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Photo Assisted Fenton in a Batch and a Membrane Reactor for Degradation of Drugs in Water

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Abstract: Some advanced oxidation processes (AOP's) such as Fenton H_2O_2/Fe^{2+}, photo assisted Fenton $UV/H_2O_2/Fe^{2+}$, UV photolysis, and photo assisted Fenton—like $UV/O_2/Fe^{2+}$ have been tested for the degradation of Gemfibrozil in aqueous solution in a batch system and then in a membrane reactor. A nanofiltration/reverse osmosis type cross-linked polyamide, UTC-60 (Toray) membrane (19 cm^2) was used. In the batch degradation tests, the gemfibrozil, used at 5 mg/L, was degraded by employing the four AOP's but numerous peaks of intermediates were observed at the HPLC. Indeed DOC analyses showed poor mineralization in the case of photolysis (3.1%) and $UV/O_2/Fe$ (10%), while it was 62% using the photo assisted Fenton and 24% using the Fenton. Thus in the membrane reactor only the Fenton and the photo assisted Fenton were tested. Obtained results showed a drug degradation higher than 92%, a mineralization higher than 55%, and a membrane retention of the catalyst in solution higher than 95%.

Keywords: Advanced oxidation processes, batch membrane reactor, degradation, drug removal from aqueous media, Fenton processes, intermediates

INTRODUCTION

In recent years pharmaceuticals have emerged as a novel class of water contaminants. So, public and scientific interest is quickly increasing because

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of the potential impact on human health and the environment even at trace levels (1–3). These molecules are annually used for therapeutic purposes in amounts of thousand of tons (4, 5). The presence of pharmaceuticals in aquatic environments typically results from hospitals, animal farms, and human excretion of metabolized and unmetabolized drugs passing into sewage systems and subsequent discharge of wastewater (6). Recent data from Europe indicate that the normal operation of sewage treatment plants (STPs) results in the non complete removal of pharmaceuticals, hence as much as 80% of their total load, entering in sewage treatment plants, may be discharged into surface water (7–12). The concentration measured in surface water samples downstream from sewage treatment plant discharges typically have been found in tens of nanograms per liter, although concentrations in the order of $\mu g/L$ are possible. These amounts are much lower than typical maximum concentrations reported for typical industrial contaminants but the effects of continuous exposure to mixtures of pharmaceuticals on aquatic environment is unknown (13).

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Gemfibrozil is a persistent and highly stable pharmaceutical under normal environmental conditions present in STPs. It is a fibrate lipid regulating agent that is clinically effective in reducing serum cholesterol and triglyceride levels, decreasing low density lipoprotein (LDL), and increasing high density lipoprotein (HDL) levels (14). It is still a drug of choice in the treatment of hyperlipidaemias involving raised triglyceride levels and has been effective in reducing the incidence of coronary heart desease. Renal extraction is the most important elimination pathway for the respective carboxylic acid as well as such glucorinides in men. Indeed, a total of 60–70% of the gemfibrozil dose is found in urine (14).

Recent progress in chemical water treatment has led to the development of advanced oxidation processes (AOPs) (15, 16). These processes have been defined as those which involve the generation of hydroxyl radicals in sufficient quantity to carry out the destruction of toxic pollutants. OH radicals are extraordinarily reactive species, they attack the most part of organic molecules with rate constants usually in the order of 10^{-6}–$10^{-9}\ M^{-1}\ s^{-1}$. These methods are also characterized by poor selectivity which is a useful characteristic for an oxidant used in wastewater treatment and for pollution problems solving. AOPs have a good versatility because they offer different possible ways to produce OH radicals, thus allowing a better acceptance with the specific requirements of the treatment (15).

Because AOPs are based on chemical destruction, when they are properly developed, they give complete solution to the problem of pollutant abatement differently from those processes in which only a phase separation is realized with the consequent problem of the final disposal. A combination of membrane and AOPs, thanks to their synergy, could have many advantages (17). Use of a membrane reactor generally permits the reuse of the catalyst, the control of contact time of organic substrates in the oxidant environment, and confining of the pollutants and their intermediates in the reaction

ambient thus carrying out, in a single step, both reaction and separation. Good results on this approach have been already obtained in a photocatalytic membrane reactor (18). In such a reactors three factor, like absorption, rejection, and degradation should cooperate permitting to obtain a permeate with a low organic content.

