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Minimization of organic pollutant content in aqueous solution by means of AOPs: UV- and ozone-based technologies

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Abstract

The study involved comparative investigations of the efficiency of several ozone- and/or UV-based processes: O_3, O_3/H_2O_2, UV/H_2O_2, UV/O_3 and UV/H_2O_2/O_3, for the minimization of phenol as a model hazardous pollutant in wastewater. For all applied AOPs the best experimental conditions concerning selected varied process parameters, initial pH and H_2O_2 dosage, were determined. Different AOPs were evaluated on the basis of their eco-effectiveness, by the means of phenol decay and TOC value decrease, and their cost-effectiveness. It was established that the complete phenol removal can be achieved by adjusting the pH and H_2O_2 dosage. The overall mineralization extent depended on the type of process, number and type of oxidants and/or UV light, and their studied processes parameters as well. The highest overall mineralization extent, 58.0% TOC removal, was achieved by UV/H_2O_2/O_3 process. From the aspect of both eco- and cost- effectiveness, UV/H_2O_2/O_3 was shown as the most suitable process.

Keywords: Phenol; AOP; UV irradiation; Ozone; Mineralization

1. Introduction

Different types of organic compounds discharged into the environment mostly through industrial effluents, present serious danger for humans and aquatic life due to their toxic nature. There is continuing need for the development of efficient and cost-effective technologies for hazardous organic contaminants such as phenol, benzene, polychlorinated biphenyls, etc. from groundwater and wastewater [1,2]. Conventional methods for water remediation, including biotreatment, carbon adsorption, air stripping, pure ozone oxidation and chlorine treatment, suffer from various limitations [3–6]. For example, treatment based on aerobic and anaerobic digestion tends to be very large due to the slow rate of the biological reaction. Furthermore, wastewater treatment methods based on physical processes such as reverse osmosis and adsorption on activated carbon are non-destructive and merely transfer the pollutants to the other media, thus causing secondary waste [5]. Chemical methods such as chlorine or pure ozone oxidation have been also shown as limited. Chlorine oxidation produces carcinogenic halogenated hydrocarbons, while pure ozone oxidation is limited by high selectivity and slow kinetics [6–8].

A number of alternative technologies, so-called advanced oxidation processes (AOPs), are considered to be promising methods for the treatment of hazardous toxic organic pollutants in aqueous solutions. AOPs involve the generation of hydroxyl radicals, highly reactive and unselective species, in sufficient quantities to oxidize the majority of organics present in the effluent water. Common AOPs could be broadly classified into chemical, e.g. O_3 and/or H_2O_2, photochemical and photocatalytic, e.g. UV/oxidant or UV/photocatalyst, mechanical, e.g. ultrasonic, and electrical, e.g. corona discharge [8,9].

Treatments of organic compounds by O_3 or H_2O_2 are possible throughout two different pathways, direct and indirect. Direct ozonation involves degradation of organics by ozone molecule under acidic conditions, while the term indirect ozonation consider degradation mechanism of organics throughout hydroxyl radicals and it occurs under basic conditions [10]. In direct mechanism, hydrogen peroxide participates in redox reactions where it can behave as an oxidant or as a reductant, while indirect mechanism consider formation of free radicals throughout reactions by other inorganic compounds, such as Fe ions or ozone, or when is photolyzed [11]. In both direct mechanisms, the oxidants ozone and hydrogen peroxide have much lower standard redox

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potential, 2.07 and 1.77 V, respectively, than 2.80 V of hydroxyl radicals, species formed by both indirect mechanisms of above oxidants [12]. By combining UV irradiation with either O_3 or H_2O_2, or both, the oxidation power of the systems for organic pollutant degradation could be significantly enhanced [1,13–18].

The main goal of the study was to determine the best experimental conditions in investigated ranges of selected varied process parameters (initial pH and H_2O_2 concentration) in order to establish those, which provide the highest phenol decay and the highest mineralization of model phenol solution. In further step, processes were evaluated on the basis of the cost-effectiveness criteria in order to find the most suitable process for the treatment of model phenol solution.

2. Materials and methods

Chemicals used in this study were supplied by Fluka, Germany (phenol, acetonitrile and acetic acid) and Kemika, Croatia (H_2O_2, 30%; sulfuric acid, >95% and sodium hydroxide, p.a.). All solutions were prepared with deionized water with conductivity less than 1 $\mu S\,cm^{-1}$. The concentration of model phenol solution was 0.1 $g\,L^{-1}$ ($TOC_{initial} = 8.01 \times 10^{-2}\,g\,L^{-1}$).

