

## DIRECT ELECTROCHEMICAL REDUCTION OF HEXAVALENT CHROMIUM IN A FILTER-PRESS REACTOR

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*The direct electrochemical reduction of toxic Cr(VI) species was studied by cyclic voltammetry, rotating disk electrode and in a flow-by filter press reactor. The key voltammetric reduction peak was found at -340 mV (vs. Ag/AgCl), whereas the limiting current under hydrodynamic conditions was observed at ca. - 850 mV. A continuous flow filter-press reactor with a reticulated vitreous carbon (RVC) cathode was used to achieve Cr(VI) reduction. It was found that the RVC itself reduces part of the Cr(VI) in the absence of an applied potential and becomes oxidized to CO<sub>2</sub>. The application of a relatively small potential (-1 V) to 200 mL of a 100 ppm Cr(VI) solution circulating at a flow rate of 40 mL min<sup>-1</sup> achieves the reduction of c.a. 99% of the Cr(VI) initially present in only 8 min.*

*Keywords: Chromate reduction, Filter-Press Reactor, Filter-Press Cell, Environmental Electrochemistry*

### List of symbols

A = electrode geometrical area, C = concentration of the electroactive species, C<sub>0</sub> = initial concentration, C<sub>t</sub> = concentration of the electroactive species after a given reaction time, D<sub>0</sub> = diffusion coefficient of the electroactive species, F = Faraday constant, I<sub>L</sub> = limiting current, K<sub>m</sub> mass transfer coefficient, t = operating time, V<sub>e</sub> = electrolyte volume, V<sub>R</sub> = reactor volume, X<sub>A</sub> = fractional conversion, z = number of transferred electrons, ν = kinematic viscosity, τ<sub>ST</sub> = space-time, ρ<sub>ST</sub> = space-time yield, φ<sup>e</sup> = normalized space-velocity and ω = electrode rotation frequency

### INTRODUCTION

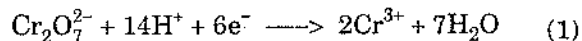
The toxicity of Cr(VI) species has been widely documented [1]. A myriad of physical, chemical

and biological schemes have been utilized to remove or reduce chromate ions from aqueous media. Electrochemical techniques have also been utilized with different degrees of success [2]. A typical electrochemical process consists of the reduction of chromate at the cathode of a cell to chromium (III) ions, which are precipitated and removed as highly insoluble species [3] (normally Cr(OH)<sub>3</sub>) at a later stage. Since this precipitate is capable of blocking the cathode surface, different approaches have been devised for its removal either by chemical dissolution (e.g., with a complexing agent) [4] or by electrochemical means through potential inversion as to reoxidize it to soluble chromate, and produce a more concentrated Cr(VI) solution for reuse [5-6]. Reduction of Cr(VI) all the way to Cr(O) requires very specific conditions that prevent its widespread utilization for remediation purposes. On the other hand, the

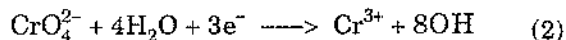
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reduction of Cr(III) to Cr(O) is kinetically hindered due to its strong hydration.

The main reactions for chromate reduction in acid and alkaline media are as follows:



and



From both equations it can be anticipated that low pH values favor the reduction reaction. Unfortunately, a high pH is required for the deposition of Cr(OH)<sub>3</sub>. This apparent contradiction can in principle be solved by using a cell with a separator between the anodic and cathodic compartments while electrochemically producing the necessary pH gradients [4].

