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ASSESSING SOME ADVANCED OXIDATION PROCESSES IN THE ABATEMENT OF PHENOL AQUEOUS SOLUTIONS

In this work, phenol oxidation in aqueous solution promoted by the effect of the oxidizing agents H_2O_2, O_3 and UV radiation and their synergy in four different advanced oxidation processes (O_3, O_3/UV, H_2O_2/O_3 and O_3/H_2O_2/UV) were assayed. Studies were performed with a closed-loop hydraulic circuit set up with a relatively high volume of solution (500 cm^3) during 90 min of treatment time. Parameters such as concentration for oxidizing species, pH, presence of UV irradiation were evaluated. The resulting degradation efficiencies were evaluated using GC-MS. The agents here used were selected considering their ease of handling and low toxicity, generation of deposited matter or sludge, so a filtration treatment for the analysis of the samples was not required. In all cases, it was observed that with increasing treatment time better degradation efficiencies were obtained. The best results were obtained with the combination of O_3/H_2O_2/UV where up to 95% degradation was attained at pH 9, which is due to active species generated in the process, e.g., O_3 and OH$^\bullet$, on the contaminant. SPE was performed for determining the presence of several by-products, mainly: catechol, resorcinol and hydroquinone, which were identified.

1. INTRODUCTION

One of the current problems related to water is its pollution, which is caused by natural or anthropogenic sources. In the last one, the chemical industry can be mentioned, since liquid effluents generated can contain organic compounds at low concentrations, so their recovery is not feasible. The inadequate disposal of wastewater without

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prior treatment represents a source of pollution that affects the bodies of water and consequently the aquatic organisms and other natural systems with which they have interaction.

Phenol is a contaminant present in water derived from various chemical processes, mainly used in the manufacture of resins, cosmetics, pharmaceuticals, paints, pesticides, solvents and household cleaning products [1, 2]. It is a hydroxylated derivative of benzene. Phenol is a white powder of high stability, great solubility and low biodegradability [1, 2]. It is classified as priority hazardous pollutant by EPA [2, 3]. In humans, the health effects at low concentrations exposition are toxic causing skin and eye burns, damages to liver and pancreas, respiratory, gastrointestinal and circulatory systems alterations. Phenol is considered a carcinogenic agent [3] which can cause death. Since phenol physicochemical characteristics, its degradation by conventional methods is not totally effective. It has been reported that phenolic compounds are resistant to biological degradation and after been exposed to chlorination process they generate toxic by-products [2, 4]. There are several methods for the treatment of phenol [5, 6], however, their application depends on the characteristics of the effluent and its final disposal. Thus, it is important to study other alternatives that synergistically achieve the degradation of the pollutant into less toxic byproducts or total mineralization.

Advanced oxidation processes (AOPs) have been used as an alternative for the treatment of contaminants in water. These methods are applied at atmospheric pressure and at room temperature, and are characterized by the use of compounds that accelerate the formation of chemical species due to their high oxidizing potential, e.g., $OH^\bullet$ radical [2, 3]. Among the main utilized AOPs, it can be mentioned: O_3, H_2O_2/O_3, O_3/UV, H_2O_2/UV, Fenton reactions (Fe_2^+/H_2O_2), photocatalysis using Fe, Mn and TiO_2. The choice of any of them depends principally on the characteristics of the pollutant, its concentration and the volume of the effluent [7].

Overall degradation of phenol by AOPs is mainly established through two oxidation routes: (a) direct reactions by the collision of the contaminant and the added oxidizing reagent, commonly O_3, known to be a selective chemical species; nonetheless the effectiveness of the process is affected when by-products of oxidation are generated and (b) indirect reactions through the hydroxylation of phenol by $OH^\bullet$ radicals, generated from the decomposition of H_2O_2 or water photolysis. Several authors even used more than one method simultaneously to obtain better degradation efficiencies [8, 9] applying external sources of energy such as ultraviolet radiation, that leads to the photolysis of water and the dissociation of the oxidizing agents used as H_2O_2 and O_3 for the generation of reactive species such as the $OH^\bullet$ radical.

Hydroxyl radical ($OH^\bullet$) is known to have a higher oxidation potential (2.85 eV) than other widely used oxidants such as hydrogen peroxide (1.77 eV), ozone (2.07 eV) [10], atomic oxygen (2.42 eV) and chlorine (1.6 eV) [11]. $OH^\bullet$ radicals are non-selective and their reactivity with most organic contaminants is higher than that of other oxidizing agents. $OH^\bullet$ radicals are responsible for initiating the oxidation of phenol; if its radicals

are not generated in sufficient quantity during the process, the degradation of phenol diminishes, this same effect can be observed during an excessive generation of OH$^\bullet$ radicals where reactions of inhibition take place. Generation of OH$^\bullet$ radicals depends on various parameters such as agents used, treatment time, pH, and concentration of the pollutant, just to mention some of them.

Various authors demonstrated significant effectiveness of AOPs in the treatment of dyes [12], pesticides [13], bisphenol A [14], pharmaceutical products [15], and personal care products [16]. However, the current challenges in this field are the diversification of studies to other toxic pollutants and the analysis of the process parameters under normal working conditions that until now have not been reported; both characteristics must be taken into account for the optimization of any process.

In this work, the study of phenol degradation by different combinations of AOPs using oxidizing agents such as O_3, H_2O_2 and ultraviolet light was performed. Ozone was produced by a generator using atmospheric air reducing the production cost, whereas H_2O_2 is a low-cost non-toxic agent easy to use. Ultraviolet light emitted from a low--pressure mercury lamp was used. The effect of oxidizing agents separately and their synergistic effect was analyzed. From the obtained results considering the functioning parameters, the optimal process conditions were established. Aqueous solutions at relatively high parameters in volume and concentrations of the contaminant were processed to determine the applicability of the studied methods. As they do not generate sludge or sediment, it does not require conditioning of the sample before or after the analysis. Characterization of the samples and determination of the by-products generated at each case of study was performed by gas chromatography and mass spectrometry (GC-MS).

