Towards integrated water management system in petrochemical site

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E4WATER – Economically and Ecologically Efficient Water Management in the European Chemical Industry

INTRODUCTION

The study carried out on a petrochemical site industry aims the demonstration of **reduction of withdrawal intake** while improving the **quality of the wastewater** for compliance with future regulations particularly on micropollutants discharge. The objective is to develop combination of treatment technologies for complex industrial wastewater streams for recycling and reuse within cooling water make up and/or in other operation/production processes, by ensuring an innovative and cost effective water scheme. The current wastewater treatment plant consists in deoiling.

Considering the limits of background technologies [1] [9] [10] [11] and the improvements offered by the latest developments [2] [3] [4] [5] [6] [7] [8], the extended treatment line proposed includes complementary and synergistic stages arranged in a treatment train able to combine **pollution concentration and degradation** into cycles. The whole results in an innovative **Low Liquid Discharge system**: Ozonation to increase biodegradability of the effluent, Biofiltration to remove organic compounds and suspended solids, Ultrafiltration to protect reverse osmosis membrane, Reverse osmosis to demineralize water, Brine recycling to reduce volume of discharge.

METHODS

Preliminary **water stream audit** on the petrochemical site provides a detailed overview of the flows and their quality entering and leaving the plant (Table 1).

Table 1 – Freshwater usage

Application	Cooling towers	Demineralized water	Fire water	Cleaning
Use of resource	55.0 %	42.1 %	1.6 %	1.3 %

The main stream regarding discharges rate is wastewater treatment plant outlet (Table 2). The main specific components to be controlled for final discharge are aromatic compounds including PAHs and BTEX.

Table 2 – Water quality summary

COD mg/L	BOD mg/L	DOC mg/L	Turbidity NTU	pH	Conductivity µS/cm	TSS mg/L
65 ± 30	14 ± 6	14 ± 8	8 ± 5	7.7 ± 0.5	896 ± 415	8.7 ± 5

Field tests are carried out at pilot scale with treatment units of capacity in the range 1 to 2 m^3/h. Water flows first into the ozonation unit. Once ozonated, water goes through an aerated biofiltration unit. The filtered water then enters the ultrafiltration module of polyethersulphone membranes. The final unit of the treatment line uses reverse osmosis technology. System pressures, effluent and gas flow rates, analytical parameters concentrations were controlled all along the experiments.

Figure 1 – In field pilot units

RESULTS

After biomass acclimatization upon water velocity increase up to 10 m/h, results obtained for the direct application of biofiltration to the deoiled wastewater confirm:

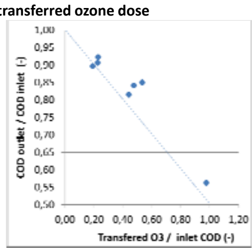
- Almost **full biodegradable organic matter removal** (BOD removal rate > 98%)
- Good **solids retention** performances with outlet TSS concentration below 10 mg/L.

It shows very good removal rates for most of the micropollutant detected in the influent like BTEX (>97%) with contribution of non-biotic processes, i.e. adsorption onto the biofilm. As a result, only 4 PAHs occur outlet the treatment. Nonylphenols are however still detected after the biofiltration (< 1 µg/L).

Regarding ozonation treatment of deoiled wastewater, ozone appears highly reactive towards the organic matter in relation to the occurrence of unsaturated and aromatic compounds.

- The variation of the ozone dose in the range 15 to 78 mg/L makes possible **COD reduction** by more than 40%.
- The oxidation extent is consistent with a shift towards the accumulation of compounds of acidic type with lower molecular weight and thus more easily biodegradable.
- In the first reaction stage, the impact of ozone dose predominates over the impact of contact time between 22.5 and 35 min suggesting that reaction rather proceeds under the **diffusion regime**.

Figure 2 – Total COD decay according to transferred ozone dose



Ozonation was then applied with the lowest ozone dosage prior to aerobic biological treatment for a synergetic oxidation.

- Accordingly, the combined oxidation system enhances **COD removal from 50 to 70%.**
- Furthermore, balances confirm that ozone mainly serves to make recalcitrant compounds more sensitive to further biodegradation and initiates the **degradation of some PAHs and all BTEX** further completed by biofiltration.
- The control of biofiltration performances is simultaneously made easier as highlighted by the **reduction of its washing frequency** with decrease of water losses by 50%.

Figure 3 – COD removal depending on applied load

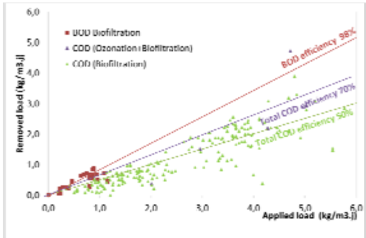
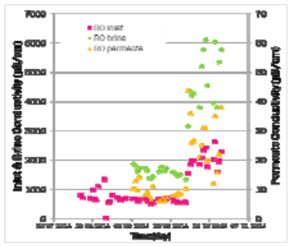


Figure 4 – Conductivity in Reverse osmosis



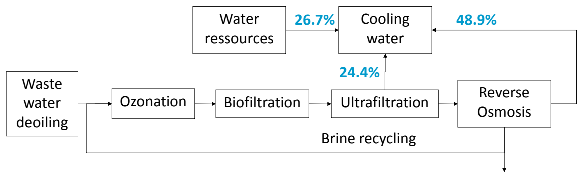
Considering background and technological limits in this application field, the implementation of the chemical/biological oxidation developed successfully upgrades the water quality in terms of organic pollution to a sufficient extent to:

- **Anticipate fouling issues** in the operation of subsequent UF/RO membrane technologies dedicated to mitigate the salt control.
- **Allow brine recycling**

In the global water treatment chain, an additional physical-chemical treatment is required to manage washwaters and biological sludge.

Recovery rate of 87% in stable operating conditions on the ultrafiltration and close to 75% for reverse osmosis obtained during pilot scale tests allow defining several full scale water management systems able to provided the water quality criteria for reuse as cooling water or steam generation. The optimized one is below (Figure 5).

Figure 5– Selected and demonstrated scheme of combined technologies tested for recycling and reuse



CONCLUSIONS

The related **integrated water management systems** are designed with a high level of **reliability**. They achieve the **reduction of the water withdrawal by 40.2 to 42.6%.** The capital and operational cost evaluations further performed favour the system involving extended wastewater treatment using after deoiling, ozonation, biofiltration, ultrafiltration and partial reverse osmosis for reuse of the mixture UF/RO permeates as cooling make-up water.

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