KMITL Sci. Tech. J. Vol. 6 No. 1 Jan. - Jun. 2006

REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS BY SCRAP IRON FILINGS

Suwannee Junyapoon* and Suttawadee Weerapong

Department of Chemistry, Faculty of Science
King Mongkut's Institute of Technology Ladkrabang
Chalongkrung Road, Ladkrabang District, Bangkok 10520, Thailand

ABSTRACT

Chromium is an important industrial metal used in various products and processes. Hexavalent chromium is relative mobile in the environment and is acutely toxic, mutagenic, teratogenic and carcinogenic. The impacts of chromium on human health and the environment is of wide concern. Therefore, it is imperative that hexavalent chromium be removed from wastewater. A removal of hexavalent chromium using scrap iron filings was studied in both synthetic wastewater, containing 30 mg l^{-1} of hexavalent chromium, and chromium plating wastewater. All experiments were evaluated in batch experiments. Effective conditions for removal of hexavalent chromium were found to be pH of 3, iron particle sizes of 35 - >200 mesh, agitating rate at 250 rpm, contact time at 180 mins., iron dosage of 1 g. According to the experiment results, almost all of hexavalent chromium was transformed to trivalent chromium. Trivalent chromium and total iron in the aqueous solution were then removed by precipitation with alkaline solutions. In this work, sodium hydroxide and calcium hydroxide were used. It was found that the use of sodium hydroxide was more effective than that of calcium hydroxide. The reaction rate constants from the results following first order reaction were calculated. In addition, it was found that nickel and copper in the aqueous solution did not affect on the reduction of hexavalent chromium.

KEYWORDS: chromium plating wastewater, hexavalent chromium, scrap iron filings

1. INTRODUCTION

Chromium is an important industrial metal used in various products and processes. Usually, chromium has been released to the environment via leakage, poor storage or improper disposal practices [1]. Generally, chromium in the environment is found primarily in two oxidation states: hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Hexavalent chromium is relatively mobile in the environment and is acutely toxic, mutagenic, teratogenic and carcinogenic. Whilst trivalent chromium has relatively low toxicity and is immobile under moderately alkaline to slightly acidic conditions [1]. According to its toxicity, chromium was classified as a primary pollutant and ranked as second among many toxic metals in the environment for frequency of occurrence at Department of Energy (DoE) sites [2]. The impacts of chromium on human health and the environment is of wide concern. The potential risk of chromium contaminated groundwater and its movement beyond compliance boundaries has been evaluated. Nowadays new technologies and treatment systems are necessary for remediation of contaminated sites. The pump-and-treat remediation technique is currently suggested for removal of chromium contaminated groundwater. However, it is

---

*Corresponding author. Tel: 662-326-4339-53 ext. 349 Fax: 662-326-4415
E-mail address: kjsuwann@kmitl.ac.th

expensive and complicated. In addition, the removal of low levels of chromium is limited. Therefore, other remediation techniques, which are cheap and convenient, are required.

A use of zero-valent iron metal (Fe(0)), which is one of the most abundant metals on the earth, as a reducer is increasingly interesting. Zero-valent iron metal is a very promising reactive medium due to its low-cost, easy-to-obtain status, effectiveness and ability to degrade contaminants. As it is a strong reducer, zero-valent iron has been used to rapidly dehalogenate a wide range of halogenated organic compounds [3-5], reduce nitro aromatic compounds [6], degrade dye solutions [7-10], and remove heavy metals [11-17]. Scrap iron filings are generated during the filing process. These iron particles are mostly composed of zero-valent iron therefore, they can be used as effectively reductive media [11]. As the use of scrap iron filings is one of waste utilization, it can reduce the cost of reactive media.

The removal of chromium by zero-valent iron is based on transformation of chromium from toxic to non-toxic forms. Hexavalent chromium (Cr(VI)), which is a strong oxidant, a potential carcinogen and more mobile in soils and aquifers, is transformed to trivalent chromium (Cr(III)), which is less hazardous and less water soluble and associated with solids [11-12]. The reduction rate of Cr(VI) by Fe(0) produces ferric ion (Fe(III)) and trivalent chromium ions (Cr(III)) (equations 1 or 2) [11]. Trivalent chromium may be removed through the precipitation or co-precipitation in terms of mixed Fe(III) and Cr(III) hydroxide as shown in equation 3 [13] or equation 4 [11].

$$Cr^{6+} + Fe^{0} \longrightarrow Cr^{3+} + Fe^{3+} \quad (1)$$

$$CrO_4^{2-} + Fe^{0} + 8\,H^{+} \longrightarrow Cr^{3+} + Fe^{3+} + 4\,H_2O \quad (2)$$

$$(1-x)\,Fe^{3+} + (x)\,Cr^{3+} + 3\,H_2O \longrightarrow (Cr_xFe_{(1-x)})(OH)_3\,(s) + 3\,H^{+} \quad (3)$$

$$(1-x)\,Fe^{3+} + (x)\,Cr^{3+} + 2\,H_2O \longrightarrow Fe_{(1-x)}Cr_xOOH\,(s) + 3\,H^{+} \quad (4)$$

The reduction rate of Cr(VI) by Fe(0) is accelerated when mineral surfaces such as goethite (α-FeOOH) and aluminium oxide (γ-Al_2O_3) are present and the pH of the solution is low [14-15]. This reaction rate is quite fast. Therefore the oxidation of the Fe(0) and Fe(II) is not only dependant on type of contaminants but also on operating conditions [14].