As for electrode materials, different forms of carbon electrodes have been used for chromate reduction. Reticulated vitreous carbon (RVC) was used with little success [4], since the extent of chromate removal after 10 passes through a potentiostatically-controlled column was only 51%. Graphite felt used in a laboratory batch cell gave a total charge efficiency of 0.39 [5]. The use of graphite felts limits the possibility of using high solution flows (that promote higher reduction rates and efficiencies by increasing mass transfer and by removing gas bubbles produced at the electrodes that reduce their effective area) [7]. To facilitate removal of the Cr(III) precipitate, avoid clogging, offer a large interface area, and promote mass transfer, a percolated porous pulsed electrode (E3P) has been proposed [8]. This concept utilizes an electrochemical reactor with a packed, granular graphite cathode that undergoes periodic pneumatic pulsation. Its application to chromate reduction, albeit promising, gives incomplete conversion (on the order of 50%) even after several hours of experimentation. A packed bed of graphite particles was also utilized in a cell divided by a PVC membrane with an applied voltage on the order of 30-35 V. For initial

chromate concentrations of 200 ppm, a reduction of up to 90% of the initial value could be achieved, albeit after approximately 6 hours. In addition, the high voltage applied produced important amounts of hydrogen gas as a by-product. Finally, since the electrolyte was recirculated through the anode compartment after reduction, part of the Cr(III) was re-oxidized, producing low reduction percentages [9]. A different concept utilizes a packed bed of carbon particles in electrical contact with a gas-diffusion electrode that oxidizes hydrogen gas to produce protons (to acidify the chromate electrolyte) plus electrons that are shuttled to the cathode to effect the chromate reduction to chromium (III) [10]. Insufficient information prevents a comparison of this procedure with the alternatives discussed above.

A rotating-cylinder hydrogen-evolving Pb electrode was used for the same purpose, with higher concentrations of chromate ions [11]. This electrode prevents the formation of gas bubbles on its surface, promotes turbulence and high mass transfer coefficients, and has a high overpotential for the production of hydrogen. Current efficiencies decrease drastically with chromate concentrations (like those typically found in effluents) and thus its application to water treatment would be rather expensive.

Indirect (mediated) electrolytic approaches have also been utilized [2,7,12,13a,13b]. For example, iron anodes produce Fe<sup>2+</sup> ions capable of reducing Cr<sup>6+</sup> in a homogeneous fashion. In another approach, a conducting polymer (polypyrrole) grown on an electrode substrate (platinum, vitreous carbon, RVC, etc) has been found to spontaneously reduce chromate. These modified electrodes are capable of exerting their reducing power for a few cycles, after which they degrade.

We report here the successful direct reduction of chromate ions in acidic media (which is common in chromate-producing processes) [11] at RVC electrodes in a flow-by configuration using a filter-press type electrochemical cell.

## EXPERIMENTAL

Characterization experiments were performed with cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements. For these, a typical three-electrode system was used in a 40 mL glass cell. The potential was applied with an Amel potentiostat-galvanostat (model 2049). Potential measurements were routinely verified with a DM-231 digital multimeter. A vitreous carbon electrode (Bioanalytical Systems, BAS) of  $0.071 \text{ cm}^2$  was used as the working electrode, and a Steadtler graphite rod (grade 2H) of  $0.5 \text{ cm}^2$  was used as the counter electrode. The reference was a Ag/AgCl electrode (BAS) in 3 M KCl. The working electrode was polished with a polishing cloth (Buehler) successively followed by  $1 \text{ }\mu\text{m}$  alumina and  $0.5 \text{ }\mu\text{m}$  alumina. Then, each electrode was immersed in deionized water and ultrasonicated for 5 min. High purity nitrogen (Praxair) was bubbled for 10 min prior to each experiment to deaerate the solutions.

The rotating disk electrode was made by mounting a vitreous carbon rod ( $d = 0.3 \text{ cm}$ , The Electrosynthesis Co.) in a threaded Teflon support and glued with N-20 conducting epoxy (EPO-TEK). Rotations were controlled with a Pine rotor (model AFASR). A filter-press type reactor (ElectroCell, Sweden) in the flow-by mode was used for the rest of the experiments (Fig. 1). The working electrode was a reticulated vitreous carbon (RVC) rectangular piece ( $7.5 \times 3 \times 0.5 \text{ cm}$ ) of 65 pores per inch (ppi), pressed against a piece of graphite felt of the same area (EGF, type GC-12), both supplied by The Electrosynthesis Co., as to facilitate a good contact with the wire connectors. A Nafion 417 cation exchange membrane was placed between the cathodic and anodic compartments. The anode consisted of a DSA oxygen evolution electrode (Electrocell), and the reference electrode was described above.

