ELECTROCHEMICAL REMOVAL OF HEXAVALENT CHROMIUM BY ELECTROCOAGULATION

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:

Chromium in wastewater is discharged from tannery, electroplating, metal finishing, dying industry and many other industries. Presence of hexavalent chromium (Cr(VI)) in the environment considerable concern because it is non-biodegradable, highly toxic and carcinogen. There are several treatments for the removal of chromium from wastewater, but the most common method involves reduction to its less toxic trivalent state. In this paper electrocoagulation was used as treatment for removing of hexavalent chromium from synthetic prepared wastewater initial concentration 50 mg/L, in presence of sodium chloride as supporting electrolyte (1 g/L). The treatment was perform in a batch electrochemical reactor 250 mL capacity and with possibility of constant stirring. It was examined the impact of electrode materials and current density (5, 10, 20 mA/cm^2) on Cr(VI) removal efficiency. The examination showed that iron has higher removal efficiency compared to aluminium. Also, it was observed high efficiency at very begin of treatment and at low current density. For 20 minutes of treatment it was achieved almost complete Cr(VI) removal at current density of 5 mA/cm^2 by using iron electrodes (E= 99.8 %).

KEYWORDS: removal efficiency, current density, irone anode

INTRODUCTION

Surface water and groundwater are recipients of various types of industrial wastewater. Organic matter of different toxicity and biodegradability and various heavy metals are the most common pollutants in wastewater. Heavy metals differ from most organic pollutants because they are not biodegradable and over time they only accumulate in certain systems [1]. Industrial pollution is the main source of all heavy metals that occur in natural surface waters. Due to its wide application in various industrial technologies, chromium (Cr), as an element from the group of heavy metals is a one of pollutant found in industrial wastewater.

Chromium can appear in two oxidation states, Cr(III) and Cr(VI). There are significant differences in physicochemical properties and toxicity between these two oxidation states. At neutral pH, Cr(III) is easily precipitated and forms $Cr(OH)_3$ which is nearly insoluble in water. Cr(VI) is much more soluble in a wide range of pH values, which increases its mobility and distribution. The toxic effect of Cr(VI) is estimated to be 100 to 1000 times higher than that of Cr(III) [2]. Trivalent chromium is naturally present in the environment and is one of the essential heavy metals necessary for the normal functioning of living organisms. The main sources of Cr(VI) emissions are mainly anthropogenic. The most common sources are pigment and paint production, galvanizing and corrosion protection plants, glass production, cement and ceramics industry, and perhaps the largest source of hexavalent chromium emissions (in some countries) - the leather industry, where large amounts of this pollutant are formed in the leather tanning process. Due to this, some members of the European Union have completely banned the operation of tanneries near water bodies [3,4,5,6].

There are different methods for hexavalent chromium removal from aqueous solutions. It can be removed either in the form of Cr(VI) or converted to less toxic Cr(III) and precipitated in the form of insoluble $Cr(OH)_3$. Methods used for Cr(VI) removal are ion exchange, chemical precipitation, adsorption, biosorption, coagulation, and electrochemical treatments (electrocoagulation, electroreduction, electrodeionization) [2,4]. The choice of technology depends on the efficiency of the Cr(VI) removal method, investment and maintenance costs of the technology and complexity of the process.

Electrochemical methods have become frequently used in environmental technology. Electrocoagulation (EC) is an electrochemical process most commonly

used in wastewater treatment. EC implies the formation of coagulants in situ by electrolytic dissolution of the electrode made of aluminum or iron, in an electrochemical reactor. The metal ions formed on the anode by hydrolysis create a large number of different compounds that are effective coagulants for the removal of pollutants. At the cathode, hydrogen is released which often carries flocculated particles to the solution surface. The EC reactor primarily produces colloidal aggregation of coagulants (increased size) and gas bubbles which are small, if the applied current is low [7].

