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Removal of Chromium from Waste Water Using Locally Available Adsorbents

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Removal of Chromium from Waste Water Using Locally Available Adsorbents

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Abstract

Different locally available adsorbents (aluminum slag, aluminum oxide hydroxide and aluminum oxide hydroxide saturated with fluoride) were tested for their efficiency in removing chromium from standard solutions prepared in the laboratory through batch mode experiments. Aluminum oxide hydroxide was found to be the most effective adsorbent for removal of Cr(III) whereas aluminum oxide hydroxide saturated with fluoride exhibited a highest adsorption efficiency for Cr(VI). Effects of pH, contact time, initial concentration and adsorbent dosage on the adsorption of Cr(III) and Cr(VI) were studied for these adsorbents. The investigation revealed almost a complete removal of Cr(III) (> 99%) over wide range of initial pH (3-10). And maximum removal of Cr(VI) (96 %) was obtained at initial pH 2. The adsorption capacities were also evaluated using Langmuir and Freundlich isotherms. Equilibrium data for adsorption of Cr(III) onto aluminum oxide hydroxide at varying adsorbent dose obeyed the two isotherms. The efficiency of the adsorbents towards the removal of chromium was tested using tannery waste effluent and found almost equally effective as the standard aqueous solution prepared in the laboratory.

Key words: Aluminum oxide hydroxide; adsorption of chromium; tannery wastewater.

1. Introduction

1.1. Chemistry of chromium and chromium compounds

Understanding of chemistry and geochemistry of chromium is important in developing remediation systems that can deal with industrial pollution. Chromium metal was discovered in 1797 by the French chemist, Louis Nicolas Vauquelin. And it was named chromium because of many different characteristic colors of its compounds (Greek word "chroma" meaning color) [1]. Chromium is a steel-gray, lustrous, hard metal. Like other transition metals, chromium has variable oxidation states. The most common oxidation states of chromium are 0, +2, +3, and +6, with +3 being the most stable. But only three oxidation states are found in nature; these are: Cr(0) which occurs in metallic form, Cr(III) which occurs in chromic compounds and Cr(VI) which occurs as soluble CrO_4^{2-} and $Cr_2O_7^{2-}$compounds. Pure Cr metal is extremely susceptible to combining with atmospheric oxygen. Therefore, it is almost impossible to have pure Cr in an oxygen-containing atmosphere because chromium is passivated by oxygen, forming a thin protective oxide surface layer that prevents oxidation of the underlying metal[1, 2].

Chromium can be combined with various nonmetals (oxygen, fluorine, chlorine, etc.) and polyatomic anions (such as nitrate, sulfate, etc.), forming relatively stable, soluble and insoluble compounds. More common are Cr(III) compounds such as chromium tribromide (insoluble), chromium nitrate (soluble), chromic hydroxide (insoluble), and chromic oxide (insoluble). In the chemical production industry, most chromium compounds are produced from sodium dichromate, which is the principal feedstock. Chemicals made from sodium dichromate include chromic acid, Cr(III) oxide, and potassium dichromate. Most Cr compounds are brightly colored and these colors are reflected in synonyms for their respective compounds. For example, basic chromium sulfate is known as chrome tan, Cr(III) oxide is known as chrome green, barium chromate is known as baryta yellow or lemon chrome, etc.

Under standard conditions, in the Cr-O-H_2O system, the Cr(III) stability zone occurs over a wide Eh (a measure of the tendency of a medium to be oxidizing or reducing) and pH field under both reducing to oxidizing and acid to alkaline conditions. Cr(III) generally forms soluble Cr^{3+} in the pH range from 0 to 8 and in the Eh range from approximately -0.4 V to 1.2 V. At a pH greater than 4 to about 7.5, Cr^{3+} dissolves to form soluble Cr(III) hydroxide cations ($CrOH^{2+}$ and $Cr(OH)_2^{+}$). At a pH of approximately 8.0, insoluble and amorphous $Cr(OH)_3$ forms, although small quantities of Cr(III) may be solubilized within this stability zone. At extreme pH and reducing conditions (above pH 12.0 and below Eh 0.0), Cr^{3+} forms soluble Cr(III) hydroxide anion, $Cr(OH)_4^{-}$. In aqueous environments under low Eh conditions, the main Cr(III) species are the Cr(III) cations: (Cr^{3+}) and $CrOH^{2+}$. In the Cr-O-H_2O system, under standard conditions, the governing reactions are [1]:

$$Cr^{3+} + H_2O \rightleftharpoons CrOH^{2+} + H^{+}$$

$$CrOH^{2+} + H_2O \rightleftharpoons Cr(OH)_2^{+} + H^{+}$$

$$Cr(OH)_2^{+} + H_2O \rightleftharpoons Cr(OH)_3 + H^{+}$$

$$Cr(OH)_3 + H_2O \rightleftharpoons Cr(OH)_4^{-} + H^{+}$$

Under standard conditions, in Cr-O-H_2O system, the Cr(VI) stability zone occurs over a much narrower range than the Cr(III) stability field. Cr(VI) species primarily occur under oxidizing (Eh > 0) and alkaline conditions (pH > 6.0). In this field, Cr(VI) generally forms soluble chromate (CrO_4^{2-}), hydrogen chromate ($HCrO_4^{-}$), or dichromate ($Cr_2O_7^{2-}$) anions depending on the concentration and acidity. At pH > 6.5 chromate ion is the dominant species. At pH < 6.5, $HCrO_4^{-}$ dominates at low concentrations (<0.03 mol/L), but at concentrations greater than 0.001 mol/L, $HCrO_4^{-}$ ions begin to change to $Cr_2O_7^{2-}$ which becomes the dominant entity at concentrations greater than 0.03 mol/L [2].

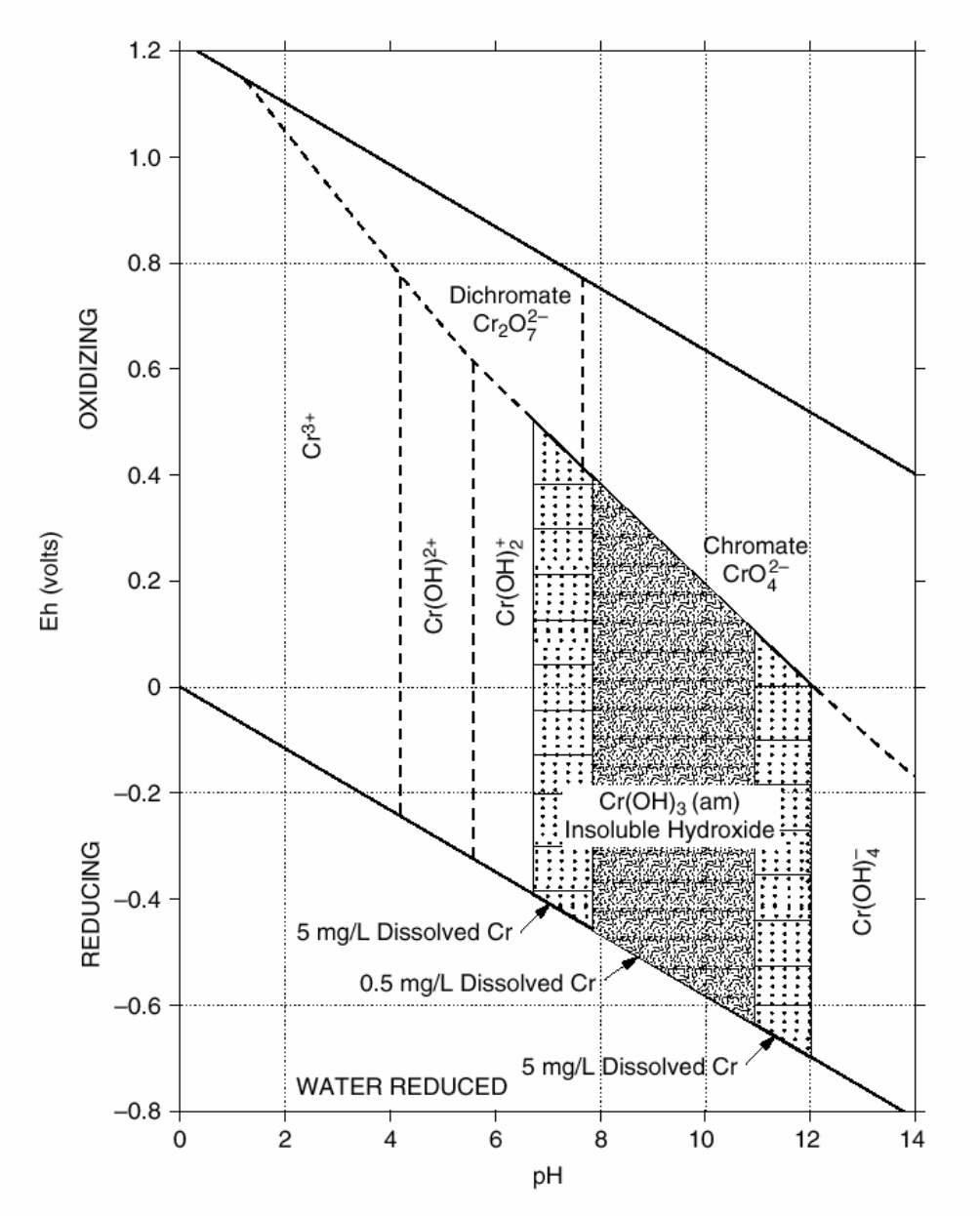

Fig. 1. Eh-pH diagram for the chromium–oxygen–water system [1].

1.2. Uses of chromium

Since its discovery, Cr has become a very important industrial metal because of its many applications in ferrous and nonferrous alloy metal fabrication, and in the chemical industry. Chromium compounds are used in a wide variety of industrial and

manufacturing applications including steel alloy fabrication, where they enhance corrosion and heat resistance and in plated product fabrication where they are used for metal decoration or increased wear resistance. They are also used in nonferrous alloy metal fabrication to impart special qualities to the alloys; in production and processing of insoluble salts, as chemical intermediates; in the textile industry for dyeing, silk treating, in the leather industry for tanning to obtain leather of desirable quality; in the manufacture of green varnishes, inks, paints, and glazes; as catalysts for halogenation, alkylation, and catalytic cracking of hydrocarbons; as fuel and propellant additives; and in ceramics [2, 3]. Uses of different forms of chromium are summarized in Table 1.

Table 1. Uses of different forms of chromium.

Form	Uses
Cr(O)	-Stainless steel production -Alloy production
Cr(III)	- Alloy manufacturing -Brick lining -Chrome plating - Leather tanning -Textiles -Copying machine toner
Cr(VI)	-Chrome plating -Leather tanning -Textiles -Copying machine toner

1.3. Toxicity and health effect of chromium

The presence of heavy metals in the environment is of major concern because of their toxicity to many life forms. Heavy metals like mercury, lead, cadmium, copper, chromium and nickel are toxic even in extremely minute quantities [5]. Since the majority of heavy metals do not degrade into harmless end products, their concentrations

must be reduced to acceptable levels prior to discharge of industrial effluents. Otherwise, they could pose threats to public health and affect the aesthetic quality of potable water. According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury, and lead [6].

