Heterogenization of Polyoxometalates on the Surface of Plasma-Modified Polymeric Membranes

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Novel catalytic membranes have been prepared by linking phosphotungstic acid $H_3PW_{12}O_{40}$ (W12), a polyoxometalate having interesting properties as photocatalyst, on the surface of plasma-modified membranes. Porous flat-sheet membranes made of polyvinylidene fluoride (PVDF) have been prepared by a phase-inversion technique induced by a nonsolvent. These membranes have been modified by plasma treatments on the surface to graft N-containing polar groups that are able to act as binding sites with W12 (PVDF−NH2−W12). A comparison of the surface and bulk properties of the native and modified PVDF membranes has been reported. Catalytic activity of the PVDF−NH2−W12 membranes has been evaluated in the aerobic degradation reaction of phenol in water. Catalytic tests have been carried out in a membrane reactor operating in continuous mode. Better catalytic performances have been observed for the W12 heterogenized on PVDF membrane than for W12 in a homogeneous phase. Moreover, PVDF−NH2−W12 membranes have given proof of their complete stability under photooxidation conditions and their good recycle. This study has shown the possibility of heterogenizing catalysts by a controlled modification of the membrane surface via a plasma technique. This new method is very versatile and can be easily extended to other catalysts. Further studies are actually in progress with other catalysts belonging to the polyoxometalates group.

Introduction

Early transition metals (V, Nb, Ta, Mo, W) in their highest oxidation states can form metal−oxygen cluster anions, commonly named polyoxoanions or polyoxometalates (POMs).[1] These compounds have interesting acid and redox properties for catalytic applications. In particular, POMs in the solid state are particularly suitable for catalyst design at the atomic and molecular level.[2] There are several large scale industrial applications of POMs as oxidation and acid catalysts, both in the solid state and in solution.[3−6] However, POMs are characterized by a low surface area that in many cases limits their applications.[2] To overcome this problem, researchers have made numerous attempts to disperse POMs on various supporting materials such as silica[7−10] and organic polymers.[11−13] The heterogenization of catalysts also has interesting implications in both environmental and industrial sectors, allowing the same catalyst to be reused several times, in many cases with higher catalytic activity.

Among the different heterogenization routes, the entrapping of catalysts in membranes offers new possibility for the catalyst design. Moreover, catalytic membranes can be easily applied in the continuous processes required in the industry. One of the main advantages of membrane reactors, in comparison to traditional reactors, is the easy recycling of the catalyst; furthermore, the selective transport properties of the membranes can be used to improve the yields of equilibrium-limited reactions, selectively remove products from the reaction mixture in order to prevent undesired consecutive reactions, and selectively supply reagents.[14,15]

In our previous work,[16] we reported the heterogenization of decatungstate ($W_{10}O_{32}^{4-}$), an interesting photocatalyst, in

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polymeric membranes made of polyvinylidene fluoride (PVDF) or poly(dimethylsiloxane). The polymeric catalytic membranes prepared have been successfully applied in the photooxidation of organic substrates in water. These photocatalytic systems are characterized by different and tunable properties depending on the nature of the polymeric microenvironment.

In this work, we have investigated the possibility of supporting phosphotungstic acid $H_3PW_{12}O_{40}$ (W12), one of the most widely used photocatalytic POMs, on the surface of plasma-activated PVDF membranes. The application of a plasma technique for the heterogenization of a catalyst on the surface of membranes is very interesting because, generally, when a catalyst is heterogenized on a solid support, it results in the catalyst being only partially active because of diffusion limitations and aggregation phenomena.

Plasma treatments (PT) represent a versatile tool for modifying only the few topmost layers of solid surfaces thus leaving the bulk properties totally unaltered.[17,18] PT allow one to graft, in a controlled way, different functional groups on solids surfaces (e.g., COOH, OH, NH_2, etc.).[19] These functionalities can be conveniently used as anchor groups for catalyst binding, which can be well dispersed on the membrane surface, overcoming diffusion and aggregation limits. In particular, in our experiments, we have used ammonia-fed discharges,[20] because the grafting of basic groups on membrane surfaces can allow the instauration of ionic interaction with the acid W12 catalyst. Moreover, the formation of hydrogen bonds with other polar groups grafted on the surface is also possible.

The membrane surfaces and cross section, before and after plasma treatment, have been examined by scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) and RX maps have been used to characterize the composition of membrane surface and to assess the initial grafting of nitrogen groups and subsequent immobilization of the W-based catalyst. The effect of the plasma modification on surface and bulk properties of the PVDF membrane was also investigated.

