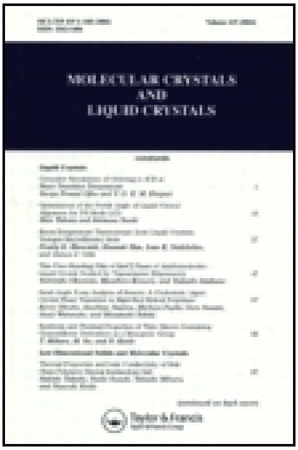


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Reduction of Cr(VI) Using Polyaniline-Polystirene-Divinyl Benzene Gels

Ramona Rad [a], Nicoleta Pleşu [a], Adriana Popa [a], Smaranda Iliescu [a], Lavinia Macarie [a], Aurelia Pascariu [a], Gh. Dehelean [a] & Liliana Pacureanu [a]

[a] Institute of Chemistry Timişoara, Romanian Academy, 24 Mihai Viteazul Ave., Romania

Version of record first published: 18 Oct 2010

To cite this article: Ramona Rad, Nicoleta Pleşu, Adriana Popa, Smaranda Iliescu, Lavinia Macarie, Aurelia Pascariu, Gh. Dehelean & Liliana Pacureanu (2004): Reduction of Cr(VI) Using Polyaniline-Polystirene-Divinyl Benzene Gels, Molecular Crystals and Liquid Crystals, 418:1, 1-9

To link to this article: http://dx.doi.org/10.1080/15421400490478623

Mol. Cryst. Liq. Cryst., Vol. 418, pp. 1/[729]–9/[737], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490478623

REDUCTION OF CR(VI) USING POLYANILINE–POLYSTIRENE-DIVINYL BENZENE GELS

Ramona Rad, Nicoleta Pleşu, Adriana Popa, Smaranda Iliescu, Lavinia Macarie, Aurelia Pascariu, Gh. Dehelean, and Liliana Pacureanu
Institute of Chemistry Timişoara, Romanian Academy, 24 Mihai Viteazul Ave., Romania.

Wastewaters generated by electroplating, Industry of Pigments, Tannins, etc. contain Cr(VI).

The removal of Cr(VI) from wastewaters is necessary due to its toxicity; the admissible concentration being 10 ppm.

This work studies quantitatively and qualitatively the possibility of treating waste waters that have a concentration of 0.1 g/l Cr(VI), by using DVB gels coated with Pani films.

The Pani films were applied on the DVB's surface both by polymerization of aniline in acid medium, using ammonium peroxodisulphate as the oxidizing agent and by treating the DVB gels with Pani solutions in N,N-dimethylformamide.

During reaction, the reduction rate of Cr(VI) decreases because the Pani films are degrading. This degradation is generated by over-oxidation, phenomenon that leads to a series of secondary hydrolysable products.

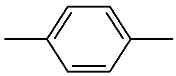
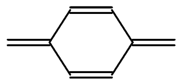
Keywords: hexavalent chromium reduction; polyaniline; polyaniline composite

INTRODUCTION

The study of conductive polymers has become a part of modern material science due to the possible technological applications. Conductive polymer composites are obtained by combining an insulating polymer or copolymer with an intrinsically conductive polymer. The most commonly used conductive polymers are polyaniline, polypyrrole, polythiophene and their derivatives. These polymers are easily synthesized and have great environmental

Address correspondence to Nicoleta Pleşu, Institute of Chemistry Timişoara, Romanian Academy, 24 Mihai Viteazul Ave. E-mail: plesu_nicole@yahoo.com

$$4x\ B - NH_2 \rightarrow -[(B\text{-}NH\text{-}B\text{-}NH)_y(B\text{-}N{=}Q{=}N)_{1-y}]^{n-}_x \quad +4xH^+ +4e^-$$

B:  ; Q : 

SCHEME 1

stability. Preparation includes mechanical mixing, casting a solution containing the components or the polymerization of one polymer into the other [1,6].

Polyaniline (Pani) is one of the most promising conductive polymers, due to electrical conductivity of doped and protonated forms and thermal stability, and it can be obtained in a relatively easy manner.

