Removal of Chromium Using Electrochemical Approaches: A Review

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In the manufacturing industry, chromium is often discharged with the effluent, which releases significant contamination to the environment. To remove chromium from wastewater, many different treatment techniques have been developed. The present work reports the treatment of chromium pollution using electrochemical-based remediation strategies, including electrodeionization, electrodialysis, electrochemical reduction, and electrocoagulation. This work also presents the principles and mechanisms of these strategies, along with research trends into the electrochemical removal of chromium.

Keywords: Chromium removal; Electrochemical; Electrodeionization; Electrocoagulation; Electrochemical reduction; Electrodialysis

1. INTRODUCTION

Chromium compounds have gained extensive applications in fields such as wood preservation, printing inks, textile dyeing, leather tanning, paints and pigments, along with metal plating [1, 2]. Because they are widely used in many fields, chromium compounds, produced from the base material of sodium/potassium dichromate, are discharged in large amounts to the environment [3]. Cr(III) and Cr(VI) are the main form of chromium discharged into aqueous systems. As a human carcinogen, Cr(VI) compounds can cause cancer at tissue sites, bone cancer, and leukaemia due to high exposure from chrome tanning, chrome plating, Cr(VI) pigments, and arc welding [4-6]. Metals differ from a majority of organic pollutants due to their accumulation in living tissues and non-biodegradability as well as their potential to enter the food chain, where they would become concentrated. Increased heavy metal doses cause detrimental health effects for the majority of living organisms, despite their necessity as micronutrients and presence at low doses in plants and animals [7, 8]. Due to the presence of chromium in aqueous systems, many scholars have studied this material and its toxic properties.
Many adsorbents have been reported to remove chromium from wastewater, including condensed tannin gel derived from a natural polymer [9], powder and granular forms of activated carbon prepared from different raw materials and by different activation procedures [10], activated carbon from cow dung [11], nanocrystalline akaganeite [12], maghemite nanoparticles [13], and activated carbo-aluminosilicate [14]. Several methods have been proposed to eliminate chromium pollution, such as electrochemical oxidation, followed by low-cost ion-exchange resins [15], nanofiltration [16] or ion-exchange processes. Cr(VI)-resistant bacteria involving a biosorption and bioaccumulation strategy have also been proposed [17]. The most common technique for the removal of Cr(VI) is the chemical reduction of Cr(VI) to Cr(III), followed by precipitation.

Porous carbon felt and graphite felt have been used as cathode materials for the electrochemical removal of chromium from wastewater [18-21]. To effectively remove chromium from plating industry effluents, iron electrodes in bipolar mode were used for the electrochemical precipitation of Cr(VI) [22]. Electroreduction consumed 10 times more power than electrochemical reduction, as displayed in the performance comparison of chemical reduction, electrochemical reduction and electroreduction of Cr(VI) [23-26]. Despite the high power consumption of electroreduction, the recovery and reuse of water and chromium could be realized, as the sludge does not suffer iron pollution. With a decrease in the initial concentration of Cr(VI) in the feed water, an increase in the Fe(II) dose exceeding the stoichiometric amount was observed, as shown in the investigation of Cr(VI) removal from ground water using the electrochemical precipitation method [27]. Cr(VI) reduction using scrap iron in a divided electrochemical cell was also presented, where the electrical energy was generated via a galvanic cell [28]. The above method reduces the overall power consumption due to the storage and further electrolysis use of the dc energy generated in the Cr(VI) reduction process. As the solution temperature and initial Cr(VI) concentration are increased, an increase in the rate of Cr(VI) reduction and energy output was observed, as shown in experiments of the cell voltage vs. cell current. Martinez and co-workers [29-31] used batch and continuous electrochemical reactors to study Cr(VI) removal from electroplating industry wastewaters. The removal kinetics of the electrochemical process involving Cr(VI) was also investigated using an electrochemical reactor with industrial and synthetic wastewater under continuous stirring, and the overall kinetic model was experimentally confirmed [32, 33]. This model was integrated with the spontaneous dissolution of Fe(II) due to corrosion under acidic conditions, and the cathodic reduction induced the conversion of Fe(III) to Fe(II). At high concentrations of Cr(VI), the experimental data were fit with a zero-order kinetics model, while at low concentrations, the data were fit with the first-order kinetics model. Based on the study of a dynamic model considering the pH and dispersion effects for electrochemical Cr(VI) removal in a tubular reactor, it can be seen that an increase in the residence time in the reactor was observed with an increase in the influent Cr(VI) pH in the range of 1.0–2.0 [34]. The optimal stirring was obtained through the kinetic rate equation and the Reynolds’ number, and it can be seen that a short treatment time and low energy requirements for agitation were obtained when the current density was increased [35-39]. A dynamic model integrated with current density, dispersion effects, and pH was developed based on the study of electrochemical Cr(VI) reduction in a tubular continuous reactor using a spiral-shaped anode [40].
In aqueous solution, Cr(VI) most likely exists in the form of CrO$_4^{2−}$, Cr$_2$O$_7^{2−}$, HCrO$_4^{−}$, and H$_2$CrO$_4$, and the factors affecting their relative distribution include the redox potential, the solution pH, and the Cr(VI) concentration [41]. Unfortunately, insoluble precipitates cannot be formed by these Cr(VI) species, and thus, separation via a direct precipitation strategy is unfeasible. The dependence of Cr(VI) species on the redox potential and pH can be seen from the theoretical distribution of the dominating chemical Cr(VI) species. Even pH changes do not lead to the formation of insoluble Cr(VI) species, as shown in the Pourbaix and predominance zone diagrams above. The metal exhibits a fairly high mobility in soil and water at this oxidation state. At this pH range, insoluble species cannot be formed from the trivalent state of Cr. These results indicate that changing the oxidation state is essential for the formation of chromium solid phases for easy separation from aqueous media.