The objectives of this study are (i) to use scrap iron filings as a low-cost reactive media for reduction of Cr(VI) and (ii) to remove trivalent chromium and total iron from the aqueous solution by precipitation with alkaline solutions. In this work, batch experiments were conducted in synthetic wastewater to examine the effects of different reaction parameters on the reduction of Cr(VI), such as initial pH, iron particle size, agitating rate, contact time and iron dosage. In addition, the amounts of alkaline solutions used to remove trivalent chromium and total iron from aqueous solutions were examined. The related kinetics were investigated. The removal efficiency of Cr(VI) from chromium plating wastewater was also evaluated under the obtained optimum conditions.

2. MATERIALS AND METHODS

2.1 Materials

Scrap iron filings were obtained from a filing shop in Bangkok, Thailand. Synthetic wastewater was prepared from potassium dichromate (Carlo Erba Co., Ltd.). Hydrochloric acid, sulfuric acid, calcium hydroxide and copper sulfate were purchased from Carlo Erba Co., Ltd. Sodium hydroxide and acetone were purchased from Lab Scan Co., Ltd. Nickel sulfate (BHD Laboratory Supplied Co., Ltd.) Phosphoric acid (J.T. Baker Co., Ltd.) 1,5-Diphenylcarbazide (Fluka Co., Ltd.) were used. All chemical reagents were analytical reagent grade. Chromium plating wastewater was obtained from effluent from a chromium plating factory in Bangkok, Thailand.

2.1.1 Scrap iron filing preparation

Scrap iron filings, used as zero-valent iron, were classified using a sieve (Laboratory Test Sieve Co., Ltd.). Fractions of iron particle sizes were obtained from a calculation of weight ratio of each iron particle size to total iron filings. The iron particles were pretreated by washing with 3% hydrochloric acid at agitating rate of 150 rpm for 30 mins. They were then washed with degas de-ionized water several times to remove the residual acid and rust, and rinsed with acetone to remove the remaining water. Next, they were quickly dried under nitrogen gas flow and finally stored in an amber glass bottle filled with nitrogen gas. The specific surface area of the iron particles were determined by Autosorb (Quanta Chrome Co., Ltd.). The components of iron particles were analyzed with an X-ray fluorescence spectrometer (XRF) model SRS 3400 (Bruker A.G.). Characteristics of iron surface before and after treatment under the obtained optimum conditions were examined by a scanning electron microscope-energy dispersive spectrometer (SEM-EDS) model 1455 VP (Leo Co., Ltd.).

2.1.2 Aqueous chromium solution preparation

One thousand milligram per liter of standard stock solution of Cr(VI) was prepared from potassium dichromate. The standard solutions were prepared by diluting the corresponding mass of potassium dichromate with de-ionized water. The standard working solutions were prepared by further dilution of the standard stock solution. Synthetic wastewater of 30 mg l^{-1} Cr(VI) was also prepared by diluting the standard stock solution with de-ionized water.

2.2 Batch experiments

Batch experiments were carried out in the laboratory to evaluate the removal efficiency of Cr(VI) using scrap iron filings. All individual experiment was carried out in a 180 ml polyethylene bottle to prevent Cr(VI) adsorbing on to the container wall. Fifty milliliters of the synthetic wastewater and 1 g of washed iron particles were added to the bottle. The mixture was agitated with a shaker at 150 rpm for 30 mins. The solution was filtered using a Whatman No. 42 filter to remove the iron particles. Cr(VI) in the filtrate was determined using the photometric diphenylcarbazide method [18]. The absorbance was measured at a wavelength of 540 nm using a UV-visible spectrophotometer model 6405 (Jenway Co., Ltd.). Absorbance was calculated according to Beer's Law. Samples were diluted with de-ionized water so that readings never exceeded 1 AU, whilst total chromium and total iron were detected with an atomic absorption spectrophotometer model AA-680 (Shimadzu Co., Ltd.). The trivalent chromium value was obtained by subtracting total chromium from hexavalent chromium.

