. At low pH functional groups of the sorbent become protonated, and easily attract negatively charged chromate ions. On the other hand, at high pH de protonation takes place because functional groups of the sorbent become negatively charged and do not attract negatively charged chromium compounds (Mohan, Pittman et al. 2006).

Sorption-coupled reduction is the mechanism that deals with the reduction of Cr(VI) to Cr(III) using a sorbent in an acidic medium. Then the resultant Cr(III) is sorbed from the solution. In the anionic and cationic sorption mechanism, part of Cr(VI) is reduced to Cr(III), and then both the chromium species are sorbed to the surface of sorbent. According to the reduction and anionic sorption mechanism, a part of the Cr(VI) is reduced to Cr(III); afterward Cr(VI) is mainly sorbed by the sorbent while Cr(III) remains in the solution (Rengaraj, Joo et al. 2003).

2.6 Alum based water treatment sludge (Al-WTS) as an adsorbent.

Water treatment processes that are used to produce safe drinking water generate a wide variety of residual products depending on the untreated water source, chemicals used for purification, and types of unit operations used. In the conventional coagulation-filtration treatment process, suspended solids and natural organic matter are removed from the raw water supply by the addition of aluminum and iron salts as coagulants, resulting in the production of water treatment residuals. In addition to the chemical coagulant used, WTS also carry minerals and elemental signature of the source water (Dayton and Basta 2001).

Most often WTS is considered as waste and usually it is chemically conditioned and mechanically dewatered before disposal in landfills. Although various alternative options for disposal, regeneration and beneficial reuse of WTS have been explored in the past decade the search for cost effective and eco-friendly disposal options has become an urgent priority due to

tighter environmental regulations, declining public acceptance of landfill solutions, increasing disposal costs and decrease in landfill capacity (Babatunde and Zhao 2007).

Water treatment residuals tend to be amorphous in nature. For example, as shown in Eq. [1], when alum is added to water it reacts with bicarbonate to form amorphous Al(OH)3(s)

$$Al_2(SO_4)_3 * 14H_2O + 3Ca(HCO_3)_2 \text{ ------- } 2Al(OH)_{3(s)} + 3CaSO_4 + 6CO_2 + 14H_2O \quad (1)$$

Ippolito (2001) 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 $Al(OH)_3$ phase in Al-WTR, suggesting that an amorphous Al form was present

WTS have shown, via scanning electron microscopy (SEM), to be of various shapes and sizes and are highly porous (Ippolito, Barbarick et al. 2011). Using SEM, Yang et al. (2006), 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. Ippolito et al. (2003) and Makris et al. (2004) used SEM to identify elements present in WTS. Ippolito et al. (2003) noted the presence of Ca and Al in Al-WTR, whereas Makris et al. (2004) 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, Sarkar et al. 2006, Ippolito, Barbarick et al. 2011).

Due to their porosity and amorphous nature and the presence of Al and Fe hydroxides, WTS have the propensity to adsorb tremendous quantities of anions. Anion sorption on to WTS should be a function of particle size, charge, and surface area. Yang et al. (2006) sieved an Al-based WTS into <0.063, 0.06- to 0.125, 0.125 to 0.25, 0.25 to 0.425, 0.425 to 1.00, and 1.00 to 2.36-mm size fractions, noting that smaller particles (<0.25 mm) sorbed greater quantities of phosphate. The authors suggested that this was related to the amount of surface area present across the size fractions studied, with smaller size fractions containing greater surface area allowing for easier access of phosphate to micropores. The findings of Yang et al. (2006) and Makris et al. (2004) support the contention that WTS micropores sorbs the majority of anions. Results are in agreement that WTS are highly porous in nature, containing a greater area of microporosity per gram as compared with macroporosity. In addition, characterization findings suggest that the dominant metals found in WTS, Al and Fe, are present as amorphous phases and their concentrations are similar to reported earlier (Yang, Tomlinson et al. 2006).

Aluminium or iron hydroxides are the important component of the sludge once it has been dewatered and this opens the possibility of reusing it to control pollutants since aluminium or iron ions can enhance their adsorption and chemical precipitation. Extensive studies have shown the effectiveness of WTS for Phosphorous immobilization in soils. Other recent studies explore the phosphorus adsorption ability of WTS (especially aluminium based WTS) and its use in other

applications. Ippolito et al. reported a high phosphorus-binding capacity of approximately 12.5 g P/kg WTS while Dayton and Basta (Dayton and Basta 2001) claimed a capacity ranging from 10.4 to 37.0 g P/kg WTS by examining 18 WTSs in the U.S. Leader et al. (Leader, Dunne et al. 2008) reported a study of the use of lime and iron sludges as potential constructed wetland co-treatment substrates for both dairy and municipal wastewater treatment.

Zhao et al. (Zhao, Babatunde et al. 2006) also studied the reuse of dewatered Al-based sludge cake as the main substrate in a reed-bed system for Phosphorus enriched wastewater treatment. In their study, alum-contained drinking water treatment sludge is extended into developing constructed wetland system using alum sludge as main substrate. Analysis of the system's performance shows that it is a unique and promising low-cost wastewater treatment system. The mean monthly removal efficiencies obtained were determined that ranged 57–84%, 36–84%, 11–78%, 49–93%, 75–94%, 73–97% and 46–83% for BOD5, COD, TN, NH4-N, TP, P and SS, respectively. More importantly, the system showcases a novel reuse alternative for the alum sludge as opposed to its land filling, demonstrating a win-win technique with a great potential for larger scale application.

Yang et al. (2007) used Al-WTS as a potential co-conditioner and dewatering agent in anaerobically digested biosolids. A 2:1 biosolids, Al-WTS ratio was the optimal mix ratio on a volume basis, resulting in 99% P reduction in reject wastewater. The authors also showed that Al-WTS enhanced the dewaterability of biosolids because the Al-WTS played a role in charge neutralization and lowered the specific resistance to filtration and capillary suction time (Yang, Zhao et al. 2007). Generally Water treatment residuals have been used to reduce wastewater and water P concentrations, and depending on the dosage, between 94 and 99.5% P removal efficiency has been realized (Ippolito, Barbarick et al. 2011).

Chu,1999 investigated the removal of dye from textile industry effluent using WTS. The author employed the alum sludge to remove the hydrophobic dye from the textile wastewater at the removal efficiency of 88%, resulting in the reduction of fresh alum requirement by one-third (Chu 1999).

Basibuyuk and Kalat reported the use of waterworks sludge for the treatment of wastewater from a vegetable oil refinery. The used the ferric chloride sludge from the water treatment plant to treat oil and grease, COD, and total suspended solids (TSS) in the vegetable oil industrial wastewater. The application of 12.5 mg/L of fresh ferric chloride and 1000 mg/L of ferric chloride sludge could effectively remove the oil and grease, TSS, and COD at the removal efficiencies of 99%, 83%, and 99%, respectively (Basibuyuk and Kalat 2004).

More recently, the use of WTS as a sorbent for perchlorate and arsenic removal was investigated by Makris et al. Perchlorate sorption isotherms showed that the greatest amount (65%) of perchlorate removed by the Al-WTS. In addition WTSs exhibited high affinities for soluble As(V) and As(III), exhibiting Freundlich type adsorption with no obvious plateau after two days

of reaction. The Al-WTS was highly effective in removing both As(V) and As(III), although As(III) removal was much slower. The Fe-WTS showed greater affinity for As(III) than for As(V) and reached As(III) sorption capacity levels similar to those obtained with the Al-WTS-As(V) system (Makris, Sarkar et al. 2006).

Generally, the generation of WTS will likely increase with increasing population and more stringent drinking water standards; therefore, finding beneficial WTS reuse options will become paramount as environmental and economic pressures limit disposal options (i.e., landfilling, lagooning, and discharging to sewers). The utility of WTS has been proven positive in a wide variety of environmental applications, from small-scale laboratory to field-scale settings. Water treatment sludges are considered an industrial waste product in some states, and as such apprehension exists in terms of using this material for environmental enhancement (Ippolito, Barbarick et al. 2011).

3. Material and Methods

3.1 Characterization of Al-WTS

Freshly generated Al-WTS was collected directly from sludge thickening unit of Legedadi water treatment plants. Prior to characterization and utilization as an adsorbent, sample was air dried, grounded and sieved (< 1mm). pH of WTS was determined in a 2:1 WTS to 0.01MCaCl. accordingly, 2g of WTS sample was weighed and transferred into a 250 mL beaker and 100 mL of distilled water and 1 g of CaCl was added and stirred for 1h. Samples were allowed to stabilize and then pH was measured using an electronic pH/conductivity meter (Jenway 430 Model). Electrical conductivity (EC) were measured in a 1:5 sludge sample/water ratio (McLean 1982).

The Isoelectric point or Zero point charge (PH_{zpc}) of the WTS samples were measured by using the pH drift method. A known quantity of a series of ten $NaNO_3$ solutions having the initial pH values ranging from 1 to 10 were prepared using dilute HCl and dilute NaOH. All the ten $NaNO_3$ Solutions taken in ten different bottles were mixed with 0.5g WTS for a specified period of time. Then the solutions were filtered off and the sludge was separated. The final pH values of the ten solutions were measured and thereby calculation of ΔpH was made by subtracting the initial pH values from final pH values. The graph was drawn by plotting the final pH values against ΔpH. From the graphs plotted, the pH_{zpc} (point of zero charge) of the WTS was determined (McLean 1982).

The elemental metal composition was carried out by carefully weighing 0.5g of the air-dried Al-WTS samples into clean vessels followed by addition of 8 mL HNO_3 + 400mL HF + 8 mL of distilled water. Samples were then digested using a low volume microwave digestion technique (Sandroni, Smith et al. 2003) and the digestates was analyzed for dissolved metals using UV spectrophotometer (Perkin Elmer lambda 950 UV vis Spectrometer). Humic acid expressed as total organic carbon (TOC) content of WTS was determined by HACH DR2800 spectrophotometer, method 10128 (HACH 2007).

3.2 Batch adsorption study

3.2.1 Preparation of chromium stock solution

Potassium dichromate ($K_2Cr_2O_7$) was used as the source for chromium stock solution. All the required solutions were prepared with analytical grade reagents and distilled water. The chromium (VI) stock solution (1000mg/L) was made by dissolving 2.835g of 99% $K_2Cr_2O_7$ in 1.0L distilled water. Synthetic samples of different concentrations of chromium (VI) were prepared from this stock solution by appropriate dilutions.

3.1.2 Chromium analysis, diphenylcarbazide method

250mg 1,5-diphenylcarbazide (1,5diphenylcarbohydrazide) was dissolved in 50mL acetone solution. 50mL sample was taken and 2mL of 3M H_2SO_4 and 1mL of diphenylcarbazide was added. Chromium (VI) concentrations was estimated by the intensity of the red brownish color complex formed, was measured using UV spectrophotometer (Perkin Elmer lambda 950 UV vis Spectrometer) at 540nm, following the 1,5-diphenylcarbazide method (APHA, AWWA et al. 1998). To estimate the percentage removal of chromium (VI), the following equation was used.

$$\text{Percentage removal of Cr (VI)} = \frac{Co - Ce}{Co} \quad (2)$$

Where, C_o and C_e are the concentrations of Cr(VI) at the beginning and at the end of the adsorption process. The metal uptake (q_e) at equilibrium time was calculated from the following equation.

$$q_e = \frac{Co - Ce}{1000w} V \quad (3)$$

Where q_e(mg/g) is the amount of chromium adsorbed per unit weight of adsorbent, C_0 and C_e are the initial and equilibrium chromium ion concentration (mg/L), v is the volume of aqueous solution (mL), and w is the adsorbent weight (g).

3.1.3 Bach adsorption study variables

pH
Adsorbent dose
Shaking time `
Initial chrome concentration
Temperature

3.1.4 Batch adsorption experimental procedure

For each experimental run 200mL of known chrome concentration (0.5, 2, 6, 10, 15.5mg/L) of aqueous solution with known adsorbent dose (0.2, 2, 6, 10, 15.5g) was placed in a 250ml conical flask. The desired pH (1, 2, 3.5, 5, 7) was adjusted by adding 0.2N H_2SO_4 and then the flask is placed in thermal shaker at required temperature (15, 25,32.5, 40, 50^oC) and speed of shaking was adjusted at 200rpm for determined time period (0.15, 1, 3.5, 6, 9hr). The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1). The final Cr(VI) concentration was determined according to diphenylcarbazide method. The amount of chrome adsorbed onto unit weight of the adsorbent was calculated using equation 3.

3.1.5 Batch adsorption experimental design.

Batch experiment study was conducted to check the influence of the study variables (pH, adsorbent dose, chrome concentration, temperature and contact time). Response surface study type with initial design of central composite was applied to generate factor combination using Design of Expert (DOE) software version 7.0.0.

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables (Montgomery and Wiley 2001). A standard RSM design called Central Composite Design (CCD) was applied in this work to study the variables for adsorption of chromium in a batch process. CCD for five variables, each with five levels, was used as experimental design model.

The model has advantage that it permits the use of relatively few combinations of variables for determining the complex response function. A total of 50 experiments were needed to determine coefficients of second order polynomial equation. In the experimental design model, initial Cr(VI) concentration (2-10 mg/L), pH (2-5), sludge dosage (2-10g), contact time (1- 6 hr) and temperature (25-40^{0}c) were taken as input variables. Percentage removal of chromium (VI) was taken as the response of the system.

$$Y = f(X1, X2, X3, X4 \ldots Xn) \tag{4}$$

Where Y is the response of the system and Xi is the variables of action called factors. The goal is to optimize the response variable (Y). It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between independent variables and the response surfaces.

The optimization of Cr(VI) adsorption was carried out by five chosen independent process variables using Central Composite Design with 42 unique runs including 8 replicates at center points. The quadratic equation model for predicting the optimal point was expressed according to Eq. 5.

$$Y = \beta o + \sum_{i=1}^{k} \beta i x i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta x i x j + \varepsilon \tag{5}$$

The Five factors studied with their low and high levels are given in Table (1). The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots. The variability of independent variables was explained by the multiple coefficient of determination, R^2 and the model equation was used to

predict the optimum value and subsequently to elucidate the interaction between the factors within the specified range (Montgomery and Wiley 2001).

Table 1: Actual and Coded values of variables of the experimental design

Factors		Low actual	High actual	Low coded	High coded
Cr(VI) concentration (mg/L)	A	2	10	-1	1
pH	B	2	5	-1	1
Adsorbent dose (g)	C	2	10	-1	1
Time (h)	D	1	8	-1	1
Temperature (^{o}C)	E	25	40	-1	1

2.1.6 Bach Adsorption Isotherm Study

The isotherms models of Langmuir and Freundlich (Langmuir 1919) were fitted to describe the equilibrium adsorption. These equations of isotherms were,

$$\text{Langmuir isotherm} \qquad q = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{6}$$

Where *Ce* is the supernatant concentration after the equilibrium of the system (mg/L), K_L the Langmuir affinity constant (L/mg), and Q_{max} is the maximum adsorption capacity of the material (mg/g) assuming a monolayer of adsorbate uptaken by the adsorbent.

