Removal of Zn(II), Cu(II), Ni(II), Ag(I) and Cr(VI) present in aqueous solutions by aluminium electrocoagulation

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Abstract

The performance of an electrocoagulation system with aluminium electrodes for removing heavy metal ions (Zn^{2+}, Cu^{2+}, Ni^{2+}, Ag^+, $Cr_2O_7^{2-}$) on laboratory scale was studied systematically. Several parameters – such as initial metal concentration, numbers of metals present, charge loading and current density – and their influence on the electrocoagulation process were investigated. Initial concentrations from 50 to 5000 mg L^{-1} Zn, Cu, Ni and Ag did not influence the removal rates, whereas higher initial concentrations caused higher removal rates of Cr. Increasing the current density accelerated the electrocoagulation process but made it less efficient. Zn, Cu and Ni showed similar removal rates indicating a uniform electrochemical behavior. The study gave indications on the removal mechanisms of the investigated metals. Zn, Cu, Ni and Ag ions are hydrolyzed and co-precipitated as hydroxides. Cr(VI) was proposed to be reduced first to Cr(III) at the cathode before precipitating as hydroxide.
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1. Introduction

Industrial wastewaters like electroplating or acid mine wastewaters contain various kinds of toxic substances such as cyanides, alkaline cleaning agents, degreasing solvents, oil, fat and metals [1,2]. Most of the metals such as copper, nickel, chromium, silver and zinc are harmful when they are discharged without treatment [1–3]. Due to their high toxicity, industrial wastewaters are strictly regulated and have to be treated before being discharged [1,3]. The most widely used method for the treatment of metal polluted wastewater is precipitation with NaOH and coagulation with $FeSO_4$ or $Al_2(SO_4)_3$ with subsequent time-consuming sedimentation [2,3]. Other methods include adsorption, ion exchange and reverse osmosis [3,4]. Although precipitation is shown to be quite efficient in treating industrial effluents, the chemical coagulation may induce secondary pollution caused by added chemical substances [3]. These disadvantages encouraged many studies on the use of elec-

trocoagulation for the treatment of several industrial effluents [3].

The electrocoagulation process is based on the continuous in-situ production of a coagulant in the contaminated water. It had been shown that electrocoagulation is able to eliminate a variety of pollutants from wastewaters, as for example metals and arsenic [1–6], clay minerals [7,8], as well as oil [9,10], chemical oxygen demand [9–12], color [13] and organic substances [13,14]. This technique does not require supplementary addition of chemicals, reduces the volume of produced sludge [14–17] and first economical studies indicate also a financial advantage compared to the conventional methods [17]. Electrocoagulation has the potential to extensively eliminate the disadvantages of the classical treatment techniques to achieve a sustainable and economic treatment of polluted wastewater [14,15,17,18].

Since the turn of the 19th century, electrocoagulation has been applied for wastewater treatment [7] and many studies attended to optimize the process for specific problems. Typically, empirical studies were done [3,9–11,13,14]. These studies show the successful treatment of the wastewaters, however, they provide little insight into fundamental chemical and physical mechanisms [15,19]. Therefore, the mechanisms involved are yet not

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clearly understood [15,20]. But exactly these physico-chemical mechanisms have to be understood to optimize and control the process, to allow modeling of the method and to improve the design of the system.

The main objectives of the present work were to gain insight into some fundamental mechanisms and possible interactions influencing the removal process of heavy metals by electro-coagulation. Therefore, we studied (i) the influence of initial metal concentration, charge loading and current density on the removal of Zn, Cu, Ni, Cr and Ag ions by electrocoagulation. We determined (ii) the removal rates of these metals and examined (iii) possible interactions between the metals during the coagulation process. These results gave indications on the removal mechanisms by electrocoagulation.

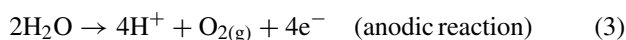## 2. Electrocoagulation process

The electrocoagulation (EC) process involves many chemical and physical mechanisms [15]. Generally, aluminium or iron is dissolved by anodic dissolution. A range of coagulant species and hydroxides are formed which destabilize and coagulate the suspended particles or precipitate and adsorb dissolved contaminants [13]. It is generally accepted that the EC process involves three successive stages [15].