2. EXPERIMENTAL

Reagent and apparatus: phenol (99.0%), hydrogen peroxide (30% W/W), acetone and methanol, all from Fermont, analytical grade, were used in the experiments.

The utilized treatment system shown in Fig. 1 is composed of: a) a cylindrical reactor of stainless steel 35 cm long and 7 cm in a diameter, an UV lamp of 30 cm long enclosed by a quartz tube of an internal diameter of 2.5 cm, b) a spectrometer of the Acton Series SP-2500i coupled to a iCCD PI-MAX®3, c) a 7 W low-power consumption ozone generator (model OEM-XEGZO-30N) directly coupled to the reactor, d) an ozone measure model 460L monitoring the supplied ozone e) a Thermo Scientific Trace 1310 gas chromatograph coupled to a single quadrupole mass spectrometer (GC-MS) via a Trace TR-5M capillary column, 0.25 mm; 0.25 µm film was used for the characterization of samples and by-product analysis, and f) pH and conductivity were measured with a Gro Line HI-9814 multi-parameters device from Hanna Instruments. The Acton SP-2500i spectrometer provided with an 1800 grooves mm^{-1} grating

and a focal length of 0.5 m was used in Czerny–Turner mode and the entrance slit adjusted to 10 μm.
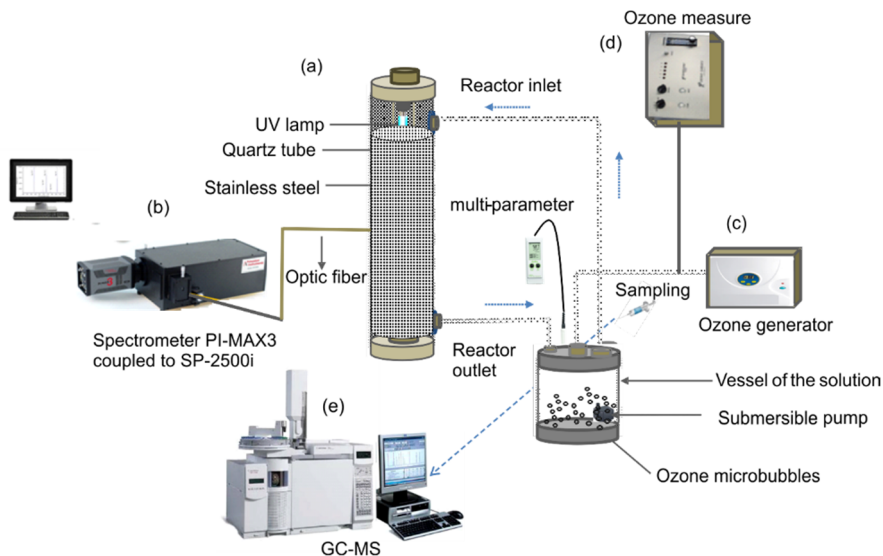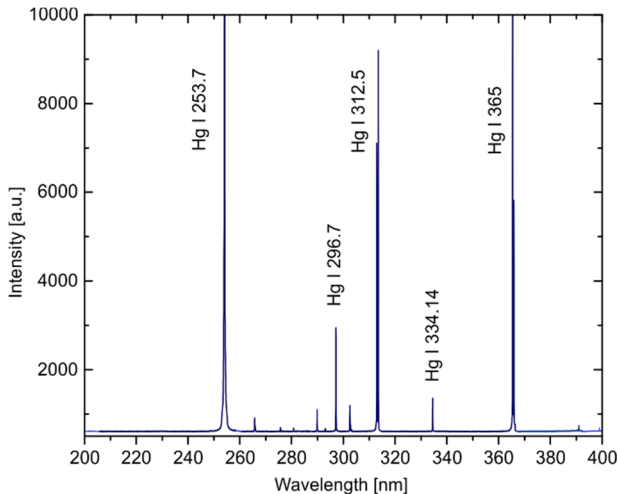

Fig. 1. Experimental set up

Fig. 2. Emission spectrum of the UV lamp

For the characterization of UV light emission generated by a 16 W low-pressure mercury-vapour lamp of type GPH330T5L/4P (Fig. 1), a spectrometer of the Acton Series SP-2500i coupled to an iCCD PI-MAX®3 1024×256 pixels from Princeton Instruments were used. The emission of the lamp was driven to the spectrometer using a quartz

optical fibre, while WinSpec/32® software was used for the data acquisition. The obtained emission spectrum of the UV lamp shown in Fig. 2. The emitted UV radiation contains the wavelength of 253.7 nm necessary to induce photolysis reactions. This characteristic certainly increases the decomposition of H_2O_2 due to the energy absorption by molecules at this wavelength.

Procedures. Synthetic phenol solutions were prepared at an initial concentration of ca. 10^{-4} mol/dm^3 in distilled water. 500 cm^3 of solution were propelled across a closed-loop hydraulic circuit by a submersible pump from the solution vessel to the reactor through an inlet port at its top, after recirculated through an outlet at the bottom of the reactor until return to the container. The circulating sense of the solution is depicted by blue arrows in Fig. 1. The imposed treatment time for each solution was ninety minutes, during this procedure every ten minutes a sample of water was taken by a needle. Then, these samples were analyzed by GC-MS. As the experiments were performed in duplicate and the chromatographic analysis was performed up to 10 times per sample, results provided in this work are depicted by the average values.

