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Removal of chromium(VI) from aqueous solutions by electrochemical reduction–precipitation

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In this work, we investigated the reduction and removal of aqueous Cr(VI) via electrotreatment in a stirred batch reactor using a low-carbon steel electrode. In addition, the capacity to remove chromium from natural seawater, synthetic seawater and wastewater was also studied. The removal of Cr(VI) was primarily based on the simultaneous reduction of Cr(VI) to Cr(III), which then precipitated and formed a $Fe(OH)_3/Cr(OH)_3$ sludge to absorb Cr(VI). The amount of Cr(VI) that was adsorbed in the sludge increased to a maximum value of 10% but decreased to a negligible level as the Cr(VI) concentration in the solution gradually decreased. The Cr(VI) concentration was reduced to the discharge limit (0.5 mg/L) in a single process without the addition of other precipitation agents.

Keywords: Cr(VI); Adsorption; Precipitation; Electrochemical; Pollution

1. INTRODUCTION

Due to the widespread application of chromium in metal processes, chromate preparation, electroplating, nuclear power plants, the textile industry and leather tanning, chromium contamination of water is a concern. There are two oxidation state of chromium, Cr(III) and Cr(VI). However, the toxicity of hexavalent chromium is 500-fold more than that of trivalent chromium [1-5]. Chromium is poisonous to microorganisms, plants, animals and human beings, and in humans, it can cause lung cancer and harm to the stomach, kidneys and liver [6-9]. The leather tanning process has been one of the largest sources of chromium discharge in the world. In particular, most tanning factories in India use the chrome tanning process due to its low cost, high processing speed, remarkable stability and the resultant light color of the leather. However, the leather only consumes approximately 60-80% of the chromium used in the chrome tanning process, and the rest of the chromium is discharged into the wastewater system, resulting in serious environmental contamination. Although the chromium ions in the tanning wastewater are primarily trivalent, they can be further oxidized into the hexavalent state by the organics present in the system.

In general, precipitation is used to remove chromium metal ions, but chromium can also be removed via adsorption [10-13] and ion exchange [14-16]. Lime is usually used to precipitate chromium ions because the hydroxides of heavy metals are typically insoluble. However, the valence state of the metal is the most essential factor in precipitating heavy metals. For instance, chromate, CrO_4^{2-}, which contains the hexavalent form of chromium, exhibits a remarkable solubility compared to trivalent chromium. In chromate, the chromium needs to be reduced to the trivalent state, which is generally accomplished at a low pH using SO_2 generated from sodium metabisulfite. Moreover, another factor for the precipitation process is the zeta potential of the original colloidal precipitant of the heavy metal.

Electrochemical precipitation was used to reduce the concentration of Cr^{6+} in the leaching solutions, and this technique has been demonstrated to be efficient for the treatment of effluents containing contaminants such as cyanide [11], Ni [17], Cr [18], Cu [19], Pb [20] and Hg [21-23]. The principle of electrochemical precipitation for the treatment of a Cr^{6+}-based solution is to transform the soluble Cr into the corresponding hydroxide or oxide species using Fe^{2+} formed at the anode and OH^- generated at the cathode [24-27]. This process can be simply described using the following chemical equations:

Anode: $Fe \rightarrow Fe^{2+} + 2e^{-}$

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2\,OH^{-}$

Generally, Cr(VI) is reduced to Cr(III) via the electrochemically formed Fe(II). Subsequently, the Cr(III)/Fe(III) precipitates due to the increased pH caused by the generation of OH^- during the electrolysis process. Notably, the reduction and precipitation occur simultaneously in a single procedure without the addition of other chemicals. However, additional chemicals are required for the precipitation when the process is performed at a low pH, i.e., strongly acidic conditions [28, 29]. The chemical equation below describes the overall reduction of Cr(VI) to Cr(III) via Fe(II) in an aqueous solution.

$$H_aCrO_4^{a-2} + 3Fe(II) + mH_2O \rightarrow Cr(OH)_b^{3-b} + 3Fe(OH)_c^{3-c} + nOH^{-}$$

In this equation, the various hydrolyzed and hydroxylated species are determined by the solution pH, which can be illustrated using the variables included, i.e., a in the pH range of 0-2, b in the pH range of 0-4 and c in the pH range of 0-4 as well as m and n, which can be calculated using the equations (4-b-3c) and (b+3c+2 m-a), respectively.