(i) Formation of coagulants by electrolytic oxidation of the sacrificial anode

The main reaction occurring at the aluminium anode is dissolution:

$$Al_{(s)} \rightarrow Al^{3+} + 3e^- \tag{1}$$

Additionally, water electrolysis occurs at the cathode and anode:

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \quad \text{(cathodic reaction)} \tag{2}$$

$$2H_2O \rightarrow 4H^+ + O_{2(g)} + 4e^- \quad \text{(anodic reaction)} \tag{3}$$

(ii) Destabilization of the contaminants, particulate suspension and breaking of emulsions

A direct electrochemical reduction of metal cations (Me^{n+}) may occur at the cathode surface:

$$Me^{n+} + ne^- \rightarrow nMe^0 \tag{4}$$

Simultaneously, higher oxidized metal compounds like Cr(VI) may also be reduced to Cr(III) in contact with the cathode:

$$Cr_2O_7{}^{2-} + 6e^- + 7H_2O \rightarrow 2Cr^{3+} + 14OH^- \tag{5}$$
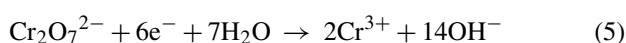
Furthermore, the hydroxide ions formed at the cathode increase the pH of the wastewater thereby inducing precipitation of metal ions as corresponding hydroxides and co-precipitation with aluminium hydroxides:

$$Me^{n+} + nOH^- \rightarrow Me(OH)_{n(s)} \tag{6}$$
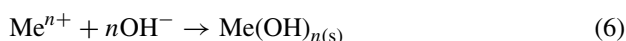
(iii) Coagulation of the destabilized phases to form flocs

In addition, anodic metal ions and hydroxide ions generated at the electrode surfaces react in the bulk wastewater to form various hydroxides and built up polymers:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_{3(s)} \tag{7a}$$

$$nAl(OH)_{3(s)} \rightarrow Al_n(OH)_{3n(s)} \tag{7b}$$
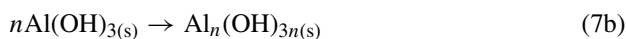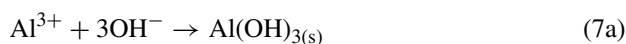
However, depending on the pH of the aqueous medium other ionic species, such as dissolved $Al(OH)^{2+}$, $Al_2(OH)_2{}^{4+}$ and $Al(OH)_4{}^-$ hydroxo complexes may also be present in the system. The suspended aluminium hydroxides can remove pollutants from the solution by sorption, co-precipitation or electrostatic attraction, followed by coagulation [15].

For a particular electrical current flow in an electrolytic cell, the mass of aluminium theoretically dissolved from the sacrificial anode is quantified by Faraday's law [15]:

$$m = \frac{ItM}{zF} \tag{8}$$

where m is the amount of anode material dissolved (g), I the current (A), t the electrolysis time (s), M the specific molecular weight (g mol^{-1}), z the number of electrons involved in the reaction and F is the Faraday's constant (96485.34 As mol^{-1}). The mass of evolved hydrogen and formed hydroxyl ions can be calculated correspondingly.

The amount of coagulant dosed into the solution can be increased by increasing the current and the reaction time. But increasing the current density leads to a decreased current efficiency. Influencing factors of the EC process are current density, conductivity, pH and electrode material [15,20].

3. Materials and methods

3.1. Model wastewater characteristics

Stock solutions of 5000 mg L^{-1} Cr(VI), Cu^{2+}, Zn^{2+} and Ni^{2+} and of 1000 mg L^{-1} Ag$^+$, were prepared by dissolving the required amounts of potassium dichromate, copper-, zinc-, nickel- and silver-sulfate in deionized water. Solutions of lower concentrations were made by proper dissolution. All chemicals were of analytical grade and supplied by Merck, Germany. The characteristics of the model wastewaters are summarized in Table 1. Conductivity of the model wastewater was adjusted to 20 mS cm^{-1} by addition of sodium nitrate in order to reduce the IR-drop or solution resistance potential η_{IR} [15,20].

Most electrocoagulation studies used chloride as anion to enhance the conductivity of the solution. We added nitrate instead of chloride and the reason for choosing nitrate was that since during an electrocoagulation process chlorides can be oxidized and organic substances be chlorinated and thereby transformed into toxic substances [21]. The added amount of sodium nitrate was 17 g L^{-1}. The synthetic wastewaters had initial pH values between 4.5 and 7.5, which were not adjusted. The effect of pH on EC will be investigated in

Table 1
Characteristics of the model wastewater

Initial pH	Conductivity (mS cm^{-1})	Zn (mg L^{-1})	Cu (mg L^{-1})	Ni (mg L^{-1})	Cr(VI) (mg L^{-1})	Ag (mg L^{-1})
7.5–4.5	20	50–5000	50–250	50–250	10–50	5–50

detail in a further study. The wastewater parameters varied were (i) initial metal concentrations and (ii) number of metals present.

3.2. Batch experiments

Batch experiments were carried out in a conventional 2000 mL beaker. Four electrodes were installed vertically with a spacer to ensure fixed distances of 5 mm in order to minimize the IR-drop [15]. The electrodes consisted of aluminium plates (AlMg3/Al 5754), 78 mm × 99 mm × 2 mm in dimension. Because these electrodes were also used in experiments with a flow through reactor, each electrode was perforated with 28 holes, each 5 mm in diameter. The active anode surface was 0.031 m^{-2}. To remove the oxide and/or passivation layer from the electrodes, the electrode surfaces were grinded with sandpaper before each experiment. The electrodes were operated in bipolar mode, so only the outer electrodes were connected to the power supply. The electrical contacts were established with crocodile clips. A defined current was applied by a DC power supply (Startron, maximum 30 V and 6.4 A). During the experiments the direction of the current was reversed every 10–30 min to limit the formation of passivation layers [20]. The solution was slowly stirred. The experimental set-up of the batch cell is schematically shown in Fig. 1.