All experiments were performed in the glass water-jacketed batch reactor (Fig. 1), the same as in our previous study [19]. The middle of the reactor was occupied with the quartz tube in which a mercury lamp (125 W, UV-C at 254 nm, UVP-Ultra Violet Products, Cambridge, UK) was placed vertically. The value of incident photon flux at 254 nm, 7.36×10^{-6} einstein s^{-1}, was calculated on the basis of hydrogen peroxide actinometry experiments [20]. In the experiments where UV irradiation was required, UV/H_2O_2, UV/O_3 and UV/H_2O_2/O_3, the UV lamp was switched on. In the experiments involving ozone, O_3, O_3/H_2O_2, UV/O_3 and UV/H_2O_2/O_3, ozone was introduced into the reactor. Ozone was generated from pure oxygen, >99.9%, by introducing it into the ozone generator, MIC Systems Inc., Valdosta, Georgia, USA to produce ozone. The outlet gas mixture, i.e. mixture of ozone and oxygen, from the ozononizer was fed into the reactor through a sintered glass plate diffuser located in the bottom half of the reactor. The outlet gas flow from the ozone generator i.e. reactor inlet stream, was fixed at 0.15 $L\,min^{-1}$. The rate of ozone generation in reactor inlet stream, $7.86 \times 10^{-3}\,g\,min^{-1}$, was determined iodometrically [21]. The constant level of ozone production during experiments was monitored by spectrophotometrical method [22]. Initial pH values and hydrogen peroxide concentration ranged from 3 to 12, and 2 to 110 mM, respectively, until the achievement of maximal mineralization extent. Initial pH was adjusted with the addition of 0.1 M NaOH or 0.1 M H_2SO_4. Added quantities of H_2SO_4, NaOH and H_2O_2 as an additional oxidizing agent, were negligible in comparison to the total volume of treated reaction mixture. The experiments were conducted by adjusting one variable, while others were held constant. The total volume of the treated solution was 0.5 L in all cases, while the mixing of the solution was provided by both magnetic stirring and peristaltic pump at a flow rate of 0.1 $L\,min^{-1}$. Experiments were carried out at 25 (±0.2) °C. The duration of each experiment was 1 h. Samples were taken periodically from the reactor (2, 5, 10, 15, 30, 45 and 60 min) and thereafter immediately analyzed. All experiments were repeated at least two times to give reproducibility of the experiments within 5%, and averages are reported.

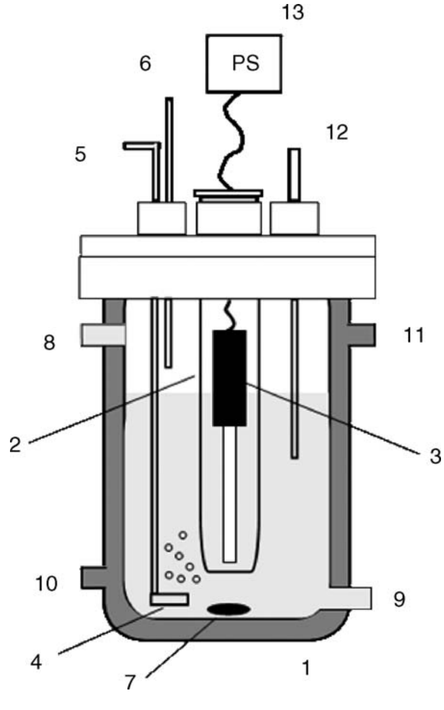

Fig. 1. Schematic diagram of experimental set-up for applied AOPs. (1) Glass water-jacketed reactor, (2) quartz jacket, (3) UV lamp, (4) sintered glass plate diffuser, (5 and 6) gas inlet and outlet, (7) magnetic stirring bar, (8 and 9) solution inlet and outlet, (10 and 11) cooling water inlet and outlet, (12) thermometer, (13) power supply.

The degradation of phenol was analyzed by HPLC equipped with Software $Class_{VP}$, Shimadzu, Japan, using a 5 μm, 25.0 cm × 4.6 mm, Supelco Discovery C18 column, USA, and detected with diode array UV detector, SPD-$M10A_{VP}$, Shimadzu, Japan. The mobile phase was 2% acetic acid/20% acetonitrile/78% water at $10^{-3}\,L\,min^{-1}$. Phenol decomposition was monitored at $\lambda = 270$ nm ($t_R = 10.05$ min), whilst the monitoring of formation and then the degradation of by-products were performed at $\lambda = 276$ nm for catechol ($t_R = 5.76$ min), at $\lambda = 290$ nm for hydroquinone ($t_R = 3.97$ min), at $\lambda = 245$ nm for benzoquinone ($t_R = 5.38$ min) and at $\lambda = 274$ nm for resorcinol ($t_R = 4.78$ min). The recorded peaks were first identified and then the concentrations of residual phenol and its formed primary by-products were determined from their calibration standards. Phenol removal was reported as a percentage, $100 \times [phenol]/[phenol]_{initial}$. The mineralization of the phenol solution was established on the basis of total organic carbon content measurements (TOC), performed by total organic carbon analyzer; TOC-V_{CPN} 5000 A, Shimadzu, Japan, and expressed as a percentage of removed organic content, $100 \times [TOC]/[TOC]_{initial}$. UV–vis spectrophotometer, Lambda EZ 201, Perkin-Elmer, USA, was used for monitoring ozone generation during the experiments. Handylab pH/LF portable pH-meter, Schott Instruments GmbH, Mainz, Germany, was used for pH measurements.