Electronically conductive Pani is a 1-4 coupling product of aniline in acid media, and belongs to a class of polymers having main chains consisting of a succession of reduced benzene nucleus B and oxidized quinoid nucleus Q (Scheme 1):

In fact, formed polymer is a mixture of polyanilines in different oxidation states (leucoemeraldine – light yellow, emeraldine – green and conductive, pernigraniline – violet) and the (1-y) oxidation state, can be continuously modified, beginning from 0, for the entire reduced polymer (a), to 0.5 when it forms the half oxidized polymer (b) or to 1 for the entire oxidized polymer (c).

The properties of this polymer depend on the synthesis method (chemical or electrochemical) and the work conditions. The conductivity of polyaniline is a result of the delocalised π electrons, and the possibility of them participating to internal acid-basic reaction [3].

In order to increase the weak processability of polyaniline, the polymers are usually dispersed or absorbed into a convenient substrate [4].

The aim of this work has been the obtainment of a composite polyaniline-Dowex1 (polyaniline-polystirene-divinylbenzene gels), and the possibility of using this composite for the reduction of hexavalent chromium to trivalent chromium, a less toxic species [9].

EXPERIMENTAL

Materials

The characteristics of reactants are presented in Table 1.

The Pani-composite was obtained using a solution of Pani-EB in DMF, by absorption onto Dowex1. The quantity of the absorbed polyaniline was

TABLE 1 Characteristics of the Reactants

Substance	Characteristics	Observations
Strong base anion type I exchanger trimethylammonium Dowex1	d = 0,72 g/cm^3 water content 68–77%	Fluka AG PS-2–7% DVB gel
Sulfuric acid, H_2SO_4	M = 98 g/mol ρ = 1,84 kg/l purity of 97%	"Chimactiv SRL" Bucureşti p.a.
Polyaniline emeraldine (Pani-EB) base	Inherent viscosity = 0,850 dl/g ρ = 1,228 g/cm^3 χ = 9,71.10^{-9} S/cm	Prepared in laboratory according to [7]
N,N-dimethylformamide (DMF)	M = 73,09 d = 0,945 g/cm^3 t_f = 153°C $n^{20}{}_D$ = 1,4303	Janssen Chimica
Potassium dichromate $K_2Cr_2O_7$	M = 294,14 Content min. 99,8%	Reactivul Bucureşti

calculated from UV-VIS data. The method was based on having a known quantity of Dowex1, in a solution of Pani-EB in DMF of known concentration. We chose, based on the experimental data, a Pani-EB/Dowex1, 1/0.3 weight ratio, a time treatment equal to 20 hours under stirring (600 rot/min.). After absorption, the composite was filtrated and washed on funnel with distilled water ($5 \times 25\,cm^3$), and ethanol ($3 \times 20\,cm^3$), and dried at 50°C, 24 hours under remanent pressure of 2 kPa. The quantity of absorbed polyaniline was calculated based on etalon curves, obtained from solutions with known concentrations and Lambert-Beer relation.

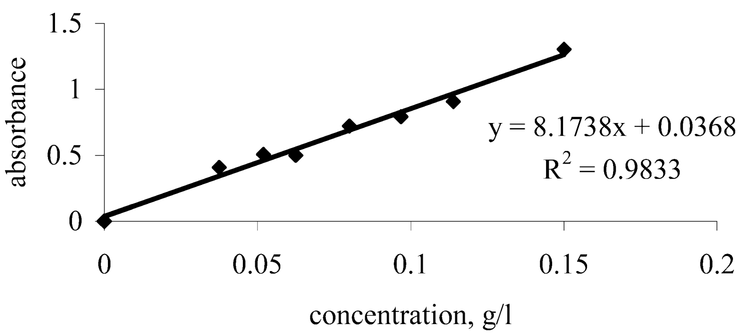


FIGURE 1 The etalon curve of the Pani-EB solutions in DMF.

