

Remediation of chromium(VI) at polypyrrole-coated titanium

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Abstract The application of conducting polypyrrole (PPy) and polyaniline (PAni) coated substrates in remediation of chromium, Cr(VI), is an area of considerable interest. Here, we discuss the implementation of PPy-coated titanium as a new material for the reduction of Cr(VI) to the less toxic trivalent state, Cr(III). An alkaline-peroxide based etching process was used to ensure the adhesion of the PPy coatings to the underlying titanium. The PPy films showed excellent resistance to acidic Cr(VI) solutions and remained adherent after continuous exposure to the solutions. In order to optimise the remediation process a number of experimental parameters were investigated, including the thickness of the PPy coating, the reduction potential used in pre-treatment of the PPy and the degree of solution agitation. The durability of the materials on exposure to the Cr(VI) test solutions made them suitable for repeated remediation experiments. Following several test-runs, the cleanup efficiency of the material was found to decrease slightly, however, increasing the exposure/experiment time resulted in significantly improved cleanup ability.

Keywords Electropolymerization · Chromium remediation · Pollution control · Polypyrrole · Titanium

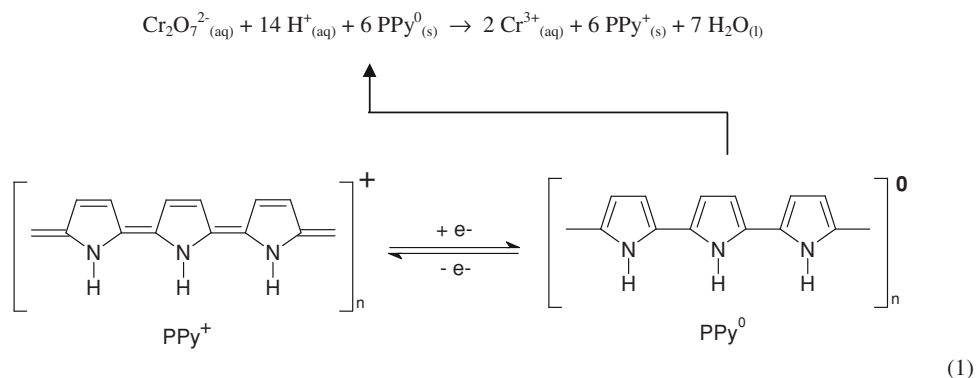
1 Introduction

Hexavalent chromium, Cr(VI), is a well-documented carcinogen, mutagen and redox active species [1–6]. However,

the use of chromium in industrial processes including corrosion inhibition, metal finishing, tanning and pigment production is still prevalent [2, 7]. Pollution due to Cr(VI) is a considerable problem due to its extremely hazardous nature and the relative ease with which it may contaminate the environment. Investigated remediation techniques include electrochemical methods [8, 9], the use of ferrous iron [7], photocatalysis utilising UV illumination of titanium [10, 11] or zinc oxides [12] and a number of other interesting methods including the implementation of copper, hydrogen peroxide, hydrogen sulphide and methylated yeast biomass [13–16]. In the past number of years the use of conducting polymer-based materials in Cr(VI) remediation has arisen as an interesting area of research [17, 18]. Typically, a substrate is coated with a layer of conducting polymer, which is then used to reduce the toxic Cr(VI) to Cr(III), Eq. 1, which can be removed by precipitation of the chromium hydroxide [19]. Unlike ferrous or photocatalytic based methods, the reducing agent, i.e. the conducting polymer coated substrate, can be easily removed from the system and be regenerated for repeated use.

