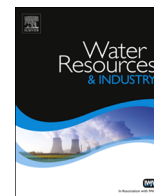




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Drivers and economic aspects for the implementation of advanced wastewater treatment and water reuse in a PVC plant



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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 €/m³ and the required flow of the recycled water exceeds 50 m³/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 m³/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 m³/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⁻¹; NH₄⁺-N < 2 mg L⁻¹; biochemical oxygen demand (BOD₅) ~ 0; electrical conductivity (EC) < 10 μS cm⁻¹; total organic carbon (TOC) < 10 mg L⁻¹ and aluminum (Al) < 0.1 mg L⁻¹. 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 BOD₅/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 m³/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⁻¹): 38 of NH₃, 0.97 of Al, 211 of Na⁺, 0.08 of VCM, 285 of Cl⁻, 0.28 of Cl₂, 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 m³. Three membrane modules with an effective filtration area

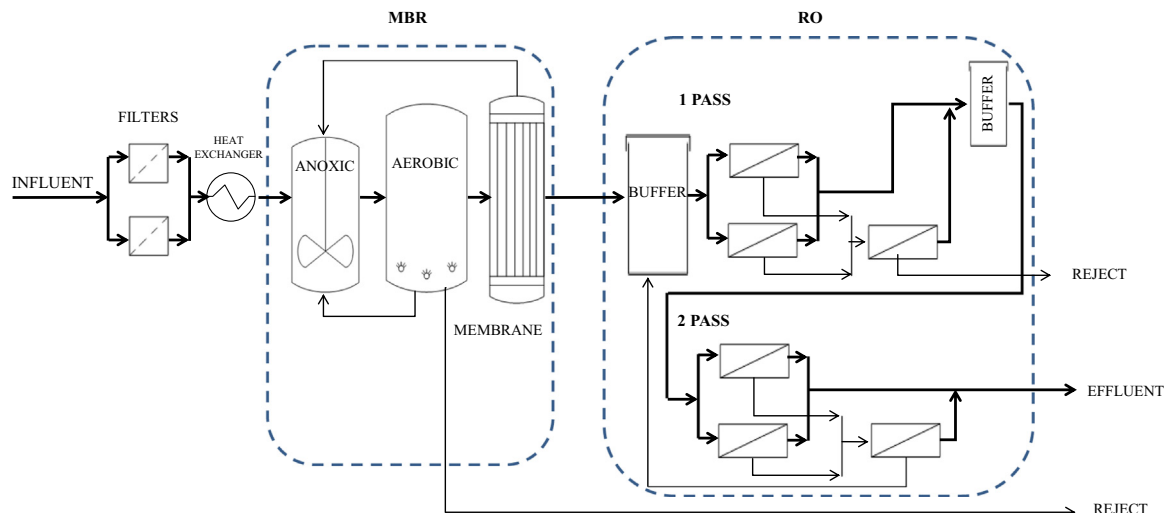


Fig. 1. Pilot plant.

of 94.8 m² (31.6 m² each) were used for permeate production. In addition, a cleaning in place (CIP) system and a heat exchanger for temperature control were installed. For the pilot phase an aero cooler was used. Even though the feed flow comes from the physico-chemical treatment, a safety filter (Y-strainer of 5 mm) was installed for the pilot trial. To start up, activated sludge was obtained from a mixture of 25% municipal biological treatment sludge and 75% sludge from the internal WWTP in the VCM process unit.

Downstream of the MBR, a storage tank was installed to collect the MBR permeate for the backpulse cycles. In this backwashing, the MBR permeate is pumped back through the membranes to remove reversible fouling and avoid a fast decrease in permeability. The cyclic mode of operation consisted of alternated filtration and backpulsing periods. CIP was performed once per day (30 min) during the trial. Cleaning consisted of successive cycles of backpulsing, chemical reagent addition (citric acid and sodium hypochlorite), relaxation with aeration and final backpulsing for chemicals removal. The main purpose was to keep high permeability values and reduce harsh chemical cleanings or recovery cleanings which means longer MBR stops and fast membrane aging. After acid CIP cleanings, effluent was directly used for feeding the RO treatment; when sodium hypochlorite was used, stream was discharged until free chloride was under detection limit, thus membranes would not be damaged.