For the reduction of hexavalent chromium Cr(VI) to trivalent chromium Cr(III), potassium dichromate solutions with concentrations of 10, 20, 40 and 50 mg/l and adjusted to pH = 2 with chlorhidric acid, were used. In order to increase the yield of reduction process and to extend the life of the composite, we have chosen a stepwise process, which allows the recycling of the solution. The working temperature was 21° ± 1°C. The residual concentration of Cr(VI) was determined from iodometric titration [8].

The UV-VIS spectra of Pani, were recorded using a spectrophotometer Specord Cecille 7200. After the reduction process, the Pani from composite was extracted with NMP (N-methylpyrrolidone) for 6 hours and the resulting solution was analysed. The thermal analyses of composite samples were performed with TG 209, from Netszch in nitrogen atmosphere with the heat rate of 25° K/min, in range 20° to 990°C.

RESULTS AND DISCUSSIONS

The etalon curve, based on the absorption values of solutions with known concentrations of Pani-EB in DMF, is presented in Figure 1.

Using the etalon curve, the percentage of Pani-EB in the composite was calculated. The experimental data is presented in Table 2.

After drying, the composite was used to reduce the Cr(VI) to Cr(III). The experiments were performed at room temperature. Figure 2 shows the reaction rate of Cr(VI) using composite Pani-Dowex1, without recycling the resulting solution.

A faster rate of reduction is observed in the beginning of the process, when the oxidation processes take place. In time, the Pani suffers a degradation process due to the oxidation, and the reaction rate decreases. With the increase of concentration of Cr(VI) in water, the reduction rate decreases faster, and the residual Cr(VI) concentration remains over the 0.1 mg/l, which is above the required limit.

In Table 3 the experimental condition for the reduction of Cr^{6+} to Cr^{3+} are presented, using Pani-Dowex1 composite, in a stepwise process, which allows the recycling of the solution.

TABLE 2 Experimental Data for Obtaining the Pani-Dowex1 Composite

$C_{initial}$ Pani, (g/l)	Dowex1, g/l	Weight ratio Dowex1/PAni	λ (nm)	$C_{remanent}$ Pani, (g/l)	Absorption yield, %	% Pani in composite
3.2	100	10/32	622	0.19	94.06	2.92

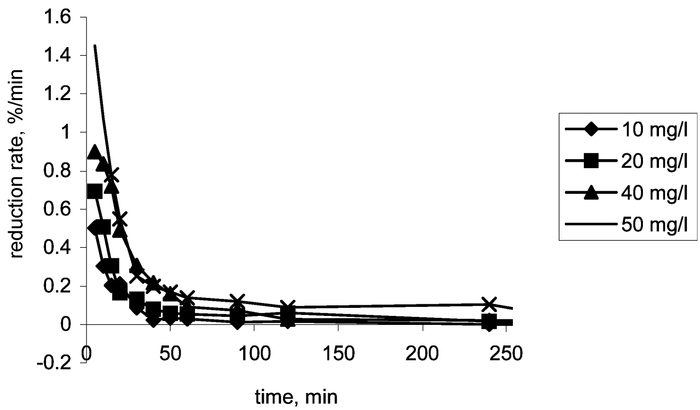


FIGURE 2 Reaction rate of chromium (VI), using Pani-Dowex1 composite, without recycling the resulting solution.

After the first cycle, the concentration of Cr(VI) decreases, the yield of reduction depends on the initial concentration of Cr(VI) in solution, and the maximum yield (67,5%) was obtained for 10 mg/l $K_2Cr_2O_7$ (Fig. 3).

The residual concentration in Cr (VI), after the first cycle, was greater than the required limit of concentration, and requires more cycles of reduction. Figure 4 shows the variation of residual concentration of Cr(VI) depending on the number of reduction cycles, and the initial concentration of potassium dichromate in water.

Experimental data shows a decrease of Cr(VI) with the increase of the number of cycles. In order to obtain the required remanent concentration of Cr(VI) under 0.001 mg/l, between 6 and 8 cycles are needed, depending on the initial concentrations of dichromate solutions. The reduction yield of Cr(VI) was over 98%.

