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Role of Iron Anode Oxidation on Transformation of Chromium by Electrolysis

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Abstract

The potential for chemical reduction of hexavalent chromium Cr(VI) in contaminated water and formation of a stable precipitate by Zero Valent Iron (ZVI) anode electrolysis is evaluated in separated electrodes system. Oxidation of iron electrodes produces ferrous ions causing the development of a reducing environment in the anolyte, chemical reduction of Cr(VI) to Cr(III) and formation of stable iron-chromium precipitates. Cr(VI) transformation rates are dependent on the applied electric current density. Increasing the electric current increases the transformation rates; however, the process is more efficient under lower volumetric current density (for example 1.5 mA L⁻¹ in this study). The transformation follows a zero order rate that is dependent on the electric current density. Cr(VI) transformation occurs in the anolyte when the electrodes are separated as well as when the electrolytes (anolyte/catholyte) are mixed, as used in electrocoagulation. The study shows that the transformation occurs in the anolyte as a result of ferrous ion formation and the product is a stable Fe₁₅Cr₅(OH)₆₀ precipitate.

Keywords

Chromium; Iron; Electrolysis; Transformation

1. Introduction

Chromium is a heavy metal with many oxidation states. The most stable states are trivalent chromium Cr(III) and hexavalent chromium Cr(VI). Cr(III) is less soluble, tends to associate with solid phases, and is considered an essential element in human and animal nutrition, while Cr(VI) is more soluble, very toxic, and carcinogenic [1]. Cr(VI) is typically present as negatively charged chromate, CrO₄²⁻, or dichromate, Cr₂O₇²⁻, ions which are highly mobile in groundwater with increased risk of human exposure. Significant amounts of chromium waste are produced every year as a result of industrial activities (e.g. wood preservative treatments, pigments, leather tanning, and electroplating) and are subsequently discharged in the environment [2]. A query at the EPA Superfund Information System showed that chromium is present in 533 of the 1255 sites listed on the National Priority List [3].

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Many techniques have been proposed to reduce Cr(VI) in wastewater and groundwater by introducing naturally occurring materials to enhance chemical transformation. These materials include iron [4–6], humic substances [7], fulvic acid [8], agricultural wastes and activated carbon [9], cellular organics [10], and iron-reducing bacteria [11]. Other techniques involve manufactured materials to treat Cr(VI), such as gel-coated silica made of epoxy-cross-linked poly(ethylenimine) [12], conducting polymers [13], polyaniline films [14], iron (III) complex of a carboxylated polyacrylamide-grafted sawdust [15], hydrogen peroxide [16], high-density phosphonic acid [17], carbon-aerogel electrodes [18], reticulated vitreous carbon electrodes [19]], and zero valent iron [20].

Various shapes and forms of iron, such as scrap iron, steel wool, ferrous ions, or iron-bearing minerals, have been proposed for transformation of Cr(VI) (chromate/dichromate). The Cr(VI) chemical reduction is assumed to be coupled with iron oxidation (or corrosion) as a single electrode redox system, i.e. oxidation and reduction occur at the same iron surface or redox site. In such cases, the redox process is spontaneous under specific pH and redox conditions. For example, Cr(VI) reduction by scrap iron [21] shows an increased reduction rate with decreasing pH, increasing temperature, and decreasing initial Cr(VI) concentration. Studies on the mechanisms of the reactivity of micro- and nano- Zero Valent Iron (ZVI) highlight the critical role of corrosion and release of ferrous ions on the chemical reduction by ZVI. The reactivity and corrosion of ZVI fillings as a single electrode system show that the kinetics of Cr(VI) reduction by ZVI is controlled by the anodic rate of iron corrosion [22]. However, due to the inevitable passivation and formation of scale, the reactivity of iron fillings decreases quickly and eventually limits contaminants transformation.

