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Removal of chromium from aqueous solutions by treatment with fibrous carbon electrodes: column effects

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The continuous removal of toxic *hexavalent* chromium from contaminated solutions by means of a graphite felt based electrochemical column was studied. The process is based on an *in situ* generation of appropriate pH gradients which allows both rapid reduction to Cr^{3+} and its precipitation within the electrode bed. Conditions for the attainment of low (< 25 p.p.b.) effluent concentrations as well as longitudinal concentration distribution of the precipitate and maximum loading capacities are presented. Treatment schemes involving two separate columns or a dual function column are also discussed.

1. Introduction

The toxicity of hexavalent chromium has been known for many years and the clinical symptoms of prolonged exposure to a chromium contaminated environment are well defined [1].

Chromium enters waterways as a result of effluent discharge from cooling towers, electroplating and tanning industries, oxidative dyeing, leaching from sanitary landfills and leaks from timber treatment sites. As a result of its high toxicity the concentration of Cr(VI) (and other highly toxic metallic ions such as cadmium, lead and mercury) in drinking water resources is restricted to several p.p.b. [2]. It is not surprising, therefore, that the development of novel procedures for the efficient removal of toxic metals from industrial wastes and contaminated water resources is an ongoing task in many laboratories dealing with environmental problems.

In the last few years, new materials have become available for use as electrodes in electrochemical reactors and filters. Among these, cloths, felts, foams and sponges of conductive materials such as graphite and carbon [3], nickel [4] or copper [5] should be mentioned. These electrode structures show the unique combination of high electrochemically accessible surface area and high permeability for solutions. This allows significant progress in reactor optimization with respect to size and efficiency.

The electrochemical removal of Cr(VI) from contaminated solutions is complex in comparison to that of other toxic metallic contaminants because the deposition should be preceded by a reduction to Cr^{3+}, a process which is pH sensitive: It proceeds faster as the pH decreases.

As was shown in a previous paper [6], there exist an electrochemical mechanism, consisting of several steps, by which it is possible to remove hexavalent chromium down to concentration levels compatible with drinking water specifications. The electrochemical principles of this process were outlined and a single column combining the necessary steps was suggested.

In the present paper, the characteristics of an electrochemical multistage process for capturing hexavalent chromium are discussed.

2. Experimental details

The electrochemical filter, of a flow-by type, is shown schematically in Fig. 1. It consisted of two identical Plexiglass enclosures, each containing an electrode made of a graphite felt, RVG-2000 (Le Carbon-Lorraine, France). The dimensions of each electrode were 300 mm (L) × 10 mm (W) × 3 mm (T) and they were separated by a Nafion® cation exchange membrane.

The electrical connections to the electrodes were made via part of the felt strips (approximately 30 mm) protruding from the enclosure at both ends. Copper foil was glued to the felt strips by a carbon conductive adhesive to ensure good contact with the current collectors and to protect the protruding felt from damage. In order to prevent the solution from penetrating through the outer parts of the felt, the vacancies within the felt in the enclosure at a length of about 20 mm from its end were filled with a liquid silicon rubber (RTV, Dow Corning) which was than allowed to polymerize fully.

A saturated calomel electrode (SCE) was used for reference. It was mounted on the effluent line as close as possible to the cell outlet. In order to prevent interruption of the electrical continuity between the SCE and the working electrode due to occasional bubbles evolved in the cell, a glass filter paper strip maintained wet by the flowing solution, was placed along the short tubing connecting the two electrodes.