Chromium contamination of soil and groundwater is one of the significant environmental problems today. Chromium is believed to be the second common inorganic contaminant after lead. The toxicity of chromium does not reside solely with the elemental form but varies greatly among a wide variety of chromium compounds. Oxidation state and solubility are crucial factors in this regard [7].

Chromium occurs in the environment primarily in two valence states, the oxidized hexavalent chromium, Cr(VI), and the less oxidized trivalent chromium, Cr(III). Under common environmental conditions of pH and Eh, Cr(III) compounds are sparingly soluble in water, whereas Cr(VI) compounds are quite soluble. Chromium(III) is considered to be essential to mammals for glucose, lipid, and protein metabolism and hence is an essential dietary element [7]. On the other hand, Cr(VI) is much more toxic and mobile in groundwater than the relatively immobile Cr(III) and possesses mutagenic and carcinogenic activity [8, 9]. In humans, Cr(VI) exposure caused marked irritation of the respiratory track and ulceration and perforation of the nasal septum in workers in the chromate producing and using industries. Ingestion of 1.0 g to 5.0 g of Cr(VI) as chromate results in severe acute gastrointestinal disorders, hemorrhagic diathesis, and convulsions. Death may occur following cardiovascular shock [1]. The maximum levels permitted in drinking water are 5 mg/L for trivalent and 0.05 mg/L for hexavalent chromium [10, 11]. But, there is still uncertainty regarding what daily dose of Cr(VI) is considered toxic and what ingestion concentration of Cr(VI) is acceptable.

1.4. Sources of chromium contaminations

Chromium contamination is primarily owing to its use in numerous industrial processes such as metallurgy, refractory, and chemical manufacturing involving numerous commercial processes like leather tanning, electroplating, manufacturing of dye, paint and paper milling, mining (ore refining), and wood preservation [12]. And human-caused one has recently been the focus of much scientific discussion, regulatory concern, and legal posturing. However, relatively high concentrations of naturally occurring dissolved Cr have been observed, usually associated with the very soluble chromates [1]. Thus, both anthropogenic and natural sources of Cr can lead to locally elevated concentrations in soils and waters. Common to many Cr contamination sites are the questions that continue to arise regarding the safety of the drinking water supply. As with most environmental challenges, questions of science compete with emotional and political responses and financial interests.

Chromium from anthropogenic sources is commonly released as Cr-bearing liquid or solid wastes such as chromate byproducts, ferrochromium slag, or Cr plating wastes. Such wastes can contain any combination of Cr(III) or Cr(VI) with various solubility. The nature and behavior of various forms of Cr found in wastewaters can be quite variable. The presence, form and concentration of Cr in discharged effluents depend mainly on the Cr compounds utilized in the industrial process, on the pH, and on the presence of other organic and inorganic processing wastes.

Chemicals containing Cr(VI) are principally used for metal plating (which use chromic acid H_2CrO_4), as dyes, paint pigments, and leather tanning. Thus, Cr(VI) will dominate in wastewater from the metallurgical industry, metal finishing industry (Cr hard plating), refractory industry and production or application of pigments (chromate color pigments and corrosion inhibition pigments). Cr(III) found mainly in wastewaters of the tannery, textile (printing, dying) and decorative plating industries. However, there is exception to these generalities owing to several factors. For example, in waste water where Cr(III) is the most expected form, the redox reactions occurring in sludge because of presence of

oxidized impurities can increase the concentration of Cr(VI). That is why adsorbents which have both cation and anion-exchangeable possibilities, are the objects of many studies.

Cr(VI) can be transported great distances in groundwater owing in part to its high solubility. But, if the transported Cr(VI) enters an area with relatively low Eh (in the presence of organic matter, Fe(II) and dissolved sulfides especially where pH is low) it may be transformed by reduction to, and precipitated as, Cr(III). Cr(III) generally is not transported great distances by groundwater because of its low solubility. However, Cr(III) can be transformed to the more soluble Cr(VI) if the redox conditions along the transport pathway change from reducing to oxidizing. Under natural conditions, Cr(III) has been found to be oxidized to Cr(VI) by Mn.

1.5. Chromium Remediation technologies

There are a number of different techniques of chromium remediation methods such as adsorption, chemical precipitation, solvent extraction, electrolytic extraction and ion exchange [1, 3, 13]. Since the biogeochemical properties of Cr and the associated matrix can affect the efficiency of many treatment strategies, an understanding of these properties is essential for choosing an effective treatment method. Once the properties of Cr, the associated matrix and treatment environments are understood, remedial alternatives for Cr can be addressed. Common chemical processes that occur in the remediation techniques are summarized in Figure 2. These chemical processes can be biologically mediated either directly through metabolic processes or indirectly as microorganisms change their geochemical environment. Chromium(VI) is far more mobile than Cr(III) and more difficult to remove from water. As a result, the equilibrium concentration of dissolved Cr(III) in natural waters is small compared to Cr(VI) concentration.

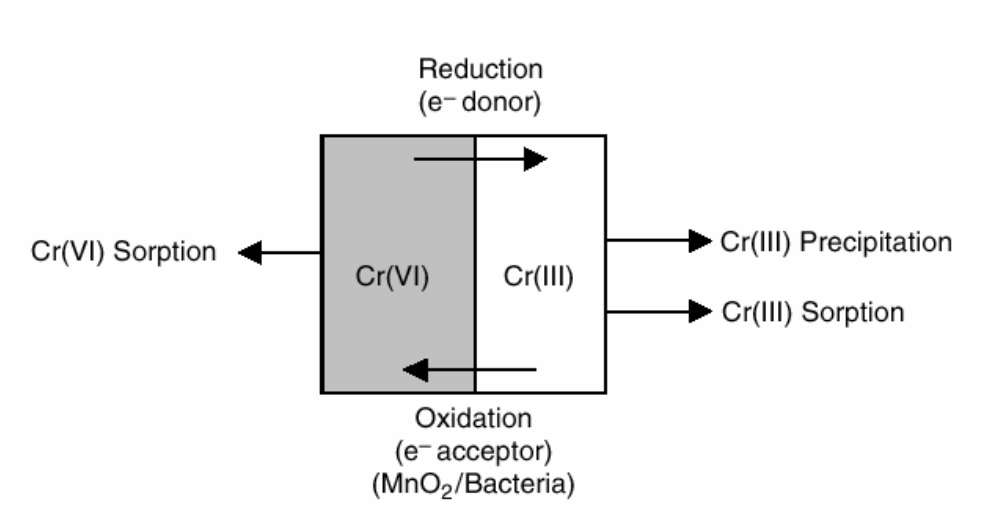

Fig. 2. Reactions for Cr(VI) and Cr(III)[1].

In recent years, the use of low-cost adsorbents has been considered to reduce chromium concentration from industrial waste effluents. Several such adsorbents have been examined by many scientists. Cr(III) is the primary form of Cr that is retained by adsorption. Cr(III) behaves like a positively charged ion when adsorbing onto surfaces. As pH increases, surfaces get deprotonated, increasing the attraction between Cr(III) and the surface. Adsorption of Cr(III) is therefore enhanced as pH increases. If the adsorbent has a high organic content, adsorption is also enhanced, as more sites are present for sorption to occur [1]. Although Cr(VI) is usually mobile in groundwater, it can be adsorbed, under some conditions. Cr(VI) behaves like an anion, so sorption of Cr(VI) decreases with increasing pH, in general. At low pH values, surfaces will be neutral or positively charged, leading to charge attraction. In addition, sorption of Cr(VI) becomes less important as the concentration of competing anions sorbed to solid surface increases. In such conditions, adsorption of Cr(VI) is negligible and hence adsorption processes are used indirectly to remediate Cr(VI); i.e., Cr(VI) is first reduced to Cr(III) [2].

Adsorption is a cost-effective and very important, particularly for developing countries, method of chromium removal from water and wastewater. Several adsorbents such as eucalyptus bark, saw dust, sand, clay mineral, charcoal, and various agricultural by products like peanut shell, wheat husk, sugarcane bagasse, etc, have been studied for their

chromium removal efficiencies in different parts of the world [3, 6, 8, 9, 12-33]. But, no study has been reported in the literature on the chromium removal using local adsorbents in Ethiopia. Hence there is a need to develop a method for removal of chromium from wastewater using local (Ethiopian) adsorbents. No study has been reported from any part of the world on chromium removal using the adsorbents used in the present study. Thus, this study also focused on putting locally available alternative adsorbents with better efficiency and lower cost.

1.6. Objectives and scope of the present study

1.6.1. General Objective:

The overall objective of this study was to develop a method for removal of chromium from wastewaters using locally available low-cost adsorbents.

1.6.2. Specific Objectives:

1. To examine chromium adsorption efficiencies of different locally available adsorbents (aluminum slag, aluminum oxide hydroxide and aluminum oxide hydroxide saturated with fluoride) following batch experiment.

2. To investigate the effect of different parameters such as contact time, pH, amount of adsorbent and initial concentration on chromium removal efficiencies of the selected adsorbent.

3. To apply the selected effective adsorbents to the real sample, collected from tannery waste effluent.

2. Experimental

2.1. Materials and method

2.1.1. Adsorbents

Different locally available adsorbents that were tested for their chromium removal efficiency are: aluminum slag which was obtained from Awash Melkasa Aluminum Sulfate and Sulfuric Acid Factory, aluminum oxide hydroxide synthesized from aluminum sulfate and aluminum oxide hydroxide saturated with fluoride. Aluminum sulfate used for preparation of aluminum oxide hydroxide was obtained from the Addis Ababa Water Supply and Sewerage Authority that is produced locally by Awash Melkasa Aluminum Sulfate and Sulfuric Acid Factory.

The adsorbent (aluminum oxide hydroxide) was prepared by mixing 100 g of $Al_2(SO_4)_3$ in 500 mL of distilled water while stirring with magnetic stirrer. These amounts were taken arbitrarily for the time being without considering stoichiometry. The resulting lower pH of 2.72 was adjusted to pH of 7.00 using 2 M NaOH. This pH was chosen based up on the literature value at which hydrated alumina ($Al(OH)_3$) becomes stable. The precipitated solid material was filtered and dried at 50 ^{0}C in an oven. Then, the fractions of the dried material were treated at temperature of 200 ^{0}C using a furnace (calbolite, ELF modern). The heated adsorbents were cooled in a descanter until later use

2.1.2. Chemicals, reagents and standard solutions

Chromium(III) chloride hexahydrate (Riedel-deHaen, Germeny) and potassium dichromate (BDH, England) were used as sources of Cr(III) and Cr(VI) ions. All solutions were prepared in distilled and de-ionized water to avoid errors in the results. Stock standard solution of chromium metal (1000mg/L, BUCK SCIENTIFIC PURO-GRAPHIC^{tm}, USA), prepared as nitrates in 2% HNO_3, was used as calibration standards

for determination of chromium concentration using flame atomic absorption spectrometer. 0.2 M NaOH and 0.2 M HCl were used to adjust pH.