In this work the following AOPs processes are tested for the degradation of Gemfibrozil in aqueous solution: Fenton (H_2O_2/Fe^{2+}), photo assisted Fenton ($H_2O_2/Fe^{2+}/UV$), photolysis (UV), and photo assisted Fenton–like ($O_2/Fe^{2+}/UV$). These processes were previously carried out in a batch reactor, to optimize the operating conditions (e.g. pH, concentrations) and to estimate the best processes. Then, they were compared in a batch membrane reactor.

EXPERIMENTAL

Materials

Gemfibrozil (5-(2,5-Dimethylphenoxy)-2,2 dimethylpentanoic acid, $C_{15}H_{22}O_3$, MW = 250.3 g/mol, melting point 58–61°C, pKa 4.7, Fig. 1) was purchased from Sigma. It is a white solid, insoluble in acidic media. Gemfibrozil solutions were prepared by dissolving it in ultrapure water (Elix 5, Millipore).

Sulphuric acid (H_2SO_4, 96% w/w solution in water) by Carlo Erba, hydrochloric acid (HCl, MW = 36.46 g/mol, 37% w/w solution in water) by Riedel-De Haën, and sodium hydroxide (NaOH, MW = 40.00 g/mol, purity = 98%) from Sigma, were used to correct the pH of aqueous phases. In many tests the pH of the aqueous phases were controlled by using a phosphate buffer (50 mM) prepared with Sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$, MW = 137.99 g/mol, purity = 99%) by Fluka.

Iron (II) chloride tetra hydrate ($FeCl_2 \cdot 4H_2O$, MW = 198.8 g/mol, purity > 99%) from Fluka was used as the catalyst.

Hydrogen peroxide (H_2O_2, MW = 34.02 g/mol, 3% w/w solution in water) from Sigma was used as the oxidant.

Flat sheet Reverse Osmosis type membranes of grafted polyamide (UTC-60 FLAT (SU-6xx) by Toray-Romembra Industries) were used in the membrane reactor.

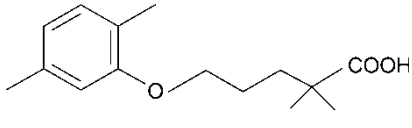

Figure 1. Structure formula of Gemfibrozil.

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Equipments and Methods

Gemfibrozil concentration and the relative area of picks of its degradation products were detected by high performance liquid chromatography (HPLC, Agilent 1100 Series instrument) using a Phenomenex Synergi 4u Fusion–RP 80 A (4.60 × 250 mm, 4 μm) column by UV readings at 280 nm wavelength. The mobile phase consisted of an acetonitrile/phosphate buffer at pH 3.1 solution 70/30 v/v fed to a flow-rate of 1.0 mL/min. The column pressure was 82 bar and the injection volume was 20 μL.

Gemfibrozil mineralization was evaluated by dissolved organic carbon (DOC) measurements, performed by using a TOC-VCSN from Shimadzu.

Determination of iron (II) concentration was carried out by using an analytical kit (Carlo Erba Reagenti), based on a colorimetric reaction and absorbance reading at 562 nm wavelength. The absorbance reading was performed by using a Recording Spectrophotometer (UV-1601 by Shimadzu Corporation–Analytical Instruments Division).

A pH meter (WTW Inolab Terminal Level 3) with a glass pH-electrode SenTix 81 (WTW), was used for pH measurements.

Dissolved oxygen concentration was determined by using an oxygen meter HI 9143 purchased from Hanna Instruments.

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Apparatus

Preliminary degradation tests were carried out in the experimental set up reported in Fig. 2 excluding the membrane cell loop. This part of the set up is constituted by a jacket batch reactor thermostated by means of a water bath at 30°C temperature, so that the process took place in isothermal condition. The UV lamp is situated above the open-air reactor, so that the UV radiation impinges on the free liquid surface. A magnetic stirrer placed below the reactor guarantee system mixing. A stainless steel tube is put in the reactor for oxygen feeding. At established time intervals samples were withdrawn from the reactor and Gemfibrozil and DOC concentrations were measured. The membrane cell loop contains the permeation cell and a diaphragm pump (Lewa MD 0.18, Qmax = 60 l/h, Pmax = 14 bar) that permits the recirculation of the aqueous solution in the membrane reactor. The permeation cell was made to promote turbulent flow in order to avoid membrane fouling. Indeed aqueous flow enters in the bottom of the cell tangentially, thus promoting a good mixing minimizing cake deposition on the membrane. The permeation cell is a chamber (V = 0.095 L) in stainless steel, closed at the top with a transparent polycarbonate septum. In the bottom of the permeation cell is situated the membrane placed on a porous support that guarantees mechanical resistance. The permeate is collected in a container or it is sent to the batch reactor while the retentate is recirculated to the batch reactor. Pressure regulation on the membrane is obtained by

