Polymer Bulletin 37, 531-537 (1996)

Polymer Bulletin

© Springer-Verlag 1996

Heterogeneous photocatalysis treatment of Kraft and textile effluents using metallic and polymeric semiconductors (ZnO and polyaniline)

P. Peralta-Zamora, S. Gomes de Moraes, J. Reyes, N. Durán *

Instituto de Química, Biological Chemistry Laboratory,
Universidade Estadual de Campinas. C.P. 6154, Campinas-SP, CEP 13081-970, Brazil

Received: 24 April 1996/Revised version: 17 June 1996/Accepted: 18 June 1996

Summary

When Kraft E_1 and textile effluents are illuminated with UV light in the presence of polyaniline, the color fades gradually until decolorization ratios of over 80% are attained for a single step of irradiation (1 hour). A chemometrics study show very little influence of pH, mass of polyaniline and presence of oxygen on the efficiency of this process. Complementary experiments indicated that the great intensity of preliminary adsorption of chromophores prevent the subsequent photocataytic destruction when UV light is used.

Introduction

One of the main problems associated with industrial activity is the generation of large volumes of effluents which contain a great number of toxic and persistent chemicals. In pulping and bleaching, the paper and cellulose industry produce brown or black effluents with high organic charge and significant concentration of high and low molecular weight chlorinated organic compounds (chlorolignins and chlorophenols, respectively). In addition, the textile industry produces effluents which contain organic dyes (i.e. azo compounds) and inorganic salts of great environmental importance (i.e. chrome salts).

In recent years, *clean technology* and *zero discharge* have become very popular concepts, because they reduce the volume and the concentration of toxic substances in effluents[1-6]. For the moment, this technology is available only in limited situations and the development of methodologies for industrial effluent treatment is necessary.

Photocatalysis, one of the most promising waste-water treatment systems, permits the decomposition of many organic materials to carbon dioxide and other inorganic products without the use of chemical oxidants[7-10].

Many metallic semiconductors used for photocatalyzed treatment of industrial wastes (eg.TiO_2, ZnO, CdS, etc.) have a bandgap in the UV region, and for this reason practical application imply the use of artificial UV light sources. Previously, ZnO was used for the decontamination of Kraft effluent together with biological treatment[11,12].

Semiconducting conjugated polymers [i.e., poly(p-phenylene)] were extensively used for photocatalytic reduction of water, carbonyl compounds, carbon dioxide and oleofines[13-15]. Polyaniline is a semiconductor with a conducting band in the visible region, and therefore can be activated by solar radiation[16]. Polyaniline was reported to decolororize a Kraft effluent in the presence of light[17]. Recently it was found that the

---

* Corresponding author

presence of oxygen was not a critical variable[18] . Since oxygen is very important for photocatalytic reactions, because oxygen act as electron acceptor to inhibit recombination of the hole-electron pair, this fact suggested that the main mechanism of decolorization was the adsorption[18].

In this work, we report a study of the photocatalytic treatment of an effluent from the paper and textile industries, using polyaniline catalyst in the presence of UV light and demonstrate the importance of absorption in the decolorization mechanism. A systematic study of bleaching performance for different experimental parameters was carried out using factorial design.

Experimental

1 - Effluents

The first caustic extraction E1 liquor, pH 9,5-13, was obtained from RIPASA Papel e Celulose (SP, Brazil). The textile effluent, obtained from a textile plant of the São Paulo region (Brazil), contains a mixture of many organic dyes. Both effluents were stored at 0°C in plastic flasks and were used without filtration.

2 - Synthesis of polyaniline

The polyaniline resin was obtained by polymerization of aniline according to Mattoso et al.[19].

3 - Photocatalytic reaction

The reaction was carried out in a open beaker containing 10 or 20 mL of effluent, at various initial pHs. An adequate amount of photocatalyst was added (50-300 mg of ZnO or polyaniline, depending on the experiments) and the solution was illuminated from the top using a 250W Philips lamp (without the glass cover) at a distance of 12 cm (108 $kJm^{-2}s^{-1}$ at $\lambda > 254$ nm) for a convenient time. During the irradiation, the solution was magnetically stirred and oxygen was bubbled through at a rate of about 20 $mLmin^{-1}$.

