

The Efficiency of Toxic Chromate Reduction by a Conducting Polymer (Polypyrrole): Influence of Electropolymerization Conditions

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Studies of pollution due to hexavalent chromium are important because it represents a risk to human health and the environment. Hexavalent chromium is a toxic substance and has been found to be carcinogenic. Fortunately, its reduced form, Cr(III), is much less toxic. This paper discusses the remediation Cr(VI) by its reduction in aqueous media by polypyrrole (PPy)-coated reticulated vitreous carbon substrates (RVC). The study is focused on the effect of PPy-film electropolymerization conditions and its efficiency toward the reduction of toxic chromate. We have studied parameters such as the influence of the polymerization electrolyte, the scan rate, the potential limits, and the polymerization cycles concerning the reduction capability of the film. Key results obtained in the present study show that in the presence of different anions during formation of the PPy film, the efficiency of chromate reduction depends on the nature of the anion. We found that the films prepared and treated in the presence of KI performed much better and lasted much longer than those prepared in the presence of KF. Films synthesized at lower scan rates, and higher positive potential limits showed higher chromate reduction efficiencies. Some of our results show reduction of ca. 100% of Cr(VI) from a 10 mg/L solution, even after using the film in 20 contacts with the chromium solution, with films synthesized in KBr and KI electrolytes, at a scan rate of 20 mV/s, between -0.3 and 0.9 V and 40 polymerization cycles. Our study shows that remediation of Cr(VI) by reduction with PPy-coated substrates could be developed into an effective method toward the solution of this problem.

Introduction

Selected properties of conducting polymers make them suitable for a variety of applications. This has made their

production technology and the study of their properties relatively well-known. Novel schemes for environmental remediation applications involving conducting polymers have been proposed. Most of these are based on the use of polypyrrole (PPy) due to its inherent features that include its capacity to form adhesive coatings at different substrates, the possibility of growing it in aqueous media, easiness for chemical substitution to modify its properties, sufficient porosity to enable exchange of ions with the surrounding medium, high electronic conductivity, high chemical stability, thickness controllability, ease of electrochemical polymerization, and good reversibility between its conducting and insulating states (1, 2).

Such properties have led to the proposal of environmental remediation schemes based on the following principles.

(a) Charge Compensation Effects. Ionic pollutants can be concentrated by ion trapping with a PPy matrix and subsequently released by the application of an electric field. Cationic (e.g., M^{n+}) or anionic (e.g., ML^{m-}) species can be removed, depending on the type of ion dynamics dominating in the system (3).

(b) Electrocatalytic Oxidation. An electrocatalyst suitable for the oxidation of pollutants can be incorporated into the PPy matrix to provide befitting oxidation sites. The polymer goes into its reduced (neutral) state and is then regenerated by electrochemical oxidation for reuse (4).

(c) Electrocatalytic Reduction. Electrogenerated PPy (in its oxidized form) is reduced by imposing a negative potential on the substrate electrode. An oxidized pollutant (e.g., chromate ion) is then exposed to the neutral PPy, and spontaneous electron transfer occurs. The (neutral) polymer is then electrochemically regenerated for reuse (5-10).

In this paper we report work in connection to this last application related to the electrocatalytic reduction of Cr(VI) to Cr(III) by polypyrrole.

Chromium(VI) is used in a variety of applications including electrodeposits, steel production, metal finishing, dye production, water cooling, etc. Toxic effects of Cr(VI) moieties are well documented as well as their high mobility in Nature (11). Important amounts of Cr(VI) residues are generated in many parts of the world, which warrant the need for their treatment before discharge. As an example, U.S. regulations have set the following limits for chromium discharges: 170 mg/L of Cr(III) and 0.050 mg/L of Cr(VI) (12) and the U.S. EPA Drinking Water regulations limit total chromium in drinking water to less than or equal to 0.1 mg/L (13). Treatment strategies include biological, physical, chemical, and electrochemical routes. Each one has its own merits and challenges. For example, biological treatment can be limited by the sensitivity of microorganisms to temperature changes, high salinity, and extreme pH (14). Physical treatment of Cr(VI) involves its adsorption on substrates such as activated carbon (15); however, the resulting product must receive further treatment, and normally it amounts to a phase transfer, which does not offer a final solution to the problem. Chemical treatment is generally accomplished by the use of a reducing agent (e.g., sulfite, hydrogen sulfite, metabisulfite, Fe^{2+} , organic materials) which can produce important amounts of sludge and increase the salinity of the wastewater. An alternative involving the use of iron filings has been shown to reduce chromates effectively (16, 17). Electrochemical treatment by direct reduction of Cr(VI) to Cr(III)—which is much less toxic and can be easily made insoluble as $Cr(OH)_3$ —suffers from slow kinetics that require a considerable amount of energy (i.e., high electrode potentials). For