In EC processes, Cr(VI) ions are first reduced to Cr(III) ions at the cathode and then combine with the generated OH^- ions and precipitate as insoluble $Cr(OH)_3$. The reaction mechanism of the EC process in the case of using an iron anode is formation of $Fe(OH)_3$ or $Fe(OH)_2$ on anode and evolution of hydrogen gas on cathode. Chromium is isolated in the form of a precipitated $Cr(OH)_3$ or is adsorbed on iron hydroxide particles [8,9]. When aluminum electrodes are used in the EC process, the process of removing hexavalent chromium takes place mainly by the adsorption mechanism of Cr(VI) on amorphous $Al(OH)_3$ [5].

The efficiency of the EC process of chromium wastewater depends on the applied current density, treatment duration, used electrodes and conection modes, electrolyte pH and composition, initial pollutant concentration [5, 8-18]. Since Fe and Al hydroxides are very good coagulants that have an affinity to adsorb different organic and inorganic compounds, the EC process is proved to be effective in simultaneous removal of several different pollutants, together with Cr(VI) (reducing the BOD and COD, simultaneous removal of heavy metal ions, turbidity) [5,12].

The main advantages of the EC process and its use in wastewater treatment are the reduced amount of chemical reagents required for precipitation, the reduced amount of sludge formed in the process. The Fe and Al hydroxide flocs formed in the electrolysis process have a large particle size, are stable and easy to separate from treated water, and the material used for this process, metal iron and aluminum plate, are available and relatively inexpensive [15,16]. In this paper diferent process parameters on EC of synthetic prepared wastewater containing Cr(VI) was examined.

MATERIALS AND METHODS

Experimental part of the research is contained by the application of EC for removing of hexavalent chromium from simulated wastewater.

Electrochemical batch reactor (Fig. 1) is made of polypropylene of capacity 250 cm^3 with possibility of constant mixing (300 rpm/min), which contains two electrodes of the same dimensions (area), $A=24$ cm^2, and distance between electrodes, $d=20$ mm. Electrodes were connected to programmable DC power supply (GW INSTEK, PSP-2010; 20V, 10A). Before each treatment electrodes were cleaned and degreased.

Used electrode materials are made out of metals known compositions, and comply with prescribed standards, respectfully, steel (EN10130-91), stainless steel (EN 1.4301/AISI 304) and aluminum (Al 99.5/EN AW-1050 A). Steel and aluminium were used as anode and stainless steel as cathode. For the experimental purpose it was used commercially available chemicals *p.a.* (Lachner, Czech): 99,5% sodium chloride, NaCl, 35% hydrochloric acid, HCl, acetone, $(CH_3)_2CO$, 97% sodium hydroxide, NaOH and 99,5% potassium chromate, K_2CrO_4.
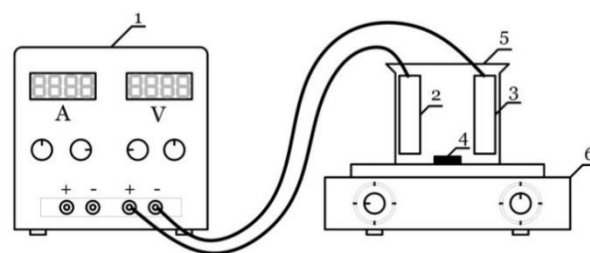

Figure 1. Schematic view of electrochemical reactor: 1 – source of electric power; 2 – anode; 3 – cathode; 4 – magnetic stir bar; 5 – electrochemical cell; 6 – magnetic stirrer)

All the experiments were performed at an ambient temperature and with synthetic wastewater volume of 250 cm^3. Initial wastewater concentration was 50 mg/L of Cr(VI) and it was added sodium chloride (0.5 or 1 g/L) as supporting electrolyte. Initial pH was 5.13 (without adjustment) and electric conductivity was 2.5 mS/cm. Before each treatment, current density was set at desirable value (5; 10 and 20 mA/cm^2).