The catalytic membranes have been successfully applied in the aerobic photooxidation of phenol in water, providing stable and recyclable photocatalytic systems. These results have been compared to those of a similar reaction carried out in the homogeneous phase.

This reaction has been chosen because phenol and its derivatives constitute one of the main organic pollutants to be removed from wastewater.[21] The development of new effective and environmentally benign methods for phenol
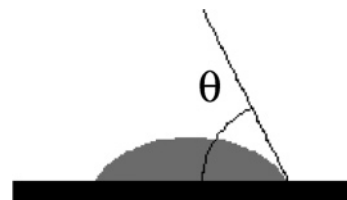

Figure 1. Geometrical definition of the contact angle (θ).

degradation is an important research area; advanced oxidation processes (AOP) are very promising methods for wastewater treatments.[22,23] These methods, mainly based on the photoinduced generation of hydroxyl radicals, can lead to complete mineralization of organic pollutants. POMs have been largely used as efficient photocatalysts for the complete degradation of organic pollutants, including phenols.[24−26]

Experimental Section

Materials and Methods. Phosphotungstic acid hydrate ($H_3PW_{12}O_{40}$ aq), phenol, and *N,N*-dimethylacetamide (DMA) were used as received from Sigma-Aldrich without further purification. MilliQ deionized water was used in the experiments. PVDF homopolymer was supplied from Elf Atochem under the trade name Kynar 460. The cross section and surface morphology of the membranes were examined by a Cambridge Instruments Stereoscan 360 scanning electron microscope. Cross sections were prepared by fracturing the membrane in liquid nitrogen. All the samples were coated with a thin layer of gold before SEM observations. RX maps on the membrane surface, coated with a thin layer of graphite, were performed on an EDAX-Phoenix instrument (detector Super Ultrathin Window, Si/Li crystal analyzer).

XPS analyses were performed on a PHI ESCA 5300 equipped with a nonmonochromatic Mg K_α radiation (1253.6 eV) at an operating power of 300 W. The measurements have been performed at a takeoff angle (TOA) fixed at 45° (measured with respect to the sample surface).

The casting knife was supplied by Braive Instruments. The membrane thickness was determined by a Carl Mahr D7300 Esslingen a.N digital micrometer. Results reported are the mean of 10 measurements from different regions of each membrane.

The contact angle (θ) is a quantitative measure of the wetting of a solid by a liquid.[27] It is defined geometrically as the angle formed by a liquid at the three-phase boundary where a liquid, gas, and solid intersect as shown in Figure 1.

Low values of θ indicate that the liquid spreads, or wets the surface well, whereas high values indicate poor wetting. Contact angles (CA) and surface tension of the liquid tested were measured by a CAM 200 contact angle meter (KSV Instruments, Ltd., Helsinki, Finland). The measurements were performed by the sessile drop method at ambient temperature. The sessile drop was formed by depositing the used test liquid (water or phenol solution, 0.002 M) from above, using a motor-driven microsyringe on the membrane surfaces. Results are the mean of four measurements from different regions of the membrane surfaces.

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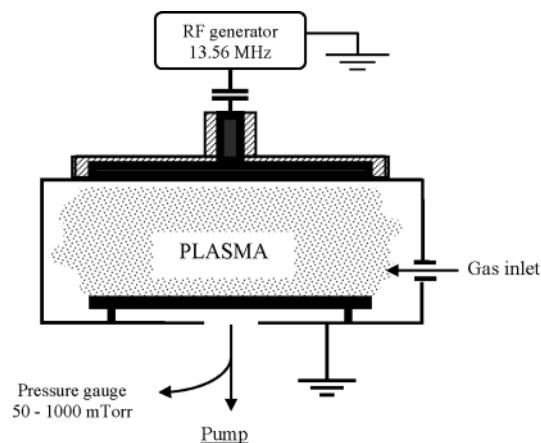
Figure 2. Schematic diagram of the plasma reactor.

Cross-flow water filtration experiments were carried out at 30 °C using bench lab ultrafiltration equipment, constituted by a flat-sheet membrane cell that was assembled in our laboratory and fed with distilled water at different transmembrane pressures.

The mean pore diameters, the pore diameter at the maximum distribution, and the pore size distribution were determined by a CFP 1500 capillary flow porometer, Porous Materials, Inc., Ithaca, NY.