The solutions were pumped through each compartment by a dual channel peristaltic pump at a flow rate of 1 ml min^{-1}. Typically, different solutions were

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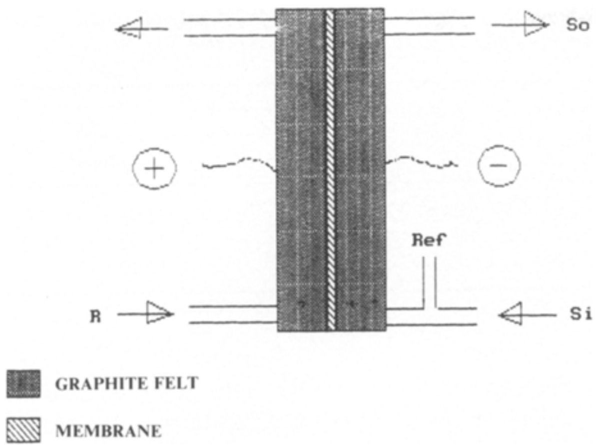

Fig. 1. A schematic representation of a flow-by electrochemical filter. Ref – Reference electrode; R – Anodic solution; Si – Feed inlet; So – Feed outlet.

used for the cathodic and anodic compartments: The cathodic solution contained 0.05 M Na_2SO_4 and Cr^{3+} or Cr(VI) (as CrO_3) at the concentration range 1–60 p.p.m. and at various pH values adjusted by titration with H_2SO_4 or NaOH. The solution flowing through the anode contained all the components except chromium. However, when the dual function column concept was utilized (see Section 3.4) only a chromium contaminated solution was used. This solution flowed first through the anode and then through the cathode of the same column. When the separate column concept was studied (Section 3.4), two identical columns, operating under different voltages were used and the chromium containing solution was passed through the cathodes of both columns according to the flow path shown in Fig. 7b. The solution flowing through the anodes was the same as described above.

Potentiostatic and galvanostatic experiments were performed using a basic Potentiostat/Galvanostat Model 30-05, Opal–Israel.

Total chromium and Cr(IV) concentrations were determined by atomic absorption. Cr^{3+} concentration was determined from the difference between the two above concentrations after extracting it from the aqueous phase with acidic methyl isobutyl ketone (MIK) [7].

The concentration distribution of chromium hydroxide precipitated along the column was determined under galvanostatic conditions (due to partial deactivation of the electrode bed caused by the nonconductive heavy precipitate, the current decreased gradually with time under potentiostatic conditions, thus galvanostatic conditions allowed a more accurate and faster charge consumption calculations). Each run was arbitrarily terminated whenever concentrations higher than 100 p.p.b. were detected in the effluent. The cathode was then taken out of the cell and cut into 1.5 or 2 cm longitudinal segments which were treated separately in 10 ml of 0.5 M citric acid at 50° C. Typically, complete dissolution of the precipitate took about 60 min under these conditions. The solution was then filtered in order to separate it from felt pieces and chips and the chromium content was analysed as outlined above.

3. Results and discussion

3.1. *Removal of* Cr^{3+}

The removal of Cr^{3+} ions from aqueous solutions by chemical means is a simple, highly efficient and inexpensive process. The adjustment of the pH to values above 7 assures the precipitation of this ion as $Cr(OH)_3$ which, in the pH range 6.5 to 10 and 0.01 M ionic strength, exhibits an equilibrium constant of 1.44×10^{-7} with its dominant soluble form [8]. This implies that the highest chromium concentration that should be present in the solution under the above conditions is 2.8 p.p.t.

The continuous precipitation of Cr^{3+} as a hydroxide in an electrochemical column is based on the cathodic production of hydroxyl ions by water electrolysis and by the reduction of oxygen when present as a soluble species in water, according to the following equations,

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad \text{water reduction} \tag{1}$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad \text{oxygen reduction} \tag{2}$$

$$Cr^{3+} + OH^- \longrightarrow Cr(OH)_3 \downarrow \quad \text{precipitation} \tag{3}$$

The reaction at the anode is

$$2H_2O - 4e^- \longrightarrow O_2 + 4H^+ \tag{4}$$

Figure 2 shows the current, the pH and Cr^{3+} concentration at the effluent as a function of the voltage. At voltages above 1.1 V/SCE the current increases sharply as the voltage is increased. This is accompanied by a dramatic increase in the pH and a decline in chromium concentration which, at voltages above 1.6 V, reaches values lower than 25 p.p.b.

