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The ‘‘Watercatox’’ process: Wet air oxidation of industrial effluents in a catalytic membrane reactor
First report on contactor CMR up-scaling to pilot unit

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Abstract

A new and innovative method for oxidation of dissolved compounds in water – the ‘‘Watercatox’’ process – has been developed in order to reduce the chemical oxygen demand and the total organic carbon in industrial wastewaters. This process is the result of a European Fifth Framework Program project. It can operate at much lower temperatures and pressures than conventional wet air oxidation or incineration, and it offers much smaller volume requirements than biological treatment plants. The operating principle of the Watercatox process is the oxidation of the dissolved molecules using oxygen from air within a catalytic membrane reactor in an interfacial contactor configuration. The catalytic contactor membranes, as well as the operating conditions, have been up-scaled from lab-scale to pilot unit. The technological efficiency was demonstrated by the results obtained using the pilot test unit on different industrial effluents from several origins.

Keywords: Wet air oxidation; Catalytic membrane reactor; Contactor; Wastewater; Industrial effluent

1. Introduction

When treating wastewater industrial effluents, three basic options can be presented. In the first case, when the effluent is non-toxic, biological processes are the most economical. When the composition of the effluent makes it toxic to the microorganisms, the most common option is incineration. However, when the pollutant is in low concentration, incineration is not cost nor energy effective. With the current concern on environmental issues, regulations about toxic waste regularly straighten the accepted concentrations in wastewaters. As a result, there is an increasing need for an economically alternative to incineration for dilute wastewaters.

Wet air oxidation represents a nice choice for this alternative. It has been developed in recent years over three types of processes. Non-catalytic WAO implies the use of high air pressure and treatment temperature, and therefore its energy saving with regards to incineration is limited. Catalytic WAO processes are divided into two groups. The first one uses homogeneous catalysts, usually based on copper or iron salts, still using rather high temperature and pressures, and moreover leading to difficult catalyst recollection, or leaching to the environment. Heterogeneous catalysis is also an option, generally based on Pt or Ru dispersed metal [1,2]. This process still involves high energy costs, complex equipment and difficult catalyst recovery and maintenance.

The ‘‘Watercatox’’ process [3] represents an alternative to the above, in order to treat particularly toxic but dilute wastewater. It is based on a catalytic membrane reactor (CMR) configuration. In the previous publications from our group [4–6], CMRs have been divided into extractors, distributor and contactors. In extractor CMRs, the membrane is used to remove one of the products from the reaction zone, usually allowing higher conversion or selectivity through an equilibrium shift, for example in dehydrogenation [7] or isomerization reactions [8]. In distributor CMRs, the membrane is used to spread one of the reactants to the catalyst in a homogeneous way, limiting its

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concentration to a constant minimum all around, and therefore avoiding side reactions, for example in selective oxidations [9–12]. In contactor CMRs, the membrane is used to enhance the contact between the reactants and the catalysts, usually located inside the membrane pores. In a first option, contactors can be set up as flow-through membranes, leading to a better control of the contact time and therefore selectivity [13–15]. For the Watercatox process, the CMR is used as an interfacial contactor. In this mode, the gas and liquid reactants are separately introduced into the membrane from each side. The wastewater is pumped along the contactor on one side, while air flows along the other side of the contactor. The gas–liquid interface is then located within the membrane by means of a trans-membrane differential pressure that compensates for the gas/liquid capillary pressure within the membrane pores. This configuration favours three-phase contact, leading to a better accessibility of the reactants to the catalyst that can improve the conversion rates [4,16–18]. The membrane structure and properties have to be adapted to the catalytic process, while the active phase deposition must be controlled [19,20]. Using appropriate overpressure conditions, and taking into account the specific porous structure of the membrane, the operation of the CMR can be optimised [21].

The Watercatox process is expected to be quite robust, since the contactor is made of ceramics that can withstand high temperatures and pressures and tough chemical environment. Actually, a large part of previous works on this project [3] was devoted to chemical-physical material design, in order to reach a high degree of resistance. Previous papers presented the work carried out at lab-scale [17,21].

This paper gives an overview of the recent progress of the Watercatox European project, and in particular describes the process of technology transfer from research laboratories to a pilot unit. This collaboration included academic groups and companies from France, Slovenia, Belgium, Germany, the U.K. and Norway.

