



# Drivers and economic aspects for the implementation of advanced wastewater treatment and water reuse in a PVC plant

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## ABSTRACT

This paper shows the economic feasibility of water reuse within a polyvinyl chloride (PVC) plant. A two-step treatment of the current primary effluent consisting of an aerobic membrane bioreactor followed by a double pass reverse osmosis process, validated at pilot scale, was used to estimate the costs of the industrial water treatment plant. The economic feasibility of the treatment and reuse concept remained unclear because the required investment of 2.5 M€ was high and the discounted payback time of 5 years was long.

The proposed solution is profitable for sites where fresh demineralized water production costs are currently higher than 1.5 €/m<sup>3</sup> and the required flow of the recycled water exceeds 50 m<sup>3</sup>/h. The water reuse concept allows decoupling the production from fresh water use. In this case, anticipating that a drought would lead to a 3% reduction of the production, the amortization period would be lowered to one year.

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## 1. Introduction

Water stress is nowadays a major risk for industry and it is expected to aggravate within the next decades due to population growth coupled with industrialization and urbanization. If an integral sustainable water management is not assured, the increasing demand for water will have serious consequences on the environment. As the resource is becoming scarce, tensions among urban, industrial and agricultural stakeholders will intensify and, in periods of severe droughts, industry may lose the right to use water with serious effects on the competitiveness of companies in water stressed regions such as Spain [1]. To contain this risk, the use of alternative water sources becomes an indispensable element in industrial water management.

Under this scenario, industries need to become more independent of the supply of fresh water for their production

processes. For the last four years the EU FP7 project E4Water has promoted methods for sustainable water use in the chemical sector by demonstrating the technical and economic feasibility of advanced wastewater treatment and reuse in different plants.

Polyvinyl chloride (PVC) is the third most important polymer, slightly behind polyethylene and polypropylene. It is used in most industrial sectors (e.g. packaging, automotive, building, agriculture, medical care) and main applications include pipes, flooring, window and door frames, as well as electric cables. The production in Europe amounts to around 5 million tons [2] and the demand is increasing. Within the three different processes used in the manufacture of PVC, suspension, emulsion and bulk polymerization, the suspension process is the most applied one for large-scale productions (> 80% of total production).

PVC is produced in batch, by polymerization of vinyl chloride monomer (VCM) accompanied by catalyst at a certain temperature and pressure in aqueous medium. Poly(vinyl alcohol) (PVA) is used as dispersing agent during the polymerization step. VCM is produced by thermal cracking of ethylene dichloride (EDC). The chlorine used in the manufacture of EDC is derived electrolytically from NaCl by the chlor-alkali process. Finally, PVC particles are separated by centrifugation [3].

The average water consumption required to produce the polymer is 3 m<sup>3</sup>/t PVC according to the BREF [3]. VCM

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contaminated water (e.g. water used for the cleaning of reactors containing VCM, transfer lines and suspension or latex stock tanks), pass through a water stripper to remove the VCM which is recycled while the water is sent to the waste water treatment plant (WWTP) as well as the final effluent containing residual PVC particles and PVA. This effluent is characterized by being slightly alkaline (ammonia), having low chemical oxygen demand (COD), high PVA/COD ratio, and containing both aluminum and solids made of fine PVC particles, as shown in Section 2.1. The WWTPs of PVC plants are usually based on a two-step process comprising flocculation and removal of suspended solids by sedimentation or flotation. In some plants, the treated water is reused for rinsing purposes, although the water demand for rinsing is small compared to the water required for the polymerization of the PVC [3]. Thus water consumption can be reduced, but more than 100 m<sup>3</sup>/h are still discharged after the physico-chemical treatment in a plant producing 35 t of PVC/h. Moving towards a more sustainable water use in the PVC industry and reducing its dependence on external water sources requires a further closure of the water circuit, which itself implies the need to implement additional wastewater treatment processes integrated in the current WWTP to allow the reuse of the final effluent. The water generated through the upgraded treatment plant shall be reused as process water in the polymerization process step that takes 30% of the plant water consumption. However, a very high quality demineralized water is required for this reuse option: polyvinyl alcohol (PVA) < 1 mg L<sup>-1</sup>; NH<sub>4</sub><sup>+</sup>-N < 2 mg L<sup>-1</sup>; biochemical oxygen demand (BOD<sub>5</sub>) ~ 0; electrical conductivity (EC) < 10 µS cm<sup>-1</sup>; total organic carbon (TOC) < 10 mg L<sup>-1</sup> and aluminum (Al) < 0.1 mg L<sup>-1</sup>. Hence, the new treatment must remove the residual PVA and other COD, ammonia, salinity and aluminum.