When ozone was used as an oxidizing agent, it was supplied to the vessel via a diffuser generating micro-bubbles in the volume of the solution, which was previously adjusted with three different initial pH values (4, 7, and 9) used in order to analyze the reactive effects of the oxidizing chemical species according to the acidity or alkalinity of the solution. While hydrogen peroxide was added directly to the phenol solution at one of the four different initial concentrations: 0.5, 1.0, 2.0, and 3.0 mmol/ dm^3, before starting the treatment.

The identification of by-products from phenol degradation was performed for each one of the four studied cases (O_3, O_3/UV, O_3/H_2O_2 and O_3/H_2O_2/UV). The tC18 solid extraction cartridges previously conditioned with methanol were used to filter by dripping at atmospherics pressure all the residual aqueous solution after its treatment. Thereafter cartridges were washed with methanol and acetone before to carry the elution of compounds of interest out by their analysis with GC-MS. Unlike other exhaustive methods [17], the extracted phase is not subjected to a derivatization and was injected as such.

3. RESULTS AND DISCUSSION

3.1. OPTICAL EMISSION SPECTROSCOPY AND OZONE GENERATION

The emitted UV radiation in the analyzed wavelength range guaranteed that UV-induced chemical processes in the O_3/UV, H_2O_2/UV, O_3/UV/H_2O_2 systems can be accomplished. Moreover, the cylindrical reactor wall offers a reflective feature promoting photolysis processes.
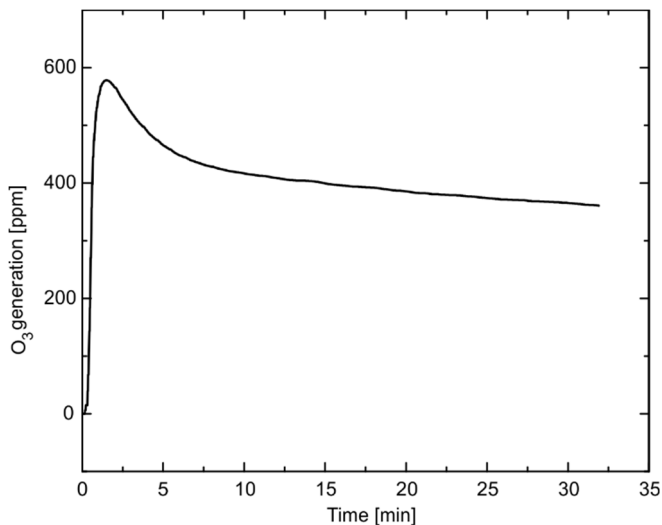
Fig. 3. Ozone generation as a function of time

Figure 3 shows the characteristic ozone generation versus time using a portable low--cost ozone generator, which, in addition, consumes oxygen directly from atmospheric air. A considerable ozone concentration was detected at the ozone generator output. This concentration facilitates the chemical processes promoted by ozone considering the absorption in aqueous solutions after ozone is injected.

3.2. DEGRADATION OF PHENOL BY O_3

The results obtained for the degradation of phenol using O_3 at the initial pH of 4, 7, and 9, are shown in Fig. 4. For all cases, as the treatment time increases, the higher degradation efficiencies are obtained. The highest degradation efficiency obtained was 76% for an initial pH of 9 and 90 min treatment time.

The chemical mechanism of phenol degradation by ozone is due to two possible oxidation courses [11, 18] (a) direct ozonation mechanism (reaction 1) and (b) by indirect mechanism, which O_3 reacts with H_2O to generate $OH^{\bullet}$ radicals and subsequently, the latter react with the contaminant (reaction 2). Moreover, some authors [11, 18] have observed that the two possible oxidation paths depend on pH magnitude; on the one hand, in acid solutions is promoted a direct oxidation process. On the other hand, in basic solutions is booted the indirect oxidation process.

$$O_3 + C_6H_5OH \rightarrow \text{by-products} \tag{1}$$

$$OH^{\bullet} + C_6H_5OH \rightarrow \text{by-products} \tag{2}$$
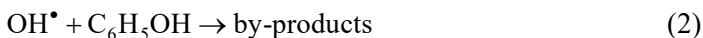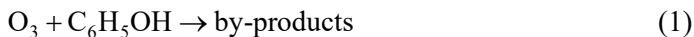
In an alkaline medium (pH 9) the generation of OH$^\bullet$ radicals mainly results from the decomposition of O_3 by reaction (3). Other active chemical species such as H_2O_2 and $HO_2^\bullet$ can also be generated, which contribute to process improvement generating OH$^\bullet$ radicals (reactions (4)–(6)) [11, 18, 19].
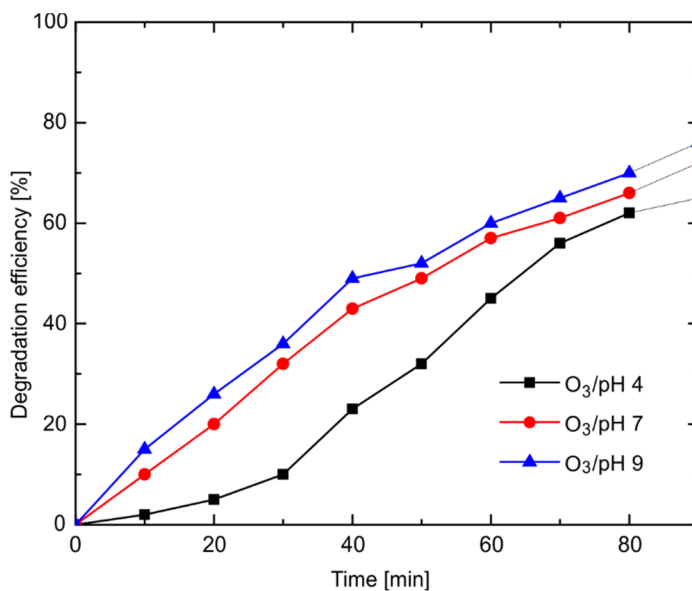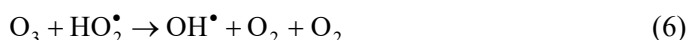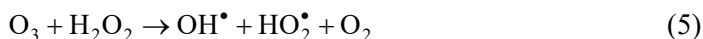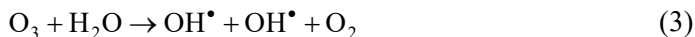
$$O_3 + H_2O \rightarrow OH^\bullet + OH^\bullet + O_2 \tag{3}$$