Both polypyrrole (PPy) and polyaniline (PAni) deposited on a variety of substrates, have been investigated with regards to reduction of Cr(VI). Wei et al. [18] described the use of a PPy-coated platinum mesh in reducing the Cr(VI) concentration in acidic solutions. The process involved first depositing PPy on the platinum substrate then reducing it in a conducting solution, in this case 0.1 mol dm^{-3} KCl. The coated mesh was then placed in the Cr(VI)-containing acid solution where the reduction of Cr(VI) was monitored using UV–Vis spectroscopy. The PPy-modified platinum showed excellent cleanup efficiency in comparison to the uncoated mesh. Further development of this work, performed by Senthurchelvan et al. [17], involved the investigation of a glassy-carbon substrate modified with

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PPy and provided further insight into the kinetics of the system and the effect of film thickness and Cr(VI) concentration. The catalytic properties of the film were investigated with cyclic voltammetry as was the stability of the film on exposure to Cr(VI). Other substrates used in investigations into the Cr(VI) reducing properties of PPy include carbon black, a highly dispersed form of elemental carbon [20], reticulated vitreous carbon [21] and aluminium [22]. However, titanium possesses several benefits over other previously investigated substrates which include lower cost, its robust nature and resistance to aggressive acidic Cr(VI) solutions and it is possible to deposit extremely adherent PPy coatings which remain intact after repeated exposure to Cr(VI) solutions. Additionally, when the PPy coating becomes ineffective through repeated remediation processes it can easily be removed through polishing or sandblasting, allowing the repeated use of the same titanium substrate.

PAni has also been investigated with regards to the remediation of Cr(VI) [23] and successfully reduces Cr(VI) to Cr(III). However, in the case of titanium substrates we found electrochemically deposited PAni coating to be inferior in comparison to PPy with regard to its poor adhesion properties. Here we present the results concerning the remediation of Cr(VI) with PPy-coated titanium electrodes including the effect of coating thickness, solution agitation, pre-treatment and durability of the coatings. The PPy was deposited potentiostatically using a method previously described in order to obtain extremely adherent coatings on the underlying titanium [24]. The PPy coating was found to be quite resistant to acidified Cr(VI) solutions used over the course of the investigations and was easily regenerated for repeated use by implementing potentiostatic reduction.

2 Materials and methods

Pyrrole (Lancaster) was distilled and stored in the dark at $-20\text{ }^{\circ}\text{C}$ prior to use. Oxalic acid di-hydrate (99%, Aldrich)

was made to a concentration of 0.2 mol dm^{-3} in distilled water. The alkaline-peroxide etch was composed of sodium hydroxide (BDH, technical grade) and hydrogen peroxide (Aldrich, 30%) diluted in distilled water to the desired concentrations of 0.5 mol dm^{-3} NaOH and 1.0 mol dm^{-3} H_2O_2 . A 0.1 mol dm^{-3} aqueous H_2SO_4 (BDH, 98% general purpose reagent) solution was used to make acidified Cr(VI) solutions with the addition of sodium dichromate-2-hydrate (99.5%, Riedel de Haën). Chemically pure (99.6+%) titanium wire with a diameter of 1.0 mm was obtained from Goodfellow Metals Limited.

The titanium wire was prepared by abrading with p1200 grade SiC paper, cleansing with distilled water and ultrasonic degreasing in acetone for 15 min. Following this, the wire was etched in the alkaline-peroxide solution for 10 min after which it was thoroughly rinsed in distilled water. The PPy coatings were deposited potentiostatically at 0.8 V (SCE) in a solution of 0.2 mol dm^{-3} pyrrole in 0.2 mol dm^{-3} aqueous oxalic acid. When the PPy coatings were formed the coated electrode was then potentiostatically reduced in 0.1 mol dm^{-3} H_2SO_4 for a period of 30 min at -0.4 or -0.8 V (SCE). When the reduction process was completed, the PPy-coated titanium was placed in a UV-Vis quartz cell, containing a known concentration of Cr(VI), ($\text{Na}_2\text{Cr}_2\text{O}_7$), in 3.0 cm^3 of 0.1 mol dm^{-3} H_2SO_4 solution. All electrochemical procedures were performed using a Solartron 1285 potentiostat. UV-Vis spectroscopy was performed with a Varian Instruments Cary 50 Conc UV-Vis spectrophotometer.

