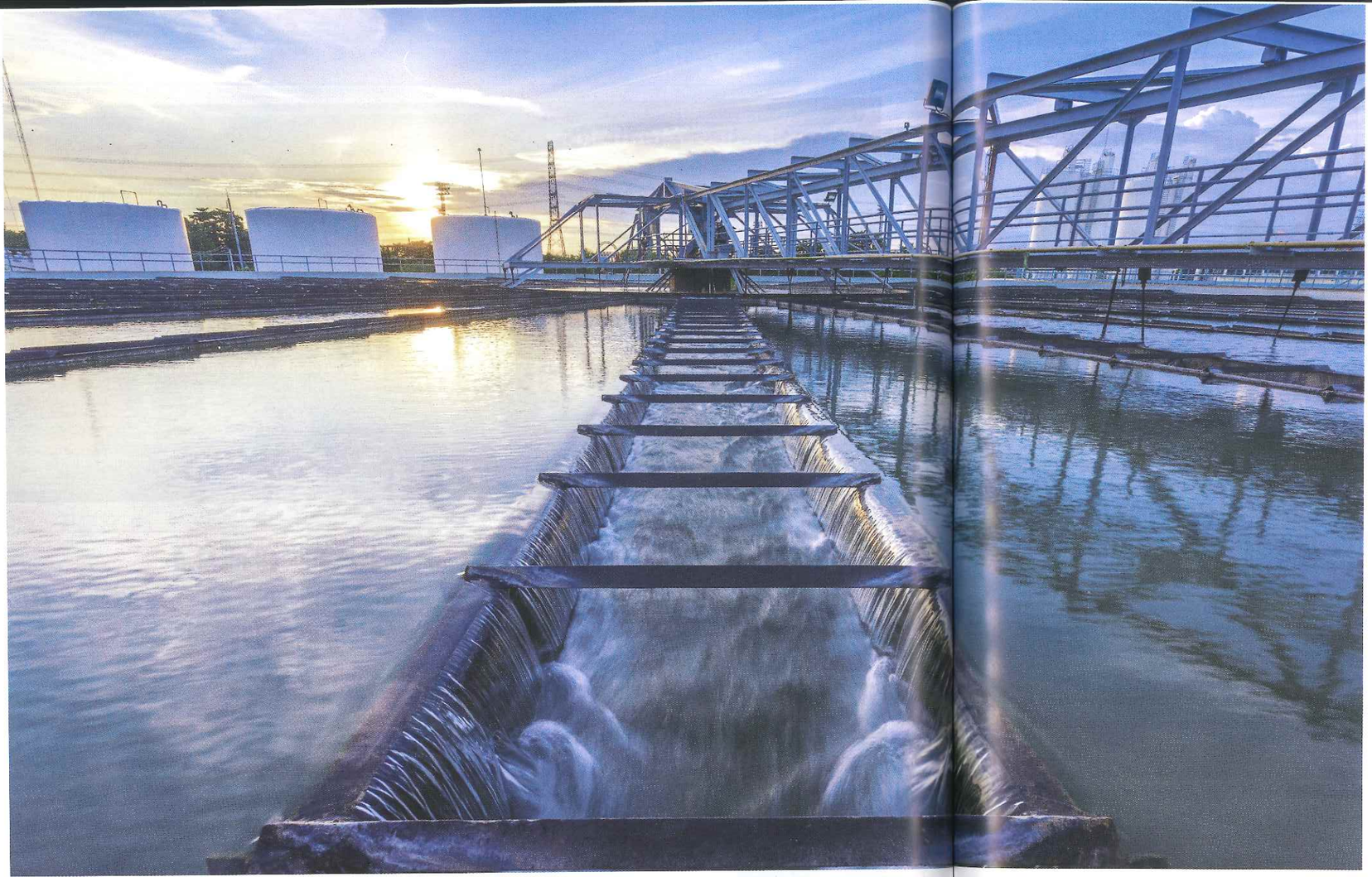

Advanced Oxidation Processes for Recalcitrant Pollutants from Refinery Waste Water