The concentration profile of OH^- ions at the cathode can be calculated as follows.

It is assumed that plug flow prevails in both the cathode and the anode and all the current I is consumed in water electrolysis. [This assumption is valid in the present case because the reduction of Cr^{3+} to Cr^{2+} is thermodynamically improbable at pH values above 6.5 [9]. The assumption of plug flow is commonly used in flow systems and is valid also for the present one as it can be shown that due to the relatively short residence time of the solution in the column, the contribution of the diffusion term in the flux equation is negligible.] Accordingly, the mass balance equation for the cathode is,

$$u\left(\frac{\mathrm{d}\,C_{OH}}{\mathrm{d}x}\right) = \frac{IL(1 - t_H)}{gVnF} \tag{5}$$

where $v = 0.056\,\mathrm{cm\,s^{-1}}$ is the solution linear velocity;

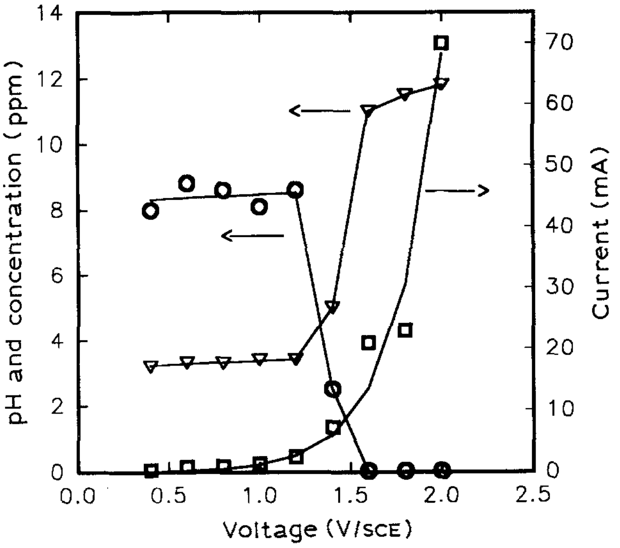

Fig. 2. Removal of Cr^{3+}: effluent pH, chromium concentration and current as a function of voltage. Flow rate 1 ml min^{-1}; solution: 0.05 M Na_2SO_4, initial Cr^{3+} concentration 9.5 p.p.m., initial pH 3.2; (○) concentration, (▽) pH, (□) current.

C_{OH}, the local concentration of OH^- ions; I, the current (A); $L = 30$ cm, the electrode length; t_H, the transport number of H^+ ions generated at the anode, through the cation exchange membrane; $g = 0.7$ g, the electrode mass; $V = 10\,cm^3\,g^{-1}$, the specific void volume; n, the number of electrons taking place in the reaction ($n = 1$); F, the Faraday number and x, a dimensionless distance along the electrode.

The concentration profile of H^+ ions at the anode is independent of the cathode reactions since no OH^- ions are transferred through the membrane. Therefore, the H^+ concentration along the anode, C_H, can be expressed as,

$$C_H = C_H^0 + \frac{ILx}{gVvnF} \qquad (6)$$

where C_H^0 is the inlet H^+ concentration.

If it is assumed that the concentration ratio of H^+ to Na^+ ions in the membrane is equal to that in the solution, the transport number of H^+ ions through the membrane takes the form,

$$t_H = \frac{\alpha(C_H/C_{Na})}{\alpha(C_H/C_{Na}) + 1} \qquad (7)$$

where, α is the ratio of H^+ to Na^+ mobilities in the membrane and C_{Na} is the (constant) concentration of Na^+ ions in the solution. [Following Mackay *et al.* [11], the H^+ to Na^+ specific conductivity ratio in a cation exchange membrane at 25° C is 6.5. This value also accounts for the mobility ratio.]