The hydraulic system consisted of two MasterFlex peristaltic pumps, two 0.5 L beakers and two high-resolution Teflon flow meters (Cole Parmer) with incorporated valves. The reactor catholyte outlet was connected to a UV-Vis

spectrophotometer (Spectronic 21 D, Milton Roy) as to continuously monitor the concentration of Cr(VI) remaining in the solution at all times. Absorbance data acquisition was performed with a LabView system installed in a Digital DECpc 325 Sx CP personal computer. The entire system is shown in Fig. 2. It was tested with water for possible hydraulic leaks before each run.

All the reagents were J. T. Baker reagent grade and were used as supplied. A 100-ppm dichromate solution (prepared from potassium dichromate) was used, with sulfuric acid as the supporting electrolyte as needed as to achieve a pH c.a. 2 in all runs. Sulfuric acid in the same concentration as in the catholyte but without Cr(VI) ions was used as the anolyte. Deionized water ( $12 \text{ }\mu\text{mhos}$ ) was used in all the experiments.

The potential required for the reduction of the dichromate ions was investigated under unstirred conditions (cyclic voltammetry, CV) and under hydrodynamic conditions (rotating disk electrode, RDE). Cyclic voltammetry was used to obtain an initial estimate of the reduction potential. The RDE experiments were used to determine the potential at which dichromate reduction is mass transfer controlled in order to select adequate conditions for the electrochemical operation of the reactor [14]. Continuous dichromate reduction was performed by imposing a constant potential on the RVC cathode in this reactor.

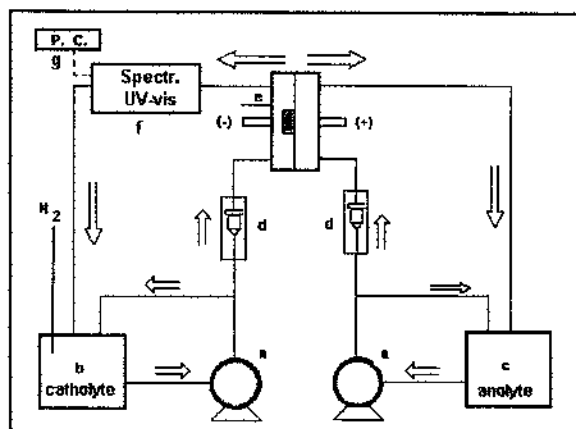


Fig. 1: Cross sectional view of the flow cell  
 a) Teflon cover (interior), with stainless steel (exterior),  
 b) Viton gaskets, c) Acrylic blocks, d) Nafion(417) membrane,  
 e) Back cover and oxygen DSA

**RESULTS AND DISCUSSION**

The diffusive behavior of an electroactive species can be described as a function of the rotation frequency of the working electrode, according to Levich's equation [15-16].

$$I_L = -0.62 z A F \omega^{1/2} \nu^{-1/6} D_0^{2/3} C \quad (3)$$

For this, we use the following values:  $z = 6$ ,  $A = 7.1 \times 10^{-6} \text{ m}^2$ ,  $F = 96500 \text{ C mol}^{-1}$ ,  $\nu =$  approximately equal [7] to  $1.172 \times 10^{-6} \text{ (m}^2 \text{ s}^{-1})$  and  $C = 1.9 \text{ mol.m}^{-3}$ .