The Langmuir equation can be presented to linear form for the convenience of plotting and calculating the Langmuir constants (K_L). The values of q_m and K_L can be calculated from the linear plot of Ce/q_e versus *Ce*. Eq.7.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} . C_e \tag{7}$$

The essential characteristics of the Langmuir isotherm may also be expressed in terms of a dimensionless separation factor of equilibrium (R_L) which may be calculated from Eq. 8

$$R_L = \frac{1}{1 + K_L C_O} \tag{8}$$

The parameter (R_L) is related to the shape of the isotherm according to the following characteristics: $R_L > 1$ represents unfavorable adsorption; $R_L = 1$ corresponds to a linear relationship; $0 < R_L < 1$ is favorable adsorption and $R_L = 0$ is irreversible.

$$\text{Freundlich isotherm} \qquad q = K_F C_e^{1/n} \tag{9}$$

Where K_F is the Freundlich constant related with adsorption capacity (mg/g) and n is the Freundlich exponent (dimensionless): Equilibrium constants evaluated from the intercept and the slope, respectively, of the linear plot of log q_e versus log Ce based on experimental data. A linear form of the Freundlich expression will yield the constants K_F and $1/n$ Eq. (10) .

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (10)$$

3.3 Fixed bed column study

Fixed bed column study was conducted to assess the effect of flowrate, bed depth, and initial Cr(VI) concentration through one factor at a time study. Fixed bed column was prepared from cylindrical borosilicate glass of internal diameter 2.4cm and height 40cm. Prepared adsorbent was packed to the column at required bed height. In order to prevent adsorbent loose, a glass wool was used at column outlet for support and filtration purpose. Flowrate was regulated by peristaltic pump. The effluent samples were collected at a regular time interval of 0.5h. All the experiments carried out at room temperature. The residual concentration of chromium in the effluent sample was determined using UV vis spectrophotometer. After that the related graphs are prepared from which the design parameters were found out using suitable mathematical models.

3.3.1 Effect of flow rate

The effect of flow rate on adsorption of Cr(VI) by alum sludge in fixed bed column experiment was studied by varying feed flow rate at 5, 10 and 15mL/min respectively while keeping the bed depth at 20cm and feed Cr(VI) concentration 20mg/L.

3.3.2 Effect of bed depth

The effect of bed depth was assessed by varying the column depth at 10, 20, and 30cm while keeping flow rate at 5mL/min and feed Cr(VI) concentration of 20mg/L.

3.3.3 Effect of feed concentration

The effect of feed concentration was assessed by varying feed concentration at 10, 20, 30mg/L while keeping the flow rate at 5mL/min and bed depth at 20cm.

3.3.4 Column adsorptive capacity

Column adsorption capacity or breakthrough capacity ($Q_{0.5}$) is defined in terms of breakthrough time (t_b). The breakthrough time for each column to determine adsorptive capacity is the time when the outlet concentration of chromium (C_{out}) reached 50% of the initial concentration (C_{in}).

(Goel, Kadirvelu et al. 2005). $Q_{0.5}$ (at 50% or $C_o/C_i = 0.5$) expressed in mg of Cr(VI) adsorbed per gram of the adsorbent was calculated using Equation given by Treybal in 1980 (Treybal 1980).

$$Q_{0.5} = \frac{\text{Breakthrough time tb,(at 50\%) (min)x flow rate mL/min) x feed conc.(mg/L)}}{\text{mass of adsoebent (g)}} \quad (11)$$

The total amount of metal ions sent to the column can be calculated from the Equation (6):

$$M_{total} = C_o . F . t_e \quad (12)$$

where: C_o is the inlet metal ion concentration (mg/L), F is the volumetric flow rate (mL/min) and t_e is the exhaustion time (min).

The total amount of metal adsorbed in the column (M_{ad}) is found by the amount of flowrate multiplied by the area above the breakthrough curve. By dividing metal mass (M_{ad}) by the mass of adsorbent (M) will be give the uptake capacity (Q) of the mass.

Using the ratio of Cr(VI) adsorbed, (M_{ad}) to the total amount of Cr(VI) sent to the column (M_{total}), total metal removal (%) can be calculated as Eq. (12). (Hasani, Farnam et al. 2015)

$$\text{Total metal removal \%} = \frac{M_{ad}}{M_{total}} \text{ x } 100 \quad (13)$$

3.3.5 Evaluation of the Experiment by fixed bed column adsorption models

In order to facilitate the adsorption column design it is necessary to fit the adsorption data using established models and subsequently determine parameters associated with those models to determine their influence for optimization of the fixed bed adsorption process. Modeling of break through curves was carried out using three established models, namely, bed-depth-service-time (BDST), Thomas and Yoon – Nelson models.

3.3.5.1 BDST model

The BDST model was formulated by Hutchins (Hutchins 1973). He modified the Bohart Adam model and named it bed depth service time (BDST) model, which is obtained based on different breakthrough values by varying bed depth and flowrate. According to these model the relation of service time and the packed bed depth of column is expressed as

$$C_O = \frac{N_O\, h}{u} - \frac{1}{k} \ln\left[\frac{C_O}{C_t} - 1\right] \quad (14)$$

Where, C_0 is the influent concentration (mg/l), C_t (mg/l), is the effluent concentration at time t, k is the adsorption rate constant (l/(mgmin)), N_0 is the adsorption capacity (mg/l), u is the linear flow rate (cm/min), h is the depth of fixed bed, t is the service time to breakthrough (min).

A linear plot between C_0t and $\ln[C_o/C_t-1]$ was employed in order to determine the values of N_0 and k. In the linear plot we get an equation of general form y = a–bt from which we can obtain the values of N_0 & k by equating a = $\frac{kN0h}{v}$, b = kC_0.

3.3.5.2 Thomas model

The Thomas model formulated by Thomas, is used to determine the maximum solid phase concentration of solute on the adsorbent and the adsorption rate constant an adsorption column (Hutchins 1973). The linearized form of the model is given as,

$$\ln[\frac{C_O}{C_t}-1] = \frac{k_{Th}\, mq_o}{Q} - \frac{k_{Th}C_O V_{eff}}{Q} \quad (15)$$

Where, C_0 is the influent concentration (mg/L), C_t (mg/l) is the effluent concentration at time t, Q is the volumetric flow rate (ml/min), k_{Th} is the Thomas rate constant (ml/min mg), V_{eff} is the volume of effluent (m/L), m is amount of adsorbent in the column (g), q_0 is the equilibrium Cr (VI) uptake per gram of the adsorbent (mg/g).

A linear plot of ln $[\frac{Co}{Ct}- 1]$ and $\frac{V_{eff}}{Q}$ was employed in order to determine the values of k_{Th} and q_o from the intercept and slope of the plot. Then we get an equation of general form y = a-bt then by equating a = $\frac{kThmq0}{Q}$ & b = $k_{Th}C_0$ the values of k_{Th} and q_0 are determined.

3.3.5.3 Yoon Nelson model

Yoon and Nelson proposed a less complicated model based on the assumption that the rate of decrease in the probability of sorption for each sorbate molecule is proportional to the probability of sorbate breakthrough on the sorbent (Yoon and Nelson 1984)

The linearized model for a single component system is expressed as,

$$\ln [\frac{C_t}{C_o - C_t}] = k_{YN} - \tau k_{YN} \quad (16)$$

where, k_{YN} is the rate constant (per min), τ is the time required for 50% adsorbate breakthrough (min). A linear plot of $\ln[C_t/(C_0 - C_t)]$ against sampling time (t) was employed to determine values of k_{YN} and τ from the intercept and slope of the plot. In the linear plot a general equation of the form y = a – bt is obtained from which the values of k_{YN} and τ are obtained by equating a = τk_{YN} & b = k_{YN}

3.4 Data analyses

Batch adsorption data was analysed using experimental design Expert software 7.0.0 and the analysis of variables and process optimization was presented using tables, and graphs. For fixed bed column study, Microsoft excel was used for data analysis.

4. Result and Discussion

4.1 Characteristics of alum based water treatment sludge (Al-WTS)

The Al-WTS has a residual pH of 6.56, 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 Aluminium toxicity due to the quantity of Aluminium 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 Aluminium speciation is highly pH dependent, with soluble species present in higher concentrations at pH levels less than 6 (Dayton and Basta 2001).

The solution pH at which the surface of a soil particle carries no charge is called the zero point of charge (ZPC). The ZPC values of Al-WTS used in this study is 5.8. At pH below ZPC value, the adsorbent carry the overall positive surface charges in suspension (Kumar and Chakraborty 2009). Chromium below pH 6 exists as an ionic form of Cr(VI). So adsorption occurs below the PZC were the adsorbent will develop positive surface charges.

Table 2: Physicochemical characteristics of Al-WTS

Parameters	Value	Unit
pH	6.56	-
pH_{PZC}	5.82	-
EC	1.3	mS/cm
Aluminum	196.45	mg/g
Calcium	4.21	mg/g
Chromium (VI)	0.06	mg/g
TOC(humic acid)	98.68	mg/g

TOC of Al-WTS is 98.86mg/g. These values may be attributed to humic substances contained in the raw water being treated (Yang, Tomlinson et al. 2006). The raw water is highly turbid with turbidity up to 900NTU, which contains high humic substances. It is clear that the primary coagulant (aluminium sulphate) used during the water treatment process is reflected in the composition of the Al-WTR. The compositions of Aluminium in the Al-WTR is high (196.45). This is because the treatment plant uses large amount of Aluminum Sulfate as a coagulant to treat raw water (120mg of alum per liter of raw water).

4.2 Batch adsorption study

The five variables, Cr(VI) concentration, pH, adsorbent dose, shaking time and temperature are chosen for batch adsorption experiment. A five-factor-five-level CCD design is used to determine the optimal values of these factors. The factor range and level of variables investigated in this study is listed in Table (3).

Table 3: Experimental range and levels of the independent variables in terms of actual value

Variable		Low axial ($-\alpha = -2$)	Low factorial (-1)	Center point (0)	High factorial (+1)	High axial ($+\alpha = +2$)
Initial Cr(VI)concentration (mg/L)	A	0.5	2	6	10	15.5
pH	B	1	2	3.5	5	7
Adsorbent dose (g)	C	0.5	2	6	10	15.5
Time (h)	D	0.25	1	3.5	6	9.5
Temperature (^{o}c)	E	15	25	32.5	40	50

Once the desired value of variables has been defined, they were coded to lie at ±1 for the factorial points, 0 for the center points, and ± α for the axial points. In this case a CCD for five independent variables each at five levels was employed to fit the model in which 50 experiments were required for this procedure. Central Composite Design experimental matrix, experimental and predicted values of Cr(VI) removal by alum based water treatment sludge via batch adsorption is presented in annex (4).

4.2.1 Mathematical model development and evaluation

Experimental result of batch adsorption was feed to DOE software for multiple regression fitting. Quadratic polynomial model was fitted with backward elimination regression with alpha to exit 0.10. The sequential model sum of squares is presented in Table (4). Model summary statistics is presented in Table (5). Analysis of variance is presented in Table (6).

Table 4: Sequential Model Sum of Squares

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	288860.80	1	288860.80			
Linear vs Mean	6508.38	5	1301.67	17.642	< 0.0001	
2FI vs Linear	880.10	10	88.01	1.264	0.288	
Quadratic vs 2FI	***1085.19***	***5***	***217.03***	***4.913***	***0.00223***	***Suggested***
Cubic vs Quadratic	608.48	15	40.56	0.844	0.627	Aliased
Residual	672.60	14	48.04			
Total	298615.58	50	5972.31			

Sequential Model Sum of Square selects the highest order polynomial where the additional terms are significant and the model is not aliased. From sequential model sum of squares it was found that quadratic model was the most suitable model to describe effect of selected process condition in removal of Cr(IV) by Al-WTS.

The final obtained model equation for prediction of response variables based on coded factor was as follows;

Chrome Removal (%) =

$$72.48 - 3.97 * A - 3.81 * B + 8.46 * C + 6.91 * D - 2.73 * A * B + 2.08 * A * C + 3.12 * B * C + 3.05 * A^2 + 2.50 * B^2 - 1.47 * D^2$$

The magnitude of the coefficient in the above quadratic equations denotes the intensity while the sign indicates nature of influence (positive or negative) of the particular variable on the response. A positive effect of a factor means that the response is improved when the factor level increases and a negative effect of the factor revealed that the response is inhibited when the factor level increases.

Table 5: Model Summary Statistics

	General model	Reduced model
R- Squared	0.868	0.912
Adjusted R-Squared	0.778	0.901
Predicted R-Squared	0.645	0.862
Adequate Precision		17.474
Mean	76.008	76.008
Std. Dev.	6.646	6.281
C.V. %		8.264
PRESS	3454.773	2316.214

To assess the adequacy of a model, the coefficient of determination (R^2) and the lack of fit test were commonly used. Coefficient of determination (R^2) refers to the changes described by the model to the overall changes. Therefore, when R^2 is closer to 1, the power of fitted model is greater to describe the response changes as a function of the independent variables.

From the model summary statistics table, it can be seen that the regression coefficient of the quadratic model developed for reduced response is 0.912 which shows that the model explains 91.2% of the variation and also the adjusted R^2 of 0.901 is in reasonable agreement with the predicted R^2 of 0.862.

Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. As can be seen from model summary statistics table, this ratio is 17.474 indicating an adequacy of signal, implying that the model can be used to navigate the design space (Montgomery and Wiley 2001).

The ANOVA result (Table 6) shows that the Model F-value of 20.82 implies the models is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. The associated p value is used to estimate whether F is large enough to indicate statistical significance. The values of p, less than 0.05 indicates that the model is considered to be statistically significant whereas values greater than 0.05 indicate the model terms are not significant variable (Montgomery and Wiley 2001).

Table 6: The Analysis of variance (ANOVA) table

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	**8215.82**	**10**	**821.58**	**20.82**	**< 0.0001**	**significant**
A-initial Cr(VI) concentration.	682.91	1	682.91	17.30	0.0001	
B-pH	628.37	1	628.37	15.92	0.0002	
C-Adsorbent dose	3102.36	1	3102.36	78.62	< 0.0001	
D-shaking time	2069.98	1	2069.98	52.45	< 0.0001	
AB	335.63	1	335.63	10.93	0.0053	
AC	239.25	1	239.25	6.06	0.0183	
BC	139.02	1	139.02	3.52	0.0580	
A^2	534.09	1	534.09	13.53	0.0007	
B^2	356.99	1	356.99	9.04	0.0045	
Residual	1538.94	39	39.46			
Lack of Fit	**1048.64**	**32**	**32.77**	**0.46**	**0.932**	**not significant**
Pure Error	490.29	7	70.04			
Cor Total	9754.7768	49				

The ANOVA result also presents p - values of individual model terms. According to the result four linear terms, initial Cr(VI) concentration, pH, adsorbent dose and shaking time; interaction term, initial Cr(VI) oncentration and pH, initial Cr(VI) concentration and adsorbent dose, pH and adsorbent dose and second order terms of initial Cr(VI) concentration, and pH (A, B, C, D, AB, AC, BC, A^2, B^2) are significant model terms.