$$O_3 + H_2O \rightarrow H_2O_2 + O_2 \tag{4}$$

$$O_3 + H_2O_2 \rightarrow OH^\bullet + HO_2^\bullet + O_2 \tag{5}$$

$$O_3 + HO_2^\bullet \rightarrow OH^\bullet + O_2 + O_2 \tag{6}$$

$$O_3 + M \rightarrow O_2 + O^\bullet + M \tag{7}$$

$$O^\bullet + H_2O \rightarrow OH^\bullet + OH^\bullet \tag{8}$$

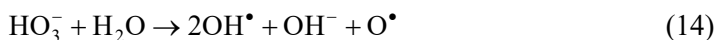Fig. 4. Efficiency of phenol (1.0×10^{-4} mol/dm^3) degradation by ozonation

Figure 4 shows that the highest efficiencies were obtained at pH 9. In this case, O_3 is an unstable molecule and ozone can be easily decomposed in O_2 and $O^\bullet$ (reaction (7)). These in their turn can recombine to form OH$^\bullet$ radicals (reaction (8)), promoting an

indirect oxidation process of phenol. In our case, O_3 was continuously supplied to the reactor which could contribute to maintaining a constant generation of $OH^{\bullet}$ radicals. They are characterized by a high oxidation potential (2.8 eV) [10], being not selective and reacting with phenol ($k = 6.6 \times 10^9$ $dm^3/(mol \cdot s)$) faster than O_3 ($k = 1.3 \times 10^3$ $dm^3/mol \cdot s$) [18], k being the rate constant for reactions (2) and (1), respectively. Furthermore, it has been demonstrated that the selectivity of O_3 with phenol decreases when pH is increased [18] because the oxidation process occurs by indirect reactions.

3.3. DEGRADATION OF PHENOL BY O_3/H_2O_2 (PER OZONE)

The results of phenol degradation at pH 9 are shown in Fig. 5 for the combination of two oxidizing agents. H_2O_2 in alkaline aqueous solution can generate the decomposition of O_3 (reaction (5)) initiating a chemical pathway that can achieve the phenol degradation (reactions (9)–(14)) [11, 19]:

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{9}$$

$$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^- \tag{10}$$

$$HO_2^- \rightarrow O_2^{2-} + H^+ \tag{11}$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \tag{12}$$

$$O_3^- + H^+ \rightarrow HO_3 \tag{13}$$

$$HO_3^- + H_2O \rightarrow 2OH^{\bullet} + OH^- + O^{\bullet} \tag{14}$$

The effectiveness of this process depends mainly on the initial concentration of H_2O_2. Whereas the H_2O_2 concentration was increased, an initial increase of the degradation efficiency occurred. However, at higher H_2O_2 concentration (3.0 $mmol/dm^3$) radical species were generated in excess limiting the oxidation course and promoting chemical reactions among them, instead to react with phenol. As a consequence, the resulting efficiency is minor. This inhibitory effect is mainly driven by the following chemical reactions [18, 19]:
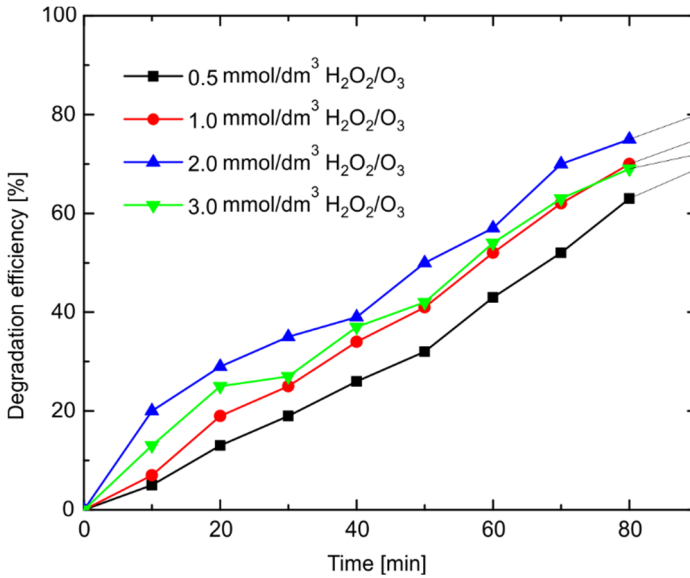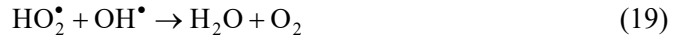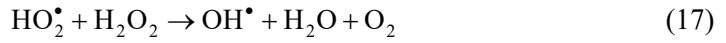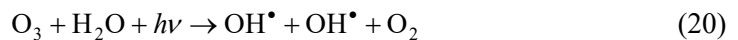
$$OH^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2 \tag{15}$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{16}$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow OH^{\bullet} + H_2O + O_2 \qquad (17)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (18)$$

$$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2 \qquad (19)$$

Fig. 5. Efficiency of phenol (1.0×10^{-4} mol/dm^3) degradation by O$_3$/H$_2$O$_2$ at pH 9