From Equations 6 and 7, an expression for the variation of the transport number with the current and location is obtained. Introducing this expression into Equation 5 and integrating, gives

$$C_{OH} = C_{OH}^0 + \beta \ln\left[\frac{B_t + x}{B_t}\right] \qquad (8)$$

where, C_{OH}^0 is the OH^- inlet concentration, $\beta = C_{Na}/\alpha$, $Bt = (1/\beta_H)(C_H^0 + \beta)$ and $\beta_H = IL/gvVnF$.

Table 1. Calculated and measured effluent pH values. The experimental conditions are the same as in Fig. 2.

Voltage (V)	*Current (mA)*	*Effluent (pH)*	
		Measured	*Calculated*
−1.6	21.5	11.0	11.93
−1.8	23	11.75	11.95
−2.0	70	11.8	12.19

The concentrations of OH^- ions along the column as calculated from Equation 8 has to be corrected for their consumption due to the precipitation of Cr^{3+} ions (by the ratio $3OH^-$ ions to one Cr^{3+} ion). However, it can be shown that when considering the worse situation, namely, that the precipitation occurs mainly close to the outlet (in other words, a solution with the initial chromium concentration reaches the end of the electrode), the correction does not exceed 6% of the calculated OH^- concentration. This results in a maximum correction of 0.25% in the effluent pH values which is negligible with respect to the ± 10% accuracy of the pH measurements.

The effluent pH values as calculated from Equation 8 under the conditions of Fig. 2 are summarized and compared to the measured values at high voltages in Table 1. As can be seen, even though the calculated pH values are larger than the measured ones, they are within the accuracy of the measurements as mentioned above.

3.2. *Removal of Cr(VI)*

As mentioned above, the complete removal of Cr(VI) in a cathode column is a pH dependent process. This emerges not only from the dependency of the Cr^{3+} precipitation on the pH but also from the mechanism of the electro-reduction reactions of Cr(VI) as shown by the following equations,

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad (9)$$

and

$$CrO_4^{2-} + 4H_2O + 3e^- \longrightarrow Cr^{3+} + 8OH^- \qquad (10)$$

It is clear from the above equations that the reduction rate of Cr(VI) to Cr^{3+} increases when the pH decreases. This is clearly shown in Figs 3, 4 and 5 which present the chromium effluent concentration, the current and the pH values respectively, as a function of voltage and inlet pH.

Figure 5 shows that, regardless of the inlet pH, due to the very high currents attained at high voltages (Fig. 4), the effluent pH reaches values as high as 11.5–11.9. The peculiar behavior of the pH profile in the case of high (60 p.p.m.) feed Cr(VI) concentration should be noted. The earlier increase (with respect to the potential) of the effluent pH is nonetheless due to the consumption of H^+ ions in the reduction reaction of chromium [10].

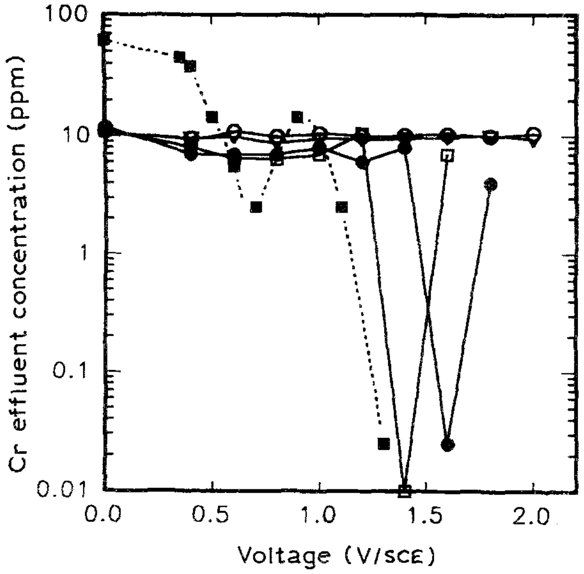

Fig. 3. Removal of Cr(VI): chromium effluent concentration at various initial pH values as a function of voltage. Flow rate 1 ml min^{-1}; solution: 0.05 M Na_2SO_4; initial chromium concentration and pH: 11 p.p.m., (○) 7.0, (▽) 4.0, (□) 3.5, (●) 3.0; 60 p.p.m. and (■) 2.9.

