

CHAPTER 1

INTRODUCTION

1.1 Introduction

Industrial wastewaters often contain considerable amounts of heavy metals that would endanger public health and the environment if discharged without adequate treatment. Heavy metals such as Pb, Hg, Zn, Ni, Cd, Cu, and Cr which are usually associated with toxicity (Rengaraj *et al.*, 2001). Pollution by chromium is of considerable concern especially Cr (VI) because this form has been demonstrated to be a public health hazard (Aoki and Munemori, 1982). Cr (VI) is believed to be a carcinogen in human while Cr (III) is actually a micronutrient (Parks *et al.*, 2004).

1.2 Background of chromium

1.2.1 Chemical and Physical property

Chromium occurs in the subgroup of group VI that contains molybdenum and tungsten. It is a hard, blue-white metal crystallizing in the cubic system. The mineral, chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$) is its only important source (Hampel, 1982). Some properties of chromium are given in Table 1-1.

Table 1-1 Chemical and physical property of chromium

Type	Value
Atomic number	24
Atomic mass	51.996
Group	Transition Metal
Melting point	1857 °C
Boiling point	2199 °C
Specific heat	0.45 J/gK
Heat of fusion	16.90 kJ/mol
Heat of vaporization	344.30 kJ/mol
Thermal conductivity	0.937 W/cmK
Density (293 K)	7.19 g/cm ³
Crystal structure: Cubic	Body centered

Source: Hampel, 1982

1.2.2 Distribution of chromium in aquatic systems

In aquatic systems chromium occurs in two oxidation states, Cr(III) and Cr(VI). It depends on the redox potential (pE) and pH (see Figure 1-1). The simple ionic form of Cr(III) is Cr^{3+} , which predominates at $\text{pH} < 4$. At $\text{pH} > 4$, Cr^{3+} forms hydroxide complexes in a stepwise fashion as pH increases ($\text{Cr}^{3+} \rightarrow \text{Cr}(\text{OH})^{2+} \rightarrow \text{Cr}(\text{OH})_2^+ \rightarrow \text{Cr}(\text{OH})^0 \rightarrow \text{Cr}(\text{OH})_4^-$). These complexation reactions control the ionic state of aqueous Cr(III) with the ionic charge changing from +3 to -1 between pH 4 and pH 10. At the typical natural water pH range of 6-8, the predominate aqueous species is $\text{Cr}(\text{OH})_3^0$.

Cr(VI) is highly soluble at pH 8. At low concentrations, Cr(VI) is present in water as diprotic chromic acid (H_2CrO_4 , $\text{pK}_{a1} = 0.81$, $\text{pK}_{a2} = 6.49$). In natural water two Cr(VI) oxyanion species predominate, monovalent HCrO_4^- below pH 6.5, and divalent CrO_4^{2-} above pH 6.5. An additional Cr(VI) species, dichromate ($\text{Cr}_2\text{O}_7^{2-}$), predominates at concentration greater than 1000 mg L^{-1} (National Water Research Institute, 2001). And in wastewater Cr(VI) exists in two anion forms, HCrO_4^- and CrO_4^{2-} (Aoki and Munemori, 1982).

pE pH Diagram

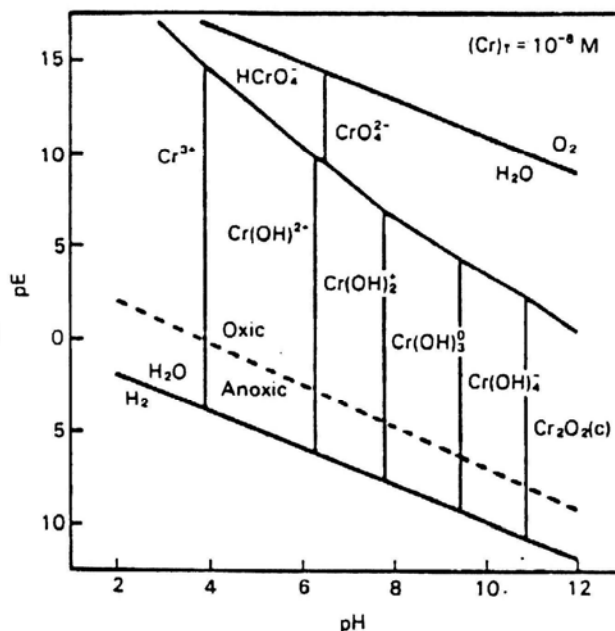


Figure 1-1 pE-pH diagram Cr in aquatic systems (National Water Research Institute, 2001)