After each EC process, treated synthetic wastewater was filtered through filter paper, Filtres Fioroni, France (Ref.:0015A00007; size: 125 mm, qty.: 1000) and it was collected formed sludge. The samples of wastewater before and after treatment were analyzed on the following parameters: pH, conductivity (κ) and Cr(VI) concentration. The chromium concentration before and after treatment was determined spectrophotometrically ($\lambda_{max}=540$ nm) on UV-VIS spectrophotometer (Perkin Elmer, Lambda 25) according to standard methods [19] and pH and κ are determined on the multimeter (Consort C861). The IR spectrum of the resulting sludge was

analyzed by Fourier transform infrared spectroscopy (FTIR) in the range of 400–4000 cm^{-1} (Bruker, Tensor 27).

In order to improve the EC treatment, from three in practice represented current regime it was used pulsed current regime. The regime is a schematic represented in Figure 2. A pulsed current regime is defined by the cathode current density (j_k), time cathode deposition (t_k), anodic current density (j_a), and time of anodic dissolution (t_a). The period of pulsed current waves, (T), is the sum of the time of cathode deposition (t_k) and time of anodic dissolution (t_a) [20].
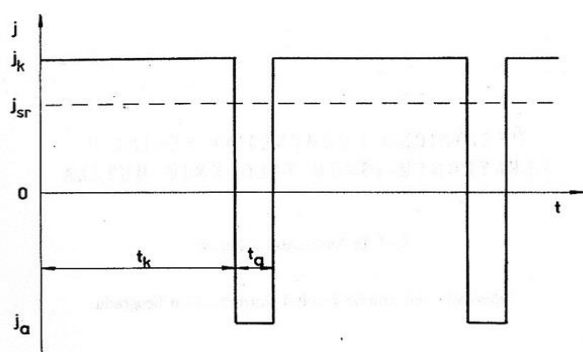

Figure 2. Schematic view of pulsed current regime [20]

RESULTS AND DISCUSSION

Results of the EC process are shown through chromium removal efficiency $E_{Cr(VI)}$ (%) calculated by following equation:

$$E_{Cr(VI)} = \frac{\gamma_i - \gamma_f}{\gamma_i} \times 100 [\%] \qquad (1)$$

where are γ_i and γ_f the initial and the final concentration of Cr(VI) expresed in mg/L.

The energy consumed to remove pollutants unit is one of the most important technological performance indicators of electrochemical reactor, because it affects the overall cost of treatment. Specific energy consumption (W_{sp}) is calculated by the following equation:

$$W_{sp} = \frac{\int_0^\theta IE_r dt}{3600 \times 1000m} \left[\frac{kWh}{kg_{polutant}} \right] \qquad (2)$$

where: E- voltage (V), I- current (A), t- time (h), m- mass of removed chromium (kg).

This research investigates the impact of: anode material, stirring, electrolysis duration, current density, cathode material, supporting electrolyte concentration and reverse current regime.
During wastewater treatment, special attention is paid to the choice of electrode material. In the case of EC,

the choice of anode material is reduced to a choice between an iron and an aluminum electrode. In the first set of experiments, electrode pairs (anode - cathode) made of steel (Fe - Fe) and aluminum (Al - Al) were used. Iron electrodes achieve higher Cr(VI) removal efficiency compared to aluminum electrodes, under the same experimental conditions, which is in accordance with previous research [17,18]. In 30 minutes of treatment with Al-Al electrode pair it was achieved 43.9% removal efficiency, while with Fe-Fe pair, 97.9% removal of chromium was achieved in 5 only minutes of treatment (Figure 3).
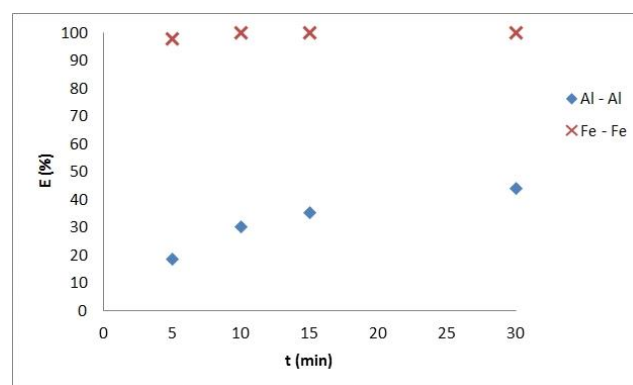