Every EC experiment was started with 1200 mL of metal solution. The desired current was applied and 5 mL samples were taken near the anode and the cathode from the bulk solution every 2.5–30 min. The coagulation parameter varied were

(i) charge loading by reaction time and (ii) current density by applied current.

3.3. Measurements

The pH was monitored with a pH meter (Suntex TS-1, Germany) and the conductivity was measured with a multimeter (Dr. Lange, Germany). Samples were filtered (CME 0.45 μm, Rotalibo, Germany) and acified with HNO$_3$ Suprapur (Merk, Germany) directly after the sampling. The total concentrations of Zn, Ni, Cu, Ag and Cr in solution were determined with flame AAS (Perkin Elmer 1100B).

The amount of Cr(VI) in solution was analyzed photometrically using 1,5-diphenylcarbazide according to the standard method for the examination of water and wastewater (AWWA 3500-Cr D colorimetric method) [22].

4. Results and discussion

4.1. Influence of coagulation time

The electrocoagulation process is controlled by many parameters, like pollutant concentration and composition, initial pH and conductivity. Additionally, electrode material, current density, charge loading and coagulation time are influencing the process. In order to elucidate the removal processes of the different metals, the initial wastewater characteristics and the EC operating variables were held constant and only one parameter varied by time. We started with synthetic wastewaters containing one single metal at different initial concentrations. Fig. 2 shows the residual metal concentrations of each the five metals at three different initial concentrations and the corresponding pH against coagulation time. The applied current was 1.0 A and the current density was 33 A m^{-2}. Different scales of the *x*- and *y*-axes are used for the different metals.

The concentrations of Zn, Ni and Cu (Fig. 2) decreased almost linearly by time. 50, 100 and 250 mg L^{-1} of each metal in 1200 mL were nearly completely removed after 5, 10 and 15 min respectively, which corresponds to charge loading of 300, 600 and 900 As. During the first stage of EC the pH decreased slightly from the initial value to around 5–6. When the metals were almost completely removed, the pH increased quickly to values around 10.

Similarly, the concentration of Ag decreased linearly by time (Fig. 2). But the removal of Ag was much less effective than of Zn, Ni and Cu. No experiment lead to a complete removal of Ag, although the initial concentrations of 10, 20 and 50 mg L^{-1} were much lower. Also the development of the pH was different with Ag compared to Zn, Ni and Cu: the pH increased quickly during the first minutes to values around 9–10. No initial pH decrease was observed as in the other experiments.
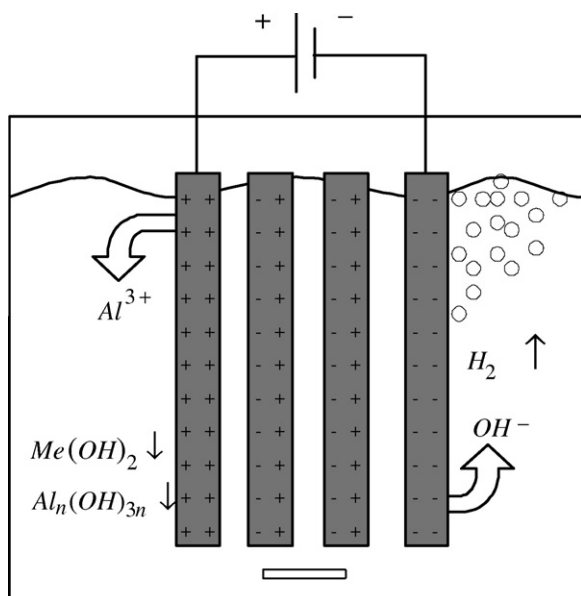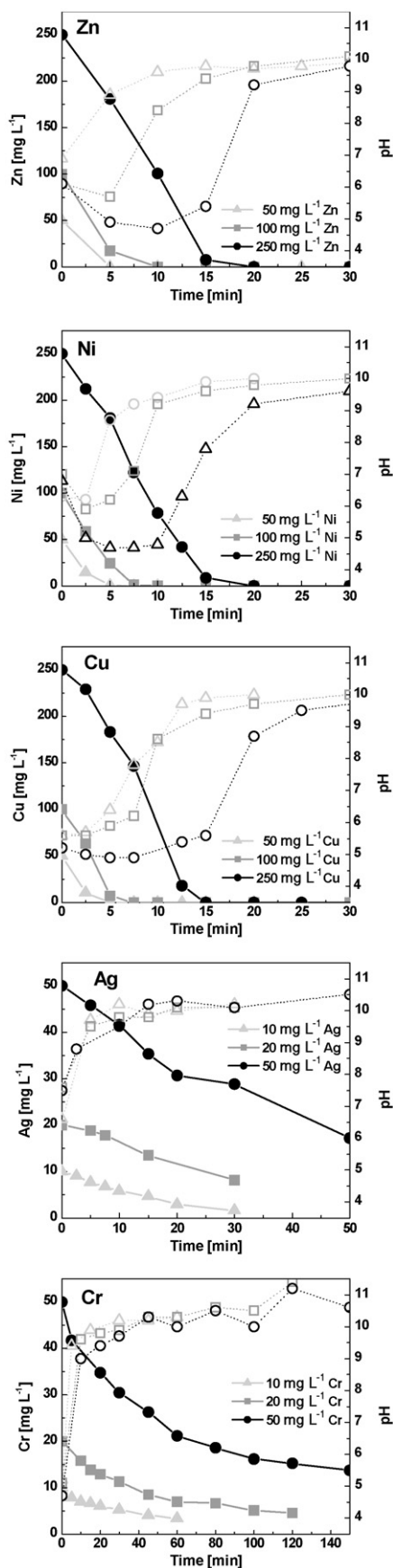

