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DEGRADATION OF MEMBRANE CONCENTRATES OF THE TEXTILE INDUSTRY BY FENTON LIKE REACTIONS IN IRON-FREE SOLUTIONS AT BIOCOMPATIBLE pH VALUES (pH \approx 7-8)

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ABSTRACT

Degradative oxidation of membrane concentrates of textile waters were carried out in batch reactors in the dark and under visible light. H_2O_2 and Nafion- Fe^{3+}/H_2O_2 as an immobilized Fenton reagent were used as ecological oxidants. The results observed with the Nafion/ Fe^{3+} system lead to a kinetically faster and more complete oxidation than H_2O_2 alone and comparable to the homogeneous Fenton reaction in solution. This study reports on the Fenton treatment of membrane concentrates resulting from nanofiltration of biologically treated secondary textile effluents produced in a large scale in Northern Italy. The degradation of the membrane concentrates is accelerated under light due to the recycling of the Fe^{3+} -ion in the Nafion avoiding the drawbacks of the homogeneous treatment. A reduction of \sim 50% is seen in the TOC and of \sim 20-50% in optical absorbance after 3 hours pretreatment under light for end of pipe membrane concentrates under light and the process was stable over many cycles. The observed degradation depended on the amount of H_2O_2 , the intensity of the visible light applied. But it varied very little on the pretreatment pH which makes the Fenton immobilized systems suitable to pretreat membrane concentrates up to pH 8. The membrane concentrates showed a decrease in their toxicology when undergoing oxidative pretreatment under visible light mediated by Nafion- Fe^{3+} (1.78%) adding in solution H_2O_2 (10 mM). Mathematical modeling of the degradation parameters is presented by constructing a single exponential polynomial function. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Biocompatibility, degradation recalcitrant organic compounds, immobilized membrane Fenton reactions, toxicology, modeling of reaction parameters.

INTRODUCTION

Increasing water use for all purposes is leading to water shortages in countries of Southern Europe. Considerable volumes of water are used in textile processing and this textile-water contains dyes, detergents, insecticides, fungicides, grease and oils, solvents and inorganic salts. The usual biological treatment of waste-waters is not able to abate non-biodegradable toxic compounds of industrial origin. To comply with

the E. U. water use directives (EEC Directives, 1982) the membrane concentrates have to be recycled back to the biological stage or discharged into water bodies after additional treatments like ozonation (Rozzi, 1997) or Advanced Oxidation Technologies (AOT's) (Ollis, 1995). In this study we use a new approach that seeks mild ecological and environmentally friendly conditions for membrane concentrates pretreatment producing a minimum of by-products at a kinetically acceptable rate at low cost. The energy demand should be minimal as well as the reagents used and the reaction time. This will be modeled to attain the most rational utilization of the approach taken.

Membrane related research has attracted much attention during the last decade (Bard, 1994; Ollis and Al-Ekabi 1993, Bellobono *et al.*, 1994). Nafion perfluorinated membranes are resistant to $\cdot\text{OH}$ radical attack ($\cdot\text{OH}/\text{OH}^-$ E° 1.90 V vs NHE) which is not the case with polymer containing C-H bonds. These $\cdot\text{OH}$ radicals are generated in solution in the presence of H_2O_2 and iron salts which is the most common catalyst for H_2O_2 decomposition in an aqueous system (Walling, 1975). The present study is directed toward the Nafion- Fe^{3+} mediated degradation of membrane concentrates in Fe^{3+} free solutions. The present regulations (EEC Directives, 1982) allowing an iron upper limit of 2 ppm makes the use of Fe^{3+} as in homogeneous solution as practiced until now needing removal at the end of the treatment. This is expensive in terms of chemicals and labor. Also the pH had to be adjusted to a value of pH 3 to avoid iron precipitating out of the solution. This is not the case when membranes are used as in this study. We aimed therefore at an efficient, kinetically acceptable process showing long term stability for the degradation of membrane concentrates to attain bio-compatibility modeling the reaction parameters. This approach allows further degradation of the recalcitrant membrane concentrates through biological treatment at the lowest possible cost.