4-Analytical procedures

Total organic carbon (TOC) was analyzed by the TOC - 5000 Total Organic Carbon Analyzer (Shimadzu), according to ISO standard 8245. For decolorization measurements of the tested effluent, the mixture was adjusted to pH 7.6 with a phosphate buffer solution, centrifuged for 15 minutes at 3500 rpm and the absorbance measured at 465 nm for Kraft E_1 effluent (according to CPPA Standard Method H5P) and at 515 nm for textile effluent (maximum absorption wavelength), in a Hitachi U-2000 Spectrophotometer. Decolorization is expressed as a percentage of the initial absorbance.

Results and discussion

In order to determine the effect of pH and mass of polyaniline on the Kraft E_1 effluent decolorization, with and without UV irradiation, we performed the 2^3 factorial design show in Table 1. In the first section of this factorial design (experiments performed without irradiation) we can observe a high degree of adsorption of colored species. This process is strongly influenced by the mass of polyaniline (main effect of the mass: about 60 %), whereas no influence is shown for pH changes.

In the second section (experiments performed with UV irradiation) we can observe an average decolorization of about 80 %, and a very limited influence of pH and mass of polyaniline on the efficiency of effluent decolorization. Based on these results, we assume that the photocatalytic process with polyaniline involves, as for TiO_2 catalyst, an important preliminary stage of adsorption and then the photocatalytic reactions. If we consider the complete factorial design, we can observe a very important increase of decolorization (main effect of irradiation: about 50 %) when the system is irradiated.

Table 2 shows a similar experiment for the textile effluent. In the first section (without catalyst) we observed an important degree of decolorization in the presence of

Table 1 - Factorial design for mass of polyaniline, pH and irradiation variables.

Effluent: Kraft E_1 ; volume: 10 mL ; Irradiation: 1 hour

PARAMETER	(+) LEVEL	(-) LEVEL
A: MASS (g)	**0,3**	**0,1**
B: pH	**7,0**	**3,0**
C: IRRADIATION	**YES**	**NO**

Section	Run	A	B	C	Decolor. (%)
1	1	-	-	-	0.0
	2	+	-	-	56.1
	3	-	+	-	6.6
	4	+	+	-	62.9
2	5	-	-	+	58.8
	6	+	-	+	84.0
	7	-	+	+	84.8
	8	+	+	+	84.1

Main effects: Section 1: A: 56.2 ± 1,5% - B: 6.7 ± 1,5% ; **Section 2**: A: 12.2 ± 1.5% - B: 13.0 ± 1.5% ; **Complete factorial**: C: 46.5 ± 1.5%

Table 2 - Factorial design for presence of oxygen, catalyst and irradiation variables.

Effluent: Textile ; volume: 20 mL ; Irradiation: 1 hour ; pH: 8.0

PARAMETER	(+) LEVEL	(-) LEVEL
A: OXYGEN	**YES**	**NO**
B: IRRADIATION	**YES**	**NO**
C: CATALYST	**YES**	**NO**

Section	Run	A	B	C	Decolor. (%)
1	1	-	-	-	0.0
	2	+	-	-	2.2
	3	-	+	-	22.1
	4	+	+	-	18.7
2	5	-	-	+	80.6
	6	+	-	+	93.5
	7	-	+	+	92.9
	8	+	+	+	86.2

Main effects:Section 1:A: -0.6 ± 1,5% - B: 19.3 ± 1,5% ; **Section 2**: A: 3.1 ± 1.5% ; B: 2.5 ± 1.5% ; **Complete factorial**: C: 77.6 ± 1.5%

irradiation (about 20%), probably due to a homogeneous reaction, when the substrate is directly converted in CO_2 by absorbing the light in the presence of dissolved oxygen. In the second section (with the use of polyaniline) the effect of irradiation is not evident. This observation implied that the adsorption occurs to an important extent.

