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Chromium removal using a porous carbon felt cathode

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Abstract

Removal of hexavalent chromium by an electrochemical process using a carbon felt electrode in a flow-through electrochemical cell was studied. Optimum operating conditions, such as pH and current density were investigated. It was found that at pH 3.5, current density 400 A m^{-2} and flow velocity of 1.11 cm s^{-1}, the total chromium and Cr(VI) concentrations can be reduced to less than 5 mg l^{-1} within 230 min operation for 5 l of solution with an initial concentration of 50 mg l^{-1}. It was found that the solution pH is a critical factor for the chromium removal process. To achieve high chromium removal efficiency, pH and current density must be carefully controlled.

List of symbols

C_0	initial total chromium concentration (g m^{-3})
C_{III}	estimated concentration of chromium species in oxidation state three defined by Equation 11 (g m^{-3})
C_{VI}	concentration of chromium species in oxidation state six (g m^{-3})
C	total chromium concentration (g m^{-3})
E°	standard electrode potential (V)
F	faradaic constant (96 487 C mol^{-1})
i	current density based on projected area (A m^{-2})
I	applied current (A)
K_{sp}	solubility product
M	relative atomic mass of chromium (52)
pH_{eq}	the equilibrium pH for the $Cr(OH)_3$ precipitation reaction (Equation 7) defined by Equation 12
t	time
u	superficial velocity of solution through the electrode (m s^{-1})
V	volume of solution circulated through the cell (m^3)
Φ_{VI}	percentage current efficiency for Cr(VI) reduction defined by Equation 9
Φ_T	percentage current efficiency for chromium removal defined by Equation 10

1. Introduction

Chromium is widely used in electroplating, leather tanning, paint manufacturing, pigments and dye production and cooling water systems. However, chromium, particularly hexavalent chromium, Cr(VI) is highly toxic. Conventional treatment of Cr(VI) involves a complex chemical process including reduction, precipitation and sedimentation [1]. Chromium removal by means of electrodeposition on a reticulated vitreous carbon electrode under potentiostatic control was studied as early as 1984 [2]. A very poor performance for chromium removal was obtained when compared to other metals such as copper and lead.

Electrochemical reduction of Cr(VI) species has been the subject of several studies. The species formed depend on the operating conditions, particularly the solution pH but typically Cr(III) species are formed. Under stongly acid conditions, Cr^{3+} is formed [3], while in mildly acidic, neutral or alkaline conditions a film of $Cr(OH)_3$ forms on the electrode surface [4, 5]. This layer tends to inhibit further Cr(VI) reduction. Electrodeposition of chromium metal is only possible for a limited range of electrolyte compositions [6].

The possibility of removing hexavalent chromium from wastewater by electrochemical treatment was considered by Golub and Oren [7]. They carried out cyclic voltammetry experiments using a graphite felt electrode and found that Cr(VI) could be reduced to oxidation state three, Cr(III), and adsorbed on to the electrode surface, probably as colloidal $Cr(OH)_3$. Their results suggested that under suitable conditions the adsorbed Cr(III) deposit can be reoxidised to Cr(VI) and recovered. Based on their results, Golub and Oren [7] proposed a single stage process for Cr(VI) removal, with minimised addition of chemicals and sludge disposal.

Packed bed electrodes of carbon of graphite particles have also evaluated for removal of Cr(VI) [8, 9]. However, the performance of these packed bed cells was unsatisfactory. An alternative process using an unstable iron or steel anode has been reported [9, 10]. The chromium concentration was reduced from the initial concentrations of 570–2100 mg l^{-1} to less than 0.5 mg l^{-1} [10], but large amounts of Fe/Cr sludge were produced.

Recently Njau and Janssen [11] have shown that Cr(VI) species in 1 M H_2SO_4 can be electrochemically reduced to Cr^{3+} with high efficiency at low concentration (less than 20 mg Cr l^{-1}) using a packed bed cathode. However, to our knowledge there have been no further studies on the removal of Cr(VI) based on the process suggested by Golub and Oren [7] whereby a $Cr(OH)_3$ deposit is collected on a carbon felt electrode surface. This paper focuses on a laboratory scale investigation of this Cr(VI) removal process. The aim is to evaluate the process of Cr(VI) removal using a single stage electrochemical process whereby the chromium is removed as a hydroxide deposit on the electrode surface. The reoxidation of the deposit has not been considered, and this will be the subject of a later study.

2. Experimental details

This work was carried out using an electrochemical cell with a flow through porous carbon felt cathode, which is shown schematically in Figure 1(a). The porous carbon felt (Sigratherm, KFA5) cathode had a projected area (i.e., the cross sectional area perpendicular to the direction of flow) of 25 cm^2 and thickness of 0.5 cm. The current feeder for the cathode was a stainless steel 316 mesh underneath the carbon felt. The anode was Pt/Ir oxide coated titanium mesh with a titanium current feeder. Experiments were carried out under constant current conditions using a precision d.c. power supply.