2. Experimental

2.1. Material

The chemical compositions of the materials used within this project have been presented previously, in reports of the laboratory work progress [4,21]. Let us present below the characteristics of the two main final structures. These two were first developed as single tubes for lab work (as described earlier [21]), and later declined as multichannel tubes for pilot applications. Each channel would then reproduce the asymmetric structure of the corresponding single tubes shown in Fig. 1.

Inocermic provided membranes based on pure titania support and two intermediate layers (one 46-μm thick, 0.8-μm pore size layer, and one 27-μm thick, 0.25-μm pore size layer), under a ceria-doped-zirconia-covered titania, 8-μm thick, 80-nm pore size toplayer. Single tubes were 10-mm diameter 250-mm long, and 19-channel tubes were 25-mm diameter and 250-mm long (lab-scale) or 500-mm long (pilot unit scale), each channel showing 3.3-mm diameter.

Pall-Exekia provided ceramic membranes based on titania covered α-alumina support and intermediate 15-μm thick, 0.8-μm pore size layer, under a zirconia 6-μm thick, 50-nm pore-size top layer. Single tubes were 10-mm diameter 250-mm long, and 37-channel hexagonal tubes were 31-mm width and 250-mm long (lab-scale) or 1020-mm long (pilot unit scale), each channel showing 3-mm diameter.

The Pt catalyst was prepared using a protocol presented in previous papers [4,19,20], involving an impregnation of the porous membrane into a Pt salt precursor solution, followed by careful solvent evaporation and hydrogen high temperature reduction. This protocol was adapted to multichannel tubes, with a particular attention to the reduction of precursor solution volume, in order to optimise the costs. The deposition of the metal catalyst was scaled up from single tube to multichannel supports first at lab-scale in CNRS/IRC laboratories. Then the longer membranes used for the pilot unit were impregnated at Inocermic (Germany), using a protocol as close as possible to the previous one [4,21].

The amount of metal deposited was in the range of 6.2 (Inocermic supports) to 7 g_{Pt}/m^2 (Pall-Exekia supports), as measured by weigh uptake and precursor solution elemental (ICP) analysis. Previous electron microscopy characterisations have shown that the platinum particles obtained are distributed mainly within the membrane toplayer and with high dispersion (particle size of a few nm). More details can be found elsewhere on the preparation results [20,22].

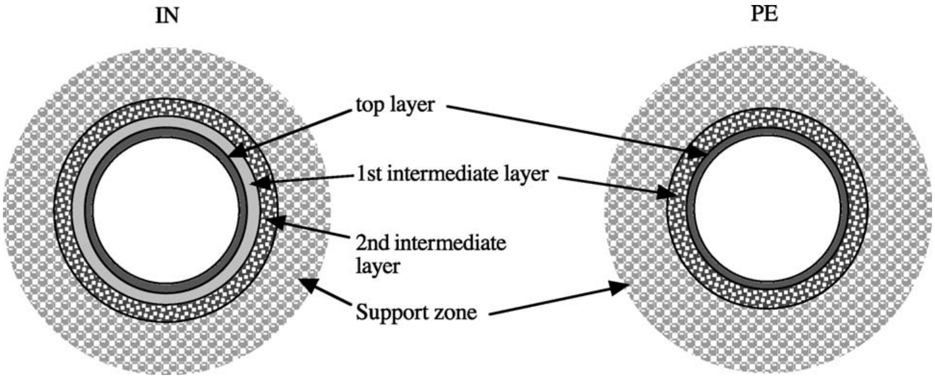

Fig. 1. Asymmetric structures of the two types of membrane material used in this work. (Left) Structure from Inocermic (IN), and (right) structure from Pall-Exekia (PE).

Table 1
Composition and origin of the effluents used in this work

Ref.	Type	Origin	Composition	TOC (mg/l)	COD (mg/l)
A	Model	Laboratory made	HCOOH 5 g/l	≈1300	≈1730
B	Chem. Ind.	Monsanto	H_2CO 0.3% + HCOOH 0.15% + ···	≈1130	≈3200
C	Chem. Ind.	Norway	H_2CO + formiates	≈1100	–

2.2. Used effluents

Apart from a reference model effluent, made of a 5 g/l formic acid solution in deionised water, many industrial effluents were treated, both at lab-scale and into the pilot unit. Table 1 shows the characteristics of the test samples presented in this study:

Total organic carbon and chemical oxygen demand are relevant parameters from the point of view of the application in industrial environment.