TABLE 3 Experimental Conditions for the Reduction of Cr^{6+} to Cr^{3+} Using Composite Pani-Dowex1

No.	Working temperature [°C]	$K_2Cr_2O_7$/Pani composite weight ratio*	Initial concentration of $K_2Cr_2O_7$ solutions, mg/l	Total volume of recycled solution, l
1	21° ± 1°C	0.01/3	10	1.0
2		0.02/3	20	1.0
3		0.04/3	40	1.0

*calculated based on Pani-EB quantity in composite.

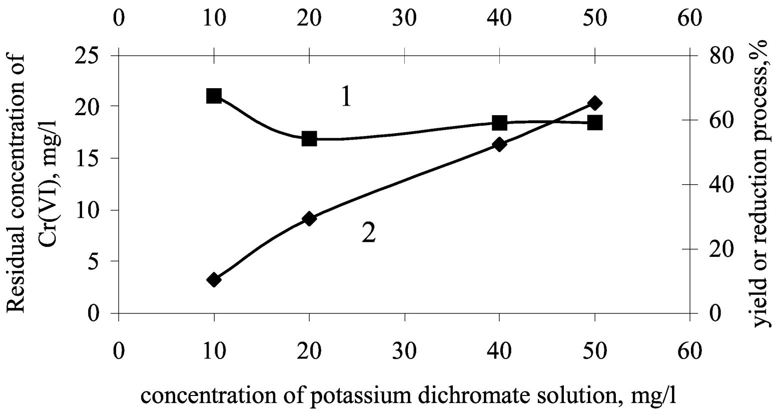


FIGURE 3 Variation of the residual Cr(VI) (curve 2) using composite Pani-Dowex1 and yield of the reduction process (curve 1) depending on the concentration of potassium dichromate in solution.

After the reduction, the UV-VIS spectra of the Pani-solution (Table 4), indicate a decrease of absorption peak at 330 nm, due to a decrease in the number of benzene rings, and an increase of absorption peak at 620 nm, due to the an increase in the number of quinoid rings in polymer chain.

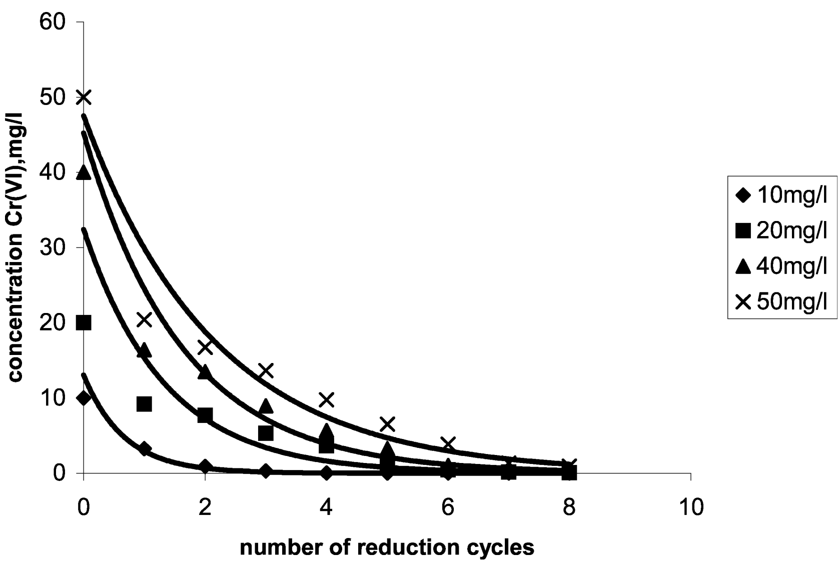


FIGURE 4 Variation of residual Cr(VI) using composite Pani-Dowex1 with number of reduction cycles and concentration of potassium dichromate in solution.