In addition to the ZVI system, two-electrode system, driven by an external electric power, is an option for transformation of Cr(VI). In two-electrode electrolytic treatment of aqueous solution, the transformation of Cr(VI) to Cr(III) is typically evaluated at the cathode or in a circulated anolyte-catholyte system using non-reactive electrodes such as carbon, and the redox is dependent on electrode types and electrolyte chemistry. Porous electrode reactors were widely studied in the 1970s and 1980s for electrolytic metal removal. Most notable is the work that provided a cost estimate associated with a pilot plant [23]. Such techniques have been explored for treatment of wastewater; their implementation for *in situ* treatment of groundwater is limited because of cost, practicality, and heterogeneity of the hydro- and geo-chemical system and transformation kinetics.

A two-electrode system using affordable iron electrodes has been proposed for treatment of wastewater by electrocoagulation under electric current and then filtering and separating the precipitated solids. Electrocoagulation for treatment of wastewater was patented in 1906 [24], but did not receive attention for treatment of wastewater until recently. The types of wastewater treated by the process include mixtures of phenol compounds [25], nitrogen and phosphorous [26], dairy waste waters [27], heavy metals and radionuclides [28–30]. Wastewater containing chromium (VI), such as electroplating wastewater and leather plant wastewater, can be effectively treated by iron electrocoagulation. In addition to electroreduction on the cathode, the ferrous species generated by the iron anode are capable of reducing Cr(VI) to Cr(III) through chemical reactions. The reactivity of this system is similar to that developed by ZVI fillings, except that iron oxidation is controlled and manipulated by the type and intensity of the applied electric current. In other words, the uncontrolled oxidation of ZVI fillings as a single electrode (with anodic and cathodic sites) system is converted in this process into two electrodes with controlled redox rates.

Although applications of iron electrocoagulation for the treatment of Cr(VI)-containing wastewater have been reported, the specific role of an iron anode by itself is still not well

investigated, especially the temporal chemical changes of electrolytes that an iron anode may induce in the anolyte. The chemical changes of treated water, such as pH and oxidation-reduction potential (Redox potential, ORP), are relevant because these variables can greatly impact the biotic and abiotic processes in groundwater when the iron electrolysis is applied for groundwater remediation. The objective of this study is to evaluate the role of iron anode oxidation in a two-electrode electrolysis system for reduction of hexavalent chromium Cr(VI) to trivalent chromium (Cr(III)) and formation of immobile precipitate in an aqueous system. Different from previous (e.g. electrocoagulation) studies, the electrolytic cell is designed to be divided or undivided, allowing accurate assessment on the role of anode oxidation and temporal chemical changes (oxidation/reduction potential, pH) in the electrolytes as a result of continuous application of the electric current.

2. Materials and Methods

The experimental program, summarized in Table 1, includes a set of electrolysis experiments using either Mixed Metal Oxide (MMO) (Group A) or iron (Groups B and C) anodes. In most of these tests, the anolyte and catholyte are separated by an ion exchange membrane. Tests were also conducted with iron anodes without membranes to separate the anolyte/catholyte (labeled open or mixed electrolytes).

The experimental setup (Figure 1) consists of two acrylic chambers (anodic compartment and cathodic compartment) that are separated by a Nafion-112 membrane, and each compartment is 15cm long, 10cm high and 5cm wide. The membrane is used in most experiments to physically separate the electrolytes into two compartments with separate solution. In some experiments, the membrane is removed (electrolyte solutions are mixed). There are three ports in the upper side of each chamber for pH and Oxidation/Reduction Potential (ORP) measurements and to sample the electrolyte. For all the experiments, the liquid in the each chamber is 650 mL. The iron electrodes are 12 cm long cylindrical iron rods, 1 cm in diameter. MMO-titanium-coated electrodes are a mesh strip 1 cm wide, 1mm thick and 12 cm long. MMO-titanium electrodes are used to assess the impact of inert (non-corrosive) electrodes on the transformation process. Ferrous chloride (Fisher Scientific) is introduced in the control experiments as an electrolyte, in order to compare with the experiments using iron anode. In this case, 9.9×10^{-3} M FeCl_2 was added to the deoxygenated solution prior to the electrolysis. A lab bench DC power supply (HPE3612A) is used to apply the direct electric current. Experiments are conducted in duplicate.