Fig. 1. Sketch of the batch cell and some basic processes.

In contrast to the experiments with Zn, Cu, Ni and Ag, the total concentration of Cr did not decrease linearly by time during EC (Fig. 2). Also the development of pH was different compared to Zn, Cu and Ni and increased quickly during the first minutes to values around 9–10. The ratio of Cr(VI) to Cr_{total} in solution decreased over time, e.g. in the experiments with initial Cr concentrations of $10 \, mg \, L^{-1}$, the ratio decreased from 1.00 at the beginning to 0.91 after 15 min and 0.87 after 30 min.

Generally, an abundant evolution of H_2 gas bubbles was observed at the cathode during all the EC experiments, whereas at the anodes only few O_2 gas bubbles were evolved. The main reactions at the anode were aluminium dissolution (Eq. (1)) and at the cathode hydrogen and hydroxyl ion formation (Eq. (2)). The minor oxygen formation at the anode (Eq. (3)) competes with the aluminium dissolution and lowers the dissolved amount.

These observations underline the following removal mechanisms for Zn^{2+}, Cu^{2+} and Ni^{2+}. Besides the direct reduction of the metal cations at the cathode surface, OH^- ions produced at the cathode precipitate metal ions as hydroxides. This reaction buffers the pH as long as all metal ions are precipitated. Subsequently that the pH increases. During EC of electrolyte solution without any metal addition (data not shown), the pH increased within 5 min to values >9. It seemed that not all hydroxyl ions formed at the cathode were bound by Al^{3+} dissolved from the anode, which lead to a fast pH increase. Even if the pH of the bulk solution is too low for formation of thermodynamically stable hydroxides, the metals can precipitate within the local zones of high pH around the cathode [23].

Ag^+ was precipitated as hydroxide too but EC does not remove Ag as efficiently as Zn, Cu and Ni. The pH increased much faster, because only one hydroxide ion is bound per Ag^+ ion.

The removal mechanism for the chromate anion is different. Chromate has to be reduced before Cr is precipitated as hydroxide $Cr(OH)_3$. In a study about electrochemical Cr removal with iron electrodes, Barrera-Diaz et al. [24] postulated besides the Cr(VI) reduction by Fe^{2+} an additional electrochemical reduction reaction at the cathode surface. Because a reduction of Cr(VI) by Al^{3+} is not possible, the only mechanism with Al electrodes is the direct reduction at the cathode surface (see Eq. (5)), followed by precipitation as $Cr(OH)_3$. According to Eqs. (5) and (6) this process would produce net 4 mol hydroxide ions per precipitated mol Cr, which explains the fast pH increase.

4.2. Influence of initial metal concentration

The Zn and Cr removal ($\mu mol \, L^{-1}$) in dependence of the charge loading ($As \, L^{-1}$) is shown in Fig. 3 as a function of initial metal concentration. The data for Zn are also representative for Cu and Ni. The removal of Zn was independent from ini-