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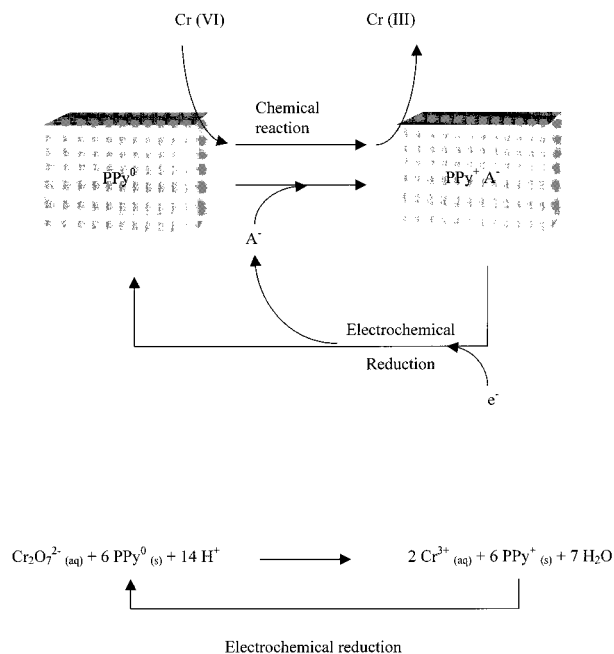


FIGURE 1. Process for the reduction of hexavalent chromium with polypyrrole. Note that the final removal of the Cr(III) produced is not addressed here.

example, only 51% of chromate in water was reduced and deposited after 10 cycles of electrochemical reduction on a reticulated vitreous carbon electrode (18). A 100% reduction in a 60 mg/L Cr(VI) solution has been reported, albeit at quite high potentials (-1.3 V vs SCE) (19).

Recently, a new concept has been proposed in which a conducting polymer (polypyrrole, PPy) is electrochemically synthesized in its positive (oxidized, conducting) state (5, 20). Then, it is subject to a negative potential as to reversibly transform it to its neutral (reduced, insulating) state and then placed in contact with a chromate solution (5–8). A spontaneous electron transfer occurs from the polymer to the Cr(VI) reducing it to Cr(III). (For a mechanistic scheme, see Figure 1). At the same time, the polymer becomes oxidized, and an anion (A^-) diffuses into the positively charged polymer matrix to accomplish charge compensation. Upon reduction of the polymer, the anion is ejected from the matrix into a different (smaller volume) solution, and the whole cycle can be initiated again. The behavior of PPy films is known to be strongly dependent upon the polymerization conditions, and this can also affect the proposed Cr(VI) electrocatalytic reduction process (7, 21, 22).

The efficiency of PPy films deposited on microelectrodes for the reduction of Cr(VI) has been investigated and demonstrated (8, 23). For porous matrices, high reduction percentages of Cr(VI) (ca. 90%) were obtained (7). In the present study we focus on the influence of anions (I^- , Br^- , Cl^- , F^- , NO_3^- , SO_4^{2-}) and other experimental conditions used during the preparation of PPy films on the Cr(VI) reduction process. We have previously investigated the influence of the number of potential cycles used during the preparation of PPy on the percentage of chromate reduction in synthetic solutions (7), which can also lead to a better understanding of the factors involved in PPy film durability.

Experimental Section

The detailed experimental sequence is shown in Figure 2. Conditions reported earlier give an indication of the key parameters for the present application (7). PPy films were synthesized in 0.1 M solutions of pyrrole (Sigma) by applying

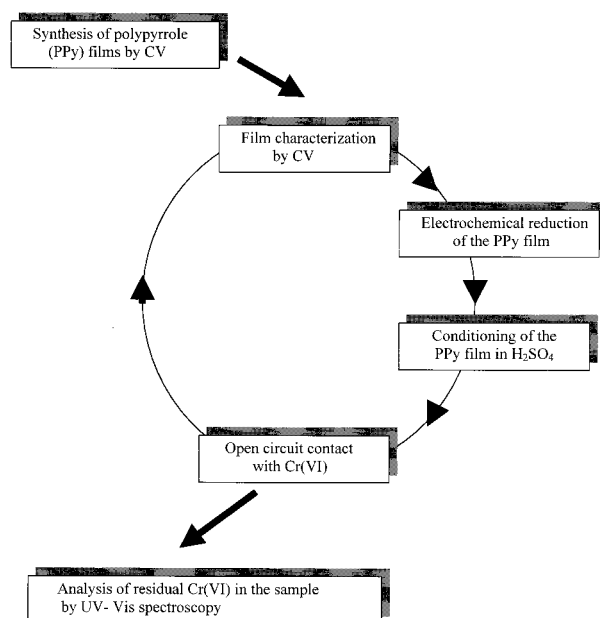


FIGURE 2. Experimental scheme used for the reduction of hexavalent chromium.