Fig. 3. The impact of anode material on Cr(VI) removal efficiency at different electrolysis time
(j=20 mA/cm^2, $\gamma_{Cr(VI)}$=50 mg/L, γ_{NaCl}=1 g/L stirring 300 rpm)

After this experiments it was examined whether the stirring has an impact on the efficiency of chromium removal. For 15 minutes of treatment with stirring (300 rpm), an efficiency of 71.9% was achieved, while without stirring under the same conditions, the efficiency was 54.1%. In further research, stirring was performed since it was confirmed that the removal chromium efficiency is diffusion controlled.
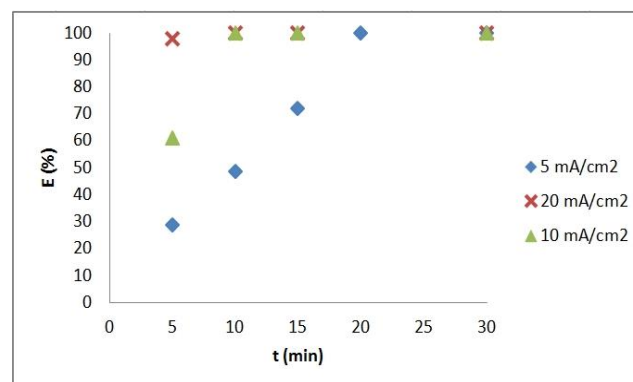

Fig. 4. The impact of current density on Cr(VI) removal efficiency at different electrolysis time
($\gamma_{Cr(VI)}$=50 mg/L, γ_{NaCl}=1 g/L stirring 300 rpm)

Figure 4 shows Cr(VI) removal efficiency at different current densities (5; 10; 20 mA/cm^2) and different treatment time. The treatment is characterized by high efficiency at the very beginning of the process, since complete removal of chromium was achieved in 30 minutes at all tested current densities. At the lowest current density (5 mA/cm^2), the efficiency increases linearly with increasing treatment time and reaches a maximum at 20 min (99.8%). Since at the lowest current density the energy consumption is the lowest and a good removal efficiency is achieved, current density of 5 mA/cm^2 was used in further research.

In order to examine the influence of cathode materials, as the cathode was used steel (Fe) and stainless steel (SS). Figure 5 shows removal efficiency with cathodes of Fe (Fe:Fe) and SS (Fe:SS), where slightly higher efficiency is observed by using a cathode made of stainless steel. Iron electrodes can be successfully replaced by cathodes of stainless steel which make process more efficient and easier to maintain.
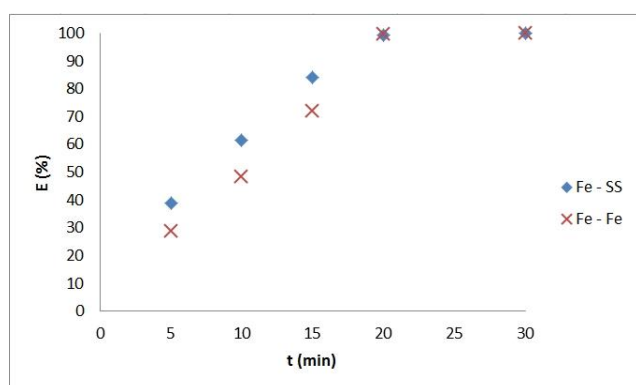

Fig. 5. The impact of cathode material on Cr(VI) removal efficiency at different electrolysis time
(j=5 mA/cm^2, $\gamma_{Cr(VI)}$=50 mg/L, γ_{NaCl}=1 g/L stirring 300 rpm)