The MBR permeate was treated in a two-pass RO system supplied by Nalco. The FILMTEC™ LC HR-4040 spiral wound membranes were supplied by Dow Chemical. The first pass treatment consisted of three pressure vessels with five RO elements each one, with a total area of 130.99 m². Concentrated streams from the first two pressure vessels feed the third pressure vessel. The permeate was used for backflushing and for feeding the second pass treatment with three pressure vessels of three RO elements

Table 1

Effluent quality in the pilot plant.

PVA	0.73 ± 1.4 mgL ⁻¹
BOD ₅	2.5 ± 1.2 mgL ⁻¹
Conductivity	3.8 ± 1.5 µScm ⁻¹
TOC	0.94 ± 0.64 mgL ⁻¹
NH ₄ ⁺	1.2 ± 1.7 mgL ⁻¹

each one, with a total area of 78.59 m². Concentrated streams from the first two vessels fed the third pressure vessel. Part of the concentrated stream was recirculated to feed both, first and second pass treatments, in order to increase the overall recovery (Fig. 1). The permeate was analysed before it was reused in the polymerization trials (pH, conductivity, TOC, COD, PVA, Al).

Different phases were tested in the RO pilot: recoveries in first and second pass were set in the range of 60–75% and 75–85%, respectively, concentrate stream from the second pass was totally recirculated to both first and second pass treatments as well as part of the first pass reject. Permeate flow and flux were set in the range of 1.6–1.7 m³ h⁻¹ and 12–21 LMH, respectively (Fig. 1). Final reject stream that was not recirculated was directly discharged and mixed with the current effluent of the plant. As flow and Trans Membrane Pressure (TMP) kept very stable during the piloting, no chemical cleanings were done; however, biocide shocks (PC-11, from Nalco) were occasionally performed especially when MBR stopped for maintenance/problems to keep RO membranes in good condition and to avoid membrane biofouling.

All chemicals and nutrients used were supplied by MERCK KGaA (Darmstadt, Germany) and PANREAC S.A. (Barcelona, Spain). Sample preservation and all analyses were performed according to the standard methods for the examination of water and wastewaters [9–11].

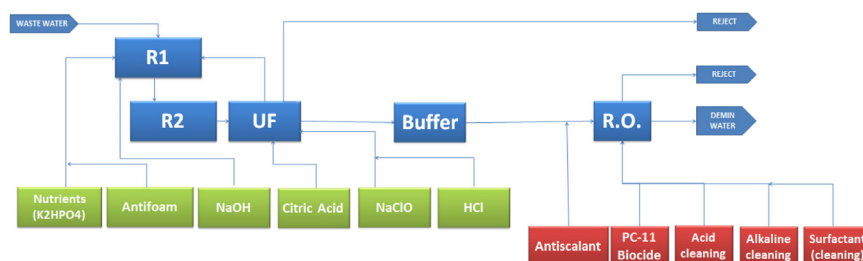


Fig. 2. MBR+RO simulator to estimate chemical consumption in the industrial plant.

Table 2

Specific consumptions taken from the pilot data and estimated in the simulation of the industrial plant.

