Journal of Environmental Protection,
Safety, Education and Management
2015, Number 6, Volume 3, date of issue 28th November 2015 ISSN 1339-5270

PHENOL DEGRADATION BY OXIDATION PROCESSES

Maroš SOLDÁN - Marek LIPOVSKÝ - Michaela KLAČANSKÁ

ABSTACT

Phenolic compounds constitute a group of chemicals found in many industrial waste water processes such as pulp mills, manufacture of pesticides, dyes and others. However, industrial wastewater in many cases contains the biorecalcitrant chemical species that resist biological treatments. For this reason, other methods are being studied as an alternative to biological and classical physico-chemical processes. Advanced Oxidation Processes (AOPs) will probably constitute the best option in the near future.

KEY WORDS

phenol, advanced oxidation process, HPLC, degradation

1. Introduction

Phenolic compounds constitute a group of chemicals found in many industrial waste water processes such as pulp mills, manufacture of pesticides, dyes and others. The concentration of these chemical compounds is usually below 1 ppm in seawater and half in river water without dilution capacity. This is in agreement with the regulation dealing with the evolution of phenolic compounds to the environment, regulated by different governmental agencies. The most used and economic alternative of wastewater treatment is based on biological methods. However, industrial wastewater in many cases contains the biorecalcitrant chemical species that resist biological treatments. The biological treatments depend on many factors including pH, temperature, organic charge measured as biological demand of oxygen and the presence of the inhibitors such as phenol species.

For this reason, other methods are being studied as an alternative to biological and classical physico-chemical processes. Of these, Advanced Oxidation Processes (AOPs) will probably constitute the best option in the near future. AOPs have been described broadly as those aqueous phase oxidation processes which are based primarily on the intermediacy of the hydroxyl radical in the mechanism resulting in the destruction of the target pollutant or xenobiotic or contaminant compound [1]. The AOPs are pollutant treatment processes, which use ozone, UV, ozone in combination with UV (O_3/UV), ozone plus hydrogen peroxide (O_3/H_2O_2), hydrogen peroxide and ultraviolet light (UV/H_2O_2), Fenton's reagent and photocatalysis, which uses titanium dioxide (TiO_2) in combination with light (UV) and oxygen. The main problem of AOPs lies in the high cost of reagents such as ozone, hydrogen peroxide or energylight sources like ultraviolet light. However, the use of solar radiation as an energy source can reduce costs. Moreover, should be pointed out that AOPs lead normally to the best yields in pollutant destruction when biological treatments are unfeasible [2].

AOPs have considerable similarities due to the participation of hydroxyl radicals in most mechanisms that are operative during the reaction. Hydroxyl radicals are extremely unstable and reactive because of their high reactivity. Given that the hydroxyl radical is such an unstable and reactive species, it must be generated continuously through chemical or photochemical reactions [3].

In an ozonation process two possible ways of oxidizing action may be considered: the direct way, because of the reaction between the ozone and the dissolved compounds, and the radical way owing to the reactions between the generated radicals produced in the ozone decomposition (hydroxyl radicals) and the dissolved compounds [4].

In spite of the fact that chemical oxidation reactions can be more expensive than the other procedures, they have the advantage that they can eliminate the pollutants, whereas in the others they are removed from the effluents but not degraded. In catalytic oxidation processes, ozone can be used as an oxidant agent capable of degrading the phenolic species. However, this alternative can be expensive due to the cost of production of ozone, generated in situ, and also because of the low solubility of ozone in aqueous solutions. The use of combined UV radiation and ozone is an attractive route because of the enhancement of the performance for both agents by means of the hydroxyl radical generation, a powerful oxidant agent that can oxidize completely the organic matter present in aqueous systems [5].

High pressure liquid chromatography (HPLC) is a unique technique that allows detection of phenol degradation products. The principle detected products are described at figure 1 [5].