Moreover, the capacity of the electrochemical cell to efficiently generate Fe^{2+} is an essential step in this process because the reduction of Cr^{6+} to Cr^{3+} requires Fe^{2+}. Meanwhile, H_2 gas was prepared to perform electroflotation to separate the $Cr(OH)_3$ precipitant. Herein, we report on the removal of aqueous Cr(VI) using an electrochemical treatment with low-carbon steel electrodes in a batch reactor and the diverse factors influencing the removal.

2. EXPERIMENTS

Batch electrochemical precipitations were performed, and single distilled water was used to prepare the aqueous Cr(VI) solutions. $K_2Cr_2O_7$ was commercially available (Merck, Mumbai). The stock solution (2000 mg/L) was produced using fresh $K_2Cr_2O_7$. The purity of the salt was measured to 99.6% using an atomic absorption spectrophotometer (AAS), and a CentiPUR Cr standard solution with a concentration of 1000 mg/L was obtained from Merck and used as the reference. In addition, the diphenyl carbazide method was used to measure the concentration of Cr(VI). Here, analytical grade NH_4Cl (2%) was added to eliminate the chromium suppression by Fe in the AAS measurements.

Furthermore, AAS and a ferrozine approach were used to measure the amount of Fe and Fe(II) [30]. The purity of $FeSO_4 \cdot 7H_2O$ purchased from Merck was 98.8%, and a CentiPUR Fe standard solution with a concentration of 1000 mg/L was obtained from Merck. For the determination of Fe(II), dissolved-oxygen water was used for the preparation of all the reagents and dilutions. The absorbance was 562 nm. In addition, the molar extinction coefficient agreed with the values reported in the literature [30].

The modified alkaline digestion method was utilized to measure the Cr(VI) content in the sludge. Na_2CO_3 was not added, and the mixture was not boiled. The electrodes were taken out of the solution at the end of the run and gently rinsed with water. Then, the rinse water was poured back into the reactor. After the run, 10 mL of a 25% (w/v) NaOH solution, 2 mL of 1 M phosphate buffer (0.5 M K_2HPO_4 and 0.5 M KH_2PO_4) and 1 g of $MgCl_2$ were quickly added into the reactor. The pH of the solution was increased to approximately 13 by adding a NaOH solution. At this pH, the oxidation reaction of Fe(II) caused by dissolved oxygen is remarkably fast, and the reaction hindered the availability of Fe(II) to instantly reduce Cr(VI) [31]. In addition, the reaction also decreased the reduction of Cr(VI) when the pH was higher [32]. The oxidation of Cr(III) was suppressed by adding Mg(II) dissolved in a phosphate buffer into the alkaline solution. The pH of the solution was adjusted to 1.5 ± 0.5 by adding a 25% H_2SO_4 solution gradually 2 min after the NaOH aqueous solution was added to completely dissolve the sludge in the reactor. AAS was used to measure the total concentrations of Cr and Fe in the digested solution. As described before, ferrozine and DPC were used to measure Fe(II) and Cr(VI), respectively. According to the mass balance, the Cr(III), Cr(VI), Fe(II) and Fe(III) contents in the sludge were obtained. The lack of Fe(II) in the solution further confirmed that the oxidation of Fe(II) was complete.