A linear  $I_L$  vs.  $\omega^{1/2}$  plot indicates that the process is mass-transfer controlled. For the characterization of an electrochemical reactor one needs to know the mass transfer coefficient,  $K_m$  associated to the electrode specific area.  $K_m$  can be calculated in at least two ways [15].

a) Measuring  $I_L$  at different flow rates with the equation:

$$I_L = z F K_m A C V_e \quad (4)$$

b) Measuring the concentration change of the electroactive species with time and applying the model for a batch reactor:

$$\frac{C(t)}{C(0)} = \exp\left(\frac{-K_m A_e V_e t}{V_R}\right) \quad (5)$$

Here,  $C_t$  is the concentration of the electroactive species after a given reaction time,  $C_0$  is its initial

concentration,  $K_m$  is the mass transfer coefficient,  $A_e$  is the active area of the electrode,  $V_e$  is the electrolyte volume,  $t$  is the operating time and  $V_R$  is the reactor volume. In the present work we have used the method of the limiting current to calculate  $K_m$ , which can be used later to calculate the figures of merit. The results thus obtained are compared to a set of results achieved using direct electrolysis on a graphite-particle packed bed electrode.

**Cyclic voltammetry**

Fig. 3 shows a cyclic voltammogram obtained in a potassium dichromate solution under the conditions mentioned earlier. The parameters were: scan rate =  $100 \text{ mVs}^{-1}$ , initial potential =  $0.6 \text{ V}$ , final potential =  $0.9 \text{ V}$ . The working electrode was a vitreous carbon rod. The only peak observed ( $-340 \text{ mV}$ ) is assigned to the irreversible  $\text{Cr}_2\text{O}_7^{2-}$  reduction, and it can be observed that this reduction starts much earlier (approximately at  $500 \text{ mV}$ ).

**Rotating disk electrode (RDE)**

This technique was used to find the cathodic potential range where the conversion of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  is mass-transfer controlled, and to determine the diffusion coefficient of the electroactive species that will be used later to calculate figures of merit. Fig. 4 shows the response of the dichromate solution using the RDE technique at  $10 \text{ mVs}^{-1}$ . The working electrode was a vitreous carbon disk (described earlier).

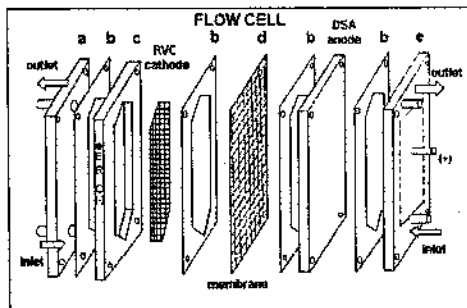


Fig. 2: Hydraulic circuit. a) Centrifuge pumps, b) Catholyte c) Anolyte; d) Teflon flow-meters, e) Capillary for the reference electrode, f) UV-Vis spectrophotometer g) Personal computer, with Lab View installed

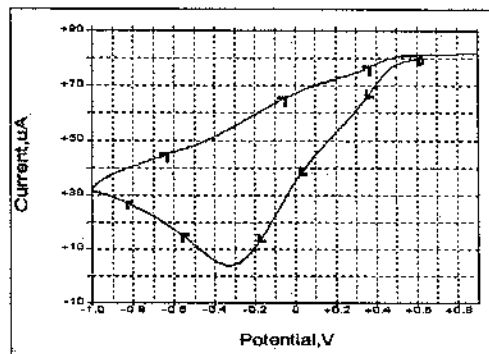


Fig. 3: Cyclic voltammogram of a potassium dichromate solution in sulfuric acid

Fig. 5 shows the relationship between the limiting current and the square root of the rotation frequency. The limiting current is obtained from the most horizontal region of each I-E curve (Fig. 4), and signals the region where dichromate reduction is mass-transport limited. As a reasonable approximation, the current was evaluated in the middle of this region (c.a. at -850 mV). The resulting plot is highly linear ( $r = 0.9928$ ), which means that dichromate reduction is under mass-transport control.