Experiments were conducted to determine the pH range at which the maximum reduction of Cr(VI) occurred. The pH was varied from pH 3, 4, 5, 7 to 9 by the addition of 0.1 M HCl or 0.5 M NaOH. In this work, parameters affecting the reduction rate of Cr(VI) were investigated including iron particle size (35-50, 50-70, 70-100, 100-200 and 35->200 mesh), agitating rate (100, 150, 200 and 250 rpm), contact time (30, 60, 90, 120 and 180 mins.), and iron dosage (0.1, 0.5, 1, 1.5 and 2 g). After the reduction of Cr(VI) to Cr(III) under the optimum conditions obtained from the batch experiments, Cr(III) and total Fe in the aqueous solution were removed by precipitation with alkaline solutions at pH 6.7 [19]. In this study, 50% w/v sodium hydroxide and 50% w/v calcium hydroxide were used as alkaline solutions. The amounts of sodium hydroxide and calcium hydroxide used were examined. The removal efficiency of Cr(VI) in chromium plating wastewater was also studied under the obtained optimum conditions. A control was set, to which no iron particles were added to determine if the Cr(VI) was adsorbed by the walls of the container and suspended solids present in the aqueous solution. De-ionized water was used as a blank. All experiments were carried out at room temperature in triplicate. The relative standard deviation was calculated. A set of kinetic experiments was also conducted under obtained optimum conditions. In addition, the effects of nickel and copper on the reduction of Cr(VI) were also investigated under the obtained optimum conditions. A ratio of concentrations of chromium to nickel, chromium to copper and chromium to nickel and copper used in this study was obtained from the report of these components in chromium plating wastewater in Bangkok and its boundaries between 1994-1998 [20].

3. RESULTS AND DISCUSSION

3.1 Characteristics of scrap iron filings

Surface area and fractions of iron particle sizes are listed in Table 1. The surface area increased with decreasing size. In this work, the particle size of 200->200 mesh was too small to pre-treat with acid and therefore, it was ignored. It was found that the iron particle size of 35->200 mesh, without sieving, had highest surface areas as indicated in Table 1.

Table 1 Surface area (measured by Autosorb) and fractions of particle sizes of scrap iron filings

Size (mesh)	Surface area ($m^2 g^{-1}$)	Fractions of iron particle sizes (%)
35-50	1.85	10
50-80	2.05	17
80-100	3.02	16
100-200	4.28	34
200->200	*	22
35->200	5.55	100

*Remarks: Scrap iron filings could not be pre-treated with acid since the particle size was too small.

Chemical constituents of scrap iron filings, determined by XRF, were composed mainly of iron (III) oxide followed by chromium (III) oxide and silicone respectively as indicated in Table 2.

Table 2 Chemical constituents of scrap iron filings (35->200 mesh) determined by XRF

Chemical constituents	Percentage by weight
Fe_2O_3	90.70
Cr_2O_3	5.41
SiO_2	1.16
Al_2O_3	0.42
MnO	0.55
MoO_3	0.86
Others	0.90

3.2 Batch studies

3.2.1 Effect of pH

To study the effect of pH on the reduction of Cr(VI) using scrap iron filings, the effect of variation of pH value was investigated. Figure 1 shows that the reduction of Cr(VI) increased with decreasing pH and then remained nearly stable at pH 7. This is possibly due to increasing oxidation of Fe(0) under acidic condition as indicated in equation 2. This is consistent with the results of Lee and co-workers [11]. In this study, the effective pH for Cr(VI) reduction was 3. The removal efficiency of Cr(VI) was 82.2 ± 0.6%. This experiment was not observed below pH 3 because the corrosion rate of iron would be increased rapidly which is not suitable for industrial applications.

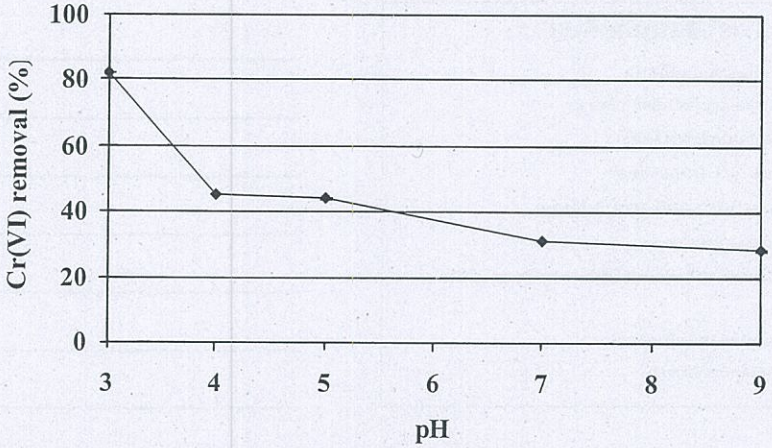


Figure 1 Effect of pH on the reduction of Cr(VI); [Cr(VI)] 30 mg l^{-1}, iron size 35->200 mesh agitating rate 150 rpm and contact time 60 mins.

3.2.2 Effect of iron particle size

The effect of iron particle size on Cr(VI) reduction was examined. Figure 2 shows that the removal of Cr(VI) increased with increases in the surface area of iron. It is possible that a higher iron surface area contained higher reactive sites. Therefore, Fe(0) was oxidized to Fe(III) increasingly. In this study, the effective iron particle size for the reduction of Cr(VI) was a 35->200 mesh because it had the highest surface area (Table 1). The removal efficiency of Cr(VI) was 82.8 ± 2.9%.