3.4. DEGRADATION OF PHENOL BY O$_3$/UV

The obtained results for the phenol degradation at pH of 4, 7 and 9 are shown in Fig. 6. In all cases, the resulting degradation efficiency was increased in comparison with that when only O$_3$ was used. The highest degradation efficiency was 82% for pH 9 and 90 min of treatment time. This can be attributed to the fact that the presence of UV radiation promotes the generation of OH$^{\bullet}$ radicals mainly by the photolytic breakdown of the molecules of O$_3$ at $\lambda = 254$ nm (reactions (20), (21)) and water for λ between 200 and 280 (reaction (22)) [20].

Intermediate species such as H$_2$O$_2$ can also be generated, which dissociated or recombined contribute to the formation of OH$^{\bullet}$ radicals (reactions (23), (24)), increasing the efficiency of the phenol degradation process [20].
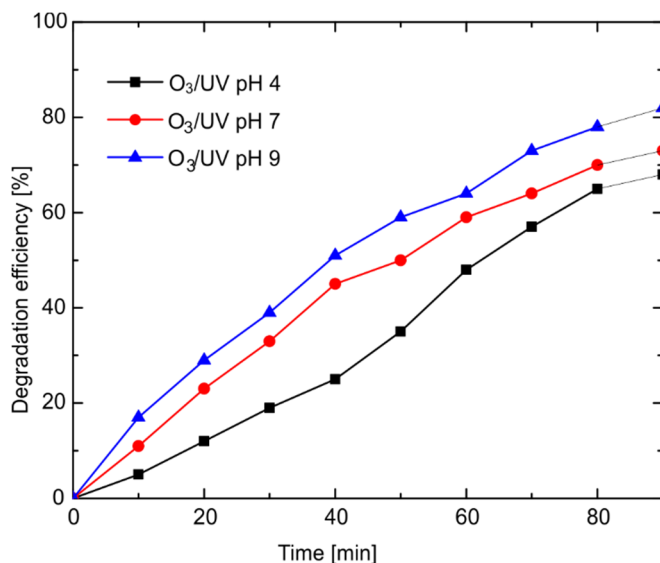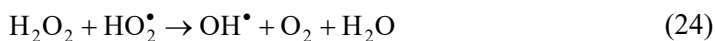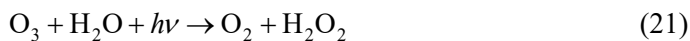
$$O_3 + H_2O + h\nu \rightarrow OH^{\bullet} + OH^{\bullet} + O_2 \qquad (20)$$

$$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2 \tag{21}$$

$$H_2O + h\nu \rightarrow OH^\bullet + H^\bullet \tag{22}$$

$$H_2O \rightarrow OH^\bullet + OH^\bullet \tag{23}$$

$$H_2O_2 + HO_2^\bullet \rightarrow OH^\bullet + O_2 + H_2O \tag{24}$$

Fig. 6. Efficiency of phenol (1.0×10^{-4} mol/dm^3) degradation by O$_3$/UV at pH 3

3.5. DEGRADATION OF PHENOL BY O$_3$/H$_2$O$_2$/UV

Figure 7 shows the degradation of phenol, in all cases for an initial concentration of 2.0 mmol/dm^3 of H$_2$O$_2$ pH 4, 7 and 9. The highest degradation efficiencies were obtained for all these processes (up to 90, 91 and 95% for pH 4, 7 and 9, respectively) compared to those previously studied (Figs. 4–6). A favorable degradation effect is observed with the increase of treatment time. However, a saturation effect is produced after 70 min of treatment time. The presence of more than one oxidizing agent (O$_3$ and H$_2$O$_2$) guarantees a favorable generation of active chemical species. The mechanism of phenol degradation involves direct and indirect oxidation pathways. In this sense, species like O$_3$ can directly attack the aromatic rings of phenol and indirectly via its hydroxylation. In addition both oxidizing agents (O$_3$ and H$_2$O$_2$) can be rapidly decomposed to OH$^\bullet$ radicals by absorbing UV radiation.
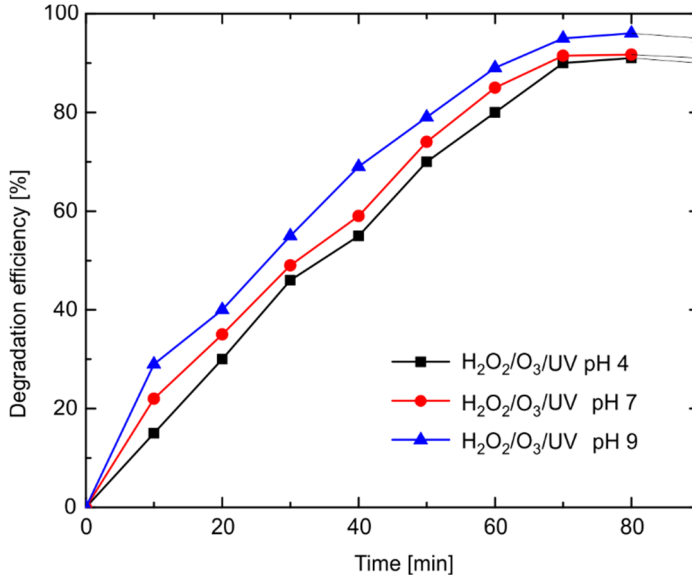
Fig. 7. Efficiency of phenol $(1.0 \times 10^{-4}$ mol/dm$^3)$ degradation
by O$_3$/H$_2$O$_2$/UV at various pH and 2.0 mmol/dm^3 of H$_2$O$_2$