Recalcitrant organic constituents, such as phenols and aromatics, can often be found in refinery effluents. Phenols in particular can seriously affect living organisms by bioaccumulation. For this reason very strict limits are set on water discharge. Starting from a laboratory scale, Artes Ingegneria (Cannon Group) has developed an innovative cost effective industrial scale solution for a refinery plant facing the Caspian Sea

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Recalcitrant compounds are organic molecules very difficult to be degraded through a biological process. Such compounds include aromatics, phenols and phenol-derivatives such as o-, m- and p-cresol. Phenols in particular are the organic constituents in effluents of coal conversion processes, coke ovens, petroleum refineries, phenolic resin manufacturing, plastics, adhesives, steel, aluminium, leather, pulp & paper and petrochemicals. In particular many refinery processes produce phenol-rich water as an effluent: catalytic cracking, crude desalting, thermal cracking and catalytic hydrotreating.

When phenols are incorporated in the food chain, they cause relevant environmental troubles since they are toxic, recalcitrant and bioaccumulating in organisms. Phenols accumulation in water proved to be toxic for both the flora and fauna, mortal for fishes for concentrations higher than 5 mg/l.

Due to the high toxicity, phenols are subjected to specific regulations:

- the European Union considers phenol a priority substance (EC 1179/94, OJ L131, 26.5.94) under Regulation 793/93 on the evaluation and control of the risks of existing substances;
- according to the Italian law (D.L. 152/99) phenols shall be limited to less than 0.5 mg/l in treated effluent disposed into surface water;
- according to the "German Framework Administrative Guideline for Minimum Requirements on the Discharge of Waste Water into Water Bodies" (Rahmen-AbwasserVwV of 1.6.2000) a phenol index value of ≤ 0.15 mg/l is set for waste water before mixture with other waste water for the production of hydrocarbons and oil processing;
- phenol ranked 11th place under 129 specific priority chemicals that are considered toxic under the 1977 Amendments to the Clean Water Act and for which the US Environmental Protection Agency (EPA) has issued water quality criteria; in USA the discharge limit is fixed to less than 1 mg/l in the treated effluent.

It is clear that the wastewaters containing phenols require careful treatment before release into the receiving water sources.

In 2014 Artes Ingegneria has been awarded the engineering, procurement, shop construction and supervision contract for the effluent treatment & water re-use plant of a refinery on the Caspian Sea. For this specific job it was mandatory to meet, among other parameters, the extremely strict limit of less than 1 ppb of phenols in the treated water in order to fulfil at the same time the requirements for water re-use and discharge into the Caspian Sea.

The overall Refinery Effluent Treatment Plant, whose capacity is more than of 300 m^3/h, includes:

- a *primary treatment* focusing on the removal of free and emulsionated oil; the treatment is realized through a Corrugated Plates Interceptors (CPIs) and Dissolved Air Flotation (DAF);
- a *secondary treatment*, targeted to re-using the largest share of treated water, implements a biological oxidation unit through Membrane BioReactor (MBR);
- a *tertiary treatment*, needed to remove organic residues, that resulted efficient in the phenol compounds removal.

The request of very long times for phenols degradation by conventional treatments affects the adoption of huge reactor volumes, having a negative impact on capital (Capex) and operative (Opex) processing related costs. For this reason the application of an Advanced Oxidation Process (AOP) has been developed according to the following steps: an accurate theoretical

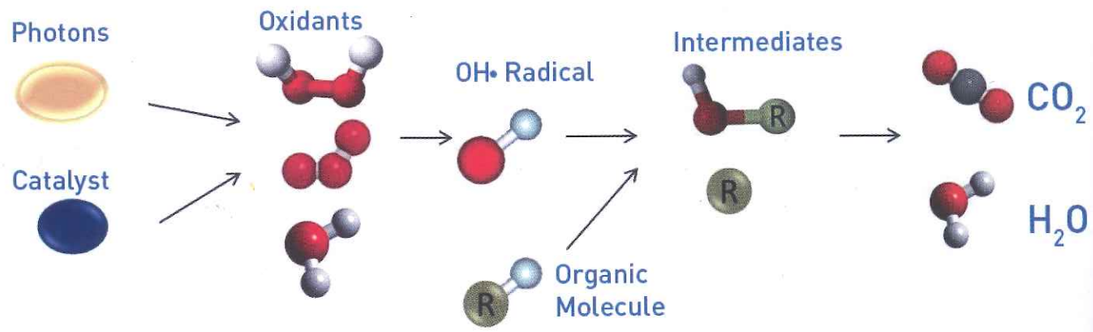

Fig. 1 – The Advanced Oxidation Process (AOP) reaction

investigation on the available AOPs, followed by a laboratory test of two of the preferred AOP technologies and the industrial implementation of the selected technology as a tertiary treatment.