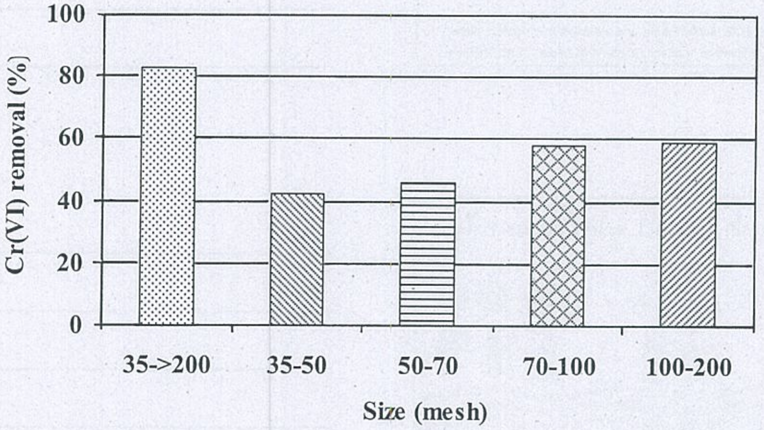


Figure 2 Effect of iron particle size on the reduction of Cr(VI); [Cr(VI)] 30mg l^{-1}, pH 3, contact time 60 mins. and agitating rate 150 rpm

3.2.3 Effect of agitating rate

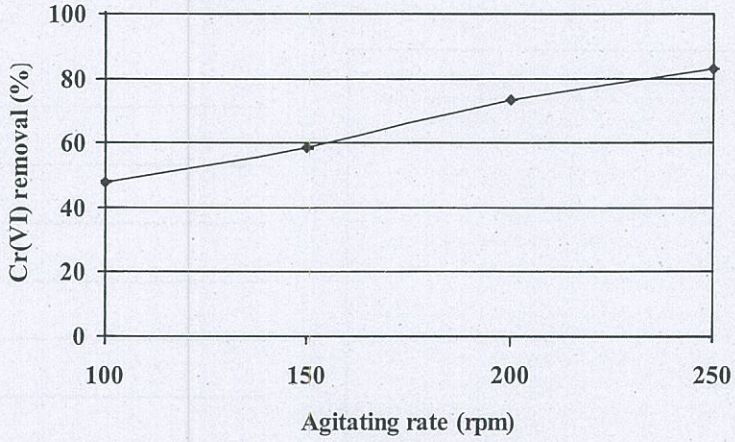


Figure 3 Effect of agitating rate on the reduction of Cr(VI); [Cr(VI)] 30 mg l^{-1}, iron size 35->200 mesh, pH 3 and contact time 60 mins.

The agitating rate was varied to observe Cr(VI) reduction efficiency. Figure 3 illustrates that the reduction of Cr(VI) increased with an increase in agitating rate. This may be due to the increase of diffusion rate of Cr(VI) solution through metal-oxide layer coated on the iron surface enhancing iron reactivity. The removal efficiency was 82.9 ± 1.5% at 250 rpm. In this study, the maximum agitating rate was 250 rpm because of the limited capacity of the agitator.

3.2.4 Effect of contact time

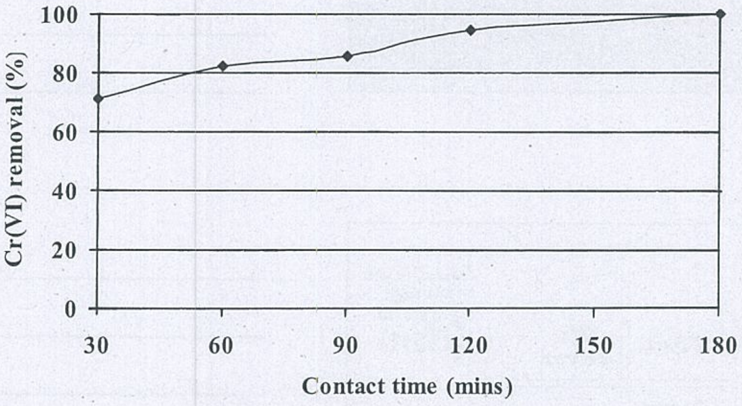


Figure 4 Effect of contact time on the reduction of Cr(VI); [Cr(VI)] 30 mg l^{-1}, iron size 35->200 mesh, agitating rate 250 rpm and pH 3

A variation of contact times was examined to investigate its effect on the reduction of Cr(VI). Figure 4 shows that the reduction rate increased with increasing contact time. This result is consistent with the results of Lee and co-workers [11]. At 180 minute - contact time, the removal efficiency was nearly 100 %. This may be explained by the increase of contact time resulting in continuing reduction of Cr(VI) until it reached its equilibrium.