METHODS

Materials and techniques employed

The membrane concentrates in the Northern Italian plants showed COD of 496 ± 20 mg O_2/L equivalent to a TOC of 110 ± 5 mg C/l. The natural pH of the membrane concentrates was ~ 8.0 . About 50% of the material in the concentrate had a MW $> 300\,000$ (range of 200 000 to 500 000). Less than 30% had a MW between 3000-10 000.

The Fenton reagent used Mohr's salt as an iron II source (ammonium ferrous sulfate hexa-hydrate) and H_2O_2 (30% w/w) were Fluka p.a. and used as received. The Fe^{3+} -ions were added at the beginning of each run. The consumption of H_2O_2 during the reaction was followed by the Merckoquant® test for peroxides which detected peroxides between 0.4 and 25 mg /L. The waste-waters were acidified to the desired pH by addition of H_2SO_4 1M. Total organic carbon (TOC) was monitored with a Shimadzu 500 provided with an automatic auto-sampler. Spectrophotometric measurements were carried out with a Hewlett-Packard 386/20 N diode array. The toxicity was measured using the Microtox® technique. The decrease in bioluminescence of *Photobacterium phosphoreum* in the presence of pretreated membrane concentrates was followed as a function of pretreatment time.

The Nafion perfluorinated membrane (Dupont 117, 0.007 inches thick, Aldrich #7.467-4) containing hydrophilic sulfonate groups immobilized on the fluorocarbon matrix. This cation transfer membrane was exchanged a few minutes with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Fluka) at room temperature. The membranes were immersed in HCl before the ion-exchange and after the ion-exchange, the membranes were washed with water followed by immersion in NaOH (1 M) to convert the exchanged- Fe^{3+} to its hydrated form. The Fe-content in the Nafion was determined after digesting the membrane in concentrated HNO_3 (Teflon coated autoclave) under pressure and temperature. This solution was subsequently diluted and the Fe-content measured by atomic absorption spectroscopy (AAS) in a Philips 20 AS instrument provided with a flame detector. The membranes used throughout this work had a loading of 1.78% by weight. The state of oxidation the Fe incorporated in the Nafion membrane was carried out by XPS in a Leybold Heraeus instrument applying the Shirley correction for particle charging.

Reactor and irradiation procedures

Figure 1 shows the schematic of the Suntest lamp cavity used to simulate solar radiation. The short uv radiation from the Suntest solar simulator ($\lambda < 310$ nm) was prevented from reaching the samples by the Pyrex wall of the reaction vessels. The radiant flux reaching the solutions in the photolysis vessels (60 ml Pyrex) was set at values of 10, 48 and 80 mW/cm². The Nafion iron loaded membrane were positioned immediately behind the wall of the reaction vessel to act as the only light absorber as shown in Figure 1 in the two phase system.

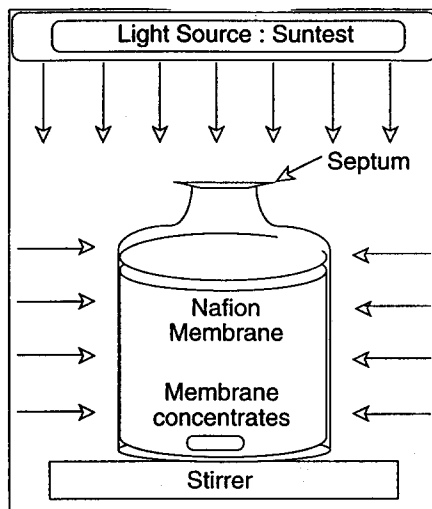


Figure 1. Reactor used during the light activated degradation/decoloration of membrane concentrates mediated by Nafion-Fe³⁺ membranes.