2.3. Catalytic membrane reactor operation

As previously mentioned, the catalytic membrane is mounted as an interfacial contactor, using a gas-tight module, allowing to independently regulate pressures of both gas and liquid sides. Fig. 2 shows the operational principles of the configuration used.

The optimal operating conditions as well as the catalytic performance on model and real effluents have been investigated at lab-scale, using a catalytic bench already presented elsewhere [4], operated in continuous mode.

The Norwegian company Due Miljø AS, with Stratos Systems, UK, as a subcontractor, has built a pilot unit for the Watercatox process of 0.35 m^2 contactor area and over 300 l/h capacity. It includes a fast recycling loop on the CMR side. The plant have been operated in a continuous or recirculation mode (50 l tank), using temperatures from 20 to 80 °C and trans-membrane differential pressures in the range of 5–15 bar. The pilot unit is automatically controlled and monitored by a fully computerised system. Fig. 3 shows schematics of both lab- and pilot-scale systems.

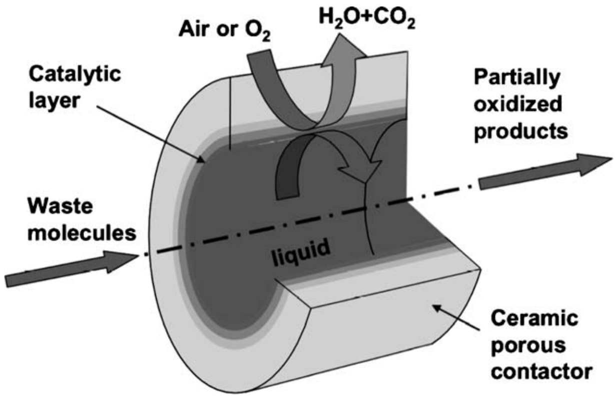

Fig. 2. Principle of operation of the interfacial contactor CMR used for Watercatox operations.

The effluents are stored in a tank at 30–90 °C, and are filtered on line and pumped to the CMR. The system acts as a continuous batch reactor or at low rates could operate in continuous mode. The time and/or the volume processed will be determined by the catalytic efficiencies. Should gas bubbles appear into the liquid side, they are continuously removed from the secondary loop using a safety release valve. The air fed to the CMR is saturated with water and pre-heated using a saturator. The feeding velocity along the membrane is in the range of 1–4 m/s. At these flow rates a maximum pressure drop of 0.3–1 bar can be expected along the liquid side of the membrane. Ceramic modules are assembled vertically so a further differential pressure of 0.1 bar from the top to the bottom of the CMR is present.

Model solutions (formic acid) as well as real industrial effluents have been tested. The catalytic performance has been evaluated at lab- and pilot-scales, in conditions as similar as possible.

2.4. Analysis

In the lab-scale experiments, the effluents were analysed using a Shimadzu total organic carbon analyser TOC5050A. The pilot unit being located into an industrial wastewater plant primary used the available semi-manual chemical oxygen demand analysis, and, on some samples a total organic carbon analyser. A few industrial effluent samples were also sent back to their respective providers for dedicated analysis by GC/MS and elemental analysis in order to detect which components from complex mixtures have been converted.

3. Results

3.1. Lab-scale unit: from single tubes to multichannels

Before scaling up the CMR to pilot, lab-scale research was necessary to implement multichannel membranes. More details on this process can be found elsewhere [22]. However, let us show the evolution of catalytic activity of the membranes, as per surface area unit. Fig. 4 shows typical results obtained under 3.6 bar air overpressure at 20 °C.

The results presented here are typical, but do not show the optimised conditions for each particular pair effluent-catalytic membrane. The conditions chosen here allow some comparison between laboratory- and pilot-scales.

Let us recall that in the case of single tubes, a significant increase of the reaction rate was observed when increasing the air overpressure, as reported in a previous paper [4]. Both types of membranes, Inocermic and Pall-Exekia revealed then a similar reaction rate of ca. 0.9 $mmol/s/m^2$ (Effluent A) at a