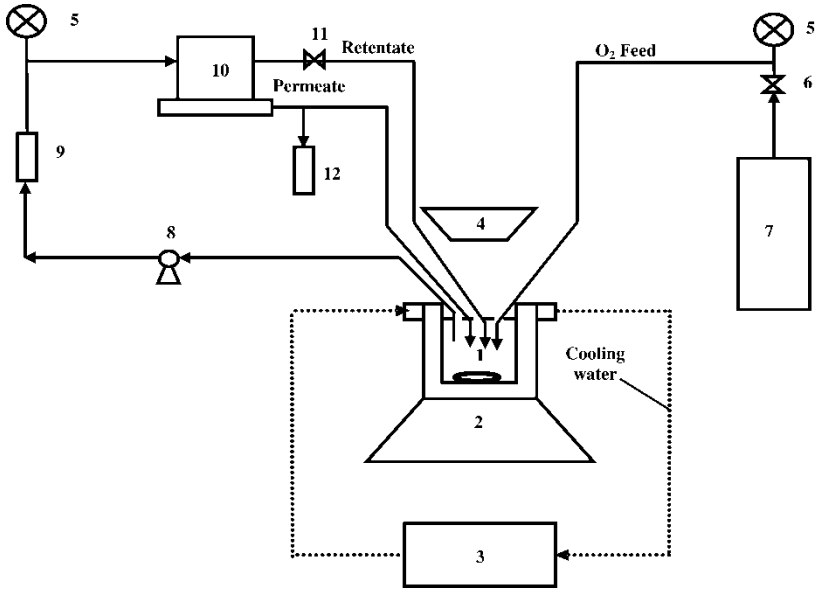

Figure 2. Scheme of the batch membrane reactor operating in continuous recirculation flow: (1) open water jacket beaker containing the reaction mixture; (2) magnetic stirrer; (3) water thermostat; (4) UV lamp; (5) manometer; (6) gas-valve; (7) O_2 cylinder; (8) diaphragm pump; (9) flowmeter; (10) pressure cell containing the membrane; (11) retentate valve; (12) graduate cylinder for permeate sampling.

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means of a valve situated between the permeation cell and the batch reactor. Exposed membrane area is 19 cm^2. The volume of the initial feed solution is 0.500 L.

A 500 W medium pressure Hg lamp (Helios Italquartz) emitting a light intensity in the UV-Vis range (maximum centred at $\lambda = 366$ nm with the emission profile between 240 and 440 nm) equal to 6.4 mW/cm^2, was used to irradiate from top the batch reactor.

RESULTS AND DISCUSSION

Tests in the Batch Reactor

All the tests in the batch reactor were performed by using the following general operating conditions: Gemfibrozil concentration in the feed 20 mg/L or 5 mg/L; iron catalyst and hydrogen peroxide concentrations respectively equal to 5.6 and 34 mg/L; temperature in the reactor hold at 30°C. Those values were chosen according to a previous work found in literature, in which degradation by different AOPs was considered (1).

Photolysis at 20 mg/L

In order to compare the effect on using only light irradiation with respect to the other two photo assisted AOPs, some photolytic tests were carried out by irradiating the aqueous solution containing the drug. Photolysis is a common method for generating free radicals through sigma bond cleavage. These radicals are most often the precursors that generate other free radicals (19). The first step in a photochemical reaction is the excitation of a molecule through absorption of one photon. This step happens normally by UV irradiation, but the actual trend is to use natural energy sources like solar radiation (7). The excited molecule leads to a chemical reaction. Thus the organic substrate is progressively degraded. In the case of gemfibrozil tested in this work the absorbance spectrum of the molecule shows some absorption in the wavelength range 210–310 nm. Because the UV-Vis lamp has an emission profile covering part of the absorption spectra of GEM, some effects on degradation should be expected.

To this aim some photolytic tests were carried out at initial Gemfibrozil concentration of 20 mg/L to evaluate both drug degradation and mineralization. Obtained data (Fig. 3) show about 90% GEM degradation after 4 hours of irradiation. The trend of some degradation products, expressed as area of the main peaks at the retention time, is reported in Fig. 4. It can be observed that there is a mineralization only of the degradation product with a retention time 5.2 minutes. The little mineralization was confirmed also by DOC measurements being the initial value 14.4 mg/L and the final one 13.9 mg/L corresponding to 3.5% mineralization. This result confirms the negligible mineralization using the UV radiation only indicating that the simple light irradiation on GEM mineralization can be neglected.