3.2.5 Effect of iron dosage

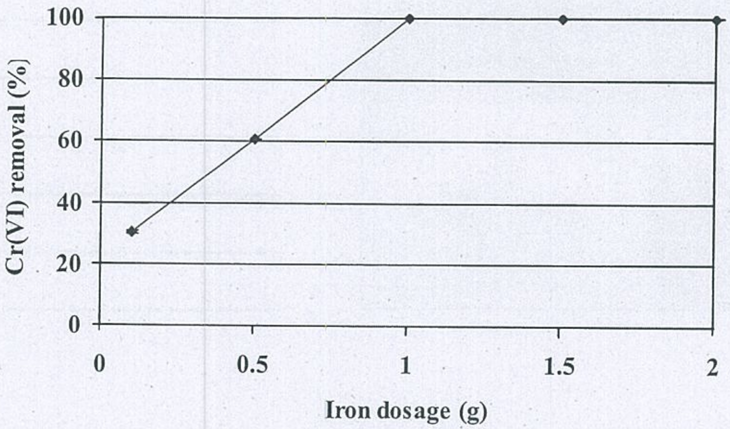


Figure 5 Effect of iron dosage on the reduction of Cr(VI); [Cr(VI)] 30 mg l^{-1}, iron size 35->200 mesh, pH 3, contact time 180 mins., agitating rate 250 rpm

Iron dosage was varied to investigate its effect on the reduction of Cr(VI). Figure 5 illustrates that the reduction of Cr(VI) rapidly increased with an increase in the dosage of iron particles and then remained stable at 1 g of iron. This may be because of the greater availability of surface area or reactive sites of higher iron dosages. However, the reaction remained stable when it reached the equilibrium.

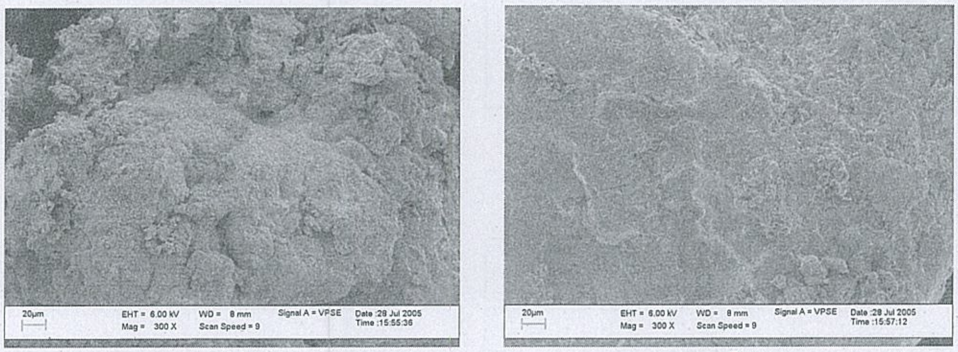
3.2.6 Removal efficiency of synthetic wastewater

Characteristics of synthetic wastewater before and after treatment are illustrated in Table 3. pH value of the synthetic wastewater after treatment was about 6. This is probable because Fe(0) is thermodynamically unstable in acidic condition and its corrosion results in the increase of pH. Therefore pH adjustment before releasing wastewater into the river was not required. Under obtained optimum conditions, almost all Cr(VI) was transformed to Cr(III). Cr (III) may be then removed through the precipitation or co-precipitation in terms of $(Cr_xFe_{(1-x)})(OH)_3$ and/or $Fe_{(1-x)}Cr_xOOH$ as illustrated in equations 3 and 4. However, some Cr(III) still remained in the solution and its concentration was over the standard limit (Table 3). The amount of total Fe in the solution increased due to its corrosion (Table 3). Figure 6 shows that the iron surface after treatment was smoother than that before treatment. This may be because iron particles after treatment were corroded and coated with metal oxides. As a result of this, the reduction of Cr(VI) decreased after treatment for awhile of period.

Table 3 Parameters of synthetic wastewater before and after treatment by scrap iron particles

Parameters	**Synthetic wastewater**	
	Before treatment	**After treatment**
pH	3.01*	5.75
Cr(VI) (mg l^{-1}) (Std. 0.75 mg l^{-1})	30.0±0.01	n.d.
Cr(III) (mg l^{-1}) (Std. 0.75 mg l^{-1})	-	4.5 ± 0.02
Total Chromium (mg l^{-1})	30.0±0.05	4.5 ± 0.02
Total Fe (mg l^{-1})	<0.02	13.85±0.04

*Remark: pH of Cr(VI) solution before treatment adjusted with 1 M HCl



(a) (b)

Figure 6 Characteristics of iron surface before (a) and after (b) treatment under the obtained optimum conditions examined by SEM-EDS with 300 X

As concentrations of Cr(III) and total Fe were still over the limit of the standard, removal of these heavy metals were required. In this study, NaOH and $Ca(OH)_2$ were used to precipitate the remaining heavy metals by adjusting the pH to 6.7 [19]. The amount of NaOH used for precipitation was less than that of $Ca(OH)_2$. It was found that almost all of the total Fe was removed as indicated in Table 4. However, the amount of total Cr although reduced was still over the standard limits. This may be because Cr(III) could not be reduced by Fe(0) but some of Cr(III) may be removed through precipitation or co-precipitation in terms of $(Cr_xFe_{(1-x)})(OH)_3$ and/or $Fe_{(1-x)}Cr_xOOH$ as mentioned above. Optimum amount of alkaline solution used or other techniques for the removal of total Cr should be examined in future work.