	Nutrients	Antifoam	NaOH	Citric acid	NaClO	HCl	Antiscalant	Biocide	Acid cleaning	Alkaline cleaning	Surfactant
Spec. Cons. (mg/L)	3.1	8.3	167	3.9	8.8	0.8	5	25	0.4	0.6	0.3

2.3. Feasibility study

An economic analysis of the new industrial wastewater treatment plant was performed using net present value (NPV) and discounted payback period (DPP) calculations to account for the time value of money. For that, after finishing the pilot studies, a computational simulator using Excel software was built to make a full scale-up extrapolation in terms of raw materials and utilities consumption, i.e., to determine variable costs (Fig. 2 and Table 2). The main values considered for this analysis are: consumer price index of 2% (European Central Bank objective), depreciation time of 15 years (suggested by AEMA MBR constructor) using linear depreciation method for the DPP estimation, energy cost between 70 and 80 €/MWh (Inovyn Spain average value for 2015), fresh demineralized water production cost between 1 and 2 €/m³, 35–55 €/h for person-months and a possible technical production of 290 kt/year.

3. Results and discussion

3.1. Pilot trials

In the MBR, for the design of a treatment with denitrification and nitrification processes, using a single biological tank with separated anoxic plus aerobic zones, the hydraulic retention time should be at least 6 h and solids retention time in the range of 15–20 days [12]. Mixed liquor suspended solids (MLSS) content in the pilot was in the range of 8–10 mg L⁻¹, the optimal flux was in the range of 22–26 LMH (during the piloting, flux was increased from 10 to 26 LMH) and recirculation rate was 4–6. The pilot plant was operated for 15 months. Samples were taken for lab analysis 3–4 times per week. Once it was optimized the quality of the final effluent, after the MBR and two pass RO, was high enough to enable the use of water in the PVC polymerization step, main average values are summarize in Table 1 [11]. This reclaimed water was tested in real polymerization trials and it was confirmed that it can be successfully reused in the polymerization plant without affecting the process or the final PVC quality.

An acclimatization period of about 1 month was needed in the MBR for achieving an almost total PVA removal, starting with a non-adapted activated sludge culture. Once the MBR was running stably, removal of PVA and BOD₅ was close to 100%, and removal of COD and TOC was in the range of 85–95% and 85–90%, respectively. CIP cleanings will be necessary for daily/weekly basic/acid cleaning and pH control by continuous caustic soda addition and phosphorus dosage for assuring a good biological treatment and foaming control will be also required, with occasional antifoam addition to avoid solid losses as well as operational problems in pipes and equipment. At stable conditions and with adequate pH and dissolved oxygen control, ammonia was completely nitrified to nitrate, matching the quality required for the MBR effluent. Details of the pilot trials are given by Blanco et al. [11].

The operation of the hollow fiber UF was very stable during the piloting. Most of the membrane fouling was reversible as permeability was very well restored after recovery cleanings. Daily CIP seemed to avoid irreversible fouling on the membrane surface.

Recirculation ratio (recirculation/MBR effluent) had a significant influence on the permeability due to the high quantity of solids accumulated in the membranes during the period when recirculation ratio was 3. This means that higher values will have to be used in real installations to avoid irreversible fouling in the membranes and reduce the need for frequent chemical cleanings.

As mentioned before, two pass RO treatment was needed for obtaining permeate with conductivity lower than 10 µS cm⁻¹. Moreover, RO permeate quality was within specifications independently of the quality of the MBR effluent. Due to the high quality of the MBR permeate and the use of high salt rejection polyamide membranes, RO showed a very good performance during the piloting, with no significant transmembrane pressure drop values (ranging from 6.5 to 7.9 bar when recovery was increased) [11].

Table 2 shows the average chemical consumptions of the industrial plant (~100 m³/h) estimated based on the pilot plant data.

Regarding the RO, two pass plus two stages are needed to achieve the targeted water quality for polymerization. Antiscalant and biocide additions were required as shown in Table 2. The recovery rates were kept in the range of 60–75% to reach the foreseen membrane lifetime and minimize cleaning requirements. Concentrates will be discharged because they are below the current limits.

3.2. Economic feasibility study

The economic feasibility was evaluated on the basis of CAPEX, OPEX and DPP.

3.2.1. CAPEX

Based on the offers received from different suppliers, the capital expenditure for a turnkey project for the requested specifications amounts to 1.5 M€, plus 1 M€ of erection and installation costs in terms of connection to the site, utilities supply and site preparation. Within the turnkey scope, civil works, bioreactors, membranes and all pumping and instrumentation equipment are included.

