Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Scrap iron packed in a Ti mesh cage as a sacrificial anode for electrochemical Cr(VI) reduction to treat electroplating wastewater

Vinh Ya[a,b], Esther Le Guillou[a,c], Yi-Ming Chen[d], Jui-Hsuan Yu[e], Kwang-Ho Choo[f], Sheng-Ming Chuang[g], Shou-Jen Lee[g], Chi-Wang Li[a,*]

[a] *Department of Water Resources and Environmental Engineering, Tamkang University, 151 Yingzhuan Road, Tamsui District, 25137 New Taipei City, Taiwan*
[b] *Faculty of Environment and Natural Resources, Dalat University, Dalat, Viet Nam*
[c] *Ecole Nationale du Génie de l'Eau et de l'Environnement de Strasbourg 1 quai Koch, 67000 Strasbourg, France*
[d] *Department of Environmental Engineering, Vanung University, No.1, Wanneng Rd., Zhongli District, 32061 Taoyuan City, Taiwan*
[e] *Department of Marine Leisure and Tourism, Taipei University of Maritime Technology, No. 150, Sec. 3, Binhai Rd., Tamsui District, 251 New Taipei City, Taiwan*
[f] *Department of Environmental Engineering, Kyungpook National University, 80 Daehak-ro, Buk-gu, 702-701 Daegu, Republic of Korea*
[g] *Department of Mechanical Engineering, Yuan Ze University, Taoyuan City, Taiwan*

ARTICLE INFO

Article history:
Received 30 December 2017
Revised 9 March 2018
Accepted 9 March 2018
Available online xxx

Keywords:
Cr(VI) removal
Scrap iron
Oxidation–reduction
Titanium mesh

ABSTRACT

A novel sacrificial anode comprised of scrap iron packed inside a cage made of titanium mesh was developed for Cr(VI) reduction. With electric currents applied, the surface passivation of scrap iron electrode could be avoided. Due to the large surface area with open structures provided, the applied current densities (1.18–3.54 mA/cm^2) were low, resulting in low operating voltage and energy consumption. Complete Cr(VI) removal was achieved with electric currents applied, whereas only 20% of the Cr(VI) was removed without electricity. Direct Cr(VI) reduction on the iron surface was a dominant mechanism for the system operated at low (0.25 A) or no current. Acidic pH levels were more effective in Cr(VI) removal, due to more adsorption of Cr(VI) onto the precipitated Fe hydroxide. The trend in total Cr removal was almost the same as that of Cr(VI) removal, but time required to complete total Cr removal was extended. With intermittent electricity supply at a high electric current intensity, the energy consumption of the system was more efficient. Using scrap iron as a sacrificial anode under the intermittent current condition can save 72–77% of the total operational costs required by the conventional plate electrode.

1. Introduction

Scrap iron is a low-cost material generated from the drilling or turning processes in metal processing plants, being produced with different shapes and sizes, such as iron powder, iron shavings, and iron spiral fibers, etc. [1]. Scrap iron packed columns were employed previously to treat Cr(VI)-containing water [1–8]. The removal of Cr(VI) in a scrap iron packed column involves the direct reduction of Cr(VI) on the iron surface which generates ferrous ions, followed by the precipitation of Cr(III) as $Cr(OH)_3$ precipitates. These ferrous ions generated will subsequently react with Cr(VI) in the solution [5]. The reduction of Cr(VI) on the iron surface is denoted as direct Cr(VI) reduction, and the overall reaction of the direct Cr(VI) reduction is written as Eq. (1), showing that 1 mol of iron is consumed for each mole of Cr(VI) reduced.

$$7H^+ + Fe^0 + HCrO_4^- \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O. \tag{1}$$

In highly acidic media, hydronium ions could oxidize iron generating ferrous ions [9,10] as shown in Eq. (2) and, the generated ferrous ions will then react with Cr(VI) in solution (see Eq. (3)). This is denoted as indirect Cr(VI) reduction and the overall reaction is shown in Eq. (4) which indicates that each mole of Cr(VI) reduced consumes 3 mol of iron. Gould [9] reported a 1.33 mol iron were dissolved for a mole of Cr(VI) reduced regardless of pH levels. Although the reaction mechanism was not demonstrated by the authors, the value of 1.33 mol iron consumed per mole of Cr(VI) removal suggests that direct Cr(VI) reduction should be the dominant mechanism.