The solution pH at the end of degradation tests was equal to 6.9. Considering that the initial pH was higher than 8, a slight phase acidification was

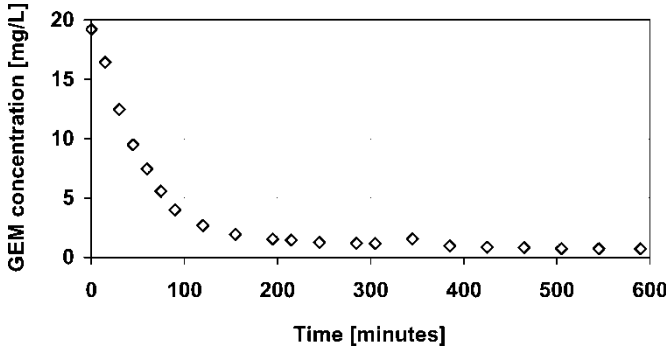

Figure 3. Gemfibrozil concentration versus the time in photolysis tests ($[GEM]_{IN}$ = 20 mg/L; T = 30°C).

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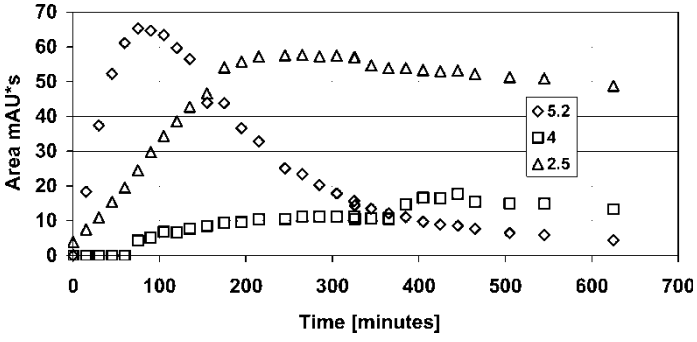

Figure 4. Area of three degradation products at retention time of 2.5, 4, and 5.2 minutes, versus the time in photolysis tests ($[GEM]_{IN} = 20$ mg/L; $T = 30°C$; UV wavelength = 366 nm).

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obtained. This pH behavior shows that also during Gemfibrozil degradation the formation of acidic species takes place, similar to that which is reported in literature for Diclofenac degradation (1) and for water pollution abatement (15).

Because GEM is not soluble at acidic pH, and considering phase self-acidification during the degradation process, a slight solution clouding was observed operating at a GEM concentration of 20 mg/L. This suspended material reduced the irradiation efficiency during the photolytic treatment, since a fraction of the irradiated energy was scattered/absorbed by these particles (15). In order to minimize this phenomenon, the successive degradation tests were carried out at a GEM concentration of 5 mg/L.

Comparison of the Four Different AOPs for GEM Degradation at 5 mg/L

In Fig. 5 and in Table 1 the results obtained by using the four different processes for GEM degradation are reported. Better results were obtained by using Fenton and the photo assisted Fenton processes showing a very fast degradation. Working with Fe at basic-neutral pH it precipitated as hydroxide, but it continued to mineralize the GEM as it can be observed in Fig. 6 where the DOC for the two AOPs decrease in the time. Because only Fenton and photo assisted Fenton processes lead to some mineralization of Gemfibrozil, they were tested in the membrane reactor. The observed mineralization agrees with expected results: indeed Fenton processes are destructive during the mineralization of organic pollutants since they generate oxidative radicals in solution in the dark. Fenton processes becomes faster and more efficient when light is applied due to the photodecomposition of $Fe(OH)^{2+}$ rendering additional OH-radicals in solution (15, 20).

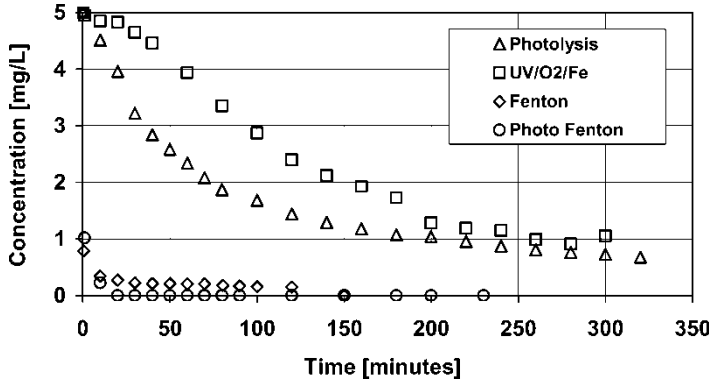

Figure 5. Gemfibrozil concentration versus the time in the degradation tests using four different AOPs ([GEM] = 5 mg/L; iron catalyst and hydrogen peroxide concentration respectively equal to 5.6 and 34 mg/L; temperature in the reactor hold at 30°C).