Stock solutions of Cr(III) and Cr(VI) at a concentration of 1000 mg/L were prepared by dissolving 5.1240 g of analytically pure $CrCl_3.6H_2O$ and 2.3725 g of $K_2Cr_2O_7$ in 1L volumetric flask and diluted to the mark with de-ionized water. Further working solutions were made by appropriate dilutions. Standard solutions of chromium metal were prepared by diluting secondary stock solution of 10 mg/L.

2.2. Instrumentation

Studying chromium removal efficiency of adsorbents involves determination of amount of chromium in the effluent solutions before and after adsorption takes place. This was done using Flame Atomic Absorption Spectroscopy (FAAS) BUCK SCIENTIFIC MODEL 210 VGP, East Norwalk, USA) equipped with deuterium ark background corrector, nebulizer and hallow cathode lamp corresponding to metal of interest, in this case chromium, using air-acetylene flame. The operating conditions of AAS employed for each analyte are given in Table 2.

To determine concentration of chromium in the filtrates, four series of standard chromium solutions in the range of 0.05 – 3 mg/L were prepared by diluting the stock solution of chromium with de-ionized water. A blank (de-ionized water) and standards were run in flame atomic absorption spectrometer and four points calibration curves were established (Table 3). Then, sample solutions were aspirated in to the AAS instrument and direct readings of total chromium concentrations were recorded. Three replicate determinations were carried out on each sample. The amount of Cr adsorbed was then calculated from the difference between the amount before and after adsorption.

Table 2. Instrumental operating conditions for flame atomic absorption spectrometer.

Element	λ	DL	SW	Lamp energy (eV)
Cr	357.9	0.05	0.7	3.7

λ; wavelength (nm), DL; detection limit (mg/L), SW; slit width (nm)

Table 3. Series of working standards for determination of chromium in filtrates using flame atomic absorption spectrometer.

Experiments	Concentration of standards, in mg/L	Correlation coefficient
Contact time optimization for Cr(III)	0.05, 0.3, 1.5, 3.0	0.9992
pH optimization for Cr(III) and Cr(VI)	0.05, 0.3, 1.5, 3.0	0.9994
Experiments on dose of adsorbent for Cr(III)	0.05, 0.3, 1.5, 3.0	0.9998
Experiments by varying initial conc. of Cr(III)	0.5, 1.0, 1.5, 3.0	0.9996
Varying contact time and dose of adsorbent for Cr(VI)	0.05, 1.5, 3.0	0.9997
Varying initial conc. for Cr(VI) and real sample analysis	0.05, 0.3, 1.5, 3.0	0.9997

Mass of adsorbents and mass of different chemicals whenever the stock solutions were prepared from solid chemicals was measured using analytical balance of 0.01 g accuracy (Adam Equipment Co. Ltd, Mil Ton Kenyes, U.K.; Model No. WL3000). pH of different solutions was measured using pH meter (pH 301 GLP Bench pH/mv/Ion/^{0}C meter microprocessor, PC compatible, Serial No. 511919, HANNA instruments, Portugal). Magnetic stirrer with hot plate (Model 04803-02, Cole-Parmer Instrument, U.S.A.) was used for stirring the mixture of adsorbent and Cr solution in 250 mL conical flask at

known time intervals. After the adsorption experiments the mixture was centrifuged for 10 minutes using LABOFUGE I (Heraeus-Christ GMBH Osterode, HC121).

2.3. Adsorption experiments

2.3. 1. Adsorption experiments of Cr(III)

Batch mode experiments for Cr(III) were carried out in 250 mL conical flask at room temperature (22 ± 2). Chromium adsorption as a function of equilibrium time, pH, amount of adsorbent and initial concentration was studied. In order to optimize contact time, 2 g of the adsorbent was stirred with 50 mL of 40 mg/L of Cr(III) solution at different time intervals (0, 2, 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, and 100 min). At the end of the stirring period the samples were centrifuged at 8000 rpm for 10 min and filtered through Whatman No. 1 filter paper. The concentrations of Cr in the filtrate were determined using flame atomic absorption spectroscopy. The same experiment was repeated using 50 and 60 mg/L of Cr(III) solutions. To study the effect of pH on Cr(III) adsorption, the initial pH of 50 mL of 40 mg/L Cr(III) solutions were adjusted to different pH values (2, 3, 4, 5, 6, 7, 8, 9 and 10) using 0.2 M NaOH and 0.2 M HCl. Then, 1 g adsorbent was equilibrated with these solutions for 60 min and the filtrates were analysed for the effect of pH on Cr(III) adsorption. The effect of adsorbent dosage was also studied by varying the amount of adsorbent (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.8, 2.2, 2.6, 3.0, and 3 g) on an initial concentration of 40 mg/L at pH 3.8 for a contact time of 60 min. In another set each 50 mL of Cr(III) solutions at varying concentrations (0, 10, 20, 40, 60, 80, 100 mg/L) were introduced into the conical flask containing 1 g of the adsorbent and stirred for 60 min and the filtrates were analysed for the effect of Cr(III) concentration.

2.3.2. Adsorption experiments of Cr(VI)

In similar manner as Cr(III), batch experiments for Cr(VI) were carried out in 250 mL conical flask at room temperature. Chromium adsorption as a function of pH, equilibrium time, amount of adsorbent and initial concentration was studied. To study the effect of pH, 50 mL of 10 mg/L Cr(VI) solution was stirred for 60 min with1.5 g adsorbent, at room temperature and at different initial pH values (2, 3, 4, 5, 6, 7, 8, and 9) of the solution. At the end of the stirring period the samples were centrifuged at 8000 rpm for 10 min and filtered through Whatman No. 1 filter paper. The concentrations of Cr in the filtrate were determined using flame atomic absorption spectroscopy. 1 g of the adsorbent was stirred with 50 mL of 10 mg/L of Cr(VI) solution for different time intervals (0, 2, 5, 10, 20, 30, 40, 60, 80, and 120 min) in order to see the effect of contact
time. The effect of adsorbent dosage was studied by varying the amount of adsorbent (0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.8, 2.2 and 2.6 g) on an initial concentration of 10 mg/L at pH 2 for a contact time of 60 min. For the effect of Cr(VI) concentration, various initial concentrations of 50 mL of Cr(VI) solution such as 10, 20, 30 , 40 and 50 mg/L were used.

2.3.3. Adsorption experiment with real sample

Chrome tan effluent was collected from Hafde Tannery PLC which is a private leather tanning industry in Addis Ababa around Alemgena, at discharge point. The chrome tan liquor had pH 3.8 and 5520 mg/L total chromium concentration. In order to study the efficiency of the adsorbent for this real sample, the effluent was diluted 25 times and the resulting solution was stirred with 2 g of aluminum oxide hydroxide for 60 min at initial pH of 3.8 and 5.0.

3. Results and Discussion

3.1. Preliminary test and selection of adsorbent

The first objective of this study was selecting the most efficient locally available adsorbent for the removal of both forms of chromium. To achieve this objective, different locally available adsorbents were tested for their effectiveness in removing chromium. Note that for the time being different parameters such as dose of adsorbent, contact time, initial concentration and initial pH were taken without any knowledge of optimum quantity as these parameters were not yet optimized for those adsorbents.

The first adsorbent tested was aluminum slag obtained from Awash Melkasa Aluminum Sulfate and Sulfuric Acid Factory. The results obtained (Table 4 and 5) show that aluminum slag is not efficient in removing both forms of chromium. After stirring for about 3 h with 4 g of the slag, only about 20% removal efficiency for Cr(VI) and 0 % for Cr(III) was obtained.

Table 4. Results of preliminary adsorption experiments for chromium(VI) with aluminum slag (contact time 3 h, initial pH 4.8)

Exp. No.	Amount of adsorbent (g)	Initial conc.(mg/L)	Final conc. (mg/L)	Average final conc. (mg/L)	% Removal
1	4	36	26.70 29.00 31.60	29.40 ± 2.45	18.33
2	4	20	15.90 15.50 16.00	15.80 ± 0.50	21.00
3	20	36	17.00 17.30 17.00	17.10 ± 0.17	52.50

Table 5. Results of preliminary adsorption experiments for chromium(III) with aluminum slag.

Exp. No.	Contact time (hour)	Amount of adsorbent (g)	Initial pH	Initial conc. (mg/L)	Final conc. (mg/L)	Average final conc. (mg/L)	% Removal
1	3	4	3.8	22	21.00 22.00 23.00	22.00 ± 1.0	0

The next adsorbent that was tested for removal efficiency of chromium was aluminum oxide hydroxide. The results obtained for this experiment (Table 6 and 7) show that only about 10 % Cr(VI) removal efficiency was obtained with 4 g of aluminum oxide hydroxide after stirring for 2 h. But about 100% Cr(III) removal efficiency was obtained with 3 g of aluminum oxide hydroxide after stirring for 2h. Thus, aluminum oxide hydroxide was found to be very efficient for removal of Cr(III), but not for Cr(VI).

Table 6. Results of preliminary adsorption experiments for chromium(VI) with aluminum oxide hydroxide (contact time 2h, initial pH 4.8, initial conc. 25 mg/L)

Exp. No.	Amount of adsorbent (g)	Final conc. (mg/L)	Average final conc. (mg/L)	% Removal
1	4	21.85 21.64 21.96	21.82 ± 0.16	12.7
2	8	17.55 17.38 16.99	17.31 ± 0.29	30.8
3	12	13.78 13.57 13.25	13.53 ±0.27	45.9

Table 7. Results of preliminary adsorption experiments for chromium(III) with aluminum oxide hydroxide (contact time 2h, initial pH 3.8, initial conc. 50 mg/L)

Exp. No.	Amount of adsorbent (g)	Final conc. (mg/L)	Average final conc. (mg/L)	% Removal
1	1	0.14 0.13 0.14	0.136 ± 0.01	99.73
2	2	ND	ND	99.99
3	3	ND	ND	99.99

Finally, the adsorbent tested was aluminum oxide hydroxide saturated with fluoride (Table 8 and 9). As one can easily see from the results tabulated below, aluminum oxide hydroxide saturated with fluoride seems very efficient adsorbent for removal of both forms of chromium. About 90 % and 99 % removal of Cr(VI) and Cr(III), respectively was achieved with 4 g of the adsorbent after 2 h of stirring. This is very interesting because the adsorbent was initially used for removal of fluoride exhaustively and still effective in removing both forms of chromium.