Electric current density is used in electrochemistry to refer to current applied per surface area of the electrode because the objective is usually to assess changes that occur directly at the electrode surface. In the present study, we are assessing changes in a specific volume of electrolyte due to a continuous application of electric current. Therefore, instead of evaluating current density per electrode surface area as commonly used, the current per volume of electrolyte is evaluated; this is referred to as volumetric current density (VCD). This facilitates calculating the chemical changes in electrolyte. Experiments are conducted by applying three VCDs: 1.5, 7.5, and 15.0 mA L^{-1} with respect to the total volume (1300 mL) of each electrolysis experiment.

Electrolytes are prepared using analytical grade reagents and deionized water. The Cr(VI) stock solution (1 mg mL^{-1}) is prepared from potassium dichromate powder (Fisher Scientific). The diphenylcarbazide (DPC) solution is prepared according to EPA Method 7196 for colorimetric analysis of Cr(VI) using the Milton Roy Spectrophotometer 20 D. Precipitated products after treatment are analyzed by X-ray photoemission spectroscopy (XPS) using a PHI 10-360-4-015 hemispherical analyzer. XPS was performed using a PHI 04-173-0-077 Mg/Al dual anode non-monochromated x-ray source. XPS peak processing is

performed using a full width at half maximum of 1.4 eV with an 80% Gaussian and 20% Lorentzian peak shape, as determined from a clean Au_{4f7/2} photoelectron peak. Depth profile on a 4×4mm area is performed using an Ar ion gun at 1 to 3 keV source voltage and 25 mA filament current with a gun pressure of 10 mPa. The samples measurements of pH are conducted using a ThermoOrion combination electrode with a VWR Scientific, Model 200 m. Oxidation/Reduction Potential of the electrolytes is determined using a Cole-Parmer combination Ag/AgCl reference electrode with a platinum (Pt) band and an Accumet Basic meter. Millivolt readings are converted to ORP, using the electrode readings plus the standard potential of a reference electrode at a given temperature. Conductivity measurements are conducted using Cole-Parmer conductivity cell (Model 19550-60) and Cole-Parmer conductivity meter (Model 30).

3. Results and Discussion

3.1 Inert Anodes

Electrolysis by non-corrosive (MMO) electrodes (Group A Experiments) produced inefficient and unstable Cr(VI) transformation at both the anode and cathode chambers. Introducing ferrous ions to the electrolytes improved Cr(VI) reduction to 75 percent at the catholyte, where reducing conditions predominate due to the release of hydrogen gas and hydroxyl ions (Eq. 1). Because oxidation occurs at the anode (Eq. 2), introducing ferrous ions into the anolyte did not impact Cr(VI) transformation. Oxidation of ferrous ions in the anolyte by oxygen produced from electrolysis (Eq. 2 and Eq. 3) is more favorable than reduction of Cr (VI) by ferrous ions.

3.2 Iron Anodes

Electrolysis at the iron anode using a system with iron electrodes separated by a Nafion membrane produced significant changes in Cr(VI) concentration in the anolyte (Figure 2). Concentrations of Cr(VI) decreased to below detectable levels within 8, 15, and 24 hours under volumetric current densities of 15 (initial concentration is 21.1 mg L⁻¹), 7.5 (initial concentration is 20.6 mg L⁻¹), and 1.5 mA L⁻¹ (initial concentration is 20.8 mg L⁻¹), respectively. Average transformation rates under 15 mA L⁻¹ were measured to be 8.9, 3.6, 1.7, and 0.1 mg L⁻¹h⁻¹ after 1, 3, 5, and 8 hours, respectively. Under 7.5 mA L⁻¹, the average reduction rates decreased from 5.3 to 2.3 and 0.03 mg L⁻¹ h⁻¹ after 1, 7, and 15 hours of operation, respectively. A comparison between the three current densities shows that the reduction rate is proportional to the applied current. The half-life values for Cr(VI) concentration are 2, 5 and 10 hours under 15, 7.5 and 1.5 mA L⁻¹, respectively.

