## Optimization of coupled advanced oxidation processes and activated carbons for purification of salt water

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Photocatalysis, ozonation and activated carbons were investigated separately and in combination as tools for the purification of polluted salt water. Coupling different processes enables to overcome many drawbacks related to the use of the single technologies and at the same time to exploit possible synergistic effects. In this work a kinetic analysis was performed for modelling the degradation of 4-nitrophenol (4NP) as a probe pollutant molecule in synthetic seawater. Thus, the optimum synergistic conditions of the three processes acting together were determined and discussed.

One of the main source of marine degradation is represented by the disposal at sea of oily waste water. This is primarily generated by the washing operations of the ship's fuel tanks containing petroleum products (slops) and by bilge water which originates from seawater infiltration and leakage of engine oil and fuel. The discharge into the marine environment of oily wastewater is an issue of considerable technical and scientific interest, in relation to the toxic effects that such substances may have on the environment and human health.

For these reasons, the International Maritime Organization (IMO) has enacted MARPOL 73/78 convention in which effluents from ships are now limited to a maximum oil content of 15 ppm [1]. This type of wastewater shows high variability in the composition, depending on the type of petroleum products transported, and contains large amounts of organic contaminants, mainly aliphatic, alicyclic and aromatic hydrocarbons. Furthermore, as the washing operations of ship's fuel tanks are performed through the use of sea water pumped at high pressures, the wastewater shows high levels of salinity and relevant amounts of other pollutants, including emulsifiers, corrosion inhibitors, heavy metals and other inorganic compounds (e.g. halides, sulphates, phosphates, sulfides) [2], present both in solution and in the suspended solid phase.

Several technologies have been proposed for facing this problem. Nevertheless the degradation efficiency is strongly affected by the high salinity of the effluent. For these reasons, in this work it is proposed an integrated treatment system, obtained by combining ozonation, photocatalysis and granular activated carbon (GAC) adsorption and the optimum working conditions have been investigated.

The bench-scale experimental setup is schematically depicted in the Graphical Illustration. A simulated seawater solution of 4NP is moved by the pump (F) from the tank (E) to the photocatalytic fixed bed reactor (G). The photoactive bed, made of $TiO_2$-covered Pyrex spheres, is both internally and externally irradiated through a 125W medium pressure Hg-lamp (power supplied by (A)) and through 6 fluorescent tubes (8W each), respectively. The effluent exiting the photocatalytic reactor splits through the valve (I) flowing partially through the activated carbons bed (H) being the rest recycled into (E). The ozone produced by means of the ozonator (C) bubbles into the tank (E). The ozone concentration and its mass flow values are monitored by means of a spectrophotometer (D) and a mass flow controller (A), respectively.

GAC adsorption is particularly useful as it allows separation of big amount of pollutant and it is quite easy to scale up. In this work GAC were previously employed alone for purification of simulated seawater in the presence of 4NP as the probe pollutant and the equilibrium parameters were determined and reported in Table 1.

**Table 1.** Equilibrium data for the adsorption of 4NP (as Total Organic Carbon due to 4NP) onto GAC, by using Langmuir-Freundlich (LF) model. $q_e$: amount of 4NP adsorbed per gram of GAC at equilibrium; $q_{mLF}$: adsorption capacity of the system; $C_e$: concentration of 4NP at equilibrium; $K_{LF}$: affinity constant for adsorption; $m_{LF}$: index of heterogeneity.

| | LF-model | $q_{m_{LF}}$ [mg·g$^{-1}$] | $m_{LF}$ | $k_{LF}$ [mg·L$^{-1}$] |
|---|---|---|---|---|
| Simulated seawater | $q_e = \dfrac{q_m \cdot (k_{LF} \cdot C_e)^m}{1+(k_{LF} \cdot C_e)^{m_L}}$ | 189.7 | 0.9 | 0.08 |

**Table 2.** Pseudo first order kinetic constants (k'), adsorption constants of 4NP ($K_{4NP}$) and of oxygen ($K_{ox}$), and $O_2$ fractional surface coverages ($\theta_{ox}$) obtained from 4NP photocatalytic degradation runs carried out in distilled water and in simulated seawater.

| | k' [mol/m$^2$·s] | $K_{4NP}$ [M$^{-1}$] | $K_{ox}$ [M$^{-1}$] | $\theta_{ox}$ |
|---|---|---|---|---|
| Distilled water | $2.04 \cdot 10^{-9}$ | 3336 | 25728 | 0.97 |
| Simulated seawater | $1.18 \cdot 10^{-9}$ | 723 | 1697 | 0.56 |