The electrochemical precipitation experiments with a 500 mL solution of Cr(VI) were performed in a cylindrical borosilicate container with a capacity of 1 L at a defined pH, and the Cr(VI) solution was produced using the stock solution. In general, the conductivity was increased by the addition of NaCl at a concentration of 1000 mg/L. However, the capacity of the process might be influenced by the addition of NaCl because Cl_2 may be generated, and this was not taken into account in the results [33]. A rectangular, Perspex spacer block with a width of 20 mm was used to separate the electrodes, and the electrodes were submerged in the solution and immobilized on a stand using an insulted clamp. Low-carbon steel purchased from the local market was used as the electrode material. The iron content of the electrode material was measured to be 98.4% using a digestion method with concentrated H_2SO_4 for a sample piece. The volume of the electrodes was 6.0 cm × 5.0 cm × 0.05 cm to minimize the effect of the surface quality, and the surfaces were conditioned for the final runs. The electrodes were conditioned in a 500 mL solution of 50 mg/L Cr(VI) and 1000 mg/L NaCl for 3 h at a cell current of 270 mA, pH of 5 and a stirring rate of 450 rpm. The submerged area of the electrode for the conditioning period was approximately 20% higher than that used for the chromium removal in this paper. In addition, the polarity of the electrode pair was reversed four times during the conditioning period. During the successive runs, the electrodes were cleaned with emery paper and then washed with a H_2SO_4 solution (5%, v/v) to eliminate influences from the previous experiments. A regulated D.C. power source, which was provided by M/s Agrawal Electronics (Mumbai), was connected to the outer edges of the electrodes. Moreover, a pre-calibrated regulator was used to maintain the required cell current under a constant current mode. The small volume samples were collected using a pipette during the experiments and filtered when the sludge was present, and the supernatant was divided into two parts. One part was immediately measured to analyze the Fe(II) and Cr(VI) content. The other part was acidified to a pH of less than 2 using a H_2SO_4 solution to prevent further sludge formation and used to determine the total Cr and Fe content. Various sets of experiments were conducted to investigate the Fe and Cr content in sludge prepared under the same conditions. Generally, the experiments were performed for 20, 40 and 60 min, and in some cases, they were conducted for 50 min.

3. RESULTS AND DISCUSSION

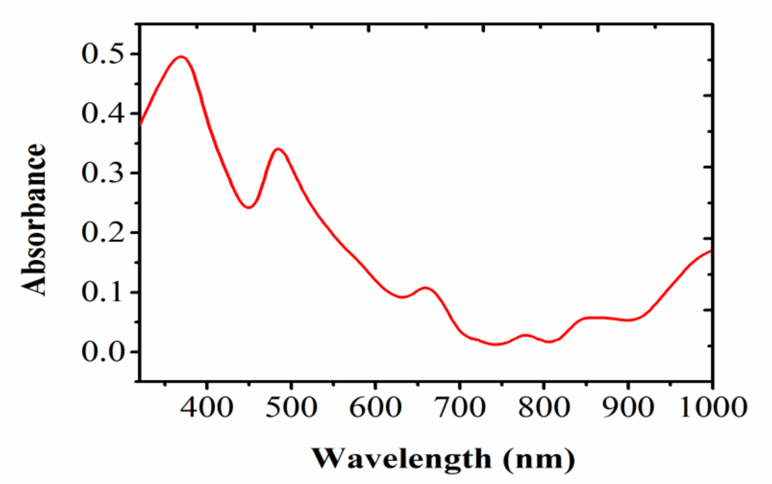

Figure 1. (A) UV-Vis spectrum of a 53 mg/L Cr^{6+} solution. (B) Calibration curve of the relationship between the concentration and absorbance of a Cr^{6+} aqueous solution at 450 nm.

Cr^{6+} exhibits a deep brown yellow color when dissolved in water. A UV-vis spectrophotometer was used to determine the Cr^{6+} concentration in the solution. Figure 1A shows the spectrum of Cr^{6+} in the aqueous solution, and the spectrum of water was subtracted as the background. The standard solution was produced by dissolving reagent grade CrO_3 in deionized water. Figure 1B illustrates the calibration curve for the solution concentration at 450 nm. Normally, the local maximum of a spectrum is used to improve the analytical method and results in a more sensitive signal and lower limit of detection. The Cr^{6+} concentration in the leaching solutions was high, as much as 100 mg/L. Thus, a local minimum at 450 m was used to construct a calibration curve and avoid the errors generated by dilution and over-scale absorbance readings, and the maximum absorbance was 2 AU. However, the instrument was typically used in a low AU range, less than 0.25 AU, to maintain the linearity of the calibration curve.