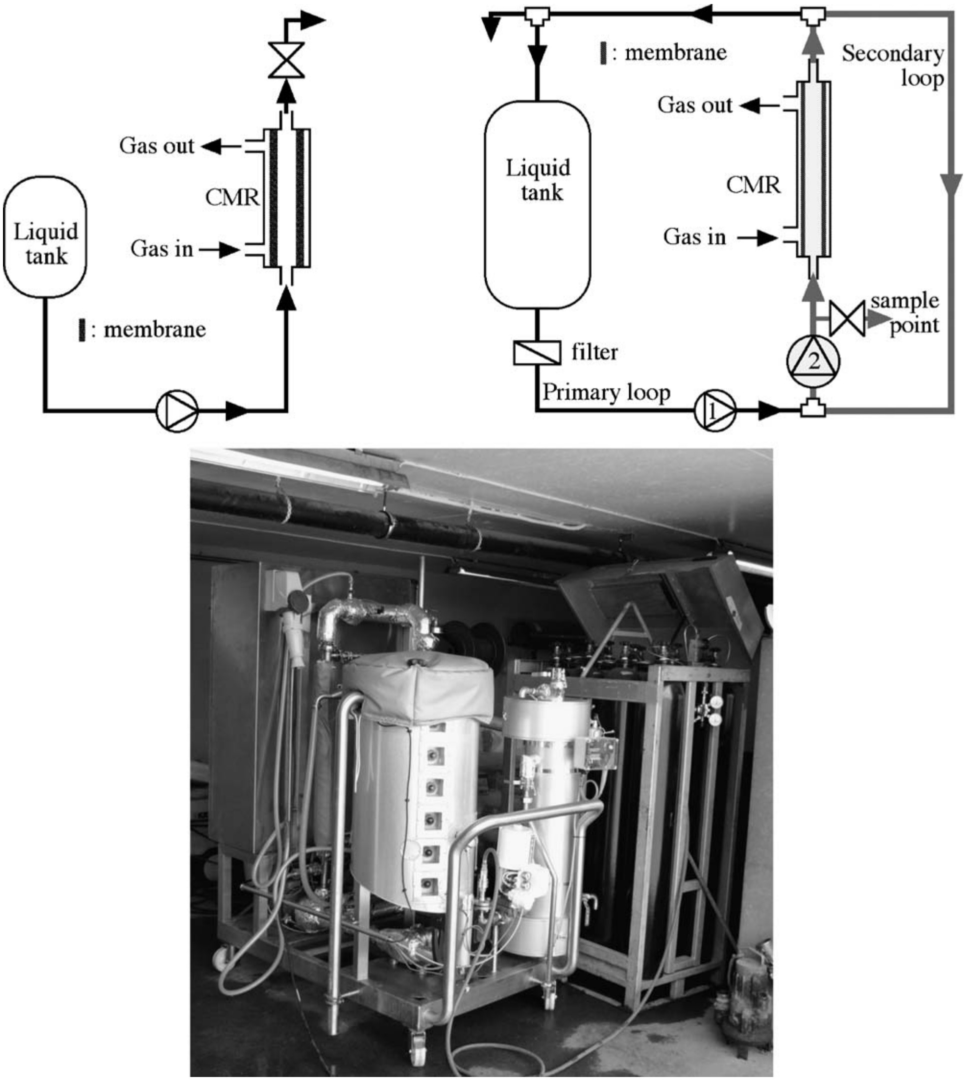

Fig. 3. Lab-scale (left) and pilot-scale (right) schematics of the test rigs used in this work. Please note the two liquid recycling pumps on the pilot test unit. (Below) Photograph of the pilot unit on the industrial site, close to Oslo (Norway).

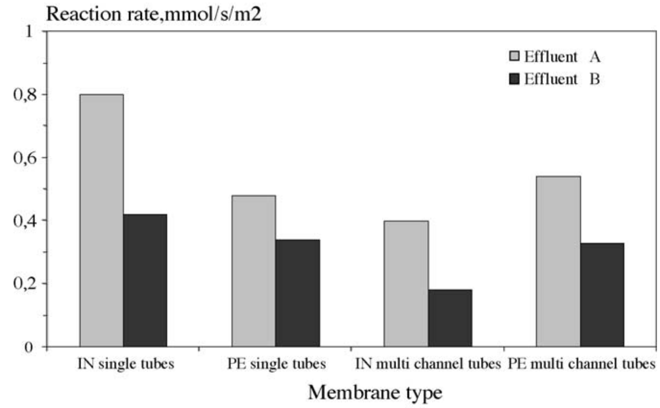

Fig. 4. Catalytic activity on the effluents A and B in lab-scale experiments on different membrane types and geometries. IN, Inocermic material; PE, Pall-Exekia material; temperature, 20 °C; air overpressure, 3.6 bar.

