

Electrochemical reduction of dilute chromate solutions on carbon felt electrodes

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Abstract

Carbon felt is a potential material for electrochemical reduction of chromates. Very dilute solutions may be efficiently treated due to its large specific surface area and high porosity. In this work, the up-scaling of this technology is investigated using a new type of separated cell and once-through flow of industrial rinse water. A significant enhancement of the process is obtained due to copper deposition during long-term operation. The co-deposition and re-solution of copper occurs depending on the inlet chromate concentration. When previously deposited copper is present a current-free reduction of chromate takes place resulting in current efficiencies apparently above 100%. Very high space time yields are obtained even for effluents at low concentration and optimised conditions (high flow rates and pH 2). The economic feasibility of the technology is also considered. Continuous, single-pass operation results in lower energy requirements than batch processing. The economic potential of the process is also evaluated in comparison with chemical detoxification of chromate. The operating costs for the electrochemical treatment of very dilute effluents on a carbon felt electrode are 30% lower than for the chemical method.

1. Introduction

Rinse water containing chromic acid is almost exclusively treated by chemical reduction, followed by neutralisation and sedimentation. Alternatively, electrochemical chromate reduction can help meet the needs of the industry, as well as, environmental aspects. This process offers detoxification without chemical reducing agents, minimization of salt freight and a lower sludge production. This technology has been under investigation for many years using either planar electrodes [1–4], mesh type electrodes [3, 5] or packed beds with granular carbon [6–9]. Ibl and Frei [4] reported promising results with two-dimensional electrodes. Chromate concentrations below 0.5 ppm and current efficiencies around 95% were obtained, when using 100–1000 ppm CrO₃ solutions and pH below 1.5. For the treatment of 1 m³ wastewater per day, 1.25 m² electrode area was necessary. Robertson et al. [2] developed an up-scaled system, the so called “Swiss Roll Cell” obtaining a current efficiency of 59% with 100 ppm Cr(VI) and space time yield of 0.31 g h⁻¹ l⁻¹. Systems with soluble anodes were also studied. These systems used divalent iron to reduce the chromates [10–13]. However, the anode was steadily consumed and additional iron ions loaded the effluent.

Recent work, however, has focused on highly porous materials, since space time yields obtained with very dilute waste effluents are often lower than the industrial requirements. Therefore, the treatment of these streams is still ineffective. Chromate reduction on carbon felt was investigated by several groups [14–18]. Carbon felt provides a high specific surface area (app. 22000 m² m⁻³ [19]). High porosity enhances the convection of electroactive species to the electrode surface resulting in high conversion rates and extremely low outlet concentrations even for very dilute solutions. Both single and two stage processes for the reduction and precipitation of chromium on carbon felt were investigated [14, 15]. The single stage process is promising since detoxification, precipitation and separation can be performed in a single step without addition of chemicals. A recent study [16] reported that the most critical factors in terms of current efficiency are the pH and current density. For effluents containing 50 ppm Cr(VI) the current efficiency was low (12%) at the optimum pH (pH 3.5) and the final Cr(VI) concentration achieved was relatively high (5 ppm). Moreover, the risk of plugging the carbon felt was rather high. Therefore, a two stage process, consisting of (i) reduction in a sulphuric acidic environment and (ii) separate neutralization and separation, should

be considered. To the best of our knowledge, there is only one publication on the up-scaling of this technology [20]. In this work, a 50 ppm Cr(VI) solution was maintained over 17 days by continuous reduction of chromate on a carbon felt cathode cartridge (geometric surface area of 150 cm²). At pH 2.6 reduction rates of Cr(VI) between 12 and 22 mg h⁻¹ were obtained, corresponding to a space time yield of about 0.2 g h⁻¹ l⁻¹. The present work focuses on the improvement of this technology to achieve higher space time yields and downsize equipment. The process parameters influencing the mass transport to the surface (e.g. flow rate and initial Cr(VI) concentration) as well as the efficiency of reduction are evaluated. Furthermore, other distinctive features for up-scaling are taken into account. Performance limitations due to non-uniform current distribution, gas evolution, higher pressure drop or channelling in the material [21] are considered and finally a cost estimation for the treatment of very dilute chromate containing solutions is discussed.

2. Experimental

2.1. Material and equipment

A new type of separated plug-flow electrolytic cell was used (Figure 1). The cell was divided into anode and cathode compartments with a cation exchange membrane (CEM, type fumasep[®] FTN by FuMA-Tech GmbH, Germany) preventing Cr(III) re-oxidation at the anode. The current flows perpendicular to the electrodes (flow-by reactor). The distinctive feature of this cell was the use of only one electrolyte cycle – the cathodic cycle.

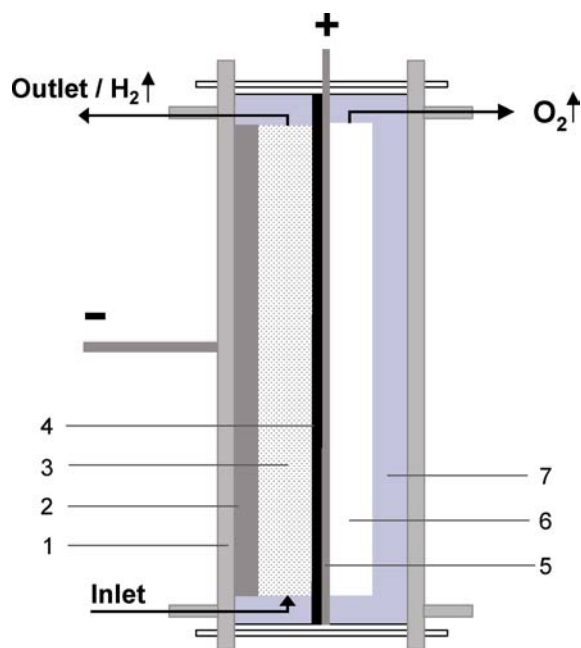


Fig. 1. Pilot plug-flow electrolytic cell (1: endplates, 2: cathode power supply, 3: carbon felt, 4: CEM, 5: anode power supply, 6: anode compartment, 7: frame).