Membrane porosity was measured by the gravimetric method, which determined the weight of water contained in the membrane pores. The porosity ϵ was calculated by the following equation:

$$\epsilon = \frac{(w_2 - w_1)/D_w}{((w_2 - w_1)/D_w) + (w_1/D_p)} \qquad (1)$$

where w_1 is the weight of the dry membrane, w_2 the weight of the wet membrane, D_w the water density, and D_p the polymer density (1.76 g/cm^3).

Membrane Preparation. Flat-sheet membranes made of PVDF were prepared by a phase-inversion process induced by a nonsolvent. DMA was used as the solvent and distilled water as the nonsolvent. A solution (15.0 wt %) of PVDF was prepared by dissolving the polymer in DMA (85.0 wt %) with magnetic stirring at room temperature for about 24 h. The solution was cast on a glass plate by setting the knife gap at 250 μm and then immersed for 2 h in a coagulation bath containing distilled water at 20 ± 2 °C. Finally, the membranes were removed from the coagulation bath and dried in a oven at 60 °C under vacuum for 24 h.

Plasma Treatments. Plasma treatments have been performed in a quasiparallel tubular pyrex glass reactor equipped with two electrodes. The upper external electrode is conformal to the reactor and connected to a radiofrequency generator (RF, 13.56 MHz, ENI-ACG-10) through an impedance matching network, and the lower internal electrode (substrate holder) is connected to the ground. A simple sketch of the reactor is shown in Figure 2. The gases have been fed into the chamber through a calibrated MKS mass flowmeter. A rotative pump allowed for chamber evacuation; the pressure has been controlled with an MKS baratron.

The membranes have first been plasma treated in RF glow discharge fed with Ar (20 sccm, 800 mTorr of pressure, 30 W, 1 min) to induce a cross-linking of the membrane surface and reduce the hydrophobic recovery of the PVDF chains.[29] Hydrophobic recovery is a phenomenon that can occur when polar groups are
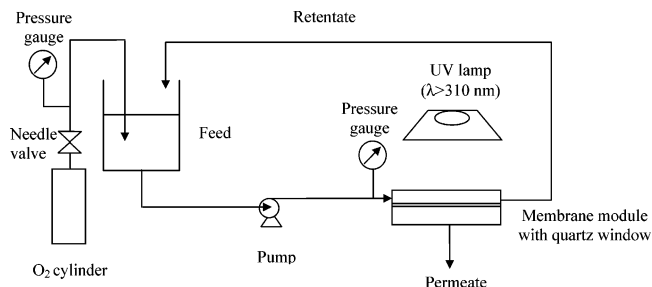
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Figure 3. Scheme of the membrane photoreactor used in the catalytic tests.

grafted by the plasma technique on hydrophobic polymeric surfaces.[29] It consists of the orientation of the untreated polymeric chains outward from the modified interface, and that of the grafted polar groups inward, leading to the recovery of the surface properties of the original polymer and to the reduction of the polar groups available on the surface.

Ar pretreated membranes have then been plasma treated in a NH$_3$ RF glow discharge (20 sccm, 300 mTorr of pressure, 20 W, 5 min) to obtain stable N- containing groups grafted to the surface. (In the following text, a PVDF membrane submitted to Ar/NH$_3$ treatment will be indicated by PVDF−NH$_2$.) As a consequence of the plasma pretreatment, the hydrophobic recovery of the PVDF chains is reduced after the NH$_3$-plasma-grafting process of N-containing groups, and the modified surfaces remain more stable with time.

Catalyst Heterogenization. The PVDF-NH2 membrane has been immersed in an aqueous solution of W12 (0.086 mM) for 24 hours; after it has been washed three times with water and finally has been dried at room temperature (in the following this membrane will be indicated as PVDF−NH2−W12).

Photooxidation Experiments. The photocatalytic experiments were carried out in a flat-sheet membrane reactor (Figure 3).

The membrane module, equipped with a quartz window, has an active surface area of 4.5 cm^2. In the catalytic test, an aqueous phenol solution (150 mL; 0.002 M) was fed to the membrane with a tangential flow rate of 65 mL/min. Retentate and permeate samples were collected at regular time intervals. The feed solution was hosted in a thermostated bath held at 30 °C, under magnetic stirring, and pure oxygen was bubbled into the reacting mixture at 0.3 bar. Irradiation was performed with a 500 W quartz UV mercury vapor lamp, emitting from 310 nm to visible light (Helios Italquarz, Milan, Italy), placed 10 cm from the membrane surface. In all experiments, the membranes were irradiated on the upper surface. Homogeneous catalytic tests were carried out using an aqueous phenol solution (150 mL; 0.002 M) in the presence of phospho-tungstic acid (7.0 × 10^{-4} M). To better compare the homogeneous and heterogeneous reactions, we also carried out homogeneous tests in the reactor shown in Figure 3, but in this case, the permeate side was closed, putting a thin stainless steel sheet in place of the membrane position. The photocatalytic reactions were monitored by HPLC determination of phenol. Analyses were performed on a HPLC Hitachi D7000 System Manager, equipped with an L-7400 UV detector; the column was Hypersil C 18, 250 × 4.6 mm^2, 5 μm (Alltech, Italy). The mobile phase was 65:35 (v/v) acetonitrile: water. The operating conditions were as follows: flow rate = 0.8 mL/min; $T = 25$ °C, $P = 73$ bar, $\lambda = 254$ nm.