Figure 3 clearly indicates that at feed pH 7 and 4 the effluent concentration is not affected even at the highest electrode potential (−2 V). As the feed pH decreases, the effluent concentration decreases and reaches values as low as 10 p.p.b. and 25 p.p.b. at pH 3.5 nd 3, respectively.

As the potential is increased, the concentration increases again and reaches values close to those in the feed. This unexpected increase also results from the pH sensitivity of the reduction reaction: When the potential increases, that section of the column in which the pH of the solution is sufficiently low to allow a reasonable reduction reaction rate, is reduced. Therefore, the removal efficiency decreases.

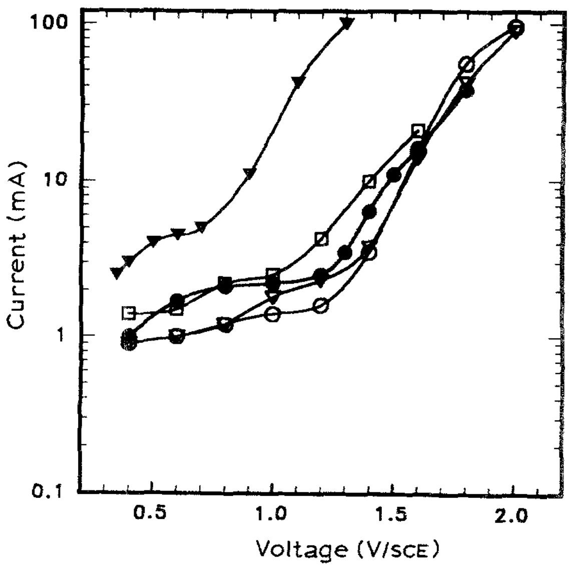

Fig. 4. Removal of Cr(VI): filter current at various initial pH values as a function of voltage. pH: (○) 7.0, (▽) 4.0, (□) 3.5, (●) 3.0 and (▼) 2.9.

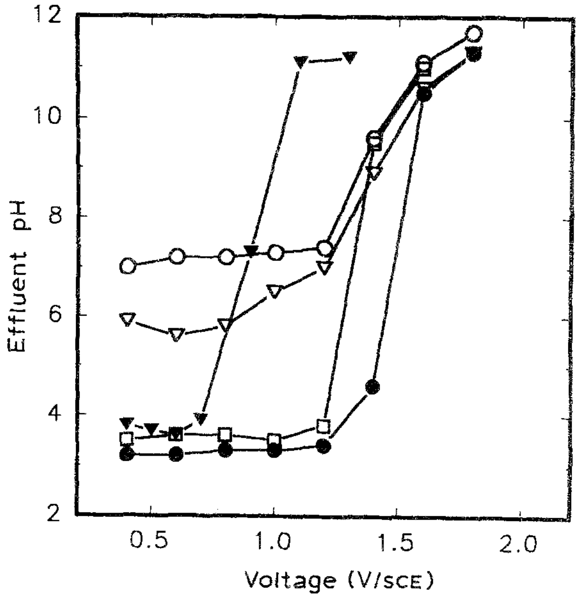

Fig. 5. Removal of Cr(VI): Effluent pH as a function of voltage and initial pH values. Other conditions are as in Fig. 3 and legend as in Fig. 4.

In order to confirm this, some of the effluent samples were analysed for both Cr^{3+} and Cr(VI). The results, summarized in Table 2, reveal that at the lower voltages, the conversion to Cr^{3+} is almost complete due to the low pH values prevailing within the column. For the same reason, the removal of chromium is not complete. The fact that the total chromium concentration decreases to about half its initial value, in spite of the low (average) pH values measured at the outlet, may be attributed to the existence of local higher pH values near the solution/electrode interface.