The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. Lack of Fit test showes that the "Lack of Fit F-value" of 0.46 which implies the Lack of Fit is not significant relative to the pure error. There is a 93.2% "Lack of Fit F-value" this large could occur due to noise.

4.2.2 Model diagnosis

Model diagnosis was conducted by cheking assumptions of normal distribution of error, abcense of constant error and outliers. Graphs of Normal probability plot of the studentized residuals to check normality of residuals, Studentized residuals versus predicted values to check for constant error, Externally Studentized Residuals to look for outliers and Box Cox plot to chech wether data transformation is needed is shown below.

The Normal probability plot shows that error is normaly distributed confirming assumption for normality of error Figure (2). As observed from probabiity plot of residuals, error is normally distributed.

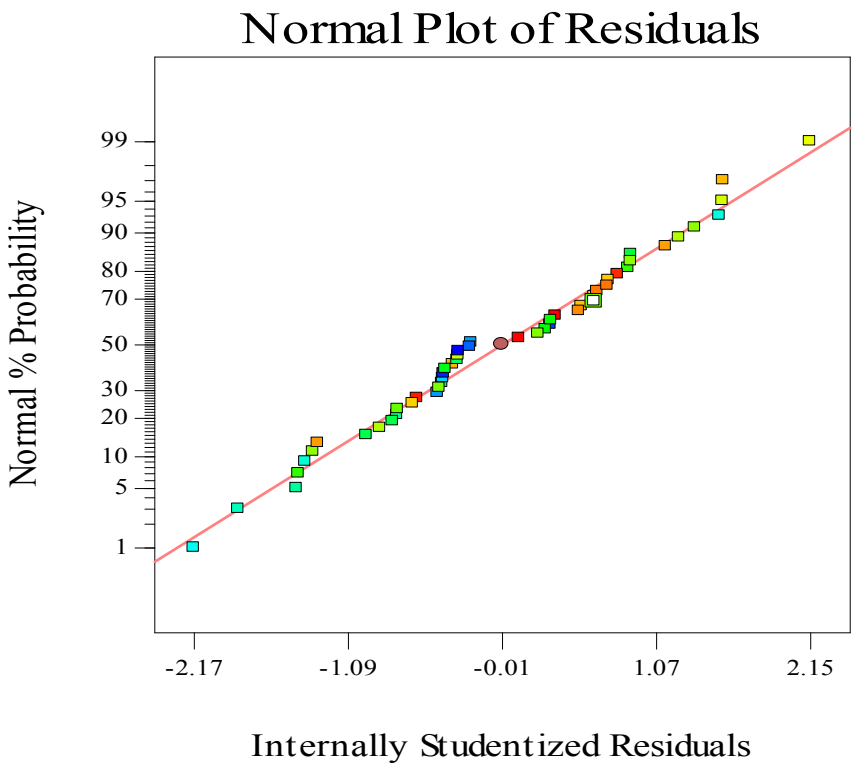

Figure 2: Normal probability plot indicating meeting of normal assumption

Similarly Figure (3), Internally and Externaly sudetized plots asserts absence of constant error and influential outlier respectively. While Figure (4) shows that no transformation of data was needed.

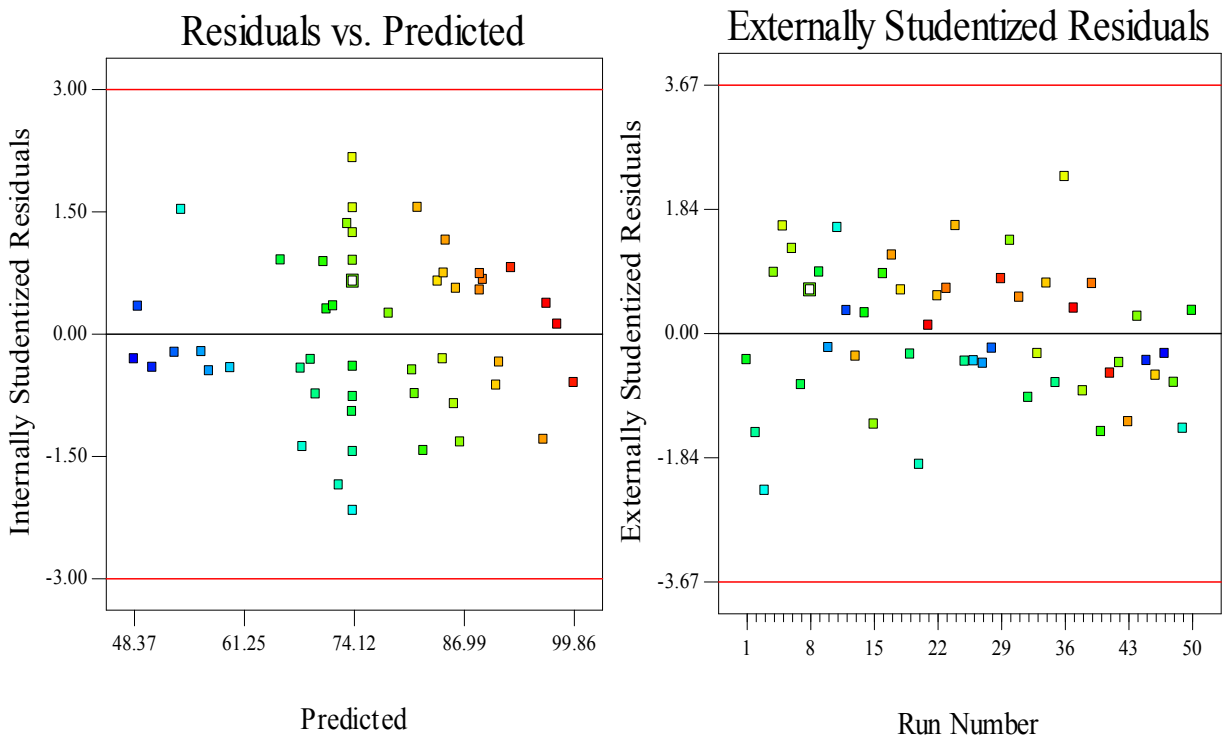

Figure 3: Internally and Externally studentized plots indicating absence of constant error and influential outlier respectively.

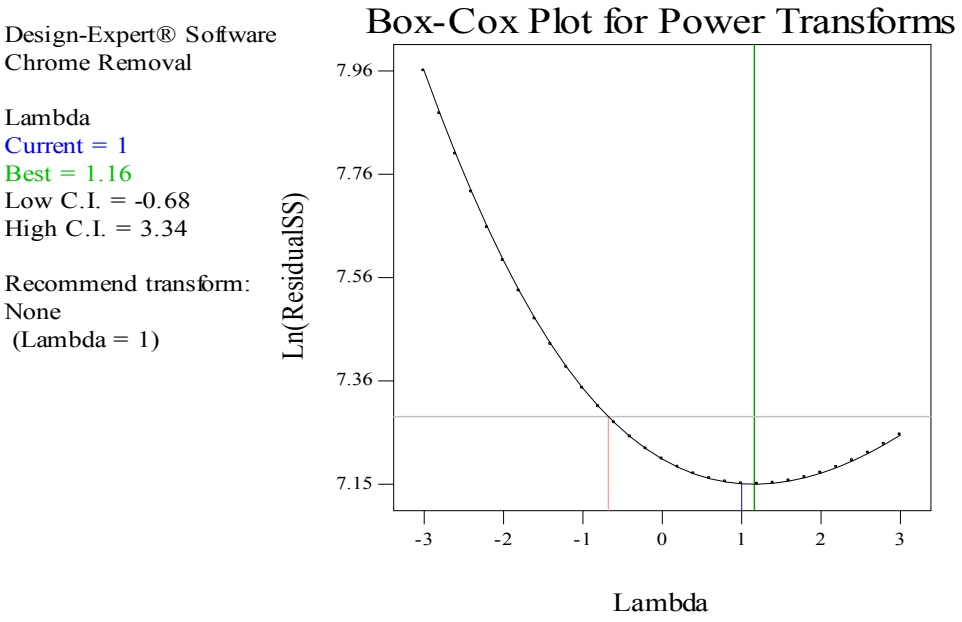

Figure 4: Box-Cox plot indicating no transformation of data is needed

4.2.3 Effect of independent variables

In order to study the interaction among different independent variables and their corresponding effect on the response; interaction, contour and 3D plots were drawn. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response.

According to ANOVA, the linear effects of four independent variables (A,B,C,D) are significant ($P < 0.0002$). Thus, each variable in turn can affect removal of chrome by alum sludge. In the investigated experimental region chrome removal decrease with increasing initial chrome concentration and pH. While removal increase with increase in adsorbent dose and shaking time. Temperature has insignificant effect according to ANOVA result.

Perturbation plot (Figure 5) is an important diagrammatic representation to compare all effects of all factor at particular point in design space. The response is plotted by changing only one factor over its range while holding other factors constant. Steepy slope or curvature for a factor shows that response variable is sensitive to that factor. A relatively flat line shows insensitivity of response for that particular factor (Montgomery and Wiley 2001).

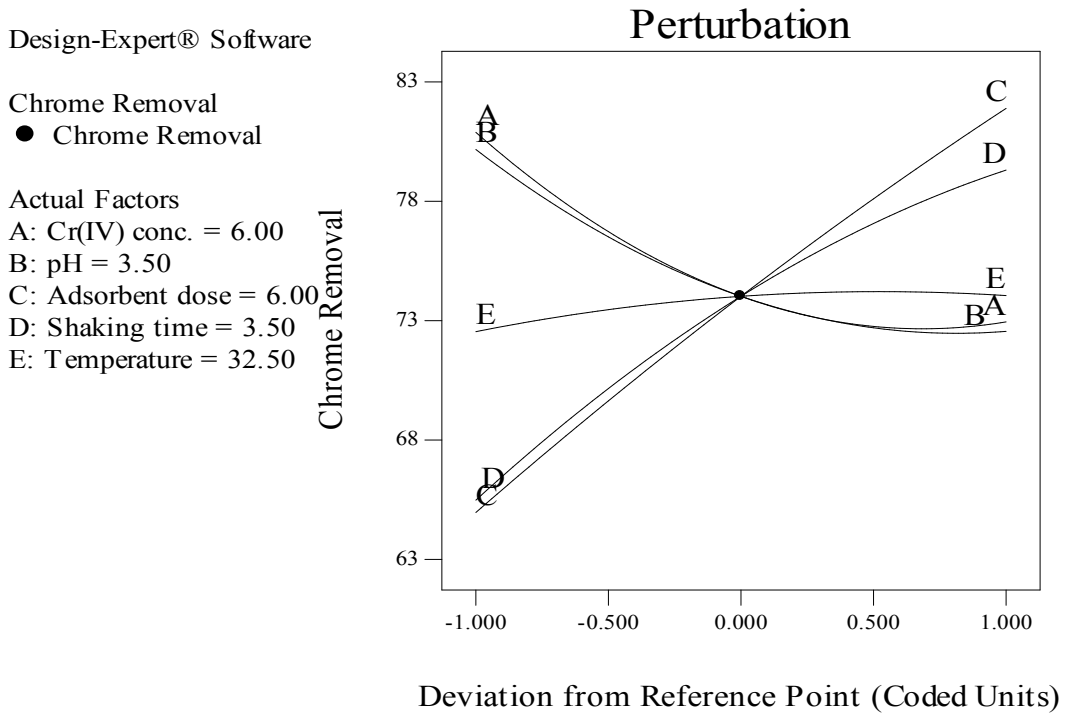

Figure 5: Perturbation plot showing effect of factors on chrome removal.

Perturbation plot shows factors (A,B,C,D) have effect on response variable (chrome removal). It can be seen that chrome removal increase with increasing adsorbent dose and contact time (C,D),

while it decreases with increasing concentration and pH (A,B). This can be also evidenced by ANOVA result.

4.2.4 Effect of Concentration

Effect of concentration was studied by varying the Cr(VI) concentration from 0.5-15.5mg/L. The percentage removal decreases with increasing Cr(VI) concentration beyond 6 mg/L. This is due to the fact that the adsorbent has a definite capacity and can adsorbs only a maximum specific amount. Therefore additional adsorbate does not get adsorbed and hence the percentage removal decreases (Hasani, Farnam et al. 2015). Changing concentration from 2mg/L to 10mg/L of Cr(VI) can decrease removal percentage from 80.89 to 72.95%.

4.2.5 Effect of pH

The effect of pH on the removal of Cr(VI) was studied by changing pH values in the range, 1 to 7. 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 2, 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 2. Maximum adsorption at pH 2.0 indicates that it is the $HCrO_4^-$ form of Cr(VI) which is the predominant species and adsorbed preferentially on Al-WTS (Cimino, Passerini et al. 2000, Mohan, Singh et al. 2005).

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 removal was studied by varying adsorbent dose from 0.5 to 15.5g and it was seen that removal increase with increasing adsorbent dose, The change in adsorbent dose from 2g to 10g can increase removal from 64.96% to 81.89% keeping other factors at the center. This trend was due to increase in surface area and adsorption sites available for adsorption.

Equilibrium time is an important parameter for economical wastewater treatment. As the contact time increases, the rate of adsorption decreases depending on the chemical characteristics of the surface (Chergui, Bakhti et al. 2007). In the study removal percent increase with in increasing shaking time.

Generally, Figure (6) shows the single variable effect on percentage removal of Cr(VI). It should be understood that effect of single variable alone did not shows the removal trend. Factor interaction should be considered.