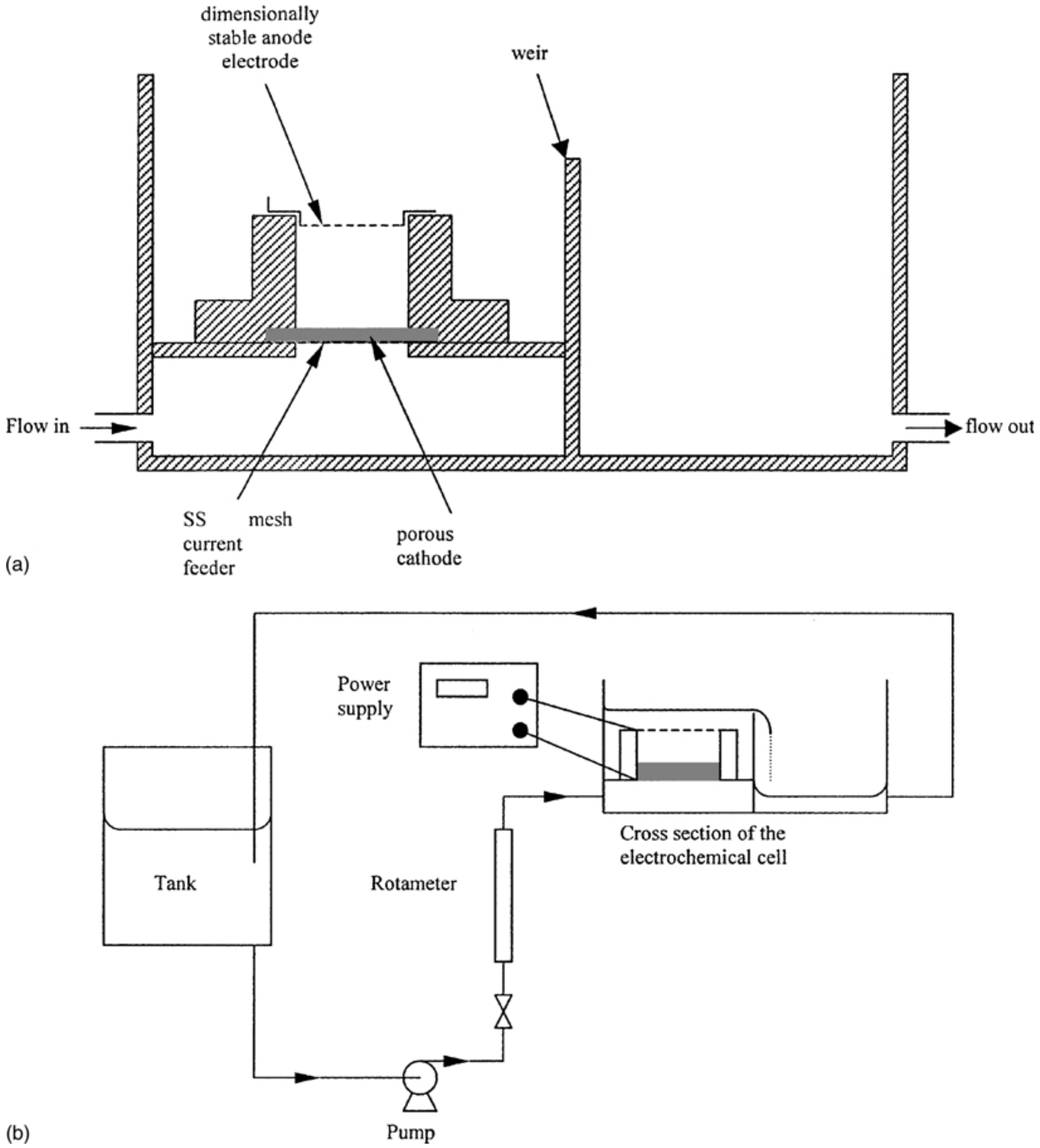

Fig. 1. Schematic diagrams of (a) the electrochemical cell and (b) experimental set-up and flow system.

Current densities in the range 250–800 A m^{-2} (based on the projected area of the felt electrode) were used. During each experiment the solution was circulated through the cell (Figure 1(b)) using a centrifugal pump, and the flow rate was measured with a rotameter. The solution pH was controlled during each experiment with a pH controller using a pH electrode in the tank.

Five litres of 50 mg Cr(VI) l^{-1} in 0.1 M Na_2SO_4 solution was prepared using potassium dichromate and the solution pH was adjusted to the required value between 3.0 and 4.0 before each experiment. The chemicals used were reagent grade anhydrous sodium sulfate, Na_2SO_4, potassium dichromate, $K_2Cr_2O_7$, sulfuric acid and sodium hydroxide. Solutions were prepared using deionized water. The solution was circulated through the cell at a flow rate of 100 l h^{-1}, giving a superficial velocity u of 1.11 cm s^{-1} through the porous electrode. Samples were taken at five minute intervals for the first half an hour and afterwards at ten minute intervals. The duration of the experiments was up to 240 min. The pH, total chromium concentration and chromium(VI) concentration of samples were measured (Section 2.2). A fresh carbon felt cathode was used for each experiment. To ensure that the surface of the carbon fibres was wetted, the felt was soaked in deionized water and any trapped air removed by vacuum before each experiment.