In the process of electrochemically reducing and precipitating Cr(VI), the pH was a significant factor. As shown in Figure 2, the influence of the initial pH on the dynamics of the Cr(VI) reduction, the total removal of Cr and the adsorption of Cr(VI) on the sludge was experimentally investigated in the pH range of 2 to 10, and these experiments were performed using the same original concentration of Cr(VI). Figure 2A shows that the total chromium removal was higher at pH 5 than at pH 2, 7 and 10. Nevertheless, Figure 1B shows that the reduction rate was higher when the pH was lower. The reduction rate reached a maximum of 3.8 mg/L/min when the electrotreatment time was less than 1 min and decreased to 0 when the reduction of Cr(VI) was complete. The Cr(VI) reduction rate varied between 1.41 and 1.33, 1.38 and 1.07 and 1.19 and 0.91 mg/L/min when the initial pH was 5, 7 and 10, respectively. Figure 2B shows the Cr(VI) reduction rate that was calculated using the experimental results. Here, the term '*reduction*' is used to represent the reduction of Cr(VI) to Cr(III).

The current efficiency was calculated to be 123%, 107%, 106% and 104% when the initial pH was 2, 5, 7 and 10, respectively. Using Faraday's law, the efficiency was calculated after a 60 min run, and the entire reactor container was submerged in concentrated H_2SO_4 at the end of run to estimate the Fe concentration. The reduction of Cr(VI) was catalyzed by H^+, and the rate of the reduction was higher at pH 2, as expected. At this pH, the reduction of Cr(VI) in an aqueous solution was nearly complete in 45 min (Figure 1B). However, when the initial pH was 5, 7 and 10, the reduction took 64.0, 57.9 and 52.7 min, respectively.

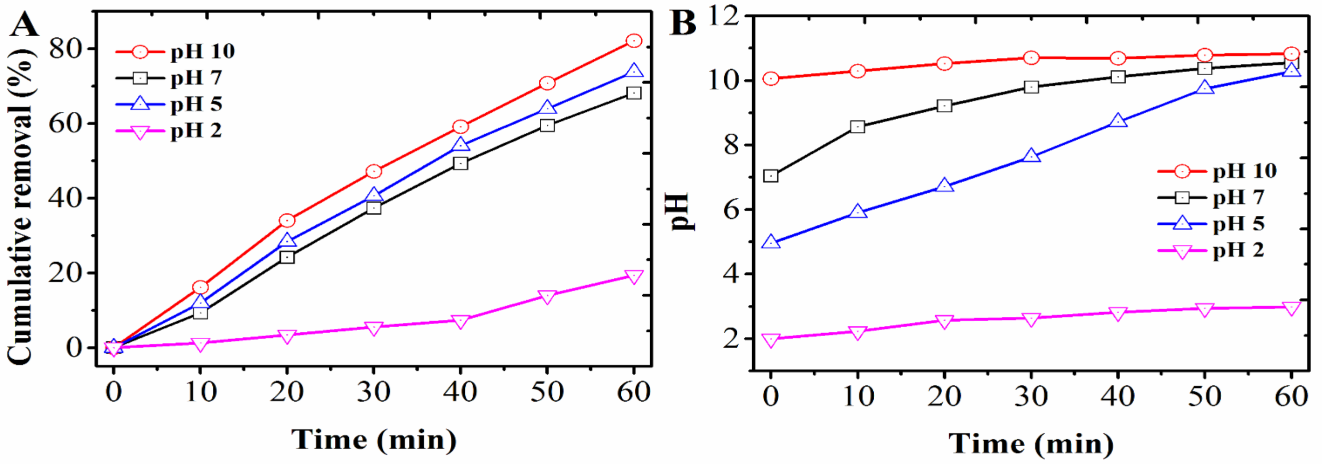

Figure 2. The effect of the original pH on the cumulative removal percentage of the total chromium (A) and the cumulative reduction percentage of Cr(VI) (B).