RESULTS AND DISCUSSION

Dark and photo-assisted degradation/decoloration of membrane concentrates. Effect of the solution pH

Figure 2a shows the decrease of the TOC with time for membrane waters in the dark and in photo-assisted light reactions using 80% of the simulated light intensity equivalent to the radiation of one sun. It is readily seen that the decrease in TOC is about the same as a function of time for different solution pH values. After an initial steep decrease a 30-33%, the initial degradation observed in the dark seems to produce intermediates in solution precluding further degradation. Under light, the degradation reached about 58% (pH 2.8) due to the higher generation of ·OH radicals in solution (Bauer, 1993) due to the fastest recycling of the Fe³⁺/Fe²⁺ embedded in the Nafion (Fernandez *et al.*, 1998). The fact that at pH 7 a considerable reduction in TOC is observed is a crucial finding unreported until now since it allows to apply the oxidative pretreatment found during this study at bio-compatible pH values. This avoids the costly neutralization of the pretreated solution required during subsequent biological degradation. The decoloration of the membrane concentrates occurs along the TOC decrease and this is shown in Figure 2b. Drastic reduction of the absorbance (A) under light is observed at pH 2.8 where the Nafion-Fe³⁺ has been shown to reduce efficiently the TOC of dyes (Fernandez *et al.*, 1998). The reduction in absorbance of OD=1 (T=10%) at time zero to OD 0.40 (T=40%) after 24 hours (pH 2.8) reflected a decoloration in solution that was easily followed visually. The full points in Figures 2a/2b show the addition of H₂O₂ in the dark and the open points show the times at which the oxidant has been added during light activated degradation runs.

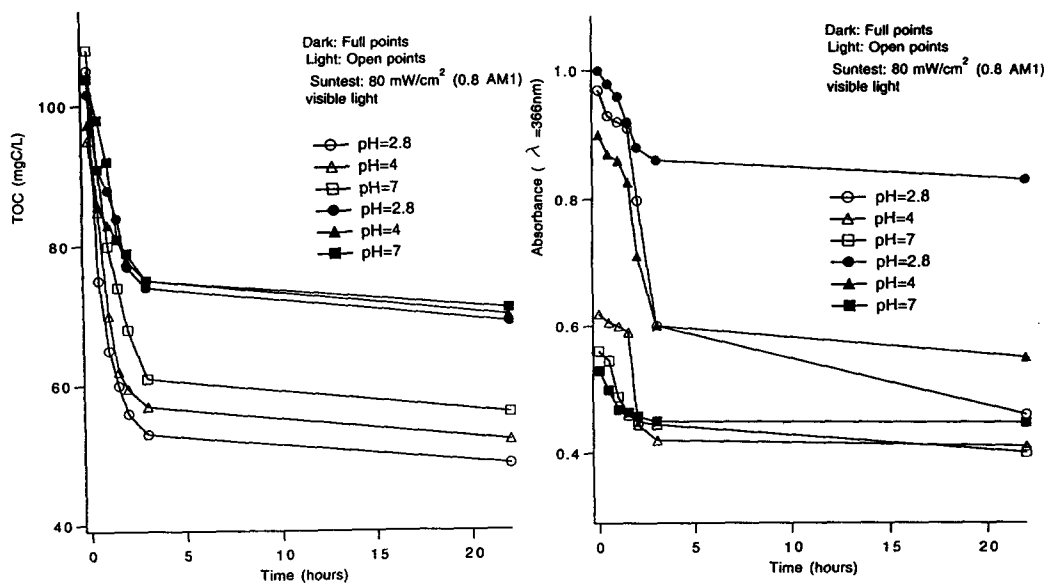


Figure 2. (a) TOC decrease as a function of time for membrane concentrates in the dark and under light at different pH values in a solution H₂O₂ (10 mM) mediated by Nafion-Fe³⁺ (1.78%); (b) Absorbance (A) in a 1 cm cell with time at $\lambda=366$ nm for membrane concentrates at different pH values in a solution H₂O₂ (10 mM) mediated by Nafion-Fe³⁺ (1.78%).