2.1. *Analysis*

To determine both total chromium and Cr(VI) concentrations, each sample was divided into two parts. The total chromium concentration was determined from the first using flame ionization atomic absorption spectroscopy (AAS), with samples diluted into the linear range of the instrument as necessary. Any Cr(III) or Cr(II) species present were precipitated from the second sample by adjusting to pH 10. The sample was then filtered and the remaining chromium concentration (assumed to be Cr(VI)) determined using AAS, after dilution if necessary. This technique was found to be accurate to within ±0.5 mg l^{-1}, which is similar to the detection limit of AAS.

3. Results and discussion

3.1. *Influence of bulk pH*

Reactions which may be occurring on the electrodes include:

Cathode:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O \quad E^\circ = 1.33\,V \tag{1}$$

$$HCrO_4^- + 4\,H^+ + 3\,e^- \rightarrow Cr^{3+} + 4\,H_2O \quad E^\circ = 1.35\,V \tag{2}$$

$$Cr^{3+} + e^- \rightarrow Cr^{2+} \quad E^\circ = -0.407\,V \tag{3}$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \quad E^\circ = 0.00\,V \tag{4}$$

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O \quad E^\circ = 1.229\,V \tag{5}$$

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \quad E^\circ = 0.695\,V \tag{6}$$

$$Cr^{3+} + 3\,OH^- \rightarrow Cr(OH)_3 \quad K_{sp} = 7 \times 10^{-31} \tag{7}$$

Anode:

$$H_2O - 2e^- \rightarrow \frac{1}{2}O_2 + 2H^+ \tag{8}$$

The removal of Cr(VI) in an electrochemical process is a pH dependent process. The effect of pH is not only associated the formation of the $Cr(OH)_3$ precipitate (Reaction 7), but also with the electroreduction of Cr(VI) (Reactions 1 and 2). While the thermodyanamic standard electrode potentials of Reactions 1 and 2 are large and positive, the kinetics of these reactions are slow [3], and a large overpotential is often required to achieve significant reaction rates. Furthermore these reactions are strongly pH dependent and tend to passivate with the formation of a $Cr(OH)_3$ film for pH > 2 [4]. It is likely that any Cr^{2+} formed by Reaction 3 will be unstable due to oxidation by H^+ or Cr(VI) species. In the following discussion it is assumed that only Cr(III) species are generated by the reduction of Cr(VI).

At the start of each experiment the rate of reduction of Cr(VI) to Cr^{3+} on carbon felt electrodes did not vary significantly with the solution pH. However as the experiments progressed the pH had a significant effect on the decay of the Cr(VI) concentration. Figure 2(a) shows the decay in the normalized Cr(VI) concentration for experiments carried out at a range of pH between 3.0 and 4.0 and with a current density of 400 A m^{-2}. In all cases the Cr(VI) concentration falls rapidly initially at a similar rate. However, as time progresses the rate of reduction falls rapidly, and a strong pH effect is observed. At pH 3.0, the Cr(VI) concentration was reduced rapidly from 49.1 to 6.4 mg l^{-1} within 60 min. After 240 min of treatment, the Cr(VI) concentration was further reduced to 2.2 mg l^{-1}. At pH 4.0, the reduction of Cr(VI) concentration was much slower than at lower pHs. After 240 min the Cr(VI) concentration was still as high as 41 mg l^{-1} (the initial Cr(VI) concentration C_0 was 60.8 mg l^{-1}). This pH effect is probably associated with the formation of the $Cr(OH)_3$ layer inhibiting the progress of the Cr(VI) reduction [5].

Figure 2(b) shows the same data plotted logarithmically. The exponential decay observed for pH 3.0, 3.3 and 3.5 at low concentrations suggests a mass transport limited reduction. However, the gradients suggest that there is a higher mass transport coefficient at pH 3.5, even though the flow conditions are the same in all cases. This may be explained by a difference in