Nevertheless, reduction of the Cr(VI) species does not signify the removal of chromium from the solution. Figure 3A shows the pH elevation progress. A logarithmic relationship between the solubility of the individual species of Cr(III) or Fe(III) and the pH was found. $Cr(OH)_3$ and $Fe(OH)_3$ exhibited increasing solubilities when the pH was higher than 9.5 or lower than 7. Nevertheless, the influence of the pH on the hydroxide solubility was greater when the pH was lower. The removal of Cr was remarkably lower when the pH of the solution was 2. Thus, the addition of alkali was required to precipitate $Fe(OH)_3/Cr(OH)_3$ when the pH of the effluents was low.

A combined effect induced the pH elevation during the electrotreatment, i.e., the OH^- ions generated at the cathode and the incomplete precipitation of the Fe^{2+} hydroxides with an equivalent amount generated at the anode, which resulted in an oversaturated solution of Fe(III) [34]. This was confirmed by a further decrease in the iron concentration after the cell current was stopped.

Figure 3B clarifies the cumulative adsorption of Cr(VI) in the sludge with the progressive treatment. The presence of Cr(VI) in the sludge was caused by adsorption, which increased with the progressive ECRP and sludge formation. The cumulative reduction of Cr(VI) and the solution pH gradually increased. The Cr(VI) concentration in the solution decreased because of the conversion of Cr(VI) to Cr(III), and the pH increased beyond the pH at which Cr(VI) desorbs from the sludge. As shown in Figure 3B, the cumulative adsorption of Cr(VI) in the sludge initially increased but then decreased after 20 min. The adsorption of Cr(VI) reached a maximum of approximately 10% at 20 min, and the pH increased to 6.5 from 5. The adsorption of Cr(VI) decreased when the pH increased, and the concentration of the residual Cr(VI) was high. However, when unconverted Cr(VI) was present in the solution, it adsorbed at a solution pH higher than the pH_{zpc} of 8.3 [35], and this might be due to the anion exchange of Cr(VI) with the surface hydroxyl groups, OH^-, in the sludge formed by the metal hydroxides, $Fe(OH)_3/Cr(OH)_3$ [36]. The adsorption of Cr(VI) became negligible as the ECRP progressed due to the reduction of Cr(VI). These results were in accordance with those reported by Gao et al. [29]. They found that an acidic pH was favorable for the reduction of Cr(VI) to Cr(III), and neutral conditions were efficient for the precipitation of $Cr(OH)_3$ (s)/$Fe(OH)_3$ (s) in a combined electrocoagulation-electroflotation process using iron electrodes.

No Cr(VI) was observed in the sludge after 40 min, even though the initial sludge formation occurred after approximately 30-34 min when the initial pH was 2, and this was probably because of the nearly complete reduction of Cr(VI) in solution. As shown in Figure 2A, approximately 5.4% of the total chromium was removed without the sludge forming (treatment time < 35 min) when the initial pH was 2. This was attributed to the deposition of hydrated Fe_2O_3 and Cr_2O_3 by the anode [37]. According to the mass balance equation, the chromium content in the deposited layer was calculated when the sludge formed by subtracting the chromium content in the solution or digested solution from the initial chromium concentration. After 60 min, approximately 11% of the original Cr(VI) was present in the deposited layer, which represents almost half of the total chromium removal when the initial pH was 2. Under these conditions, the Cr(III) in the solution after 60 min exhibited a higher solubility at a pH of 3.3 compared to the concentration expected for the process of completely reducing Cr(VI). Thus, the removal of Cr(III) might be caused by generating the complex $(Cr_xFe_{1-x})(OH)_3(s)$, and the solubility of the complex was determined by the composition and increased depending on the molar fraction of Cr(III) in the solid [38].