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Tests in the Batch Membrane Reactor

Fenton and photo assisted Fenton processes were tested in the batch membrane reactor (see Fig. 2) to evaluate the feasibility to use a membrane for recovering and reusing the catalyst, for controlling the contact time of the organic substrate in the oxidant environment, and for carrying out, in a single step, both the reaction and the separation of the purified water.

All the tests were realized by using an UTC-60 FLAT (SU-6xx) membrane by Toray-Romembra Industries at a Trans Membrane Pressure (TMP) of 1 bar.

This being an explorative phase of the work the tests on Fenton and photo assisted Fenton were carried out for a relatively long time to check the operating membrane stability, GEM degradation and GEM mineralization

Table 1. Comparison of the four AOPs tested in GEM degradation expressed as abatement % and mineralization % at 600 minutes ($[GEM]_{IN}$ = 5 mg/L; iron catalyst and hydrogen peroxide concentrations respectively 5.59 and 34 mg/L; temperature in the reactor 30°C)

	Abatement (%)	Mineralization (%)
Photolysis	86	3.1
$UV/O_2/Fe$	79	10
Fenton	97	24
Photo Fenton	100	62

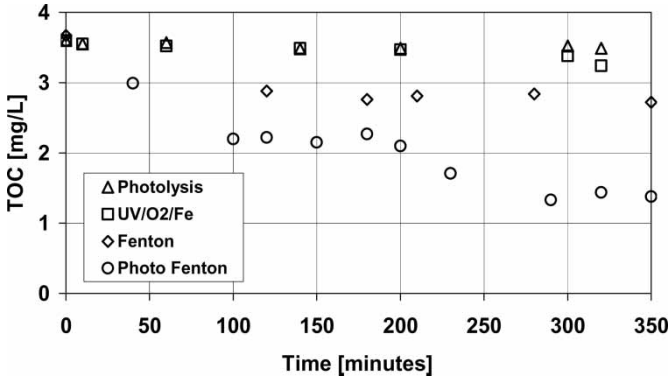

Figure 6. DOC concentration versus the time in the four different AOP degradation tests ([GEM] = 5 mg/L; iron catalyst and hydrogen peroxide concentration respectively equal to 5.6 and 34 mg/L; temperature in the reactor hold at 30°C).

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(DOC behavior in the time). The following four steps were performed in carrying out the experimental runs:

1. feeding of the GEM aqueous solution at 5 mg/L and pH $\approx$ 8 in the membrane batch reactor without Fenton reagents, in order to evaluate drug adsorption on the membrane (120 minutes);
2. first addition of hydrogen peroxide (0.568 mL of H_2O_2; 3% w/w solution in water), thus evaluating if the presence of the oxidant without the catalyst gives GEM degradation (60 minutes);
3. addition of iron (II) catalyst starting the drug degradation (90 minutes);
4. second addition of hydrogen peroxide (0.568 mL of H_2O_2; 3% w/w solution in water), for evaluating if increasing the oxidant concentration during the run brings to an additional drug degradation (120 minutes).

Fenton Process

The results of the Fenton degradation tests in the batch membrane reactor, reported in Fig. 7, showed in the first step of 120 minutes, a drug adsorption on the membrane equal to 38%. At that time the first hydrogen peroxide addition was made, and the GEM concentration decreased in 1 minute from 3.1 to 2.9 mg/L. Then it remained constant till the time of iron (II) catalyst addition at 180 minutes. At this point, the Fenton degradation started, and the GEM concentration drastically decreased in only one minute from 2.9 to 0.6 mg/L. After 90 minutes of the degradation test, the drug concentration was practically constant, and equal to 0.3 mg/L, corresponding to an abatement of 94%. This value did not reach 100% probably because of intermediates formation that precluded further degradation of the drug. In this