To develop a better understanding of the transformation rates, the change in concentration is measured as a function of electric charge applied to the electrolyte. Normalized concentration versus the electric charge (Figure 3) shows the same transformation rate under the three current densities at early stages of the process. However, rates vary after that, and the low current density of 1.5 mA L⁻¹ results in the most efficient reduction rate. The normalized concentration follows a zero order transformation rate, given by

$$\frac{dc/c_0}{dt} = -kI_v \quad \text{or} \quad \frac{dc/c_0}{d(I_v t)} = -k$$

where c is the concentration, c_0 is the initial concentration, k is the zero order transformation coefficient per Coulomb (mg/C) and I_v is the VCD (mA L⁻¹). The most efficient transformation under 1.5 mA L⁻¹ shows a zero order rate constant (k) of 0.159 mg C⁻¹.

Reduction of Cr(VI) in the anolyte was a surprise because electrochemical oxidation (not reduction) typically occurs at the anode. However, the explanation is that iron oxidation produces ferrous ions in the anolyte which tend to increase the potential for chemical reduction in the anolyte (Eq.4 and Eq.5). This is different than using inert (e.g. MMO) anodes which produce oxygen (and protons), increasing the anolyte potential for chemical oxidation. Comparisons of pH and ORP measurements using iron anodes versus MMO anodes support this analysis.

The average initial pH value for the electrolytes was 5.7. The initial pH is less than neutral pH because of the dissolution of potassium dichromate in distilled water. The pH was relatively stable and did not show significant changes during treatment under 7.5 mA L⁻¹ and 1.5 mA L⁻¹. The reason for the limited change in pH (as compared to inert electrodes) is that the release of ferrous ions to the anolyte is the dominant electrolysis reaction and the production of protons by water electrolysis is not significant when iron electrodes are used. Under 15 mA L⁻¹, the pH was steady for the first 8 hours, then followed a slight decrease to 4.5. The decrease in pH under 15 mA L⁻¹ indicates the possibility of water electrolysis (Eq. 5) occurring as the system becomes saturated with ferrous ions.

Fig. 4 shows the ORP changes over time in anolyte under different volumetric current densities. The average ORP value under 15 mA L⁻¹ decreases from 219 mV to below zero and reaches -94 mV after 8 hours. The same behavior is observed under 7.5 mA L⁻¹ where a slight increase appeared in the first 2 hours, followed by a significant drop in ORP values. The initial average value was 195 mV at 7.5 mA L⁻¹, which dropped to a negative value after 9 hours of operation. By the end of the reduction process, duplicate experiments under 7.5 mA L⁻¹ showed negative ORP values with an average of -136 mV. The behavior under the lower current density of 1.5 mA L⁻¹ was different. An increase was noted in the ORP to about 400 mV after 9 hours. However, a significant drop in ORP occurred after the ninth hour. After three days the final average ORP under 1.5 mA L⁻¹ value was -19 mV (not shown in Fig. 4), indicating the buildup of a reducing electrolyte environment. Generally, the ORP changes in Fig. 4 are consistent with applied current densities: increasing the current density increases the production of ferrous ions into the anolyte, yielding a decrease in the ORP. The behavior is completely different than the case with MMO anodes, where the ORP increases to more than 1000 mV [31] under similar conditions. The difference between the two cases highlights the value of using iron anodes for chemical reduction of contaminants. The results of Cr(VI) reduction validate this hypothesis.