different numbers (10, 20, 30, and 40) of successive potential scan cycles carried up to different potential limits (-0.2 to 0.8 V and -0.3 to $0.9 \text{ V vs Saturated Calomel Electrode, SCE}$) and with different potential scan rates (20 and 100 mV/s). (Note: to convert the SCE values to the Standard Hydrogen Electrode values, SHE, simply add 0.2415 V). Experiments were performed at room temperature ($22 \pm 2 \text{ }^\circ\text{C}$) in the presence of 0.1 M solutions of the following salts: KI, KBr, KCl, K_2SO_4 , KNO_3 , KF (J. T. Baker). The chromate solutions and the sulfuric acid solution were prepared with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 also from J. T. Baker. Deionized water was used throughout all the experimentation.

The polymeric films were grown on reticulated vitreous carbon substrates (RVC) of 100 ppi (pores per inch) of dimensions $1 \times 1 \times 0.6 \text{ cm}$ (RVC-100), supplied by the Electroynthesis Co., U.S.A. A saturated calomel electrode (SCE) was used as the reference electrode throughout this study, and a graphite rod (Johnson Matthey) was used as the auxiliary electrode. A homemade potentiostat-galvanostat, coupled to a 200 XY Houston Instruments recorder, was used. Cr(VI) concentrations were measured with a Spectronic Array 3000 UV-vis spectrophotometer using the standard method of the diphenylcarbazide (24).

The quality of the PPy films was characterized electrochemically by obtaining cyclic voltammograms (CV) in the same (monomer-free) electrolyte as it was used for the film formation. Then, the films were "activated" by subjecting them to a potential of -0.9 V for 15 min in the same electrolyte, and then they were immersed in a 0.1 M H_2SO_4 solution for 1–2 min in order to permit equilibration of the PPy film with an acidic medium before contacting with the chromate solution. Last, the films supported on the RVC were placed in contact (in a batch mode) with 10 mL of a Cr(VI) solution (10 mg/L in 0.1 M H_2SO_4) for 2 h in a 20 mL reaction vessel. After each contact (hereby termed a *reduction cycle*), a cyclic voltammogram was again performed on the PPy film as to verify whether the quality of the polymer films was sufficient for further cycling. When the obtained area in the resulting voltammetric curve decreased to less than 10% of the original area, the film was discarded, and a new one was prepared for further testing. The resulting Cr(VI) concentrations were then measured as described earlier.

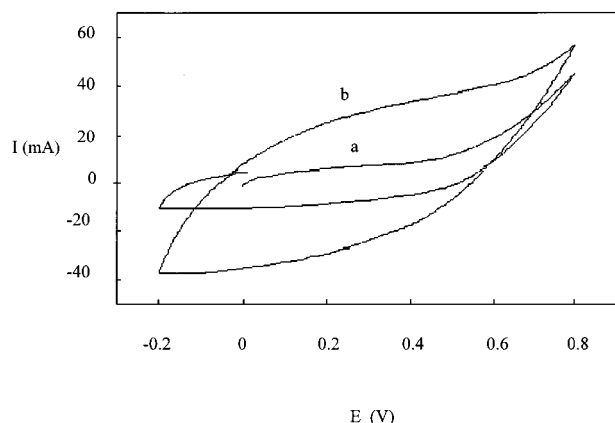


FIGURE 3. Typical voltammogram obtained during the polymerization of pyrrole: (a) first cycle and (b) 40th cycle. Conditions: -0.2 to 0.8 V/SCE, 0.1 M pyrrole in 0.1 M KBr, 100 mV/s.

Results and Discussion

(a) Cyclic Voltammetry of Polypyrrole Film Polymerization.

Figure 3 shows a typical PPy polymerization voltammogram on an RVC electrode in a KBr medium, in a potential interval of -0.2 to 0.8 V vs SCE obtained with a scan rate of 100 mV/s. Curve (a) shows the first polymerization cycle (with oxidation of the monomer) where polymerization is initiated at around 0.6 V. Curve (b) represents the 40th polymerization cycle, where a relatively large current is observed due to the oxidation–reduction of the formed polymer. Polymerization of PPy in the presence of other anions shows voltammograms of similar shape but with currents strongly dependent on the nature of the anion. This issue will be discussed at a later stage in this paper.