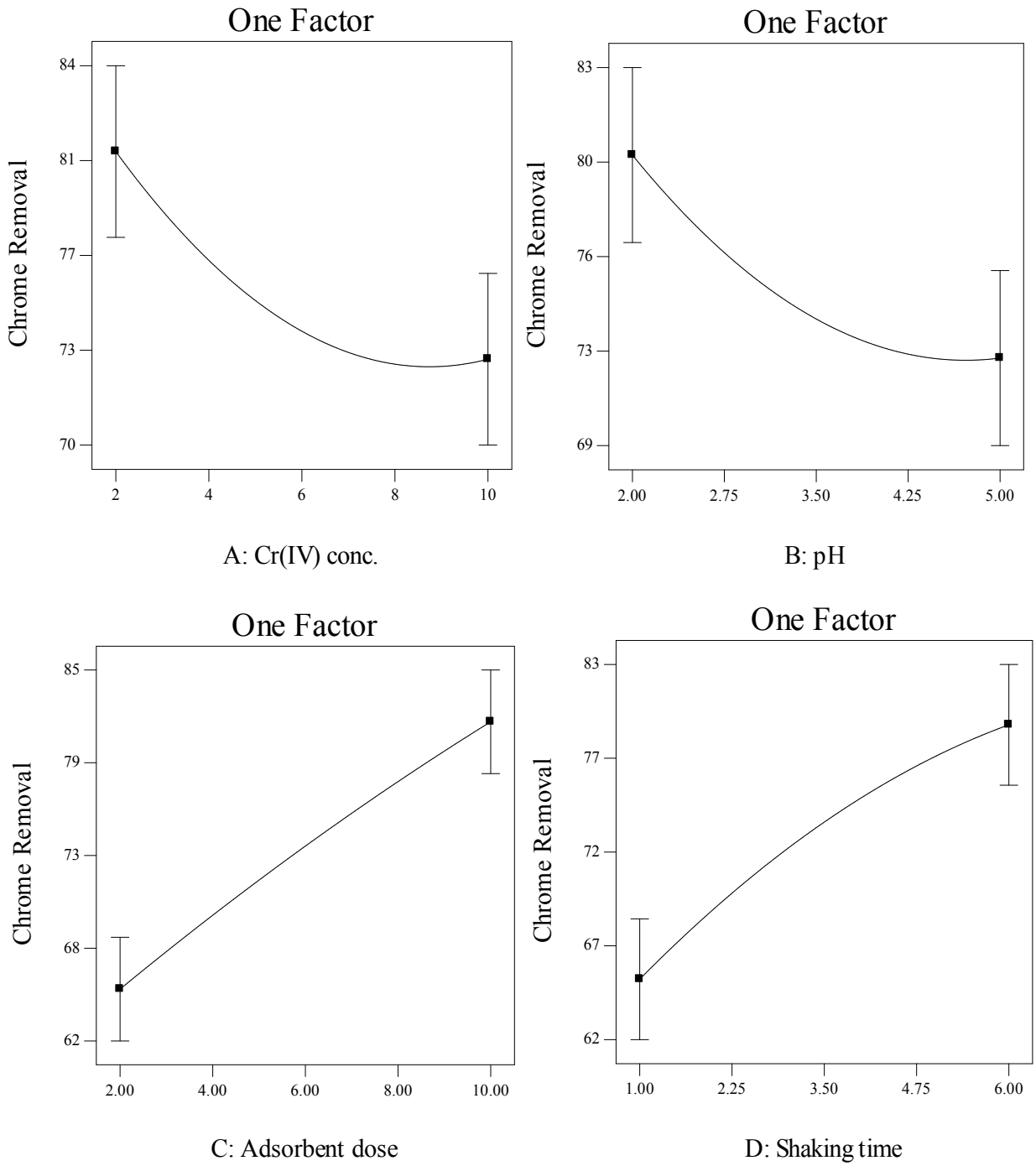

Figure 6: Single factor plots showing individual factor effect on Cr(VI) removal: Effect of Cr(VI) concentration, pH, Adsorbent dose and shaking time respectively.

4.2.6 Effects of factor interaction

In order to study the interaction among different independent variables and their corresponding effect on the response variable, contour plots were drawn. A contour plot is a graphical representation of a three dimensional response surface as a function of two independent variables, maintaining all other variables at fixed or different level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response variable.

Interaction effect of initial Cr(VI) concentration and pH (AB) was shown in contour plot of Figure (7). Removal percentage increases with decreasing both initial Cr(VI) concentration and pH. 85.35% chrome removal is achieved at Cr(VI) concentration of 2.5mg/L, pH 2.4, adsorbent dose of 6g and contact time 3.5h. The effect of AB can also be optimized by increasing adsorbent dose and contact time (Figure 7b). 94.45% chrome removal can be attained at Cr(VI) concentration of 2.4, pH 2.45, adsorbent dose 10g and shaking time of 6hr.

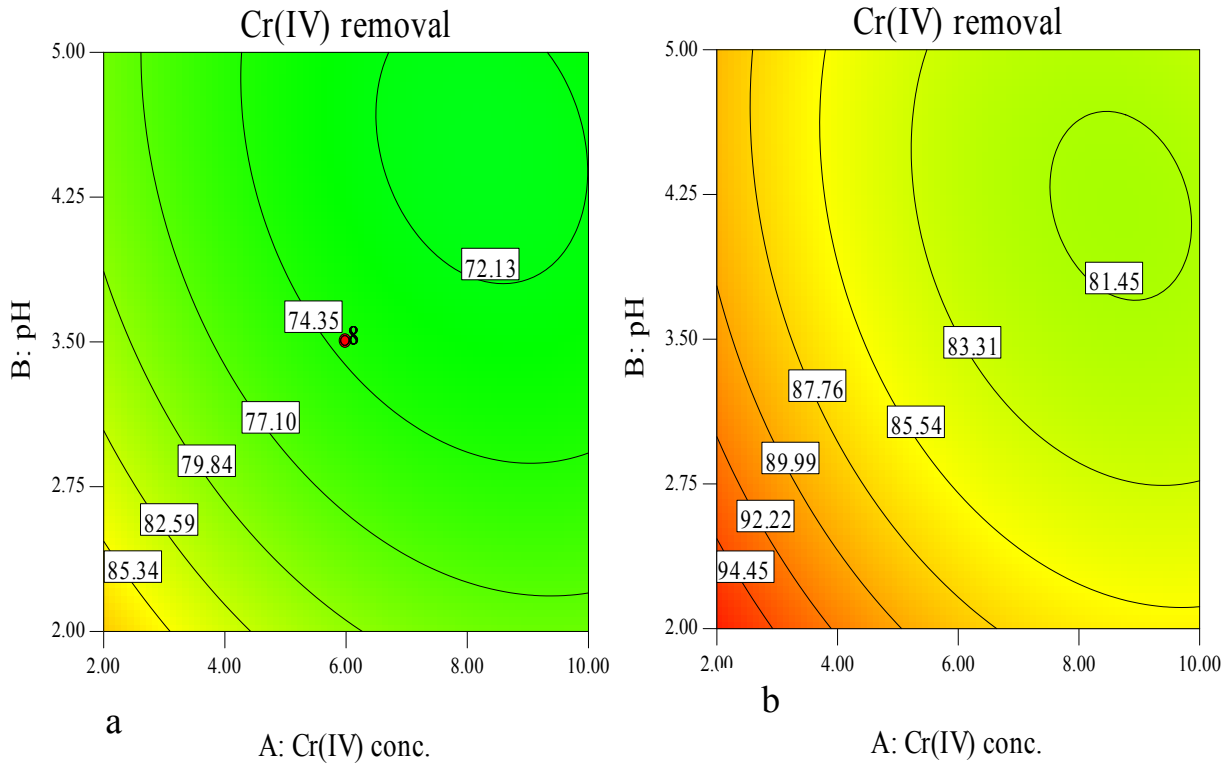

Figure 7: Contour plot showing the combined effect of Cr(VI) concentaration and pH (AB), at adsorbent dose 6g, shaking time 3.5hr, temperature 32.5^{o}C (a) and at optimized adsorbent dose of 10g, shaking time 6hr and temperature 32.5^{o}C (b)

In general, at higher Cr(VI) concentration, the Cr(VI) removal decreased as pH increased from 2 to 5, while at lower Cr(VI) concentration, removal increases first and then decreases. Possible explanations may lie in the states of the chromium ion, protonation level and surface charge of the adsorbent. The predominant Cr(VI) species were $HCrO_4^-$ and CrO_4^{2-}. Below pH 4.0, the $HCrO_4^-$ complex was the major form, while at pH above 4.0, the most abundant species was CrO_4^{2-} (Mohan, Singh et al. 2005). From low adsorption obtained at high pH, it can be inferred that the amount of Cr(VI) adsorbed by other adsorption mechanism was limited, which confirmed that at low pH, the electrostatic attraction played an important role in the removal of Cr(VI) by Al-WTS. This might be due to the reason that at low concentration, the ratio of available surface to the Cr(VI) concentration is larger, so the removal is higher. However, in case of higher concentrations, this ratio is low; hence the Cr(VI) removal percentage is lesser (Jain, Garg et al. 2011)

The combined effect of Cr(VI) concentration and adsorbent dose (AC) is shown in contour and 3D plot of Figure (8)**.** From interaction of AC, chrome removal increase with; adsorbent dose increase and Cr(VI) concentration decrease. 80.3% chrome removal was obtained at Cr(VI) concentration of 3.5mg/L, adsorbent dose 7.4g, pH 3.5, and shaking time 3.5h. But, removal increases up to 97.19% at Cr(VI) concentration of 3.3mg/L, adsorbent dose 6.3g, pH 2 and shaking time 6h. The interaction of both factors (Cr(VI) concentration and adsorbent dose) can be analyzed by checking the hot spotted formed in contour and 3D plot of Figure (8). The increase in percent adsorption with increase in adsorbent dose might be due to availability of more surface area with more functional groups at higher mass of adsorbent (Jain, Garg et al. 2011).

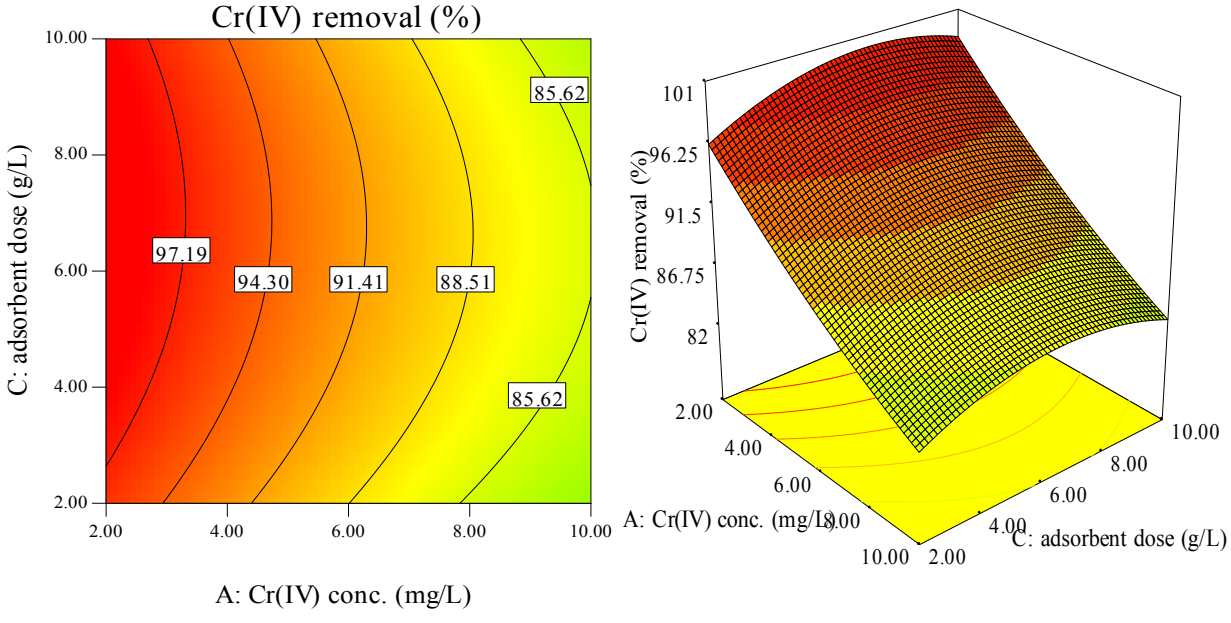

Figure 8: Contour (a) and 3D (b) plot showing combined effect of Cr(VI) concentration and adsorbent dose (AC) at pH 2, shaking time 6h and temperature 32.5°C

Figure (9) represents the effect of pH and adsorbent dose (BC) on removal of Cr(VI) under conditions given by model. The graph shows that the maximum adsorption (92.2%) occurs under acidic conditions, pH 2.4 and adsorbent dose of 6g. Increasing the solution pH from 2 to 5, decreases removal to 78.87%. The higher adsorption at acidic pH range is mainly due to ionizable surface charge of the adsorbent. Perusal of literature on Cr(VI) shows that dominant species is $HCrO_4^-$ which leads to electrostatic attraction between positively charged adsorbent surface and negatively charged Cr(VI) species $HCrO_4^-$.

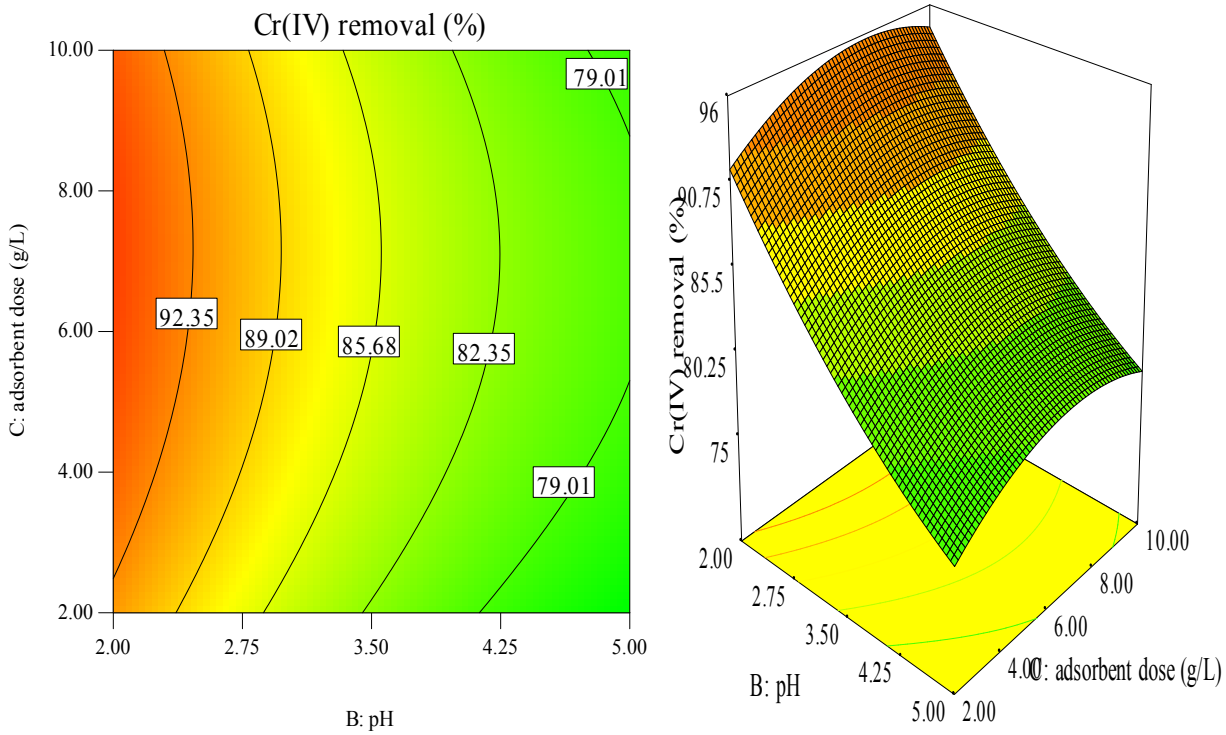

Figure 9: Contour (a) and 3D (b) plot showing the combined effect of pH and adsorbent dose (BC) at Cr(VI) concentration 2mg/L, shaking time 6h and temperature 32.5^{o}C

Meanwhile, at lower pH, the adsorbent surfaces might be highly protonated which favor the uptake of Cr(VI) anion. Besides, as the pH was lowered, the overall surface charge on the adsorbent became positive or less negative, which will promote a stronger columbic attraction towards negatively charged Cr(VI) complex ions in the solution. Hence, adsorption increased with an increase in the acidity of the solution. In this study, the pH_{PZC} value of alum sludge was 5.86. So at low pH adsorbent surface acquires positive charge, making the electrostatic attraction towards Cr(VI) anion better.