The diffusion coefficient of the electroactive species is then calculated by using Levich's equation (eq. 3). The data used are:

slope,  $m = 0.04 \text{ A s}^{-1/2}$ ,  $z = 6$ ,  $F = 96500 \text{ A.s.mol}^{-1}$ ,  $A = 7.1 \times 10^{-6} \text{ m}^2$ ,  $C = 1.9 \text{ mol.m}^{-3}$ ,  $\nu = 1.172 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ .

From here,  $D_0$  for  $\text{Cr}_2\text{O}_7^{2-}$  is calculated to be  $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ .

In order to verify this value, a series of linear potential scans (at  $5 \text{ mV s}^{-1}$ ) with different rotation frequencies was also performed. From the limiting current vs. the square root of the rotation frequency, a linear plot was obtained ( $r = 0.9730$ ) with a slope of 0.03 that yields a diffusion coefficient of  $1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , which is in close agreement to the one obtained above. The former was used for the calculation of  $K_m$  employed in the figures of merit (see below), due to the fact that it gave a better correlation coefficient ( $r$ ) than the later.

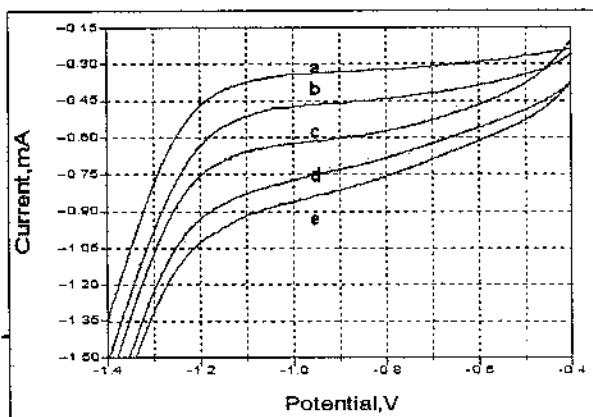


Fig. 4: I-E curves for the reduction of dichromate in acidic medium at  $10 \text{ mV s}^{-1}$  and different rotation rates (in rpm) a) 500, b) 1000, c) 1500, d) 2500, e) 3500

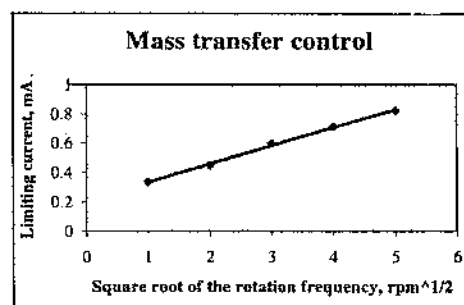


Fig. 5: Relationship between the limiting current,  $I_L$  and the square root of the rotation frequency,  $\omega^{1/2}$

### Reactor operation

The final objective is to obtain a high reduction of the  $\text{Cr(VI)}$  species in a short period of time and with a low applied voltage. Since RVC was used, we tested for a possible contribution of the electrode itself towards  $\text{Cr(VI)}$  reduction. To this end, an RVC piece (65 ppi) was used in the flow cell with a catholyte flow of  $40 \text{ mL.min}^{-1}$  and without an applied potential. The decrease in  $\text{Cr(VI)}$  concentration was evaluated with time (see Fig. 6). It can be seen that the RVC does indeed reduce the  $\text{Cr(VI)}$  concentration. We then tested for the possibility that  $\text{Cr(VI)}$  could be oxidizing the RVC to  $\text{CO}_2$ . We performed a qualitative test by immersing a piece of RVC in a dichromate solution (500 ppm) contained in a small test tube (target test). The tube was then capped with a rubber stopper equipped with a glass tube connected by a small diameter hose to a 10 mL Erlenmeyer flask (sealed with Parafilm) containing a filtered, saturated solution of  $\text{CaO}$ . A similar system without RVC was used as a blank test. The observed appearance of insoluble  $\text{CaCO}_3$  only