Results and Discussion

Membrane Characterization. One of the main issues in the selection of polymers for the heterogenization of catalysts is their stability under reaction conditions. As reported in our previous work,[16] membranes made of PVDF, a polymer
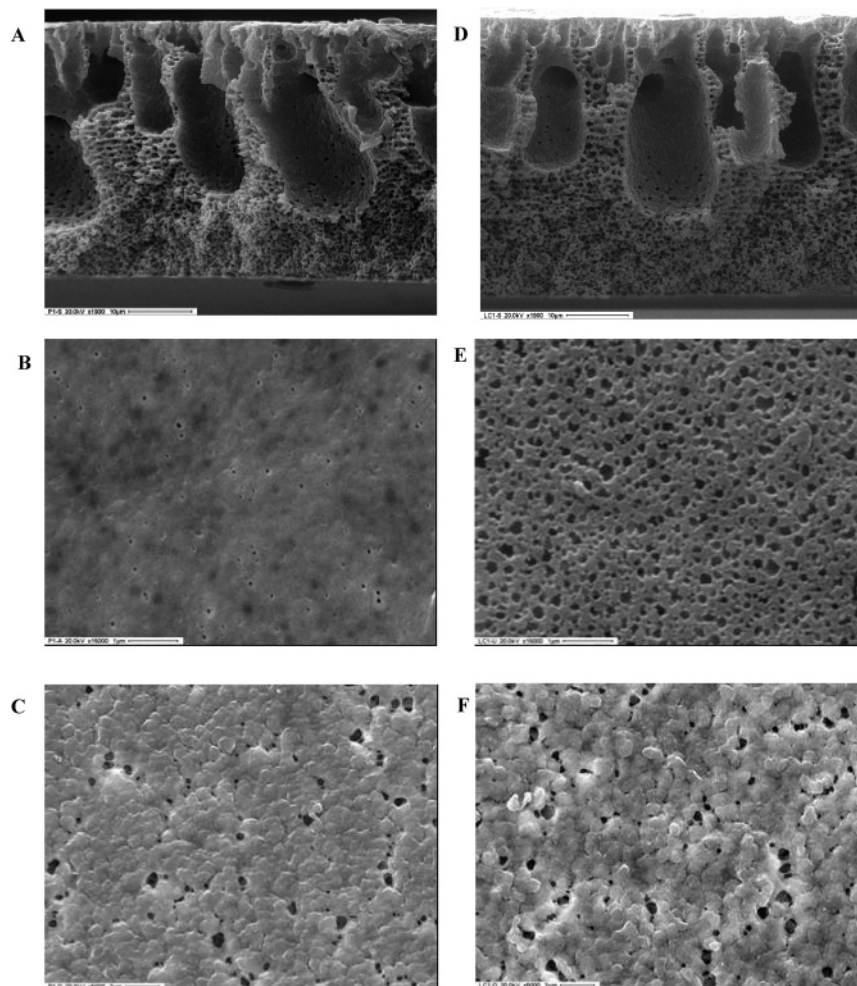
Figure 4. SEM images of the native PVDF membrane: (A) cross section (×1900), (B) top layer (×15 000), (C) bottom layer (×500). SEM images of the PVDF−NH2−W12 membrane: (D) cross section (×1900), (E) top layer (×15 000), (F) bottom layer (×5 000).