Table 4 Amounts of NaOH and $Ca(OH)_2$ used, and characteristics of synthetic wastewater after treatment under obtained optimum conditions

Parameters	**50% w/v NaOH**	**50% w/v $Ca(OH)_2$**
Amount of alkaline solution used (ml)	0.20	2.33
Amount of sediment (mg)	30.70	43.10
Cr^{6+} (mg l^{-1})	n.d.	n.d.
Total Cr (mg l^{-1})	1.07	1.56
Total Fe (mg l^{-1})	n.d.	n.d.

3.2.7 Removal efficiency of chromium plating wastewater

Cr(VI) contained in chromium plating wastewater was removed under obtained optimum conditions. Characteristics of chromium plating wastewater before and after treatment are illustrated in Table 5. The pH value of the chromium plating wastewater after treatment was about 5.4. It was found that almost all Cr(VI), total Cr and Cu was removed. Cr(VI) could be reduced by Fe(0) whilst Cr(III) and Ni may be removed through precipitation or co-precipitation in terms of $(Cr_xFe_{(1-x)})(OH)_3$ and/or $Fe_{(1-x)}Cr_xOOH$ as mentioned above. Only small amounts of Cu was found in chromium plating wastewater. The amount of total Fe in the solution increased due to its corrosion. This is consistent with the results of synthetic wastewater.

Table 5 Characteristics of chromium plating wastewater before and after treatment under obtained optimum conditions

Parameters	Before treatment (mg l^{-1})	After treatment (mg l^{-1})
pH	3.0*	5.36
Total Cr	5.75	<0.01
Cr^{6+}	2.51	n.d.
Ni	1.15	0.44
Cu	<0.01	<0.01
Fe	<0.02	6.54

3.2.8 Kinetic studies

A variation of estimated values of k at 10 to 100 mg l^{-1} Cr(VI) concentrations was observed. The results in Table 6 reveal a reasonably good fit of the first-order kinetic model. It was found that the rate of Cr(VI) reduction was accelerated by an increase in time but decelerated with an increase in initial Cr(VI) concentration (Figure 7).

The kinetic model of Cr(VI) reduction by iron particles under acidic conditions can be represented by the following equation:

$$\ln [C]/[C]_0 = -k\,t \qquad (5)$$

Where $[C]_0$ is the initial concentration of Cr(VI), [C] is the concentration of Cr(VI), t is the time, and k is slope of a plot of $\ln [C]/[C]_0$ against t.

Table 6 The rate constant of Cr(VI) reduction at different concentrations

Concentration of Cr(VI) (mg l^{-1})	First order kinetics		Second order kinetics		Zero order kinetics	
	k	R^2	k	R^2	k	R^2
10	-	-	-	-	-0.0222	0.3000
30	-0.0211	0.9885	0.0059	0.8611	-0.0959	0.6600
50	-0.0071	0.9910	0.0004	0.9604	-0.1544	0.8832
100	-0.0028	0.9879	0.0001	0.9854	-0.1968	0.9595