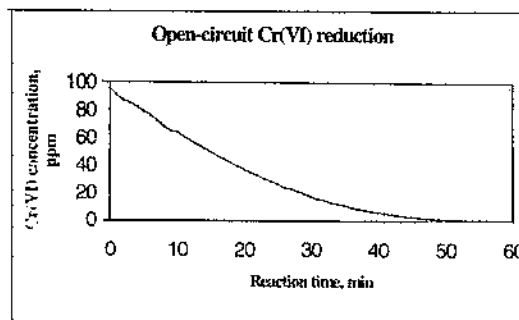


Fig. 6:  $\text{Cr(VI)}$  elimination by the RVC (no applied potential)

in the target test after an overnight period is taken as a proof of our hypothesis. To the best of our knowledge, this conclusion has not been reported elsewhere. It remains to be analyzed whether the application of potential can exert a "cathodic protection" on the RVC.

Next, the effect of the applied potential on the Cr(VI) concentration reduction was investigated in the flow cell with a catholyte flow of 40 mL.min<sup>-1</sup>. The results are shown in Fig. 7. It can be seen that the higher the applied potential, the faster the concentration drops. At -0.8 and -0.6 V, the behavior is almost identical since the reaction is not limited by the applied potential.

Lastly, the influence of the flow rate on the Cr(VI) concentration reduction was analyzed. The results are shown in Fig. 8. For a flow of 10 mL.min<sup>-1</sup> the concentration changes are greater at the beginning of the reaction than when using larger flows (40 and 80 mL.min<sup>-1</sup>). This is probably due to the longer residence time that occurs in the former. However, as the Cr(VI) concentration becomes smaller, the concentration changes are greater for the higher flows, indicating that mass transfer becomes a more important factor.

**Figures of merit**

In order to evaluate our system's performance, we looked in the literature for work with a the same chemical system reported earlier that will be taken as a reference in this section [9]. Several figures of merit were calculated and are compared below. In this reference work, a PVC packed-bed

reactor composed of a graphite particles cathode (70 cm<sup>3</sup>, 41% porosity) and separated from the anode by a sintered PVC membrane was used in the flow-by mode to treat a 100 ppm Cr(VI) solution in H<sub>2</sub>SO<sub>4</sub> at a pH of 1.5. The flow rate was varied from 100 to 250 mL.min<sup>-1</sup> and the applied potential from 30 to 90 V. Such conditions were reported to produce an undesirable heating of the electrolyte and considerable hydrogen evolution. Several figures of merit were then evaluated for both systems and are compared in Table I [15,17].

It can be seen that several figures of merit were considerably improved when using reticulated vitreous carbon and a filter-press reactor (RVC/FPR). More pollutant is converted per unit of time (approximately a factor of 6). Since two reactors of different size are compared, the amount of substance converted must be weighted per unit of volume; this is why we calculated the space-time yield (in the RVC/FPR case is better roughly by a factor of 10). This means that the mass of pollutant transformed per unit of time is much higher with the RVC/FPR, although the volume treated is smaller this case. The electrolytic power (directly related to operation costs) is much smaller with the RVC/FPR (by a factor greater than 10<sup>3</sup>). Likewise, the current efficiency is higher with the RVC/FPR by a factor of 4 since a very high potential is applied in the case of graphite- packed bed reactor that causes heating of the electrolyte and hydrogen production. Finally, the normalized space-velocity is also much higher with the RVC/FPR due to the higher mass

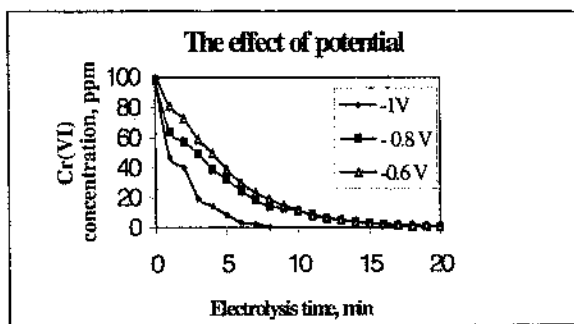


Fig. 7: Cr(VI) concentration vs. electrolysis time for different applied potentials