In the present work, basic electrochemical routes toward the detection of Cr(VI) are shown, including electrodeionization, electrodialysis, electrochemical reduction, and electrocoagulation approaches.

**2. ELECTRODIALYSIS**

Electrodialysis is considered a remarkably potential strategy for wastewater treatment. Some previous works have proposed the removal of chromium ions using electrodialysis involving solid ion-exchange membranes. Three detachable cells were employed, where Cr(III) can be recovered simultaneously with Cr(VI) by charged ion-exchange membranes [42]. For static rinse water purification, chromic acid recovery, and metallic impurities removal, one-step electro-electrodialysis, in which electrodialysis is combined with electrolysis, was carried out [43]. For the recovery of Cr(III) from aqueous solutions, a cation-exchange membrane modified by polyethyleneimine electrodeposition was used in a two-step separation-concentration procedure [44]. For Cr(VI) removal from the simulated mixture and the production of good-quality drinking water, an electrodialysis pilot setup was applied [45]. It was supposed that chromate could be recovered from electroplating wastewater with low pH using the two-stage electrodialysis configuration [46]. In the first step, HCrO$_4^{−}$ was concentrated, and the monovalent ions were separated from CrO$_4^{2−}$ during the second step due to their monovalent/divalent features at varying pH values. The concentration of chromate ions in chrome plating rinse water was realized by a method combining ion exchange and electrodialysis [47, 48]. The synergistic effect of solid synthesized membranes and electrodialysis on chromium removal from metal finishing and tannery effluents was also reported [49, 50].

Electrodialysis involving liquid membranes combines electrodialysis and carrier-mediated transport. During electrodialysis, membrane extraction was mainly driven by the electric field gradient. Compared with the solid ion-exchange membranes in traditional electrodialysis, liquid membranes are more permeable and selective. Ion exchange via liquid membranes can be dramatically enhanced by applying a direct electric field, which can also promote metal stripping from the organic phase [51, 52]. Purin [53] reported the concentration of rhenium from industrial solutions and carried out electrodialysis with liquid membranes for the first time. Bustero and co-workers [54] used supported liquid membranes to extract the electro-assisted solvent and separate Cd(II), Ni(II), and Cu(II) ions.
The extraction of copper from nickel, copper, and iron sulphate solutions was carried out using di(2-ethylhexyl)phosphoric acid (D2EHPA) by electrodialysis with liquid membranes [55]. Several years ago, a specimen preparation method for mass spectrometry, chromatography, and electrophoresis was reported based on electromembrane potentiostatic microextraction through supported liquid membranes [56] for the extraction of Mn(II), Ni(II), Cu(II), Cd(II), Zn(II), and Co(II) cations [33, 57] and for the removal of lead ions from various biological fluids [58]. Unfortunately, there are certain disadvantages for the electromembrane extraction strategy [59-61]. Instability, bubble generation at the electrodes, puncture of the liquid membrane and sparking arise when the voltage exceeds 300 V.

3. ELECTRODEIONIZATION

Electrodeionization (EDI) or continuous electrodeionization (CEDI), aiming at minimizing the phenomenon of concentration polarization, dates back to the late 1950s and usually involves electrodialysis systems [62]. The dilute compartments packed with an ion-exchange material are commonly used to bridge the gap between the ion-exchange membranes and a conductor, since they have functional groups. The maximum ion-separation efficiency was observed to increase from 50% to 90%, which suggested that ED concentration polarization could be successfully counteracted by this method. Thus, the synergy between ion exchange and ED could efficiently compensate for the inherent disadvantages of each strategy [63-65].