Chloride ions, which exhibit catalytic activity [39, 40], increase the conductivity of a solution. In addition, they can reduce the passivity of electrodes by removing the oxide layer that forms on the surfaces of electrodes. Nevertheless, the presence of Cl^- ions improved the solubility of Cr(III) ions in solution. Especially for higher concentrations of Cl^- ions, the solubility enhancement of chromium hydroxide was remarkably strong compared to the de-passivation of the electrode surfaces. Thus, the influence of the anions on the efficiency of the reduction and removal of Cr(VI) at a cell density of 5.24 mA/cm^2 was investigated by adding an appropriate amount of electrolyte to control the concentration of the corresponding anion, such as Cl^-, NO_3^-, SO_4^{2-}. The nearly complete reduction of Cr(VI) to Cr(III) was necessary for the total removal of Cr, which was achieved via adsorption in the sludge, and the concentration of Cr became negligible (<2%) with treatment beyond 40 min. The total Cr removal in the presence of Cl^- was slightly higher than the removal in the presence of NO_3^- and SO_4^{2-}, which might be due to the higher electrode deposition and reduction in the dissolution of Fe in the presence of NO_3^- and SO_4^{2-}.

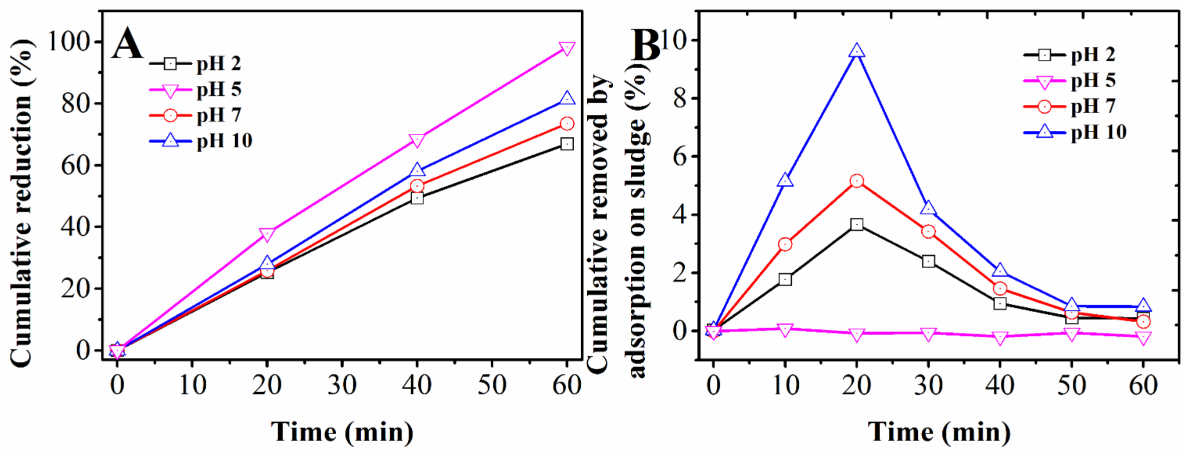

Figure 3. The effect of the original pH on the pH elevation (A) and fraction (%) of the cumulative Cr(VI) (B) adsorbed on the sludge.

The stoichiometric reduction of Cr(VI) by Fe(II) using $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ occurred at a pH lower than 10 with electrolytes. Due to the easy oxidation of Fe(II) by the dissolved oxygen, it is difficult to establish the stoichiometry of the Cr(VI) reduction through experiments. The stoichiometric oxidation reaction of Fe(II) with O_2 follows the chemical equation described below:

$$\mathrm{Fe(II)} + (1/2)O_2 + 2OH^- \rightarrow (1/2)H_2O + Fe(OH)_3$$

The rate of the Fe(II) oxidation was first order in relation to the partial pressures of Fe(II) and oxygen. Furthermore, the oxidation was second order in relation to the concentration of the OH^- ion. The concentrations of Fe(II) in the solution were measured at various time intervals immediately after collecting the samples when the initial pH was 5, 7 or 10. No color was observed in the samples after adding ferrozine and a buffer solution with a dilution ratio of 5 to 6, which demonstrated that Fe(II) was absent in the samples. The anodic evolution of oxygen was caused by the higher cell potential, which is described by the following equation:

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2\uparrow + 4e \ (E^0 = -1.23\ \mathrm{V})$$

The increase in the pH of the solution was rapid when the initial pH was 5 and 7, and the rate of the Fe(II) oxidation was accelerated by the progressive treatment when the initial pH was larger than or equal to 5. However, because of the competing oxidation of Fe(II) by DO at higher pH values, determining the amount of Fe(II) that reduced Cr(VI) was difficult. During this process, Cr(VI) was also removed via adsorption on the sludge over a wide range of pH values, and Fe(II) could be removed via precipitation.

In general, the stoichiometric reaction during the electrochemical reduction and precipitation depended on the pH, current density and Cr(VI) concentration. In all the experiments, the initial pH was the same and varied between 2 and 3 ± 0.1. However, attempts to perform the experiments with a constant pH by adding manually acid failed because of the quick increase in the pH. The ratio of the amount of oxidized Fe(II) to reduced Cr(VI) is the stoichiometric ratio for the reduction of Cr(VI), and this was in accordance with the ratio of Fe(III) to Cr(III) in the system, including the sludge, solution and electrode deposits. As shown in Figure 4, the experiments were carried out using various concentrations of Cr(VI) and diverse current densities. Each experiment was performed in triplicate. One experiment was used to determine the total content of Fe, Fe(II), Cr and Cr(VI) in the solution, and the experiments were used to determine the Fe(II) and Cr(VI) content in the sludge. Notably, the sludge appeared after approximately 30-34 min in all the experiments. However, no Fe(II) was detected in the sludge, which indicated that the removal of Fe(II) through precipitation was negligible. Moreover, no Cr(VI) was observed when the original Cr concentration was 50 mg/L. The amount of Cr(VI) adsorbed in the sludge was 1.912, 2.396, and 3.777 mg and 2.253, 1.608, and 0.209 mg at 40, 50 and 60 min with a current density of 4.55 and 8.67 mA/cm^2, respectively. The stoichiometric ratio in Figure 4 is based on the cumulative amounts, which varied between 2.38 and 2.89, and only the Cr(III) present in the deposits of the electrodes was taken into account for the calculation.

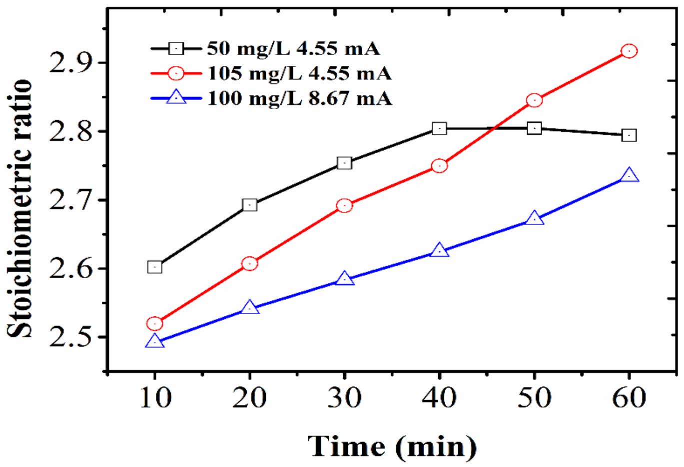

Figure 4. The stoichiometry of the Cr (VI) reduction using different applied current density.