Nevertheless, this physical treatment does not afford pollutant degradation and carbons require to be substituted or regenerated once saturated. Furthermore, small organic species as formate or acetate are only slightly adsorbed onto the GAC. In order to overcome these problems ozonation was employed in combination with GAC. In fact, ozonation affords fast oxidation of organic pollutants both in solution and when these species are adsorbed onto their surface. In this way ozonation not only allows water purification but also extends the lifetime of activated carbons which thus can be used for longer times before being reactivated. These factors entail lower operating costs of the process.

However ozonation of seawater presents a major drawback. In fact, seawater contains bromide ions (ca. 67 mg/L) which are almost quantitatively oxidized to bromate ions in the presence of ozone. Bromate was classified as carcinogenic species from the IARC (International Agency for the Research on Cancer) and the USEPA (United States Environmental Protection Agency) fixed at 10 µg/L its minimum lethal concentration.

$TiO_2$ photocatalysis was proposed as a tool to overcome this problem [3]. In fact the electrons photogenerated under UV irradiation are able to reduce bromate to bromide ions being, at the same time, the back reaction hindered. On the other hand, photocatalysis alone suffers of very slow purification rates for high salinity solutions as it can be seen from the kinetic parameters shown in Table 2. This is mainly because of the presence of chloride ions and of the low oxygen concentration in solution, due to the high ionic strength of the reacting medium.

However, photocatalysis allows to control the bromate ions formed during the ozonation step and, in the presence of ozone affords degradation rates higher than the sum of the rates of the single technologies acting in series. This feature was rationalized by Parrino et al. [4] for distilled water solutions of formate as the model pollutant. Similar considerations are presented in this work for simulated seawater solutions. In fact, it is possible to define two parameters: an intensification factor ($E_i$) and $\delta$. $E_i$ is the ratio between the rate of the integrated process (ozonation and photocatalysis acting together) and the sum of the rates of photocatalysis and ozonation acting separately, whereas $\delta$ is the ratio between the photocatalytic and ozonation 4NP degradation rates.

Notably, for distilled water formate solutions, it was found that the integrated process is 1.6 times more efficient than the sum of the single technologies. On the other hand, for 4NP simulated seawater solutions the synergistic effect between photocatalysis and ozonation is very low (almost 10% when the photocatalytic rate is 0.3 times the ozonation one, i.e. $\delta=3$, see dashed line in Figure 1) so that it is necessary to couple the two advanced oxidation processes with adsorption onto GAC in order to make the seawater purification process reasonably practicable. To this purpose, as shown in the Graphical illustration, in our system part of the effluent to be treated passes through an activated carbons bed whilst photocatalysis and ozonation act at the same time at the optimum conditions previously determined ($\delta=0.3$).

Analogously, an intensification factor can be defined as the ratio between the degradation rate of the integrated process (activated carbons+ozonation+photocatalysis) and the sum of the rate of the three technologies acting separately. The parameter $\delta$ is in this case defined as the ratio between the rate of photocatalytic ozonation and

the adsorption rate on the activated carbons. The parameter δ was varied by changing the amount of activated carbons in the adsorption bed so that the curve shown in Figure 1 (solid line) could be obtained. It is worth to note that the maximum value of the intensification factor is reached at δ = 0.3 in different experimental conditions. This result is also in agreement with the relevant literature [4].

One can observe that it is sufficient an adsorption rate on the activated carbon 0.3 times the degradation rate obtained by photocatalytic ozonation to get the best synergy between the three technologies. In particular the integrated process is almost 60% more efficient than the sum of the rate of the three technologies acting in series.
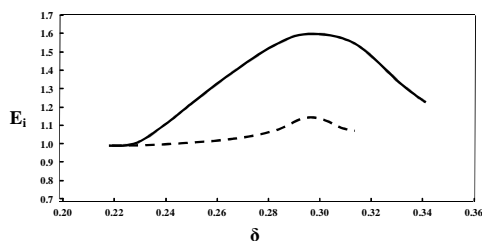
*References*

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**Figure 1.** *Experimental trend of the intensification factor for the purification process in the presence of photocatalytic ozonation, with (solid line) and without (dashed line) activated carbons, vs the parameter δ.*