To compare the advanced AOP oxidation processes that make use of an external energy source, Eq. (25) was considered [10], where the required E_{EO} electric power (kWh/m^3/order) to degrade the pollutant by one order of magnitude in a unit volume of contaminated water was determined. Table 1 shows the results on the degradation of phenol obtained in this work and other works that used AOPs.

$$E_{EO} = \frac{1000 P_{\mathrm{elec}} t}{60 V \log \left(\dfrac{C_0}{C_t} \right)} \tag{25}$$

where P_{elec} is the applied electric power (kW) to the AOPs system, t is the treatment time (min), V is the volume (dm^3), C_0 is the initial concentration of the phenol, and C_t is its concentration at time t (mol/dm^3), 1000 and 60 are conversion factors.

The supplied energy depends on the method applied to the degradation of phenol. In this work, a low-power ozone generator (7 W) and a 16 W low-pressure ultraviolet lamp were used. In Table 1, the E_{EO} values obtained are lower than the other reported results. Table 1 shows results of other methods using catalysts, and these values are slightly lower than the values reported in this paper. The supplied power from an external source will have a direct effect on E_{EO} (Eq. (25)). The use of O$_3$, H$_2$O$_2$ and UV are considered methods of easy application providing highly efficient results on the degradation of contaminants in water.

Comparison of reported studies of phenol degradation using AOPs

Process	P_{elec} [kW]	t [min]	V [dm^3]	C_0 [mol/dm^3]	C_t [mol/dm^3]	E_{EO}	Source
O$_3$ (pH 9)	0.007				2.90×10^{-5}	39.08	
O$_3$/H$_2$O$_2$ (2.0 mmol/dm^3)	0.007	90	0.50	1.0×10^{-4}	1.90×10^{-5}	29.13	present work
O$_3$/UV(p H9)	0.023				1.79×10^{-5}	92.53	
O$_3$/H$_2$O$_2$/UV (pH 9) (2.0 mmol/dm^3)	0.023				5.00×10^{-6}	53.07	
O$_3$	0.105	120	0.25	1.06×10^{-3}	1.60×10^{-4}	1026.69	[21]
UV/H$_2$O$_2$	0.150	90	0.75	1.17×10^{-2}	5.88×10^{-5}	130.51	[22]
US/UV/O$_3$	0.076	12.84	0.10	2.50×10^{-3}	2.50×10^{-4}	132.67	[23]
US/H$_2$O$_2$/CuO	0.0182	136	0.15	6.18×10^{-4}	9.38×10^{-5}	335.92	[24]
UV/ZnO	0.125	30	2.00	1.50×10^{-4}	3.80×10^{-6}	25.00	[2]
O$_3$/UV/TiO$_2$	0.0105	90	0.50	5.36×10^{-4}	4.06×10^{-4}	28.10	[10]

3.6. IDENTIFICATION OF INTERMEDIARY BY-PRODUCTS

By-product identification was performed for each one of the studied methods by GC/MS. The obtained chemical compounds are listed in Table 2.
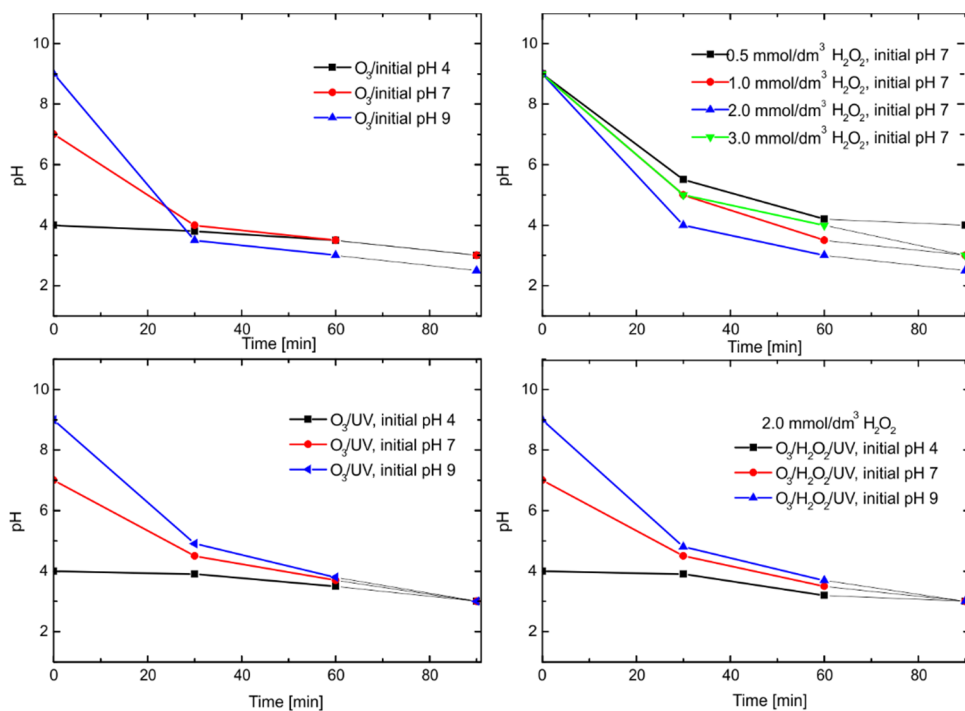
Identified intermediary by-products