The cathode electrode material was commercial carbon felt (GFA-10 from SGL Technologies GmbH, Germany). It was cut in 1 cm thick strips and placed crossways in the cell to prevent channelling. Various studies [22–24] showed that the current distribution within porous electrodes is determined by the ratio of conductivity between electrolyte and electrode material. The more these conductivities converge the more uniform the current distribution. The specific type of graphitised felt was used because its electric conductivity in the transverse direction (25 to 33 mS cm⁻¹) is in the same order than that of the acidified rinse water (4 to 5 mS cm⁻¹). The projected felt area was 180 cm². The other components were: cathode current connection made of a stainless steel plate and an impregnated graphite plate, which protects the stainless steel from chromic acid attack. The set-up of the anode consisted of a titanium mesh type electrode with mixed oxide coating (Ir) together with a titanium perforated plate for the anode current connection. All components were pressed together using PVC frames and stainless steel endplates.

During our study the anode compartment was wetted only once at the very beginning of the run by rinsing it with water. Thereafter, it was kept empty. The membrane remained humidified by water diffusion from the cathode compartment. The open cell design and perforated lid ensured that anodic gas (oxygen) could easily escape from the reaction zone at the electrode. The pilot plant (Figure 2) was placed in a plating company producing decorative and hard chromium plated parts (Hartchrom GmbH, Karlsruhe, Germany). It consisted of a tank with mixer, an impeller pump for the feed supply to the cell, a flow controller, flow meter, rectifier and PC for data acquisition (current, voltage, temperature, pH and conductivity). Samples were taken directly from the tank and the outlet stream. The Cr(VI) concentration was determined by UV/VIS spectrophotometer (CADAS 200, Dr. Bruno Lange GmbH, Germany, Test No. LCK 313 for 0.03–1 ppm Cr with formation of complexes with 1,5-diphenyl-carbazide). Selected samples were analysed for Cu, Fe, Ni, Zn and Al content by ICP-OES.

2.2. Process conditions

The experiments followed the task plan earlier proposed by Simmrock [25] and previously used for electrochemical investigations of packed bed electrodes by Kreysa [26]. The rinse water (inlet stream) was manually mixed in a tank close to the production line ensuring constant initial conditions for this study. The concentration was adjusted to 3, 16 or 50 ppm Cr(VI) by dilution of exhausted chromium etching solution (see composition in Table 1). The pH was adjusted using technical grade sulphuric acid (pH 1.8 to 2.5). The experiments were either performed as continuous, single-pass experiments or batch experiments where the outlet stream was totally recycled to the tank until the discharge level was reached. Current densities were calculated based on

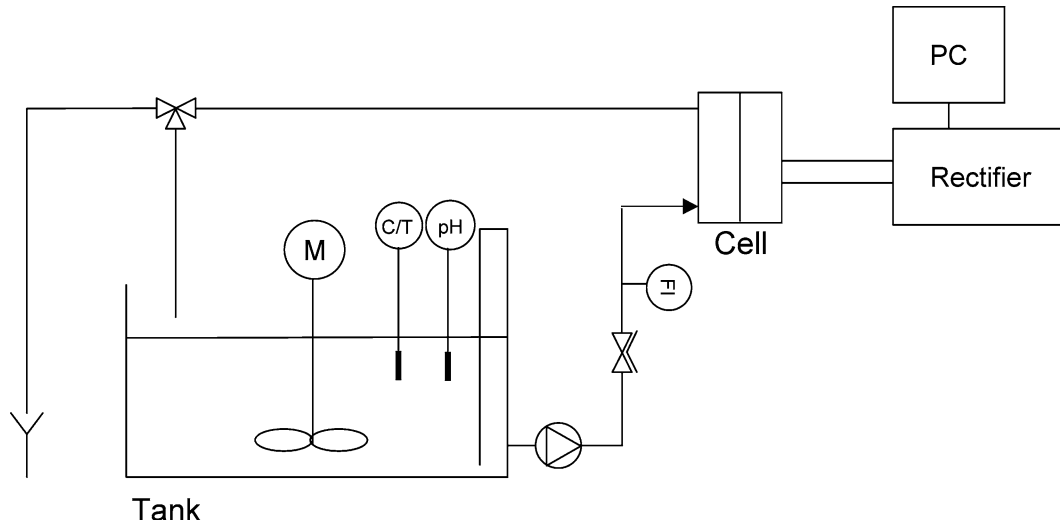


Fig. 2. Pilot plant for electrochemical chromate reduction (tank capacity: 400 l, FI – flow indicator, C/T – conductivity and temperature measurement, M – motor).

Table 1. Composition of the exhausted chromium etching solution used for preparing synthetic rinse water

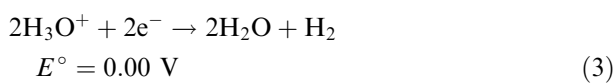
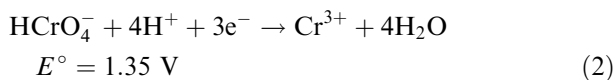
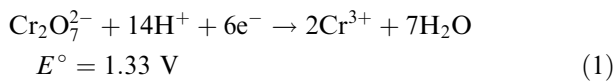
Cr(VI)/g l ⁻¹	Cr total/g l ⁻¹	Fe/g l ⁻¹	Cu/ppm	Zn/ppm	Ni/ppm	Al/ppm
113	136	15.1	571	43	160	49

the projected area of the carbon felt electrode. Throughout the tests the same carbon felt was used. First, the optimum current density at each Cr(VI) concentration was experimentally determined using the fresh carbon felt. The later experiments were performed with the same felt and with the optimum current density at the specific concentration. The feed flow rates ranged from 10 to 50 l h⁻¹ corresponding to linear flow velocities from 0.3 to 1.5 cm s⁻¹ in accordance with other studies [16, 18]. The felt electrode was kept in contact with the process solution for total of 530 h from which 120 h were under operation.

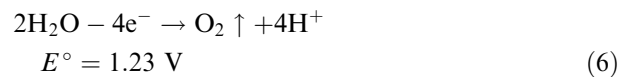
2.3. Theoretical background

The following reactions may occur at the electrodes:

Cathode



Anode



The presence of Cr(II) according to reaction (4) is generally not expected due to its fast oxidation by H⁺ and chromate. The formation of Cr(OH)₃ is excluded due to the acidity of the solution. Various parameters may be used to describe the process performance [21, 27]:

1. Fractional conversion, X_A , defined as

$$X_A = 1 - \frac{n_A}{n_{A,0}} \quad (7)$$

where $n_{A,0}$, n_A is the starting and final molar amount of chromate, respectively.