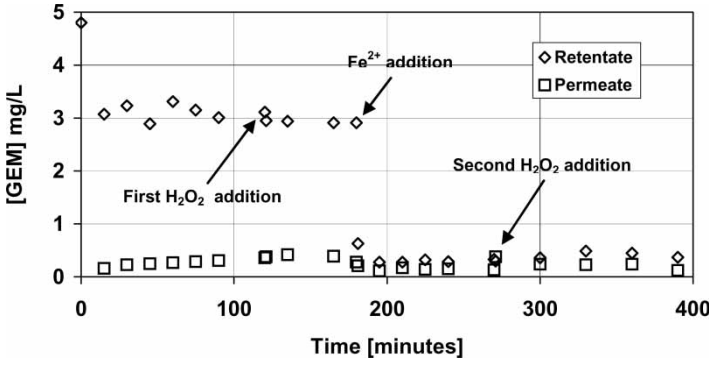

Figure 7. Gemfibrozil concentration versus the time in Fenton tests in the batch membrane reactor ([GEM] = 5 mg/L; iron catalyst and hydrogen peroxide concentration respectively equal to 5.6 and 34 mg/L; temperature 30°C; TMP = 1 bar).

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situation the second addition of the oxidant did not further decrease the GEM concentration.

Regarding the membrane performance, interesting results were obtained in terms of catalyst recovery in the retentate: indeed, membrane rejection to iron (II) was higher than 95%, meaning good possibility for catalyst reuse. Satisfactory GEM and degradation intermediate rejections (higher than 90 and 99% respectively) were obtained, thus showing the feasibility to use a membrane to maintain the catalyst in the oxidant environment and to control the contact time of the organic substrate.

Considering GEM mineralization, the results confirmed that the use of a membrane reactor significantly increase the performance of the oxidizing process, with a final mineralization in the retentate of approximately 55% instead of 24% obtained in the batch tests.

After 390 minutes (run stop time) a slightly yellow but clear aqueous solution at pH 6.3 was obtained, confirming phase self-acidification due to formation of acidic intermediates.

Another degradation test was carried out by using the same membrane without the iron (II) catalyst addition, in order to evaluate the possibility to have persistent catalytic activity due to catalyst deposition and/or adsorption on the membrane in the previous run. The obtained results showed, in the first step of the test, a GEM adsorption on the membrane of 40%. This experimental data, equal to the adsorption obtained in the previous run, indicated the degradation of GEM initially adsorbed on the membrane in the previous run. So, when the membrane is reused it adsorbs again the organic substrate. Unsatisfactory results were obtained in terms of GEM degradation after oxidant addition showing no catalyst deposition on the membrane.

Photo Assisted Fenton Process

The results of the photo assisted Fenton degradation tests in the batch membrane reactor are reported in Fig. 8. In these tests a drug adsorption on the membrane approximately equal to 25% was obtained in the first run step of 120 minutes. After the first hydrogen peroxide addition (t = 120 minutes) the GEM concentration did not show variation (3.5 mg/L), and practically did not change till the iron (II) catalyst addition (t = 180 minutes). Simultaneously the UV lamp was turned on, and the drug photo assisted Fenton degradation started. Also in this test a fast degradation happened in the first minute: indeed at the time of 181 minutes the GEM concentration drastically decreased from 3.5 to 0.4 mg/L. After 90 minutes of the degradation test, drug concentration was equal to 0.2 mg/L (abatement of 96%), and did not change. Also in this test the second oxidant addition did not cause further GEM degradation, as previously observed for the simple Fenton process.

Good results were obtained by considering membrane performance: indeed, both catalyst and organic substrates rejections were very encouraging (both higher than 95%). Thus, also for this process, the membrane was able to control the contact time of the substrates in the oxidant environment, and to reuse the catalyst.

By using the photo assisted Fenton process a drug mineralization in the retentate of approximately 60% was achieved, this value is practically similar to that one obtained in the batch tests.

After 390 minutes (run stop time) a slightly yellow but clear aqueous solution was obtained at a pH 6.0, confirming phase self-acidification due to acidic intermediates formation.