Advanced Oxidation Process, a promising technology for the degradation of refractory chemical pollutants

Innovative treatments could represent a valid alternative method for the degradation of recalcitrant chemical pollutants. Among these, Advanced Oxidation Processes (AOPs) could be adopted for that chemicals like phenols and aromatic compounds which are resistant to biological and conventional physical-chemical treatments.

AOPs treatments are based on a pollutants degradation mechanism which consists in the production of intermediate hydroxyl radicals. These are very reactive species that are continuously generated and able to react in a quick and non-selective manner with the most part of water chemical pollutants.

The organic compounds are transformed by the hydroxyl radical in the same moment in which it is produced and, consequently, the effluent is degraded to other intermediate products (**figure 1**). Major AOP processes are the following:

- UV irradiation;
- ozone;
- ozone in combination with UV;
- ozone in combination with hydrogen peroxide (H_2O_2);
- hydrogen peroxide in combination with UV;
- Fenton and Fenton-like reactions.

The Advanced Oxidation Process reaction

The advantages of the AOP process are:

- efficient destruction of pollutants, in particular those recalcitrant to conventional treatments (pesticides, chlorinated solvents);
- alternative process to mass-transfer treatments where pollutant is transferred from liquid phase to solid (like adsorption on activated carbons) or liquid one (stripping).

Among the AOPs, Artes decided to investigate two treatments:

- the use of hydrogen peroxide with UV light (H_2O_2 + hv);
- the use of hydrogen peroxide with a liquid catalyst (H_2O_2 + catalyst).

The other AOP treatments were not eligible: with UV irradiation alone is not possible to reach the 1ppb limit requested by the customer, the ozone based technology is very energy consuming and critical for safety issues, Fenton reaction produces sewage sludge to be disposed.

In the first case, the ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical (**figure 2**).

$$H_2O_2 + hv \rightarrow 2HO\bullet$$
$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O$$
$$H_2O_2 + HO_2\bullet \rightarrow HO\bullet + H_2O + O_2$$
$$2\ HO\bullet \rightarrow H_2O_2$$
$$2\ HO_2\bullet \rightarrow H_2O_2 + O_2$$
$$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2$$

Fig. 2 – AOP reaction using hydrogen peroxide and UV light (hv) competitive reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO\bullet$$
$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + HO^-$$
$$HO\bullet + RH \rightarrow H_2O + R\bullet$$
$$R\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+}$$

Fig. 3 – AOP reaction using hydrogen peroxide and ferrous catalyst

In the second case, a mixture of ferrous catalyst and hydrogen peroxide (oxidizing agent) can be considered as a powerful oxidant for organic contaminants (**figure 3**).

The two different AOPs treatments were investigated, with the collaboration of Naples "Federico II" University:

- the adoption of hydrogen peroxide in combination with UV light;
- the combination of hydrogen peroxide with a liquid catalyst.

In particular, the degradation kinetics of both the two treatments was evaluated at different concentrations of both liquid catalyst and hydrogen peroxide.

Experimental plan

A synthetic solution was prepared as surrogate of the real wastewater produced by the refinery. It contains phenols but also sulphides and chlorides for a better simulation of the wastewater characteristics and in order to include all the possible interferences among various compounds.

The chemical composition of the synthetic water is reported in the **table 1**.

Compounds	Concentration
Phenols	100 ppb
Sodium chloride	8000 ppm
Sulphates	5500 ppm
COD	100 ppm
Dodecylbenzenesulfonate	500 ppm

Table 1 - Chemical composition of the synthetic water

The synthetic solution was submitted to the two different AOPs treatments. After being processed at different reagents composition, the content of phenols concentration was evaluated by HPLC (High Performance Liquid Chromatography) analysis.