2. Overall current efficiency, Φ^e , defined as the current required for chromate reduction relative to the total current applied:

$$\Phi^e = \frac{m v_e F}{M I t} \times 100 \quad (8)$$

where m is mass of the reduced chromate, M its molar weight, F the Faraday constant, I the applied current during time, t and v_e the stoichiometric number of electrons necessary for the reaction. For the reduction of one mole of chromium, three electrons are required (see reactions 1 and 2). Therefore, the stoichiometric number, v_e , is 3.

3. The space time yield (STY) ρ_{ST} , is the reduction rate per cell volume and may be expressed as:

$$\rho_{ST} = \frac{\Delta c M}{\tau_{ST}} \quad (9)$$

where Δc is the change in Cr(VI) concentration and τ_{ST} is the space or residence time, defined as the ratio of cell volume to volumetric flow rate. Generally the STY is used for comparison of different systems and is expressed in $\text{kg m}^{-3} \text{s}^{-1}$ or in $\text{g l}^{-1} \text{h}^{-1}$. However, it is important to note that Equation 9 contains no information about the initial effluent concentration, which is one of the most important factors influencing the process.

4. The specific energy consumption, $E_{S,m}$:

$$E_{S,m} = \frac{U_c \nu_e F}{M \Phi^e} \quad (10)$$

where U_c is the total cell voltage between the anode and cathode.

3. Results and discussion

3.1. Determination of optimum current density

The limiting current densities could not be determined by direct measurement of current at different single electrode potentials using reference electrodes, because a pilot electrolytic cell was used. Instead, the outlet concentrations (conversion rate) and current efficiencies at various current densities and at three inlet concentrations (3, 16 and 50 ppm Cr(VI)) were determined. Theoretically, the curves show maximum efficiency and maximum conversion rate at a certain current density, which is considered as the optimum current density. Figure 3 presents the typical conversion rate and current efficiency at 16 ppm Cr(VI). The current efficiency is close to 100% at 3 mA cm^{-2} and the conversion rate is the highest between 3.5 and 4.5 mA cm^{-2} . Therefore,

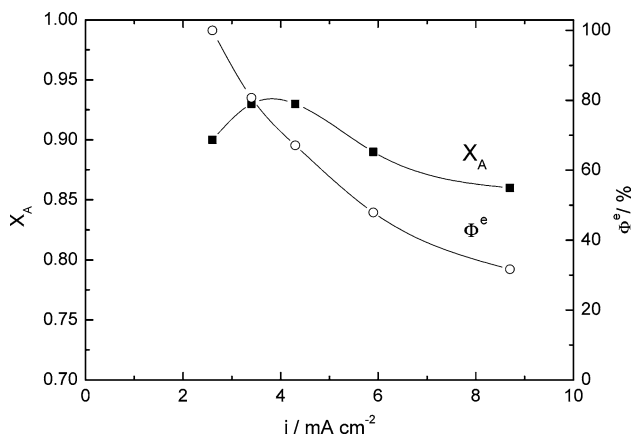


Fig. 3. Conversion rate, X_A , and current efficiency, Φ^e , at various current densities using fresh carbon felt as electrode. Process parameters: Cr(VI) inlet concentration $c_i = 16$ ppm, pH 2.1, feed velocity $u = 0.6 \text{ cm s}^{-1}$, $T = 26$ °C.

the optimum current density for operation is assumed at 3.5 mA cm^{-2} . Similarly, at 50 ppm the optimum current density is found to be 8.6 mA cm^{-2} . At very low Cr(VI) concentration (3 ppm) no maximum conversion rate is found (the conversion rate is 0.99 at each current density). Therefore, 1.4 mA cm^{-2} is chosen as optimum current density, where the current efficiency is the highest.

3.2. Influence of contaminants

Rinse water contaminants, especially copper, can have a strong effect on the process performance due to their deposition on the cathode even in acidic environment [20]. Copper coated fibers could lower the specific surface area of the porous felt acting as solid electrode surface. This will result in a decreased limiting current density and lower reactant conversion [28]. During our experiments, a green coloured metal deposit was formed on the carbon felt. This deposit was removed with concentrated nitric acid and analysed. The analysis showed that it was copper. SEM pictures of the carbon felt were taken (see Figure 4). Figure 4a shows an unused felt and Figure 4b shows a sample of the electrode used for 120 h of operation with an obvious

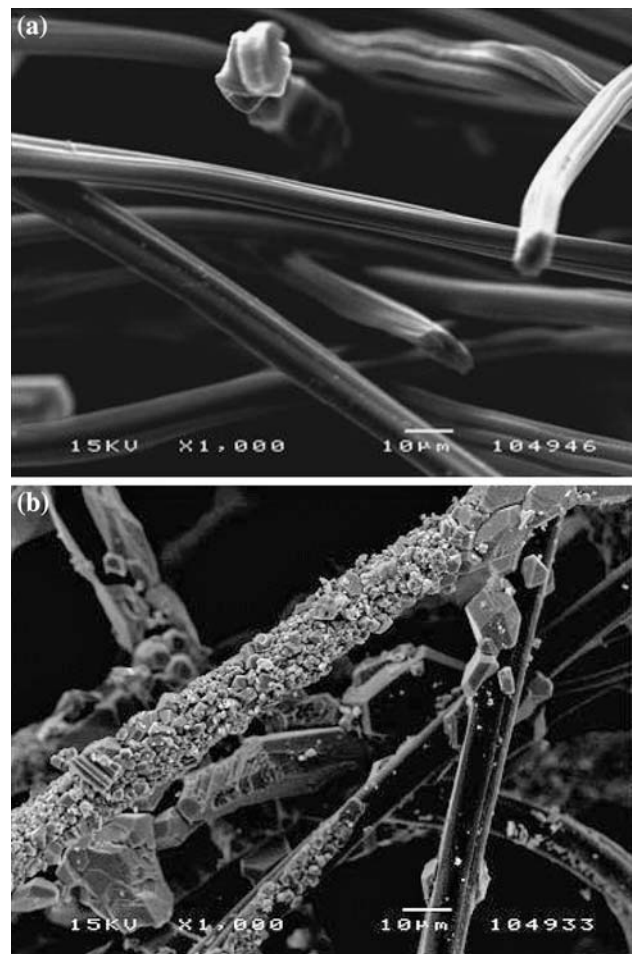


Fig. 4. SEM photographs of carbon felt GFA 10. (a) Unused carbon felt and (b) After 120 h of operation.