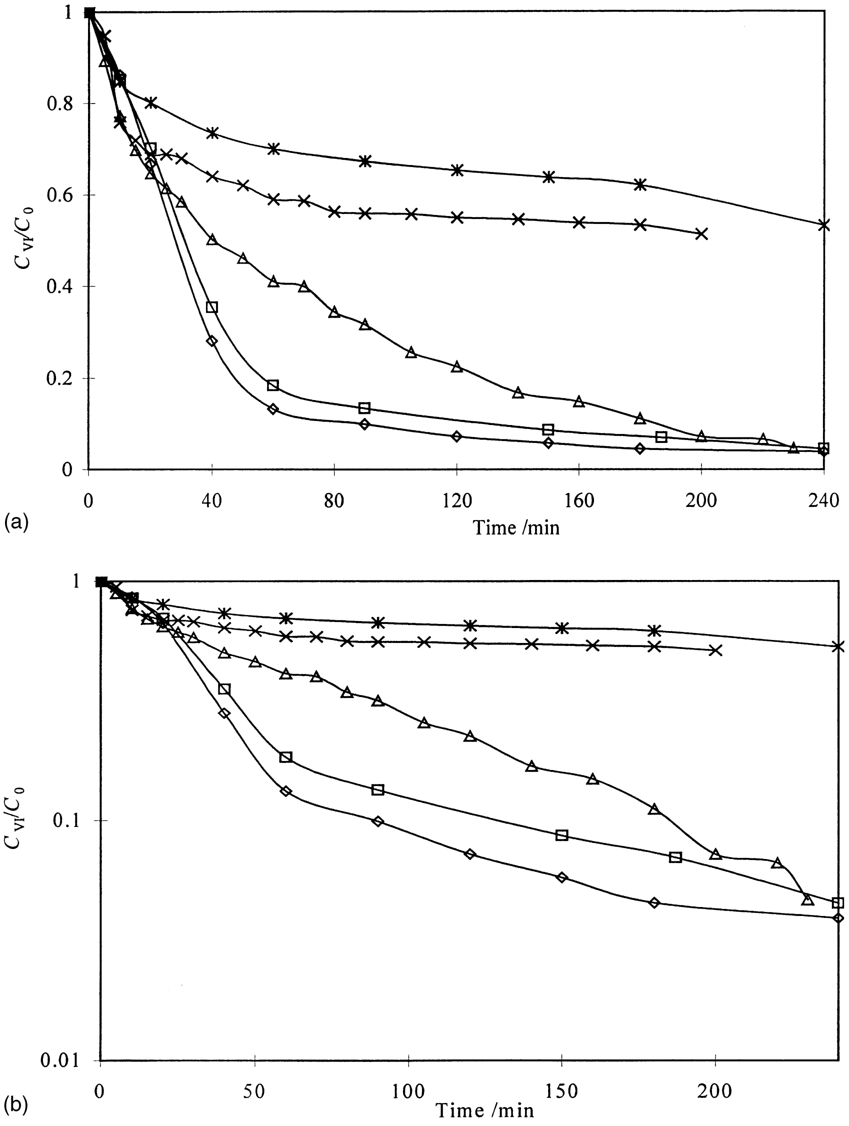

Fig. 2. Effects of pH on electrochemical reduction of Cr(VI) using carbon felt at a range of pH values, with $i = 400$ A m^{-2}, $u = 1.11$ cm s^{-1}, in 0.1 M Na_2SO_4. C_{VI} is the concentration of Cr(VI) and C_0 is the total chromium concentration at the start of each experiment. pH: (◇) 3.0, (□) 3.3, (△) 3.5, (×) 3.7 and (✱) 4.0.

active species concentration with pH (by complexation) which is not detected by the analytical method. Alternatively, there may be changes in the active surface area with pH.

The total chromium concentration was found to be more strongly influenced by the solution pH, and an optimum pH for chromium removal was observed for a given current density and flow rate. Figure 3 shows the decay in the normalized total chromium concentration for the same conditions as Figure 2. At low pH (pH 3.0) the total chromium concentration remains at a high level throughout the experiment. Although the Cr(VI) was rapidly reduced to low levels under these conditions (Figure 2), the resulting Cr(III) species remain in solution. At pH 3.5 the total chromium concentration falls to a low level (4.7 mg l^{-1} after 240 min) as the Cr(III) species are collected on the electrode as a hydroxide precipitate. At higher pH (pH 4.0) the total chromium concentration is close to the Cr(VI) concentration, indicating that any reduced species are removed from solution. At the optimum pH it is apparently possible to form the $Cr(OH)_3$ precipitate without significantly inhibiting the Cr(VI) reduction. It is possible that at this pH a more porous deposit was formed, which allowed the Cr(VI) to access the electrode surface. Alternatively the hydroxide may not have been deposited throughout the region of the electrode surface which was active for Cr(VI) reduction.

This optimum pH for chromium removal is a compromise between the low pH required for Cr(VI) reduction and the high pH required for hydroxide precipitation. The optimum can be illustrated more clearly by comparing the percentage removal of Cr(VI) and total chromium (after say 180 min) at each pH examined (Table 1).

The performance can also be considered in terms of overall current efficiencies. Two current efficiencies are defined, Φ_{VI} for Cr(VI) reduction and Φ_T for chromium

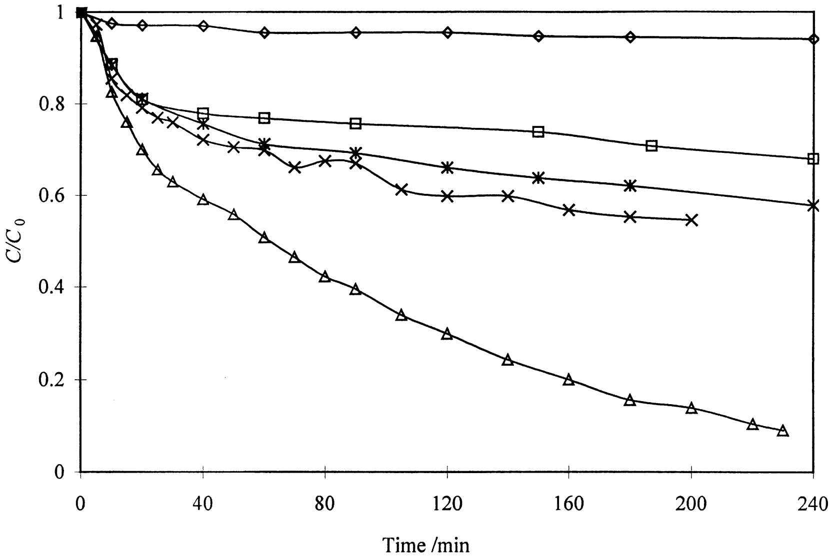

Fig. 3. Effects of pH on electrochemical removal of chromium using carbon felt at a range of pH values, with $i = 400$ A m^{-2}, $u = 1.11$ cm s^{-1}, in 0.1 M Na_2SO_4. C is the total chromium concentration and C_0 is the total chromium concentration at the start of each experiment. pH: (◇) 3.0, (□) 3.3, (△) 3.5, (×) 3.7 and (✱) 4.0.