TABLE 4 UV-VIS Data for Pani Removal from Composite After Reduction Process

	(I_Q)			(I_B)			$(I_Q)/(I_B)$	
		A			A			
$C_{initial}$ $K_2Cr_2O_7$, (mg/l)	λ, nm	Without recycling	With recycling*	λ, nm	Without recycling	With recycling*	Without recycling	With recycling*
0	621	0.904	0.904	338	0.985	0.985	0.89	0.89
10	620	1.256	0.987	332	0.745	0.972	1.69	1.02
20	620	1.325	1.023	330	0.725	0.945	1.83	1.08
40	618	1.124	1.085	330	0.356	0.940	3.16	1.15
50	605	0.987	1.112	329	0.295	0.810	3.35	1.37

*determined after 8 cycles of reduction.

After 8 cycles, because the dichromate solution is extremely aggressive, the Pani becomes over-oxidized and it participates to the hydrolysis reaction. The UV-VIS spectrum of the solution indicates that *p*-benzoquinone is the main degradation product of the polymer.

The thermal analysis shows a different thermal curve (Fig. 5) for the Pani (Fig. 5 curve A), composite (Fig. 5 curve B) and Dowex1 (Fig. 5 curve C). We noticed a weight loss of 3.73% for Pani; 5.08% for composite and 55.06% for Dowex1, in a temperature domain from 50°C and 150°C. The

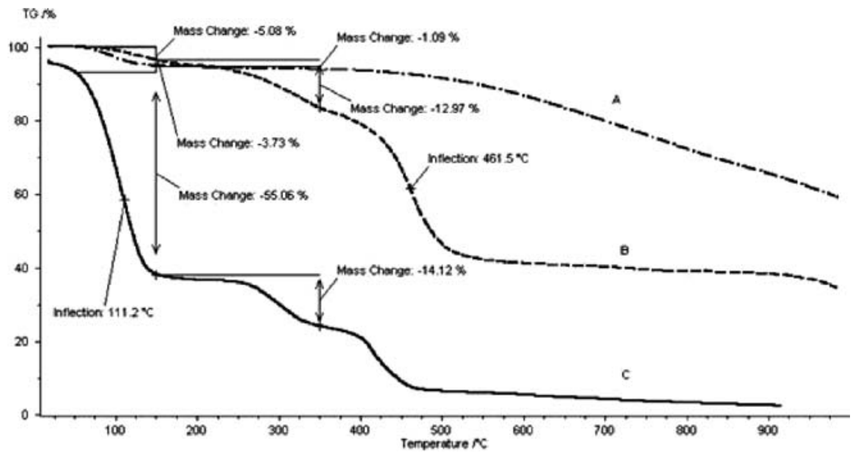


FIGURE 5 Thermogramme of Pani (A), composite Pani-Dowex1 (B) and Dowex1 (C).

weight loss was associated with the loss of water and dopant for Pani and composite, and the loss of Cl^- from Dowex1. In the domain from 150°C to 350°C the loss of weight was almost insignificant: 1.09% for Pani, 12.97% for composite and 14.21% for Dowex1. These weight losses were due to thermal decomposition, associated with the thermal degradation of the polymer chain of Pani (insignificant), of Dowex1 and composite. In comparison with Pani, which did not present rapid decomposition in the studied domain, the Dowex1 presented an inflexion point at 111.2°C, and the composite presented a major inflexion point at 461.5°C. This fact proved that the composite was formed (Fig. 5).

In Figure 6 the TG curves for composites after the reduction of dichromate solution with different concentration, are presented.

It was noticed that in the temperature domain from 50° to 150°C, the weight loss was maximum of 10%, being more accentuated for the composite used in the reduction of dichromate solution with a higher concentration (50 mg/l).

The major loss of weight takes place above 350°C, due to the degrading process. The maximum degradation rate depends on the concentration of Cr(VI) at which the composite was used. With the increase of Cr(VI) in solution, the maximum rate of degradation (the inflexion point) is recorded at a lower temperature, which indicates an advanced degradation of the composite due to the oxidation of Pani from the composite.