copper deposit on the fibres. The copper mainly deposits in the region near the entrance and the outlet of the electrode, in agreement with previous studies [28]. During the study, the apparent current efficiency was sometimes higher than 100%. For instance, it was 150% for an inlet concentration of 16 ppm Cr(VI), at pH 2.1 and 50 l h^{-1} . This indicates that current-free reduction of Cr(VI) must occur by alternative reduction. In order to investigate this, we placed two felt samples (one fresh and one used in the process for 120 h) in synthetic hexavalent chromium solution (50 ml, 16 ppm Cr(VI) prepared from chromic acid anhydride) for 50 h, under stirring. No hexavalent chromium is reduced with the unused felt, but the chromate is reduced almost completely (99%) with the felt having the copper deposit. This clearly shows that copper acts as a reductant of the chromate. Moreover, it seems that both Cr(VI) reduction and copper deposition/resolution happen simultaneously influenced by the chromate concentration in the feed. This behaviour is not surprising and can be explained by the difference in the electrode potentials of reaction (1) (1.33 V) and the copper deposition reaction (5) (0.35 V). The concentration dependence of the equilibrium potential of a redox couple ($A + e^- \rightleftharpoons A^-$) is given by the Nernst equation:

$$E = E^0 + \frac{RT}{F} \ln \frac{c_A}{c_{A^-}} \quad (11)$$

where E^0 is the standard electrode potential, R the gas constant, T the temperature, F the Faraday constant and c_A/c_{A^-} the redox couple (Cr(VI)/Cr(III) and/or Cu^{2+}/Cu) [27]. At constant temperature, the equilibrium potential shifts depending on the species concentration. At a low chromate concentration, when the chromate is nearly completely reduced, the equilibrium electrode potential decreases and reaches that of copper (0.35 V) resulting in copper deposition on the felt. If the inlet concentration is above 10 ppm Cr(VI), redissolution of previously deposited copper takes place. Figure 5 shows the course of a batch experiment lasting for 21 h. The initial 300 l rinsing solution contained 50 ppm Cr(VI) and 0.3 ppm Cu. The felt was previously used in other experiments for 80 h but the amount of the deposited copper was not known. In the beginning of the experiment, the copper concentration in the tank increases whereas the hexavalent chromium concentration decreases as desired. After approximately 6 h the copper concentration in the tank reaches a maximum and after 15 h it starts to decrease due to deposition on the felt (Figure 5a). Interestingly, despite the low initial copper concentration in the tank (0.3 ppm) the outlet stream contains 26 ppm Cu^{2+} (Figure 5b). This is due to the redissolution of copper from the felt. As a result, the chromate concentration decreases relatively fast, the process has an apparent current efficiency higher than 100% and the Cr(VI) outlet concentration practically becomes zero after 13 h. At this point the copper concentration in the outlet starts to decrease (Fig-

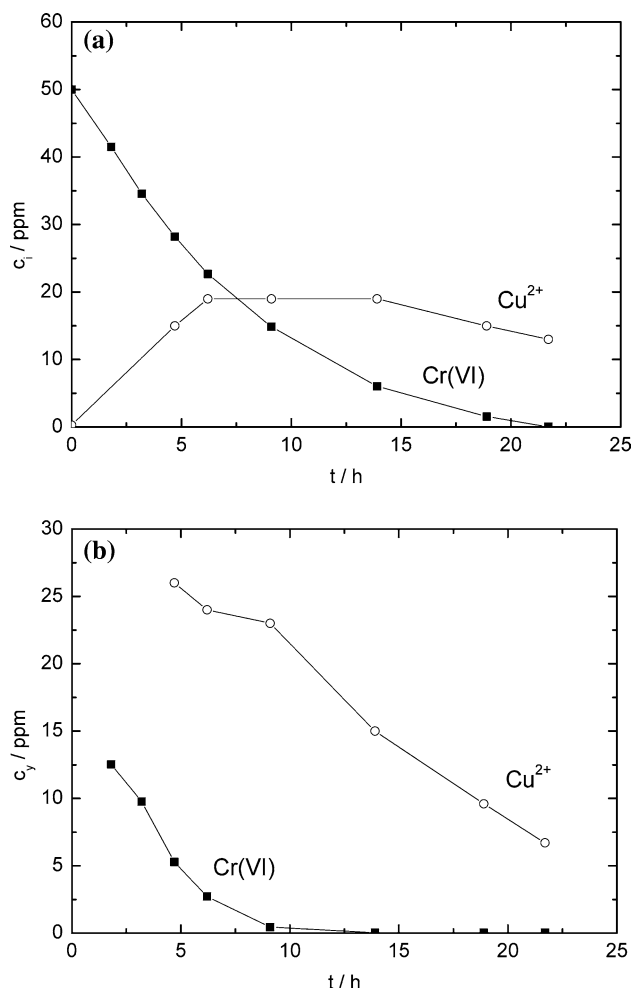


Fig. 5. The changes of Cr(VI) and Cu^{2+} concentration during a batch experiment. (a) In the tank (c_i =cell inlet concentration) and (b) in the outlet stream (c_y =cell outlet concentration). Process parameters: $U_C=2 \text{ V}$, $u=1.5 \text{ cm s}^{-1}$, $i=7.8 \text{ mA cm}^{-2}$ ($t=0 \text{ h}$) and 5.2 mA cm^{-2} ($t=21 \text{ h}$), pH 2.1, $T=26 \text{ }^\circ\text{C}$.

ure 5a), showing that the deposition of copper becomes the main reaction again. These phenomena have a significant importance for the long-term operation. Either deposited copper should be reduced at the start of batch mode operation (self-cleaning) or the felt cathode could be cleaned when process solution flows current-free through the cell (potential cleaning procedure). Finally, it is worth noting that during all experiments we used the same cathode felt and the copper deposition and dissolution could not be controlled. Therefore, the measurement series taken at different operation times can not be directly compared. However, the reactor performance in each measurement series always shows the same behaviour for the different conditions (c_i , u and pH) even if the parameters X_A , Φ^e and ρ_{ST} are fluctuating over the whole pilot study. Figure 6 presents a typical example, where the influence of the feed velocity on the process performance is studied at different operation times (all other process conditions remain constant). As expected, lower outlet concentrations (higher current efficiencies and conversion rates) are obtained when the felt is in use for a long