3. Results and discussion

In order to establish the best operating conditions for each of AOPs studied, the series of experiments were conducted. The degradation of organics by ozone process through direct or indirect mechanism is strongly influenced by pH of treated media. Therefore, in O_3 process initial pH values were varied from 3 to 12 at constant ozone feed into the reactor. Results are presented in Fig. 2. Constant increase in phenol decay in pH range from 3 to 6 can be observed. Further increase of pH value up to 8 caused the lowering of process efficiency. By the increasing initial pH value from 8 into the more basic conditions, process efficiency was again started to increase. At initial pH values 11 and 12 the complete phenol removal was achieved by ozonation process. Phenol decomposition is obviously favored in strong basic conditions, where significant increase of TOC removal can be observed. Drop of pH values of treated phenol solution by O_3 process in comparison to initial pH values, indicates the formation of organic acids as products of phenol decomposition. Due to the weak character of formed acids, this effect is not such pronounced in strong basic conditions, particularly at pH 12. Hoigne and Bader [23] pointed out that organic acids with low reaction rate constants, such as acetic and oxalic, always accumulate as final products when any type of reactive organic aqueous solutes are ozonized in water. Hence, the overall oxidation of organic material to CO_2 will be delayed whenever the oxidations lead to oxalic or acetic acid as intermediates. In cases where the oxidations form formate ions, mineralization to CO_2 will be less delayed, i.e. TOC removal will increase. Therefore, the occurrence of a full mineralization of organic solute will largely depend on whether formate or oxalate and acetate ions are formed as intermediate products. As mentioned earlier, by O_3 process organic compound could be degraded through two main oxidation mechanisms. One is oxidation by molecular ozone which is predominant at lower pH. Direct mechanism involves organic compound degradation by molecular ozone [23,24], shown in the following equation:

$$C_6H_5OH + O_3 \rightarrow \text{by-products}, \quad k_1 = 1.3 \times 10^3\,M^{-1}\,s^{-1} \tag{1}$$

According to the literature, in the case of phenol degradation by molecular ozone (1), the direct formation of organic acids, such as muconic, maleic, oxalic, etc., is favored to their formation through degradation of aromatic by-product formed by phenol decomposition [23,25,26]. This could be explanation why the monitored aromatic by-products (catechol, hydroquinone, benzoquinone and resorcinol) of phenol decomposition were not detected at pH 3 and 4 (results not shown). Chu and Ma [27] pointed out that direct ozonation rarely produces complete mineralization due to the selective nature of ozone toward formed by-products, which is in accordance with low TOC removal obtained in acidic conditions. On the other hand, the significant improvement in the oxidation power of ozonation process at strong basic conditions could be attributed to the predominant indirect mechanism which includes generation of OH radicals by ozone decomposition in aqueous solution, specially catalyzed by OH^- (i.e. higher pH), the following equation [28]:

$$O_3 + H_2O \xrightarrow{OH^\bullet} OH^\bullet + O_2 + HO_2^\bullet \tag{2}$$

Gurol and Vatistas [29] demonstrated that selectivity of ozone for phenolic compounds decrease as the pH is increased. Such observation supports the conviction that OH radical would be predominant oxidant at high pH. Phenol can be degraded by formed OH radicals according to the following equation [30]:

$$C_6H_5OH + OH^\bullet \rightarrow \text{by-products}, \quad k_2 = 6.6 \times 10^9\,M^{-1}\,s^{-1} \tag{3}$$

The reaction of phenol with OH radical (3) is much faster than with molecular ozone (1), which is obvious from the comparison of rate constants, $k_1 \ll k_2$. Also, the pathway of phenol decomposition by indirect ozonation is different than that of direct ozonation. Degradation of phenol by OH radicals favors the formation of aromatic by products, and the subsequent formation of organic acids and thereafter partial mineralization [31]. Hence, at least one of monitored aromatic by-products was detected in complete range of basic pH values. Due to the fact that OH radical is strong and non-selective oxidant, TOC removals were increased by increasing the initial pH values. The highest TOC removal, 36.1%, was obtained at initial pH 12. The established and proposed optimal pH value of ozone process for the degradation of phenol, pH 12, is in accordance with the literature. Wu et al. [32] showed that the fastest phenol degradation occurred at pH 12.9. Furthermore, Alaton et al. [33] reported the highest COD removal in their study of the treatment of penicillin formulation effluent by ozone process at pH 12. Generally, degradation of phenol always occurs by both direct and indirect mechanisms, which are competitive and dependent of process conditions. According to Gurol and Vatistas [29], radical mechanism is predominant even at neutral pH. However, due to the slow rate of self-decomposition of ozone initiated by OH^- ion at neutral pH, they came to the conclu-