3 Results and discussion

3.1 Preparation of polypyrrole films

Figure 1 shows a typical current–time transient associated with the potentiostatic deposition of PPy at titanium using an applied potential of 0.8 V (SCE). A high density of polypyrrole nucleation on the electrode surface is indicated by the rapid rise in current giving the current peak observed

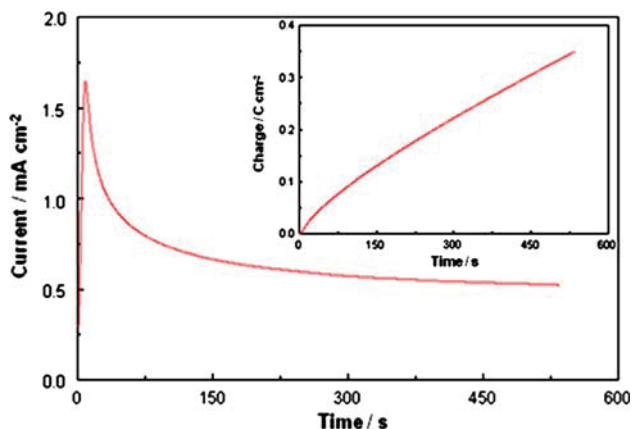


Fig. 1 Typical current–time transient observed on potentiostatic deposition of PPy on titanium. Inset: Charge–time transient obtained from the potentiostatic deposition

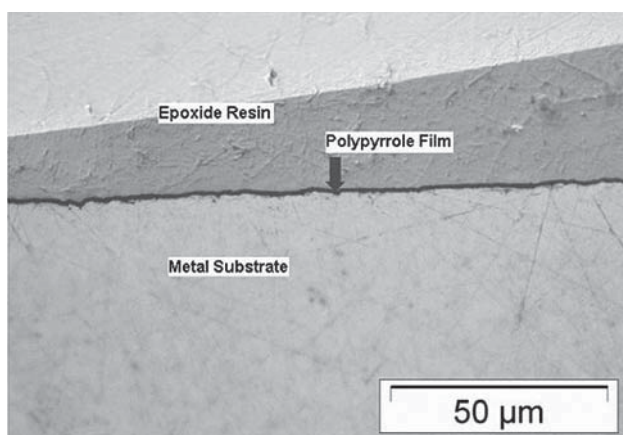


Fig. 2 Example of the cross section of polypyrrole-coated titanium used to estimate the thickness of the coatings

at ca. 30 s. This is followed by unidirectional growth of the coating indicated by a significant drop in current values over the remainder of the electrodeposition. The inset shows the corresponding charge–time plot. In order to determine the thickness of the polypyrrole coatings cross sections of PPy-coated Ti–6Al–4V were obtained. Figure 2 shows an example of the cross section micrographs used to estimate the charge–thickness relationship. Assuming a linear relationship and 100% current efficiency it is estimated that a charge of 0.35 C cm^{-2} will deposit PPy to a thickness of $1.0 \mu\text{m}$.

3.2 Cr(VI) reduction

Figure 3 shows the typical UV–Vis response of $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ Cr(VI) in 0.1 mol dm^{-3} H_2SO_4 during exposure to a $1.0 \mu\text{m}$ oxalate-doped PPy coating on titanium. Scans of the solution were obtained every 10 min over a period of 3 h and show the removal of Cr(VI) from

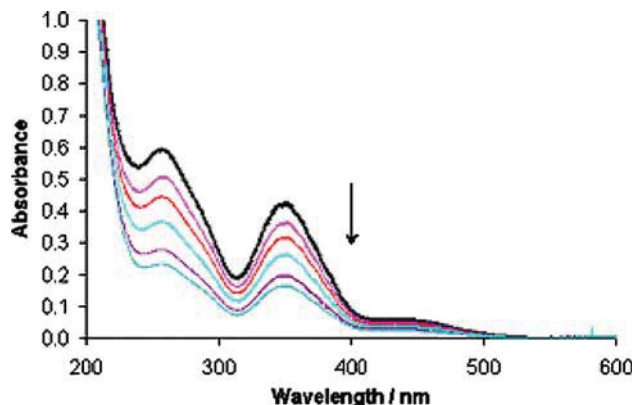


Fig. 3 UV–Vis spectra of $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ Cr(VI) in 0.1 mol dm^{-3} H_2SO_4 during exposure to a $1.0 \mu\text{m}$ oxalate-doped PPy coating on titanium. The traces were recorded at $t = 0, 10, 30, 60, 120$ and 180 min . The solution was agitated with nitrogen bubbling throughout