In natural water Cr(III) and Cr(VI) can be coprecipitated by iron hydroxide. Both Cr(III) and Cr(VI) can strongly sorb to iron hydroxide solids forming particulate Cr(III) and Cr(VI) in water (Figure 1-2). This reaction is routinely exploited in industry to remove mgL^{-1} levels of both Cr(VI) and Cr(III) from wastewaters using iron coagulants and materials such as iron oxide coated sand. We operationally define three fractions of chromium in association with iron hydroxide as follows:

- (1) "Soluble" chromium passes through a 0.45 mm pore size filter.
- (2) "Sorbed" chromium is the fraction of chromium that is chemisorbed to the iron hydroxide, but which could be released in either acidic or basic solution without complete dissolution of the iron hydroxide solid.
- (3) "Fixed" chromium is the fraction of chromium associated with the iron hydroxide that is not released unless the solid is completely dissolved.

Each of these fractions can occur for Cr(III) and/or Cr(VI) (Parks *et al.*, 2004).

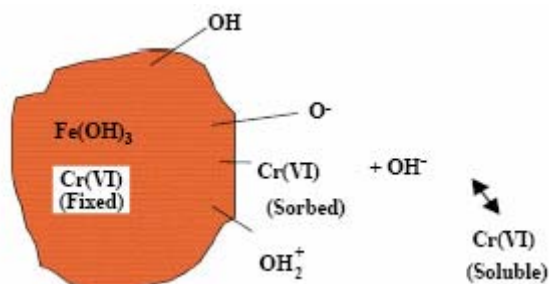


Figure 1-2 Possible forms of chromium (VI) in solution in the presence of iron particles. Cr (VI) can be in solution (soluble), Cr (VI) can stick (sorb) to the surface of iron oxide particles, or Cr (VI) can be held deep inside the iron in a form of “fixed” Cr. (Parks *et al.*, 2004)

1.2.3 Toxicity and Health Effect

Chromium and certain chromium compounds are classified as substances known to be carcinogenic. In the national Toxic Release Inventory, EPA classifies chromium as a "de minimis" carcinogen. Chromium compounds vary greatly in their toxic and carcinogenic effects. Trivalent chromium compounds are considerably less toxic than the hexavalent compounds and are neither irritating nor corrosive. There is inadequate evidence for carcinogenicity of chromium oxide, and chromium acetate. There is sufficient evidence for carcinogenicity of barium chromate, calcium chromate, chromium trioxide, lead chromate, sodium dichromate, and strontium chromate. These compounds have not been evaluated for their carcinogenicity: chromium carbonate, chromium phosphate, cobalt chromium alloy, lead chromate oxide, potassium chromate, potassium dichromate, sodium chromate, and zinc chromate.

The major acute effect from ingested chromium is acute renal tubular necrosis. Exposure to chromium, particularly in the chrome production and chrome pigment industries, is associated with cancer of the respiratory tract. Hexavalent chromium compounds are corrosive and cause chronic ulceration and perforation of the nasal septum. They also cause chronic ulceration of other skin surfaces. The general populations can be exposed to chromium through the air, water, soils, and food (PHG, 1999).

1.2.4 Application

Chromium and its salts are used in the leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic and glass industry and in photography, and for chrome alloy and chromium metal production, chrome plating, and corrosion control. Occupational sources of chromium exposure (with chemical forms of interest shown in brackets) may occur in the following industries: (Slooff, 1989).