Table 8. Results of preliminary adsorption experiments for chromium(VI) with aluminum oxide hydroxide saturated with fluoride (amount of adsorbent 4g, initial pH 4.8, initial conc. 25 mg/L)

Exp. No.	Contact time (hour)	Final conc. (mg/L)	Average final conc. (mg/L)	% Removal
1	2	2.10 2.03 2.42	2.18 ± 0.21	91.27
2	6	1.81 1.85 1.84	1.83 ± 0.02	92.67
3	12	1.29 1.17 1.25	1.24 ± 0.06	95.05

Table 9. Results of preliminary adsorption experiments for chromium(III) with aluminum oxide hydroxide saturated with fluoride (amount of adsorbent 4g, initial pH 3.8, initial conc. 22 mg/L)

Exp. No.	Contact time (hour)	Final conc. (mg/L)	Average final conc. (mg/L)	% Removal
1	2	0.10 0.21 0.14	0.15 ± 0.06	99.25
2	6	ND	ND	99.99

Here the interesting finding is that the original material, aluminum oxide hydroxide, was found ineffective towards removal of Cr(VI), but when saturated with fluoride it became very effective adsorbent. This is probably due to poor exchange of OH^- ion for Cr(VI) because of strong bond of hydroxide group of the adsorbent. And when fluoride is added to the surface through specific interaction, bond of hydroxide group to the adsorbent surface will be weakened and easily exchange for hexavalent chromium species.

Based on the above experiments, aluminum oxide hydroxide was found to be the most effective adsorbent and selected for removal of Cr(III) whereas aluminum oxide hydroxide saturated with fluoride exhibited a highest adsorption efficiency for Cr(VI). Then, further experiments were conducted using these selected adsorbents to study effects of different parameters (contact time, initial pH, amount of adsorbents, and initial concentration).

3.2. Adsorption of Cr(III) onto aluminum oxide hydroxide

3.2.1. Effect of contact time

In order to optimize equilibrium time for the removal of Cr(III), adsorption experiments were carried out at an initial concentration of 40, 50 and 60 mg/L with 2 g adsorbent at different time intervals (2 – 100 min). Percent removal of Cr(III) for 40 mg/L solution (Table 10) and the plot of percent adsorption of Cr(III) on these various initial concentration at different time intervals (Fig. 3) reveals that the rate of percent chromium removal is higher at the beginning. This is probably due to larger surface area of the adsorbent being available at the beginning for the adsorption of chromium [3].

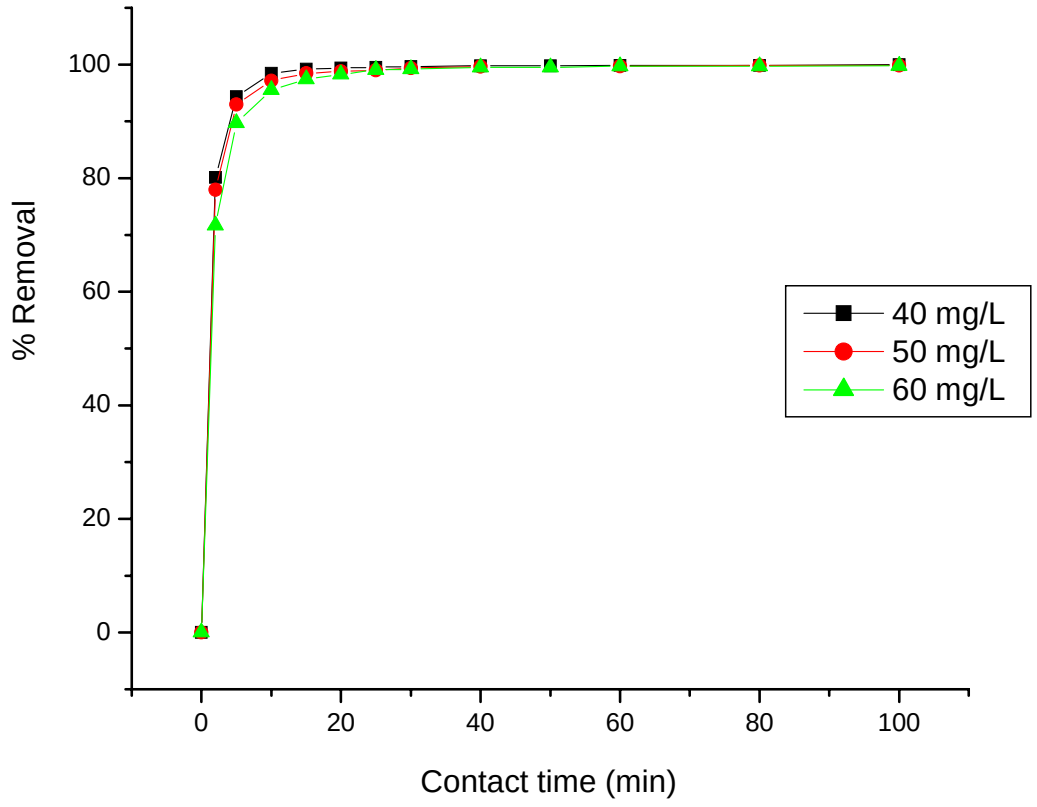

Fig. 3. Percent removal of Cr(III) as a function of equilibrium time (adsorbent dose 40 g/L, initial pH 3.8).

Table 10. Percent removal of Cr(III) at different time intervals (initial concentration 40 mg/L, adsorbent dose 40 g/L, initial pH 3.8).

Exp. No.	Contact time (min)	Final conc. (mg/L)	Average final conc. (mg/L)	% Removal
1	0	40	40	0
2	2	8.25 7.64 7.93	7.94 ± 0.31	80.15
3	5	2.27 2.15 2.38	2.27 ± 0.12	94.32
4	10	0.64 0.61 0.59	0.62 ± 0.03	98.46
5	15	0.34 0.33 0.33	0.33 ± 0.01	99.17
6	20	0.23 0.25 0.26	0.25 ± 0.02	99.39
7	25	0.19 0.19 0.21	0.20 ± 0.01	99.51
8	30	0.14 0.14 0.15	0.14 ± 0.01	99.65
9	40	0.07 0.10 0.12	0.09 ± 0.03	99.77
10	50	0.09 0.08 0.10	0.92 ± 0.01	99.77
11	60	0.05 0.05 0.05	0.05 ± 0.00	99.87
12	80	0.06 0.06 0.05	0.06 ± 0.01	99.86
13	100	ND	ND	99.99

Measurement of percentage Cr(III) adsorption as a function of time indicates that percentage adsorption of Cr(III) increased with an increase in contact time and attained equilibrium after 15 min irrespective of the concentration of Cr(III). But, the time taken to reach apparent equilibrium was increased at higher initial concentrations.

3.2.2. Effect of initial pH

pH value of the solution is an important factor that controls the uptake of Cr(III). The experimental results revealed that the percentage adsorption increased as the pH increases and reached 98% at pH 4 (Fig. 4). When pH was decreased below 3, the percent removal decreased, with only 0.1% removal at pH 2 indicating that the adsorbent is totally ineffective at very low pH.

Adsorption of Cr(III) at different pH can be explained by the species distribution of chromium in water and the nature of adsorbent surface. In acidic pH, the predominant species of Cr(III) cations are: Cr^{3+}, $CrOH^{2+}$ and $CrOH_2^{+}$ and under acidic conditions, the surface of the adsorbent becomes protonated and hence there is a decrease in the electrostatic attraction between the Cr(III) species and the adsorbent surface, with a consequent decrease in percentage adsorption. But as pH increases, the adsorbent surface becomes less protonated and will have strong attraction for cationic species of Cr(III). Another possibility for the increase in percentage removal of Cr(III) with increasing pH is formation of insoluble hydroxide precipitate. Generally adsorption of Cr(III) was higher at higher pH and decreased with decreasing pH for the reasons explained above. The removal efficiency curve shows that aluminum oxide hydroxide was effective over a wide pH range (3 –10).

Table 11. Percent removal of Cr(III) at different initial pH (initial concentration 40 mg/L, contact time 60 min, adsorbent dose 20 g/L).

Exp. No.	Initial pH	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal	Equilibrum pH
1	2	39.91 40.24 39.67	39.94 ± 0.29	0.15	4.56
2	3	3.66 3.46 3.51	3.54 ± 0.10	91.14	5.28
3	4	0.91 0.89 0.81	0.87 ± 0.05	97.83	5.57
4	5	0.47 0.44 0.43	0.4417 ± 0.02	98.90	5.68
5	6	0.77 0.70 0.69	0.717 ± 0.04	98.20	5.80
6	7	 1.77 1.81 1.81	1.80 ± 0.02	95.51	6.30
7	8	ND	ND	99.99	6.00
8	9	0.62 0.62 0.69	0.64 ± 0.05	98.39	6.10
9	10	0.14 0.12 0.14	0.13 ± 0.01	99.67	6.13

In the present study, the equilibrium pH was found to be greater than that of initial pH for initial pH values less than 6. But, final pH values were decreased to around 6 for initial pH values greater than 6. The resultant equilibrium pH as a function of initial pH is shown in Table 11. Increase in pH can be explained by protonation of adsorbent. When the initial pH values are less than 6, the adsorbent acts as a base and gets protonated. This process decreased H^+ ion concentration and resulted in increased pH. But, the adsorbent acts as an acid and gets deprotonated when the initial pH values are less than 6. As a

result, pH was decreased. Decrease in the pH may also be due to formation of insoluble Cr hydroxide which takes away OH^- ion from the solution.

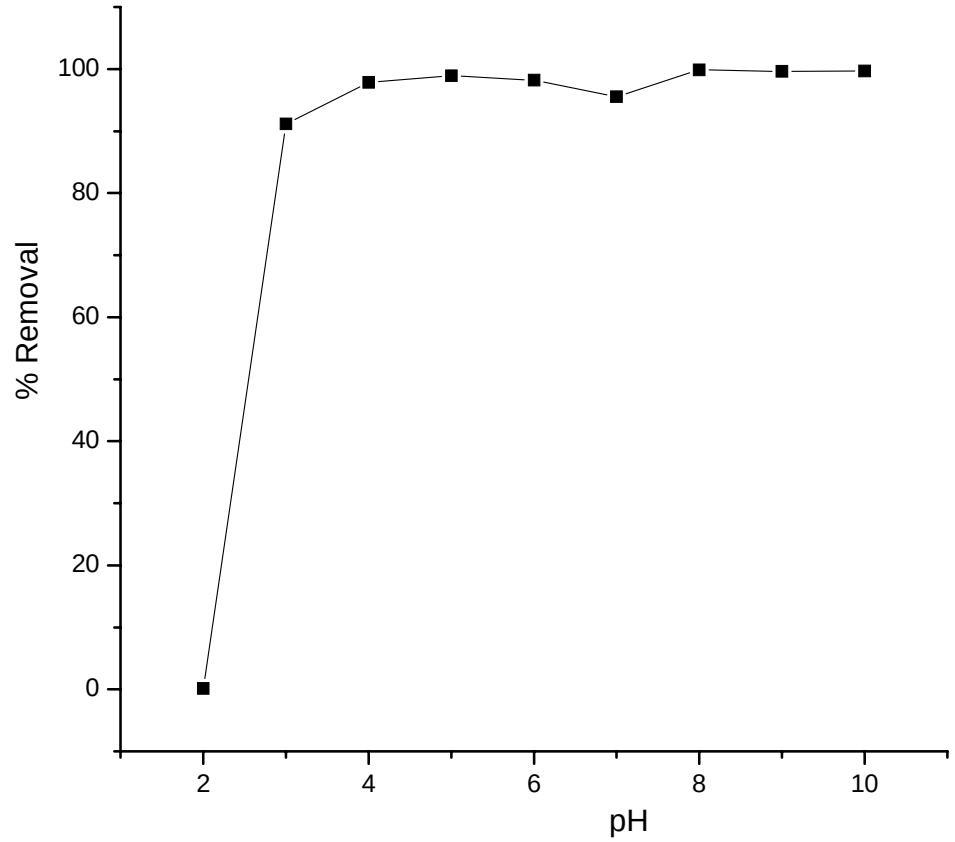

Fig. 4. Percent removal of Cr(III) as a function of initial pH (adsorbent dose 20 g/L, initial concentration of 40 mg/L, contact time 60 min).