In 1955, Walters and co-workers [66] proposed, for the first time, the use of electrodeionization for the removal of radioactive elements (trace level) from water from the Argonne National Laboratory. The Permutit Company invented the first apparatus containing a mixture of anionic and cationic resins in the late 1950s. In addition, Sammons and Watts measured the correlation among current, flow rate, and concentration in the deionization of a saline (NaCl) solution with an EDI module. To confirm the reliability of this mechanism, further investigations were carried out using solutions containing detergents, phosphates, iron, and calcium [67]. Unfortunately, the study on this configuration neglected to consider different parameters in the cell design process. The commercial use of EDI for ultrapure water production began in the late 1980s. With the development of EDI, its application has spread to many other fields. For example, the first production of ultrapure water was realized by this configuration in 1971. Then, novel membranes began to be developed, along with the integration with other configurations (e.g., UV). This technique has been significantly improved over the past decade and its applications extended beyond the production of high-purity water, which is beneficial for future studies.

Hexavalent chromium, produced during the electroplating and mining process, is a common detrimental ion in industrial wastewaters. The removal of different species of this ion has been studied, and many strategies have been applied, including EDI. Considering the high toxicity of hexavalent chromium, EDI and other methods play vital roles in environmental protection [68]. Cr(VI) removal can reach over 98% in methods integrating electrodialysis and ion exchange [69, 70]. Furthermore, three kinds of resins and conditions were used for the removal of CrO$_4^{2-}$ by Bergmann and co-workers [71], and an ion-exchange bed was used for determination of the transport number and
conductivity. Moreover, the diffusion coefficients of ion-exchange materials applied in the electrodeionization of this compound were assessed by Dzyazko and co-workers [72]. A comparative study of IX, EDI, and ED for Cr(VI) removal showed that 99.8% Cr(VI) removal was realized by EDI, suggesting the best performance [73]. Xing and co-workers [74, 75] presented the successful use of CEDI for the removal of Cr(VI) with an operation time of over 50 h, and the concentrations of 0.09 and 0.49 ppm were obtained from 40 and 100 ppm Cr(VI) solutions, respectively (energy consumption, 4.1-7.3 kWh/mol Cr(VI)) [74, 75]. For the continuous treatment of wastewater containing hexavalent chromium, a novel route was developed by Alvarado and co-workers [76], in which electrodeionization was combined with ion exchange. Upon thorough saturation of the mixed resin bed, the continuous removal of more than 98.5% of Cr(VI) was observed using the continuous electrodeionization (CEDI) process (10% over limiting current), and the continuous removal of Cr(VI) from the dilute compartment was enhanced along with the in situ electro-reproduction of the resin; meanwhile, Cr(VI) was recovered in the concentrate compartment before re-application. The proposed CEDI route exhibited an extremely low energy consumption of <0.07 kWh/m$^3$.

4. ELECTROCOAGULATION

The electrocoagulation (EC) process involves the electrochemical generation of metal ions, which function as destabilization agents and result in the removal of pollutants through electric charge neutralization. In this process, oppositely charged particles agglomerate by binding with each other like small magnets. In addition, considering the ease of operation, lack of reagents, and decreased production of sludge, this method was confirmed to be efficient in the removal of pollutants from water. During the 20$^{th}$ century, EC was extensively used in wastewater treatment, but without much popularity or success. Over the past ten years, its application to industrial wastewater treatment has extended to Europe and South America [77]. The main sources of wastewater treated by EC were the mining, pulp and paper industries [78, 79] as well as the metal processing industry [80]; other sources include petroleum refining wastewater, textile mill wastewater, arsenic-containing smelter wastewater, nitrate-containing wastewater solutions, tar sand and oil shale wastewater, restaurant wastewater, urban wastewater, yeast wastewater, and potable water [81, 82]. In particular, to determine the main factors influencing other polluted waters, empirical investigations for EC have been carried out. This strategy was optimized to obtain the maximum effluent throughput rate and minimum electrical power consumption.

For the EC experiment, a pair of electrodes is placed into a container/reactor with a well-defined capacity. The simplest EC system contains an electrolytic cell with one cathode and one anode. Upon connection of this cell to an external power source, electrochemical corrosion of the anode material occurs as a result of oxidization, where the “sacrificial electrodes” refer to the conductive metal plates. The sacrificial cathodes and anodes could be different materials or the same material, such as Fe [83], Al/Fe [84-86] and so on. The uniformity of the slurries and liquid in the reactor is ensured by a stirrer. In the electrolysis process, the cathodic reactions and anodic reactions occur on
the negative side and the positive side, respectively. Usually, the sacrificial electrodes used for the continuous production of ions in water are consumable metal plates (e.g., aluminium, iron, etc.). These produced ions would activate coagulation by neutralizing the particle charges. For the removal of undesirable pollutants, the released ions work to coalesce the colloidal materials or induce chemical reaction and precipitation, followed by flotation. Moreover, free-radical formation, hydrolysis, electrolysis, and ionization occur with the movement of water containing colloidal particulates, oils, or other pollutants under an applied electric field, which change the chemical and physical features of the water and pollutants. In addition, the pollutants could be released from water, damaged, or show low solubility due to the excited and reactive state [87].