The average electric potential or voltage is proportional to applied current density and ionic conductivity, which is a function of electrolysis products and dichromate concentration in the solution. All treatments showed an increase in the voltage over time. The voltage

increased from 50 to 61 V under 15 mA L^{-1} ; from 20 to 61 V under 7.5 mA L^{-1} ; and from 7 to 10 V under 1.5 mA L^{-1} . The increase in the potential is due to the decrease in the electric conductivity of the system. A possible reason for increasing the resistance is the precipitation of ferrous ions with dichromate ions. In particular, precipitation on the Nafion membrane will significantly minimize its electrical conductance and increase the total applied potential.

3.3 Iron electrodes in a mixed electrolyte reactor

Cr(VI) reduction also occurred in the experiments with mixed electrolyte where the anode and cathode compartments are not separated by a membrane. The reactor allows for mixing the anolyte and the catholyte in a single chamber. Transformation of Cr(VI) in the mixed electrolyte under 15 mA L^{-1} is displayed in Figure 5. In the first 5 hours, the reduction rate increased to $5.9 \text{ mg L}^{-1} \text{ h}^{-1}$ and complete Cr(VI) reduction occurred after 11 hours of processing under electric current.

In the mixed electrolyte, the initial pH increased from an initial value of 5.6 to above 10 after 11 hours. The increase is primarily due to the production of hydroxyl ions (and hydrogen gas) as a main electrolysis reaction at the cathode (Eq.1). If an inert anode is used, proton generation would neutralize the hydroxyl ion generation (Eq.1 and Eq.2). However, because iron anodes are used, the pH of the electrolyte is dominated by the water electrolytic reduction at the cathode.

Although the ferrous ions will combine some hydroxyl ions and form precipitates (Eq. 6), free hydroxyl ions still exist in the solution and resulting in alkaline pH ($K_{sp}(\text{Fe}(\text{OH})_2) = 7.9 \times 10^{-15}$) [30]. Theoretically, the final pH of mixed electrolyte can reach 11.3 if anodic reaction (iron dissolution, Eq.4) and cathodic reaction (hydrogen evolution, Eq.1) both proceed at 100% current efficiencies and no other redox processes are considered.

The ORP (Figure 6) of the mixed electrolyte under 15 mA L^{-1} decreased from an initial value of 192 mV to -264 mV after 11 hours of operation. The decrease of redox potential to reducing conditions is attributed to the combined effect of production of hydrogen gas at the cathode and the released ferrous ions at the anode. In a mixed electrolyte system, the net effect will be production of ferrous hydroxyl, hydrogen gas and development of a reducing electrolyte environment.

The total electric potential in the mixed electrolyte system increased from 9.2 to 14.3 V throughout the experiment. This is significantly smaller than the voltage measured in the membrane cell experiments, which ranged from 50 to 60 volts. The significant reduction in the voltage is mainly due to the removal of the membrane.

3.4 Assessment Experiments

The last set of experiments (Group C) is conducted to confirm that chemical transformation occurs in the electrolyte. Clean anolyte without Cr(VI) is prepared using iron anode under 15 mA L^{-1} for 2 days. The anolyte is then collected and isolated in separate vials and potassium dichromate is mixed with the isolated anolyte: 98 mL of the solution was transferred into a serum bottle prefilled with 2 mL dichromate stock solution to have a final concentration of 20 mg L^{-1} . After 2 hours, analysis showed a complete reduction of Cr(VI). This experiment verified that the reaction mainly occurred in the solution. It also indicates

that this application has great potential for use on contaminated groundwater, where ferrous ions can be introduced into the groundwater to react with contaminants.

To assess the stability of the products, the chromium precipitate is filtered from the solution and mixed with 10% sulfuric acid solution and in another experiment 10% potassium hydroxide solution. The solutions are stored for two days, and then analyzed for Cr(VI) concentration. No traces of Cr(VI) concentrations were detected in the solution, indicating that the transformation precipitate is very stable and the method is reliable for wastewater and groundwater treatment.