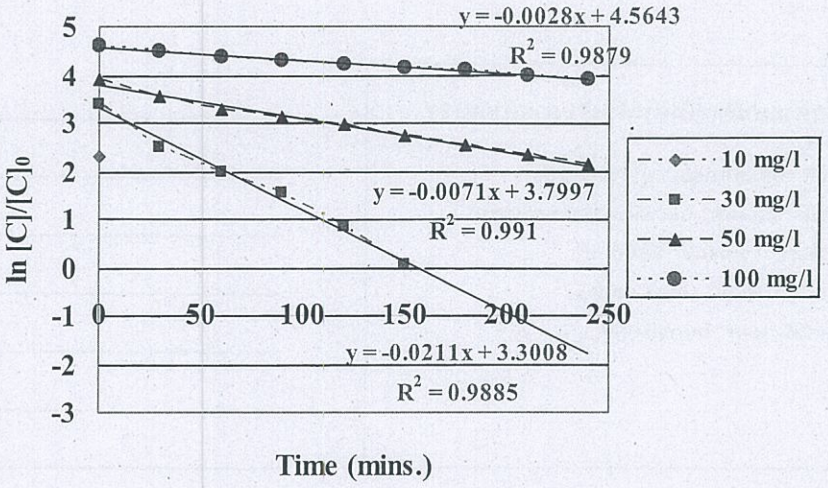


Figure 7 First order reaction of Cr(VI) reduction for different concentrations

3.2.9 Effects of nickel and copper concentrations on the reduction of hexavalent chromium

Apart from chromium, nickel and copper are main components used in chromium plating processes. The effects of nickel and copper on the reduction of hexavalent chromium was studied under several concentrations of mixtures of chromium and nickel, chromium and copper and chromium, nickel and copper. Figures 8-10 show that Ni and Cu did not affect on the reduction of Cr(VI). This may be explained by the electrical potential (E^0) of these components [21]. Ni and Cu had electrical potentials of -0.25 volts and 0.34 volts, respectively. Therefore, they could not be reduced with Fe(0) (E^0 = -0.44 Volts). However, concentrations of Ni and Cu were decreased by co-precipitation with metal hydroxides. It was found that almost all Cr(VI) was removed. This may be because Cr(VI) (E^0 = 1.33Volts) could be reduced by Fe(0) whilst Cr(III) (E^0 = -0.74 Volts) may be removed through the precipitation or co-precipitation in terms of $(Cr_xFe_{(1-x)})(OH)_3$ and/or $Fe_{(1-x)}Cr_xOOH$ as mentioned above. The amount of total Fe in the solution increased due to its corrosion.

4. CONCLUSIONS

Scrap iron filings appear to be a very good metallic system (a non-toxic substance and a low cost material) for the rapid removal of Cr(VI) contained in chromium plating wastewater. The main factors affected the reduction rate were pH and iron surface area. Increasing acidity and iron surface area led to an increase in degradation rates. The removal rate of Cr(VI) follows first order kinetics with respect to concentration of chromium solution. After the reduction of Cr(VI), the removal of total Cr and total Fe by precipitating with alkaline solution was required. Apart from chromium, nickel and copper are main components used in the chromium plating process. It was found that nickel and copper did not interfere with the reduction of hexavalent chromium.

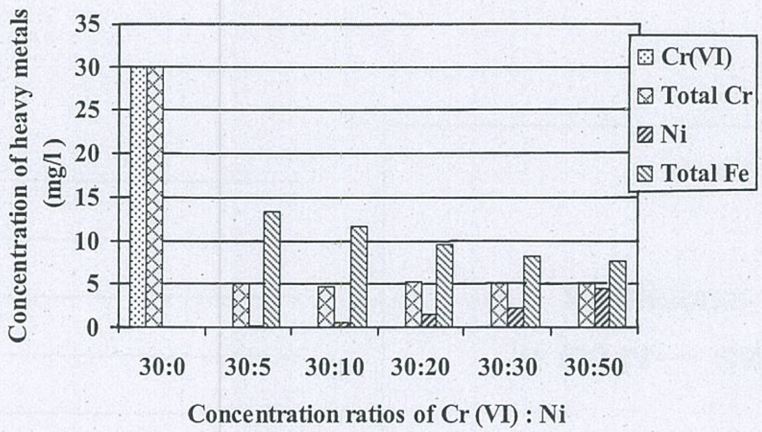


Figure 8 Effect of nickel on the reduction of hexavalent chromium

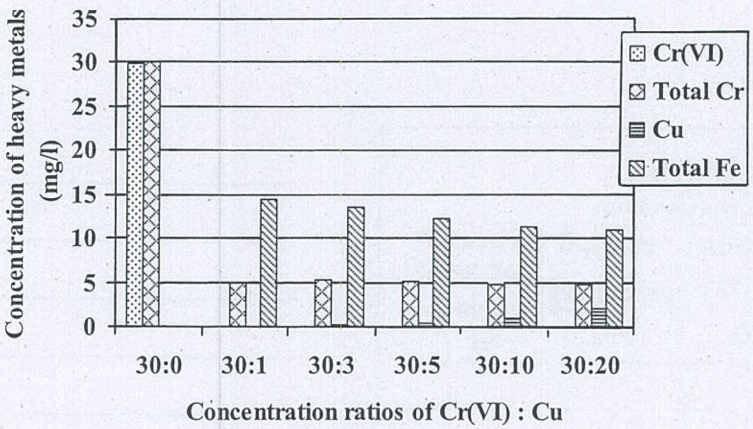


Figure 9 Effect of copper on the reduction of hexavalent chromium

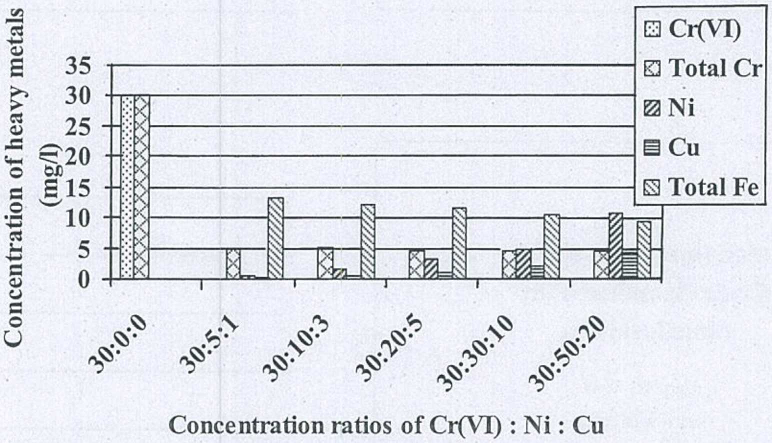


Figure 10 Effect of nickel and copper on the reduction of hexavalent chromium

5. ACKNOWLEDGEMENTS

The authors are grateful to the Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Thailand for supporting this work.