Table 1. Removal of chromium and Cr(VI) after 180 min of electrochemical treatment using a carbon felt electrode

pH	Cr(VI) removed /%	Total chromium removed /%	Φ_{VI}* /%	Φ_T† /%
3.0	95.5	5.5	11.9	0.7
3.3	93.0	29.2	11.2	3.6
3.5	88.9	84.4	11.7	11.3
3.7	46.9	44.7	6.7	6.4
4.0	37.9	37.9	5.9	5.9

*Φ_{VI} is the current efficiency for Cr(VI) reduction after 180 min based on a three electron reduction.

†Φ_T is the current efficiency for chromium removal after 180 min based on a three electron reaction.

removal, both based on a three electron transfer reaction.

$$\Phi_{VI} = \frac{3FV(C_{VI} - C_0)}{MIt} \times 100 \tag{9}$$

$$\Phi_T = \frac{3FV(C - C_0)}{MIt} \times 100 \tag{10}$$

where F is the faradaic constant, V is the volume of solution circulated, C_{VI} and C are the concentration of Cr(VI) and total chromium respectively after time t, C_0 is the initial concentration of total chromium, M is the relative atomic mass of chromium, and I is the applied current.

The overall current efficiencies for Cr(VI) and total chromium after 180 min of each experiment in Figures 2 and 3 are shown in Table 1. For pH 3.0 to 3.5, Φ_{VI} was around 11–12%, while at higher pH it fell to around 6% at pH 4.0 (Table 1). The current efficiency of total chromium reached a maximum of around 11% at the optimum pH of 3.5. These values compare with typical current efficiencies for electrochemical metal recovery processes of around 10%.

It is conjectured that the chromium was removed as precipitated chromium hydroxide $Cr(OH)_3$. To explore this premise further, the Cr^{3+} concentration, C_{III}, has been estimated for the experiments described above as

$$C_{III} = C - C_{VI} \tag{11}$$

Equation 11 assumes that the only chromium species present are hexavalent chromium and Cr^{3+}. It is likely that other chromium species are present, and C_{III} can be taken to be the concentration of soluble chromium species excluding hexavalent chromium. It is likely that this will be largely trivalent chromium, but some Cr^{2+} may also be present.

At low pH, C_{III} was observed to rise to a steady value, while at pH 3.5 and above, C_{III} remained at low values of a few mg l^{-1} throughout each experiment. Figure 4 shows C_{III} observed at a range of pH and with $i = 400$ A m^{-2}. At pH 3.0 and 3.3 C_{III} rose rapidly and reached values of around 44 and 31 mg l^{-1} respectively. At pH 3.5 and 3.7 C_{III} settled at values of around 3 and 2 mg l^{-1}, respectively, while at pH 4.0 C_{III} was close to, or below the detection limit of the measurement (~0.5 mg l^{-1}).

To test this conjecture further, the pH corresponding to a $Cr(OH)_3$ precipitate in equilibrium with the Cr^{3+} concentrations which were observed in the experiments has been calculated:

$$\mathrm{pH_{eq}} = 14 + \left\{ \frac{\log_{10}(K_{sp}) - \log_{10}\left(\frac{C_{III}}{M}\right)}{3} \right\} \tag{12}$$

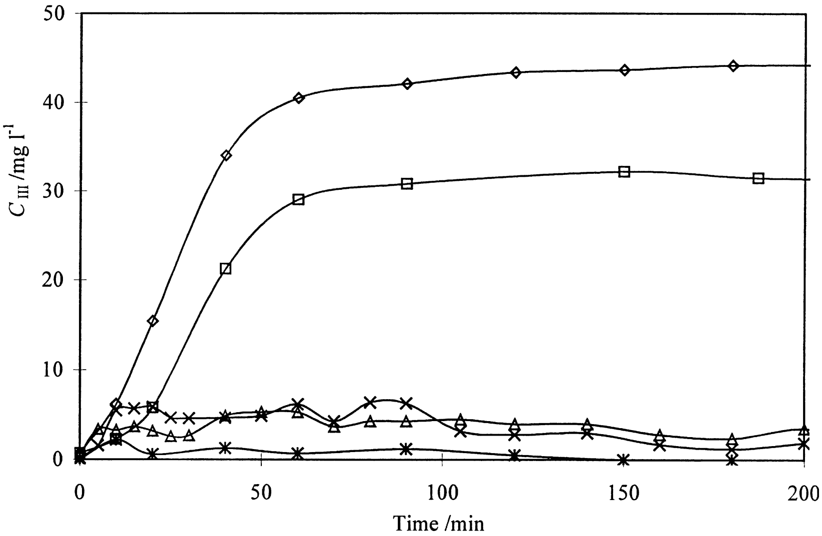

Fig. 4. Effects of pH on electrochemical removal of chromium using carbon felt at a range of pH values, with i = 400 A m^{-2}, u = 1.11 cm s^{-1}, in 0.1 M Na_2SO_4. C_{III} is the difference between the total chromium and Cr(VI) concentration. pH: (◇) 3.0, (□) 3.3, (△) 3.5, (×) 3.7 and (✱) 4.0.