Table 1. XPS Analysis of the PVDF Native Membrane, the Membrane Treated with Ar/NH₃ Plasma (PVDF−NH2), and the Membrane Immersed in W12 Solution after the Ar/NH₃ Treatment (PVDF−NH2−W12)

substrate	C%	O%	W4f%	P2p%	F%	N%	O/C (±0.03)	N/C (±0.04)	N/F (±0.04)	W/C (±0.03)	F/C (±0.03)
PVDF	54.2	1.9			43.8		0.04				0.80
PVDF−NH2	57.6	4.7			28.0	9.4	0.08	0.16	0.33		0.48
PVDF−NH2−W12	53.1	18.3	3.5	0.4	19.3	5.1	0.34	0.10	0.26	0.07	0.36

characterized by a high chemical, thermal, and mechanical stability, are also stable under aerobic photooxidation condition. The hydrophobic properties of this material can also positively influence the approach, near the catalytic sites, of organic substrates dissolved in water. PVDF is of particular interest in photocatalytic applications because of its optical transparency; moreover, the fluorinated environment can promote oxidation reactions.[30]

Porous flat-sheet membranes have been prepared by a phase-inversion technique induced by a nonsolvent,[31] as described in the Experimental Section.

The surfaces and the cross sections of the native PVDF membrane and catalytic PVDF−NH2−W12 have been examined by SEM (Figure 4). The SEM images show an asymmetric structure for both the membranes. The membrane cross sections (Figure 4a,d) are characterized by macrovoids with a drop-shaped structure extending from the upper surface toward the bottom surface. Microphotographs of the upper and bottom surfaces of the PVDF native membranes (Figure 4b,c) reveal significant differences between the two sides. The pore size in the bottom surface is much larger than that of the upper one. This difference is due to the initial evaporation of solvent, during the membrane preparation process, from the upper surface and the consequent formation of a denser skin layer. The permeability and selectivity of the membrane depend on this skin layer, and the porous substructure acts only as a support.

Polar chemical groups (we hypothesize principally NH₂, together with OH, CN, NH, and CO) have been grafted by NH₃ plasma discharge on the upper surface of a PVDF membrane pretreated with Ar in order to control hydrophobic recovery.[32,28] The groups grafted on the surface can act as anchor sites for immobilizing the acid catalyst W12.

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Figure 6. Contact angles (±standard deviation) with water and a phenol solution (0.002 M) on the upper surface of the PVDF-based membranes

Figure 7. Water flux (*J*) at 30 °C of the native PVDF membrane and PVDF−NH2−W12.
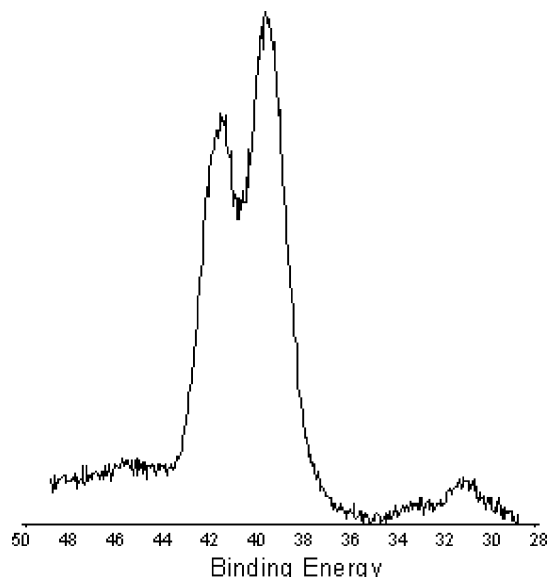
Figure 5. XPS W4f component.

Surface-diagnostics techniques such as X-ray photoelectron spectroscopy, contact angle measurements, and RX maps have been used to attest to the surface modification by plasma treatment.

The XPS N% value can be taken as a measure of the efficiency of the grafting of N-groups after the NH_3 plasma treatments. The N content is lowered from 9.4 for PVDF−NH2 to 5.1 for PVDF−NH2−W12 surfaces. When W12 is added to the surface, W%, O%, and P% XPS values increase, whereas C%, F%, and N% values are lowered. W-based catalyst binding can be monitored by the XPS W%. The W4f peak shows two major components; this behavior is typical of tungsten oxides[33] (See Table 1 and Figure 5).

RX maps (data not shown) on the upper surface of the PVDF−NH2−W12 membrane underline a good dispersion of the catalyst with a homogeneous W and F surface distribution.

We hypothesize that principally ionic interaction between W12 and the NH_2 groups, together with hydrogen bonding and different interactions with the other polar groups also grafted by plasma treatments, link the catalyst on the membrane surface. CA measurements on the upper surface of the membranes confirm the presence of polar groups by decreasing the water contact angle with respect to the native membrane (Figure 6). The water CA values further decreased after the immobilization of W12 occurred, probably because of the presence of many oxygen moieties (Figure 6).