(b) Kinetics of Cr(VI) Reduction by PPy Films. Figure 4 shows an example of reduction kinetics of Cr(VI) with a PPy film synthesized on an RVC electrode in a chloride-containing medium. In this figure, the residual amount of Cr(VI) vs time of PPy film contact with Cr(VI) solution is plotted. It can be seen that most of the reaction occurs during the first hour. This result is in agreement with literature reports (8) where a pseudo-first-order reaction for the same process was demonstrated. We also found that reaction time is practically

independent for different anions used during the polymerization stage.

(c) Cr(VI) Reduction Efficiency as a Function of Electrochemical Conditions of PPy Film Polymerization. Figure 5 shows the influence of the number of potential scan cycles during polymerization on the efficiency (percentage) of chromate reduction. The PPy films for these experiments were prepared in a chloride medium utilizing 10, 20, 30, and 40 polymerization cycles, respectively. Each PPy film was exposed to the Cr(VI) solution up to 10 times (10 contacts). With PPy films formed by 40 polymerization cycles, an almost complete chromate reduction was observed even after 10 reduction cycles. When a smaller number of polymerization cycles was used, the percentage of reduction decreased considerably, both in the first and subsequent cycles. This clearly indicates a limited capacity (ability) of PPy films for the Cr(VI) reduction process. Note that based on our previous knowledge and literature reports, an increase in the polymerization cycles means an increase in polymer thickness (7). For example, PPy films prepared by using only 10 cycles are only capable of reducing about 20% of the Cr(VI) present in the solution during the first contact with the Cr(VI) solution. Also, we found that the efficiency of these PPy films decreases rapidly, and after six contacts with a new Cr(VI) test solution the polymeric films appear to be exhausted. For this reason, all the PPy films in this study were grown using 40 polymerization cycles (unless stated otherwise).

To investigate the influence of different anions used in the polymerization process upon the efficiency of chromate reduction by PPy and to determine the durability of PPy films, we extended the number of reduction cycles up to 20. Of the six anions tested, five gave quite high reduction percentages even after 20 reduction cycles. See Table 1. Fluoride was the only anion that yielded PPy films with an extremely low capacity toward Cr(VI) reduction (about five times smaller than the others), which was the first indication that the nature of anions could also play an important role in this process.

Since it is well-known that polymer properties depend on the anodic polymerization potential limit (25, 26), we also investigated its possible influence on the chromate reduction efficiency. To this end, PPy polymerization was performed using two sets of potential scan ranges: (a) -0.2 to $+0.8$ V and (b) -0.3 to $+0.9$ V. The percentages of reduction

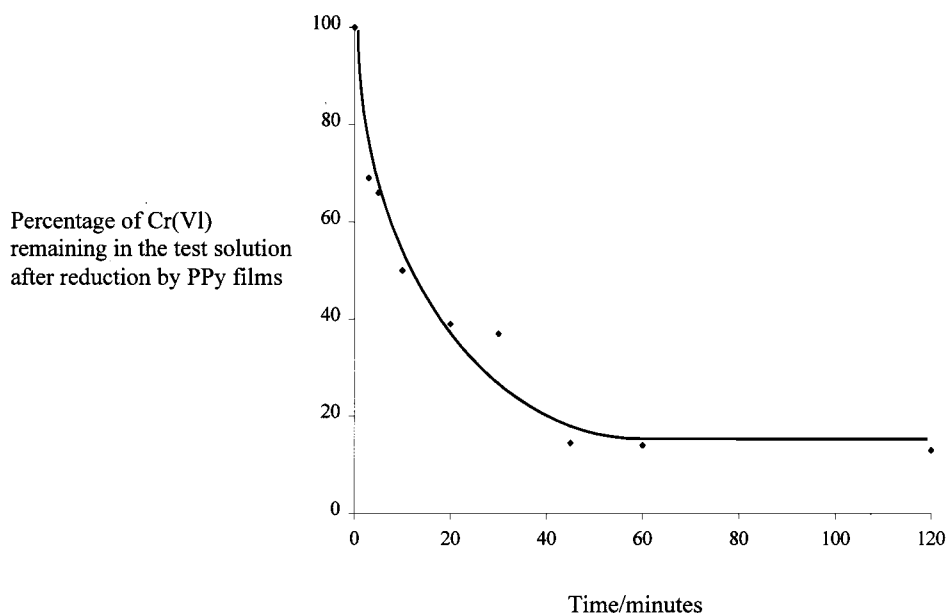


FIGURE 4. Variation of the percentage or reduction of Cr(VI) as a function of contact time between the hexavalent chromium solution and the polymer: 30 polymerization cycles. Conditions: -0.3 to 0.9 V, 20 mV/s, 10 mg/L of Cr(VI).