3.2.3. Effect of adsorbent dose

The percentage adsorption of Cr(III) was studied by increasing adsorbent dose from 4 g/L to 60 g/L at 40 mg/L initial concentration of Cr(III) solution. The results indicated a complete (> 98 %) removal of Cr(III) with 20 g/L adsorbent dose after 60 min of contact time. It is observed that within the range of adsorbent dose studied, the percent removal increases with an increase in the amount of adsorbent up to an optimum amount of the adsorbent beyond which the percent removal remains nearly the same (Fig. 5). The

increase in the percentage adsorption with increase in the adsorbent dosage is due to the increase in the number of adsorption sites.

Table 12. Percent removal of Cr(III) at different adsorbent dose (initial concentration 40 mg/L, contact time 60 min, initial pH 3.8).

Exp. No.	Adsorbent dose (g/L)	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal	Removal capacity (mg/g)
1	0	40	40	0	
2	4	18.80 19.40 19.40	19.10 ± 0.35	52.25	5.23
3	8	13.75 13.36 13.71	13.61 ± 0.21	65.98	3.30
4	12	4.11 4.03 3.91	4.02 ± 0.10	89.95	3.00
5	16	1.46 1.42 1.43	1.44 ± 0.02	96.41	2.41
6	20	0.61 0.65 0.62	0.62 ± 0.02	98.44	1.97
7	24	0.30 0.28 0.29	0.29 ± 0.01	99.28	1.65
8	28	0.15 0.15 0.15	0.15 ± 0.00	99.63	1.42
9	36	0.11 0.12 0.10	0.11 ± 0.01	99.72	1.11
10	44	ND	ND	99.99	0.91
11	52	ND	ND	100	0.77
12	60	ND	ND	100	0.67

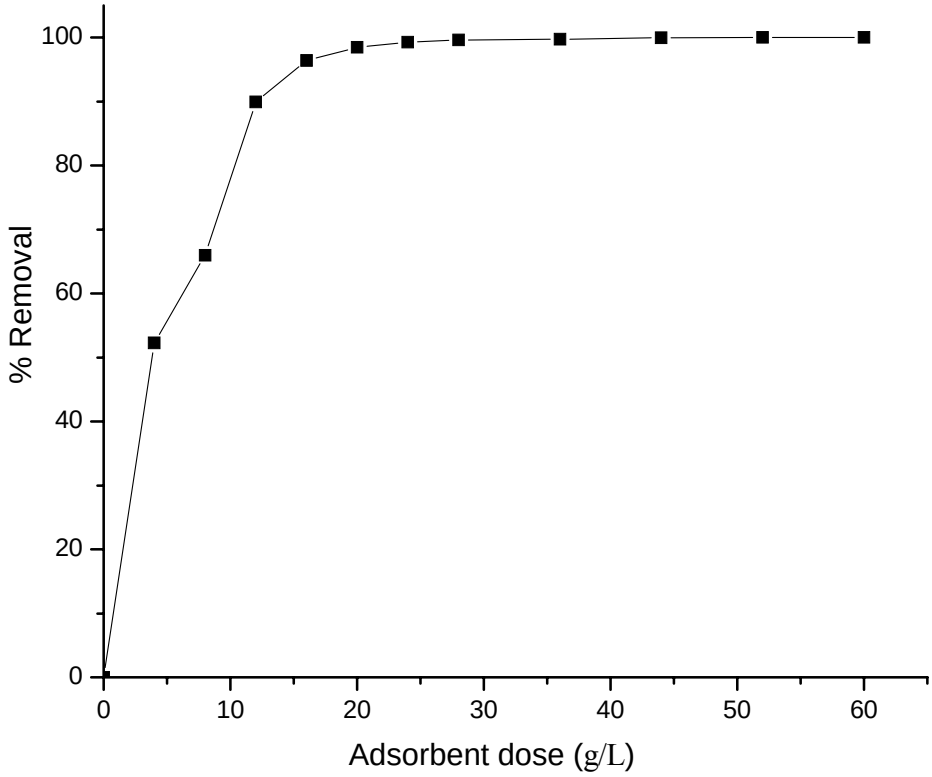

Fig. 5. Percent removal of Cr(III) as a function of amount of adsorbent (initial concentration 40 mg/L, contact time 60 min, initial pH 3.8).

3.2.4. Adsorption Isotherm

The adsorption equilibrium data obtained at a fixed initial concentration and varying adsorbent dose have been fitted into the linearized Langmuir and Freundlich adsorption isotherms. The simplest adsorption isotherm, Langmuir isotherm, is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. Linear form of Langmuir adsorption equation is given by:

$x/m = 1/X_m + 1/bX_mC_e$ or $C_e(x/m) = C_e /X_m + 1/bX_m$

which is in the form of $y = bx + a$ with slope $1/X_m$ and y-intercept $1/bX_m$. Where x/m is adsorption capacity, amount of solute adsorbed (in mg) per amount of adsorbent(in g), X_m is amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface also called monolayer capacity and b is a constant related to the heat of adsorption and C_e is equilibrium concentration [8].

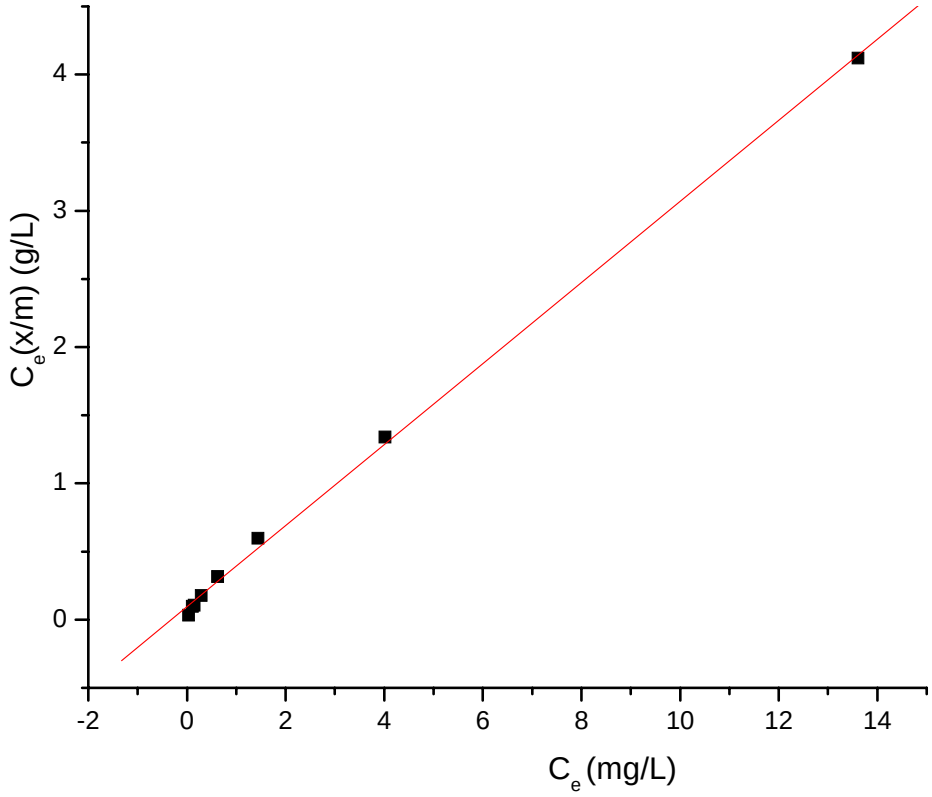

Fig. 6. Langmuir adsorption isotherm for adsorption of Cr(III) onto aluminum oxide hydroxide (initial concentration 40 mg/L, contact time 60 min, initial pH 3.8).

X_m and b were determined from the slope and intercept of the plot to be 3.36 mg/g and 3.35 L/mg, respectively. The adsorption capacity obtained in this experiment is in agreement with the results reported in the literature (maximum sorption capacity in the range of 3.23–11.8 mg/g [5]. Linear plot of $C_e/(x/m)$ versus C_e (Fig. 6) with 0.9994 regression coefficient (R^2) showed that the adsorption equilibrium obeyed Langmuir model exhibiting monolayer adsorption

Freundlich adsorption isotherm, which assumes heterogeneous surface conditions, states that the adsorption capacity, x/m is a function of the equilibrium concentration of the solute.

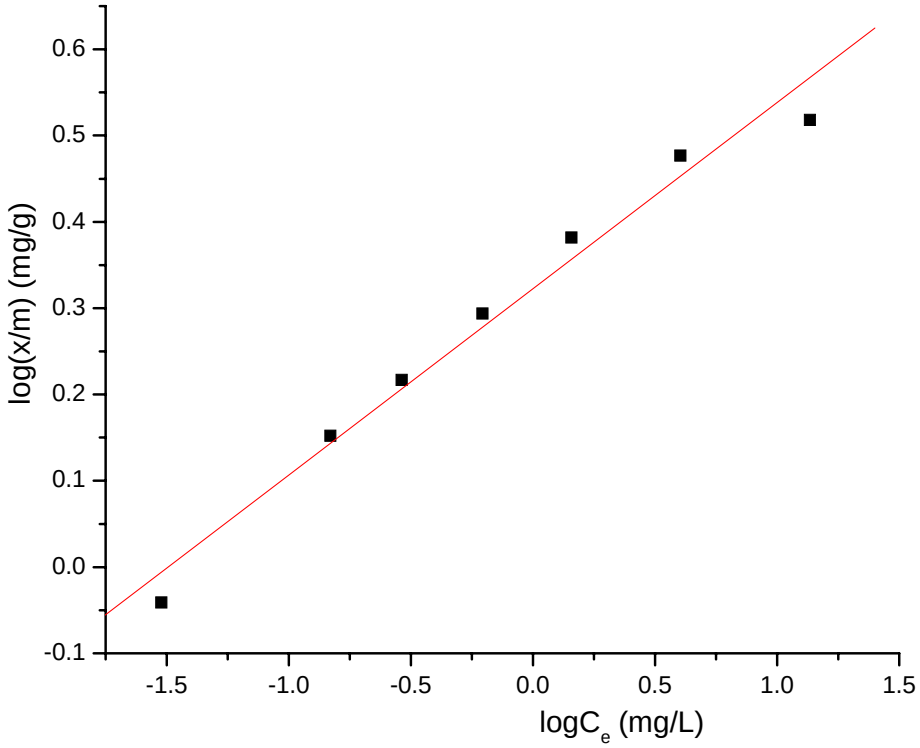

Fig. 7. Freundlich adsorption isotherm for adsorption of Cr(III) onto aluminum oxide hydroxide (initial concentration 40 mg/L, contact time 60 min, initial pH 3.8).