4.2.7 Process optimization

One of the main objectives of RSM is the determination of the optimum settings of the control variables that result in a maximum (or a minimum) response over a certain region of interest (Khuri and Mukhopadhyay 2010).

In the Design Expert software's (DOE) numerical optimization, the possible goals are maximize, minimize, target, in range and set to an exact value (factors only). Therefore, in present study, the desired goal for each factor as well as for the response function was selected from the menu. A weight is usually assigned to each goal in order to adjust the shape of the particular desirability function. The goals are then combined to an overall desirability function. Desirability is an objective function. It can normally range from zero to one for any given response. A desirability value of one represents the ideal case while a zero indicates that one or more responses fall outside the desirable limits. The numerical optimization identifies a point that will maximize the desirability function. The possibility of finding the best local maximum can generally be increased by starting from several points in the design space (Amini, Younesi et al. 2008).

Therefore, in the present study, the desired goal for each factor as well as for the response function was selected. We want our experiment to treat maximum Cr(VI) concentration so it was set a goal maximum for initial Cr(VI) concentration, pH in a range, time minimum, adsorbent dose minimum so we can treat maximum concentration with minimum adsorbent dose, and finally temperature in range. The DOE software output for the desired goal is presented in Table (7) below.

Table 7: Criteria of setting factors to be optimized

Factor	Goal	Lower Limit	Upper Limit	Importance
Initial Cr(VI) conc.(mg/L)	maximize	2	10	4
pH	is in range	2	5	1
Adsorbent dose(g)	minimize	2	10	4
Shaking time(hr)	minimize	1	6	3
Temperature(^{o}c)	is in range	25	35	1
Cr(IV) removal (%)	maximize	53	98.5	5

Finally, 10 optimum factor combination were generated by DOE software and five optimum were selected and presented in Table (8).

Table 8: Numerically optimized variables

No .	Cr(VI) conc. (mg/L)	pH	Adsorbent dose (g)	Shaking time (h)	Temperature (oc)	Cr(VI) removal (%)	Desirability
1.	9.98	5	2.81	1	25	72.73	0.749
2.	10	5	2.18	1	34.55	72.28	0.760
3.	10	4.75	2	1	34.59	71.20	0.751
4.	10	2	2.59	1.02	25.29	70.74	0.730
5.	10	3.96	2.02	1	34.96	69.55	0.728

4.2.8 Confirmatory experiment

Model validations has been conducted at five experimental combinations from output of DOE in Table (8). The result was used for validation of the statistical model with experimental value. The results of analysis which is presented in Table (9) indicates that, the experimental values were in good agreement with the predicted ones with maximum error of 1.75%.

Table 9: Confirmatory experiment result showing percent removal for optimized factor combination

Factor combination					Removal %	
A	B	C	D	E	Predicted	Experimental
9.98	5	2.81	1	25	72.73	71.63
10	5	2.18	1	34.55	72.28	71.57
10	4.75	2	1	34.59	71.20	69.98
10	2	2.59	1.02	25.29	70.74	70.5
10	3.96	2.02	1	34.96	69.55	68.52

4.3 Adsorptive capacity of Al-WTS

The Langmuir and Freundlich isotherm models was used to determine the adsorptive capacity of Al-WTS. The Langmuir model was used for monolayer sorption onto surface of sorbent containing finite amount of identical sorption sites which is indicated by Eq.(5). The values of q_m and K_L can be calculated from the linear plot of Ce/qe versus Ce (Eq. 6). Freundlich isotherm assumes that the uptakes of adsorbate occur on a heterogeneous surface by multilayer adsorption and the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is given by Eq. (8). A linear form of the Freundlich expression will yield the constants K_F and 1/n Eq. (9). The slope and the intercept correspond to (1/n) and K_F, respectively, where K_F is roughly an indicator of the adsorption capacity and 1/n is the adsorption intensity. Equilibrium constants are evaluated from the intercept and the slope of the linear plot of log qe versus log Ce respectively based on experimental data (Langmuir 1919).

The equilibrium data of Cr(VI) sorption were evaluated by the linearized form the Langmuir and Freundlich sorption isotherms. The Langmuir constants, K_L and monolayer sorption capacity, q_m were calculated from the slope and intercept of the plot between Ce/qe and Ce (Figure 12).The results of fitting the equilibrium data to Langmuir isotherm are shown that values of q_m and K_L are 33.4 and 0.164 respectively and the R^2 is 0.984. The results of fitting the equilibrium data onto Freundlich isotherm are presented that values of n and K_F are 0.43 and 2.49 respectively and the R^2 is 0.969.

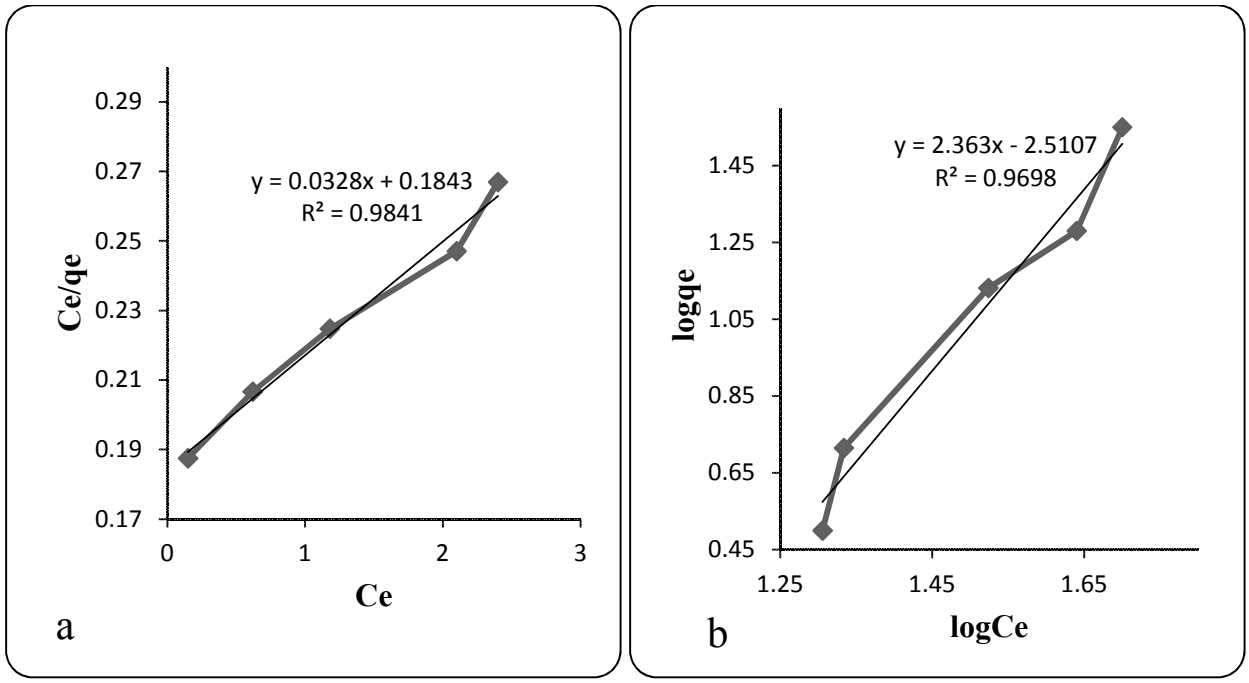

Figure 10: Langmuir (a) and Freundlich (b) isotherm plots

Figure (10) shows, the fitted equilibrium data in Langmuir and Freundlich isotherms. The fitting results, i.e. isotherm parameters and the coefficients of determination, R^2 are shown in Table (10). It can be seen that Langmuir isotherm fits the data better than Freundlich isotherm. This is also confirmed by the high value of R^2 in case of Langmuir (0.9841) compared to Freundlich (0.9698) and this indicates that the adsorption of Cr(VI) on Al-WTS takes place as mono layer adsorption on a surface that is homogenous in adsorption affinity.

Table 10: Langmuir and Freundlich isotherm constants

Langmuir isotherm constants			**Freundlich isotherm constants**		
q_m (mg/g)	K_L(L/mg)	R^2	K_F(mg/g)	n	R^2
33.33	0.164	0.9841	2.49	0.43	0.9698

The essential characteristics of the Langmuir isotherm may also be expressed in terms of a dimensionless separation factor of equilibrium (R_L) which may be calculated from Eq. (8). The

parameter (R_L) is related to the shape of the isotherm according to the following characteristics, $R_L > 1$ represents unfavorable adsorption, $R_L = 1$ corresponds to a linear relationship, $0 < R_L < 1$ is favorable adsorption and $R_L = 0$ is irreversible. In the present study, R_L is 0.0296, which indicates that alum sludge are good adsorbent for Cr(VI) ion removal (Attia, Khedr et al. 2010).

In this study the maximum adsorptive capacity of Al-WTS is 9.86mg/g. Adsorptive capacity of different adsorbent on chrome adsorption is listed in Table (11). Ya-Feng, Z and Richard, H, 2010 used alum derived water treatment sludge for sorption of Pb(II), Cr(III) and Cr(VI) from aqueous solution in one factor at time batch adsorption study (Ya-Feng and Richard 2010). They obtained adsorptive capacity of Cr(VI), 0.22 mg/g. Adsorptive capacity obtained in this study is larger, compared to Ya-Feng, Z and Richard, H, 2010. This might be from difference in adsorbent characteristics and adsorbent affinity towards the adsorbate. As a low cost adsorbent, Al-WTS in these work has appreciable adsorptive capacity in adsorbing chrome from both aqueous and real wastewater. More over compared to other low cost adsorbents it can be freely available without charge from water treatment plants and it can be easily used as an adsorbent without further complicated preparation modification procedure.

Table 11: Comparison of adsorption capacities of various low-cost adsorbents for Cr (VI) removal.

Adsorbent type	Modification	qe (mg/g)	Cr(IV) conc. (mg/L)	Reference
Coconut shell carbon	Chemical	10.88	25	(Babel and Kurniawan)
Rubber wood Sawdust activated carbon	Chemical	44.5	200	(Karthikeya, Rajagopal et al.)
Silica based adsorbent	Radiation	68	50-250	(Qiu, Wang et al.)
Fe-modified activated carbon	Iron	11.83	3.5-250	(Liu, Zhang et al.)
Magnesia cement	Chemical	18.8	70-100	(Gasser, Morad et al.)
Micelle-clay complex	Chemical	9.43	10-500	(Qurie, Khamis et al.)
Coal	Chemical	23.6	100	(Dakiky, Khamis et al.)
Water treatment sludge	None	0.21	0.4-8	(Ya-Feng and Richard)
Water treatment sludge	Activated carbon	0.22	0.4-8	(Ya-Feng and Richard)
Al-WTS	None	9.86	0.5-15.5	this work

4.4 Application of Al-WTS for removal of Cr (VI) from Tannery wastewater

For more understanding of Al-WTS capacity for Cr(VI) removal from real wastewater, batch adsorption experiment was conducted on real wastewater. Wastewater sample was collected from a local tanning factory (Addis Ababa Tannery). The pH and initial Cr(VI) concentration of this tannery wastewater were determined at the beginning of adsorption experiments, and found 3.34 and 8.64mg/L respectively. Adsorption process was conducted on 200mL of wastewater with Al-WTS dose of 2g. The suspensions were stirred at 200rpm, at 34.5°C and 1h, according

to optimum temperature, shaking time and adsorbent dose obtained from optimization study of batch experiment (No. 5 factor combination in Table 8). Cr(VI) removal efficiency of Al-WTS was found 78.96%. The result is indicative that, Al-WTS is an efficient adsorbent for the removal of Cr(VI) from wastewater too.

4.5 Fixed bed column study

Fixed bed column study was conducted to assess the effect of flow rate, bed depth, and Cr(VI) concentration on chrome adsorptive capacity of Al-WTS.

4.5.1 Effect of hydraulic loading rate

Flow rate of any wastewater stream is an important parameter in evaluating the adsorption capacity of metal effluents in continuous mode on an industrial scale (Sarin, Singh et al. 2006). To determine the effect of hydraulic loading rate, the experiments were conducted at a constant bed height of 20cm, and constant feed concentrations of 20mg/L, with hydraulic loading rate of 5, 10 and 15mL/mint. The effect of loading rate on the adsorption of Cr(VI) is shown by the breakthrough curve in Figure (11). Breakthrough generally occurred faster with higher flowrate of 15mL/min. The reason is that at higher flow rate, the rate of mass transfer increased, thus the amount of Cr(VI) adsorbed onto the unit bed height increases.

The adsorption capacity was lower as shown in Table (12), due to insufficient residence time of the solute in the column and diffusion of the solute into the pores of the adsorbent, therefore the solute left the column before equilibrium occurred. Adsorptive capacity decrease from 2.42 to 1.84 and 1.23mg/L, for flowrate of 5, 10, 15mL/min respectively. These results were in agreement with findings reported in Ko Porter, 2000 and Taty Castody et al, 2005 which was conducted for removal of metal ions by bone char and for removal of lead by sawdust in fixed bed study respectively (Ko, Porter et al. 2000, Taty-Costodes, Fauduet et al. 2005).

The increase in the steepness of the breakthrough curve and the decrease in adsorption capacity with the increase in flow rate (5-15mL/min) may be due to the fact that, when the residence time of Cr(VI) in the column is short because of higher flowrate, the contact time for Cr(VI) is less. Hence, chromium solution leaves the column before equilibrium is achieved. This reduces the removal efficiency. However, at lower flowrate, the residence time of Cr(VI) in the column is sufficient enough to diffuse into the adsorbent and reach the active sites of the adsorbent.