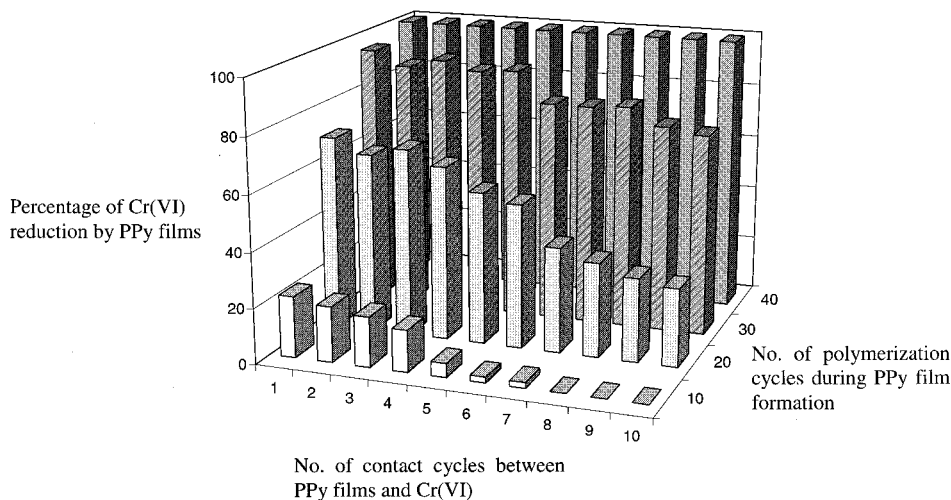


FIGURE 5. Variation of the percentage or reduction of Cr(VI) as a function of the number of cycles for polymerization and the number of contacts with a hexavalent chromium solution. Conditions: -0.3 to 0.9 V/ESC, 20 mV/s, 10 mg/L of Cr(VI).

TABLE 1. Percentage of Reduction of Cr(VI) by PPy after 20 Cycles as a Function of the Electrolyte Utilized in the Electrosynthesis^a

electrolyte	percentage of Cr(VI) reduction	electrolyte	percentage of Cr(VI) reduction
KI	100	KNO ₃	100
KBr	100	KCl	90
K ₂ SO ₄	100	KF	20

^a The films were synthesized at 20 mV/s and -0.3 to 0.9 V. The concentration of Cr(VI) was 10 ppm.

TABLE 2. Effect of the Anodic Potential upon the Percentage of Reduction of Cr(VI) after the First Cycle^a

electrolyte	anodic potential (V)		electrolyte	anodic potential (V)	
	0.8	0.9		0.8	0.9
KI	85%	100%	KClO ₄	32%	100%
KBr	78%	100%	K ₂ SO ₄	27%	100%
KNO ₃	70%	100%	KF	15%	18%
KCl	38%	100%			

^a The films were prepared at 100 mV/s and the concentration of Cr(VI) was 10 mg/L.

obtained during the first contacts are shown in Table 2. As can be seen, the narrower potential limit used during film formation yielded lower percentages of reduction. Again, films grown in the presence of fluoride ions gave the lowest yields during this first cycle. However, since literature reports show that at higher anodic potential limits the growth of PPy can be accompanied by a polymer overoxidation process (which would certainly change PPy properties and even cause film damage), we then proceeded our evaluation under the narrower potential range (-0.2 up to $+0.8$ V). Although the overoxidized polymer shows higher efficiency for Cr(VI) reduction, we decided to perform experiments in the narrower potential range to avoid possible ambiguity in the interpretation of results. (The issue of the influence of polymer overoxidation process on the Cr(VI) reduction efficiency is under further investigation in our laboratories).

An additional factor that influences the percentage of chromate reduction is the polymerization scan rate used during film formation (7). For example, PPy films prepared in 0.1 M KI solution and grown at scan rates of 20 or 100 mV/s show different efficiencies for Cr(VI) reduction. For

example, films prepared at 20 mV/s gave ca. 100% efficiency even after 20 contacts with Cr(VI) test solutions (see Table 1), while films prepared at faster polymerization scan rates (i.e., 100 mV/s) show only ca. 40% chromate reduction after just 12 cycles. With reference to our previous results obtained only in KCl electrolyte, these new results with six different anions show that independently of the anion used during polymerization, higher chromate reduction efficiencies are obtained at slower scan rates. This scan rate effect has been interpreted as being the result of a better chain rearrangement during the slower polymerization that results in thicker, better conducting, and better reducing films (7).