The experimental plan can be summarized as following:

- preparation of the synthetic solution;
- sample processing by AOP 1 (hydrogen peroxide and UV light);
- sample processing by AOP 2 (hydrogen peroxide and liquid catalyst);
- post processing analysis: determination of residual phenols concentration by HPLC;
- design of the AOP basin of the best treatment and at selected operative conditions.

AOP treatment 1: hydrogen peroxide and UV light

A UV quartz laboratory scale lamp with mercury vapours was used with the operative conditions reported in **table 2**.

Reactor H_2O_2 + UV	Operative conditions
Reactor volume	500 ml
Lamps type	mercury vapours
Chamber	quartz
Light wavelenght	254 nm
Energy power	2.87 10^{-6} Es^{-1}
Average optical path	2,2 cm

Table 2 – Operative conditions of a UV quartz laboratory scale lamp with mercury vapours

AOP tests were conducted at two different hydrogen peroxide concentrations (10 and 100 ppm). The samples were analysed at different reaction times thus having the phenols degradation kinetics.

The graph in **figure 4** reports the degradation of the phenols: it can be observed that at higher treatments times, higher degradation can be reached at both H_2O_2 concentrations. Furthermore, the effect of the concentration on phenols degradation in not very strong: if hydrogen peroxide concentration is reduced

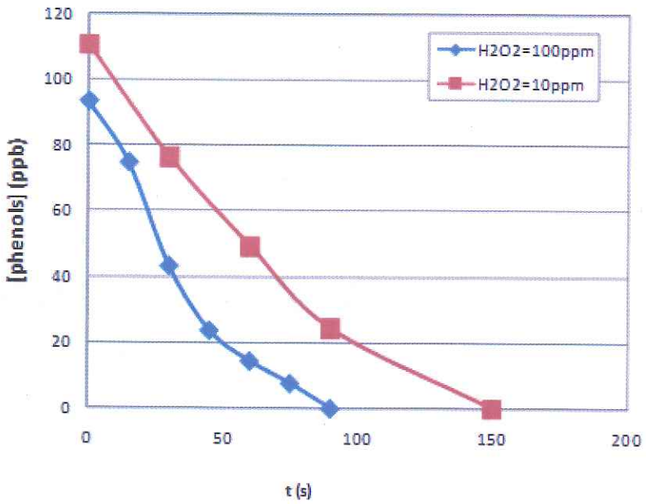

Fig. 4 – Phenols degradation AOP treatment 1

TEST	H_2O_2 ppm	CATALYST mL_{SM}/L	pH
A	1	0.017	8.0-8.5
B	30	0.510	8.0-8.5
C	50	0.850	8.0-8.5
D	100	1.700	8.0-8.5

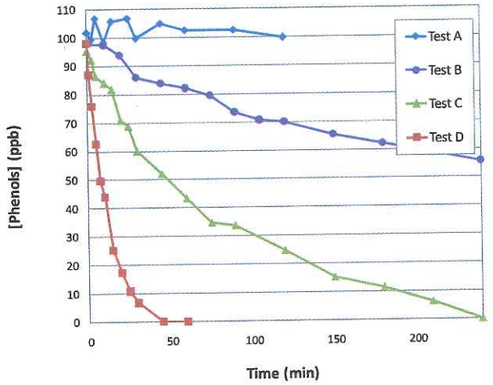

Fig. 5 - Phenols degradation-AOP treatment 2 at highest hydrogen peroxide and lower catalyst concentrations

TEST	H_2O_2 ppm	CATALYST mL_{SM}/L	pH
1	100	0.85	8.0-8.5
2	100	0.57	8.0-8.5
3	50	1.70	8.0-8.5
4	50	0.57	8.0-8.5

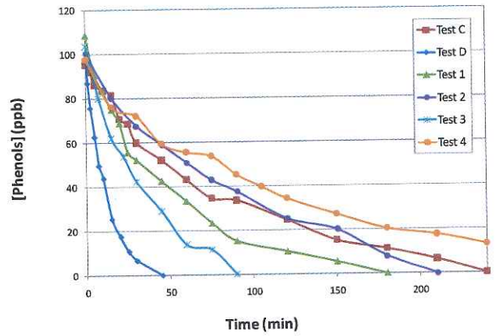

Fig. 6 – Phenols degradation AOP treatment 2

from 100 ppm to 10 ppm, the reaction time request for the complete degradation of the phenols compounds is increased only of the 66%. This can be explained by the competitive reaction occurring between OH radicals and hydrogen peroxide molecules (figure 2).