Interesting results were obtained considering the contact angle with a 0.002 M phenol solution (Figure 6). As expected, the surface tension of the phenol solution was lower than that of the pure water (73.47 and 75.24 mN/m, respectively); consequently, the plasma-modified membranes have a higher contact angle with the phenol solution than does the native PVDF membrane, but the values are still less than 90° (Figure 6).
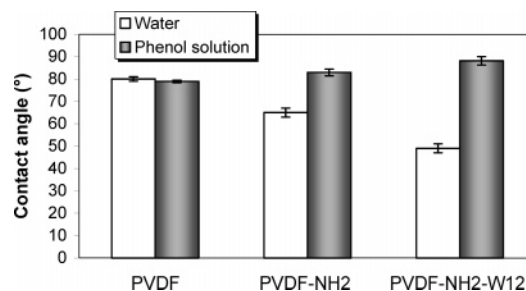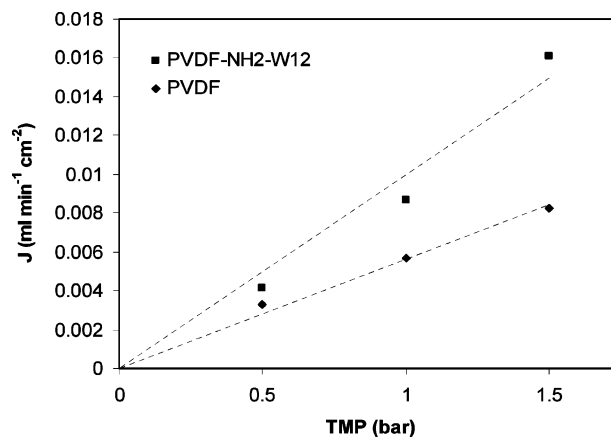
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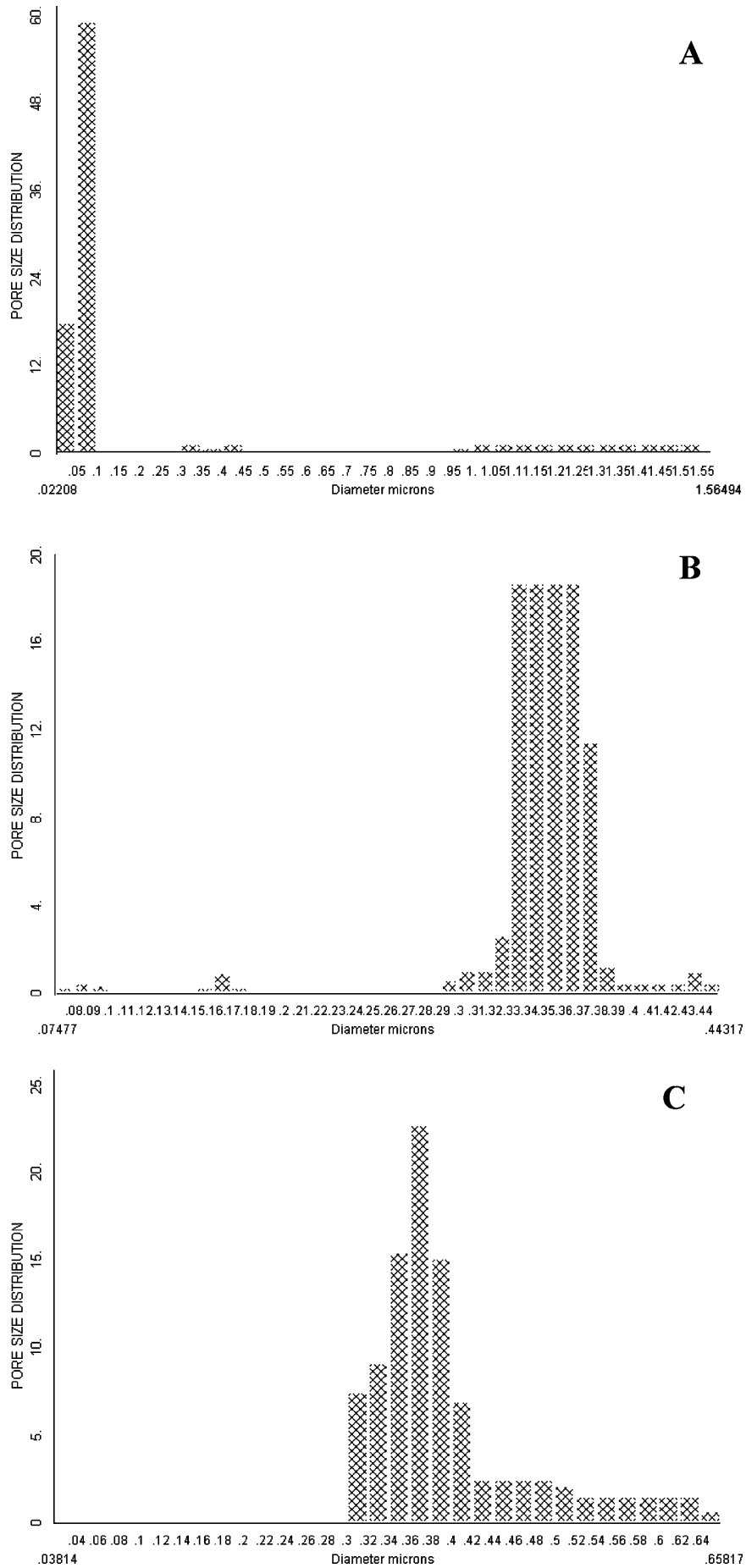
Table 2. Properties of the PVDF, PVDF−NH2, and PVDF−NH2−W12 Membranes