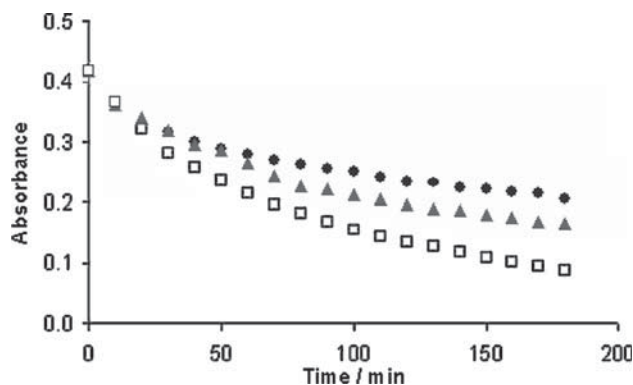


Fig. 4 Absorbance values at 351 nm shown as a function of the exposure time of PPy-coated titanium to $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ Cr(VI) in 0.1 mol dm^{-3} H_2SO_4 . Polymer thickness: $0.5 \mu\text{m}$ ●, $1.0 \mu\text{m}$ ▲, $5.0 \mu\text{m}$ □. The solution was agitated with nitrogen bubbling throughout

the solution. This is consistent with the reduction of Cr(VI) by PPy at other substrates [17–22]. The PPy was grown to a thickness of 0.5, 1.0 and $5.0 \mu\text{m}$ and similar UV–Vis experiments were performed in order to assess the effect of polymer thickness. The thickness of the PPy coatings was estimated based on the charge/thickness relationship determined from cross section measurements of PPy coatings on titanium [25]. Inspection of Fig. 4 shows the increasing ability of the coatings to reduce the Cr(VI) with increasing thickness, particularly during the later stages of the exposure period. After a 3 h exposure period the percentage cleanup efficiencies were calculated as 41, 50 and 82% in order of increasing thickness. The increasing efficiency of the thicker coatings is most likely a result of the increased quantity of PPy available for the redox reaction with Cr(VI). Also, thicker PPy coatings exhibit a rougher morphology and tend to be more porous in nature [26],

resulting in a higher surface area and improving the capacity of the reaction with Cr(VI).

The reduction process of chromium at the PPy-coated titanium follows pseudo first-order kinetics with respect to the change in Cr(VI) concentration. The rate law for the reduction of Cr(VI) is shown in Eq. 2. Since the concentration of H₂SO₄ is significantly higher than that of the Cr(VI) species, its concentration is expected to vary little during the course of the reaction, likewise the concentration of PPy⁰ can be taken as a constant. Based on this, Eq. 3 can be derived, where k^1 represents a pseudo first-order rate constant. Plotting the logarithm of the Cr(VI) concentration as a function of time allows the calculation of the rate constants for the reduction of Cr(VI) by the PPy. Inspection of Table 1 indicates a 2.5-fold increase in the rate of Cr(VI) reduction with increasing thickness of the PPy from 0.5 μm to 5.0 μm, highlighting the effect of increasing the thickness of the PPy coating.

$$R = k[\text{Cr(VI)}]^1 [\text{PPy}^0]^n [\text{H}^+]^p \quad (2)$$

$$R = k^1 [\text{Cr(VI)}]^1 \quad (3)$$

The potential at which the PPy is reduced prior to immersion in the Cr(VI) solution can also affect the efficiency of the redox process, as this determines to what extent the PPy coating will be reduced. As summarised in Fig. 5, the percentage cleanup efficiencies of PPy reduced at -0.8 V (SCE) increased by over 10% after exposure to

Table 1 First-order rate constants obtained for PPy coatings on exposure to 2.5×10^{-4} mol dm⁻³ Cr(VI) in 0.1 mol dm⁻³ H₂SO₄

Coating thickness/μm	k/min ⁻¹
0.5	$(3.3 \pm 0.2) \times 10^{-3}$
1.0	$(4.9 \pm 0.2) \times 10^{-3}$
5.0	$(8.3 \pm 0.2) \times 10^{-3}$