5-bar gas overpressure and 20 °C. Using this overpressure at 80 °C, the reaction rate even reached 3.8 mmol/s/m^2.

As shown in Fig. 4, maximal reaction rates on multichannel membranes at lab-scale were found to be in the range of 0.4–0.5 mmol/s/m^2 for effluent A and 0.2–0.3 mmol/s/m^2 for effluent B. Effluent C showed no significant conversion in lab tests (reaction rates lower than 0.1 mmol/s/m^2). Some membrane fouling was observed.

One can see the activity is either constant or decreased when switching from single tubes to multichannel catalytic membranes.

3.2. From lab-scale to pilot unit

Whereas the lab-scale test bench operates in continuous mode, the pilot-scale unit, for practical reasons, operates in

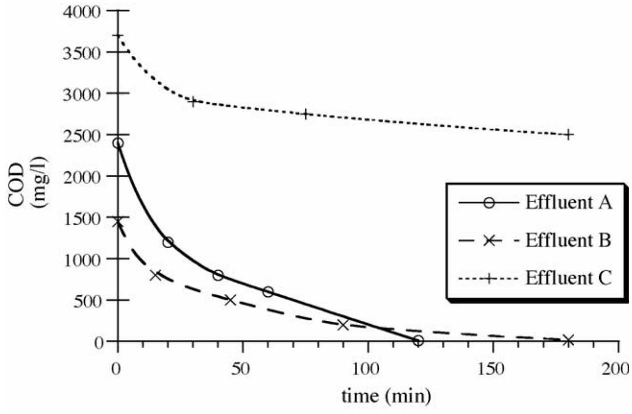

Fig. 5. Chemical oxygen demand of three effluents A–C treated into the pilot unit, as a function of time (recycling mode). Temperature, 53 °C (A and B) to 57 °C (C); gas overpressure, 5 bar; tank recycling flow rate, 40 l/h (A and B) and 65 l/h (C); fast recycling loop flow rate, 5.3 (A and B) and 2.8 m^3/h (C); multichannel membrane, Inocermic (6.2 mg Pt/m^2).

double recycling mode. This difference makes difficult direct comparisons of bulk performances. Therefore, on each case, one must rely on the conversion rate to compare both systems. However, in order to illustrate the time-scale performance achieved in the pilot-scale, Fig. 5 gives a plot of concentration (expressed as chemical demand of oxygen) as a function of time, obtained in the pilot unit.

One can see full conversion is achieved in a couple of hours for the model effluent A and the industrial effluent B, whereas the effluent C shows a partial conversion of about 25% after 1 h (35% after 2 h).

From the type of result shown in Fig. 5, and also from the continuous analysis of the lab-scale continuous down streams (as for Fig. 4), one can extract the catalytic activity of the membranes for different effluents. This should allow a direct comparison of both test rigs. However, due to differences in the parameter ranges of both systems, only a limited number of runs were carried out that share exactly similar experimental conditions. Actually, the approach of this project was to obtain first information on the CMR activity at lab-scale for a series of industrial effluents, and then conduct a more extended study of these selected samples in the pilot unit, in order to optimise the treatment conditions of each effluent. Fig. 6 gives typical results obtained on both systems.

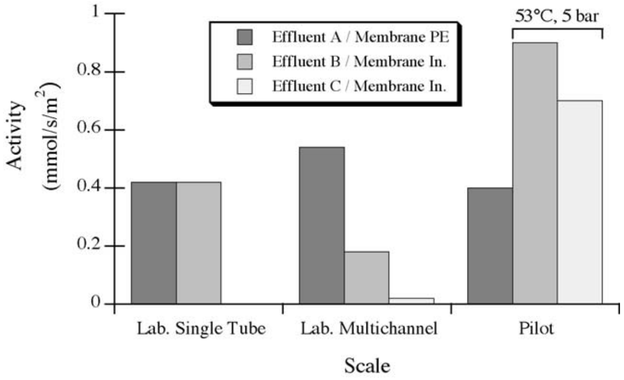

Fig. 6. Comparison of performances of different effluent/membrane systems in wet air oxidation in lab-scale single tubes, lab-scale multichannel tubes and pilot-scale multichannel tubes. PE, Pall-Exekia; IN, Inocermic; temperature and air overpressure, 20 °C and 3.6 bar if not stated otherwise.

On the model effluent A, a complete comparison was achieved and used as a reference. In other cases, Fig. 6 shows results obtained with slightly different experimental conditions.