PVA has been found to interfere in membrane based separation processes such as microfiltration (MF) or ultrafiltration (UF) producing fouling and foaming [4]. Moreover PVA is difficult to remove by microorganisms due to its polymeric structure. Because the biodegradability of these effluents with BOD<sub>5</sub>/COD values below 0.01 is very poor, this compound is frequently removed chemically instead of biologically [5]. These chemical processes, however, entail high costs, result in large amounts of solid waste and produce final effluents of poor quality [6]. In previous studies, Blanco et al. have demonstrated that the residual PVA can be successfully removed by aerobic biological treatment if the adaptation and treatment conditions are adequate [7]. It has also been demonstrated that under anoxic-aerobic conditions nitrogen could be efficiently removed up to 80%. This is important since ammonium diffuses through reverse osmosis (RO) membranes deteriorating the permeate quality below the final quality requirements and thus necessitating additional polishing which might question the economic feasibility of the full treatment. Finally, own laboratory experiments have shown that the quality of the effluent from the combination of membrane bioreactor (MBR) with RO technology meets the requirements for water reuse in the PVC polymerization steps.

MBR is a well-established technology for treating industrial effluents. It couples the activated sludge process at a higher sludge concentration with membrane separation (MF or UF) and produces a permeate free of particles and almost disinfected, which can feed the RO directly. Moreover, MBRs have a small footprint, produce less sludge, and achieve superior effluent quality compared to conventional activated sludge, due to the longer sludge retention time, that allows the direct reuse of the treated water for a range of applications [8].

After the technical validation of the proposed solution to treat the PVC plant effluent at pilot scale, the next step for the implementation of this sustainable water alternative at industrial scale is the evaluation of the economic aspects of the alternative

studied.

The present study had the objectives (a) to estimate the costs of the industrial water treatment plant based on the aerobic MBR/RO treatments validated at pilot scale and (b) to analyse the potential drivers for the implementation of this solution at industrial scale in different PVC plants.

## 2. Materials and methods

### 2.1. PVC plant

A PVC plant operated by INOVYN Spain in Martorell with a capacity of 290 kt/y has been selected for this study for three main reasons:

- 1) The plant is located in the Llobregat basin near Barcelona. This is a region where water scarcity is a pressing issue. Both fresh water abstraction and wastewater disposal are regulated by legal permits that impose very stringent limitations. Currently, the authorities are increasing the restrictions on water abstraction from existing wells, what sometimes forces the industry to operate with drinking water, which increases the costs and creates tensions between the stakeholders. Furthermore this water source is limited in cases of severe droughts.
- 2) The plant produces PVC in suspension with a high share of recycled water and therefore with a low fresh water consumption of 2 m<sup>3</sup>/t of PVC. Compared to other plants this is achieved by a water recovery system that reuses the water extracted from centrifugal decanters (first PVC drying step before fluidized bed drying) for equipment rinsing purposes.
- 3) Due to increasing demand of PVC products, an expansion of the production capacity of the plant would be required leading to a higher water demand. Due to the above limitations an alternative water source is the effluent of the plant after an advanced treatment. In this way the production capacity could be expanded without increasing the water demand.

Within INOVYN Spain site, the main uses of water are: 60% for the mercury electrolysis, where chlorine is obtained; 10% for the monomer plant, where VCM is synthesized and 30% for the polymerization process.

For the PVC process unit studied, the current WWTP includes a physico-chemical process, where PVC colloids are removed from the water. Afterwards, the clarified water is disposed of in the sea through a marine outfall.

The effluent has a pH of 7.9 and the quality is (average values in mg L<sup>-1</sup>): 38 of NH<sub>3</sub>, 0.97 of Al, 211 of Na<sup>+</sup>, 0.08 of VCM, 285 of Cl<sup>-</sup>, 0.28 of Cl<sub>2</sub>, 117 of suspended solids, and 331 of COD.

As mentioned above, the treatment objective for the pilot plant is to produce water from the current effluent meeting the requirements for the polymerization process, i.e. conductivity below 10 µS/cm. To achieve this quality, a RO treatment is required with a pre-treatment by MBR to eliminate PVA, COD and ammonia as previously validated at laboratory scale [7].

### 2.2. Pilot plant

The flow diagram of the pilot plant is given in Fig. 1. The MBR pilot was equipped with a ZeeWeed 500D system from Zenon (GE, Oroszlány, Hungary) with an outside/in UF hollow fiber membrane (PVDF with a nominal pore size of 0.04 µm). The plant consists of two biological reactors (Bioreactor 1 with the possibility of working in both aerobic or anoxic conditions and Bioreactor 2, fully aerobic) and the filtration unit, with a total effective volume of 20 m<sup>3</sup>. Three membrane modules with an effective filtration area

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