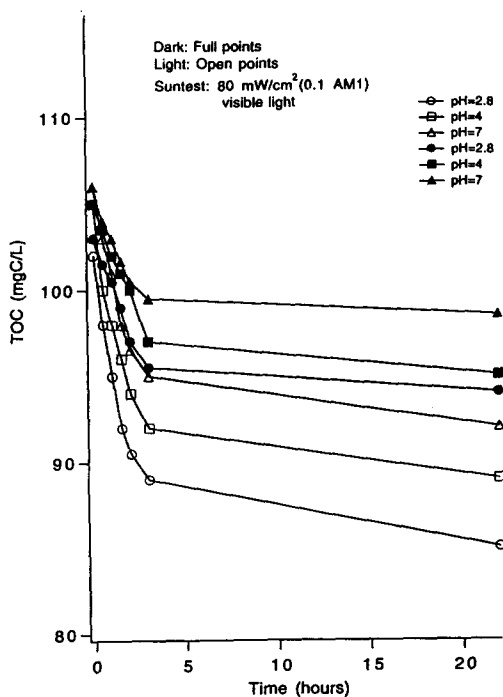


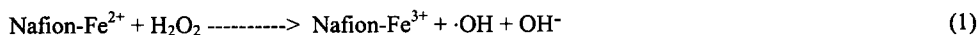
Figure 3. TOC decrease with time in homogeneous solutions of membrane concentrates in the dark and under visible light ($\lambda=310$ nm) at various pH values. The solutions contain H₂O₂ (10 mM).

TOC Reduction of membrane concentrates in homogeneous solutions with H₂O₂ (10 mM)

Figure 3 presents the results obtained in dark and light runs with membrane concentrates at different pH values in the absence of the Nafion-Fe³⁺ (1.78%) loaded membrane but in a solution with the same H₂O₂ concentration as employed in Figure 2a. It is readily seen that the dark degradation runs present the same pattern as seen previously in Figure 2a but the observed degradation was less efficient reaching in the most favorable case (pH 2.8) only 12% vs 33% in the presence of the Nafion loaded membrane (Figure 2a). In the case of the light induced runs the observed reduction was 21% (pH 2.8) vs a 58% reduction observed for the Nafion loaded membrane at pH 2.8 (Figure 2a). The beneficial effect of the highly dispersed Fe-ions on Nafion membranes is readily seen when decomposing the H₂O₂ in solution. Homogeneous solutions containing H₂O₂ (10 mM) and Fe³⁺ (30 mg/L) showed values for the TOC reduction for the membrane concentrates similar to the ones observed in Figure 2a.

Effect of the concentration of H₂O₂ and the light intensity on the TOC decrease for different pH values in nafion/Fe mediated processes

When the H₂O₂ concentration was increased to 25 mM this increase was observed to be detrimental to the degradation since after the initiation step



the propagation step eq (2) would be hindered by an excess H₂O₂ acting as an ·OH radical scavenger in solution (Walling, 1975)



During the degradation with H₂O₂ (10 mM) the pH of membrane concentrates which was initially 7 decreased to 5.8 within 24 hours. This pH change suggests that besides ·OH radical generation in eq (2), another reaction as suggested in eq (3) also takes place during the degradation of the membrane concentrates. This is indicated schematically in Figure 4.

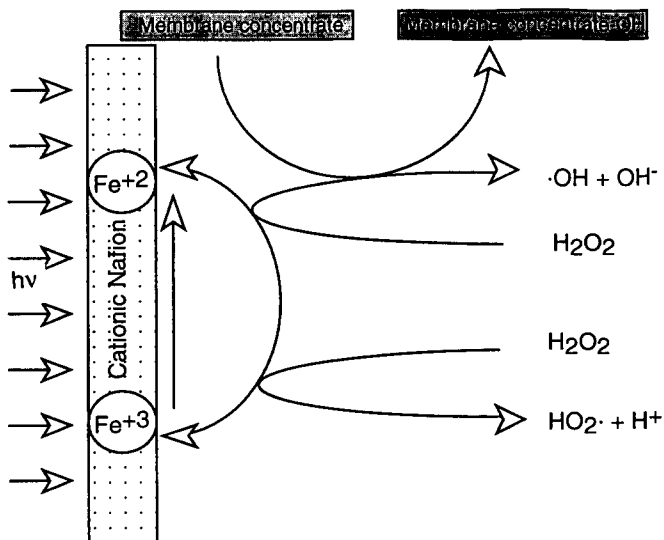
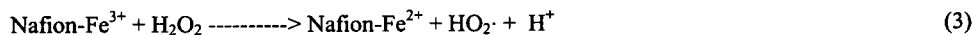


Figure 4. Photocatalytic degradation of the membrane concentrates showing the oxidative radicals intervening in the photoactivated degradation/decoloration process.