Specific wastewater treatment applications are not only based on COD/TOC abatements. For instance, see below, in the case of a toxic component waste, another result of this process: conversion of toxic compounds to non-toxic species that makes possible a subsequent biological treatment.

3.3. Example of pilot-scale application

In some cases the maximum level of certain components, e.g. phenol or formaldehyde is strictly restricted. Different samples of these types of effluents have been tested in the pilot plant, and the main components before and after the Watercatox process have been analyzed using GC/MS and IC analyses.

Treating a sample from a Norwegian chemical plant (COD of 15,800 mg/l), at 68 °C, at a flow rate of 100 l/h and a recycling loop rate of 3.1 m^3/h, at 5-bar air overpressure, a COD reduction of 10% was found after 0.5 h. After 13 h of processing, the phenol was reduced from 81 to 55 ppm. The principle of the process in converting toxic components was demonstrated, but in order to make it cost-effective, further improvement in reaction rate is needed.

4. Discussion

The main point of this paper is not to compare the performances of different membrane structures. One can note nevertheless that while offering quite different approaches to the same problem, both the Pall-Exekia and Inocermic materials offer similar membrane catalytic activities to the effluents presented here. This behaviour in lab-scale single tubes has been discussed previously [21]. Let us briefly recall that PE tubes present one layer less than IN tubes (Fig. 1). Moreover, the thickness and pore size distributions of the layers are different. As a consequence, the location of gas–liquid interface in the reactor is modified as a function of gas overpressure. That is the reason why getting similar performances on both systems requires different experimental conditions (i.e. higher gas overpressures for PE membranes).

For economical reasons, in most cases, ceramic porous membranes designed for industrial use are not single tubes. The multichannel supports used in this work are commercial geometries. They offer a lower cost per surface area unit, while maintaining a similar level of membrane quality, as could be shown by bubble point measurements. However, when up-scaling from single to multichannel tubes, the catalytic activity of the material appears decreased in some cases (Fig. 4). Without going into details, it seems the catalyst distribution over the channels is not perfect, and some channels do not offer the same amount of platinum than others. This important issue has been investigated further, and more details can be found in another paper [22]. In spite of their different structure and composition, as their single tube counterparts, Inocermic and Pall-Exekia multichannel membranes offer close overall performances according to their own best-adapted operational conditions. The discussion of the performance comparison between the two types of multichannel tubes (Fig. 4), is difficult due to differences in their characteristics: geometry, layer thickness and pore size distribution, platinum loading and distribution among channels.

However, whereas the issue of specific activity is of prime importance from the lab-scale point of view, it is not as crucial at pilot-scale. As a matter of fact, relatively soft condition changes in the pilot unit (a 10-bar pressure and 30–40 °C temperature increases) allowed to compensate for both up-scales from single tubes to multichannels and lab to pilot.

Actually, from the point of view of the industrial application, much more interesting performances in the degradation of effluents B and C were obtained in the pilot unit, using higher temperature and air overpressure conditions (Fig. 6). It is very delicate to compare lab and pilot results. However in the case of effluent C, the lab-scale tests were conducted on unfiltered samples, leading to membrane fouling and therefore a very low activity. However, the gas overpressure increase from 3.6 to 5 bar is responsible for the large activity increase observed on effluent B, as the gas–liquid interface is shifted towards the catalytic zone [22]. A catalytic membrane activity of 0.9 mmol/s/m^2 was achieved, at 53 °C and 5 bar of gas overpressure on this effluent.

Considering the techno-financial assessment presented below, this performance allows further industrial development. Based on data provided by Monsanto, one of the project partners, the following first evaluation can be estimated. For an effluent flow of 1 m^3/h, containing 1135 mg/l TOC, based on a reaction rate of 0.9 mmol/s/m^2, the Watercatox reactor would need a membrane surface area of ca. 29 m^2 to achieve full conversion. At a capital cost of about 1000–2000 €/m^2 including carters and tubing for such a membrane surface area, the treatment unit would offer investment and operative costs reduced when compared to a conventional biological wastewater treatment plant (not mentioning the effluent toxicity issue). Please note that, within this scenario, the metal catalyst, platinum, would account for less than 3% of the total investment.

Another point, which is of great importance to most applications, lies on the catalytic membrane life span. When in operation, the catalytic membrane is submitted to successive diverse effluent contents. In conventional liquid separation using membranes, CIP (Cleaning In Place) procedures are commonly used. Therefore, at lab-scale, the influence of this type of procedure on the catalyst performance and life span was thoroughly investigated. Some CIP was shown to be able to regenerate the catalyst. These procedures were scaled up to the pilot unit.