Preliminary experiments performed with PPy films grown in the presence of bromide ions and exposed to higher chromate concentrations (i.e., 100 mg/L, which is 200 times higher than that permitted by the EPA) (12), such as those that can be expected from electroplating and metal finishing applications, show the same order of reduction efficiencies.

(d) Influence of Anions on PPy Formation and Its Cr(VI) Reduction Ability. To test the influence of anions on the PPy formation process and its ability for Cr(VI) reduction, PPy was prepared under identical conditions in 0.1 M solutions of several potassium salts (I^- , Br^- , Cl^- , F^- , NO_3^- , ClO_4^- , SO_4^{2-}). Each film was exposed eight times to the Cr(VI) solution. A new Cr(VI) solution (10 mg/L) was used for each contact. As above, PPy films were regenerated ("activated") at a cathodic potential of -0.9 V in the appropriate electrolyte between contacts. The results are shown in Figure 6. These show that the efficiencies for Cr(VI) reduction are quite different. The highest efficiency in the first and the 8th cycle was obtained with polymers prepared in KI solution. The lowest efficiencies were observed with the KF solution. KI and KBr show the highest efficiencies during the eight cycles, and therefore seem to be the best electrolytes for PPy preparation for Cr(VI) reduction. In the case of KNO₃, the efficiency is very high in the first two cycles (ca. 70%) but rapidly decreases. KCl, KClO₄, K₂SO₄, and KF belong to the lower yield group with efficiencies in the first contact cycles below 40% , which makes them unsuitable for any technological proposal.

As can be deduced from the above results, several factors influence the final efficiency of chromate reduction, and they seem to be related to polymer properties. For example, it is well-known that conformational changes during the polymer doping process can translate into volume changes as a result of changes in the applied potential (27–30). During the application of a cathodic potential, the positive sites within the polymer are neutralized, and the counterions are expelled

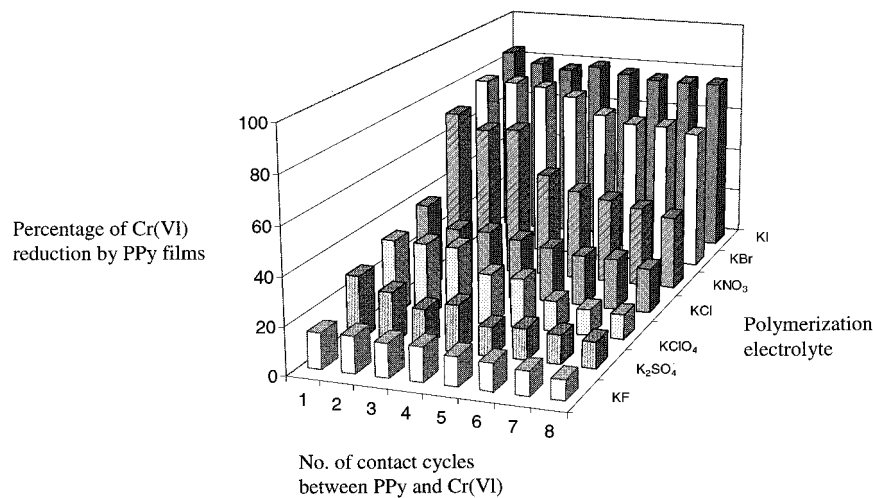


FIGURE 6. Variation of the percentage or reduction of Cr(VI) as a function of the number of contacts for PPy films synthesized in different electrolytes (KI, KBr, KNO₃, KCl, KClO₄, K₂SO₄, KF). Conditions: -0.2 to 0.8 V/SCE, 100 mV/s, 10 mg/L of Cr(VI).

from the polymer matrix. As a result, the polymeric chains undergo a rearrangement occupying the interstitial spaces left by the counterions, provoking a closure of the polymeric network and making it more compact (30). The application of an anodic potential induces a reopening or relaxation of this network and a channeling process can occur. The counterions are then allowed into the network again, and the volume increases. In view of this, we postulate that the counterion (anion) volume can play an important role in the entire process, including doping and diffusion. In fact, when the halide ion series used in our experiments is analyzed in more detail, it is found that the sizes of the hydrated ions ($F^- > Cl^- > Br^- > I^-$) (31) exactly follow the inverse of the order of chromate reduction, as can be observed in Figure 6. When the entire anion series used in this study is analyzed, the same trend is observed since those with larger hydrated radii (F^-, SO_4^{2-}, ClO_4^-) show lower reduction yields than those with smaller radii (Cl^-, NO_3^-, Br^-, I^-) (32). This clearly shows that the size of anions—and more precisely, the size of hydrated radii—is related to the chromate reduction efficiency, since larger anions are more difficult to transport in and out of the porous polymer. Further research is needed to establish the exact relationship between polymer porosity, anion size, and the anion exchange mechanism.