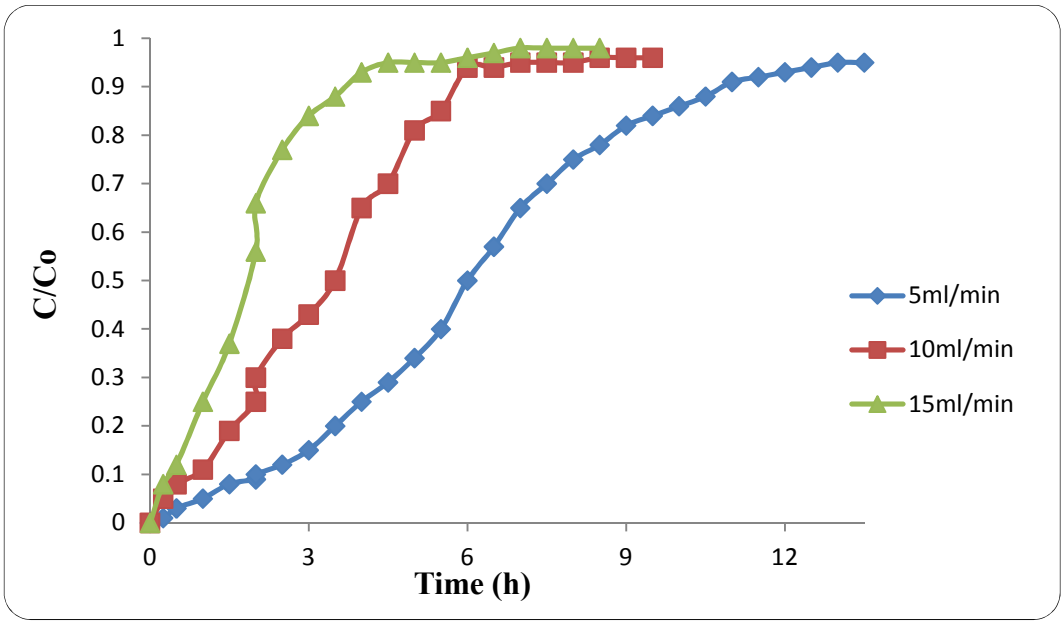

Figure 11: Breakthrough curve for hydraulic loading rate variation

Similar results have been reported by Senthilkumar et al. They reported the removal of chromium by Sargassum polycystum in fixed bed column. They found that the adsorption capacity increases from 23.5mg/g to 25.8 and 29.1mg/g at a flowrate of 15, 10 and 5mL/min, respectively (Senthilkumar, Vijayaraghavan et al. 2010).

Table 12: Adsorptive capacity of alum sludge in fixed bed column study for variation of flow rate, bed hight and initial concentration.

Flow rate (mL/min)	Bed Height (cm)	Inlet concentration (mg/L)	Adsorptive capacity (at 50% t_b) (mg/L)
5	20	20	2.42
10	20	20	1.84
15	20	20	1.23
5	10	20	1.46
5	30	20	2.81
5	20	10	1.32
5	20	30	3.36

4.5.2 Effect of Bed Height

The experiments were carried out at constant feed concentration of 20mg/L and constant hydraulic loading rate 5mL/min. and with altering bed height at 10cm, 20 and 30cm. The result is shown in Figure (12). From the graph it is seen that, the effluent Cr(VI) concentration decreases with increasing bed height. This fact can be explained by the phenomenon that with the increase of bed height, the length of bed through which the influent passes also increases,

thus the amount of adsorbate used also increases which results in the increase in breakthrough time. In addition, higher bed results decrease in the solute concentration in the effluent at the same time. The slope of breakthrough curve was slightly decreases with increasing bed height, which resulted in a broadened mass transfer zone (Zulfadhly, Mashitah et al. 2001).

It was also inferred that the adsorbent bed of lesser height was saturated quicker than the adsorbent bed having a higher bed height thus leading to lesser breakthrough time. The adsorption capacity of the adsorbent increased with the increase in bed height and was found to be at the maximum at 30cm (2.81mg/g). This increase in adsorption capacity was due to an increase in the surface area of the adsorbent and larger bed height which provided more binding sites for sorption.

Similar results have been reported by Gokhale et al. using immobilized Spirulina platensis biomass in a packed column for adsorption of Cr(VI). They reported that the breakthrough time increases with the increasing bed height since more time was required to exhaust more adsorbent (Gokhale, Jyoti et al. 2009).

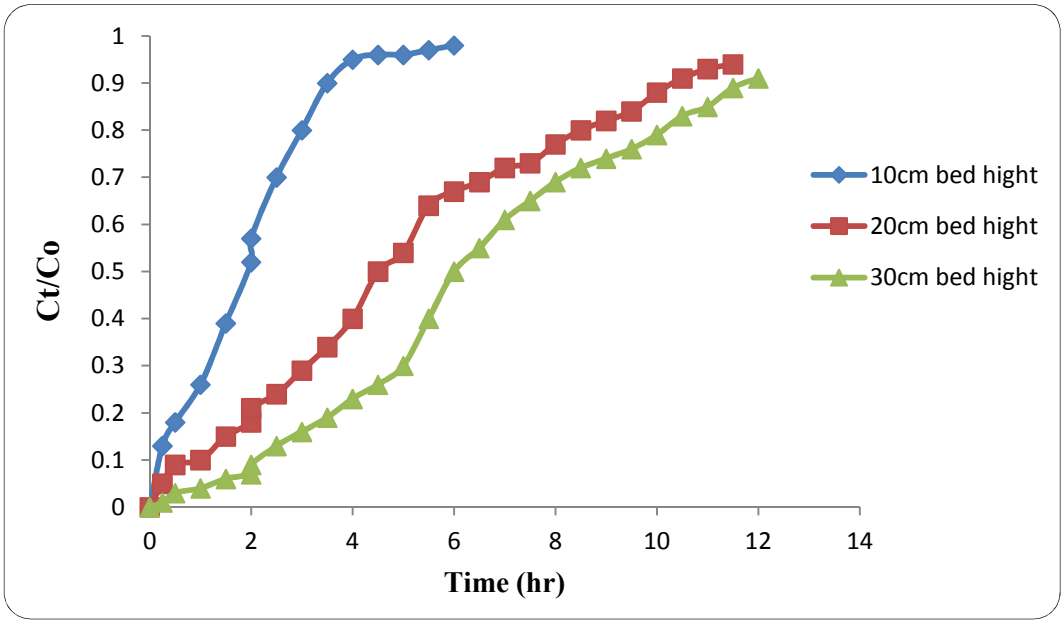

Figure 12: Breakthrough for bed height variation

4.5.3 Effect of Feed Concentration

The experiments were conducted with different initial feed concentration of 10mg/L, 20mg/L and 30mg/L with constant bed height of 20cm and hydraulic loading rate 5mL/mint. The results are demonstrated in the Figure (13), which shows that with increase of initial feed concentration, the breakthrough curve becomes steeper and the breakthrough time also decreases. At the interval of 60 minute, the value of C_t/C_o reached 0.1, 0.23 and 0.42 for inlet initial concentrations

of 10, 20 and 30mg/L respectively. As the feed concentration increases, metal loading rate increases which results in decrease of driving force for mass transfer for a fixed adsorption zone length. The larger the inlet concentration, the steeper is the slope of breakthrough curve. This is due to the increases of driving force and decreases in the adsorption zone length. Similar trends were obtained in literature for removal of lead from synthetic and real effluents using immobilized Pinus sylvestris sawdust in fixed bed column study (Taty-Costodes, Fauduet et al. 2005).

The adsorption capacity increase with increasing initial inlet concentration as shown in Table (12). This is due to the high driving force. The highest bed capacity of 3.36mg/g was obtained using 30mg/L inlet Cr(VI) concentration and flow rate of 5mL/min.

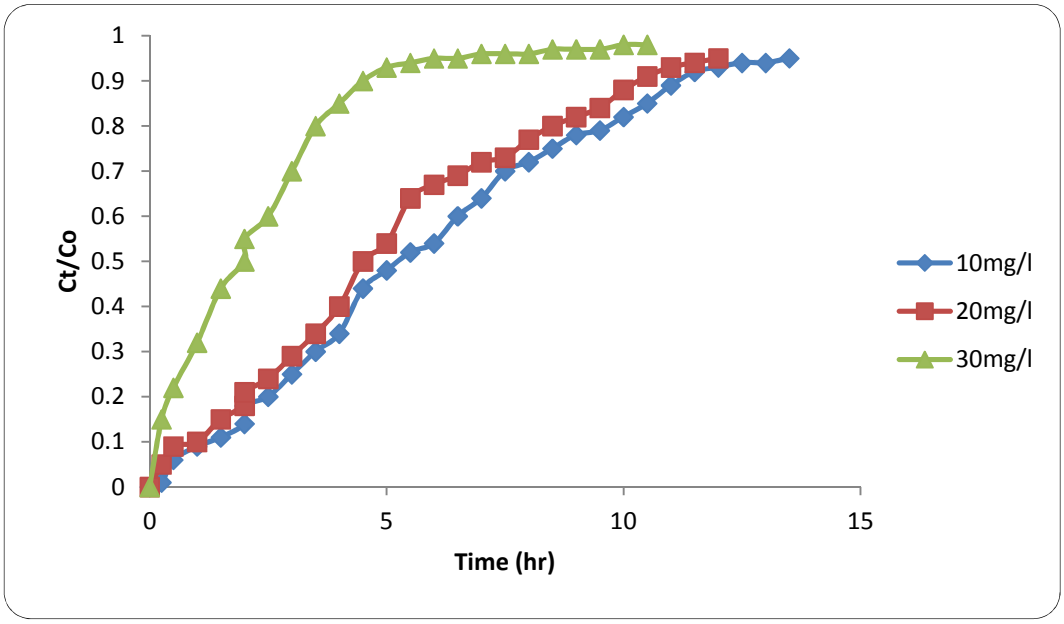

Figure 13: Breakthrough curve for Cr(VI) feed concentration variation

4.5.4 Modeling and Interpretation of Column Study

In order to facilitate the adsorption column design it is necessary to fit the adsorption data using established models and subsequently determine salient parameters associated with those models to determine their influence for optimization of the fixed bed adsorption process. Modeling of breakthrough curves was carried out using three established models, namely, bed-depth-service-time (BDST), Thomas and Yoon – Nelson models.

4.5.4.1 BDST model

The BDST model is based on physically measuring the capacity of the bed at different breakthrough values. The BDST model was formulated by Hutchins. He modified the Bohart Adam model and named it bed depth service time (BDST) model, which is obtained based on

different breakthrough values by varying bed depth and flowrate (Hutchins 1973). These model assumes that adsorbate interacts only on the surface of the adsorbent and ignores both interparticle mass transfer resistance and external film resistance. The graph was plotted against bed depth versus service time and shown in Figure (14) for 20, 50, and 50% adsorption. From the slop and intercepts model constants N_o and K_a was calculated according to Eq. (10).

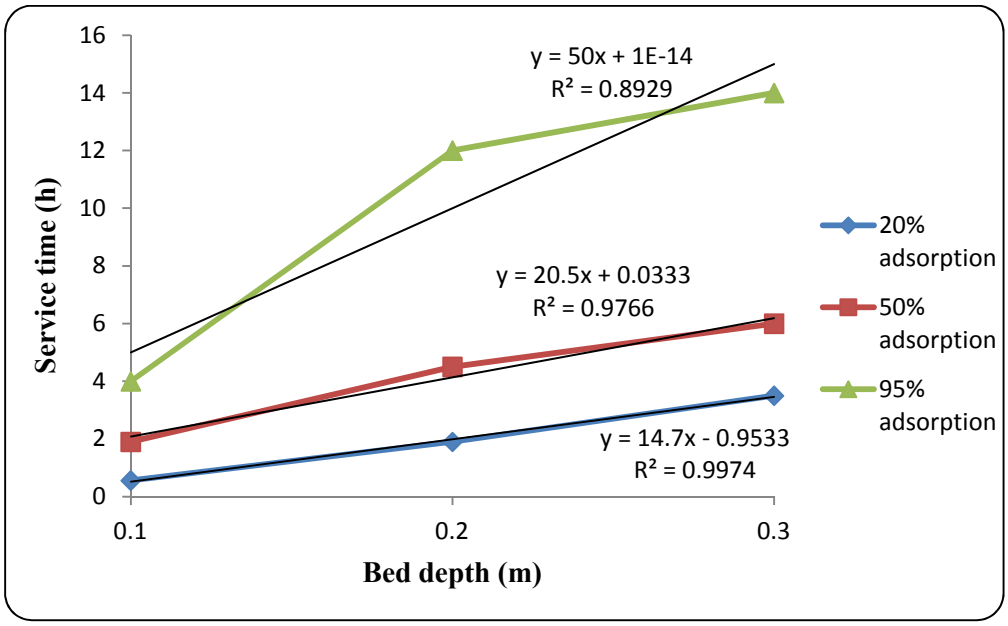

Figure 14: BDST model service time vs. bed depth plot, at flow rate of 5ml/min and feed concentration of 20mg/L

Table 13: BDST parameters at different breakthrough at flowrate 5mL/min and feed concentration of 20mg/L.

Break through adsorption	N_O mg/L	K_a L/mgmin	R^2
20%	3.25	0.028	0.997
50%	5.04	0.032	0.976
95%	10.31	0.010	0.892

A consistent increase in slopes from 1.4 to 5 for breakthroughs of 20%-95% indicate an increase in corresponding dynamic adsorption capacity N_o from 3.25 to 10.31 mg/L. On the adsorbent, some active sites remain unoccupied by metal ions at lower breakthrough value, and hence the adsorbent remained unsaturated. The dynamic adsorption capacity in such low breakthrough condition was consequently bound to be lower than the full bed capacity of the adsorbent (Kumar and Chakraborty 2009).

4.5.4.2 Thomas model

Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting steps (Taty-Costodes, Fauduet et al. 2005). Thomas model has been used by many researchers to study packed bed adsorption kinetics. The kinetic coefficient, K_T and the adsorption capacity of the bed, q_o were determined from the plot of $\ln[(C_o/C_e-1]$ against V, of Eq. (11) and shown in Figure (15,16 17). The results of K_T, R^2 and q_o are given in Table (14).

Table 14: Thomas model parameters at different conditions in fixe bed column study for removal of chromium by alum sludge.

Inlet concentration (mg/L)	Bed Height (cm)	HLR (mL/min)	k_T (L/(mgmin)	q_o (mg/g)	R^2
20	20	5	2.06	5.04	0.658
20	20	10	1.85	6.12	0.779
20	20	15	2.03	9.57	0.748
20	10	5	1.48	2.96	0.741
20	30	5	1.14	14.8	0.804
10	20	5	2.14	4.28	0.901
30	20	5	1.01	12.84	0.854

Thomas rate constant, K_T is dependent on flow rate, initial ion concentration and bed height. The maximum adsorption capacity, q_o increases with increase in flow rate and initial ion concentration but decreased with increase in bed height. The value of q_o increase from 5.04 to 9.57 mg/g for flow change from 5ml/min to 15ml/min and qo increase from 4.28 to 12.84mg/g for feed concentration change from 10mg/l to 30mg/l. These can be justified by taking into account the fact that the gradient concentration is the driving force of the sorption process. Thus, a higher driving force due to an increase in concentration of Cr(VI) results in an improved performance of the column packed with alum sludge. The value obtained also correlates with the data of other studies conducted on adsorption of chromium from wastewater by fixed bed column study (Tofan, Paduraru et al. 2015).