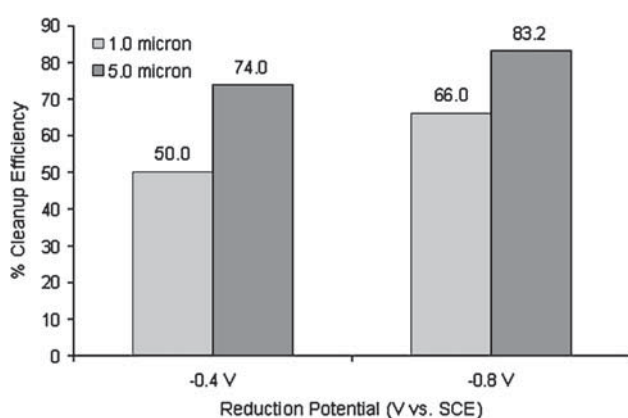


Fig. 5 Percentage cleanup efficiencies, as a function of reduction potential and polymer thickness, after exposure to 2.5×10^{-4} mol dm⁻³ Cr(VI) in 0.1 mol dm⁻³ H₂SO₄ for a period of 3 h

2.5×10^{-4} mol dm⁻³ Cr(VI) in 0.1 mol dm⁻³ H₂SO₄ for 3 h. In the case of PPy, reduction potentials of -0.9 V (SCE) have been reported [21] although it should be noted that such negative reduction potentials may significantly damage the PPy and negatively affect its redox properties.

3.3 Influence of solution agitation

The degree of solution agitation is another important consideration with regard to maximising the process of Cr(VI) reduction. Agitation of in-situ UV-Vis experiments was provided by bubbling nitrogen gas through the test solution at a controlled rate over a 3 h period. On comparison of the percentage cleanup efficiencies without and with agitation, 4.0 and 50.0%, respectively, it is clearly evident that agitation of the solution is necessary to obtain a satisfactory degree of Cr(VI) reduction. The reduction of Cr(VI) at the PPy surface is diffusion-controlled and therefore, significant agitation of the test solution will provide the most efficient reduction of the Cr(VI) in solution. In order to evaluate the effect of vigorous solution agitation, open-circuit potential measurements were used to monitor the oxidation/reduction process occurring at the PPy-coated titanium. The PPy was deposited to an estimated thickness of 1.0 μm on titanium wire and reduced at -0.4 V (SCE) prior to immersion in the 2.5×10^{-4} mol dm⁻³ Cr(VI)/0.1 mol dm⁻³ H₂SO₄ solution. A UV-Vis cuvette was used to house the electrochemical cell so as to maintain the same surface area/volume ratio used in the UV-Vis in-situ experiments. A silver wire was used as a pseudo Ag/AgCl reference. A small magnetic stirrer was used to vigorously stir the solution over the course of the experiment. Stirring was initiated 30 min after commencing the experiment so as to illustrate the impact of agitation on the rate of Cr(VI) reduction/PPy oxidation. Figure 6 shows the open-circuit potential values obtained for this experiment. The arrow

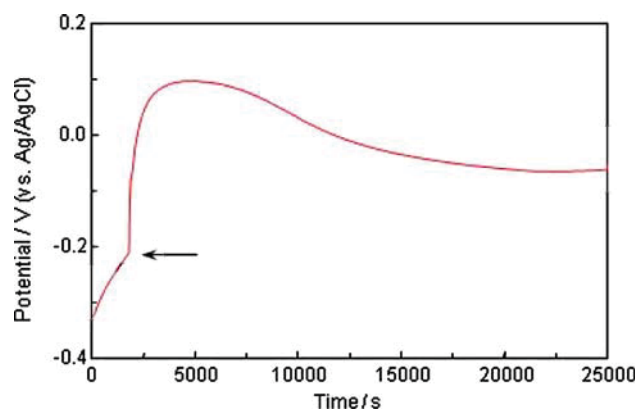


Fig. 6 Open-circuit potential of PPy (1.0 μm) on titanium in 2.5×10^{-4} mol dm⁻³ Cr(VI) in 0.1 mol dm⁻³ H₂SO₄ with solution agitation provided by vigorous stirring following 30 min. The arrow shows the time at which stirring of the solution was initiated