AOP treatment 2: hydrogen peroxide and liquid catalyst

Similarly to the previous treatment, this AOP treatment is based on the use of hydrogen peroxide, in this case hydrogen peroxide is used in combination with a liquid ferrous catalyst. The experimental tests were conducted with a laboratory scale plant at the processing conditions reported in **table 3**.

Reactor H_2O_2 + catalyst	Operative conditions
Rector volume	500 ml
Starting reactor time	addition of catalyst
Ending time	addition of catalyst (enzyme stopping the reaction)

Table 3 – Operative conditions of an experimental test using hydrogen peroxide in combination with a liquid ferrous catalyst

The tests were conducted at different hydrogen peroxide (1, 30, 50 and 100 ml_{SM}/l) and liquid catalyst concentrations (0.017, 0.510, 0.850 and 1.700 ml_{SM}/l) at pH = 8.0 – 8.5 in the following combinations: reported in **figure 5**.

The results report that higher reaction times were request for the complete phenols oxidation when using hydrogen peroxide in combination with a liquid catalyst (order of minutes). In addition, best results were performed at higher concentrations of hydrogen peroxide at 50 ppm (test C) and at 100 ppm (test D). In order to reduce reagents consumption, additional tests were performed at highest hydrogen peroxide concentrations (50 and 100 ppm) but with lower catalyst concentrations (**figure 6**).

Best results in terms of phenols degradation were reached in the following conditions:

- H_2O_2 = 100 ppm + catalyst = 1.7 ml_{SM}/l (test D)

Artes Ingegneria

Artes Ingegneria, is an Engineering and Construction Company in the water and waste water treatment business with extensive experience in the oil&gas industry, either upstream or downstream.
Artes' solutions addressing specifically the oil&gas are: produced & injection water, desalination, raw water pre-treatment, demineralization systems, condensate polishing, thermophysical deaerators, vacuum degassing package, effluent water treatment, sanitary water treatment and drinking water makers, cooling water filtration.
Artes Ingegneria is part of Cannon Group.

- H_2O_2 = 50 ppm + catalyst = 1.7 ml_{SM}/l (test 3)

Since differences in performance between the two treatments were not so high, the second condition was chosen as AOP treatment for the industrial scale up since it involves less consumption of hydrogen peroxide.

Industrial scale up of AOP treatment

The two AOPs tested and optimized in the lab-scale are now compared taking into cosideration the Capital & Operating Costs related to the industrial installation.
Even though shorter reaction times are requested by appling H_2O_2 + UV light (order of seconds) than by appling H_2O_2 + catalyst (order of minutes), the latter allows both lower Capex and Opex. Results are displayed in the **table 4**.

Treatment	Conditions	Capex (euro)	Opex (euro/m^3)
H_2O_2 + UV	H_2O_2 = 10 ppm Q J_{254} = 400 J/l	450,000	0,068
H_2O_2 + catalyst	H_2O_2 = 50 ppm catalyst = 1.7 ml_{SM}/l	100.000	0,019

Table 4 – Results of the two AOP tested and optimized in the lab-scale compared taking into cosideration Capex and Opex related to the industrial installation.