The supporting electrolyte has an important role in electrochemical wastewater treatments. If the wastewater, which is an electrolyte in this case, does not have sufficient conductivity, a supporting electrolyte is used to increase the ionic conductivity and reduce energy consumption [7]. In this paper NaCl was tested as supporting electrolyte in two concentrations: 0.5 and 1 g / L. The experiments showed that there was no significant difference in the achieved efficiencies, and for 20 min of treatment the efficiency was 98.4% with 0.5 g/L NaCl, and 99.3% with 1 g/L NaCl. Lower supporting electrolyte concentrations reduce the economic costs of the EC process.
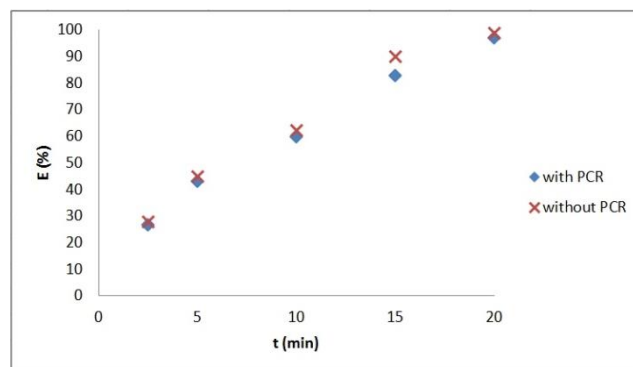

Fig. 6. The impact of pulsed current regime on Cr(VI) removal efficiency at different electrolysis time for electrode pair Fe-Fe
(j=5 mA/cm^2, $\gamma_{Cr(VI)}$=50 mg/L, γ_{NaCl}=0.5 g/L stirring 300 rpm)

In order to prevent passivation of the electrodes, it is may be necessary to replace them after a certain time. Another way to prevent passivation is to apply a reverse current regime (pulsed current regime) in which after a certain time the polarity of the electrodes changes. A change in the polarity of the electrodes is also desirable due to the uniform electrolytic dissolution of the sacrificed anodes. Figure 6 shows a slight increase in removal efficiency without the application of the pulsed current regime (PCR). This behavior is a sign that during electrolysis there is no significant passivation and "soiling" of the electrodes, so PCR regime does not have a positive impact on the efficiency of the process. Considering that the treatment time was short and it was a synthetically prepared wastewater, it is assumed that PCR would have a positive effect in longer treatments of real (more loaded) wastewater.

Based on the results shown in Figure 4, it can be seen that almost complete removal of chromium (>97%) is achieved in 5 min with the application of the highest current density (20 mA/cm^2), in 10 min with current density of 10 mA/cm^2, and in 20 min with the application of the lowest current density (5 mA/cm^2). Figure 7 shows specific energy consumption for these best achieved efficiencies. The lowest energy consumption (per mass of removed pollutant W_{sp}=2.82 kWh/kg$_{Cr(VI)}$ or per volume of treated wastewater 0.66 kWh/m^3) was at the lowest current density and high efficiency was achieved (99.8%) in a relatively short treatment time, which is favorable from the economic aspect of the process. Also, for current density of 20 mA/cm^2, energy consumption is not high, but only because the treatment time was short. In the case of loaded waters (higher initial chromium concentrations), the treatment time would be longer, and thus the energy consumption. In the paper of Kobya et al. [13] energy consumption was 1.20 kWh/m^3 for 30 minutes of

treatment with iron electrodes at current density of 30 mA/cm^2 (cocncentration of Cr(VI) in galvanizing rising water was 32 mg/L). Dermentzis et al. [8] achieved 99.9 % Cr(VI) removal efficincy from electroplating wastewater ($\gamma_{Cr(VI)}$=500 mg/L) for 50 minutes of treatment with iron electrodes at 40 mA/cm^2 and energy consumption amounts 46 kWh/m^3.
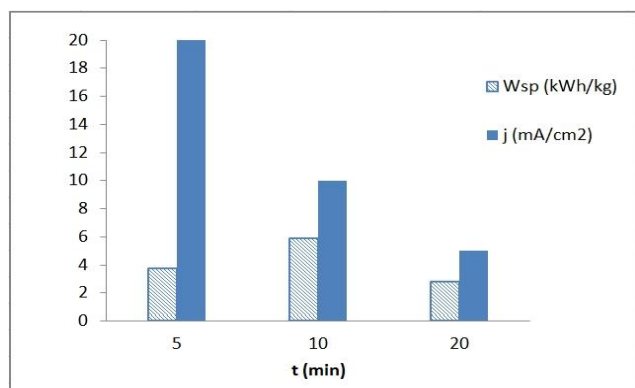