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{2}$$

$$7H^+ + 3Fe^{2+} + HCrO_4^- \rightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O \tag{3}$$

$$H^+ + HCrO_4^- + 3Fe + 8H_2O \rightarrow 3H_2 + Cr(OH)_3 + 3Fe(OH)_3 \tag{4}$$

---

[*] Corresponding author.
E-mail address: chiwang@mail.tku.edu.tw (C.-W. Li).

https://doi.org/10.1016/j.jtice.2018.03.016

Please cite this article as: V. Ya et al., Scrap iron packed in a Ti mesh cage as a sacrificial anode for electrochemical Cr(VI) reduction to treat electroplating wastewater, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.03.016

The Cr(VI) reduction capacity of scrap iron packed columns was limited by the passivation of iron particle surface by freshly formed iron oxides or mixed Cr(III)-Fe(III) oxides [1,3,4,7]. Depending on shape and size of scrap iron, contact time, solution pH, and influent Cr(VI) concentration, the reduction capacity varied from 0.51 to 41.4 mg Cr(VI)/g Fe [1,6,11], corresponding to only 0.051–4.14% of the packed iron was actually used. Several studies indicated that the treatment capacity of scrap iron packed columns could be enhanced with the column being operated at highly acidic pH values [4,5,8,11,12] or with the presence of nitrate ions [3]. Other than altering the solution chemistry, Lu et al. [13] had applied electric current to remove passivation layer to recover iron reactivity in a permeable reactive barrier system which was constructed with 8 pieces of iron meshes for treating Cr(VI)-contaminated water.

Using a sacrificial iron anode in electrolytic system (ES) for the reduction of Cr(VI) has been reported [5,14,15]. Although the direct electro-reduction of Cr(VI) on the cathode is possible, Cr(VI) is mainly reduced through indirect reduction by the anodically generated ferrous ions [16]. The effect of initial pH on the Cr(VI) reduction by ES was reported, revealing the increase of removal efficiency with decreasing initial pH [17]. The increased Cr removal at acidic pH was thought to be due to the excessive Fe(II) generated by chemical dissolution of the iron anode. Regarding the effect of solution chemistry on the Cr(VI) reduction using a sacrificial iron anode, Chuang et al. [14] reported that the rate of Cr(VI) removal increased with decreasing initial pH. The amount of Fe(II) generated per mole of Cr(VI) reduced was compared with the stoichiometric ratio between Cr(VI) reduction and Fe(II) oxidation *via* indirect Cr(VI) reduction (see Eq. (4)), i.e., 3 mol of Fe(II) oxidized per mole of Cr(VI) reduced. It was found that $Fe(OH)_3$ precipitates contributed to the additional adsorption of Cr(VI) at low initial pH values [14,18].

Currently, there is no report using scrap iron in a ES for Cr(VI) reduction except few reports using scrap iron anode for the removal of Ni [19], color and COD [20], and Ni-EDTA [21]. The scrap iron anode used in ref. [19] was metal scrap sheets which has been pre-treated (degreasing, acid pickling and alkaline treatment) and cut into a uniform surface area. In both refs. [20] and [21], scrap iron was packed in a perforated polyvinyl chloride (PVC) tube. A thin wire or a rod was buried inside the scrap iron particles to conduct electric charge from the power supply. Although the scrap iron anode having much higher surface area than traditional tubular anode, the energy consumption was still higher than that of the tubular anode due to the resistance caused by concentration polarization [20].