Fig. 2. Concentrations of Zn, Ni, Cu, Ag and Cr (closed symbols) and pH values (open symbols) during EC with model wastewater containing one single metal. Initial concentrations were 250, 100, $50 \, mg \, L^{-1}$ for Zn, Ni and Cu, and 50, 20, $10 \, mg \, L^{-1}$ for Ag and Cr. Applied current was 1.0 A, the current density was $33 \, A \, m^{-2}$.
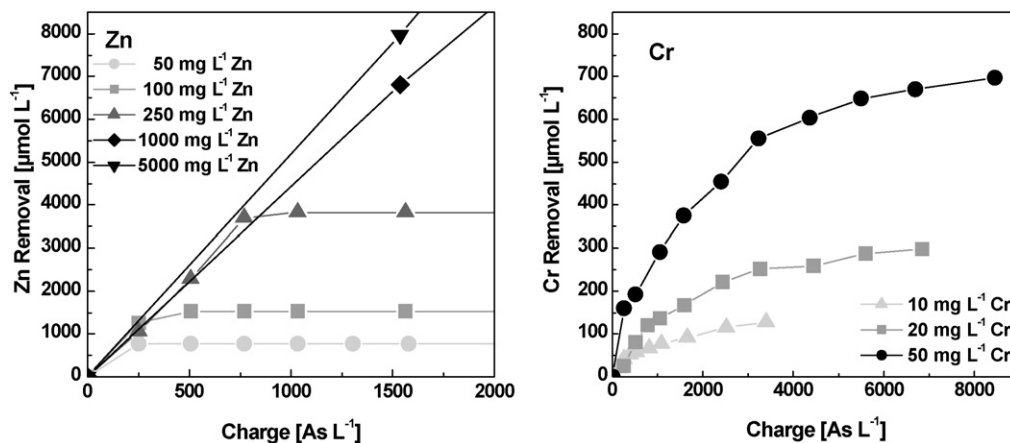
Fig. 3. Influence of initial concentration on removal of Zn and Cr (μmol L^{-1}) against charge loading (As L^{-1}) during EC with model wastewater containing one single metal. Initial concentrations were 50, 100, 250, 1000, 5000 mg L^{-1} for Zn and 50, 20, 10 mg L^{-1} for Cr. Applied current was 1.0 A, the current density was 33 A m^{-2}.

tial metal concentrations over two orders of magnitude from 50 to 5000 mg L^{-1}. The relationship between charge loading and removed Zn was almost linear. By calculating the relationship, it turned out that per applied As approximately 5 μmol Zn were removed. In contrast, the removal of Cr$_{total}$ and also the ratio of Cr(VI) to Cr$_{total}$ in solution dependend on the initial concentration. This indicates a different removal mechanism compared to Zn, Cu and Ni and supports the suggested reduction of Cr(VI) to Cr(III) at the cathode with subsequent precipitation. The more Cr$_2$O$_7^{2-}$ is present, the more Cr(VI) can hit the cathode, can be reduced to Cr(III) and then be precipitated.

To compare the removal of different metals we defined a removal rate, which describes the metal removal (μmol L^{-1}) per charge loading (As L^{-1}). The removal rates were calculated from the linear gradient between removal and charge loading. Non-linear removal of Cr was calculated for a rough comparison until 3600 As and is shown in brackets. The removal rates for Cr were strongly dependend on the initial Cr concentration and were 0.05/0.10/0.20 μmol A^{-1} s^{-1} for 10/20/50 mg L^{-1} Cr, respectively. The values for the metals are presented in Table 2. From solutions with Zn, Cu and Ni around 5 μmol L^{-1} were removed by 1 As L^{-1}, whereas with the same charge loading only around 0.1 μmol L^{-1} Ag and Cr were removed, respectively.

The maximum amount of aluminium and hydroxyl ions theoretically formed at anodes and cathodes can be calculated by

Table 2
Removal rates (μmol A^{-1} s^{-1}) as removed metals (μmol L^{-1}) by 1 As L^{-1} in single-metal solutions with initial concentrations of 50–5000 mg L^{-1} for Zn, 50–250 mg L^{-1} for Cu and Ni, 10–50 mg L^{-1} for Ag and Cr

Metal	Removal rates (μmol A^{-1} s^{-1})
Zn	4.7 ± 0.4
Cu	5.2 ± 0.3
Ni	5.0 ± 0.4
Ag	0.1 ± 0.0
Cr	(0.05/0.1/0.2)

Current density was 33 A m^{-2}. Averages from three to five experiments with standard deviation. Non-linear removal is quoted in brackets.

Faraday's law according to Eq. (8): suggesting that no oxygen is produced at the anodes, maximally 10 μmol Al^{3+} and 30 μmol OH$^-$ ions could be theoretically produced per Ampere second from the four electrodes. Calculating the Al dissolution from the electrodes by their weight loss during the EC experiments, resulted in 9.5 ± 1.3 μmol Al^{3+} per Ampere second dissolved from the electrodes (data from 32 experiments with concentrations from 10 to 5000 mg L^{-1} metal and 0.05 to 3.0 A), which is very well within the calculated range. The precipitation of all dissolved Al^{3+} ions as Al(OH)$_3$ (Eq. (7a)) would require all formed OH$^-$ ions. Because the precipitated metal ions require also OH$^-$ ions (Eq. (6)), there is a loss of OH$^-$ ions from the solution to the precipitates, which results in a pH decrease. Again, although the pH of the bulk solution is too low for the overall precipitation of metal hydroxides, hydrolysis occurs and it might be possible that the metals can precipitate within the local zones of high pH around the cathode. In the EC experiments without other metal addition, the pH increased quickly which indicates no pH buffering effect by the dissolved Al^{3+} ions.