Table 3 shows a 2^3 factorial design to compare the effect of catalyst mass and presence of oxygen on photocatalytic decolorization of Kraft effluent , using ZnO and polyaniline as catalysts. In the first section, we observed an important effect of both variables (main effect for both variables: about 15%) on the effluent decolorization with ZnO catalyst. For polyaniline, section 2, the effect of the variables is not significant. However, the effluent decolorization increase about 70 % when compared with the use of ZnO. The results for the decolorization kinetics with the use of both catalyst (Fig. 1) showed that polyaniline, even in the absence of oxygen, is responsible for an important increase in decolorization efficiency of Kraft E_1 effluent. This observation and the great significance of the adsorption process indicates two decolorization mechanisms:

1 - adsorption of organic species following by photocatalytic reaction, or
2 - only adsorption of chromophores

Table 3 - Factorial design for mass of catalyst, oxygen and catalyst variables.

Effluent: Kraft E_1 ; volume: 10 mL ; Irradiation: 1 hour
O_2: about 20 mLmin^{-1}

PARAMETER	**(+) LEVEL**	**(-) LEVEL**
A: MASS (g)	**0,2**	**0,1**
B: OXYGEN	**YES**	**NO**
C: CATALYST	**POLYANILINE**	**ZnO**

Section	**Run**	**A**	**B**	**C**	**Decolor. (%)**
1	1	-	-	-	0.6
	2	+	-	-	17.5
	3	-	+	-	17.5
	4	+	+	-	30.1
2	5	-	-	+	79.5
	6	+	-	+	79.5
	7	-	+	+	88.1
	8	+	+	+	80.1

Main effects: Section 1: A: 14.7 ± 1,5% ; B: 14.7 ± 1,5% ; **Section 2**: A: - 3.9 ± 1.5% ; B: 4.6 ± 1.5% ; **Complete factorial**: C: 65.3 ± 1.5%

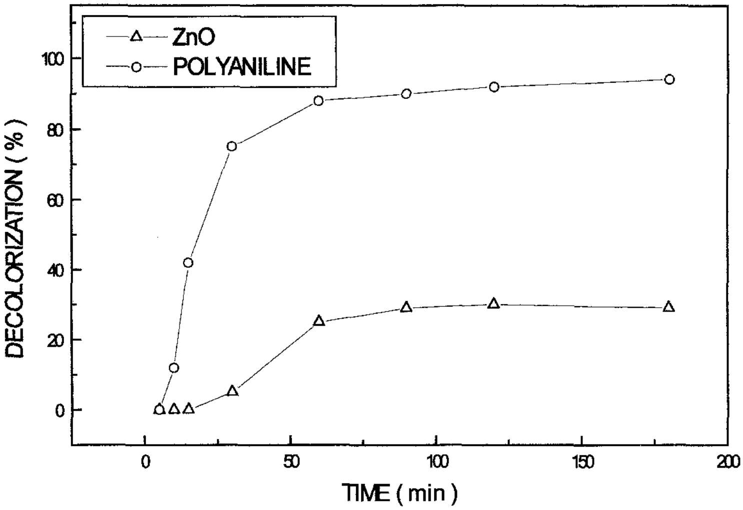

Figure 1 - Kinetics of decolorization with the use of polyaniline and ZnO.
Effluent volume: 100 mL ; Mass of catalyst: 0.3 g
pH: 7.0 ; O_2: about 20 mLmin^{-1} (only for ZnO)

To investigate the decolorization mechanism, the photocatalytic process was extended up to 5h and the resulting mass of polyaniline was extracted during 1h with aqueous solutions with several pH's. We observed in all cases (Table 4) that about 50% of the absorption signal is obtained by extraction at pH 10. When a second extraction process is done, the recovered signal reaches about 15 %.

Table 4 - Aqueous extraction of polyanile after photocatalytic treatment.
Effluent: Kraft E_1 ; volume: 20 mL ; Mass of catalyst: 0.05 g
pH: 7.0 ; O_2: about 20 mLmin^{-1} ; Inicial absorbance: 0.280

Irradiation time (min)	Absorbance after irradiation	Absorbance of first extraction pH 2.0	Absorbance of first extraction pH 10.0	Absorbance of second extraction pH 10.0
30	0.009	0.015	0.176	0.050
60	0.007	0.017	0.180	0.045
90	0.007	0.016	0.151	0.033
120	0.006	0.017	0.145	0.040
180	0.007	0.020	0.160	0.045
240	0.007	0.015	0.152	0.038
300	0.006	0.018	0.180	0.032

By elemental analysis it was found that the total carbon concentration increases about 6 % when the polyaniline alone is submitted to the photocatalytic process for 5h. Total organic carbon determination was not possible because polyaniline is decomposed in the photocatalytic process, releasing significant amounts of organic carbon (see Table 5).