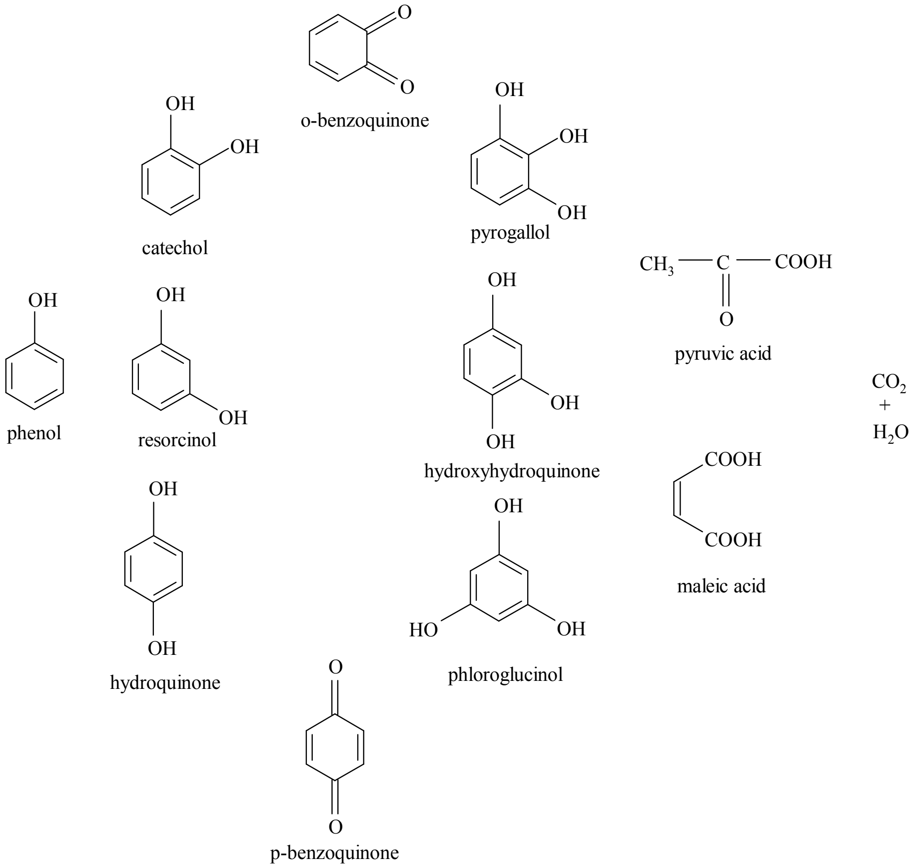


Figure 1 The products of phenol degradation

2. Experimental

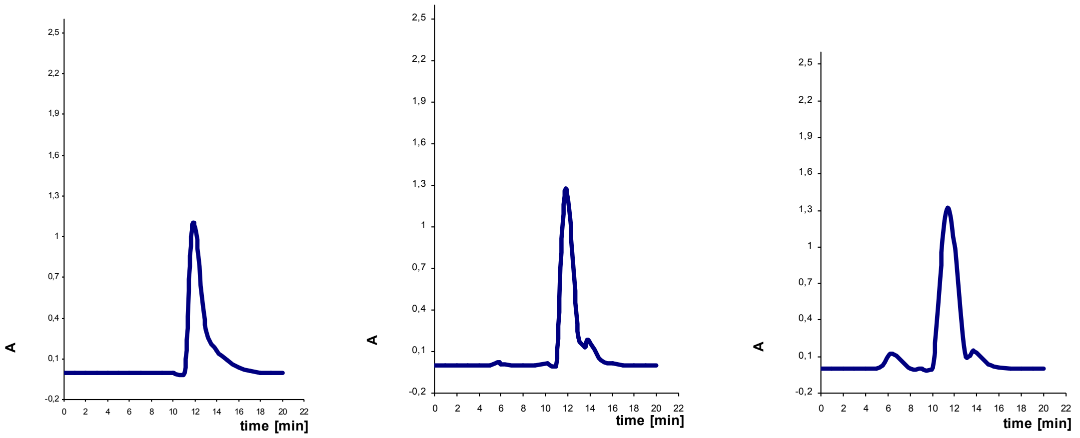
Phenol degradation process was carried out in a 250 ml reactor with 100 ml of 1 % aqueous solution of phenol. The ozone, generated by a DEZOSTER Laboratory Ozone Generator, was added to the reactor by a fibber placed at the bottom of the reactor.

Experiments with phenol degradation by hydrogen peroxide were carried out in 100 ml reactor with 10 ml of 1 % agueous solution of phenol and 5 ml of H_2O_2 (36 %).

Phenol was monitored by HPLC chromatography using a Hitachi HPLC system provided with a sampler, UV-Vis detector (280 nm) and a column SEPARON C18. The system was operated with a mixture of methanol / water buffer (70:30).

3. Results and discussion

Figure 2 shows chromatograms of phenol degraded by ozone in different times of exposure. With increasing time of ozone exposure we can observe the peaks of some phenol degradation products, which were not determined. However, the ozone concentration was not enough to degradation of phenol. Therefore in future experiments there will be the need of its optimalization.

