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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].

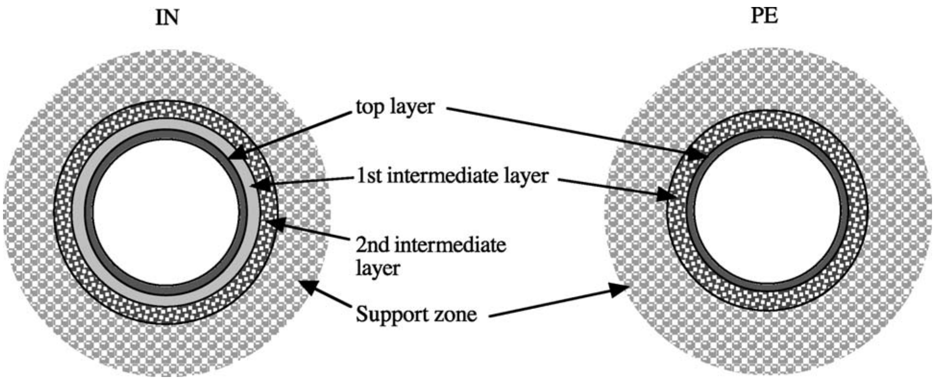

Fig. 1. Asymmetric structures of the two types of membrane material used in this work. (Left) Structure from Inocermic (IN), and (right) structure from Pall-Exekia (PE).