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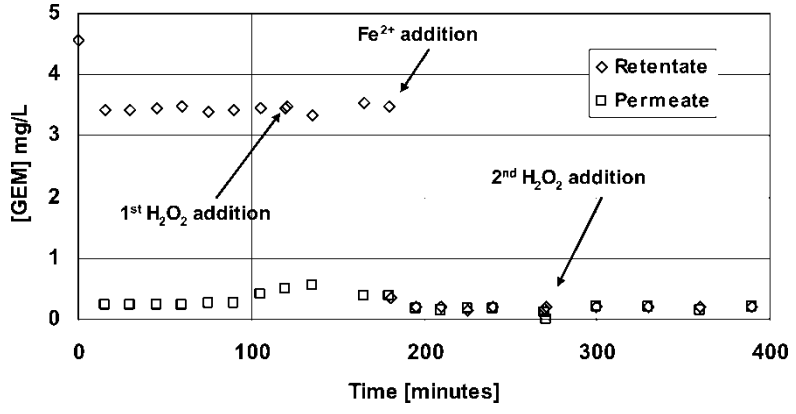

Figure 8. Gemfibrozil concentration versus the time in photo assisted Fenton tests in the batch membrane reactor ([GEM] = 5 mg/L; pH ≈ 8; iron (II) catalyst and hydrogen peroxide concentrations respectively equal to 5.6 and 34 mg/L; temperature 30°C; TMP = 1 bar).

Comparison of Fenton and Photo Assisted Fenton for GEM Degradation in the Batch Membrane Reactor

In Figs. 9 and 10 Fenton and photo assisted Fenton results are compared in terms of reduction (adsorption or degradation) percentage, and mineralization versus the time. In particular Fig. 9 is divided in two zones: the first one, from 0 to 180 minutes corresponds to steps (i) and (ii) of the batch membrane tests in which no drug degradation happens but only drug adsorption on the membrane. The second part of the graph corresponds to the real degradation tests.

Those results show a little better GEM degradation and mineralization by using the photo assisted Fenton process (96% and 60%, respectively) in agreement with the expected results.

Indeed, in both the processes OH · radicals are generated by the Fenton reagents according to the following reaction:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + HO\cdot$$

responsible for the organic substrate degradation.

When irradiation with UV light is employed, the degradation of the organic pollutant with Fenton reagents is strongly accelerated because the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration, rendering additional OH-radicals in solution by the following reaction (18):

$$Fe(HO)^{2+} \xrightarrow{h\nu} Fe^{2+} + OH\cdot\,.$$

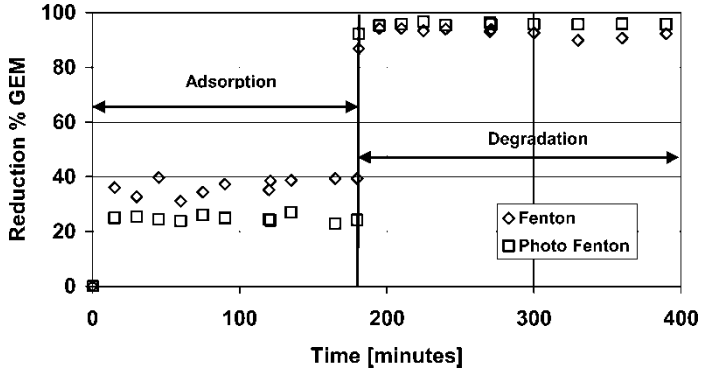

Figure 9. Comparison between Fenton and photo assisted fenton processes for GEM degradation in the batch membrane reactor ([GEM] = 5 mg/L; iron catalyst and hydrogen peroxide concentration respectively equal to 5.6 and 34 mg/L; temperature in the batch membrane reactor hold at 30°C; TMP = 1 bar).

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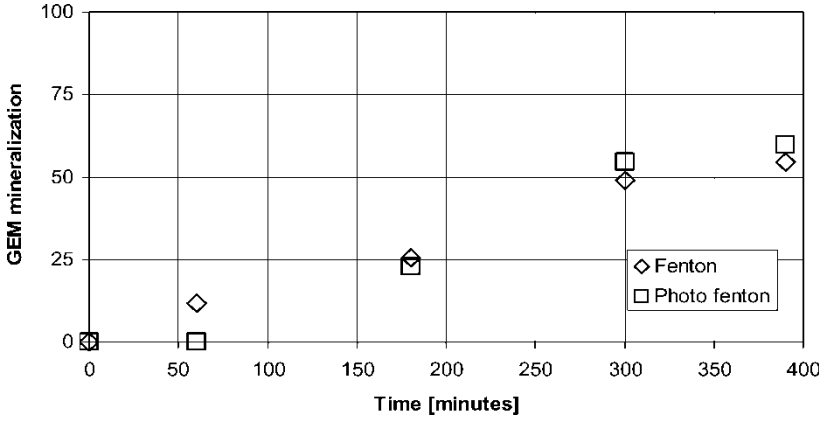

Figure 10. Comparison between Fenton and photo assisted fenton processes for GEM mineralization in the batch membrane reactor (same conditions of Fig. 9).