where pH_{eq} is the equilibrium pH for the $Cr(OH)_3$ precipitation reaction (Equation 7) and C_{III} is in g l^{-1}. The values of pH_{eq} calculated using Equation 12 for the concentration C_{III} obtained in the experiments are shown in Table 2. The results show that only a small change in pH would lead to the large differences in equilibrium concentration.

Although the experiments described above indicate the influence of the bulk pH, it is the conditions at the electrode surface which will influence the electrochemical and chemical processes. Electron transfer reactions at the cathode (Equations 1–6) are likely to generate a higher pH at the electrode surface compared to the bulk. These conditions are also likely to vary through the depth of the felt, as higher current densities associated with hydrogen evolution (Equation 4) at the surface nearest the anode, while mass transfer limited oxygen reduction (Equations 5 and 6) may occur through the depth of the electrode. It therefore seems likely that pH at the electrode surface could approach or exceed the pH_{eq} values calculated above. The proposed mechanism of Cr(VI) reduction followed by precipitation of $Cr(OH)_3$ is reasonable and seems the likely mechanism for chromium removal under the conditions studied.

Table 2. Concentration Cr(III), C_{III}, and equilibrium pH, pH_{eq} (calculated using Equation 12), after 200 min of treatment of 5 l of 50 mg l^{-1} Cr(VI) solution

pH	C_{III} (mg l^{-1}) after 200 min	PH_{eq}
3.0	44	4.97
3.3	31	5.02
3.5	3	5.36
3.7	1.5	5.46
4.0	<0.5	>5.62

It is likely that the operating conditions such as current density and flow rate will also influence the pH at the electrode surface and would therefore be expected to influence the chromium removal process. The influence of current density on Cr(VI) reduction and chromium removal was investigated.

3.2. *Influence of current density*

At pH 3.5 the current density was found to primarily influence the Cr(VI) reduction process. Figure 5 shows the behaviour of the normalized Cr(VI) concentration at a range of current densities between 280 and 800 A m^{-2}. It is clear that the maximum Cr(VI) reduction rate was achieved at 400 A m^{-2}. At lower current densities the Cr(VI) concentration fell more slowly as expected. The overall current efficiency for Cr(VI) reduction after 160 min was 12.3% at 280 A m^{-2} compared to 12.6% at 400 A m^{-2}. At higher current densities the Cr(VI) concentration fell more slowly, probably due to the higher pH conditions at the electrode surface associated with the increased rates of the hydrogen evolution and oxygen reduction reactions (Equations 4 and 5). An alternative explanation would be that the increased rate of gas evolution at the electrode surface at high current densities reduced the apparent conductivity of the electrolyte, thus reducing the penetration of the current into the electrode.

For the range of conditions studied, the total chromium concentration followed a similar trend to the Cr(VI) concentration as the current density was varied (Figure 6). The total chromium concentration remained a few mg l^{-1} higher than the Cr(VI) concentration throughout each experiment, indicating that Cr(III) species were present at low levels throughout these experiments. These results indicate that, for these conditions, the rate of chromium removal was limited

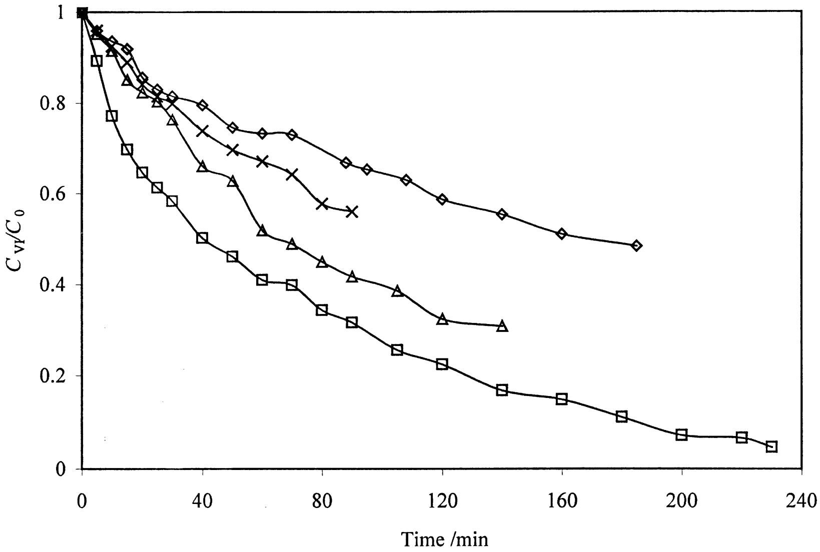

Fig. 5. Effect of current density on electrochemical Cr(VI) reduction using carbon felt at a range of current densities, with u=1.11 cm s^{-1}, in 0.1 M Na_2SO_4 at pH 3.5. C_{VI} is the Cr(VI) concentration and C_0 is the total chromium concentration at the start of each experiment. C.d.: (◇) 280, (□) 400, (△) 600 and (×) 800 A m^{-2}.