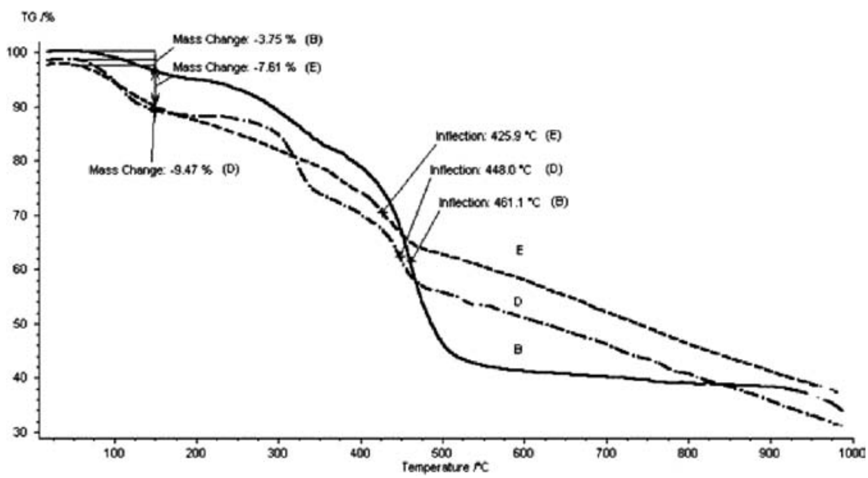


FIGURE 6 Thermograme of composite Pani-Dowex1 (B) before reduction with chromium, and after reduction with solutions of chromium having concentrations of 20 mg/l (D) and 50 mg/l (E).

CONCLUSIONS

The composite Pani-Dowex1 improves the mechanical resistance compared with the polyaniline, and allows the production, in an easy and reproducible manner, of a composite with an oxidant capacity, based on polyaniline. The final percent of Pani in composite was of 2.92%.

The waters having Cr(VI) concentrations of 10–40 mg/l are suitable for the treatment with 100 g of composite, which permits the obtainment of good remanent Cr(VI) in water. The polyaniline was susceptible to degradation, due to oxidation process, which destroyed the polymer chain. A stepwise process that allows the recycling of the solution, increases the yield of reduction process, and extends the life of the chosen composite.

REFERENCES

[1] Trivedi, D. C. (1997). Polyanilines: Blends and composites. In: *Handbook of Conductive Molecules and Polymers. Conductive Polymers: Synthesis and Electrical Properties*, Nalwa, H. S. (Ed.), John Wiley & Sons Ltd, Vol. 2, 534–535.

[2] Trivedi, D. C. (1997). De Paoli conductive polymer blends and composites. In: *Handbook of Conductive Molecules and Polymers. Conductive Polymers: Synthesis and Electrical Properties*, Nalwa H. S. (Ed.), John Wiley & Sons Ltd, Vol 2, 773–798.

[3] Anand, J., Palaniappan, S., & Sathyanayana, D. N. (1998). Conducting polyaniline blends and composites. *Polym. Sci.*, *23*, 993–1018.

[4] Malinauskas, A. (2001). Chemical deposition of conducting polymers. *Polymer*, *42*, 3957–3972.

[5] Huang, W. S., Humpfrey, B. D., & Mac Diarmid, A. G. (1986). Polyaniline, a novel conducting polymer. *J. Chem. Soc. Faraday Trans. I*, *82*, 2385–2400.

[6] Cao, Y., Smith, P., & Heeger, A. J. (1993). Processible forms of electrically conductive polyaniline. US 5.232.631.

[7] Pleşu, N., Ilia, Gh., Dehelean, Gh., Macarie, L., Păcureanu, L., Iliescu, S., Popa, A., & Pascariu, A. (2001). Polyaniline powder obtained by chemical polymerisation. *Annals of West University of Timişoara*, Series Chemistry, *10*, 1027–1031.

[8] Liteanu, C. (1964). Chimie analitică cantitativă. Volumetria, Bucureşti. Did şi Ped, Ltd. 406.

[9] Lei, W., Kocherginsky, N. M. (2000). Polyaniline film: Reaction with Fe^{3+} and H^+ permeability. *Reactive and Functional Polymers*, *45*, 65–77.