Therefore, the present study focused on a new design of a sacrificing anode for Cr(VI) reduction using scrap iron while packing it inside a cage made of titanium mesh with rhombus shape opening of the size of 7 × 7 mm. The titanium mesh cage, which is non-corrosive, lightweight, durable and strong [22], could provide multiple points of contact to conduct electricity to the scrap iron. Meanwhile, the scrap iron anode packed inside the Ti mesh had more open structures and thus was expected to enhance electrochemical reactions. The surface passivation of scrap iron could be potentially avoided as well due to electric currents [13]. With various electric current intensities applied, the Cr(VI) removal efficiency and dissolution behavior of scrap iron were investigated. More specifically, the effects of key parameters (*i.e.*, electric current density, solution pH, and intermittent electricity supply) on the Cr removal efficiency were evaluated. Finally, the energy consumption and operational costs of various ES processes were assessed.

2. Materials and methods

2.1. Scrap iron

Scrap iron materials (mainly iron shavings), collected from a local machine shop manufacturing automobile parts, were shipped to the laboratory, washed with acidified de-ionized water (adjusted to pH 2 using HCl) to remove the oxide layer on the surface, and stored in acetone solution (see Fig. S1). Before each experiment, scrap iron was taken out of the acetone solution and dried out with compressed air. Other than iron, the scrap iron contains trace amount of other elements (less than 1%) as indicated in Table S1.

2.2. Feed wastewater

To have consistent wastewater quality during the whole study, the simulated wastewater used in this study was prepared by diluting liquid collected from the electroplating bath of a local surface finishing plant. The liquid was diluted 100 times with deionized water to simulate the wastewater generated from cleaning electroplated objects. The wastewater prepared has the Cr(VI) concentraiton in the range of the actual wastewater generated in the plant. The electroplating bath liquid contained Cr(VI) as well as Ni, had a highly acidic pH level of 1.1, and contained a lot of dissolved ions with a conductivity of 74.4 mS/cm. Table 1 shows the characteristics of the concentrated liquid collected.

2.3. Electrolytic system operation

Fig. 1 shows the experimental setup and photo of the actual anode and cathode assembly. A 2.5-L reactor was mixed using a magnetic stirrer plate (Cemarec^{TM} Stirring Hot Plates, MA, USA). The scrap iron packed anode was constructed by filling 50 g of scrap iron on a cage made of titanium mesh being rolled into a cylindrial form (diameter × high of 4.78 cm × 17 cm). Two stainless steel plates with a dimension of 20 cm × 3 cm × 0.3 cm were used as the cathode. The gap between the stainless steel plate and titanium mesh is 1.1 cm. The area of scrap iron can be roughly estimated based on the average thickness of scrap iron shavings and fibers. With the average thickness of 0.06 cm and the estimated iron density of 7.87 g/cm^3, the total surface area for 50 g of scrap iron was approximately 212 cm^2, corresponding to the specific surface area of 4.24 cm^2/g. The scrap iron provided much larger specific surface areas than that of the iron plates used in our previous study (*ca.* 0.94 cm^2/g) [14].

The electric current conveyed by a power supply (GPS-3030DD, Taiwan) was set before each experiment, and voltage and oxidation–reduction potential (ORP) were recorded using two multimeters (CENTER 122, Taiwan). All experiments were carried out at room temperature (~25 °C). Samples were collected during predetermined reaction time. An aliquot of the sample was filtered through a 0.45-µm membrane filter for the determination of total chromium, Cr(VI), and Ni(II) concentrations; some were digested with concentrated sulfuric acid for the determination of the total iron generated from the anode. XPS analysis was performed for selected samples. Triplicate experiments were conducted, and the mean and one standard deviation were reported.

Table 1
Water quality of electroplating wastewater.

pH	Conductivity (mS/cm)	Cr(VI) (mg/L)	Total Cr (mg/L)	Ni(II) (mg/L)	TOC (mg/L)
1.1	74.4	11136	25176	945	271

Please cite this article as: V. Ya et al., Scrap iron packed in a Ti mesh cage as a sacrificial anode for electrochemical Cr(VI) reduction to treat electroplating wastewater, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.03.016