The linear form of Freundlich equation is expressed as:

$$\log(x/m) = \log(K_f) + 1/n \log(C_e)$$

where K_f is constant related to adsorption capacity, 1/n is constant related to adsorption intensity [3]. Linear plot of log(x/m) versus log(C_e) (Fig.7) with 0.988 regression coefficient showed that the adsorption equilibrium also obeyed Freundlich model exhibiting heterogeneous surface conditions. K_f *and* 1/*n* values as obtained from the plot (Fig.7) are 2.09 mg/g and 0.22 L/g, respectively. The low value of 1/*n* (less than 1),

indicates a greater adsorption efficiency of the newly developed adsorbent. These values are comparable with several published literature reported for various adsorbents [8].

3.2.5. Effect of initial concentration

Adsorption experiments at varying initial Cr(III) concentrations from 10 to 100 mg/L were performed with fixed doses (20 g/L) of adsorbent. The results indicates that percentage Cr(III) removal decreases as the initial concentration of Cr(III) was increased. Cr(III) removal ranged from 100% to 79% at initial Cr(III) concentration of 10–100 mg/L (Fig. 8). This can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. Since % $R = (C_o - C_e)/C_o$, another reason for decrease in percent removal is larger increase in the denominator (C_o) value in comparison to that of ($C_o - C_e$) value. And the actual amount of chromium removed (mg) per gram of the adsorbent is lager for higher concentration.

Table 13. Percent removal of Cr(III) at different initial concentrations (contact time 60 min, adsorbent dose 20 g /L, initial pH 3.8).

Exp. No.	Initial conc. (mg/L)	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal
1	0	0	0	100
2	10	ND	ND	99.99
3	20	ND	ND	99.99
4	40	0.43 0.46 0.44	0.44 ± 0.02	98.90
5	60	3.11 3.07 3.10	3.09 ± 0.02	94.85
6	80	8.63 8.50 8.72	8.619 ± 0.11	89.23
7	100	20.50 20.95 20.83	20.76 ± 0.23	79.24

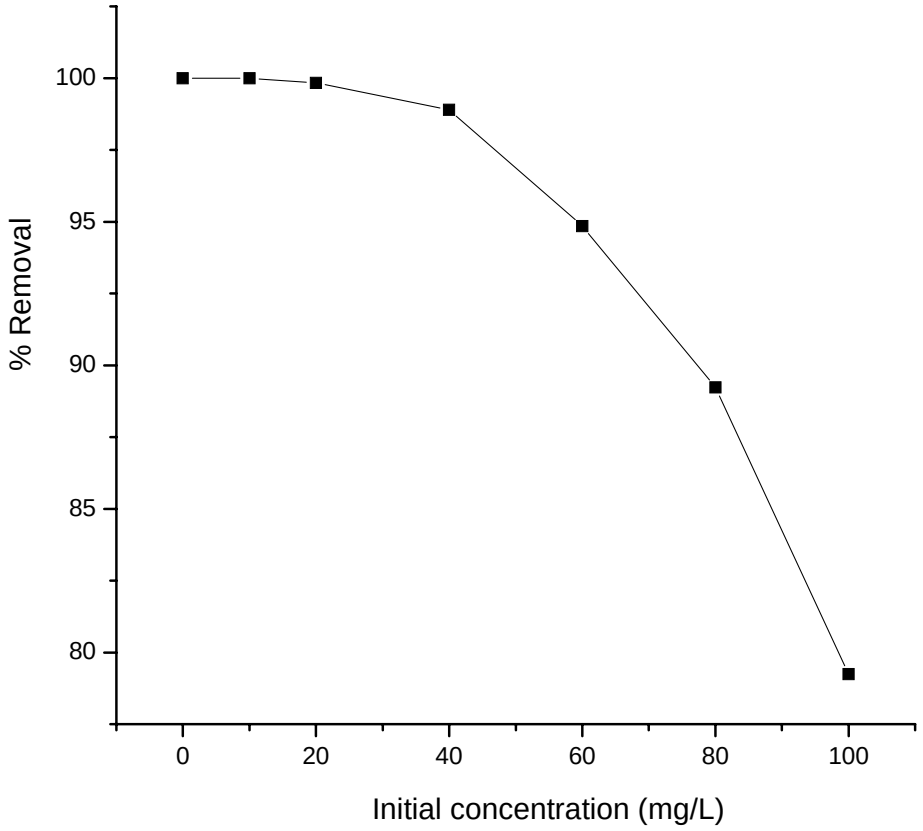

Fig. 8. Percent removal of Cr(III) as a function of initial concentration (contact time 60 min, adsorbent dose 20 g /L, initial pH 3.8).

3.3. Adsorption of Cr(VI) onto aluminum oxide hydroxide saturated with fluoride

3.3.1. Effect of contact time

The rate of adsorption of Cr(VI) on the adsorbent, aluminum oxide hydroxide saturates with fluoride, at different time intervals is depicted in Fig. 9. It was observed that adsorption of Cr(VI) from the solution proceeded very fast and attained equilibrium just after 5 min. Percent removal exceeded 90 % with in the first 5 min indicating that contact

time has very little effect on percentage removal and immediate adsorption takes place, which is one of the advantages of using aluminum oxide hydroxide saturated with fluoride for removal of Cr(VI).

Table 14. Percent removal of Cr(VI) at different time intervals (initial concentration 10 mg/L, adsorbent dose 20 g /L, initial pH 2).

Exp. No.	Contact time (min)	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal
1	0	0	10	0
2	2	0.52 0.51 0.53	0.52 ± 0.01	94.80
3	5	0.30 0.30 0.31	0.30 ± 0.01	96.96
4	10	0.30 0.31 0.32	0.31 ± 0.01	96.92
5	20	0.38 0.37 0.36	0.37 ± 0.01	96.33
6	30	0.33 0.36 0.34	0.34 ± 0.02	96.58
7	40	0.39 0.36 0.39	0.38 ± 0.02	96.19
8	60	0.27 0.27 0.26	0.27 ± 0.01	97.36
9	80	0.32 0.29 0.32	0.31 ± 0.02	96.90
10	120	0.316 0.307 0.327	0.32 ± 0.01	96.83

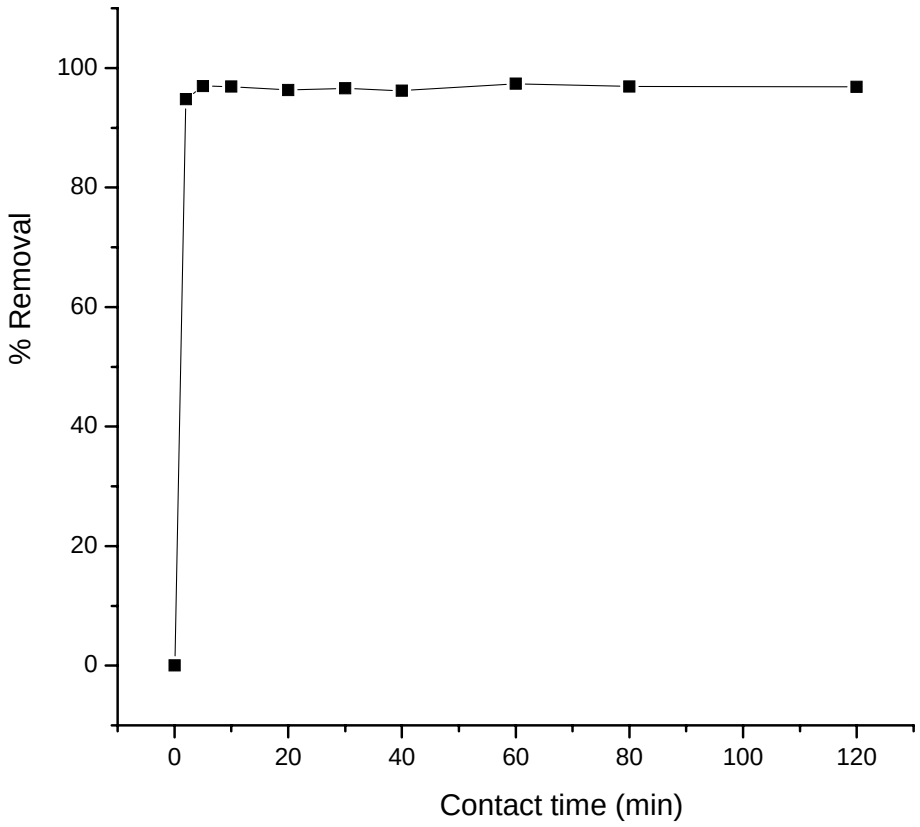

Fig. 9. Percent removal of Cr(VI) as a function of equilibrium time (initial concentration 10 mg/L, adsorbent dose 20 g /L, initial pH 2).

3.3.2. Effect of initial pH

The effect of pH was determined by studying adsorption of Cr(VI) at an initial Cr(VI) concentration of 10 mg/L with adsorbent doses of 20 g/L over a pH range of 2–9. The experimental results revealed that the percentage adsorption increased as the pH was lowered and reached 96% at pH 2 (Fig. 6). Increasing pH from 2 to 5, decreased percent removal of Cr(VI) from 96 to 59, which shows that adsorption of Cr(VI) on aluminum oxide hydroxide saturated with fluoride is strongly dependent on pH of the solution.

Table 15. Percent removal of Cr(VI) at different initial pH (initial concentration 10 mg/L, contact time 60 min, adsorbent dose 20 g/ L).

Exp. No.	Initial pH	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal	Equilibrium pH
1	2	0.37 0.37 0.41	0.39 ± 0.02	96.15	4.91
2	3	0.95 0.91 0.95	0.94 ± 0.02	90.64	6.76
3	4	3.74 3.70 3.60	3.68 ± 0.07	63.19	7.26
4	5	4.12 4.16 4.12	4.14 ± 0.02	58.64	7.29
5	6	4.29 4.26 4.33	4.29 ± 0.04	57.11	7.31
6	7	4.63 4.61 4.55	4.60 ± 0.04	54.03	7.39
7	8	4.78 4.82 4.70	4.76 ± 0.06	52.37	7.40
8	9	4.81 4.82 4.80	4.81 ± 0.01	51.91	7.41

pH dependence of metal adsorption can largely be related to type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution. High adsorption of Cr(VI) at low pH can be explained by the species of the Cr and the adsorbent surface. At acidic pH, the predominant species of Cr(VI) are $Cr_2O_7^{2-}$ and $HCrO_4^-$ and above pH 8, only CrO_4^- is stable. Further decrease in pH below 3 results in the formation of more polymerised Cr oxide species such as $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$. On the other hand, under acidic conditions, the surface of the adsorbent becomes highly protonated and favours the uptake of Cr(VI) in the anionic form because of electrostatic attraction. With increase in pH, the degree of protonation of the surface reduces gradually and hence adsorption is decreased.