On the other hand, effluents could contain aggressive species that could damage the membrane catalyst or structure. For instance, it has been shown on some industrial effluents that the efficiency of the process is maintained even in chloride-rich environment.

5. Conclusions

Better understanding of the Watercatox process has been achieved taking into account the experiments on the pilot unit. Industrially competitive conversion rates were obtained for real industrial effluents at remarkable mild conditions. Crucial technological parameters have been identified in order to allow further improvements of the process at industrial level.

An important task was the technological transfer from lab-scale to pilot unit. Apart from the unit design and optimisation, significant research efforts have been focused on the scale-up from single tube to multichannel membranes suitable to commercial use.

For future works, three directions are drawn. First, the adaptation of the preparation to the multichannel tubes needs improvement, particularly when carried out with industry realistic procedures. The distribution of catalysts among the different channels is still not homogeneous and some effort is needed here.

Second, the inherent complexity of industrial effluent composition makes necessary to study other catalytic systems than platinum. Whereas this metal was used as a proof of concept in this study, further application of this new process means more work at the lab-scale to adapt or optimise the membrane catalyst to each effluent.

Third, in order to increase the surface/volume ratio of the catalytic membranes, an evolution towards hollow fibber geometry is under study.

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References

[1] S. Imamura, Ind. Eng. Chem. Res. 38 (1999) 1743.
[2] A. Pintar, G. Bercic, M. Besson, P. Gallezot, Appl. Catal. B: Environ. 47 (2004) 143.
[3] Fifth Framework Project, no. EVK1-CT-2000-00073, http://www.sintef.no/watercatox.
[4] E. Iojoiu, S. Miachon, J.-A. Dalmon, Top. Catal. 33 (2005) 135.
[5] S. Miachon, J.-A. Dalmon, Top. Catal. 29 (2004) 59.
[6] S. Mota, S. Miachon, J.-C. Volta, J.-A. Dalmon, Catal. Today 67 (2001) 169.
[7] W. Liang, R. Hughes, Catal. Today 104 (2005) 238.
[8] L. van Dyk, L. Lorenzen, S. Miachon, J.-A. Dalmon, Catal. Today 104 (2005) 274.
[9] R. Mallada, M. Menendez, J. Santamaria, Catal. Today 56 (2000) 191.
[10] P. Kölsch, Q. Smejkal, M. Noack, R. Schäfer, J. Caro, Catal. Commun. 3 (2002) 465.

[11] A. Cruz-López, N. Guilhaume, S. Miachon, J.-A. Dalmon, Catal. Today 107–108 (2005) 949.
[12] A. Julbe, D. Farrusseng, D. Cot, C. Guizard, Catal. Today 67 (2001) 139.
[13] M. Reif, R. Dittmeyer, Catal. Today 82 (2003) 3.
[14] O.M. Ilinitch, F.P. Cuperus, L.V. Nosova, E.N. Gribov, Catal. Today 56 (2000) 137.
[15] G. Centi, R. Dittmeyer, S. Perathoner, M. Reif, Catal. Today 79–80 (2003) 139.
[16] J. Peureux, M. Torres, H. Mozzanega, A. Giroir-Fendler, J.-A. Dalmon, Catal. Today 25 (1995) 409.
[17] M. Vospernik, A. Pintar, G. Bercic, J. Levec, J. Walmsley, H. Raeder, E. Iojoiu, S. Miachon, J.-A. Dalmon, Chem. Eng. Sci. 59 (2004) 5363.
[18] G. Bercic, A. Pintar, J. Levec, Catal. Today 105 (2005) 589.
[19] D. Uzio, S. Miachon, J.-A. Dalmon, Catal. Today 82 (2003) 67.
[20] E. Iojoiu, J. Walmsley, H. Raeder, R. Bredesen, S. Miachon, J.-A. Dalmon, Rev. Adv. Mater. Sci. 5 (2003) 160.
[21] E. Iojoiu, J. Walmsley, H. Raeder, S. Miachon, J.-A. Dalmon, Catal. Today 104 (2005) 329.
[22] E. Iojoiu, E. Landrivon, J. Walmsley, H. Raeder, S. Miachon, J.-A. Dalmon, Appl. Catal. B (accepted).