shows the time at which stirring of the solution was initiated, indicating a significant increase in the rate at which the PPy is oxidised. The maximum potential value was achieved at *ca.* 83 min, after which the open-circuit potential begins to steadily drop. This indicates the point at which the oxidation of the PPy as a result of the reduction of Cr(VI) has ceased, and thus the point in time at which all of the Cr(VI) has been consumed by the redox reaction with PPy. Following the experiment the solution was analysed with UV–Vis spectroscopy and there was no Cr(VI) remaining whatsoever. This indicates that 100% cleanup efficiency was obtained after 83 min of immersion with vigorous agitation of the solution.

3.4 Durability and re-usability of PPy film

The durability of the PPy-coated titanium in Cr(VI) remediation applications is an important consideration. Cr(VI) is quite a strong oxidising agent and in combination with acidic environments can be potentially damaging to both the PPy and underlying titanium. Open-circuit potential analysis was used to evaluate the resistance of PPy-coated titanium electrodes to corrosion in acidic Cr(VI) solutions. Open-circuit potential analysis was performed in 0.1 mol dm⁻³ H₂SO₄ containing 2.5 × 10⁻⁴ or 1.0 × 10⁻³ mol dm⁻³ Cr(VI). This analysis is useful in determining the potentials adopted by the PPy/titanium electrode on exposure to Cr(VI)-containing solutions. The PPy-coated titanium was prepared from 0.2 mol dm⁻³ oxalic acid electrolyte and grown to an estimated thickness of 1.0 μm and then reduced at -0.4 V (SCE) in 0.1 mol dm⁻³ H₂SO₄ before placing in the Cr(VI) containing solution. Figure 7 compares the open-circuit potential values obtained for PPy-coated titanium wire over a period of 16 h on exposure to 2.5 × 10⁻⁴ and 1.0 × 10⁻³ mol dm⁻³ Cr(VI) in 0.1 mol dm⁻³ H₂SO₄. The initial open-circuit values indicate that the PPy coatings, which are in a reduced state, are readily oxidised by the Cr(VI) in the solution. When stirring was initiated at 30 min a rapid increase in the rate of oxidation of the polymer was observed. A maximum potential was obtained at *ca.* 83 min in the case of 2.5 × 10⁻⁴ mol dm⁻³ Cr(VI) and at *ca.* 60 min in the case of the 1.0 × 10⁻³ mol dm⁻³ Cr(VI) solution. This indicates the time required to consume all of the Cr(VI) present in the solution by the redox reaction with the PPy. Following these maximum potentials the open-circuit potential was gradually reduced, reaching steady-state values approximately 360 min after initiating the experiment. The increased rate of oxidation on increasing the Cr(VI) concentration is quite evident during the first 30 min of the experiments. Subsequent UV–Vis analysis of the solution revealed complete reduction of the Cr(VI) species. The maximum potentials

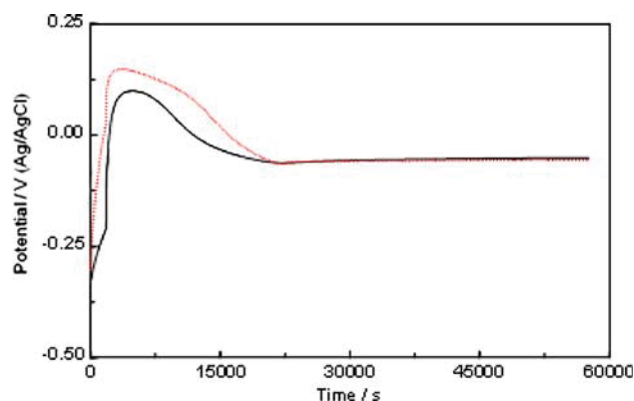


Fig. 7 Open-circuit potentials of PPy-coated titanium (1.0 μm) in 2.5 × 10⁻⁴ — and 1.0 × 10⁻³ mol dm⁻³ --- Cr(VI) in 0.1 mol dm⁻³ H₂SO₄. Vigorous stirring initiated at *t* = 30 s

achieved during the course of the Cr(VI) reduction experiments were 0.098 and 0.148 V (pseudo Ag/AgCl) for 2.5 × 10⁻⁴ and 1.0 × 10⁻³ mol dm⁻³ Cr(VI), respectively. Following the open-circuit potential experiment the PPy coatings remained adherent to the titanium and showed no visible signs of physical damage, indicating the resilience of the coating and underlying titanium in quite aggressive conditions.