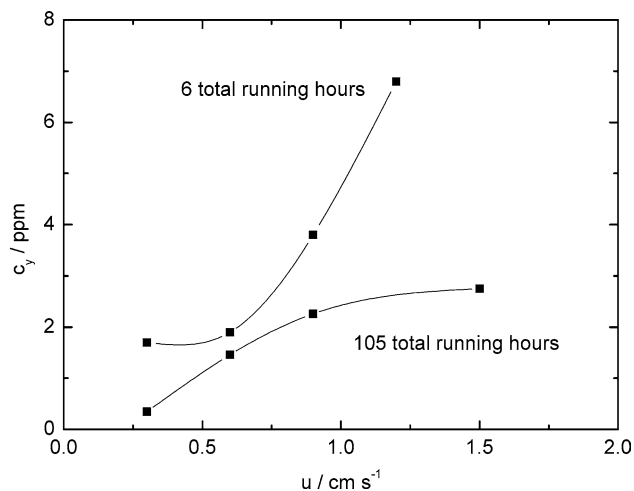


Fig. 6. Effect of feed velocity, u , on Cr(VI) outlet concentration, c_y , at different total running times. Process parameters: Cr(VI) inlet concentration $c_i = 16$ ppm, $i = 3.5$ mA cm^{-2} , pH 2.1, $T = 26$ °C.

time (105 h instead of 6 h) indicating once more the additional chromate reduction by deposited copper. Furthermore, the influence of the flow rate seems to be different in these two cases. When the felt has been used for only 6 h, the outlet concentration increases strongly with the flow rate. However, after several hours of operation (105 h), this effect weakens. It seems that increasing feed flow rates results in increasing copper resolution and therefore lower Cr(VI) outlet concentrations compared to the fresh felt are obtained.

3.3. Influence of process parameters

3.3.1. Effluent concentration and feed velocity

The concentration of waste effluent fluctuates strongly in plating shops. In some cases this may result in lower cell performance and outlet concentrations above the maximum permissible levels. Figure 7 shows the variation of the STY at three different initial Cr(VI)

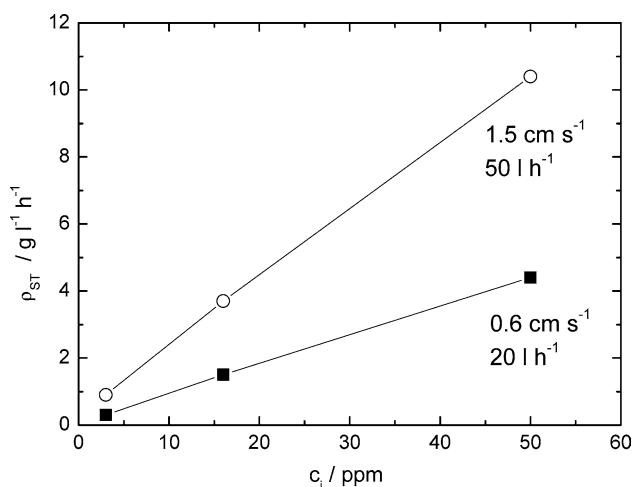


Fig. 7. Space time yield, ρ_{ST} , at different Cr(VI) inlet concentrations, c_i , and feed flow rates. Process parameters: Current density 1.4 mA cm^{-2} for 3 ppm, 3.5 mA cm^{-2} for 16 ppm and 8.6 mA cm^{-2} for 50 ppm Cr(VI), pH 2.1 and $T = 26$ °C.

concentrations for two feed flow rates. The STY increases with the increase in Cr(VI) concentration, as expected (see Equation 9). This increase is stronger at higher flow rates. The highest Cr(VI) reduction rate (10.4 g $\text{l}^{-1} \text{h}^{-1}$) is found at 50 ppm and 50 l h^{-1} (1.5 cm s^{-1}) and can be attributed to two effects. When the reactant concentration is low, the supply of reactant to the electrode surface becomes important (diffusion limitation). Therefore, the conversion improves at higher feed velocities (see Figure 6). The conversion improves at high flow rates due to increased copper dissolution resulting in a current efficiency of $\sim 130\%$. On the other hand, if the feed velocity is too high, especially at high inlet concentrations, the residence time might be too short to have sufficient conversion. Then, reduction of the flow rate (increasing residence time) might be required to reach lower outlet concentrations. Nevertheless, our results show that the outlet concentration obtained with a low concentration (3 ppm) is below the German discharge level (0.1 ppm) independent of the feed flow rates studied. Even at a feed rate as high as 50 l h^{-1} (1.5 cm s^{-1}) hexavalent chromium could not be detected in the outlet stream.

3.3.2. Influence of pH

Protons are required for chromate reduction (see reactions 1 and 2). Therefore, both chemical and electrochemical reduction of dilute Cr(VI) effluents require addition of sulphuric acid to pH < 2.5. One should always strive for optimised acid consumption. On one hand consumption of extra chemicals should be minimized, but on the other hand, the electrolyte pH must be low enough to ensure sufficient and complete chromate reduction.

Most experiments in this study were performed at pH 2.1. However, the influence of excess H_2SO_4 was also investigated using a Cr(VI) inlet concentration of 16 ppm. Samples were taken every 30 min after acid addition. Lowering the pH from 2.5 to 1.8 results in

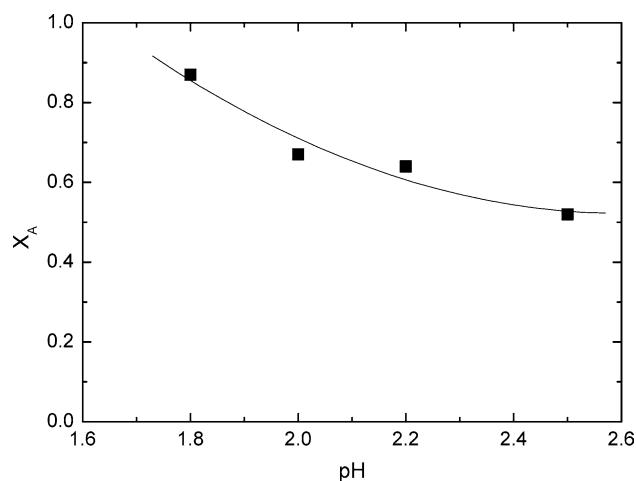


Fig. 8. The effect of rinse water pH on the conversion rate of Cr(VI). Process parameters: Cr(VI) inlet concentration $c_i = 16$ ppm, $i = 3.5$ mA cm^{-2} , $u = 1.5$ cm s^{-1} , $T = 26$ °C.