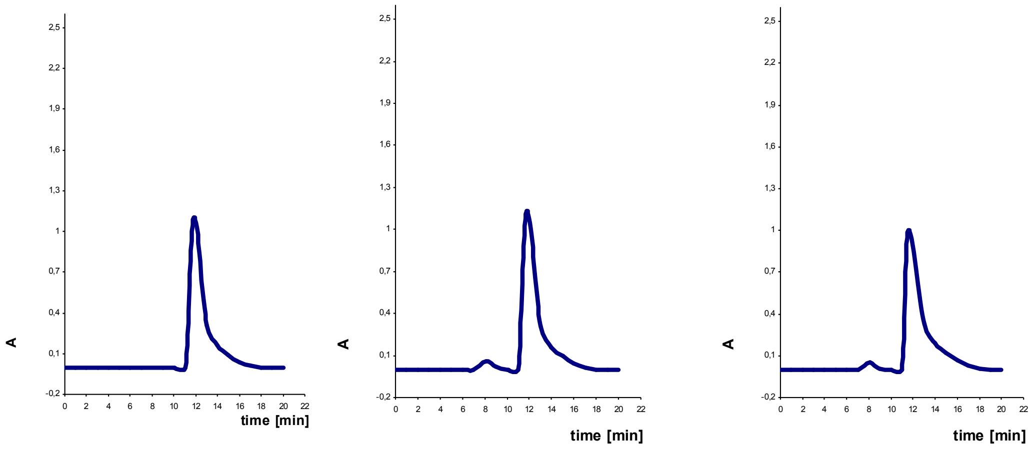


0 min. 30 min. 60 min.

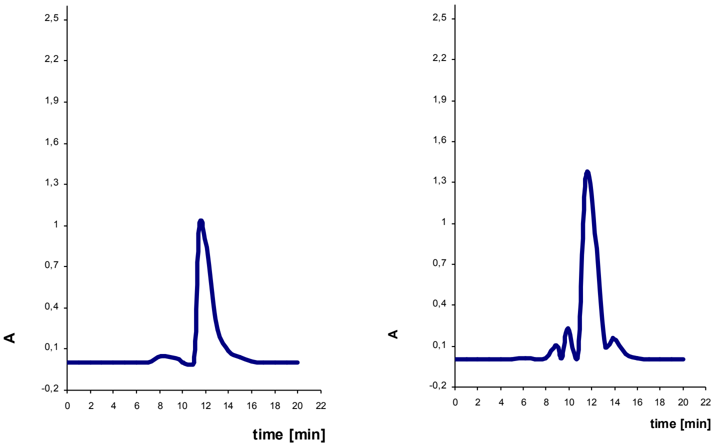
Figure 2 The chromatograms of phenol degradation by ozone after different times of treatment

Next figure shows chromatograms of phenol after different times of hydrogen peroxide treatment. It has been found out that longer time of treatment results in product of some phenol degradation products but not in decrease of its concentration.

The increase of the elution peak of phenol could be caused by its degradation products with similar elution time.



0 hours 12 hours 24 hours



48 hours 72 hours

Figure 3 The chromatograms of phenol degradation by hydrogen peroxide after different times of treatment

4. Conclusions

AOPs (ozone and H_2O_2) have been studied for the degradation of phenol in aqueous solution. It has been found that ozone has not improved the degradation rate of phenol. Nevertheless, degradation rate and the lower costs obtained with ozonation makes it the most appealing choice for phenol degradation. The degradation rate of phenol can be improved with the use of UV light with suitable wavelength.

REFERENCES

[1] Esplugas S., Gimenez J., Contreras S., Pascual E., Rodriguez E.: Comparison of different advanced oxidation processes for phenol degradation. In. *Water Research* Vol. 36, 2002, p. 1034–1042

[2] Andreozzi R, Caprio V, Insola A and Marotta R.: Advanced oxidation processes (AOP) for water purification and recovery. In: *Catal Today*, Vol. 53, 1999, p. 51–9

[3] Oussi D, Mokrini A, Esplugas S.: Removal of aromatic compounds using UV/H_2O_2. In: *Recent Res Dev Photochem Photobiol.*, Vol. 1, 1997, p. 77–83

[4] Beltrian F. J., Encinar J. M., Alonso M.A.: Nitroaromatic hydrocarbon ozonation in water. Combined ozonation with hydrogen peroxide or UV radiation. In: *Ind Eng Chem Res*, Vol. 37, 1998, p. 32–40

[5] Gimenez J, Curcio D, Queral M. A.: Photocatalytic treatment of phenol and 2,4-dichlorophenol in a solar plant in the way to scaling-up. In: *Catal Today*, Vol. 54, 1999, p. 229–43

CONTACT ADRESS

Authors: prof. Ing. Maroš SOLDÁN, PhD.
Ing. Marek LIPOVSKÝ
Mgr. Michaela Klačanská
Workplace: Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Institute of Safety, Environment and Quality
Address: Paulínska 16, 917 24 Trnava, Slovak Republic
E-mail: maros.soldan@stuba.sk