Compound	Structure	Process			
		O$_3$	H$_2$O$_2$/O$_3$	O$_3$/UV	O$_3$/H$_2$O$_2$/UV
Benzene-1,2-diol (catechol)		✓	✓	✓	✓
Benzene-1-3-diol (resorcinol)		✓	✓	✓	✓
Benzene-1,4-diol (hydroquinone)		✓	✓	✓	✓

Identified intermediary by-products

Compound	Structure	Process			
		O_3	H_2O_2/O_3	O_3/UV	$O_3/H_2O_2/UV$
Biphenyl-4,4′-diol				✓	✓
3-Phenoxyphenol			✓	✓	
Biphenyl-4-ol		✓	–	–	–

Fig. 8. pH variation for: a) O_3, b) O_3/UV, c) O_3/H_2O_2 and d) $O_3/ H_2O_2/UV$ processes

For all cases, hydroquinone, catechol, and resorcinol were identified as primary by-products of phenol oxidation based on the mechanism proposed in [10]. Later, during the process, carboxylic acids such as acetic acid, oxalic acid, and glycolic acid, were generated, concluding with their mineralization. In this study, the carboxylic acids were not identified. Nevertheless, pH of the solution was measured during the treatment time denoting a decrease, which can be attributed to the formation of these acids, as it can be observed in Fig. 8.
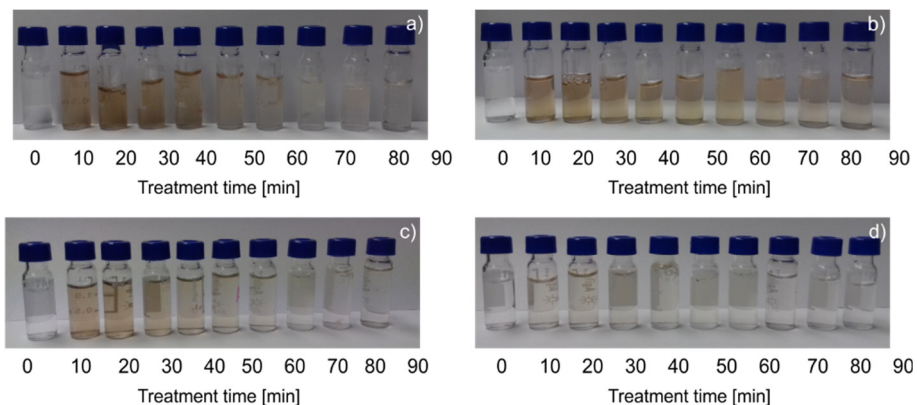

Fig. 9. Color variation for: a) O_3, b) O_3/H_2O_2 (2 mmol/dm^3), c) O_3/UV
and (d) O_3/H_2O_2 (2 mmol/dm^3)/UV processes

Figure 9 shows the color change of the samples before and after treatment. For all cases at initial pH of 9, due to the formation of oxidation by-products, a color change was observed, when the coloration has a light color after tens of minutes of treatment, the level of oxidation is higher forming small molecules such as carboxylic acids.

Other species previously not considered by the kinetic mechanism proposed in [10] were identified, as is shown in Table 2. It is possible that their generation is due to recombination reactions of the existing species in the solution; these have been earlier identified by other author [25].

4. CONCLUSIONS

Several advanced oxidation methods were studied for phenol degradation specifically O_3, O_3/UV, O_3/H_2O_2 and O_3/ H_2O_2/UV. In all cases, it was observed that with the increase of the treatment time better degradation efficiencies were obtained. When only O_3 was used efficiencies up to 76% were obtained under alkaline conditions and the degradation is mainly attributed to the indirect oxidation path promoted by OH$^•$ radicals. A favorable effect on degradation was observed when adding a second oxidant (H_2O_2) obtaining efficiencies of up to 81%. However, when the initial concentration of H_2O_2

was increased up to 3.0 mmol/dm^3, the efficiency decreased, which is attributed to inhibit reactions. For the case of O$_3$/UV the presence of the radiation contributed to the formation of a greater amount of OH$^\bullet$ radicals favoring the degradation of phenol. The best efficiency obtained in this study was for the case of O$_3$/H$_2$O$_2$/UV reaching 95% pollutant downgraded at pH 9, which is due to the existence of direct and indirect reaction path of the contaminant under effects of active species generated in the process, mainly O3 and OH●. In this work, the use of low power consumption equipment was privileged, and in those working conditions, a low energy consumption for the degradation of the pollutant was used, at the same time high removal efficiencies were obtained. Finally, hydroquinone, catechol and resorcinol were identified as oxidation by-products.

REFERENCES

[1] GODINI H., HASHEMI F., MANSURI L., SARDAR M., HASSANI G., MOHSENI S.M., ALINEJAD A.A., GOLMOHAMMADI S., MOHAMMADI A.S., *Water polishing of phenol by walnut green hull as adsorbent: an insight of adsorption isotherm and kinetic*, J. Water Reuse Desalin., 2016, 6 (4), 544.

[2] NAGHAN D.J., AZARI N., MIRZAEI N., VELAYATI A., TAPOUK F.A., ADABI S., PIRSAHEB M., SHARAFI K., *Parameters effecting on photocatalytic degradation of the phenol from aqueous solutions in the presence of ZnO nanocatalyst under irradiation of UV-C light*, J. Bulg. Chem. Commun. 2015, 47, 14.

[3] MORADI M., MANSOURI A.M., AZIZI N., AMINI J., KARIMI K., SHARAFI K., *Adsorptive removal of phenol from aqueous solutions by copper (cu)-modified scoria powder: process modeling and kinetic evaluation*, Desalin. Water Treat., 2016, 57 (1), 11820.

[4] ZENG Z., ZOU H., LI X., AROWO M., SUN B., CHEN J., CHU G., SHAO L., *Degradation of phenol by ozone in the presence of Fenton reagent in a rotating packed bed*, Chem. Eng. J., 2013, 229, 404.