An important aspect in the use of conducting polymers in the remediation of Cr(VI) is their re-usability, i.e. following reduction of Cr(VI) with the conducting polymer is it possible to regenerate the polymer by electrochemically reducing it? Figure 8 a, b summarise the percentage cleanup efficiencies of PPy-coated titanium with an exposure time of 2 h, having been recycled three times following the initial reduction experiment under gentle or vigorous stirring. The PPy was grown to a thickness of 1.0 μm and reduced at -0.4 V (SCE) in 0.1 mol dm⁻³ H₂SO₄ prior to exposure to the acidic Cr(VI) solution for a period of 2 h. After each experiment the PPy/titanium electrode was removed from the solution, rinsed in distilled water and reduced again for 30 min before placing in fresh 2.5 × 10⁻⁴ mol dm⁻³ Cr(VI) solution. In Fig. 8a the reduction of the Cr(VI) was monitored using UV–Vis spectroscopy as before. Bubbling nitrogen gas was used to agitate the Cr(VI) test solution throughout the exposure period. Figure 8b shows the percentage cleanup efficiencies obtained with vigorous stirring of the Cr(VI) solution. In this case, the progression of the chromium reduction was monitored with open-circuit potential analysis throughout and the Cr(VI) concentration was measured following the 2 h exposure period in order to calculate the percentage cleanup efficiency. Experiments 1–3 involved exposure periods of 2 h whereas Experiment 4 involved an extended exposure period of 16 h, all performed with the same PPy-coated titanium specimen. There was little difference in the

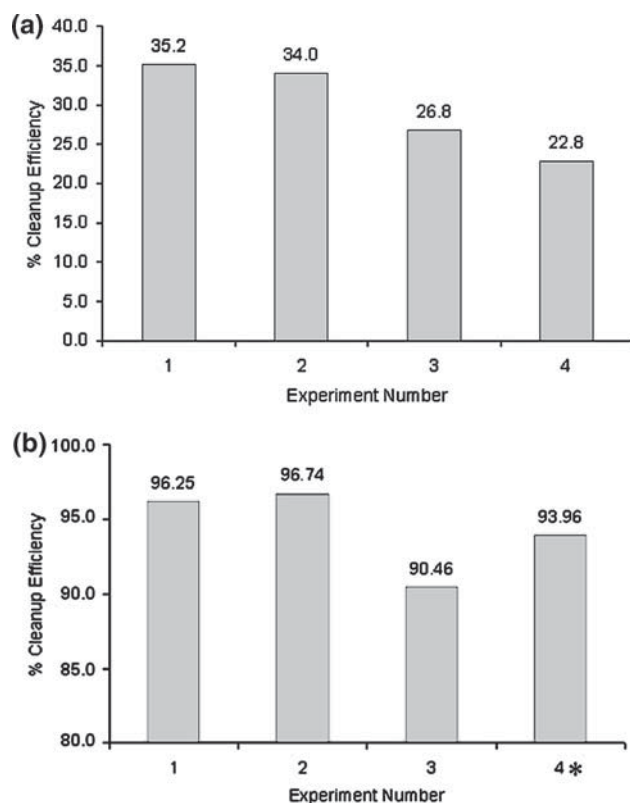


Fig. 8 Percentage cleanup efficiencies in $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ Cr(VI) in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ with exposure of the same oxalate-doped PPy/titanium electrode ($1.0 \mu\text{m}$) for each experiment. In (a) the exposure time in each case was 2 h under gentle agitation and in (b) the exposure time in each case was 2 h except for * where a time of 16 h was used, under vigorous stirring