4.3. Influence of current density

In these the experiments the initial concentrations of the metals were held constant and the applied current was varied to study the effect of different current densities on the metal removal. According to Faraday's law (Eq. (8)), increasing the current density leads to a higher Al^{3+} and OH$^-$ dosage by time. Thus the process can be accelerated. The question is if the higher current is completely converted into a higher coagulant dosage or if there are losses, which make the process less efficient, for example a higher oxygen formation at the anode.

The development of Zn and Cr concentrations and pH values corresponded to the experiments with a current of 1.0 A and the expected acceleration of the process (data not shown). The more current was applied, the more Al^{3+} and OH$^-$ were dosed into the system and the faster the Zn and Cr concentration decreased. This effect was also observed by other researchers during EC with Zn, Cr and Cu [3,4]. Again, the concentration
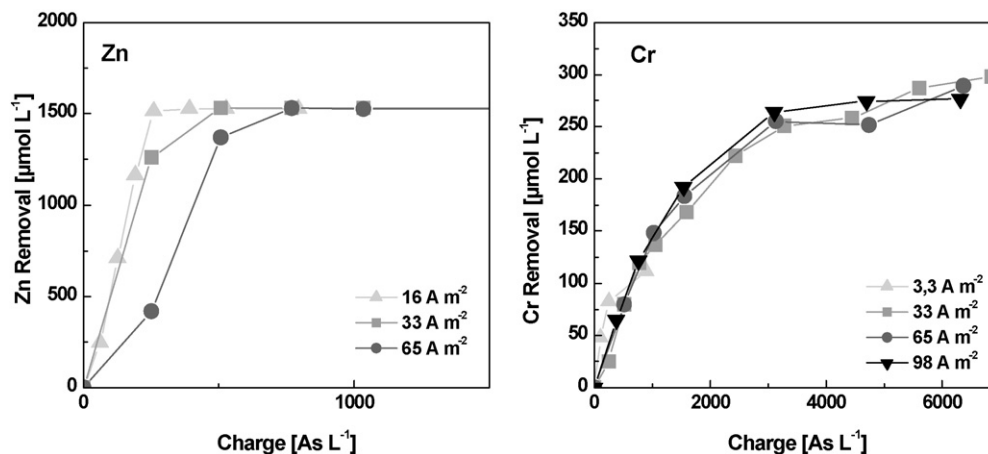
Fig. 4. Influence of current density on removal of Zn and Cr ($\mu mol\,L^{-1}$) against charge loading (As L^{-1}) during EC. Current density was 3.3–98 A m^{-2}, applied current was 0.1–3.0 A. Initial concentrations were 100 mg L^{-1} for Zn and 20 mg L^{-1} for Cr.

of Zn decreased linearly over time and the Cr concentration did not. The ratio of Cr(VI) to Cr$_{total}$ in solution was dependent on the applied current density. After 30 min the ratio was 0.98/0.92/0.64/0.42 for a current density of 3.3/33/65/98 A m^{-2}, respectively.

More information on the efficiency of the metal removal in dependence of the current density provides the relationship between metal removal and applied charge. As shown in Fig. 4, the removal ($\mu mol\,L^{-1}$) is plotted against the applied charge loading (As L^{-1}) and it can be seen that the removal of Zn in dependence on the applied charge decreased with increasing current density. When increasing the applied current density from 16 to 33 and 65 A m^{-2}, the removal rates were decreasing from 5.8 to 5.0 and 2.5 $\mu mol\,A^{-1}\,s^{-1}$, respectively. The lower removal rates might be explained with the higher kinetic over potential [15] and with energy losses by heating the water at high current densities [20]. A stronger bubble generation at the anode, which would indicate a higher oxygen formation and a reduction of the aluminium dissolution, was not observed. Also the weight losses of the electrodes did not indicate a lower aluminium dissolution in relation to higher current densities, the

relative weight losses (mg $A^{-1}\,s^{-1}$) were independent of the current density.

A different behavior could be observed for Cr: the relationship between removal and applied charge was again not linear and independent of the applied current density between 3.3 and 98 A m^{-2}. The removal rate was always 0.1 $\mu mol\,A^{-1}\,s^{-1}$ after approximately 3600 As L^{-1} (900 As L^{-1} for 3.3 A m^{-2}). This supports the assumption that the removal is limited by the reduction of chromate at the cathode. The more charge introduced into the system by the cathode, the more Cr(VI) is reduced and subsequently precipitated as Cr(OH)$_3$.