- Stainless steel welding (chromium (VI))
- Chromate production (chromium (VI))
- Chrome plating (chromium (VI))
- Ferrochrome industry (chromium (III) and chromium (VI))
- Chrome pigments (chromium (III) and chromium (VI))
- Leather tanning (mostly chromium (III))

The effluent from the industries may contains chromium at concentrations ranging from tenths to hundreds of mg L^{-1} (Rengaraj *et al.*, 2001). So it is essential for industries to treat effluents to reduce the chromium to acceptable level .The industries effluents standards shown in Table 1-2.

Table 1-2 Chromium concentration in industries effluent standards

Parameters	Standard Values	Method for Examination
Heavy metals		
1. Chromium (VI)	not more than 0.25 mg L^{-1}	Atomic Absorption Spectro Photometry; Direct Aspiration or Plasma Emission Spectroscopy ; Inductively Coupled Plama : ICP
2. Chromium (III)	not more than 0.75 mg L^{-1}	

Source: Notification the Ministry of Science, Technology and Environment, 1992

There are various treatment techniques to removal chromium from water, the most five common ones are reduction and precipitation, ion exchange, adsorption (Rengarj *et al.*, 2001) and Iron Oxide Coated-Sand (IOCS) (Benjamin *et al.*,1996). The reduction, precipitation, ion exchange and adsorption methods suffer from some drawback such as high capital and operational costs or the treatment and disposal of residual metal sludge (Rengarj *et al.*, 2001). The main advantage of IOCS was low cost, remove particulate from water, and it was simple method. After the sample passed the pretreatment. It is important to determine the residue chromium in water. Several techniques for determination of chromium are shown in Table 1-3.

Table 1-3 Techniques for determination of chromium

Technique	Pretreatment method	Type of sample	References
AAS	precipitation	wastewater	Aoki and Munemori, 1982
ICP-MS	filter	water	Parks <i>et al.</i> , 2004
IC	filter	water	Parks <i>et al.</i> , 2004
GFAAS	digestion	fish and seafood	Bratakos <i>et al.</i> , 2002

Many researches used Graphite Furnace Atomic Absorption Spectrometry (GFAAS) for determination of chromium because the sensitivity of GFAAS makes it the obvious choice for trace metal analysis application. Routine determination at microgram per liter ($\mu\text{ L}^{-1}$) level for the most elements make it ideal for environment application. The microliter sample sizes used offer additional benefits where the amount of sample available for analysis is limited, as in many clinical analyses (Beaty and Kerber, 1993).

The advantages of GFAAS are high sensitivity, using a few of sample and reducing interference in the sample by using background correction. So in this study we choose GFAAS techniques for determination of Cr (VI) in wastewater samples.

1.2.5 Graphite furnace atomic absorption spectrometry

1.2.5.1 Components of the graphite furnace system

The graphite furnace is made up of the three major components, the atomizer, the power supply and the programmer. The atomizer is located in the sampling compartment of the atomic absorption spectrometer, where sample atomization and light absorption occur. The power supply controls power and gas flows to the atomizer under the direction of the programmer, which is usually built into the power supply or spectrometer (Beaty and Kerber, 1993).

1.2.5.1.1 The graphite furnace atomizer

A basic graphite furnace atomizer is comprised of the following components:

- Graphite tube
- Electrical controls
- Enclosed water cooled housing
- Inert purge gas controls

A graphite tube is normally the heating metal of the graphite furnace. The cylindrical tube is aligned horizontally in the optical path of the spectrometer and serves as the spectrometer sampling cell. A few micro liters (usually 5-50) of sample are measured and dispensed through a hole in the center of the tube wall onto the inner tube wall or graphite platform. The tube is held in place between two graphite contact cylinders, which provide electrical connection. An electrical potential applied to the contacts cause current to flow through the tube, the effect of which is heating of the tube and the sample (Beaty and Kerber, 1993). The HGA and THGA graphite tubes with integrated L'vov platform for larger sample volumes are shown in Figure 1-3.