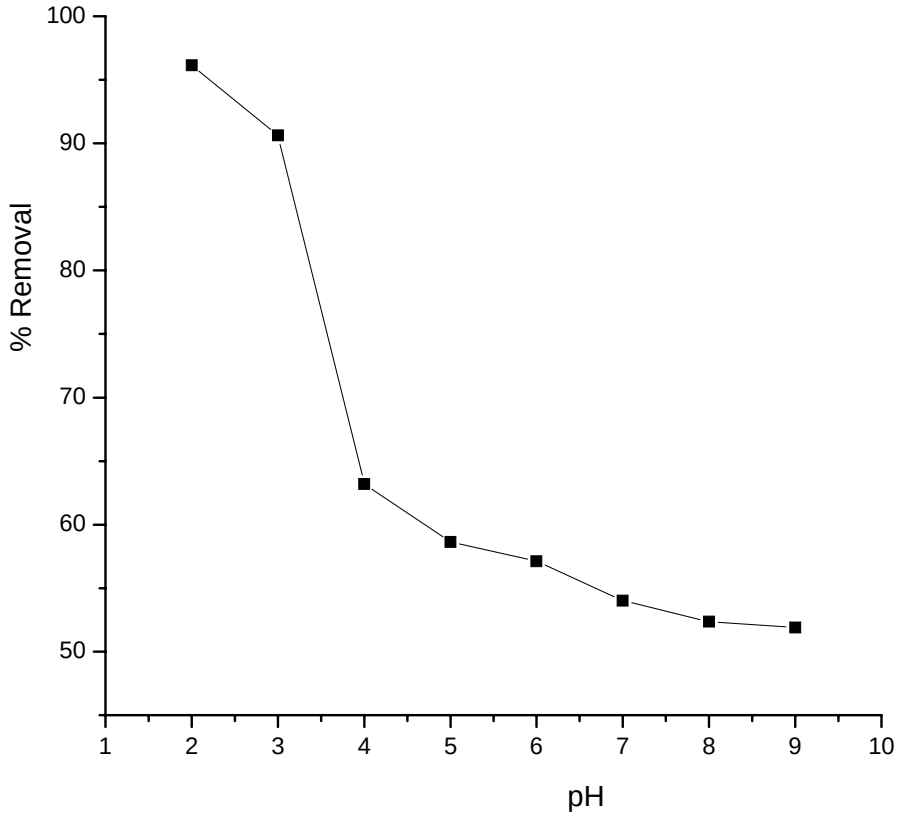

Fig. 10. Percent removal of Cr(VI) as a function of initial pH (initial concentration 10 mg/L, contact time 60 min, adsorbent dose 20 g/L).

Furthermore, as pH increases there is competition between OH^- and chromate ions, the former being the dominant species at higher pH values. The net positive surface potential of adsorbent decreases, resulting in the weakening of electrostatic forces between adsorbent and adsorbate, which ultimately leads to reduced adsorption capacity.

3.3.3. Effect of amount of adsorbent

To optimise the adsorbent dose for the removal of Cr(VI) from the solution, adsorption studies were carried out at an initial Cr(VI) concentration of 10 mg/L with different adsorbent doses at initial pH 2 (Fig. 11). Measurement of percentage Cr(VI) adsorption

as a function of amount of adsorbent indicates that sorption of Cr(VI) increased with increasing dose of the adsorbent.

Table 16. Percent removal of Cr(VI) at different adsorbent dose (initial concentration 40 mg/L, contact time 60 min, initial pH 2).

Exp. No.	Adsorbent dose (g/L)	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal
1	0	0	10	0
2	4	1.95 1.94 1.97	1.95 ± 0.02	80.46
3	8	0.68 0.69 0.72	0.70 ± 0.02	93.03
4	12	0.51 0.52 0.53	0.52 ± 0.01	94.81
5	16	0.41 0.42 0.42	0.42 ± 0.01	95.80
6	20	0.40 0.36 0.39	0.38 ± 0.02	96.18
7	28	0.31 0.35 0.39	0.35 ± 0.02	96.54
8	36	0.33 0.35 0.34	0.34 ± 0.01	96.6
9	44	0.23 0.27 0.25	0.25 ± 0.02	97.49
10	52	0.24 0.28 0.31	0.28 ± 0.04	97.24

Increase in adsorption with dose can be attributed to increased surface area and the availability of more binding sites for adsorption. The removal of Cr(VI) ranged from 80 to 97 % at 60 min time with various adsorbent doses of 12 to 52 g/L.

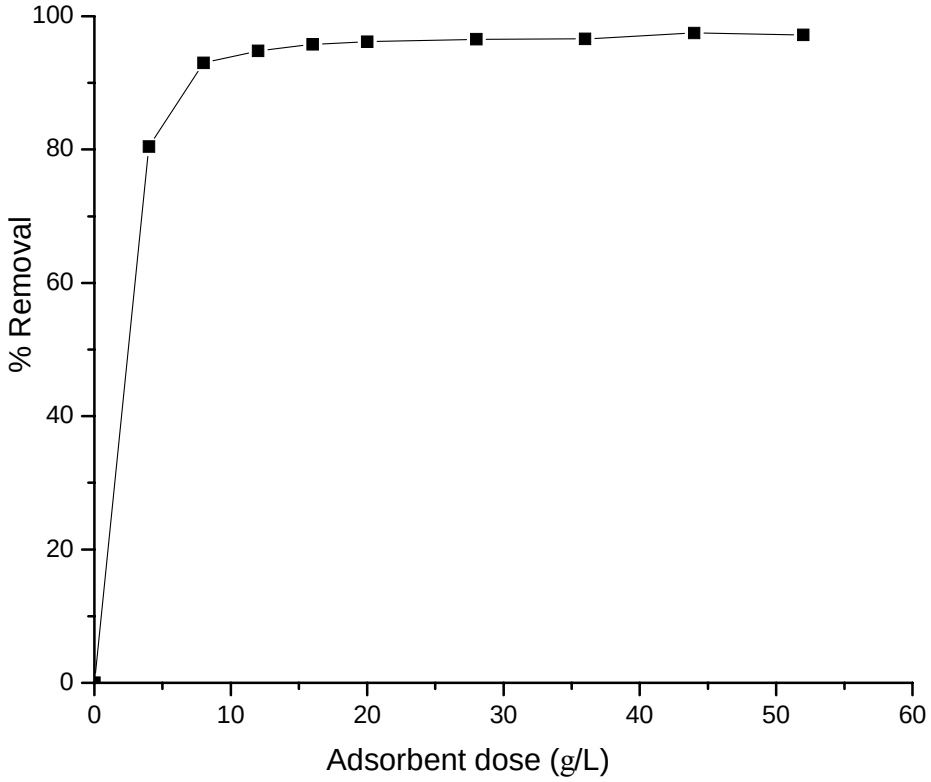

Fig.11. Percent removal of Cr(VI) as a function of dose of adsorbent (initial concentration 40 mg/L, contact time 60 min, initial pH 2).

3.3.4. Adsorption Isotherm

Adsorption isotherms, which are the presentation of the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at constant temperature, were also studied for 10 mg/L Cr(VI) solution at varying amount of the adsorbent. The equilibrium data obtained were not fitted to both Freundlich and Langmuir adsorption isotherm models.

3.3.5. Effect of initial concentration

Adsorption experiments at initial Cr(VI) concentrations from 10 to 100 mg/L were also performed with fixed dose of adsorbent (20 g/L). The results indicates that percentage Cr(VI) removal decreases as the initial concentration of Cr(VI) was increased. Cr(VI) removal ranged from 96 % to 26 % at initial Cr(VI) concentration of 10–50 mg/L (Fig. 12).

Table 17. Percent removal of Cr(VI) at different initial concentrations (contact time 60 min, adsorbent dose 20 g/L, initial pH 2).

Exp. No.	Initial conc.(mg/L)	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal
1	0	0	0	100
2	10	0.40 0.36 0.39	0.38 ± 0.02	96.18
3	20	11.30 10.10 8.50	9.97 ± 1.40	50.15
4	30	21.20 19.00 20.15	20.12 ± 1.10	32.94
5	40	25.65 26.65 29.15	27.15 ± 1.80	32.13
6	50	38.35 36.00 36.25	36.87 ± 1.29	26.26

This can be explained by the fact that the adsorbent had a limited number of active sites, which would have become saturated above a certain concentration. In the case of low concentrations, the ratio of the initial number of moles of metal ions to the available surface area is larger and subsequently the fractional adsorption becomes independent of initial concentrations. However, at higher concentrations the available sites of adsorption become fewer, and hence the percentage removal is dependent upon the initial concentration.

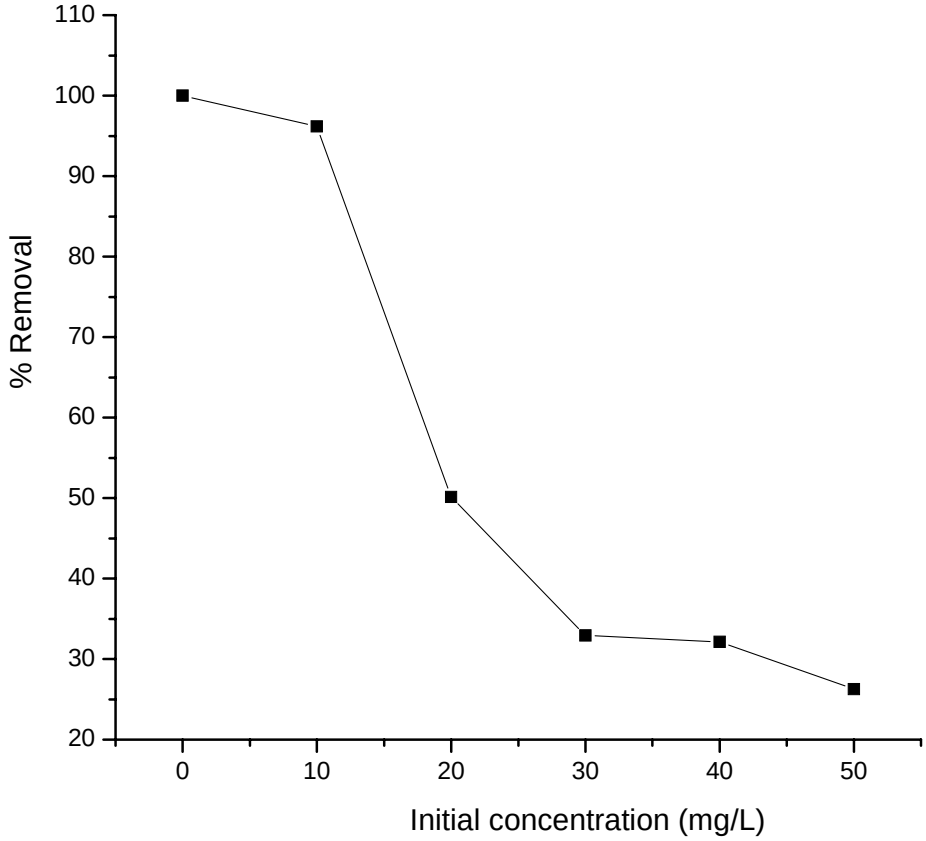

Fig. 12. Percent removal of Cr(VI) as a function of initial concentration (contact time 60 min, adsorbent dose 20 g /L, initial pH 2).