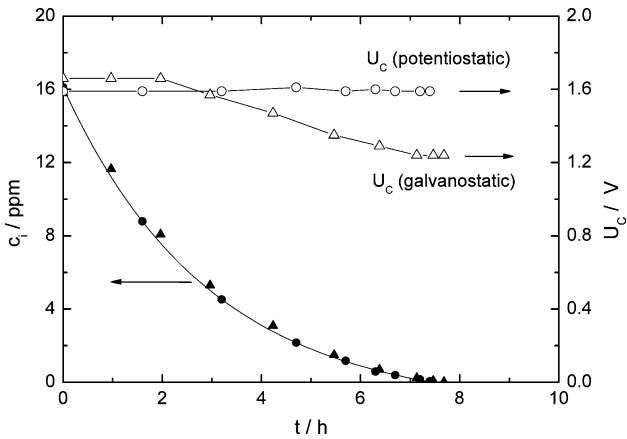


Fig. 9. Batch processing at different modes of electric operation (circles: potentiostatic, triangles: galvanostatic mode). Other process parameters: Cr(VI) inlet concentration $c_i=16$ ppm ($t=0$), pH 2.1, $u=1.5$ cm s⁻¹, $T=26$ °C.

lower outlet concentrations from 7.8 ppm to 2.0 ppm and to an increase of the conversion rate from 0.52 to 0.87 (Figure 8). The same behaviour was obtained for more dilute solutions, e.g. 3 ppm Cr(VI). In this case, the conversion rate was 0.96 at pH 2.1, but only 0.8 at pH 3 (both for 1.2 cm s⁻¹).

3.3.3. Potentiostatic vs. galvanostatic mode

For the estimation of energy requirements, we compared two batch mode experiments, where the Cr(VI) concen-

tration in the tank was reduced from 16 ppm to below 0.1 ppm. The first experiment was performed at a constant voltage of $U_c=1.6$ V (potentiostatic mode) and the second experiment at a constant current (galvanostatic mode). In the latter experiment the current was gradually lowered according to the decrease in concentration in the tank simulating constant current operation as in industrial scale experiments. This process might be advantageous since the current density can be lowered stepwise according to the particular inlet concentration which results in energy savings. Figure 9 shows that the decrease in Cr(VI) concentration in the tank is the same for both experiments despite the different modes of operation. The overall STY for both experiments is 1.9 g l⁻¹ h⁻¹ and roughly 50% lower than the STY of the continuous, single-pass experiments performed at constant Cr(VI) concentration (see Figure 7, STY~3.5 g l⁻¹ h⁻¹ for 16 ppm Cr(VI) and 1.5 cm s⁻¹). This difference can be explained by the steady decrease in Cr(VI) concentration in the tank, resulting in a decreasing STY according to Figure 7. The total current efficiency is 93% in batch mode and nearly 100% in continuous, single-pass mode showing the good performance of this technology with very dilute waste effluents and indicating the balance of copper dissolution and deposition. In conclusion, it seems that the galvanostatic mode brings no additional benefits in terms of the required carbon felt area (i.e. equipment size). However, gradual lowering of the

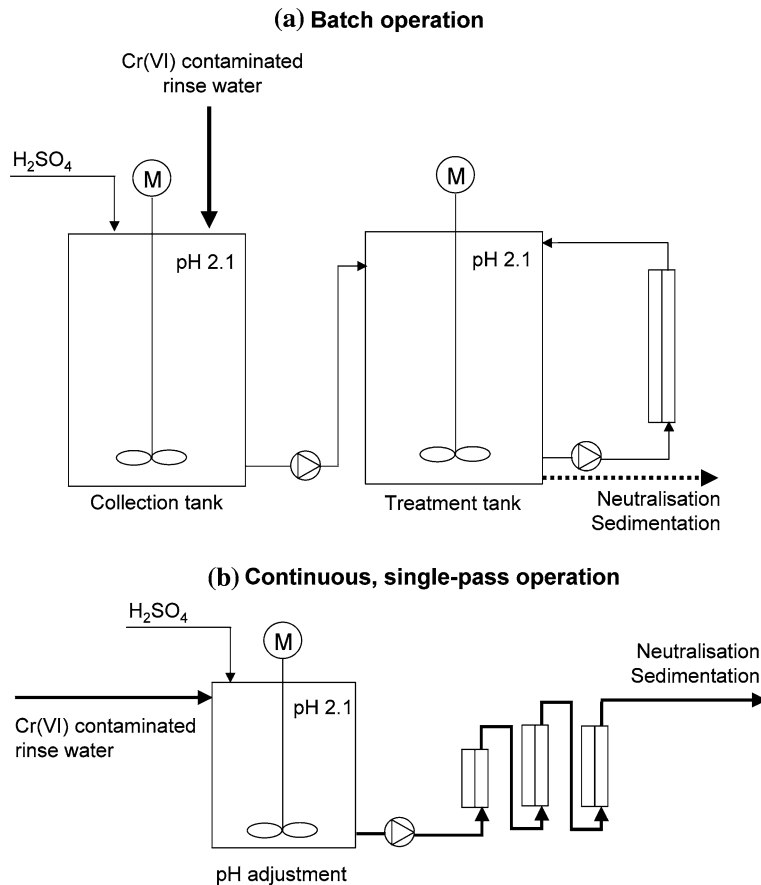


Fig. 10. Schematic presentation of electrochemical modes of operation. (a) Batch and (b) continuous, single-pass operation.