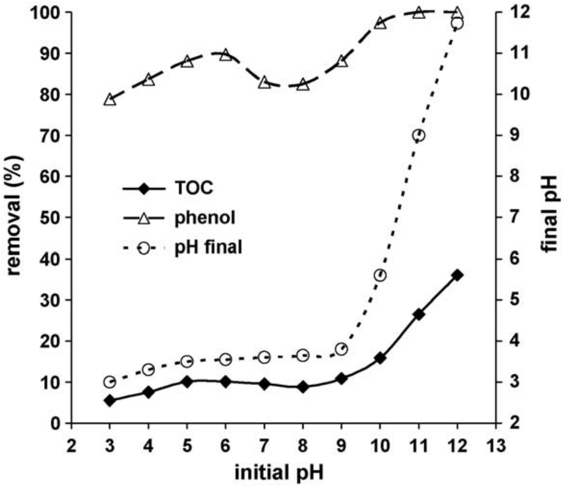

Fig. 2. Influence of the initial pH value on the phenol decomposition and mineralization efficiency and final pH values after a 1-h treatment by O_3 process.

sion that phenolic compounds themselves must be acting as the promoters of the decomposition of ozone and the formation of free radicals [29]. In this study, in pH range from 6 to 9 the drop of phenol decay can be observed. One of possible reasons for such effect could be the consumption of major oxidative species (O_3 and $OH^\bullet$) between themselves, according to the following equation [34]:

$$OH^\bullet + O_3 \rightarrow HO_2{}^\bullet + O_2, \quad k_3 = 1.1 \times 10^8\,M^{-1}\,s^{-1} \qquad (4)$$

Rather than their consumption in the reactions with phenol molecule, Eqs. (1) and (3). The result of above reaction (4) is the formation of perhydroxyl radical, $HO_2{}^\bullet$, much less reactive specie than both oxidants, with the redox potential of 1.70 V [5]. In addition, according to Mvula and von Sonntag [35], the competition of ozone between phenol and its by products should be taken into account, resulting with slower phenol removal. Accordingly, from the results presented in Fig. 2, it can be seen that in spite of the drop of phenol removal in pH range form 6 to 9, TOC removal remained constant. Such behavior corresponds to the pronounced degradation of phenol by products in comparison parent phenol molecules.

The next studied process applied for phenol degradation was peroxone process, O_3/H_2O_2. Both initial H_2O_2 concentration and pH were varied in order to determine values of those parameters producing the highest phenol decay and mineralization extent of model phenol solution. Firstly, the set of experiments was conducted at initial pH value 6 (pH value of phenol solution), while initial H_2O_2 concentrations were varied from 2 to 70 mM (Fig. 3(A)). It can be seen that an increase in initial H_2O_2 concentration from 2 to 10 mM slightly improved the efficiency of O_3/H_2O_2 process for phenol degradation, up to maximal 94.5 % of phenol removal. Further increasing of initial H_2O_2 caused a decrease in process efficiency, at the beginning very slightly, and then after 30 mM of H_2O_2, the decrease in the phenol removal efficiency of O_3/H_2O_2 process was more and more pronounced. It should be emphasized that H_2O_2 addition improved phenol removal efficiency in comparison to the case of ozone process at pH 6 (Fig. 2), but only in the cases with H_2O_2 lower than 40 mM. In the cases with initial H_2O_2 over 40 mM, obtained phenol decays were even lower than that obtained in the case without H_2O_2 addition (Figs. 2 and 3(A)). Mineralization extents achieved in the cases with lower H_2O_2 concentration followed increasing trend up to 30 mM of H_2O_2, and then in the cases with higher H_2O_2 dosages, obtained mineralization extents followed decreasing trend. Comparing obtained TOC removals through entire H_2O_2 range studied with that obtained in the case of ozone process at pH 6 (Fig. 2), it can be observed that H_2O_2 addition has improved mineralization of phenol model wastewater. The highest mineralization extent of phenol solution was achieved at initial H_2O_2 concentration of 30 mM where 18.8% of TOC was removed, whilst 93.4% of phenol was decomposed. Generally, in the case of peroxone process, both mechanisms O_3 and OH radical attack to phenol and its organic by-products could be considered. However, the mechanism including OH radicals is considered as predominant when H_2O_2 is present in reaction mixture, according to the overall Eq. (5) proposed by Glaze et al. [36]