At sufficiently high voltages (e.g., −1.5 V) the pH profile within the column allows both the complete conversion to Cr^{3+} and its removal as $Cr(OH)_3$. When the voltage increases further, the concentration of both chromium ionic species in the effluent increases significantly. The increase in the hexavalent chromium is in accordance with the above discussion. The Cr^{3+} concentration increase can be assigned to the downstream dragging of hydroxide particles by small gas bubbles evolving at high voltages.

3.3. *Chromium distribution along the electrode bed at maximum capacity*

The distribution of chromium deposit along the electrode bed when maximum capacity is reached is of

Table 2. Cr(VI) and Cr^{3+} concentrations and pH values at the effluent. Feed solution: 12 p.p.m. Cr(VI), 0.05 M Na_2SO_4, pH 3.

Voltage (V)	*Current (mA)*	*pH*	*[Cr^{3+}] (p.p.m.)*	*[Cr(VI)] (p.p.m.)*
−0.6	1.7	3.2	7	<0.025
−1.2	2.5	3.3	6	<0.025
−1.5	11	10.5	<0.025	<0.025
−1.8	38	11.3	1	3

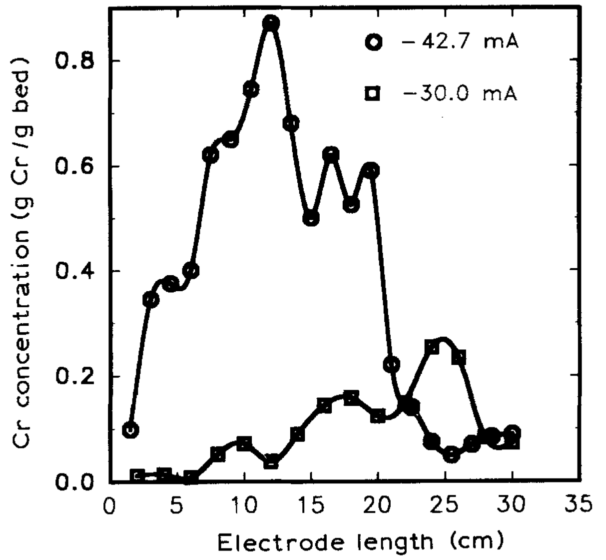

Fig. 6. Chromium concentration distribution profiles at maximum capacity under galvanostatic conditions. Flow rate 1 ml min^{-1}; Feed solution: 85 p.p.m. Cr^{3+} (as $CrCl_3$), 0.01 M Na_2SO_4, pH 3.

great importance for optimization purposes when a given solution and electrochemical column are considered. The determination of the distribution profile when full capacity is reached at a given set of experimental conditions provides important information on the minimal bed length required to reach total removal under the same conditions.

The maximum loading capacity of the electrode bed is also important when process cost is considered. It determines the regeneration or disposal frequency of the bed.

In Fig. 6, distribution profiles for Cr^{3+} precipitation determined under galvanostatic conditions are given for two currents.

Some figures extracted from these experiments are summarized in Table 3.

Table 3 reveals that the location of the precipitate peak moves towards the outlet as the current is decreased. This is due to the fact that pH values which are suitable for efficient precipitation are attained much earlier along the column at higher currents. This also explains the much higher capacity acquired at the higher current. It is estimated that under the higher loading there is a multilayer coverage of $Cr(OH)_3$ on the fibres constituting the electrode bed. Under these conditions the electrochemical efficiency of the bed is expected to decline. This capacity may therefore be considered as the highest that can be obtained for the precipitation of $Cr(OH)_3$. Since the currents were intentionally taken high, the rather low current efficiency obtained in these experiments is not surprising.

Table 3. Data obtained from galvanostatic electrode bed loadings. Feed solution: 85 p.p.m. Cr^{3+}, 0.01 M Na_2SO_4, pH 3; feed flow rate: 1 ml min^{-1}.