Table 2. Energy requirements for electrolytic chromate reduction in batch and continuous, single-pass mode for $1 \text{ m}^3 \text{ h}^{-1}$

	Batch	Continuous, single-pass
Stages	1	3
$I t/\text{Ah}$	27.4	24.7 (6.1 + 13.3 + 5.3)
U_c/V	1.6	1.6/1.5/1.3
E/Wh	44	37
$E_{s,m}/\text{kWh kg}^{-1}_{\text{Cr(VI)}}$	2.8	2.3

Calculation parameters: treatment of $1 \text{ m}^3 \text{ h}^{-1}$, $c_i = 16 \text{ ppm}$, $u = 1.5 \text{ cm s}^{-1}$, potentiostatic mode for batch operation and galvanostatic mode for continuous, single-pass operation.

current results in lower power consumption due to lower voltage drop.

3.4. Electrochemical Cr(VI) reduction at industrial scale – A case study

3.4.1. Energy requirements for batch and continuous, single-pass operation

Generally the batch processing is promoted by legislative authorities. The reason is that the risk of the toxic chromate reaching the public sewers or receiving water seems to be less than for continuous processing. By operating in the batch mode discharging levels can be safely maintained, even if the waste concentrations fluctuate. Figure 10 schematically presents future industrial-scale operations using either batch (Figure 10a) or continuous, single-pass mode (Figure 10b). The calculations are based on the STY of batch experiments of Figure 9 ($1.9 \text{ g l}^{-1} \text{ h}^{-1}$) assuming a waste water flow of $1 \text{ m}^3 \text{ h}^{-1}$. Continuous, single-pass processing requires only one small tank for pH adjustment, whereas batch processing requires two tanks able to collect the total waste stream for a certain time (1 h). For this example the carbon felt area is the same for both modes ($\sim 1.2 \text{ m}^2$) due to the same average STY ($1.9 \text{ g l}^{-1} \text{ h}^{-1}$). Batch operation is realized with one module (Figure 10a), whereas the continuous, single-pass configuration consists of three modules in series each running at different current density (Figure 10b). Accordingly, the three modules are smaller than the module used for the batch mode. Table 2 presents the calculated energy requirements for both modes of operation. The consumed current was calculated by integrating the variation of current density over time. In the continuous,

single pass operation three different electrode areas were used. The first cell has the largest electrode area since the chromate concentration is the highest. In the last cell only small amounts of chromate remain and thus, the electrode can be smaller. The projected electrode area was calculated from the STY at 1.5 cm s^{-1} (see Figure 7). We assumed chromate reduction from 16 to 10 ppm in the first stage (STY $3.5 \text{ g l}^{-1} \text{ h}^{-1}$), 10 to 3 ppm in the second stage (STY $2 \text{ g l}^{-1} \text{ h}^{-1}$) and 3 to 0 ppm in the last stage (STY $1 \text{ g l}^{-1} \text{ h}^{-1}$).

The continuous, single-pass mode has economical advantages due to the lower specific current at the inlet of each step. Besides higher current efficiency ($\sim 100\%$), this also results in a slightly lower voltage drop and power consumption in comparison to batch mode (2.3 instead of $2.8 \text{ kWh (kg}_{\text{Cr(VI)}})^{-1}$). On the other hand, batch processing has advantages in terms of operational reliability. In this mode, the deposited copper can be removed in the starting phase of the process (self-cleaning operation). In the continuous, single-pass mode most of the copper may be deposited in the last module and can only be removed by additional cleaning procedures. The successful industrial implementation requires further research focused on up-scaling of the electrolytic cell, especially on carbon felt multi-layer cathodes to provide sufficient large cross-sectional area. Due to the limited cross-sectional area, a number of repeating units should be used. Therefore, the detoxification of large streams requires high investment costs, e.g. for electrodes and power supply etc. If a multi layer cathode is used the investment costs could be reduced.

3.4.2. Electrochemical vs. chemical detoxification of chromate

There are few data published on the economics of other electrochemical methods like chromate reduction on planar or mesh type electrodes, fixed beds (granular carbon) or soluble steel anodes. Table 3 presents some of this data in comparison to our results. The power consumption of the different processes for pure electrolysis per kg Cr(VI) are compared. Our method using carbon felt shows the lowest power consumption, $2.3 \text{ kWh per kg}_{\text{Cr(VI)}}$, followed by the reduction using graphite particles in a fixed bed.

Finally, the operating costs for chromate removal from very dilute effluents are considered (Table 4). Chemical and electrochemical treatments are compared

Table 3. Energy requirements for electrolytic Cr(VI) reduction using different electrochemical treatment methods

Cr(VI) reduction method	Reference	Power consumption/kWh $\text{kg}^{-1}_{\text{Cr(VI)}}$
Membrane electrolysis with mesh type cathodes	[5]	8–11 ^a
Soluble anodes (indirect reduction by Fe^{2+})	[13]	12 ^b
Fixed bed (granular carbon)	[9]	6 ^a
Carbon felt	[this work]	2.3 ^c

^aCr(VI) concentration not specified.

^b $c_i, \text{Cr(VI)} = 500 \text{ ppm Cr(VI)}$.

^c $c_i, \text{Cr(VI)} = 16 \text{ ppm}$ (this work, Table 2).

Table 4. Operating costs for Cr(VI) removal by chemical and electrochemical reduction (in Euros m⁻³)

	Chemical treatment	Electrochemical reduction on carbon felt (continuous, single-pass mode)
Initial pH adjustment to pH 2.1	0.08 ^a	0.08 ^a
Chemical for reduction (NaHSO ₃)	0.08 ^b	–
Energy consumption for electrolysis	–	<0.01 ^c
Energy for pumping through the cell	–	0.05 ^d
Chemical for precipitation (lime milk)	0.02 ^e	0.01 ^f
Sludge disposal	0.24 ^g	0.15 ^h
Total	0.42	0.30

Process parameter: $c_i = 16$ ppm Cr(VI), treatment of $1 \text{ m}^3 \text{ h}^{-1}$, $u = 1.5 \text{ cm s}^{-1}$, continuous, single-pass operation.

^aH₂SO₄ at 100 € t⁻¹.

^bNaHSO₃ (solid) at 1.3 € kg⁻¹ (3.3 kg NaHSO₃ (kg Cr(VI))⁻¹ needed), including a factor for making-up and dosage of the liquid reduction chemical (factor 1.2).

^cExample from Table 2 (2.3 kWh per kg Cr(VI)), 0.11 € kWh⁻¹.