$$2O_3 + H_2O_2 \rightarrow OH^\bullet + O_2 \qquad (5)$$

Observed dependence of process efficiency on H_2O_2 concentration suggests that H_2O_2 act as a free radical scavenger at concentrations above optimum required, i.e. in the excess of H_2O_2 concentration. Hence, the following radical scavenging reactions (6) and (7) may become important [37]. Both reactions consider consumption of OH radicals to the formation of less reactive perhydroxyl radical, $HO_2{}^\bullet$

$$OH^\bullet + H_2O_2 \rightarrow OH_2{}^\bullet + H_2O + O_2, \quad k_4 = 2.7 \times 10^7\,M^{-1}\,s^{-1} \qquad (6)$$

$$OH_2{}^- + OH^\bullet \rightarrow OH^- + OH_2{}^\bullet, \quad k_5 = 7.5 \times 10^9\,M^{-1}\,s^{-1} \qquad (7)$$

Further experiments were carried out at above determined initial H_2O_2 concentration of 30 mM (Fig. 3(A)), while pH was varied in the range from 3 to 12 (Fig. 3(B)). It should be empha-

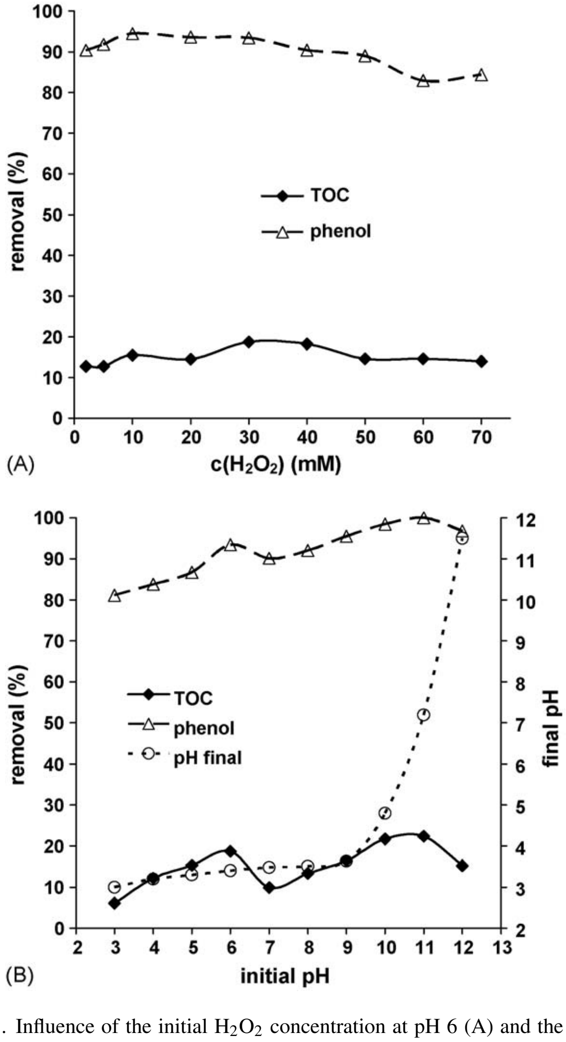

Fig. 3. Influence of the initial H_2O_2 concentration at pH 6 (A) and the initial pH value at 30 mM H_2O_2 (B) on the phenol decomposition and mineralization efficiency and final pH values process after a 1-h treatment by O_3/H_2O_2 process.

sized that the trend of the curve of phenol removal regarding pH is very similar to that obtained by O_3 process (Fig. 2) with strong exception at pH 12. This could be explained by similar degradation mechanisms involved in phenol degradation at the same pH values. Constant increasing of initial pH value up to pH 6 caused a constant increase in the efficiency of O_3/H_2O_2 process for phenol degradation. By further increasing of pH, process efficiency was firstly decreased at pH 7, but not as much pronounced as in the case of ozone process (Fig. 2), and then constantly increased until the complete phenol decay at pH 11. Further increasing up to pH 12 caused a decrease in process efficiency (Fig. 3(B)). It can be observed that the trend of curve of TOC removal with two maximums (pH 6 and 11) is very similar to that of phenol removal. The overall highest TOC removal, 23.0 %, was obtained at pH 11. Somewhat higher results of both phenol and TOC removals obtained by O_3/H_2O_2 than O_3 process through entire investigated range of pH (with exception of extreme basic conditions, pH 12) indicated the presence of additional OH radical generated throughout mechanism shown by Eq. (5). Also, it should be kept in mind that the compounds of low reactivity, such as carboxylic acids (discussed above) may be oxidized by secondary oxidants (e.g. OH radicals) produced by preliminary decomposition of ozone by H_2O_2, Eq. (5). The yields of such reactions will not only depend on the amount of decomposed ozone, but also on the total amount of aqueous solutes which scavenge these non-selective oxidants in concurrent reactions [23]. Trend of final pH values in the cases of O_3 and O_3/H_2O_2 processes are very similar, while only exceptions could be observed as lower final values in the case of O_3/H_2O_2 process at pHs 10 and 11. These results indicate the higher amount of formed organic acids than at the same pHs in the case of O_3 process, presumably due to the above mentioned additional OH radical generation.