Current (mA)	*Peak location (cm)**	*Precipitation efficiency†*	*Current efficiency‡ (%)*	*Average capacity (g_{Cr}/g_{bed})*
42.7	12	97.8	19.7	0.3
30.0	24	95.7	26.2	0.098

* Taken from Fig. 6.

† Calculated by dividing the weight precipitated by the total weight passed through the bed.

‡ Calculated by dividing the charge consumed by that required to electrolyse water for generating just enough OH^- ions for the precipitation process.

3.4. *Removal of Cr(VI) using separate columns or a dual function column*

Each of the stages in the electrochemical hexavalent chromium removal mechanism from a contaminated solution can be performed in separate columns or in the two electrodes of the same column (a dual function column). In this way, the exact conditions necessary for the completion of each step can be applied.

The setups shown in Fig. 7a to c present the basic flow schemes for the treatment of a contaminated solution according to these options.

The setup shown in Fig. 7a describes a dual function column operation which is suitable for non-acidic solutions and low flow rates. The solution flows first through the anode where it is made acidic and then through the cathode of the same column where the reduction and precipitation processes occur. Because of its dual function, this column should be operated under high potentials.

Results for this type of operation are given in Fig. 8 in which the pH of the anode and cathode effluents and the chromium concentration at the cell outlet are presented as a function of the potential applied to the cathode. The generation of low and high pH values after flowing through the anode and cathode respectively and the tenfold concentration reduction are evident.

The setup shown in Fig. 7b is suitable for the treatment of acidic contaminated solutions at high flow rates.

Typical results for this run are shown in Fig. 9. The solution, with an initial pH and chromium concentration of 3.3 and 12 p.p.m., respectively, is treated in the

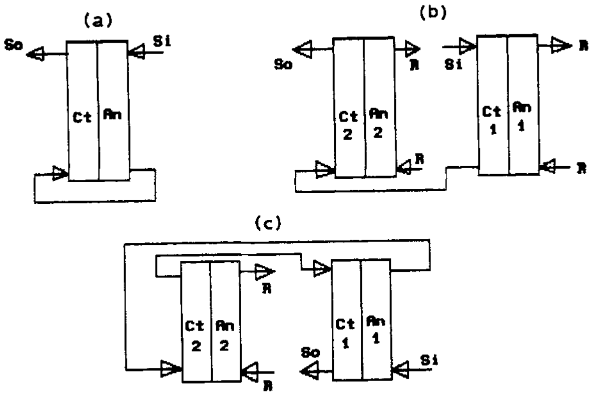

Fig. 7. The basic setups for a continuous treatment of a Cr(VI) contaminated solution: (a) A dual function column; (b) and (c) separate column operation. (An) Anode; (Ct) cathode; other notation as in Fig. 1.

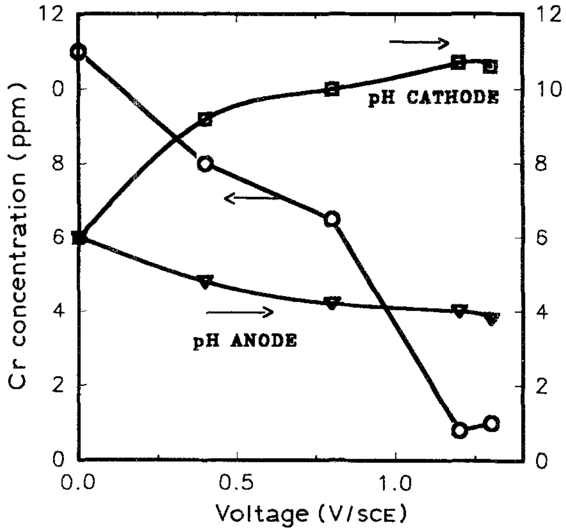

Fig. 8. A dual function column: Effluent Cr(VI) concentration and pH values at the anode and cathode outlets as a function of voltage. Flow rate: 1 ml min^{-1}; solution: 0.05 M Na_2SO_4; initial chromium concentration: 11 p.p.m.; initial pH: 6.4.