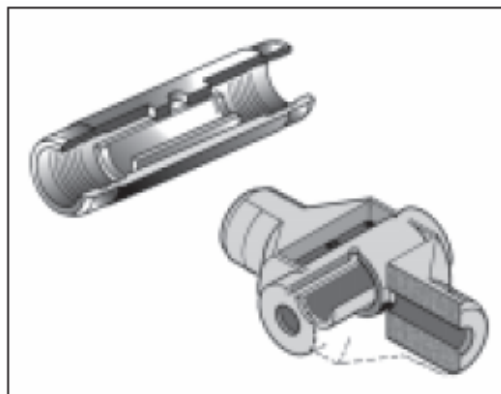


Figure 1-3 HGA and THGA graphite tubes with integrated L'vov platform for larger sample volumes (Source: The Perkin-Elmer AAnalyst 700 and 800 Atomic Absorption Spectrometer, 1997)

The entire assembly is mounted within an enclosed, water-cooled housing. Quartz windows at each end of the housing allow light to pass through the tube. The heated graphite is protected from air oxidation by the end windows and two streams of argon. An external gas flow surrounds the outside of the tube, and a separately controllable internal gas flow purges the inside of the tube. The system should regulate the internal gas flow so that the internal flow is reduced or preferably, completely interrupted during atomization. This helps to maximize sample residence time in the tube and increase the measurement signal. The transversely-heated graphite furnace (Figure 1-4) eliminates many of the problems associated with the longitudinally-heated furnace. The graphite tube of the transversely-heated graphite includes integral tabs which protrude from each side. These tabs are inserted into the electrical contacts. When power is applied, the tube is heated across its circumference (transversely). By applying power in this manner, the tubes is heated evenly over its entire length, eliminating or significantly reducing the sample condensation problems seen with longitudinally- heated furnace systems.

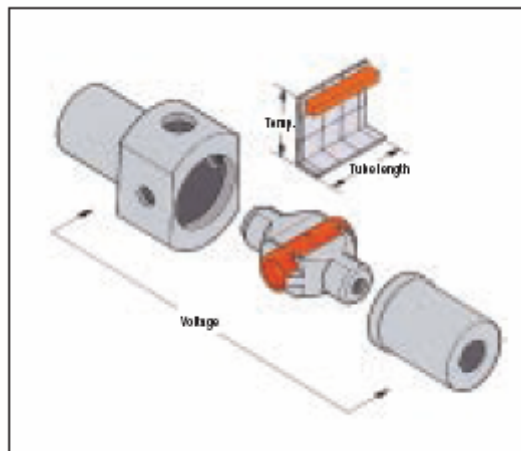


Figure 1-4 The transversely heated graphite tube provides a uniform temperature profile. (Source: The Perkin-Elmer AAnalyst 700 and 800 Atomic Absorption Spectrometer, 1997)

An additional advantage of the transversely-heated furnace is that it allows the use of longitudinal Zeeman-effect background correction. Longitudinal Zeeman offers all of the advantages of transverse Zeeman correction with put the need to include a polarizer in the optical system. This provides a significant improvement in light throughput (Beaty and Kerber, 1993).

1.2.5.1.2 The graphite furnace power supply and programmer

The power supply and programmer perform the following functions:

- electrical power control
- temperature program control
- gas flow control
- spectrometer function control

The power supply controls the electrical current supplied to the graphite tube, which causes heating. The temperature of the tube is controlled by a user-specified temperature program. Through the programmer the operator will enter a sequence of selected temperatures vs. time to carefully dry, pyrolyze, and finally atomize the sample. The program may also include settings for the internal gas flow rate and, in some cases, the selection of an alternate gas. Certain spectrometer functions, such as triggering of the spectrometer read function, also may be

programmed and synchronized with the atomization of the sample in the furnace (Beaty and Kerber, 1993).

1.3 Literature reviews

There are many conventional technologies for removing metals from solution involves precipitation of metals (typically as oxides, hydroxides, carbonates, or sulfides) and then separation of the particulate metals by coagulant such as iron hydroxide. This approach has several practical limitations, some of which are exacerbated when the metals are present in complex matrices. Among these limitations are; that precipitation is often ineffective if the metals are in complex forms or if they are present as anions (e.g., CrO_4 , SeO_3 , AsO_4) (Benjamin *et al.*, 1996).

Recently, several researchers have developed techniques for coating iron oxide onto the surface of sand to overcome the problem of using iron oxide powders in water treatment. Iron coated sand has been tested for removal of cationic as well as anionic metals from synthetic and real wastes.