membrane code	membrane thickness (μm)	mean pore diameter (μm)	pore diameter at the maximum distribution (μm)	porosity (%)
PVDF	47	0.06	0.06	24
PVDF−NH2	42	0.35	0.33	24
PVDF−NH2−W12	46	0.37	0.36	25

The plasma treatment of the PVDF membrane has changed, in a controlled way, the surface chemistry and properties of the systems without altering its bulk structure, as revealed by the comparison of the SEM image of the native PVDF membrane (Figure 4a−c) and PVDF−NH2−W12 (Figure 4d−f). The pores on the upper surface of the plasma-modified membranes (PVDF−NH2 and PVDF−NH2−W12) are larger than those on the upper surface of the native PVDF membrane (Table 2). This peculiarity, together with the more hydrophilic character of the same, can explain the higher water flux observed for these membranes compared to the native membrane (Figure 7).

However, all the prepared membranes have a narrow pore size distribution, as shown in Figure 8.

No significant differences in overall porosity have been detected between native and plasma-modified membranes (Table 2).

Photocatalytic Tests. To analyze the catalytic activity of the W12 heterogenized on the plasma-activated membranes surface, we chose oxidative degradation of phenol as a reaction test. In our study, we have compared the catalytic activity of W12 in homogeneous phase (7×10^{-4} M aqueous solution) versus heterogeneous reaction carried out with PVDF−NH2−W12 membranes.

Figure 8. Pore size distribution of the PVDF, PVDF−NH2, and PVDF−NH2−W12 membranes.

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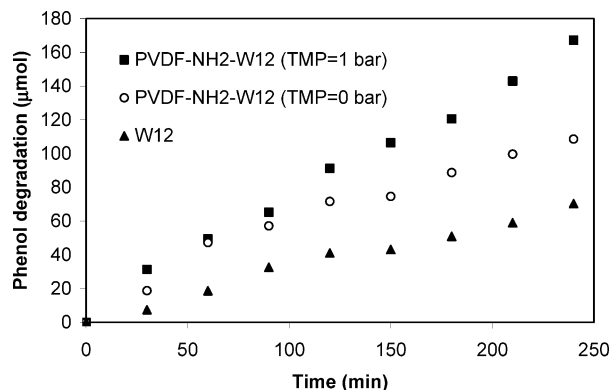
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Figure 9. Photocatalytic degradation of phenol (150 mL; 2.0×10^{-3} M; $T = 30$ °C; $\lambda > 310$ nm) in homogeneous W12 (7.0×10^{-4} M) and heterogeneous PVDF−NH2−W12 membrane.

A relevant enhancement of the phenol oxidation rate was observed for the reaction catalyzed by the PVDF−NH2−W12 membrane (Figure 9) despite the fact that the amount of catalyst present on the membrane surface is less than that used in the homogeneous phase (7.0×10^{-4} mol/L).

We can estimate, by a rough calculation on the basis of crystallographic data, that the moles of catalyst present on the membrane surface are several orders of magnitude lower than that in the homogeneous reaction. As determined by XRD, the Keggin anion $[PW_{12}O_{40}]^{3-}$ can be contained in a cube 10.27 Å on a side;[34] consequently, on a surface of 4.5 cm², no more than 7×10^{-4} μmol of catalyst can be accommodated. More work is in progress to determine the exact number of chemical groups introduced by plasma treatments.