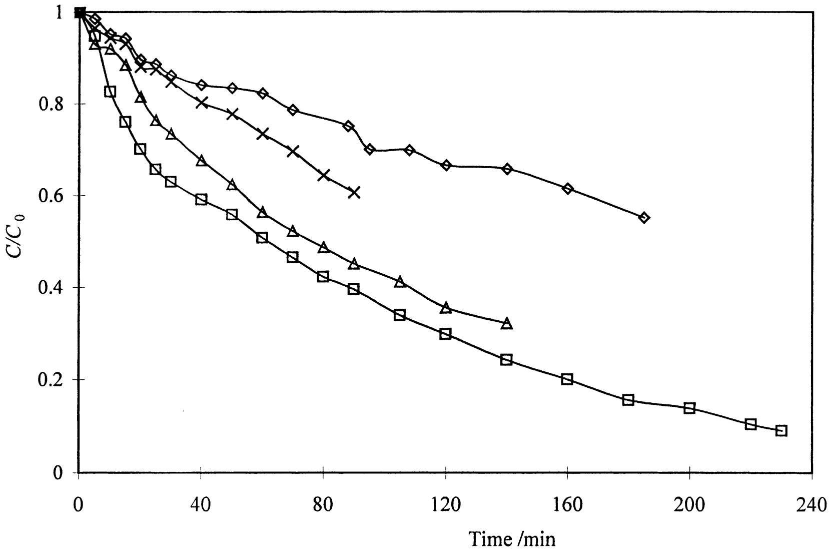

Fig. 6. Effect of current density on electrochemical removal of chromium using carbon felt at a range of current densities, with u = 1.11 cm s^{-1}, in 0.1 M Na_2SO_4 at pH 3.5. C is the total chromium concentration and C_0 is the total chromium concentration at the start of each experiment. C.d.: (◇) 280, (□) 400, (△) 600 and (×) 800 A m^{-2}.

by the Cr(VI) reduction and not the $Cr(OH)_3$ precipitation process.

3.3. *Deposit morphology*

The surface of the felt facing the anode was observed to have a grey–green colour, suggesting that a chromium precipitate was formed. E-DAX analysis of the electrode surface confirmed that the observed deposit was indeed a chromium precipitate. Scanning electronic microscopy (SEM) was used to study the morphology of the precipitate collected on the electrode surface during the experiments discussed above. Figure 7(a) shows an SEM image of a fresh carbon felt. The felt is made up of loose fibres of around 10 μm diameter. Channels can be seen on the surface of the fibres, suggesting that the structure of each fibre may be a bundle of smaller cylindrical fibres. At the end of each experiment, a deposit was observed on fibres on the surface of the felt which was facing the anode. Figure 7(b) shows an SEM image of this felt surface after treatment of 5 l of Cr(VI) solution at pH 3.0, and with a current density of 400 A m^{-2}. Many of the fibres have little or no deposit on their surface, but clumps of precipitate with a thickness of around 5 μm are apparent. The deposit is cracked, which probably occurred when the felt was dried prior to observation under the SEM. Figure 7(c) shows a SEM image of the deposit formed at pH 3.5 and i = 400 A m^{-2}, the conditions which gave the highest