When a wider potential range (with a higher anodic limit) is used, the percentages of chromate reduction increase possibly due to a greater number of positive sites available to be neutralized by the chromate and other anions as well as a better access through the channels mentioned earlier and a greater relaxation of the polymeric network. Following this logic, the possibly trapped anions with smaller hydrated radius can have higher mobility and can significantly increase the efficiency of chromate reduction. This is in fact the case for the halide series, as shown in Figure 6.

To further test the difference in using different anions, we devised the following experiment. We produced a PPy film in a 0.1 M sulfate solution and subjected it to several successive reduction cycles as described above. After the 4th–5th reduction cycles, the efficiency of Cr(VI) reduction decreased to less than 50%. Before the 6th cycle, the PPy was regenerated in an iodide medium instead of the original sulfate medium. The idea behind this change of anions was to replace the sulfate ions with iodide ions, since PPy grown in iodide ions was shown earlier to give better reduction percentages than the rest of the anions tested. Indeed, this worked well since a considerable increase in chromate reduction was observed after the 6th cycle (about 90%, see Figure 7). This means that the presence of iodide as a

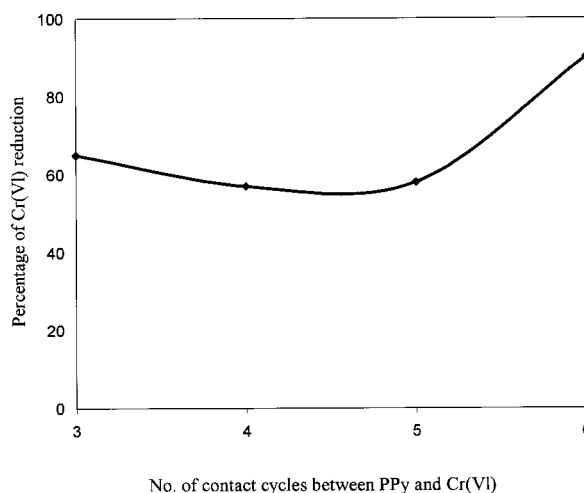


FIGURE 7. Variation of the percentage or reduction of Cr(VI) as a function of the anion utilized for PPy regeneration. PPy was synthesized and regenerated the first four cycles in K₂SO₄ and the fifth cycle in KI. Conditions: -0.3 to 0.9 V/SCE, 100 mV/s and 10 mg/L of Cr(VI).

counterion in the polymer matrix leads to an increase in the efficiency for Cr(VI) reduction. To discard the possibility of iodide adsorption effects (i.e., iodide on the electrode surface) we performed a separate experiment in which the bare electrode (i.e., RVC without polymer) was exposed to dissolved iodide ions and then subjected to the routine described above for chromate reduction; no chromate ions were reduced as a result of this procedure. We then conclude that the nature of the anion used during the growth of PPy exerts a considerable influence on the chromate reduction efficiency. In the case of iodide ions, the low standard potential of the I₂/I⁻ couple (0.62 V) (33) as compared to the other halogens is also likely to play a key role in the high percentage of chromate reduction.

Continuous-flow experiments in larger cells with synthetic and real wastewater samples are under investigation in order to evaluate the possibility of scaling-up this proposed remediation scheme.

Our study then demonstrates that the choice of anion used during the preparation of the PPy film and the positive potential limit during the electrosynthesis process have a dramatic influence on the polymer film efficiency toward chromate reduction. Films prepared using positive potential limits (i.e., +0.9 V) and prepared with anions with smaller

hydration radius (e.g., iodide or bromide) showed the highest chromate reduction efficiencies. Further work is required to fully understand all the factors involved and their interplay. In addition, the physical stability of the films grown in different electrolytes can be of importance and requires further study. In addition, the resistance to degradation of the PPy films (especially upon exposure to high chromate concentrations) must be considerably increased before they can be proposed for large scale, economically viable applications. Finally, in a similar fashion as most of the commonly used chromate reduction schemes, this process requires the additional removal of the Cr(III) species produced (normally by precipitation of the corresponding hydroxide). Although this step requires further investigation, no serious problems are anticipated in its achievement.