4.4. Metal interactions during electrocoagulation

As metal contaminated wastewaters mostly include a variety of different metals we studied the influence of other metals (various metals in different concentration ratios) on the removal of Zn and Cr during EC. The effect of different metal additions on the removal of Zn and Cr in dependence of the charge loading is shown in Fig. 5. The results showed that the removal of Zn
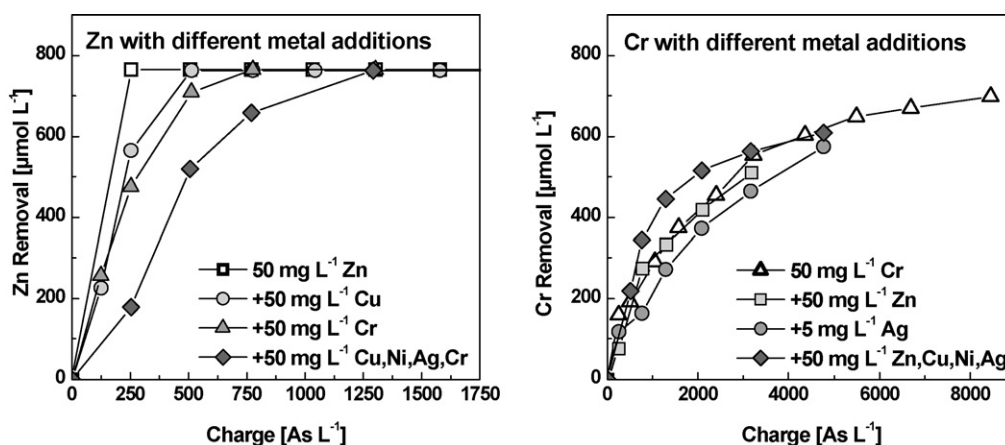

Fig. 5. Influence of metal addition on removal of Zn and Cr ($\mu mol\,L^{-1}$) against charge loading (As L^{-1}) during EC. Initial concentrations were 50 mg L^{-1} Zn and Cr, respectively, with different metal additions. Current density was 33 A m^{-2} accordant to an applied current of 1.0 A.

Table 3
Removal rates (μmol A^{-1} s^{-1}) in two-metal systems at a current density of 33 A m^{-2}

Initial concentration	Metal	Removal rate (μmol A^{-1} s^{-1})
50 mg L^{-1} Zn + 50 mg L^{-1} Cu	Zn	2.1
	Cu	2.8
100 mg L^{-1} Zn + 10 mg L^{-1} Cu	Zn	4.3
	Cu	0.6
50 mg L^{-1} Zn + 50 mg L^{-1} Cr	Zn	1.5
	Cr	(0.2)
100 mg L^{-1} Zn + 10 mg L^{-1} Cr	Zn	2.8
	Cr	(0.05)
10 mg L^{-1} Cr + 10 mg L^{-1} Ag	Cr	(0.05)
	Ag	(0.03)
50 mg L^{-1} Cr + 5 mg L^{-1} Ag	Cr	(0.14)
	Ag	0.03

Non-linear removal is quoted in brackets.

Table 4
Removal rates (μmol A^{-1} s^{-1}) in five-metal solutions with initial concentrations of 50 mg L^{-1}

Metal	Removal rate (μmol A^{-1} s^{-1})	
	1.6–3.3 A m^{-2}	33–98 A m^{-2}
Zn	1.4 ± 0.2	0.9 ± 0.1
Cu	1.6 ± 0.1	1.0 ± 0.1
Ni	1.5 ± 0.2	1.0 ± 0.1
Ag	0.6 ± 0.3	0.2 ± 0.1
Cr	0.7 ± 0.1	0.2 ± 0.0

Rates presented are average values with standard deviations at 1.6–3.3 and 33–98 A m^{-2}. Non-linear removal is quoted in brackets.

is reduced by the addition of other metals. Thereby, the addition of Cr caused a more pronounced effect than adding the same amount of Cu. Adding four other metals in all caused the greatest effect.

In contrast, the effects of the addition of other metals on removal of Cr$_{total}$ were different. The addition of 5 mg L^{-1} Ag caused a small decrease in the Cr$_{total}$ removal, the addition of 50 mg L^{-1} Zn had almost no effect, whereas the addition of 50 mg L^{-1} Zn, Cu, Ni and Ag lead to a slightly higher removal compared to the single-metal Cr wastewater. The ratio of Cr(VI) to Cr$_{total}$ in solution dropped significant below 1.00 only after Ag addition.

Calculating the removal rate of each metal in the two-metal systems (see Table 3) it turned out that indeed the removal rates decreased for each metal except for Cr with Zn and partly with Ag. By adding the removal rates of Zn and Cu the removal rate is the same as in the single-metal wastewaters. This supports the assumption of similar removal mechanisms for Zn and Cu. Both metals compete for the hydroxide ions produced at the cathode and for sorption sites at the aluminium hydroxide surface (co-precipitation).