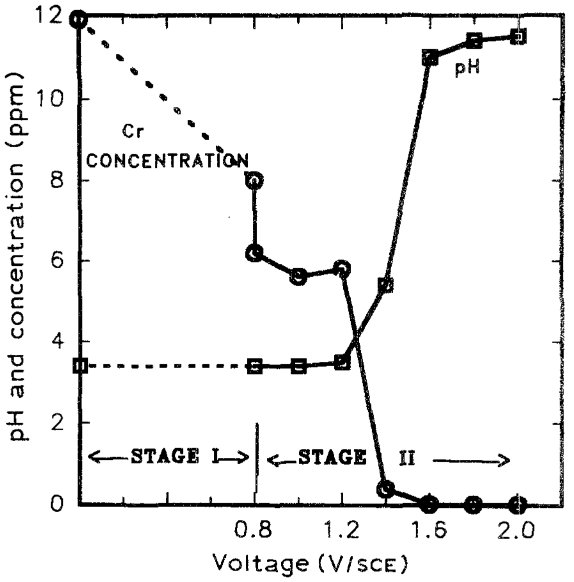

Fig. 9. A separate two-column operation: Cr(VI) concentration and pH of the effluent at the end of each stage as a function of voltage. Flow rate 1 ml min^{-1}; solution: 0.05 M Na_2SO_4; initial chromium concentration: 12 p.p.m.; initial pH: 3.3.

cathode of the first column at −800 mV/SCE where all the hexavalent chromium is converted into Cr^{3+} (analysis of the resulting solution shows 8 p.p.m. Cr^{3+} and less than 25 p.p.b. Cr(VI)). In spite of the fact that no pH change is detected in the effluent at this stage, a 30% chromium concentration reduction is evident. This may be explained by the possible occurrence of local (at the vicinity of the electrode/solution interface) high pH values which almost do not effect the average solution pH but causes a partial precipitation of chromium hydroxide. In the next step the solution is treated on the cathode of a second column at higher potentials where all the chromium is precipitated within the electrode (at potentials higher than −1400 mV) as a result of the high pH values generated there. In this case, a non contaminated reference solution flows through the anodes of both columns.

The setup shown in Fig. 7c is suitable for the treatment of non acidic solutions at high flow rates. The solution is acidified at the anode of the first column held at high potential. Then, chromium reduction occurs in the cathode of the second column; following by precipitation at the cathode of the first column. If necessary, the solution can be treated, as a last step, at the anode of the second column in order to reduce the pH of the effluent. This also eliminates the use of a reference solution in this anode. At present, no experimental data is available for this setup.

In principle, other treatment schemes, such as those involving flow-through filters in which the solution flows through anode/cathode pairs in a serial arrangement, may also be applicable for chromium removal. However, it is expected that due to to relatively short bed length per electrode pair that could be obtained and to the fact that no internal extreme pH values could be generated, only solutions carrying low (of the order of several hundreds of p.p.b.) initial Cr(VI) concentrations and neutral to slightly acidic pH values could be treated using this arrangement.

4. Conclusion

In the present study it is shown that by choosing the proper conditions, it is possible to lower the concentration of hexavalent chromium in contaminated aqueous solutions by several orders of magnitude in an all-electrochemical process. Basically, the removal is achieved in two consecutive steps: Reduction to Cr^{3+} and precipitation on the fibres constituting the electrode bed as a non soluble hydroxide. The overall process is strongly pH dependent due to the sensitivity of the reduction reaction rate to pH and the requirement for high pH for precipitation. It is shown that the proper pH values can be achieved by controlling water electrolysis rate within the anode and the cathode and by choosing the appropriate flow path within a column or a combination of columns.

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