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Literature Cited

- (1) *Electrochemistry: Science and Technology of Polymers*; Linford, R. G., Ed.; Elsevier: Amsterdam, 1987; Vol. 1.
- (2) *Handbook of Conducting Polymers*; Skotheim, T., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 265.
- (3) Hepel, M.; Dentrone, L. *Electroanal.* **1996**, *8*, 996.
- (4) Hwang, B. J. *J. Appl. Electrochem.* **1996**, *26*, 153.
- (5) Wei, Ch.; German, S.; Basak, S.; Rajeshwar, K. *J. Electrochem. Soc.* **1993**, *140*, L60.
- (6) Yun, W.; Rajeshwar, K. *J. Electroanal. Chem.* **1997**, *425*, 183.
- (7) Alatorre, M. A.; Gutiérrez, S.; Páramo, U.; Ibanez, J. G. *J. Appl. Electrochem.* **1998**, *28*, 551.
- (8) Senthurchelvan, R.; Wang, Y.; Basak, S.; Rajeshwar, K. *J. Electrochem. Soc.* **1996**, *143*, 44.
- (9) Fernández, L. F.; Ibanez, J. G.; Rajeshwar, K.; Basak, S. *189th Meet. Electrochem. Soc.* Los Angeles, CA, May 5–10, 1996.
- (10) Rajeshwar, K.; Swain, G. M.; Ibanez, J. G. *J. Appl. Electrochem.* **1994**, *24*, 1077.
- (11) Katz, F.; Salem, H. *The Biological and Environmental Chemistry of Chromium*; VCH Publishers: New York, 1994; pp 51–58.
- (12) U.S. EPA. Report No. EPA/570/9-76/003; Washington, DC, 1976.
- (13) Patterson, R. R.; Fendorf, S.; Fendorf, M. *Environ. Sci. Technol.* **1997**, *31*, 2039.
- (14) Metcalf & Eddy, *Wastewater Engineering. Treatment, Disposal and Reuse*, 3rd ed.; Tchobanoglous, G., Burton, F. L., Ed.; Rev. McGraw-Hill: New York, 1991; Chapter 8.
- (15) Leyva, R.; Juarez, A.; Guerrero, R. *Water Sci. Technol.* **1994**, *30*, 191.
- (16) Pratt, A. R.; Blowes, D. W.; Ptacek, C. J. *Environ. Sci. Technol.* **1997**, *31*, 2492.
- (17) Powell, R. M.; Puls, R. W.; Hightower, S. K.; Sabatini, D. A. *Environ. Sci. Technol.* **1995**, *29*, 1913.
- (18) Agarwal, I. C.; Rochon, A. M.; Gesser, H. D.; Sparling, A. B. *Water Res.* **1984**, *18*, 227.
- (19) Abda, M.; Gavra, Z.; Oren, Y. *J. Appl. Electrochem.* **1981**, *21*, 734.
- (20) Rajeshwar, K.; Ibanez, J. G. *Environmental Electrochemistry. Fundamentals and Applications in Pollution Abatement*; Academic Press: San Diego, CA, 1997; pp 454–458.
- (21) Fermín, D. J.; Mostany, J.; Scharifker, B. R. *Curr. Topics Electrochem.* **1993**, *2*, 131.
- (22) Stankovic, R.; Pavlovic, O.; Vojnovic, M.; Jovanovic, S. *Eur. Polym. J.* **1994**, *30*, 385.
- (23) Wang, Y.; Rajeshwar, K. *J. Electroanal. Chem.* **1997**, *425*, 183.
- (24) AWWA, APHA, WPCF. *Standard Methods for the Examination of Water and Wastewater*. APHA-AWWA-WEF 17th ed.; Baltimore, MD, 1995; pp 3–59.
- (25) Páramo, U.; Ibanez, J. G.; Guzmán P. J.; Batina, N. *Proceedings of the XII National Congress of the Mexican Electrochemical Society*; Guanajuato, Mexico, Jun 1997; p 247.
- (26) Thiéblemont, J. C.; Gabelle, J. L.; Planche, M. F. *Synth. Met.* **1994**, *66*, 243.
- (27) Inzelt, G.; Day, R. W.; Kinstle, J. F.; Chambers, J. Q. *J. Phys. Chem.* **1988**, *92*, 4592.
- (28) Pei, Q.; Inghanas, O. *J. Phys. Chem.* **1993**, *97*, 6034.
- (29) Otero, T.; Grande, H.; Rodríguez, J. *Electrochim. Acta* **1996**, *41*, 1863.
- (30) Otero, T.; Grande, H.; Rodríguez, J. *Synth. Met.* **1996**, *83*, 205.
- (31) Markus, Y.; Kertes, A., *Ion Exchange and Solvent Extraction of Metal Complexes*; Wiley-Interscience: London, 1969, 28.
- (32) Nightingale, R. E. *J. Phys. Chem.* **1959**, *63*, 1381.
- (33) Lagrega, M.; Buckingham, P.; Evans, J. *Hazardous Waste Management*; McGraw-Hill: Singapore, 1994; p 512.

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