3.4. Application of the method to real sample

The efficiency of adsorbent, aluminum oxide hydroxide, towards the removal of chromium was also tested using Hafde tannery waste effluent. Until the time of collection of waste effluent, no recycling of chromium has been used and the chromium concentration in the effluent at the discharge point is very high (5520 mg/L). Adsorption experiments on this real sample were carried out at two different pH values (Table 18 and 19): at pH 3.8, which is the pH of the waste effluent and at pH 5 which is the optimum pH for removal of Cr(III) on the adsorbent. And the adsorbent was found almost equally effective at the two pH values. Thus, the adsorbent can be directly applied without any

pH adjustment. As the waste effluent is highly concentrated adsorption experiments were carried out after dilution (25 times). Even after diluting the effluent, it is still very concentrated and contains 221 mg/L of chromium. That is why percent adsorptions tabulated below seem small (74 and 76%). But, the actual amount removed per gram of the adsorbent is as high as that of standard aqueous solution prepared in the laboratory.

Table 18. Percent removal of chromium from the real sample solution (diluted 25 times) (contact time 60 min, adsorbent dose 40 g /L, initial pH 3.8).

Exp. No.	Initial conc. (mg/L)	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal
1	220.87	56.24		
2	220.87	56.78	56.60 ± 0.31	74.37
3	220.87	56.78		

Table 19. Percent chromium removal from the real sample solution (diluted 25 times) (contact time 60 min, adsorbent dose 40 g /L, initial pH 5).

Exp. No.	Initial conc. (mg/L)	Final conc. (mg/L)	Average final conc. (mg/L)	%Removal
1	220.87	51.88		
2	220.87	53.55	52.82 ± 0.85	76.09
3	220.87	53.01		

4. Conclusion and Recommendation

In the present study, an efficient adsorption method was developed for both trivalent and hexavelent chromium based on batch mode of adsorption experiments. Different locally available adsorbents have been tested for their effectiveness in removing chromium. Aluminum oxide hydroxide was found to be the most effective adsorbent and selected for removal of Cr(III) whereas aluminum oxide hydroxide saturated with fluoride exhibited a highest adsorption efficiency for Cr(VI).

Effects of different parameters (such as contact time, initial pH, amount of adsorbents, and initial concentration) were investigated for these selected adsorbents. The investigation revealed a complete removal of Cr(III) (> 99%), with 1 g of adsorbent in 50 mL of 40 mg/L solution. And about 96 % removal of Cr(VI) was obtained with 1 g of aluminum oxide hydroxide saturated with fluoride at initial concentration of 10 mg/L and pH 2. The adsorption equilibrium data obtained for removal of Cr(III) on aluminum oxide hydroxide at a fixed initial concentration and varying adsorbent dose were well fitted into the Langmuir and Freundlich adsorption isotherms. Whereas data for removal of Cr(VI) on aluminum oxide hydroxide saturated with fluoride were not fitted to both Freundlich and Langmuir adsorption isotherm models.

The efficiency of adsorbent, aluminum oxide hydroxide, towards the removal of chromium was also tested using Hafde tannery waste effluent and found almost equally effective as that for standard aqueous chromium solution prepared in the laboratory. Thus the adsorbent can be applied to real chromium waste effluent.

Future studies should be focused on investigating the removal efficiency of chromium on these adsorbents following continuous method by packing the adsorbents in column. And even better removal efficiency can be obtained by using consecutive columns (three or more). Applicability of the adsorbents to the real situation where large volume of waste effluent is being discharged should also be studied. Moreover, desorption experiments should be carried out in order to recover chromium from the adsorbed surface. This is very important as the ultimate aim is not to dispose chromium to the environment with the adsorbent. As adsorption of Cr(III) is disfavored in strongly acidic medium, desorption of Cr(III) can be achieved by using acids and desorption of Cr(VI) with bases. The impact of other ions on the removal efficiency should also be studied as the real waste effluents are composed of a number of other ions. Adsorption experiments with samples containing both Cr(III) and Cr(VI) should also be conducted.

5. References

1. W.E. Motzer, S.M. Testa, J. Guertin, F.T. Stanin, Independent Environmental Technical Evaluation Group, *Chromium(VI) Hand Book,* 1st edition, CRC Press, New York, **2005**.

2. D. Mohan, U. Charles, J. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, *J. Hazardous Materials*, **2006**, 10, 5772-5822.

3. K.M.S. Sumathi, S. Mahimairaja, R. Naidu, Use of low-cost biological wastes and vermiculite for removal of chromium from tannery effluent, *Bioresource Technology*, **2004**, 96, 309–316.

4. J.C. Igwe, A.A. Abia, A bioseparation process for removing heavy metals from waste water using biosorbents, *African J. Biotechnology*, **2006**, 5, 1167-1179.

5. K. Selvaraj, S. Manonmani, S. Pattabhi, Removal of hexavalent chromium using distillery sludge, *Bioresource Technology*, **2003**, 89, 207–211.

6. M.A. Baig, B. Mehmood and A. Matin, Removal of chromium from industrial effluents by sand filtration, *Electronic. J. Environ. Agric. Food Chem.*, **2003**, 2 (3), 374-379.

7. A. Salimi, N. Amini, H. Danyali, R. Hallaj, Electrocatalytic reduction of chromium(VI) by thionin: Electrochemical properties and mechanistic study, *Electroanalysis*, **2006**, 17, 1664-1671.

8. V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, *Bioresource Technology*, **2006**, 97, 15– 20.

9. S.M. Nomanbhay, K. Palanisamy, Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal, *Electronic J. Biotechnology*, **2005**, 8, 1-6.

10. F.N. Acar, E. Malkoc, The removal of chromium(VI) from aqueous solutions by beech saw dustL., *Bioresource Technology*, **2004**, 94, 13–15.

11. M. Aliabadi, K. Morshedzadeh, H. Soheyli, Removal of hexavalent chromium from aqueous solution by lignocellulosic solid wastes, *International J. Enviornmental Science and Technology*, **2006**, 3, 321-325.

12. U. Kumar, Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review, *Scientific Research and Essay*, **2006**, 1, 033-037.

13. S. Chamarthy, C.W. Seo, W.E. Marshall, Adsorption of selected toxic metals by modified peanut shells, *J. Chem. Technol. Biotechnol.*, **2001**, 76, 593-597.

14. S. Samantaroy, A. K. Mohanty, M. Misra, Removal of hexavalent chromium by kendu fruit gum dust, *J. Applied Polymer Science*, **1997**, 66,1485–1494.

15. A. J.M. Barros, S. Prasad; V.D. Leite, A. G. Souza, The process of biosorption of heavy metals in bioreactors loaded with sanitary sewage sludge, *Braz. J. Chem. Eng.,* **2006,** 23, 1590-1595.

16. S. Mor, K. Ravindra, N.R. Bishnoi, Adsorption of chromium from aqueous solution by activated alumina and activated charcoal, *Bioresource Technology*, **2007**, 98, 954–957.

17. L. Krim, S. Nacer, G. Bilango, Kinetics of chromium sorption on biomass fungi from aqueous solution, *Am. J. Env. Sci.*, **2006**, 2 (1), 31-36.

18. M. G. da Fonseca, M. M. de Oliveira, L. N.H. Arakaki, Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral, *J. Hazardous Materials*, **2006**, 137, 288–292.

19. V. K. Gupta, M. Gupta, S. Sharma, Process development for removal of lead and chromium from aqueous solution using red mud – an aluminum industry waste, *Water Resource*, **2001**, 35, 1125-1134.

20. V.K. Garg, R. Gupta, R. Kumar, R.K.Gupta, Adsorption of chromium from aqueous solution on treated sawdust**,** *Bioresource Technology*, 2004, 92, 79– 81.

21. J. Lach, E. Okoniewska, E. Neczaj, M. Kacprzak, Removal of Cr(III) cations and Cr(VI) anions on activated carbons oxidized by CO_2, *Desalination*, **2007**, 206, 259–269.

22. A. Chakir, J. Bessiere, K.E. Kacemi, B. Marouf, Comparative study of the removal of trivalent chromium from aqueous solutions by bentonite and expanded perlite, *J. Hazardous Materials*, **2002**, 95, 29– 46.

23. S.P. Dubey, K. Gopal, Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: A comparative study, *J. Hazardous Materials,* **2006**, Article in press.

24. B. Mukhopadhyay, J. Sundquist, R. J. Schmitz, Removal of Cr(VI) from Cr-contaminated groundwater through electrochemical addition of Fe(II), *J. Environmental Management*, **2007**, 82, 66–76.

25. O.K. Junior, L.V. A. Gurgel, Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse, *Bioresource Technology*, **2006**, Article in press.

26. Z.R. Guo, G. Zhang, J. Fang, X. Dou, Enhanced chromium recovery from tanning wastewater, *J. Cleaner Production*, **2006**, 14, 75-79.

27. L.J. Yu, S.S. Shukla, K.L. Dorris, A. Shukla, J.L. Margrave, Adsorption of chromium from aqueous solutions by maple sawdust, *J. Hazardous Materials*, **2003**, 100, 53–63.

28. K. Csoba´n, P. Joo´, Sorption of Cr(III) on silica and aluminium oxide: experiments and modeling, *A: Physicochemical and Engineering Aspects*, **1999**, 151, 97–112.

29. Y.C. Sharma, Uma, V. Srivastava, J. Srivastava, M. Mahto, Reclamation of Cr(VI) rich water and wastewater by wollastonite, *Chemical Engineering Journal*, **2007**, 127, 151–156.

30. H.S. Altundogan, N. Bahar, B. Mujde, F. Tumen, The use of sulphuric acid-carbonization products of sugar beet pulp in Cr(VI) removal, *J. Hazardous Materials,* **2007**, 144, 255–264.

31. S.S. Baral, S.N. Das, P. Rath, Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust, *Biochemical Engineering Journal*, **2006**, 31, 216–22.

32. Z. Aksu, E. Balibek, Chromium(VI) biosorption by dried *Rhizopus arrhizus* : Effect of salt (NaCl) concentration on equilibrium and kinetic parameters, *J. Hazardous Materials*, **2007**, 145, 210–220.

33. S. S. Baral, S.N. Das, P. Rath, G.R. Chaudhury, Chromium(VI) removal by calcined bauxite, *Biochemical Engineering Journal*, **2007**, 34, 69–75.

34. P. Alvarez, C. Blanco, M. Granda, The adsorption of chromium (VI) from industrial wastewater by acid and base-activated lignocellulosic residues, *J. Hazardous Materials*, **2007**, 144, 400–405.

35. J.M. Sun, R. Li, J.C. Huang, Optimum pHs for Cr(VI)co-removal with nucleated Cu(II) precipitation in continuous-flow fluidised metal strippers, *Water SA*, **2007**, 33, 137-142.

36. S. E. Manahan, Environmental Chemistry, 8th edition, CRC Press, New York, **2005**.