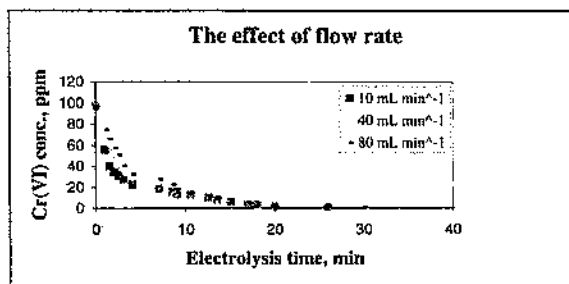


Fig. 8: Cr(VI) concentration vs. electrolysis time for different solution flow rates

TABLE 1: Comparison between two electrochemical systems for the reduction of Cr(VI) (using graphite or RVC electrodes).  $V_R$  = Volume of the solution inside the 3D electrode,  $Q_v$  = Volumetric flow rate,  $\Delta C$  = Concentration change,  $E_{\text{cel}}$  = Applied potential \* 30V,  $Q_v = 100 \text{ mL}\cdot\text{min}^{-1}$

Figure of merit	Graphite particles (ref 9)	Conditions*	RVC 65 ppi (This work)	Conditions
Fractional conversion $X_A = 1 - \frac{C_t}{C_0}$	0.15	At 15 min	0.97	At 15 min, -0.8 V vs Ag/AgCl, $80 \text{ mL}\cdot\text{min}^{-1}$
Space-time $\tau_{\text{ST}} = V_R/Q_v$	1.72s	$V_R = 28.8 \text{ mL}$ (this is the min value)	7.5 s	$V_R = 10 \text{ mL}$ , $80 \text{ mL}\cdot\text{min}^{-1}$
Space-time yield, $\rho_{\text{ST}} = \frac{\Delta CM}{\tau_{\text{ST}}}$ (Here M is the molar mass)	$6.4 \times 10^3 \text{ g}\cdot\text{m}^{-3} \text{ s}^{-1}$	15 min	$1 \times 10^5 \text{ g}\cdot\text{m}^{-3} \text{ s}^{-1}$	15 min, -0.8 V vs Ag/AgCl $80 \text{ mL}\cdot\text{min}^{-1}$
Electrolytic power $W_n^v = \frac{E_{\text{cel}} q}{V_n t}$	$4.9 \times 10^7 \text{ KW}\cdot\text{m}^{-3}$	1.4 A, 6 h	$1.4 \times 10^4 \text{ KW}\cdot\text{m}^{-3}$	1.35 A, 12 min, 22 V (max. alue) $10 \text{ mL}\cdot\text{min}^{-1}$
Current efficiency $\phi^c = q_{\text{real}}/q_{\text{theoretical}}$	15.6%	6 h	63%	8 min, -1V vs Ag/AgCl, $40 \text{ mL}\cdot\text{min}^{-1}$
Normalized space-time $S_n^{\text{batch}} = \frac{K_m A}{2.3 V_R}$	$1.66 \times 10^{-4} \text{ s}^{-1}$	15 min	$0.73 \text{ s}^{-1}$	15 min, -0.8 V vs Ag/AgCl, $80 \text{ mL}\cdot\text{min}^{-1}$

transfer coefficient as well as the larger electroactive area offered by this electrode and configuration.

### CONCLUSIONS

Cr(VI) reduction by direct electrolysis in a filter-press reactor with a high area RVC as the electrode offers a promising approach for the treatment of this hazardous substance. In the present work, c.a. 99% reduction of the pollutant was achieved in just 8 minutes with a simple set-up.

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