Based on the investigation of the reduction of synthetic chromium solution at 20 and 40 V (pH 3) containing Cr at the legal discharge limit, Bazrafshan and co-workers [88] proposed that iron electrodes showed more desirable chromium removal efficiency than aluminium. Rayman and White [89] used a Fe(II) electrode to remove Cr(VI) via a continuous process. Nouri and co-workers [86] also carried out Cr(VI) removal with iron electrodes at 40 V (pH 3). Bing-Fang [90] reported that the EC process involved metal removal, and the removal of Cu$^{2+}$ and Cr$^{6+}$ by the EC process was found to decrease to 93 and 98.91%, respectively. Narayanan and Ganesam [91] used adsorption by granulated activated carbon (GAC) along with the EC method, and the chromium concentration was remarkably decreased due to the integration of GAC and EC.

5. ELECTROCHEMICAL REDUCTION

The electrolysation of a Cr(VI) aqueous solution was carried out using iron electrodes during the electrochemical reduction–precipitation process. On the electrode surfaces, the main electrochemical reactions were as follows [27, 92-94]:

\[
\text{anode: } \text{Fe}^0 - 2e^- \rightarrow \text{Fe}^{2+}(aq) \quad (E^0 = 0.440 \text{ V})
\]

\[
\text{cathode: } 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 \uparrow + 2\text{OH}^- \quad (E^0 = -0.828 \text{ V})
\]

The pH value of the system increased after OH$^-$ was formed. The electrochemically generated Fe(II) led to the reduction of Cr(VI). With an increase in pH in the electrolysis process, Cr(III)/Fe(III) precipitated. These two reactions occurred in one step, and no reagents were added. At extremely acidic pH, it is essential to add reagents for the precipitation to proceed [93, 94]. Aqueous Cr(VI) was reduced to Cr(III) via aqueous Fe(II), and the overall reaction was as follows [95, 96]:

\[
H_a\text{CrO}_4^{-2} + 3\text{Fe(II)} + m\text{H}_2\text{O} \rightarrow \text{Cr(OH)}_b^{3-b} + 3\text{Fe(OH)}_c^{3-c} + n\text{OH}^-
\]

where the solution pH-dependent hydrolysed/hydroxylated species could be represented by \( a = 0-2 \), \( b = 0-4, \) \( c = 0-4, \) \( m = 4 - (b + 3c) \), and \( n = (b + 3c + 2m) - a \). Cr(VI) could be removed from the solution by the precipitation of reduced Cr(VI), i.e., as Cr(OH)$_3$(s); the co-precipitation of Cr(III) and Fe(III) as solid solution-like species; or the adsorption of Cr(VI) on metal hydroxide sludge.

\[
x\text{Cr(III)} + (1 - x)\text{Fe(III)} + 3\text{OH}^- \rightarrow (\text{Cr,Fe}_{1-x})(\text{OH})_3(s)
\]

Diverse anionic Cr(VI) species can be generated during dichromate ion hydrolysis in dilute solution, in which the predominate form is the chromate (CrO$_4^{2-}$) ion at solution pH >5.7, whereas the main form is the bichromate (HCrO$_4^-$) ion at pH <5.7. The adsorbent (Cr(OH)$_3$(s)/Fe(OH)$_3$(s)) sludge
shows a pH_{pzc} of ca. 8.3 [97]. When pH < pH_{pzc} (acidic region), positively charged precursors of Fe(OH)$_3$(s) and Cr(OH)$_3$(s) can be generated, and positively charged sites can be formed from these sludge-adsorbed species [98, 99]. These sites would attached/adsorb Cr(VI) that contains unconverted Cr(VI) (soluble anions). Unfortunately, this adsorbed Cr(VI) is easily leached/desorbed into the environment. The adsorption phenomenon must be taken into consideration in regard to the overall stoichiometry of Cr(VI) reduction/removal. In addition, adsorbed Cr(VI) must be studied to better understand the stoichiometry and reduction/removal rate of Cr(VI).

6. CONCLUSIONS

The discharge of wastewater containing chromium from many different industrial processes to the environment has been on the rise. To remove chromium from wastewater, varying techniques have been developed. Some effective electrochemical strategies for the reduction of Cr(VI) in aqueous solutions were reported herein, such as electrodeionization, electrodialysis, electrochemical reduction, and electrocoagulation.

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