The kinetics of the H_2O_2 + UV treatment is more performing but the costs associated with the energy consumption and UV lamps (installation and periodical replacement) makes this process less competitive when compared with the H_2O_2 + catalyst treatment.
The most cost effective solution, jointly defined by the laboratory test and the Capex / Opex analysis, is therefore the hydrogen peroxide +catalyst treatment that was preferred for scale up from laboratory scale to the industrial one.
This solution has been adopted for the supply of the tertiary equipment included in the effluent water treatment plant for the Caspian Refinery.
Once optimized the reaction conditions at a laboratory scale, the design of an advanced oxidation basin was conducted, on the basis of the client's specifications (inlet/outlet water quality and flows).
The AOP basin represents a tertiary treatment in an integrated system including Coalescent Plate Interceptors (CPI), flotation as deoling and MBR (Membrane BioReactor). The basin has been realized in order to reproduce the reaction at the optimized conditions:

- hydrogen peroxide: 50 ppm;
- catalyst concentration: 1.7 ml_{SM}/l;
- reaction time: 120 min.

The AOP basin design was conducted to guarantee the optimized reaction conditions and it was supported by a mixing system in order to ensure the reaction uniformity and by a sodium hydroxide (NaOH) dosing system to keep the continuous pH regulation.
The volume of the AOP basin was calculated by considering a volume flow rate equal to 300 m^3/h and a reaction time of 120 min, which is the time requested for the phenols oxidation below the discharge limits (< 1 ppb).
The reaction was performed in a concrete basin having an internal diameter of 16.5 m and an height of 2.8 m: the high D/H ratio (greater than 3) was due to the aquifer constrains associated to the plant (limited soil elevation and low feeding pressure to the basin).
In order to guarantee the complete mixing between the two reagents in the AOP tank, a vertical mixer was installed assuring continuous mixing during treatment thus leading such system in a CSTR (Continuous Stirred Tank Reactor) configuration.

The selected mixer moved about 24,500 m^3/h of water, in this way each fluid element had a turn-over of around 120 s and was mixed about 60 times before going out assuring a complete and homogeneous mixing.

The system was also accomplished by sodium hydroxide injection for the maintanance of the desired pH = 8.0 – 8.5 (optimum pH for the reaction) through the installation of dosing pump skid; also hydrogen peroxide was added to the tank by means of dosing pumps.

Conclusions

To comply with the strict request of phenols removal till less than 1 ppb for a Caspian Refinery Effluent Water treatment for which Artes Ingegneria has been awarded, the company investigated two Advanced Oxidation Processes:

- H_2O_2 + UV light;
- H_2O_2 + liquid catalyst.

They were first analysed in terms of degradation kinetics at different H_2O_2/catalyst. In addition, the treatments were compared in terms of both Capex and Opex costs.

The results showed that the reaction time necessary for the degradation of phenols below 1 ppb in the case of hydrogen peroxide + UV light is lower than in the case of treatment using liquid catalyst at parity of hydrogen peroxide concentration.

On the other side the process implying UV light is much more expensive because of the high energy costs associated with the UV light and the need of frequent replacement of UV lamps. For this reason, the treatment with hydrogen peroxide and liquid catalyst was implemented in the industrial scale up to the Caspian project conditions: once selected the best AOP treatment and optimized in terms of operative conditions, the AOP basin was adopted as tertiary treatment in the integrated wastewater treatment.

Results showed that lower treatment times were requested at the highest concentration of both the reagents (H_2O_2 = 100 ppm, liquid catalyst = 1.7 ml_{SM}/l) but in order to reduce hydrogen peroxide consumption, the condition of 50 ppm of hydrogen peroxide and 1.7 ml_{SM}/l of catalyst were used as optimum.

The scale up to the real waste water flow of the Caspian Refinery drove to the design and construction of a 600 m^3 AOP basin capable to guarantee the respect of the 1 ppb phenols limitation with a 300 m^3/h flow rate and a residence time of 120 minutes. An atmospheric cylindrical continuous stirred reactor hosts the reaction.

Artes Ingegneria's solution was really appreciated by the customer that, thanks to the optimized kinetics, had benefited from a significant reduction of the investment and operating costs in comparison to a conventional treatment complying the same limitations.

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Ivan Saracino

Graduated *cum laude* in Chemical Engineering in 2002 at University of Salerno, in the same year started working as a project engineer at Artes Ingegneria SpA. Project manager from 2007 up to now, in 2008 he was nominated directional consultant in HSE. From 2012 he received the assignment as R&D Manager focusing on energy efficiency, water reuse and innovative processes.