Fig. 7. Energy consumption, time and current density during EC with Fe-Fe electrode pair

($\gamma_{Cr(VI)}$=50 mg/L, γ_{NaCl}=1 g/L stirring 300 rpm, E $_{Cr(VI)}$≈100%)

The main advantage is that EC produces only 50% of the sludge chemical process, which shows more benign properties for the environment [2]. Although Cr(VI) was reduced to less hazardous Cr(III) during the EC process, the resulting sludge is certainly a problem in terms of further disposal. In this study, the sludge formed after the EC process was collected and analyzed by FTIR spectroscopy. It has been observed that with aluminium electrodes formed sludge was more voluminous, compared to sludge formed with iron electrodes.

Figures 8 and 9 show FTIR spectrum of the sludge generated after EC treatment with aluminium and iron electrodes. It can be observed that both spectrums have broad peaks in the range of 3200 - 3500 cm^{-1}, which are associated with OH$^-$ groups originate from Al and Fe hydroxides generated in this process [21,22]. Peak at 1634 cm^{-1} (Fig. 9) can confirmed presence of nondissociated H$_2$O from Cr(OH)$_3$·H$_2$O [23, 24], since according to the described mechanism, the removal of chromium takes place through the adsorption of chromium on Fe(OH)$_3$, but also through the precipitation of Cr(OH)$_3$. Peaks appearing in the range of 460 - 540 cm^{-1} (Fig. 8, Fig. 9) confirm the presence of Al and Fe, since these peaks are characteristic of Al-O and Fe-O bonds [25].
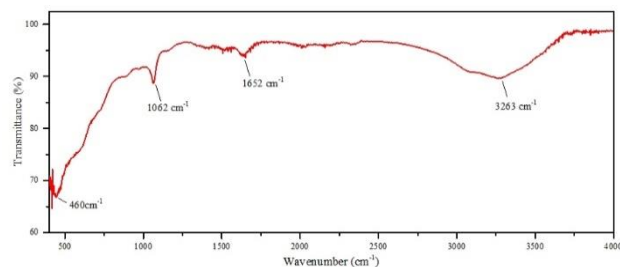

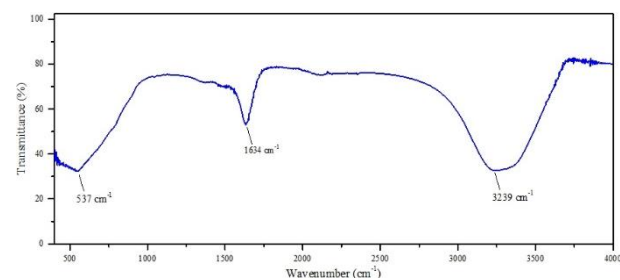**Fig. 8**. FTIR spectrum of the sludge generated after treatment with aluminium electrodes

Fig. 9. FTIR spectrum of the sludge generated after treatment with iron electrodes

CONCLUSIONS

Research has confirmed that the electrocoagulation process is very effective for removing hexavalent chromium from wastewater. Iron anodes show significantly higher efficiency compared to aluminum anodes, while the choice of cathode material does not have a great impact on the chromium removal efficiency, but only on the economic feasibility of the process. The tested initial concentration required only 20 min for almost complete removal of chromium, at a current density of 5 mA/cm^2, where the energy consumption was W_{sp}=2.82 kWh/kg$_{Cr(VI)}$ / 0.66 kWh/m^3.

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