Hydrogen peroxide can be used as an oxidant (redox potential of 1.77 V) to treat organic pollutants present in aqueous solutions [5]. Combining hydrogen peroxide with UV irradiation results with the generation of OH radicals, Eq. (8), that react with organic compounds at the much higher rate than the parent compound (H_2O_2) [11].

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet}, \quad \Phi = 0.5\,\text{mol einstein}^{-1} \tag{8}$$

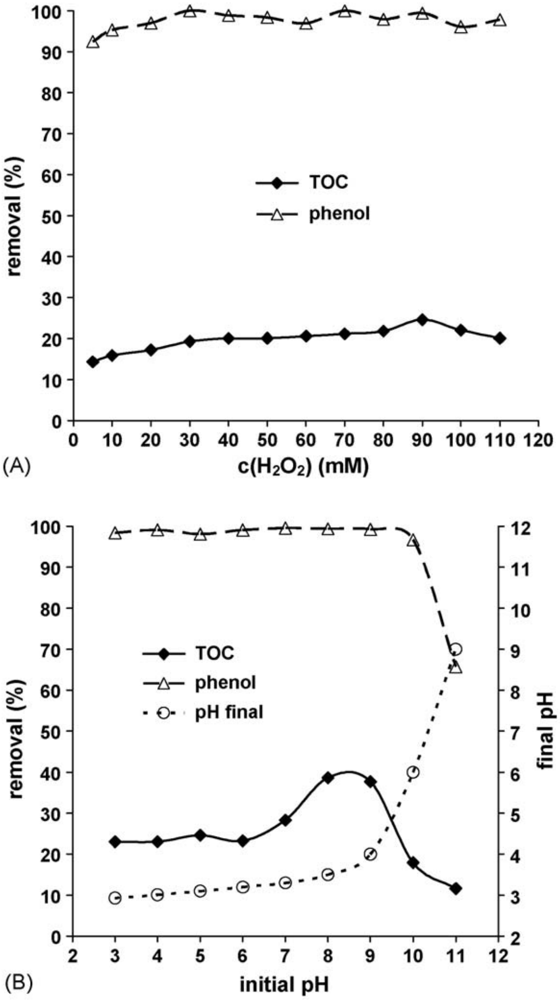

Fig. 4. Influence of the initial H_2O_2 concentration at pH 6 (A) and the initial pH value at 90 mM H_2O_2 (B) on the phenol decomposition and mineralization efficiency and final pH values process after a 1-h treatment by UV/H_2O_2 process.

Two operating parameters of UV/H_2O_2 process, initial concentration of H_2O_2 (i.e. ratio of pollutant/H_2O_2) and pH were investigated. Therefore, two sets of experiments were performed where one parameter was varied, while other was held constant. In Fig. 4(A) the influence of initial H_2O_2 concentration on phenol and TOC removal at pH 6 is presented. Relatively high phenol decay, over 90%, is obtained over entire investigated range and no significant effect of H_2O_2 concentrations on phenol decomposition is observed. However, from the mineralization point of view, influence of initial H_2O_2 concentration is more pronounced. Increasing of initial H_2O_2 concentration enhanced the oxidation process up to certain point at which H_2O_2 started to inhibit the phenol photolytic degradation. At higher H_2O_2 concentration, reactions (6) and (7) in the H_2O_2 photolysis mechanism became more important and H_2O_2 acted as a free radical scavenger thereby decreasing phenol decomposition [14]. At our operating conditions (wavelength and light intensity), it was deduced that the optimum H_2O_2/phenol ratio is 90, i.e. at 90 mM of initial H_2O_2 24.6% of treated solution was mineralized, whilst 99.4% of phenol was decomposed. In further experiments pH was varied in the range from 3 to 11 at above established initial H_2O_2 concentration of 90 mM (Fig. 4(B)). It can be seen that the efficiency of phenol decomposition was not affected by pH below 9, phenol removal >98% is achieved through range from 3 to 9. Further increasing of pH over 9 caused rapid decrease in UV/H_2O_2 process efficiency that resulted with only 65.7% of decomposed phenol at pH 11. Similar system behavior can be observed in the case of TOC removal in the pH range from 3 to 7 and pHs over 10. Exceptions were cases of pH 8 and 9 where significantly higher TOC removals, 38.7 and 37.1%, respectively, were achieved. This could be explained in terms of H_2O_2 dissociation in strong alkaline media. Also, the fast reaction of OH radicals with H_2O_2 was responsible for the observed decrease in phenol decomposition under acidic conditions [14]. This is in accordance with Lipczynska–Kochany [38] who studied phenol oxidation by the UV/H_2O_2 process and observed no significant effects in the pH range from 7 to 9. On the other hand, phenol degradation decreased rapidly when pH <7 and pH >9. Also, direct photolysis of phenol is accelerated in alkaline solutions due to the increase in "phenolate anions light absorbency" [14]. Accordingly, in this study photolysis combined with H_2O_2 was most effective in weak basic conditions. The curve of final pH values followed the same trend like in the cases of O_3 and O_3/H_2O_2 processes (Figs. 2 and 3(B)).