REFERENCES

[1] Palmer, C.D. and Puls, R.W. **1994** *Natural Attenuation of Hexavalent Chromium in Ground Water and Soils*. Chapter 4, EPA Environmental Assessment Source book, EPA/540/S-94/505 pp. 57-72.

[2] Sparks, D.L. **1995** *Environmental Soil Chemistry*. Academic Press, CA, USA.

[3] Orth, W.S. and Gillham, R.W. **1996** Dechlorination of Trichloroethene in Aqueous Solutions using Fe^0, *Environmental Science and Technology*, *30*(1), 66-71.

[4] Gotpagar J., Grulke E., Tsang T. and Bhattacharyya, D. **1997** Reductive Dehalogenation of Trichloroethylene using Zero-valent Iron, *Environmental Progress*, *16*(2), 137-143.

[5] Janda, V., Vasek, P., Bizova, J. and Belohlav, Z. **2004** Kinetic Models for Volatile Chlorinated Hydrocarbons Removal by Zero-valent Iron, *Chemosphere*, *54*, 917-925.

[6] Agrawal, A. and Tratnyek, P.G. **1996** Reduction of Nitro Aromatic Compounds by Zero-valent Iron Metal, *Environmental Science and Technology*, *30*(1), 153-160.

[7] Cao, J., Wei, L., Huang, Q., Wang, L. and Han, S. **1999** Reducing Degradation of Azo Dye by Zero-valent Iron in Aqueous Solution, *Chemosphere*, *38*(3), 565-571.

[8] Deng N., Luo F., Wu F., Xiao M. and Wu X. **2000** Discoloration of Aqueous Reactive Dye Solutions in the UV/ Fe^0 System, *Water Research*, *34*(8), 2408-2411.

[9] Nam, S. and Tratnyek, P.G. **2000** Reduction of Azo Dyes with Zero-valent Iron, *Water Research*, *34*(6), 1837-1845.

[10] Mielczarski, J.A., Atenas, G.M. and Mielczarski, E. **2005** Role of Iron Surface Oxidation Layers in Decomposition of Azo-Dye Water Pollutants in Weak Acidic Solutions, *Applied Catalysis B: Environmental*, *56*, 289-303.

[11] Lee, T., Lim, H., Lee, Y. and Park, J-W. **2003** Use of Waste Iron Metal for Removal of Cr(VI) from Water, *Chemosphere*, *53*, 479-485.

[12] Puls, R.W., Paul, C.J. and Powell, R.M. **1999** The Application of in situ Permeable Reactive (Zero-valent Iron) Barrier Technology for the Remediation of Chromate Contaminated Groundwater: A Field Test , *Applied Geochemistry*, *14*, 989-1000.

[13] Blowes, D.W., Ptacek, C.J. and Jambor, J.L. **1997** In-situ Remediation of Cr(VI) Contaminated Groundwater using Permeable Reactive Walls: Laboratory Studies, *Environmental Science and Technology*, *31*(12), 3348-3357.

[14] Buerge, I.J. and Hug, S.J. **1997** Kinetics and pH Dependence of Chromium(VI) Reduction by Iron (II) , *Environmental Science and Technology*, *31*(5), 1426-1432.

[15] Buerge, I.J. and Hug, S.J. **1999** Influence of Mineral Surfaces on Chromium(VI) Reduction by Iron(II), *Environmental Science and Technology*, *33*(23), 4285-4291.

[16] Ponder, S.M., Darab, J.G. and Mallouk, T.E. **2000** Remediation of Cr(VI) and Pb(II) Aqueous Solutions using Supported, Nanoscale Zero-valent Iron, *Environmental Science and Technology*, *34*(12), 2564-2569.

[17] Nikolaidis, N.P., Dobbs, G.M. and Lackovic, J.A. **2003** Arsenic Removal by Zero-valent Iron: Field, Laboratory and Modeling Studies, *Water Research*, *37*, 1417-1425.

[18] ASTM **1998** ASTM D 1687-92, Test Methods for Chromium in Water.

[19] Lin, Q., Zhao, G. and Yuan, W. **1990** Chemical Equilibrium Calculation in Treatment of Wastewater Containing Chromium, *Water Treatment*, *4*, 79-90.

[20] Department of Industrial Works **1999** Chromium Plating Wastewater.

[21] Hanpongpun, I. **1996** *General Chemistry for Engineers*, 6th eds., Bangkok, Chulalongkorn Publishing.