The influence of transmembrane pressure (TMP) on the reaction rate has also been investigated. The flux through the membrane depends on the TMP value and has a large influence in the performance of a catalytic membrane reactor.[35,36] When the reactor is operated at TMP = 1 bar, a higher phenol disappearance rate is observed than at TMP = 0. When the reactor is operated at higher TMP, the phenol can accumulate in proximity of the membrane surface, and thus a concentration gradient between the membrane interface and the bulk of the solution is realized. This phenomena induces the increase in the mean contact time between the phenol and the catalyst and the increase in phenol concentration around the catalytic sites. The phenol is retained on the membrane surface until its complete mineralization. However, in both cases (TMP = 0 bar and TMP = 1 bar), the heterogeneous reactions led to a faster phenol degradation than the homogeneous reaction (Figure 9). Further studies are in progress to determine the better hydrodynamic condition for the photocatalytic oxidation.

A better dispersion of the catalyst on the membrane surface, with respect to the homogeneous solution, can also contribute to an increase in catalyst efficiency in terms of both the percent active catalyst and the superficial area of the catalyst.
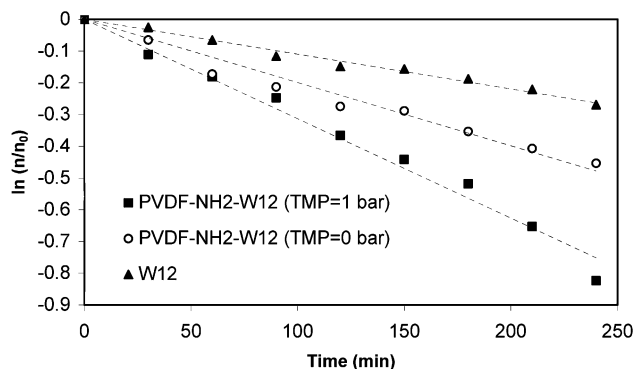
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Figure 10. First-order plot for the photocatalytic degradation of phenol in homogeneous W12 and heterogeneous PVDF−NH2−W12 reactions (n_0 is the initial moles of phenol and n_t the moles at time t).

Table 3. First-Order Rate Constant (k) for Phenol Photodegradation and Correlation Coefficient (R^2) for the First-Order Plot

process	k (min^{-1})	R^2
W12	0.00110	0.99
PVDF−NH2−W12 (TMP = 0)	0.00199	0.97
PVDF−NH2−W12 (TMP = 1 bar)	0.00313	0.98

No difference in the phenol concentration was observed between retentate and permeate in the catalytic tests.

First-order kinetics with respect to phenol concentration was found for both homogeneous and heterogeneous reactions (Figure 10).

The rate of disappearance of phenol can be described by the following equation:

$$v = -\frac{d[C]}{dt} = k[C] \qquad (2)$$

where [C] is the phenol concentration (mol/L), t is the time (min), and k is the rate constant (min^{-1}).

First-order rate constants for both the homogeneous and heterogeneous systems are reported in the Table 3.

The regeneration of the heterogeneous systems is another important subject for practical applications. The PVDF−NH2−W12 membrane can be used in further catalytic runs without a loss of activity.

No catalytic properties were observed using the membranes functionalized by Ar/NH₃ plasma treatment (PVDF−NH2) but without the catalyst linked on the surface for the phenol photodegradation.

Conclusions

In this work, novel polymeric photocatalytic membranes operating in water with O₂ have been synthesized by anchoring Keggin type phosphotungstic acid (W12) on the surface of plasma-activated polymeric membranes made of PVDF (PVDF−NH2−W12). Polar chemical groups (principally NH₂, together with OH, CN, NH, and CO) have been linked on the membrane surface by an Ar/NH₃ plasma to act as binding sites for W12, principally by ionic interaction and hydrogen bonds. Evidence of the anchoring of N-groups and, for the catalytic membranes, W-based catalyst was provided by XPS analysis. The characterization of surface and bulk properties of the plasma-modified membranes was also carried out and compared to native membranes.

Photocatalytic activity of the PVDF−NH2−W12 membranes has been tested in the aerobic degradation reaction of phenol in water. Higher photocatalytic activity was observed with the PVDF−NH2−W12 membrane than with the homogeneous W12. It was also found that the phenol degradation catalyzed by the polymeric catalytic membrane was dependent on the transmembrane pressure.

First-order rate expression can be used to describe both the homogeneous and heterogeneous photodegradation reactions of phenol.

The catalytic membranes prepared are stable and recyclable without loss of activity in successive catalytic runs; furthermore, no catalytic activity was detected for the plasma-modified membranes prepared without the catalyst.

CM051739G