The metal removal at 3.3 and 33 A m^{-2} in solutions containing the five metals Zn, Cu, Ni, Ag and Cr, each with an initial

concentration of 50 mg L^{-1}, is shown in Fig. 6. Again, the group of Zn, Cu and Ni was quickly removed, whereas Ag and Cr were still partly in solution at the end of the experiments.

The removal rates at 33 A m^{-2} (see Table 4) in the five-metal wastewater can be again grouped in the same way as the rates for the wastewater with only one single metal present. Zn, Cu and Ni exhibited removal rates around 1.0 μmol A^{-1} s^{-1}, whereas only around 0.2 μmol A^{-1} s^{-1} Ag and Cr were removed at a current density of 33 A m^{-2}. Cr and Ag exhibited a slightly higher removal rate in the presence of the other metals compared to the removal rate in the single-metal wastewater. This could again indicate a co-precipitation of Ag and Cr with other precipitated metal hydroxides. The removal rates of Zn, Cu and Ni were lowered by the presence of the other metals because of the competition for the OH^{-} ions produced at the cathode.

The influence of the current density on the removal rates is presented in Table 4. What was shown for the single-metal wastewater, is also true for the five-metal system: the lower the current density, the higher the removal rate. By lowering the current density over one order of magnitude, the removal rates of Zn, Cu and Ni increased over 50% and the removal rates for Ag and Cr were trebled. The higher removal rates at lower current densities might be explained with the lower reaction kinetics and concentration overpotential [15]. The concentration or mass transfer overpotential is caused by differences in electroactive species concentration near the electrode surface and
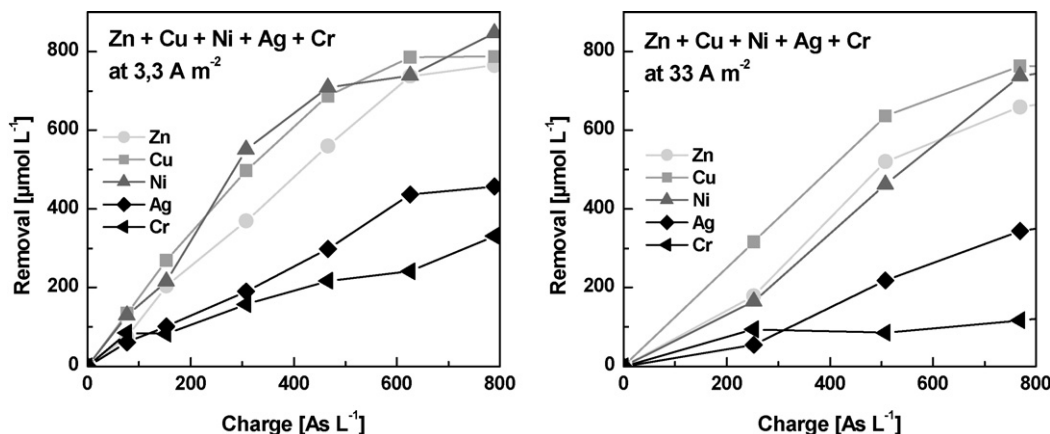

Fig. 6. Removal of Zn, Cu, Ni, Ag, Cr in a solution containing all five metals together. Removal (μmol L^{-1}) against charge loading (As L^{-1}) during EC. Initial concentrations were 50 mg L^{-1} for all metals. Current densities were 3.3 and 33 A m^{-2}, accordant to applied currents of 0.1 and 1.0 A, respectively.

the bulk solution due to the electrode reactions. The concentration overpotential decreases with decreasing currents [15]. The kinetic or activation overpotential has its origin in the activation energy barrier to electron transfer reactions and do also decrease with decreasing currents [15]. Due to the lower reaction kinetics and concentration overpotential at lower current densities, the removal was more efficient.

5. Conclusions

This work is a first step to understand systematically the processes of metal removal by electrocoagulation. From this study we attained hints on removal mechanisms of Zn, Ni, Cu, Ag and Cr. Zn, Ni, Cu and Ag are removed by direct reduction at the cathode surface, as hydroxides by the hydroxyl ions formed at the cathode via water electrolysis and by co-precipitation with aluminium hydroxides. We could calculate the amount of aluminium ions dissolved and hydroxyl ions formed, which agreed with the weight loss of the electrodes, and the amount of hydroxyl ions needed to precipitate the respective metals, respectively. The removal rates for Zn, Cu, Ni and Ag were independent of their initial concentration, which supports our thesis of the removal by precipitation as hydroxides.

Cr(VI) is proposed to be reduced directly at the cathode and precipitated afterwards as Cr(OH)$_3$. The limiting step seems to be the reduction at the cathode, because the Cr removal was depended on the initial concentration. The results from experiments with five metals indicate a co-precipitation of Cr with the other metals. These findings have to be confirmed yet with other methods, for example with Cr-speciation studies of the particles with XAFS and dissolved Cr compounds, which is in work.

Acknowledgements

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