These results show that under our experimental conditions, decolorization is due to adsorption of chromophores and not to photocatalytic destruction of organic compounds. Recent studies reported by Diaz et al.[20] indicate that the conducting properties of polyaniline are strongly influenced by the experimental conditions of synthesis (i.e. temperature, applied potential, morphology, etc.). Similar observations were realized by Shibata et al.[13], who showed that the photocatalytic properties of poly(p-phenylene) are significantly influenced by the molecular mass of the polymer and consequently by the experimental conditions of the synthesis. For this reasons, the use of polyaniline in photocatalytic process may be considered.

Table 5 - Photocatalytic decomposition of polyaniline in aqueous media

Irradiation time (min)	Total Organic Carbon (ppm)
60	6
120	10
300	100

Final remarks

Literature data and preliminary experimental studies indicate that polyaniline is a promising catalytic material for photocatalytic treatment of toxic and persistent chemicals derived from industrial effluents. However, subsequent experiments showed the existence of an important adsorption process which obstructs the photocatalytic destruction of the compounds present in the tested effluents, as was observed under our experimental conditions.

Acknowledgment

Support from CNPq and FINEP is acknowledged.

References

1 - Sundquist J (1994) Paperi Ja Puu - Paper and Timber 76: 22-26.

2 - Williamson P (1994) Pulp & Paper Can. 95: 9-10.

3 - Odendahl S (1994) Pulp & Paper Can. 95: 30-34.

4 - Evansb T, Sweet B, Manolescu D and Mason J (1995) Pulp & Paper Can. 96: 60-64.

5 - Heatley W R and Barfield MW (1995) Tappi J. 78: 197-200.

6 - Kenny R, Yampolski H and Goncharov A (1995) Pulp & Paper Can. 96: 26-28.

7 - Ohnishi H, Matsumura M, Tsubomura H and Iwasaki M (1989) Ind. Eng. Chem. Res. 28: 719-724.
8 - Kobayakawa K, Sato Y, Nakamura S and Fujishima A (1989) Bull. Chem. Soc. Jpn. 62: 3433-3436.
9 - Herrmann JM, Guillard C and Pichat P (1993) Catal. Today. 17: 7-20.
10 - Hoffmann M, Martin ST, Choi W and Bahnemann DW (1995) Chem. Rev. 95: 69-96.
11 - Durán N, Dezotti M and Rodrigues JJ (1991) Photochem. Photobiol. A. Chem. 62: 269-279.
12 - Durán N, Espósito E, Inocentini-Mei LH and Canhos VP. (1994) Biodegradation 5: 13-19.
13 - Shibta T, Kaburoto A, Shiragami T, Oshitani O, Pac C and Yanagita S. (1990) J. Phys. Chem. 94: 2068-2076.
14 - Yanagida S, Kaburoto A, Mizumoto K, Pac C and Yoshina k. (1985), J.C.S., Chem. Commun. 474.
15 - Matsuoka S, Kohzuki T, Pac C and Yanagita S. (1990) Chem. Lett. 2047.
16- Huang WS and MacDiarmid AG (1994) Polymer 34: 1833-1845.
17 - Dezotti M, Moreira M, Carvalho E, Silveira E, Araújo O and Botter W (1994) Proc. 2º Simpósio Iberoamericano de Polímeros, Vol. II: 828-830.
18 - Peralta-Zamora P, Dezotti M, Reyes J and Durán N (1996) Proc. of The Fourth Brazilian Symposium on the Chemistry of lignins and Other Wood Components (Recife- PE), in press.
19 - Mattoso LHC, Faria RM, Bulhões LOS and MacDiarmid AG. (1994) J. Polym. Sci.: Polym. Chem. 32: 2147.
20 - Diaz F, Tagle LH and Sanchez C (1996) Livro de Resúmenes XXII Congreso Latinoamericano de Química, Vol. I: 412.