The values of K_T obtained in this work are similar to the ones obtained by Sivakumar and Palanisamy, 2009 (Sivakumar and Palanisamy 2009). And also in agreement with recent literature data reporting on the sorption of chrome ions from aqueous solution by olive stone in a fixed bed column (Blázquez, Hernáinz et al. 2009). High values of regression coefficients were determined indicating that the kinetic data conformed well to Thomas model in contrast with the report of Sivakumar and Palamisamy, 2009 but in agreement with the results obtained by Baek et al,2007 (Baek, Song et al. 2007, Sivakumar and Palanisamy 2009).

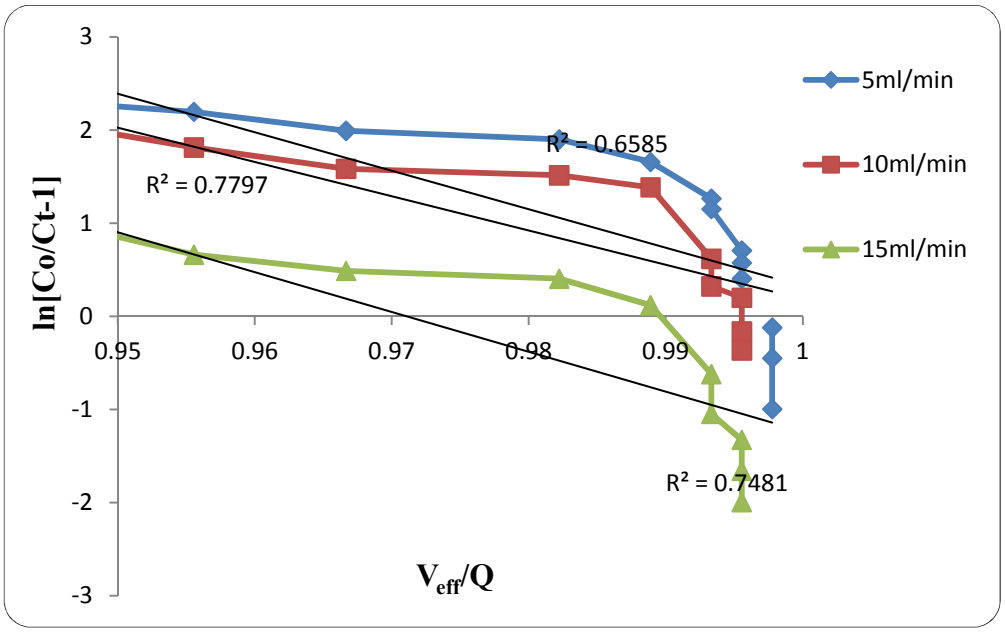

Figure 15: Graphical representation of Thomas model for loading rate variation

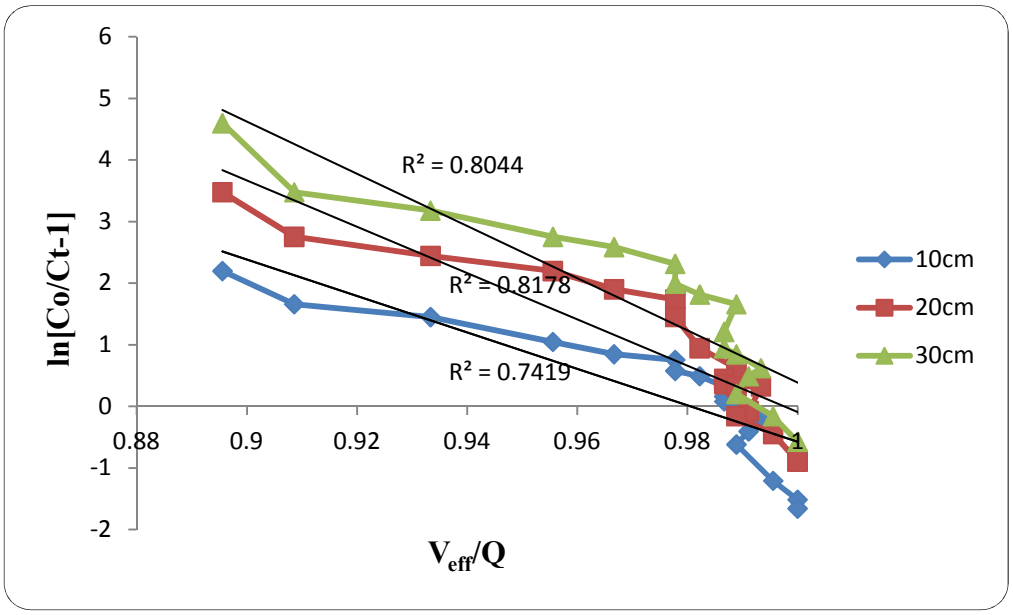

Figure 16: Graphical representation of Thomas model for bed depth variation

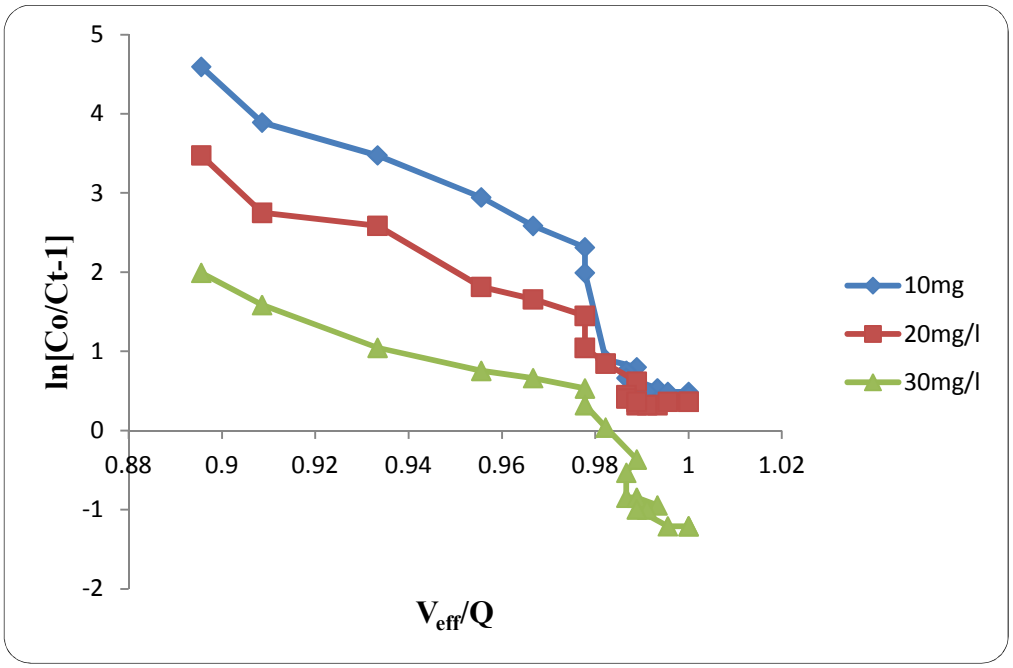

Figure 17: Graphical representation of Thomas model for feed concentration

4.5.4.3 Yoon Nelson mode

The Yoon Nelson model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and adsorbate breakthrough time on the adsorbent. Yoon and Nelson proposed a less complicated model based on the assumption that the rate of decrease in the probability of sorption for each sorbate molecule is proportional to the probability of sorbate breakthrough on the sorbent (Yoon and Nelson 1984).

The linearized model for a single component system is expressed as ln $[\frac{C_t}{C_o - C_t}]$ = k_{YN} - τk_{YN}, where, k_{YN} is the rate constant (per min), τ is the time required for 50% adsorbate breakthrough (min) which is calculated from Eq. (12). According to Yoon Nelson model the amount of metal ion sorbed in a fixed bed is half of the total metal ion entering the adsorption bed within 2τ period (Yoon and Nelson 1984).

The values of K_{YN} and τ are listed in Table (15) and the characteristics graph of Yoon Nelson for flow rate, bed depth and feed concentration was also shown in Figure (18,19,20).

Table 15: Yoon Nelson model parameters at different conditions in fixe bed column study for removal of chromium by Al-WTS

Inlet concentration (mg/l)	Bed Height (cm)	HLR (mL/min)	K_{YN} (per min)	τ (min)	R^2
20	20	5	0.009	342	0.933
20	20	10	0.012	252	0.982
20	20	15	0.013	156	0.986
20	10	5	0.017	108	0.973
20	30	5	0.009	360	0.968
10	20	5	0.008	312	0.945
30	20	5	0.013	120	0.988

It was found that the rate constant k_{YN} increases as flow rate increases. Because of less residence time of metal ion in adsorbent bed, time required for 50% adsorbate breakthrough (τ) decreased with increasing flow rate while k_{YN} shows slight decrease. The rate constant K_{YN} increases and the 50% breakthrough time τ decreased with increasing inlet concentration. With the bed height increase, the τ increases while the values of K_{YN} decreases. Linear plot of Yoon-Nelson model in different heights, flow rates, and concentrations is shown in Figures (18,19,20), respectively. As can be observed, the experimental data are fit well with the model.

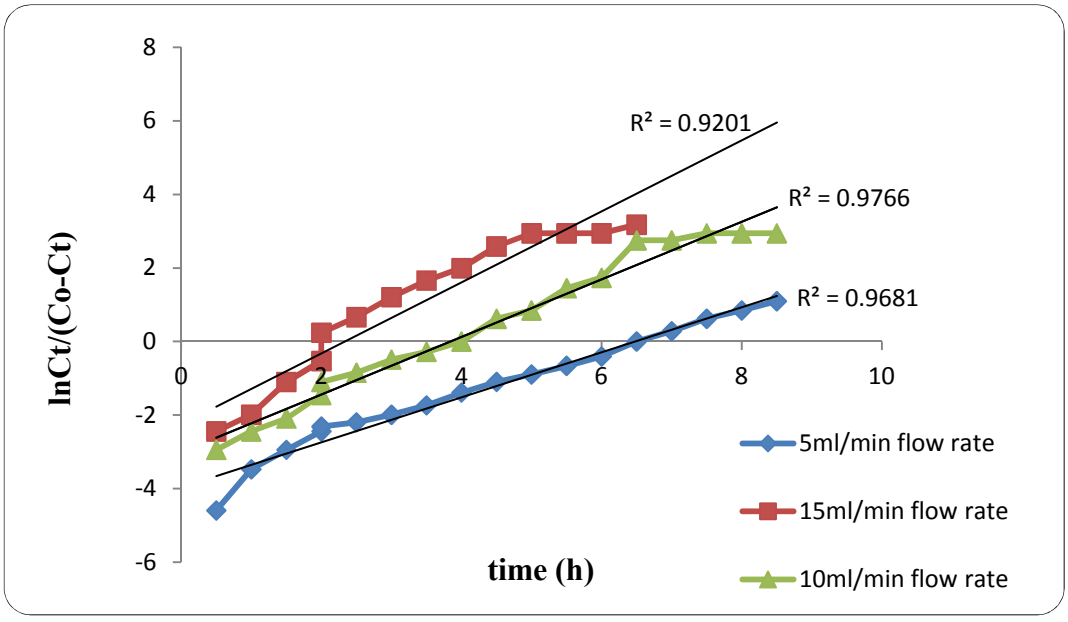

Figure 18: Graphical representation of Yoon Nelson model for hydraulic loading rate variation

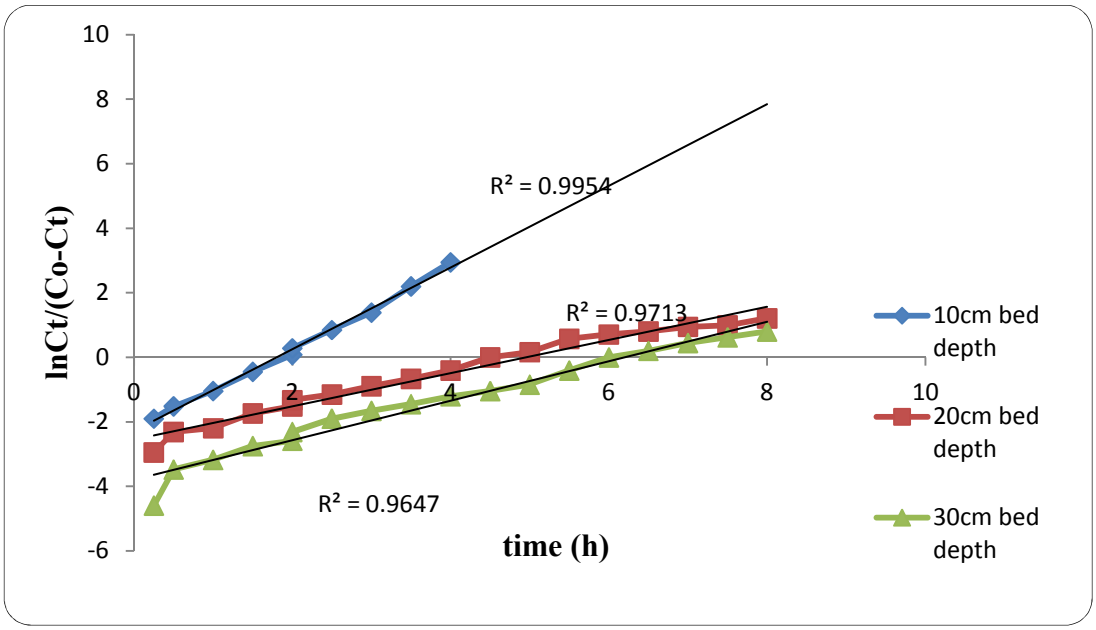

Figure 19: Graphical representation of Yoon Nelson model for bed depth variation

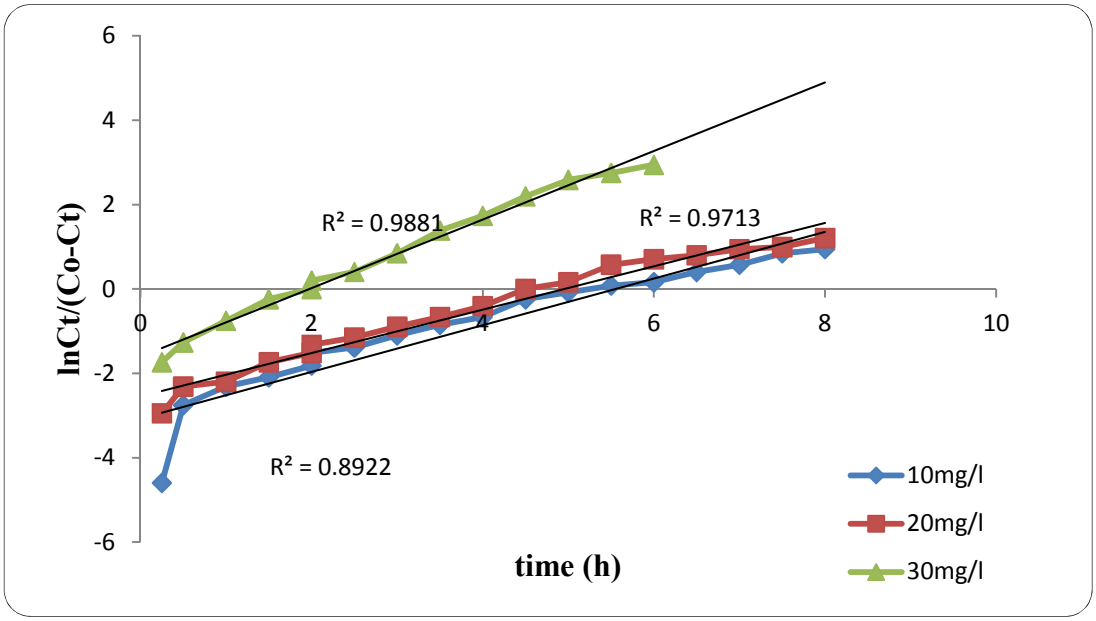

Figure 20: Graphical representation of Yoon Nelson Model For Feed Concentration

4.5.5 Application of fixed bed column for wastewater treatment

In order to facilitate large scale application, the AL-WRS was employed for the treatment of industrial wastewater (tannery wastewater) in fixed bed column study and their usability was assessed. Figure (21) shows the breakthrough curves for adsorption of Cr(VI) by AL-WTS. The t_b, t_e, q(mg/g), M_{total} , M_{ad} and removal efficiency are shown in the Table (17). As can be seen, AL-WTS show considerable ability for the removal of Cr (VI) from tannery wastewater.