cleanup efficiency in Experiments 1 and 2. However, a decrease of *ca.* 6% in the efficiency occurred with Experiment 3. Prior to performing Experiment 3, the specimen had already been exposed to the $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ Cr(VI) solution for a period of 4 h with the two previous experiments. Experiment 4 highlights the significance of exposure time with regard to the reduction of Cr(VI). Although the rate of reduction of Cr(VI) had been decreased somewhat as a result of exposure of the PPy to the solution, an increase in the exposure time was effective in providing an increase in the quantity of Cr(VI) that was reduced. These results obtained with stirring of the solution again highlight the importance of adequate agitation of the Cr(VI)-containing solution with an almost 3-fold increase in the amount of Cr(VI) reduced when the solution is under vigorous stirring compared to gentle agitation.

In tandem with the re-usability experiment, cyclic voltammetry was used to characterise the PPy coating following each exposure period in the Cr(VI) solution. The cyclic voltammetry was performed in 0.2 mol dm^{-3} oxalic acid solution in each case. Figure 9 shows the cyclic voltammograms obtained on cycling the PPy-coated titanium

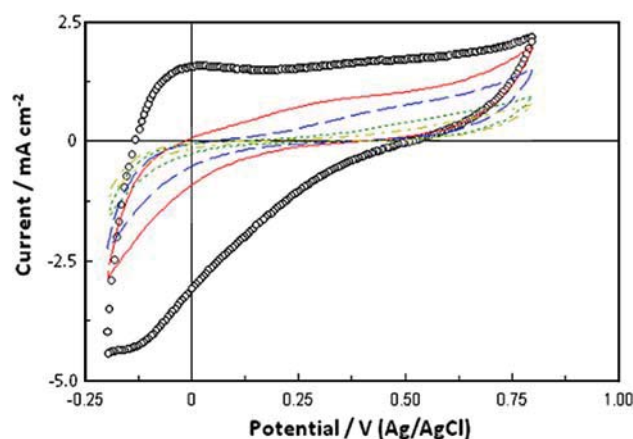


Fig. 9 Cyclic voltammograms recorded for PPy-coated titanium ($1.0 \mu\text{m}$) in 0.2 mol dm^{-3} oxalic acid after exposure to $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ Cr(VI) in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Freshly prepared PPy $\circ\circ$, Experiment 1 —, Experiment 2 - -, Experiment 3 · · ·, Experiment 4 - · - (0, 2, 4, 6 and 22 h of exposure time)

between -0.2 and 0.8 V (Pseudo Ag/AgCl) at a scan rate of 50 mV s^{-1} . For comparison purposes, a voltammogram was also obtained for freshly prepared PPy on titanium. On inspection of Figure 9 it is clear that a reduction in the current values occurs in tandem with the length of the exposure period. The oxidising nature of the Cr(VI) solution contributes to the degradation of the PPy thus, continued exposure can reduce its conducting properties and lead to the reduced current values observed. Although the current values were reduced considerably, the PPy still performed reasonably well obtaining a percentage cleanup efficiency of 93.9% having been exposed to $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ Cr(VI) in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ on three previous occasions for a period of 2 h. Following this series of experiments, the PPy coating was inspected for any signs of physical damage or reduction in its adhesion to the underlying titanium. The coating was found to remain intact and extremely adherent to the underlying titanium.

4 Conclusions

Titanium substrates provide a reasonably inexpensive and resilient substrate for the implementation of PPy coatings in the remediation of Cr(VI) pollution. We found the coated electrodes to be resistant to the acidic Cr(VI) solutions at open-circuit conditions and also suitable for regeneration, allowing a number of Cr(VI) reduction experiments from a single test specimen. Results indicate that the ideal parameters for maximising remediation of Cr(VI) are a combination of thicker PPy coatings, low pre-treatment potential (i.e. -0.8 V) and vigorous solution agitation. Additionally, there is the possibility of forming the PPy coatings on titanium substrates with a rough

surface morphology so as to increase the working surface area and improve the efficiency of the Cr(VI) reduction process at the PPy surface.

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