XPS is used to identify both the reactants and the products. The Cr-Fe complex was isolated using filter papers under negative pressure and the filtrate was exposed to x-ray. XPS analysis show that all iron species in Fe-Cr complex are ferric species and the molar ratio of Fe(III) to Cr(III) is 3:1, which represents the electron relationship or the chemical stoichiometric relationship between the two elements: three moles of Fe(II) are required to reduce one mole of Cr(VI) to Cr(III). The chemical formula of the final product is believed to be $\text{Fe}_{15}\text{Cr}_5(\text{OH})_{60}$. It is reported [32] that $(\text{Cr,Fe})(\text{OH})_3$ solubility is dependent on the mole fraction of chromium in the $(\text{Cr,Fe})(\text{OH})_3$. The higher the mole fraction, the higher is the solubility. It is also shown [33] that Fe can be substituted by Cr(III) in hydrous Fe oxides. The Eh–pH diagram of aqueous Cr species shows that Cr(VI) is transformed into Cr_2O_3 or FeCr_2O_4 when ferrous is present at reducing and alkaline conditions[34]. In the natural environment, these products are believed to be finally converted to more stable Fe-Cr oxides due to the loss of water

4. Conclusions

Complete Cr(VI) reduction can be achieved in the anolyte as a result of electrolysis by iron anodes and the transformation occurs under different rates depending upon the volumetric current density. The transformation occurs in the anolyte as it does in the mixed electrolyte, similar to electrocoagulation. Although oxidation occurs at the anode, using iron anodes generates reducing conditions in the anolyte. The final product is a stable ferric chromium hydroxide. Manipulation of the redox in separated or mixed electrolytes leads to efficient treatment of contaminated wastewater and groundwater. Iron electrolysis is expected to be applied for remediation of groundwater contaminated with Cr(VI), although the physiochemical changes of aquifer that an iron electrolysis may cause still need to be evaluated.

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Figure 1.
Schematic of experimental setup

Figure 2.
Cr(VI) concentration in the anolyte using iron electrode under 15, 7.5, and 1.5 mA L⁻¹

Figure 3. Cr(VI) ratio as a function of charge density in the anolyte using iron electrode under 15, 7.5, and 1.5 mA L^{-1} .

Figure 4.
ORP values during Cr(VI) reduction in anolyte solution using iron electrode.

Figure 5.
Cr(VI) reduction in non-membrane redox cell under a current density of 15mA L⁻¹.

Figure 6.
pH and ORP in the mixed electrolyte in non-membrane redox cell under a current density of 15mA L^{-1} .

Table 1

A summary of the experimental program

Test Group	Anode type	Current per Volume (mA L ⁻¹)	Cr(VI) Conc. (mg L ⁻¹)	Treatment Electrolyte Type	Electrolyte Solution	Test ID [*]
A	MMO	15	10	Anolyte	5.4×10 ⁻⁴ M K ₂ Cr ₂ O ₇	MMO-A1
				Catholyte	5.4×10 ⁻⁴ M K ₂ Cr ₂ O ₇	MMO-C1
	MMO	15	10	Anolyte /Catholyte	5.4×10 ⁻⁴ M K ₂ Cr ₂ O ₇	Control
					9.9×10 ⁻³ M FeCl ₂	
B	Iron Anode	1.5	20	Anolyte	1.1×10 ⁻³ M K ₂ Cr ₂ O ₇	Fe-A1-1
		7.5	20	Anolyte	1.1×10 ⁻³ M K ₂ Cr ₂ O ₇	Fe-A1-7.5
		15	20	Anolyte	1.1×10 ⁻³ M K ₂ Cr ₂ O ₇	Fe-A1-15
			25	mixed electrolyte	1.3×10 ⁻³ M K ₂ Cr ₂ O ₇	Fe-Mixed
C	Iron Anode	15	NA	Preparing Anolyte	3.8×10 ⁻³ M NaCl	Fe-A1-Pre

* All experiments were carried out with duplicates.