3.2.2. OPEX

Operational costs include electrical energy, personnel costs (one lab technician and one maintenance technician), exploitation costs (based on the chemical consumption shown in Table 2) and plant consumables reposicion. According to the performed simulations, operational costs are about 0.455 M€/year, where fixed costs represent 34% of the total amount (0.153 M€/year) and variable costs 66% (0.292 M€/year). In terms of specific operational expenditure, cost is 0.69 €/m³, with 0.24 €/m³ for fixed cost and 0.45 €/m³ for variable costs.

3.2.3. Discounted payback period

DPP calculation has been done taking into account following constructive and financial estimations: erection period time of 1 year, depreciation time of 15 years and inflation of 2% starting from 2015.

Price of demineralized water has been estimated between

Table 3
NPV (k€) estimation based on INOVYN Spain data reference.

	2015	2016	2017	2018	2019
INVESTMENT	2550	0	0	0	0
COSTS	0	463	472	481	491
DEPRECIATION	0	173	177	180	184
SAVINGS	0	1266	1291	1317	1344
NPV	–2550	–1920	–1278	–622	46

Table 4
Project profitability based on modular CAPEX investment.

Treated flowrate (m ³ /h)	DPP (years)
5	Not profitable
50	15
75	7
100	5

Table 5
Project profitability based on fresh demineralized water production price.

Fresh demineralized water price (€/m ³)	DPP (years)
0.5	Not profitable
1	23
1.5	7
2	4
2.5	4

Table 6
Payback time in months compared with production reduction forced by a drought.

Production restriction (%)	Investment recovery (months)
36	1
25	2
15	3
10	4
5	8
3	13

1 €/m³ and 2 €/m³ for the year 2015. Table 3 shows that, according to stated estimations and based on different offers, DPP is 5 years, i.e., the year where NPV becomes positive, with an initial investment of 2.5 M€.

With the aim of reducing investment costs, i.e., CAPEX, a model based simulation was performed for different treated flowrates and DPP was estimated (Table 4). The data gathered in Table 3, other estimated parameters such as fresh demineralized water cost, electrical energy cost, personnel cost and maintenance cost were kept constant.

Afterwards, another simulation was performed to make a DPP value comparison depending on fresh demineralized water production cost (Table 5).

Nevertheless, this technology cannot be considered only as a project where a quick payback is sought, but also as a strategic one. Table 6 shows the time to recover the investment in case of production reduction due to water use restrictions resulting from water scarcity.

If a drought period comes, water scarcity inflicts large damages at the business in terms of product and customers loss. Hence, looking to Table 6, it can be seen that a reduction in the production of 36% forced by a drought may give the investment back in

1 month. Even for a production reduction of 3%, the payback time would be one year approximately.

4. Conclusions

Based on a previous pilot plant study that confirms that water reclamation from PVC effluents is possible through coupling a MBR and a double pass RO process, the economic aspects for the implementation of the advanced treatment and water reuse in a PVC plant has been assessed.

Regarding the economic figures and based on INOVYN Spain CAPEX standards, the feasibility of the treatment train is not clear from a sole savings point of view, as the NPV is 5 years. Besides, the investment required is rather high, which does not match with free cash flow philosophy of the companies. Subcontracting option was not considered in this study, but it can be taken as an option if subcontractor offers recycled water at a price lower than fresh demineralized water production cost.

If DPP is lower than depreciation time of the active, the alternative considered here can be interesting from an economic point of view. Hence, for sites where fresh demineralized water production cost is higher than 1.5 €/m³, and with a treatment flow rate greater than 50 m³/h, this recovery system is potentially profitable.

However this alternative cannot be seen only by considering the payback time because it is also a strategy for the PVC production plant to become more independent from external water supply. It has been calculated that in the scenario of a drought that causes a 3% production restriction, the investment return would only be 1 year.

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