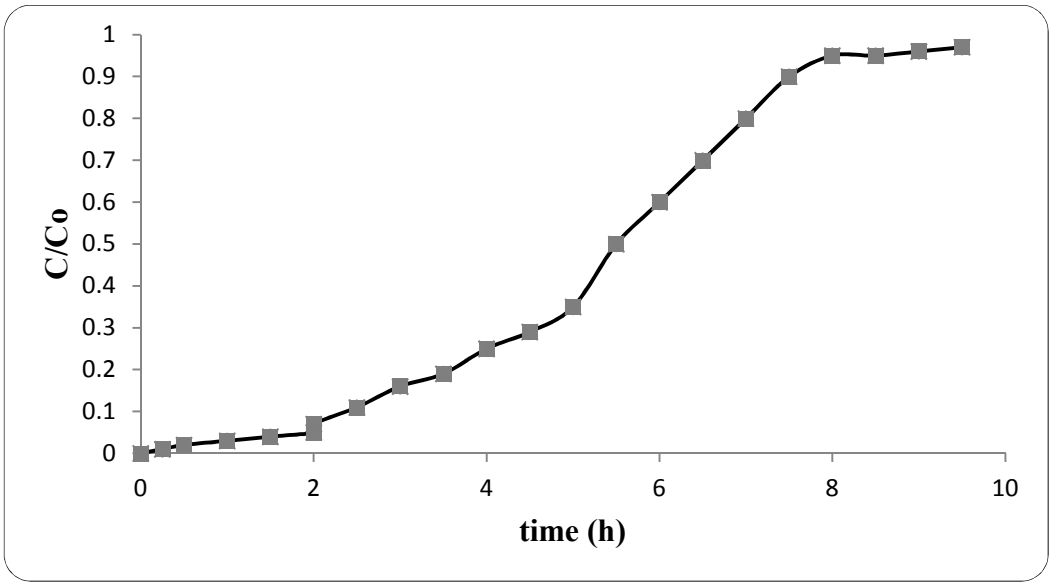

Figure 21: Breakthrough curve for Cr(VI) removal from wastewater by AL-WTS in fixed bed column study (at flow rate 5mL/min, bed height 30cm, Cr(VI) conc. 30mg/L)

Table 16: Fixed bed adsorption process parameters for adsorption of Cr(VI) from tannery wastewater by AL-WTS

Cr(VI)Concentration (mg/L)	t_b(50%) (hr)	t_e (hr)	M_{total} (mg)	M_{ad} (mg)	q (mg/g)	Removal efficiency %
30	5	8	144	112.4	7.5	78.1

For chrome removal from real wastewater by fixed bed study, the removal efficiency was found 78.8% and column adsorptive capacity was 7.5mg/g for feed concentration of 30mg/L of Cr(VI) and 30cm bed height and flowrate 5mL/min.

5. Conclusion

This work has demonstrated the application of water treatment sludge for chromium removal through batch and fixed bed column study. Response Surface methodology was used in batch wise experiment seeking to optimize Cr(VI) removal capacity of water treatment sludge. The optimum conditions for Cr(VI) removal from numerically optimized value was evaluated as pH 3.96, initial Cr(VI) concentration 10mg/L, adsorbent dose 2g, contact time 1h, temperature 35^{o}c. Under these optimum conditions, maximum Cr(VI) removal was obtained 68.52% for aqueous waste and 78.98% from tannery wastewater.

From statistical analysis (ANOVA), initial Cr(VI) concentration, the adsorbent dose, pH, contact time have significant effects on the Cr(VI) removal. The results of confirmation experiment were found to be in good agreement with the values predicted by the model. This demonstrates that to obtain a maximum amount of information in a short period of time, with the least number of experiments, RSM and CCD can be successfully applied for modeling and optimizing the adsorption process. The Langmuir and Freundlich isotherms are subjected to adsorption data to estimate adsorption capacity. The results gained from this study were well described by the theoretical Langmuir equation.

The Cr(VI) removal in the fixed bed column study was also studied. Effect of different parameter such as effect of flow rate, bed height and initial concentration were investigated. The results show that an increase in bed height and initial Cr(VI) concentration, increases the adsorptive capacity of water treatment sludge, but increasing flow rate, reduces the adsorptive capacity of the adsorbent. Meanwhile, the treatment of tannery wastewater in fixe bed column study was investigated and the result shows that 78.1% removal.

Generally, both in batch and fixed bed column experiment, the capacity of water treatment sludge for Cr(VI) removal is encouraging. Compared to other low cost adsorbents, water treatment sludge has shown appreciable adsorptive capacity. It was observed that water treatment sludge has the capacity to remove Cr(VI) from wastewater too. It was concluded that, water treatment sludge is a suitable material from which to develop a low-cost adsorbent for removal of chrome.

6. Recommendation

From the result of the study the following recommendation has been forwarded.

- As a byproduct of water treatment plant, WTS is a resource to be used for chrome removal from wastewater and it should not be simply discarded to the environment.
- From the experimental result and different literatures, WTS has shown high affinity for anions. So other research should also be conducted to evaluate the applicability of WTS for anion sorption from industrial wastewater too.

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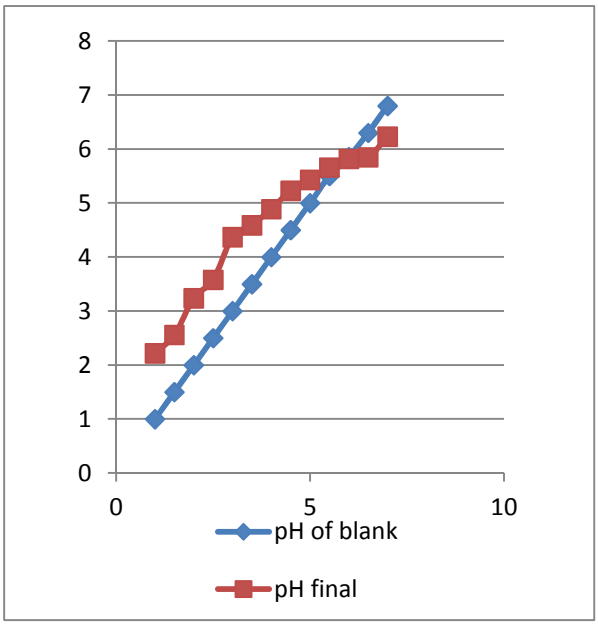
ANNEXS

Annex 1: pH at ZPC determination.



pH initial	pH of blank	pH final	pH change
1	1	2.22	1.22
1.5	1.5	2.56	1.06
2	2	3.24	1.24
2.5	2.5	3.58	1.08
3	3	4.37	1.37
3.5	3.5	4.59	1.09
4	4	4.89	0.89
4.5	4.5	5.23	0.73
5	5	5.43	0.43
5.5	5.5	5.66	0.16
6	5.85	5.82	-0.03
6.5	6.3	5.85	-0.45
7	6.8	6.23	-0.57
7.5	7.5	6.77	-0.73
8	8	7.5	-0.5

Annex 2: Aluminium determination

Several analytical techniques such as flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES) devoted to low-level metals determination, however, their present very high acquisition and operational costs. Spectrophotometry is a well-established analytical technique that provides low cost, simplicity and wide range of applications for aluminium determination in some food samples. Eriochrome cyanine R (ECR) has been used for the spectrophotometric determination of aluminium. Eriochromecyanine R (ECR), the most commonly used reagent for Al determination, was proposed as complexing agent in the presence of N,Ndodecyltrimethylammonium bromide (DTAB) as cationic surfactant.

Apparatus

Absorbance measurements were carried out with a UV-Vis spectrophotometer (Lamda 25, PerkinElmer Instrument, USA)

Reagents

All chemicals used were of analytical reagent grade. A 1000mg/L Al standard solution was used through all the experimental work. Working standard solutions of Al with different concentrations were prepared by appropriate diluting the stock solution. A 5 mmol/L eriochrome cyanine R (ECR) stock solution was prepared by dissolving 0.6704g of ECR in distilled water and makes a final volume of 250mL in volumetric flask. The 1mol/L acetate buffer solutions at different pH were prepared from sodium acetate and acetic acid.

Spectrophotometric determination of aluminium

Amount of Al in all of real samples was found by standard addition method. In order to build up analytical curves, an appropriate amount of each sample was added to different 25 mL volumetric flasks. To each flask, 1.5 mL of 0.4 mmol/LECR, 0.5mL of 1mmol/L DTAB and 5 mL of 1mol/L acetate buffer pH 5 and a known volume of a 10mg/L Al solution were added, in the sequence. After this, the obtained mixture was shaken in order to promote reaction and the volume was completed to the mark with distilled water. The absorbance of the final solution was measured at 584 nm against a blank solution containing only the reagents.

Annex 3: Calcium determination

Soluble calcium (as Ca2+ ions) in aqueous samples is usually determined by EDTA titration using Eriochrome Black T as indicator. In very dilute solutions, titration becomes impractical to use due to low levels of calcium ions which make the color change at the equivalence point difficult to see. Ultraviolet/visible (UV/vis) absorption spectroscopy is a technique that can be used to determine low levels of calcium. Because aqueous solutions of calcium salts are colorless and therefore do not absorb in the near UV and visible region, an organic complexing agent will be used in this determination. Arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)phenylarsonic acid]) forms highly colored 1:1 complexes with calcium and other metallic ions, allowing calcium levels to be determined using UV/vis spectroscopy.

Calcium-arsenazo complex is blue or purple in color, depending on pH, while uncomplexed arsenazo is wine-red.

Annex 4: Central composite design of experimental matrix with experimental and predicted value

Coded value					Actual value					% Removal	
A (mg/l)	B	C (g)	D (hr)	E (0c)	A (mg/l)	B	C (g)	D (hr)	E (0c)	Experimental	Predicted
-1	-1	-1	-1	-1	2	2	2	1	25	70	65.1
1	-1	-1	-1	-1	10	2	2	1	25	55.2	58.5
-1	1	-1	-1	-1	2	5	2	1	25	61.4	57.5
1	1	-1	-1	-1	10	5	2	1	25	50.5	50.9
-1	-1	1	-1	-1	2	2	10	1	25	89.4	93.8
1	-1	1	-1	-1	10	2	10	1	25	72.4	76.2
-1	1	1	-1	-1	2	5	10	1	25	80	86.2
1	1	1	-1	-1	10	5	10	1	25	74.9	68.6
-1	-1	-1	1	-1	2	2	2	6	25	90.5	81.1
1	-1	-1	1	-1	10	2	2	6	25	87.1	82.7
-1	1	-1	1	-1	2	5	2	6	25	67.5	73.4
1	1	-1	1	-1	10	5	2	6	25	63.2	75.1
-1	-1	1	1	-1	2	2	10	6	25	98.5	97.3
1	-1	1	1	-1	10	2	10	6	25	88.8	87.9
-1	1	1	1	-1	2	5	10	6	25	92.5	89.6
1	1	1	1	-1	10	5	10	6	25	89.2	80.3
-1	-1	-1	-1	1	2	2	2	1	40	65.8	65.2
1	-1	-1	-1	1	10	2	2	1	40	57.6	58.5
-1	1	-1	-1	1	2	5	2	1	40	54.9	57.5
1	1	-1	-1	1	10	5	2	1	40	52	50.9
-1	-1	1	-1	1	2	2	10	1	40	96.5	93.8
1	-1	1	-1	1	10	2	10	1	40	80	76.2
-1	1	1	-1	1	2	5	10	1	40	91.5	86.2
1	1	1	-1	1	10	5	10	1	40	69.2	68.6
-1	-1	-1	1	1	2	2	2	6	40	83	81.1
1	-1	-1	1	1	10	2	2	6	40	88.3	82.7
-1	1	-1	1	1	2	5	2	6	40	66	73.4
1	1	-1	1	1	10	5	2	6	40	84.6	75.1
-1	-1	1	1	1	2	2	10	6	40	98.5	97.2
1	-1	1	1	1	10	2	10	6	40	81.6	87.9
-1	1	1	1	1	2	5	10	6	40	92.5	89.6
1	1	1	1	1	10	5	10	6	40	75.2	80.3

-2	0	0	0	0	0.5	3.5	6	3.5	32.5	97.2	99.1
2	0	0	0	0	15.5	3.5	6	3.5	32.5	79	80.6
0	-2	0	0	0	6	1	6	3.5	32.5	90.6	95.6
0	2	0	0	0	6	7.0	6	3.5	32.5	79.3	77.5
0	0	-2	0	0	6	3.5	0.5	3.5	32.5	48.7	52.3
0	0	2	0	0	6	3.5	15.5	3.5	32.5	88	92.6
0	0	0	-2	0	6	3.5	6	0.5	32.5	47	47.7
0	0	0	2	0	6	3.5	6	9	32.5	78	80.5
0	0	0	0	-2	6	3.5	6	3.5	15	62	72.4
0	0	0	0	2	6	3.5	6	3.5	50	73.2	72.4
0	0	0	0	0	6	3.5	6	3.5	32.5	81.7	72.4
0	0	0	0	0	6	3.5	6	3.5	32.5	69.2	72.8
0	0	0	0	0	6	3.5	6	3.5	32.5	71.5	72.4
0	0	0	0	0	6	3.5	6	3.5	32.5	78	72.4
0	0	0	0	0	6	3.5	6	3.5	32.5	79.6	72.4
0	0	0	0	0	6	3.5	6	3.5	32.5	65	72.4
0	0	0	0	0	6	3.5	6	3.5	32.5	83.6	72.4
0	0	0	0	0	6	3.5	6	3.5	32.5	60.5	72.4