^dConsidering a pump consuming 0.5 kWh, 0.11 € kWh⁻¹.

^e4.3 kgCa(OH)₂ per kgCr(VI), 35% Ca(OH)₂, 65 € t⁻¹.

^f2.1 kgCa(OH)₂ per kgCr(VI), 35% Ca(OH)₂, 65 € t⁻¹.

^g50 kg per kgCr(VI), 20% solids content, 300 € t⁻¹.

^h32 kg per kgCr(VI), 20% solids content, 300 € t⁻¹.

using the results obtained in this work. The operating costs for electrochemical treatment are 30% lower than for the chemical treatment. This is mainly due to the lower amount of sludge produced when reducing chromate without the use of reduction chemicals. The cost for electrolysis is very low compared to that of sludge disposal and practically does not influence the total costs. However, additional costs arise for the hydraulic supply of electrolytic cell. Furthermore, it should be noted that the costs for the manufacturing of electrochemical plant is generally higher than that of chemical plant. However, suitable process design (use of thicker carbon felt and/or multi layer electrodes) could result in a financially attractive process to detoxify chromate containing effluents.

4. Conclusion

Electrochemical chromate reduction on highly porous carbon felt is an efficient treatment method, especially for very dilute solutions of chromate. In this work, high reduction rates of chromate were obtained. This especially happened when the electrode felt was running for long times and due to the copper deposition and resolution from the felt; the copper in the rinse water comes from the chromium etching process. Copper deposited on the cathode felt when chromate was completely reduced and dissolved when the chromate concentration increased, for instance when a new batch process started. The copper deposits significantly enhanced the process performance due to current-free reduction of chromate.

The economics of batch and continuous, single-pass operation were compared for effluents containing 16 ppm Cr(VI). The energy requirements of the continuous, single-pass operation were estimated to be low

(2.3 kWh per kg Cr(VI)). Finally, electrochemical Cr(VI) reduction with carbon felt was compared to the chemical removal of chromate. The operation costs of the process were estimated to be 30% lower showing the promising economic potential of this technology.

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References

1. I.M. Kolthoff and A.M. ShamsEl Din, *J. Phys. Chem.* **60**(11) (1956) 1564.
2. P.M. Robertson, F. Schwager and N. Ibl, *J. Electroanal. Chem.* **65**(2) (1975) 883.
3. A.J. Chaudhary, N.C. Goswami and S.M. Grimes, *J. Chem. Tech. Biotech.* **78**(8) (2003) 877.
4. N. Ibl and A.M. Frei, *Galvanotech. Oberflächenschutz* **5**(6) (1964) 117 (in German).
5. P. Kimmerl, H. Schade, W. Blatt and L. Schneider, *Galvanotech.* **85**(12) (1994) 4131 (in German).
6. E.C.W. Wijnbelt and L.J.J. Janssen, *J. Appl. Electrochem.* **24** (1994) 1028.
7. K.N. Njau and L.J.J. Janssen, *J. Appl. Electrochem.* **29** (1999) 411.
8. S. Reussard, J.F. Benezech and G. Lacoste, Removal of hexavalent chromium converting to chromium hydroxide by treatment in an electrochemical reactor, in "Electrochemical Engineering and the environment 1992" (1992) 97.
9. E. Langefeld, *Galvanotech.* **83**(11) (1992) 3859 (in German).
10. J. Dziejewski, S. Marczak, E. Nuttall, G. Purdy, W. Smith J. Taylor and C. Zhou, *Waste Manag.* **18** (1998) 257.

11. N. Kongsricharoern and C. Polprasert, *Wat. Sci. Techn.* **31**(9) (1995) 109.
12. N. Kongsricharoern and C. Polprasert, *Wat. Sci. Tech.* **34**(9) (1996) 109–116.
13. C. Barrera-Díaz, M. Palomar-Pardave, M. Romero-Romo S. Martínez, *J. Appl. Electrochem.* **33** (2003) 61.
14. D. Golub and Y. Oren, *J. Appl. Electrochem.* **19** (1989) 311.
15. M. Abda, Z. Gavra and Y. Oren, *J. Appl. Electrochem.* **21** (1991) 734.
16. E.P.L. Roberts and H. Yu, *J. Appl. Electrochem.* **32** (2002) 1091–1099.
17. V.K. Varenzov, *Galvanotech. obrab. poverchnosti (Russia)* **10**(1) (2002) 29 (in Russian).
18. E.O. Vilar, E.B. Cavalcanti, H.R. Carvalho and F.B. Sousa, *Braz. J. Chem. Engin.* **20**(3) (2003) 291.
19. J. González-García, P. Bonete, E. Expósito, V. Montiel, A. Aldaz and R. Torregrosa-Maciá, *J. Mat. Chem.* **9**(2) (1999) 419.
20. I.M. Dalrymple, S.J.G. and M. Hendou, The Recovery and Recycling of Cr(VI) from Dilute Waste Solutions. Canmet/Cari/ European Commission Joint Workshop on “Environmental Technologies for a Sustainable Production and Consumption” (Vancouver, Canada, 2003).
21. F. Walsh, A first course in electrochemical engineering, the Electrochemical Consultancy (1993).
22. V.S. Daniel-Bek, *J. Phys. Chem. (UdSSR)* **22**(6) (1948) 697 (in Russian).
23. V.K. Varenzov. Use of voluminous porous flow-through electrodes for increased performance of electrochemical processes in hydrometallurgy, in “Increasing performance of electrochemical processes. Collection of scientific studies”, in A.P. Tomilov (Ed.), Academy of Science of UdSSR. Institute for Electrochemistry “A.N. Frunkin”, (Nauka, Moscow, 1988), pp. 94 (in Russian).
24. F. Walsh, Electrode Potential and Current Density Distribution, in ‘A first course in electrochemical engineering’. The Electrochemical Consultancy (1993) 235.
25. K.H. Simmrock, *Chem. Ingen. Techn.* **40** (1968) 875 (in German).
26. G. Kreysa, *Chem. Ing. Tech.* **50**(5) (1978) 332 (in German).
27. H. Wendt and G. Kreysa, *Electrochemical Engineering: science and technology in chemical and other industries* (Springer-Verlag, Heidelberg, 1999).
28. E.J. Podlaha and J.M. Fenton, *J. Appl. Electrochem.* **25** (1995) 299.