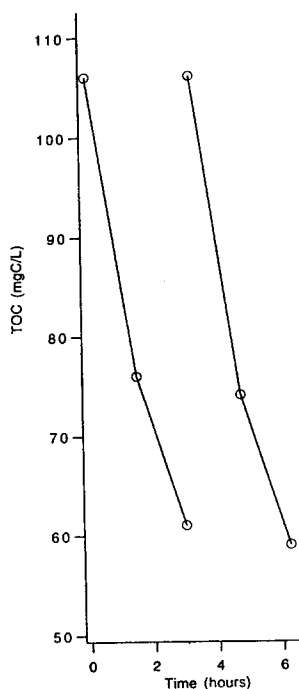
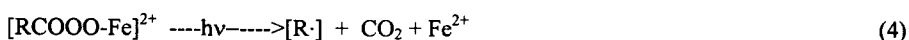


Figure 5. Stable reuse of the Nafion-Fe³⁺ (1.78%) in H₂O₂ (10 mM) during the degradation of membrane concentrates at pH 7 under simulated solar light of 80 mW/cm².

The consumption of H₂O₂ in the case of interest (pH 7, 10 mM) was followed by Merkoquant® paper. After 3 hours irradiation the oxidant went from 300 mg/L to 20 mg/L. After 24 hours, not adding any H₂O₂ after 3 hours revealed no oxidant left at all. The degradation of the membrane concentrate proceeds at an acceptable kinetic rate at pH 7. This may involve the formation of a mechanism involving iron-organic complexes (Sawyer, 1993; Herrera *et al.*, 1998)



the LMCT complex in eq(4) leads to CO₂ as observed by the decrease of TOC in Figures 2-5. This process proceeds concomitantly to other radical reactions



as mentioned in eqs (1)-(3) above. The decrease in TOC achieved during the pretreatment for 24 hours is accompanied by a reduction in the toxicology (see experimental part) of over 50% of the toxicity found initially in membrane concentrates. No complete elimination of the initial toxicity was observed within 24 hours pretreatment.

Stability and reuse of the nafion-Fe loaded membranes during the degradation of membrane concentrates

Figure 5 above shows the stable nature of the repetitive degradation processes on the membrane concentrates up to 4 cycles. The Nafion membranes were washed with distilled water after each cycle. Neither the ·OH radical nor the slower oxidizing HO₂· radical (H⁺, HO₂)/H₂O₂ E° 1.44 V vs NHE) attack the membrane or corrode the Fe-ions exchanged on the Nafion-SO₃H groups. No Fe-ions appeared in solution up to 500 hours testing in the presence of H₂O₂ and light. The color of the membrane did not change during the recycling. The Fe(II) and Fe(III) states of the Fe in the membrane have been evaluated by XPS (see experimental part). Signals at 710.0 eV B.E. comprised 78% corresponding to Fe(III) peak of Fe₂O₃. Signals

at 713.8 eV B.E. were also observed corresponding to about 22% of the total XPS Fe₃O₄ signals. Therefore, Fe(II)/Fe(III) exist on the Nafion as is the case in homogeneous Fenton systems (Ollis and Scott, 1995; Fernandez *et al.*, 1998).

Mathematical modeling of the degradation parameters exponential function

Our group has developed treatment of the degradation of pollutants aiming at the optimization of the reaction parameters to attain the most economical use of the oxidant, reaction time and applied energy (light intensity) during the degradation process. As recently published (Balanosky and Kiwi, 1998) reduced centered dimensionless variables of the parameters affecting the TOC decrease are taken and a single polynomial function is constructed to fit the experimental results obtained. Figure 6 present the calculated values in the dotted lines from the exponential model applying eq (6) as compared to the experimental result shown by the full line

$$Z(\text{TOC}) = 91.19 \exp(-112x_1 + 53.29x_2 + 43.15x_1^2 + 75.1717x_2^2 - 077x_1x_2) \quad (6)$$

in which the value of x_1 is related to the concentration of H₂O₂ (in mM) and x_2 is related to the light intensity at any time in the experiment (Figure 6). The experimental and calculated values show an agreement of 95% confirming the validity of the exponential model used in eq (6).