As shown in Figure 4, the experimental conditions influenced the stoichiometry, and it varied with the initial Cr(VI) concentration, current density and treatment time. For a defined treatment time, the stoichiometric ratio was higher when a higher current density was used. However, a slightly lower ratio was observed when the original Cr(VI) concentration was higher during the initial period, and this was explained using the current efficiency calculated based on the total dissolved Fe (Figure 5A) and the accumulation of chromium in the electrode deposits (Figure 5B). Using the mass balance equation, the chromium in the electrode deposits was calculated. After 60 min, the chromium content in the electrode deposits was 9.5, 4.2 and 6.3% when the original Cr(VI) concentrations were 50 mg/L (4.55 mA/cm^2), 105 mg/L (4.55 mA/cm^2) and 100 mg/L (8.67 mA/cm^2), respectively. A higher current efficiency was observed when the current density was lower, whereas the efficiency gradually decreased with time. The effect of the electrochemical dissolution of Fe was negligible among the current densities used. In addition, the bulk pH varied slightly in all three experiments. Because of the blanketing effect of the electrode deposit, the chemical dissolution of Fe, described by the following equation, decreased remarkably: $Fe^0 + 2H^+ \rightarrow Fe(II) + H_2$. Thus, the rate of Cr(VI) reduction by Fe decreased, and the stoichiometric ratio increased. The deposits on the surface of the electrode induced a higher current efficiency and lower original stoichiometric ratio.

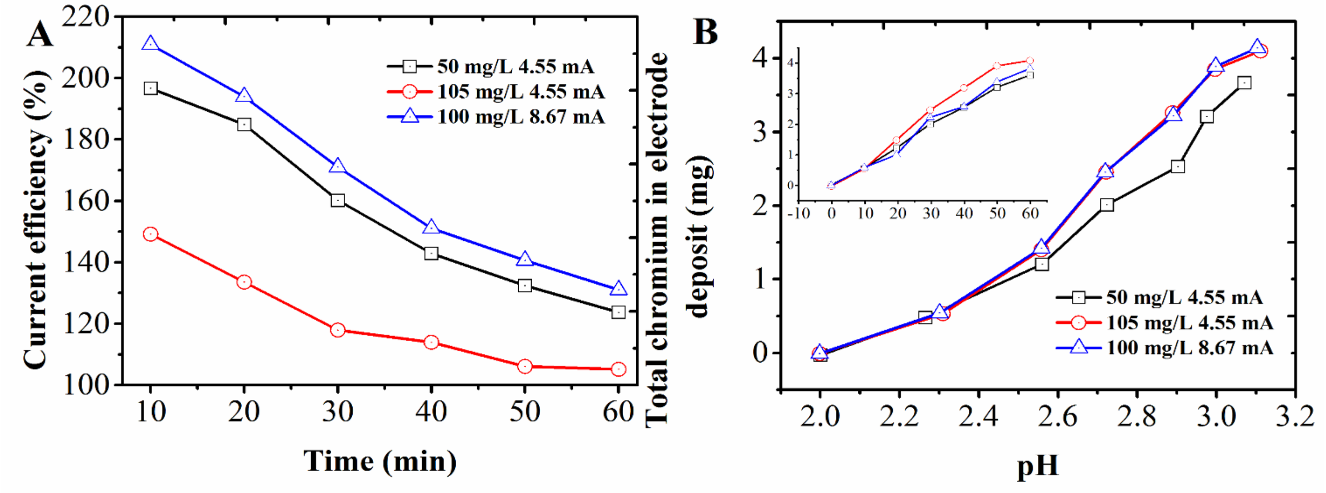

Figure 5. (A) The influences of the original Cr(VI) concentration and the current density on the current efficiency of the cell with varied treatment times. (B) The relationship between the progressive accumulation of the total chromium in the oxide layer and the pH of the solution.

4. CONCLUSIONS

In conclusion, we reduced the Cr(VI) concentration below the maximum discharge limit in a single procedure using a bath electrochemical precipitation with soft steel electrodes. The amount of Cr(VI) adsorbed on the sludge increased to a maximum during the incomplete reduction, and then decreased with the progressive ECRP. Thus, the detention time of the sludge in the ECRP instrument must be sufficient. The total stoichiometric ratio for the Cr(VI) reduction was reduced by conducting the treatment at a low pH, which also decreased the consumption of the electrode and iron, as the simultaneous reduction was primarily induced by Fe(II)/Fe.

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