Similarly like in the case of UV/H_2O_2 process, the efficiency of O_3 process can be enhanced by UV irradiation. The UV/O_3 system is an effective method for the oxidation and destruction of organic compounds in water [13,15–17]. The extinction coefficient of ozone at 254 nm is much higher than that of hydrogen peroxide ($\varepsilon_{\text{ozone}} = 3300\,\text{M}^{-1}\,\text{cm}^{-1} \gg \varepsilon_{\text{hydrogen peroxide}} = 18.6\,\text{M}^{-1}\,\text{cm}^{-1}$). The decay rate of ozone is about a factor of 1000 higher than hydrogen peroxide [39]. The AOP with UV irradiation and ozone is initiated by the photolysis of ozone. The photodecomposition of ozone leads to the formation of H_2O_2 in the following equation:

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2, \quad \Phi = 0.64\,\text{mol einstein}^{-1} \tag{9}$$

and consequently, generation of two hydroxyl radicals through Eq. (8) [11]. This system contains three components to produce OH radicals and/or oxidize the pollutant for subsequent reactions: UV irradiation, ozone and hydrogen peroxide. In this study, UV/O_3 process was investigated regarding to the pH value at constant ozone feed rate. From Fig. 5 it can be seen that the final extent of phenol decomposition was not affected by pH. The complete phenol decomposition was achieved through entire pH investigated, from 3 to 12. However, influence of initial pH on the rate of phenol decomposition was observed (results are not shown). The highest phenol degradation rates were observed in strongly alkaline media, like in the case of O_3 process. Influence of initial pH on the mineralization extent by UV/O_3 process is presented in Fig. 5, as well. It can be seen that an increase of pH value enhanced mineralization of phenol solution up to pH 8. Further pH increasing caused drop in process efficiency at pHs 9 and 10, and then again an increase to the maximal 44.3% of TOC removal at pH 11. However, in comparison to O_3 process presented in Fig. 2, higher mineralization extents were obtained by UV/O_3 process (Fig. 5) at each investigated initial pH value, as an evidence of positive effect of UV irradiation on the investigated system. The trend of TOC curve presented in Fig. 5 is a consequence of interactions of several above discussed mechanisms involved in UV/O_3 process and their predominance in dependence of pH of solution [40]. Again, the trend of the curve of final pH values was similar like in previous cases (Figs. 2, 3(B) and 4(B)).

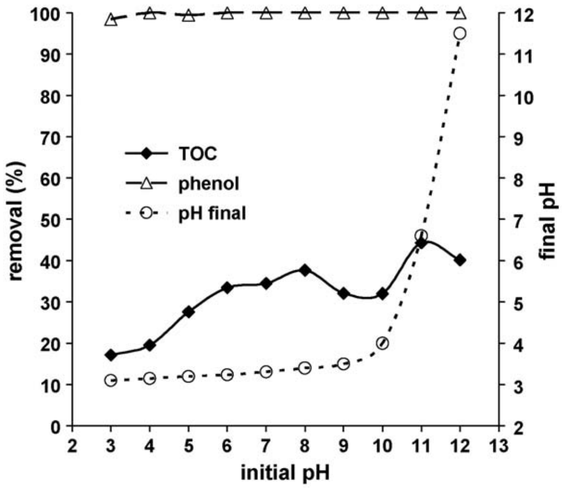

Fig. 5. Influence of the initial pH value on the phenol decomposition and mineralization efficiency and final pH values after a 1-h treatment by UV/O_3 process.

The addition of H_2O_2 to UV/O_3 process accelerates the decomposition of ozone due to the increased rate of OH radical generation. $UV/H_2O_2/O_3$ process is a very powerful method that allows a considerable reduction of TOC. This process is the combination of the binary systems UV/O_3 and O_3/H_2O_2. Influence of initial H_2O_2 concentration and initial pH values to $UV/H_2O_2/O_3$ process effectiveness was investigated (Fig. 6(A) and (B)). As it