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CONCLUSIONS

The results obtained in this explorative work on the possibility of coupling advanced oxidation processes (AOPs) and membrane processes were quite encouraging in the abatement of the drug Gemfibrozil from aqueous systems.

Degradation tests in the batch reactor showed better results by using Fenton and photo assisted Fenton processes of the four AOPs tested. Indeed these two processes gave quite a complete GEM degradation, and satisfactory results also in terms of mineralization (62 and 24% for Fenton and photo assisted Fenton processes, respectively). Thus, only these AOPs were tested in the membrane reactor.

Degradation tests in the batch membrane reactor gave a drug degradation higher than 92% and a mineralization higher than 55%. Obviously, better results were obtained by using UV irradiation because of the promotion of iron catalyst regeneration and production of additional OH radicals in one step.

Good results were obtained regarding the possibility to couple AOPs with a membrane separation step. Indeed, it was observed that the membrane was able to control the contact time of the organic substrates in the oxidant environment, and to reuse the catalyst, thus realizing in a single step both the degradation and the separation of the purified water.

Further studies are required to improve the system performance:

1. by choosing a membrane with better performance,
2. by studying the influence of some chemical parameters like oxidant and catalyst concentration on the process,
3. by studying some operating parameters like hydrogen peroxide addition mode or system fluid dynamics.

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REFERENCES

1. Vogna, D. et al. (2004) Advanced oxidation of the pharmaceutical drug Diclofenac with UV-H_2O_2 and ozone. *Water Res.*, 38: 414.
2. Heberer, T. (2002) Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. *Toxicol. Lett.*, 131: 5.
3. Halling-Sorensen, B. et al. (1998) Occurrence, fate, and effects of pharmaceutical substances in the environment—a review. *Chemosphere*, 36: 357.
4. Jones, Q.A.H., Voulvoulis, N., and Lester, J.N. (2002) Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. *Water Res.*, 36: 5013.
5. Kummerer, K. (2001) *Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks*; Springer: Berlin, Germany.
6. Cahill, J.D. et al. (2004) Determination of pharmaceutical compounds in surface- and ground-water samples by solid-phase extraction and high performance liquid chromatography-electrospray ionization mass spectrometry. *J. Chromatogr. A*, 1041: 171.
7. Andreozzi, R., Marotta, R., and Paxéus, N. (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. *Chemosphere*, 50: 1319.
8. Castiglione, S. et al. (2006) Removal of pharmaceuticals in sewage treatment plants in Italy. *Environ. Sci. Technol.*, 40: 357.
9. Carballa, M. et al. (2004) Behaviour of pharmaceuticals cosmetics and ormones in a sewage treatment plant. *Water Res.*, 38: 2918.
10. Braga, O. et al. (2005) Fate of steroid estrogens in Australian inland and coastal wastewater treatment plants. *Environ. Sci. Technol.*, 39: 3351.
11. Bendz, D. et al. (2005) Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Hoje River in Sweden. *J. Hazard. Mater.*, 122: 195.
12. Zuccato, E., Castiglioni, S., and Fanelli, R. (2005) Identification of the pharmaceuticals for human use contaminating the Italian aquatic environment. *J. Hazard. Mater.*, 122: 205.
13. Colpin, D.W. et al. (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. Streams, 1999 − 2000: A national reconnaissance. *Environ. Sci. Technol.*, 36: 1202.
14. Hermening, A. et al. (2000) Gemfibrozil and its oxidative metabolites: quantification of aglycones, acyl glucuronides, and covalent adducts in samples from preclinical and clinical kinetic studies. *J. Chromatogr. B*, 741: 129.
15. Andreozzi, R. et al. (1999) Advanced oxidation processes (AOP) for water purification and recovery. *Catal. Today*, 53: 51.
16. Esplugas, S. et al. (2002) Comparison of different advanced oxidation processes for phenol degradation. *Water Res.*, 36: 1034.

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17. Parra, S. et al. (2004) Synthesis, testing, and characterization of a novel nafion membrane with superior performance in photoassisted immobilized Fenton catalysis. *Langmuir*, 20: 5621.
18. Molinari, R. et al. (2006) Heterogeneous photocatalytic degradation of pharmaceuticals in water by using polycrystalline TiO_2 and a nanofiltration membrane reactor. *Catal. Today*, 118: 205.
19. Pine, S.H. (1987) *Organic Chemistry*; Mc Graw Hill: New York, U.S.A.
20. Kavitha, V. and Palanivelu, K. (2004) The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere*, 55: 1235.

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