Aoki and Munemori, 1982 investigated the recovery of Cr(VI) from wastewater with iron (III) hydroxide-I. Cr(VI) is adsorbed as HCrO_4^- on iron (III) hydroxide as its surface charge is positive below pH 8.5. HCrO_4^- is attracted to the iron (III) hydroxide surface by the coulomb force and is adsorbed by ion bonding. Anions such as SO_4^{2-} and SCN^- compete with HCrO_4^- for anion exchangeable sites on the hydroxide surface. The force of exchange becomes greater as the stability constants of the iron(III)- anion complexes increase. The adsorption of Cr (VI) increases in the presence of metal ions such as Cd (II), Pb (II), Cu (II) and Zn (II), because the partially coprecipitate with iron(III) hydroxide and cause the adsorption sites to increase.

However, Iron salts are commonly added as coagulants in conventional metal treatment processes. In neutral to slightly alkaline solutions, the iron forms precipitates, referred to generically as Fe oxides, that are good adsorbents for many metals (Benjamin *et al.*, 1996). And iron oxides have relatively high surface area and surface charge, and they often regulate free metal and organic matter concentration in

soil or in water through adsorption reactions. Many research have applied the iron oxide to the treatment of heavy metals and organic matter from tap or wastewater. However, the iron oxide alone is not suitable as a filter medium because of their low hydraulic conductivity (Lai *et al.*, 2001).

Benjamin *et al.*, 1996 investigated sorption and filtration of metals using iron oxide-coated sand. Iron oxide-coated sand (IOCS) was prepared by two methods that were IOCS-1 used $\text{Fe}(\text{NO}_3)_3$ and IOCS-2 used FeCl_3 . IOCS used to treat various metal-bearing waste streams. Both preparations yield products with dramatically increased surface area, a more positively charge surface and significantly greater tendency to sorb both cationic and anionic metals. Iron oxides are good adsorbents for uncomplex metals, some metal-ligand complexes, and many metal oxyanions. The process was successful in removing uncomplex and ammonia-complex cationic metals (Cu, Cd, Pb, Ni, Zn), as well as some oxyanionic metals (SeO_3 , AsO_3), from simulated and actual waste streams over a wide range of metal concentrations. The adsorbent was stable during backwashing and regeneration operations, releasing most metals quantitatively; the exception was AsO_3 , which was not efficiently recovered by regeneration with either acid or base. The composite media is inexpensive to prepare and could serve as the basis of a useful metal removal and possibly metal recovery process in variety of settings.

Lo *et al.*, 1997 studied about adsorption of Se (IV) and Se (VI) on two coating parameters were investigated: the pH at which iron-oxide was synthesized and the coating temperature. The pH (coating) played a very important role in the coating process and in Se removal. A larger quantity of iron was coated onto quartz sand in the lower pH range (0.5 – 2.0), but a greater amount of iron was dissolved from coating produced at higher pH(coating) (8.0-11.0). The IOCS produced at higher temperature (coating) because of higher temperature provided more energy to build a stronger bond between iron oxide and quartz sand. Adsorption experiments showed that Se (IV) adsorption by IOCS was specific and Se (VI) adsorption was nonspecific. In kinetic experiments, pseudo-equilibrium of Se (IV) adsorption was attained within 10 minutes while Se (VI) adsorption needed 1.5 h. Higher concentrations of NaOH solution could increase the desorption rate of Se (VI) but could not increase the total

desorbed quantity. In addition, adsorption isotherm results indicated that the adsorption capacity of IOCS from pH 4.0 to 6.5 was 0.014 – 0.017 mmole Se / g sand for Se (IV) and was 0.013 – 0.014 mmole Se / g sand for Se (VI).