[5] HEYDARI M., DARVISHMOTEVALLI K.K., KARAMI A., VASSEGUIAN Y., AZIZI N., GHAYEBZADEH M., MORARI M., *Data for efficiency comparison of raw pumice and manganese-modified pumice for removal phenol from aqueous environments. Application of response surface methodology*, Data Brief., 2018, 20, 1942.

[6] MORADI M., HEYDARI M., DARVISHMOTEVALLI M., KARIMYAN K., GUPTA V.K., VASSEGHIAN Y., SHARAFI H., *Kinetic and modeling data on phenol removal by iron-modified scoria powder (FSP) from aqueous solutions*, Data Brief., 2018, 20, 957.

[7] LIOTTA L.F., GRUTTADAURIA M., DI CARLO G., PERRINI G., LIBRANDO V., *Heterogeneous catalytic degradation of phenolic substrates. Catalysts activity*, J. Hazard. Mater., 2009, 162 (2–3), 588.

[8] SUZUKI H., ARAKI S., YAMAMOTO H., *Evaluation of advanced oxidation processes (AOP) using O$_3$, UV, and TiO$_2$ for the degradation of phenol in water*, J. Water Proc. Eng., 2015, 7, 54.

[9] BOCZKAJ G., FERNANDES A., *Wastewater treatment by means of advanced oxidation processes at basic pH conditions. A review*, Chem. Eng. J., 2017, 320, 608.

[10] SUZUKI H., ARAKI S., YAMAMOTO H., *Evaluation of advanced oxidation processes (AOP) using O$_3$, UV, and TiO$_2$ for the degradation of phenol in water*, J. Water Proc. Eng., 2015, 7, 54.

[11] LOURES C.C.A., ALCÁNTARA M.A.K., FILHO H.J.I., TEIXEIRA A.C.S.C., SILVA F.T., PAIVA T.C.B., SAMANAMUD G.R.L., *Advanced oxidative degradation processes: fundamentals and applications*, Int. Rev. Chem. Eng., 2013, 5 (12), 102.

[12] Cengiz Y.H., Diler K.S.U., *Photocatalytic efficiencies of alternate heterogeneous catalysts. Iron modified minerals and semiconductors for removal of an azo dye from solutions*, Environ. Prot. Eng., 2018, 44 (1), 5.

[13] Maddila S., Lavanya P., Jonnalagadda S.B., *Degradation, mineralization of bromoxynil pesticide by heterogeneous photocatalytic ozonation*, J. Ind. Eng. Chem., 2015, 24, 333.

[14] Sharma J., Mishra I.M., Kumar V., *Degradation and mineralization of bisphenol A (BPA) in aqueous solution using advanced oxidation processes: UV/H_2O_2 and UV/$S_2O_8^{2-}$ oxidation systems*, J. Environ. Manage., 2015,156 (1), 266.

[15] Yuqi C., Xiaoyong D., Qiuling M., Huixuan Z., Xiuwen C., Xiaoli L., Mingzheng X., Qingfeng C., Bo L., *Kinetics of photoelectrocatalytic degradation of diclofenac using N, S co-doped TiO2 nano-crystallite decorated TiO2 nanotube arrays photoelectrode*, Environ. Prot. Eng., 2018, 44 (2), 117.

[16] Gong P., Yuan H., Zhai P., Xue Y., Li H., Dong W., Mailhot G., *Investigation on the degradation of benzophenone-3 by UV/H_2O_2 in aqueous solution*, Chem. Eng. J., 2015, 277, 97.

[17] Karimael M., Sharafi K., Moradi M., Ghaffari H.R., Biglari H Arfaeinia H., Fattahi N., *Optimization of a methodology for simultaneous determination of twelve chlorophenols in environmental water samples using in situ derivatization and continuous sample drop flow microextraction combined with gas chromatography-electron-capture detection*, Anal. Methods, 2017, 9, 2865.

[18] Kusic H., Koprivanac N., Loncaric B.A., *Minimization of organic pollutant content in aqueous solution by means of AOPs: UV- and ozone-based technologies*, Chem. Eng. J., 2006, 123 (3), 127.

[19] Wang J.L., Xu L.J., *Advanced oxidation processes for wastewater treatment. Formation of hydroxyl radical and application*, Crit. Rev. Environ. Sci. Technol., 2012, 42, 251.

[20] Vilhunen S.H., Sillanpää M.E.T., *Ultraviolet light emitting diodes and hydrogen peroxide in the photodegradation of aqueous phenol*, J. Hazard. Mater., 2009, 161 (2–3), 1530.

[21] Yogeswary P., Yusof M.R.M., Amin N.A.S., *Degradation of phenol by catalytic ozonation*, Chem. Nat. Res. Eng., 2007, 2, 34.

[22] Primo O., Rivero I., Ortiz I., Irabien A., *Mathematical modelling of phenol photooxidation: kinetics of the process study*, Chem. Eng. J., 2007, 134, 23.

[23] Kidak R., Ince N.H., *Catalysis of advanced oxidation reactions by ultrasound. A case study with phenol*, J. Hazard. Mater., 2007, 146, 630.

[24] Drijvers D., Van Langenhove H., Beckers M., *Decomposition of phenol and trichloroethylene by the ultrasound/H_2O_2/CuO process*, Water Res., 1999, 33, 1187.

[25] Farzadkia M., Dadban S.Y., Nasseri S., Hossein M.A., Gholami M., Shahryari A., *Catalytic ozonation of phenolic wastewater: Identification and toxicity of intermediates*, J. Eng., 2014, ID 520929.