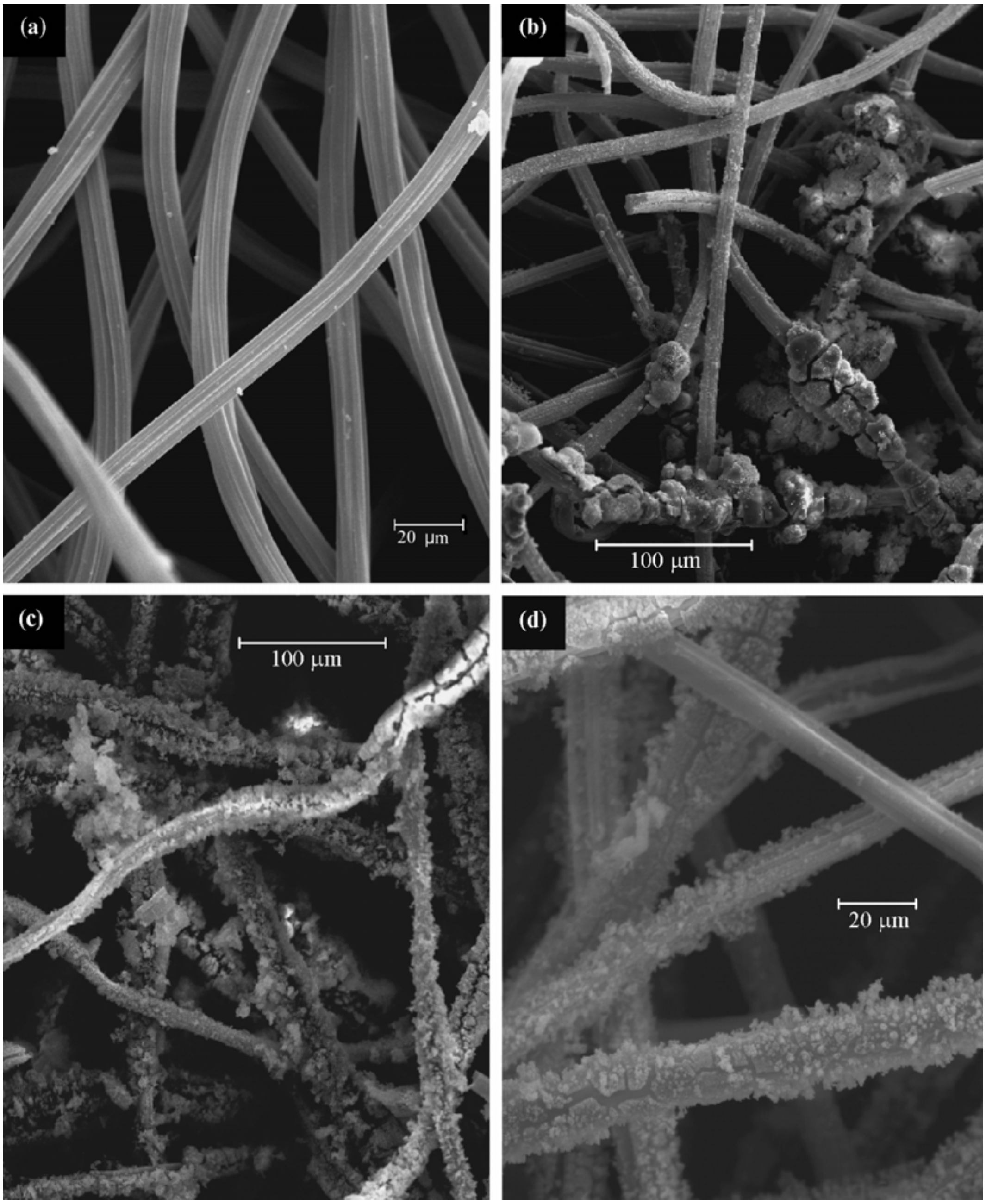

Fig. 7. SEM image of the carbon felt electrode. (a) Fresh felt, (b–d) felt after treating 5 l of 50 mg l^{-1} Cr(VI) solution at a current density 400 A m^{-2} and with (b) pH 3.0, (c) pH 3.5 and (d) pH 4.0.

levels of chromium removal. A thick deposit is apparent over most of the fibres in the image, and the deposit has a loose structure. Some of the dark fibre surface underneath the deposit is visible. The deposit has an agglomerated structure, consistent with the adsorption of colloidal $Cr(OH)_3$ particles with a size of order 1 μm. At higher pH (Figure 7(d)) a thinner coherent layer of deposit is apparent beneath a powdery deposit. These observations are consistent with the suggestion that at high pH the Cr(VI) reduction is inhibited by a layer of $Cr(OH)_3$ precipitate, while at the optimum pH a more porous deposit is formed, allowing reduction of Cr(VI) to continue while precipitated $Cr(OH)_3$ is collected on the electrode.

4. Conclusions

It is clear that pH is a critical factor in the proposed Cr(VI) removal process. This sensitivity is associated with the conflicting effects of pH on the electrochemical Cr(VI) reduction and the chemical $Cr(OH)_3$ precipitation. A lower pH favours Cr(VI) reduction, but at low pH the not all the Cr^{3+} formed is precipiated as $Cr(OH)_3$, so the total chromium concentration remains high. At higher pH, although the difference between total chromium and Cr(VI) is small (indicating high Cr^{3+} precipitation as $Cr(OH)_3$, the Cr(VI) reduction rate is slow resulting in a low removal efficiency. It is clear from the above discussion that to obtain a high chromium removal efficiency, pH must be controlled carefully. However, the results show that it is possible to remove chromium from solution to concentrations of below 5 mg l^{-1} with a current efficiency of around 12%.

Increasing the current density was found to influence the performance. At high current density the Cr(VI) reduction rate was found to be reduced. This effect may be associated with an increased pH at the electrode surface, associated with an increased rate of hydrogen evolution and/or oxygen reduction. However, the current density was observed to have little effect on the hydroxide precipitation, as the total chromium concentration followed a similar trend to the Cr(VI) concentration for the range of conditions studied. It is possible that the Cr(VI) reduction and the Cr^{3+} reduction reactions are occurring in different parts of the felt electrode, and it is likely that the current density only effects the electrode surface pH in a small part of the felt. The results suggest that conditions of low current density ($\leqslant 400$ A m^{-2}) combined with a solution pH controlled at around 3.5 will be optimal for total chromium removal. It may be possible to operate at higher pH with lower current densities.

Although high levels of chromium removal were obtained by optimization of solution pH and current density, further work on other operating parameters, in particular the solution flow rate, is desirable. The solution flow rate will affect mass transport rates, and will thus influence the at the electrode surface. It is possible to envisage a two stage process with two electrodes operating under different conditions optimized for Cr(VI) reduction and hydroxide precipitation, respectively. Further work is also needed to establish the potential for the reoxidation and recovery of the deposited chromium.

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