Muhammad *et al.*, 1997 investigated about removal of metals by slow sand filtration (SSFs). SSFs can be used to remove heavy metals from surface water. Although a conventional filtration rate (0.1 m h^{-1}) and filter bed depth (1.2 - 1.5 m) are adequate for all four metals (Cu, Cr, Pb and Cd), optimization of parameters depends on the individual metal. The removal efficiency of heavy metals increases with the increase of total organic carbon (TOC) and the maximum removal is achieved at 12 mgL^{-1} of TOC. The positive influence of TOC is more significant for Pb and Cd than Cu and Cr. The removal efficiency of heavy metals decreases as the filtration rate increases. It has been observed that a filtration rate of 0.4 m/hr could be adopted for Cu and Cr but for Pb and Cd, the conventional filtration rate of 0.1 m/hr is recommended. Heavy metal removal efficiency by SSF decreases with a decrease of sand bed depth. It indicates the importance of adsorption in removing heavy metals by SSF. A filter bed depth of 0.4m is enough to remove Cu and Cr whereas Pb and Cd are removed through the whole sand bed. So SSF acts as a deep bed filter for Pb and Cd.

Lai *et al.*, 2001 investigated the removal of metal ions and humic acid from water by iron-coated filter media. Iron – coated sand was investigated for adsorbing metal ions and natural organic matter from water by batch and column experiments. Chemical analysis (energy dispersive analysis of X-ray, EDAX) was used for characterizing the copper and lead adsorption sites on iron – coated sand. From the batch experiment results, the copper and lead ions could be removed simultaneously by iron – coated sand. Adsorption behavior of copper ions, lead ions and humic acid on iron – coated sand may include pores diffusion and chemical reaction. The maximum adsorption capacities of iron – coated sand for copper and lead were 0.259 mg Cu/g sand and 1.21 mg Pb/g sand, respectively. The presence of humic acid led to the increase of the adsorption of copper and lead. Results from the column experiments indicated that the copper ions, lead ions and humic acid could be removed completely before the breakpoint. So Iron – coated sand is excellent

adsorbent and may be applied for the adsorption/filtration of metal ions and natural organic matters from water.

Thirunavukkarasu *et al.*, 2002 investigated about removal organic arsenic from drinking water. The column studies were conducted by using manganese greensand (MGS), iron oxide-coated sand (IOCS-1 and IOCS-2) and ion exchange resin in Fe^{3+} form. And the residual of arsenic after passing the column was determined by Varian type Spectro AA600 Zeeman GFAAS.

From this study, they concluded that IOCS-2 was the best method, the result showed that the organic arsenic adsorption capacity was $8 \mu\text{g/g}$. In the part of ion exchange resin, it was higher bed volumes (585 BV) and high arsenic removal capacity ($5.7 \mu\text{g/cm}^3$).

The preparation of IOCS has two methods; IOCS-1 and IOCS-2. The sand was sieved to a geometric mean size of 0.6–0.8 mm, acid washed (pH 1; 24 h), rinsed with distilled water three times and dried at 110°C for 20 h before use.

IOCS-1 was prepared by adding 40 ml of 1M $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ solution per 500 g of sand and the mixture was allowed to remain in the column for 12 h. The column was backwashed for a short duration before starting the run (Thirunavukkarasu *et al.*, 2002).

IOCS-2 was prepared in two steps. In step 1, the solution containing a mixture of 80 ml of 2M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1 ml of 10 M NaOH was poured over 200 g dried sand placed in a heat resistant dish, and the mixture was heated at an elevated temperature. Then the sand was cooled and washed with distilled water. In step 2, the solution containing the same mixture of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NaOH was poured over 100 g of the coated sand from step 1, and heated for a desired duration. Further the coated sand from the second step was subjected to five more drying cycles, which consisted of drying at 110°C for 4 h followed by 20 h at room temperature. The coated sand was stored in capped bottles (Thirunavukkarasu *et al.*, 2002).

IOCS-1 was simple method, take time for preparing sand at least, low cost and can be removed particulate from water. So in this study we choose IOCS-1 method for removal Cr (VI) from wastewater.

1.4 Objective

The aims of this research are:

- 1.4.1 To optimize conditions of graphite furnace atomic absorption spectrometry (GFAAS) for determination of chromium.
- 1.4.2 To optimize conditions for removal chromium (VI) by Iron Oxide-Coated Sand (IOCS).
- 1.4.3 To use conditions for removal and optimum conditions of GFAAS for the determination of Cr (VI) in wastewater sample.