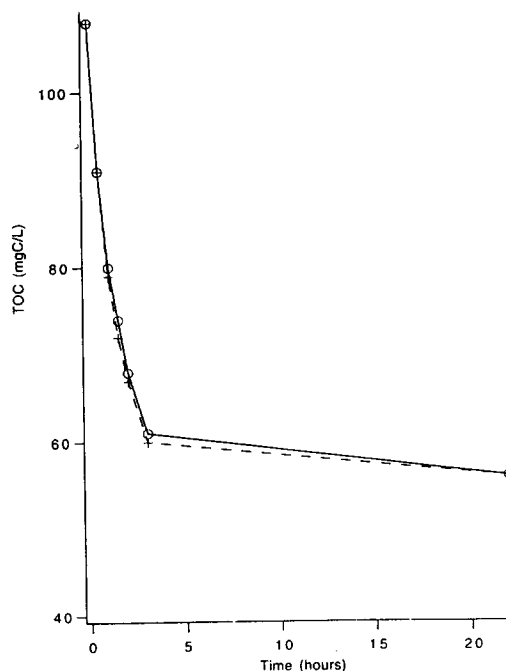


Figure 6. Reduction of the TOC showing calculated values (dotted lines) and experimental values (full lines) for membrane concentrates under simulated solar irradiation (80 mW/cm²) with H₂O₂ (10 mM) H₂O₂ added to the membrane concentrates up to 3 hours at pH 7.

CONCLUSIONS

Fe-Nafion membranes have been shown to be catalytically active during oxidative treatment of membrane concentrates at a bio-compatible pH. This new type of membranes resist OH-radical attack, do not release Fe-ions in to the solution and intervene with fast kinetics in oxidation processes. The cluster composition does not correspond to Fe-oxides or Fe-hydroxides.

ACKNOWLEDGMENTS

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REFERENCES

- Balanosky, E. and Kiwi J. (1998). Mathematical modeling of the photochemical reactor degradation of p-Nitrotoluenesulfonate. *Ind. Eng. Chem. Res.*, **37**, 347-356.
- Bard, J. (1994). *Integrated Chemical Systems*. John Wiley and Sons, New York.
- Bellobono, I., Carrara, A., Barni, B. and Gazzotti, A. (1994). Laboratory- and pilot-plant-scale photodegradation of chloroaliphatics by photocatalytic membranes immobilizing TiO₂. *Photochem. Photobiol A* **84**, 83-90.
- Fernandez, J., Bandara, J., Lopez, A., Albers, P. and Kiwi, J. (1998). Efficient photo-assisted catalysis mediated by Fe-ions on Nafion membrane active in the abatement of nonbiodegradable azo-dye. *Chem. Comm.* 1493.
- Herrera, F., Pulgarin, C., Nadochenko, V. and Kiwi, J. (1998). Accelerated photo-oxidation of concentrated p-coumaric acid in homogeneous solution. *Appl. Cat. B.* **435**, 1-15.
- Lopez, A., Ricco, G., Ciananarella, R., Rozzi, A., Di Pinto, A. and Passino, R. (1998). Textile wastewater reuse: ozonation of membrane concentrated secondary effluent. *Wat. Sci. Tech.*, **40**(4-5), 99-105 (this issue).
- Ollis, D. and Al-Ekabi, H. (1993). *Photocatalytic Purification and Treatment of Water and Air*. Elsevier, Amsterdam.
- Ollis, D. and Scott, J. (1995). Integration of chemical and biological oxidation processes for water treatment: review and recommendations. *Environmental Progress*, **14**(2), 89-103.
- Ruppert, G., Bauer, R. and Heisler, G. (1993). The photo-Fenton reaction - an effective photochemical waste water treatment process. *J. Photochem. Photobiol. A* **73**, 75-78.
- Sawyer, D., Sobkowiak, A. and Matsuchita, T. (1966). Metal/hydroperoxide induced activation of dioxygen for the oxygenation of hydrocarbons. *Acc. Chem. Res.* **29**, 409-416.
- Walling, Ch (1975). Fenton's reagent revisited. *Acc. Chem Res.* **8**, 125-131.