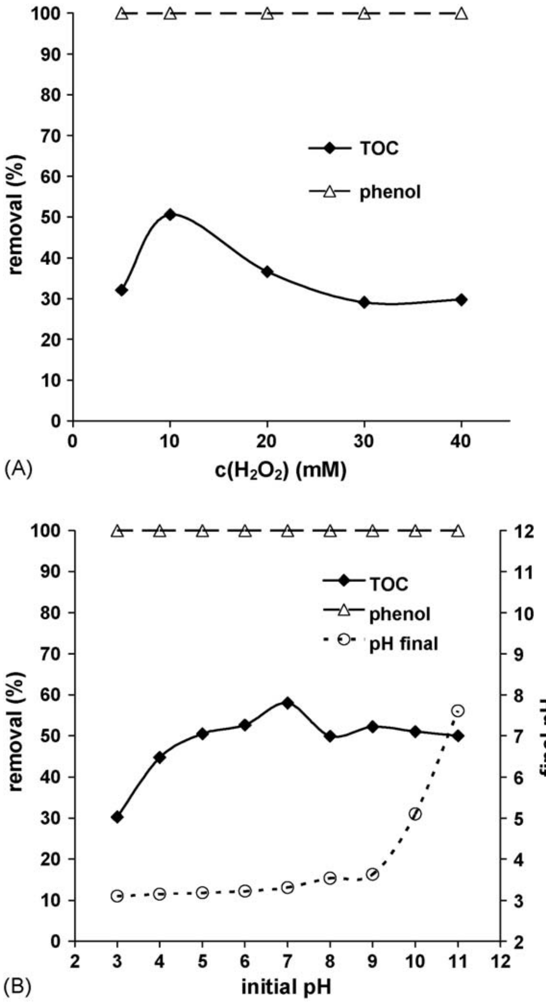

Fig. 6. Influence of the initial H_2O_2 concentration at pH 6 (A) and the initial pH value at 10 mM H_2O_2 (B) on the phenol decomposition and mineralization efficiency and final pH values process after a 1-h treatment by $UV/O_3/H_2O_2$ process.

was expected due to the previous presented results, the complete phenol decomposition was achieved in complete investigated H_2O_2 and pH range. From Fig. 6(A) it can be seen that mineralization extents strongly depended on initial H_2O_2 concentration at constant initial pH value. Maximal TOC removal was obtained by 10 mM H_2O_2. It can be assumed that at lower H_2O_2 concentration, insufficient amount of OH radicals is generated (Eqs. (5), (8) and (9)), while at higher concentrations, scavenging nature of H_2O_2 became predominant (Eqs. (6) and (7)). In Fig. 6(B) mineralization extents of phenol solution after the treatment by $UV/H_2O_2/O_3$ process (10 mM H_2O_2) at different pH values are presented. Maximum TOC removal, 58.0%, is obtained at pH 7. Obtained TOC curve is a result of several competitive pH dependant mechanisms involved in phenol and its by-products oxidation by $UV/H_2O_2/O_3$ process. All these degradation mechanisms should be taken into consideration: OH radical attack as predominant, direct ozone attack, direct photolysis of organics by UV irradiation and direct oxidation by H_2O_2 [18]. The generation of OH radicals from following sources could be considered: (a) from the photolysis of added H_2O_2, (b) from the photolysis of formed H_2O_2 by ozone photolysis, (c) from the reaction of H_2O_2 (either added or formed) with ozone and (d) by indirect ozonation. In addition, different radical species, either inorganic or organic, formed during the oxidation treatment can participate in chain reactions thus influencing overall process efficiency [11].

In the next step of study, kinetics of phenol decomposition, mineralization of model phenol solution and pH changes during the treatment at above established best conditions for each studied AOP were investigated. Fig. 7(A) shows phenol degradation and the subsequent formation of oxidation by-products during a 1-h treatment by O_3 process (pH 12), while in Fig. 7(B) the mineralization of phenol solution and changes of pH during that treatment are presented. It can be seen that complete phenol degradation was achieved after 45 min of treatment, while only the presence of hydroquinone as an aromatic by-product of phenol oxidation was observed. Formed hydroquinone was not completely degraded even after 60 min of treatment (Fig. 7(A)). From the mineralization kinetics, shown in Fig. 7(B), it can be observed that TOC removal was somewhat faster in first 15 min of treatment, and then almost negligible inhibition in process efficiency was occurred, while thereafter the curve has the linear trend. That small decrease in process efficiency could be attributed to the small decrease of pH value (from 12.0 to 11.8) in that first treatment period, due to the formation of organic acids as by-products of phenol decomposition [31,41]. In further treatment period, pH value remained almost constant, around 11.8, which could be connected with the liner trend of TOC curve in that period. It could be expected that an extension of treatment time will result with the further mineralization of phenol solution at the same rate due to the constant ozone feed rate and expected constant pH. From the wide discrepancy at each time point between the amount of degraded phenol and the produced hydroquinone, and on the other side the mineralized part of phenol solution the formation of other by-products, either aromatic or aliphatic, could be presumed. Mostly of that part could be attributed to the formation of aliphatic organic acids (HAA), which can be formed through degradation of aromatic by-products [15,31]. But according to the results presented in Fig. 7, HAA may also be formed directly by the indirect ozonation of phenol solution.

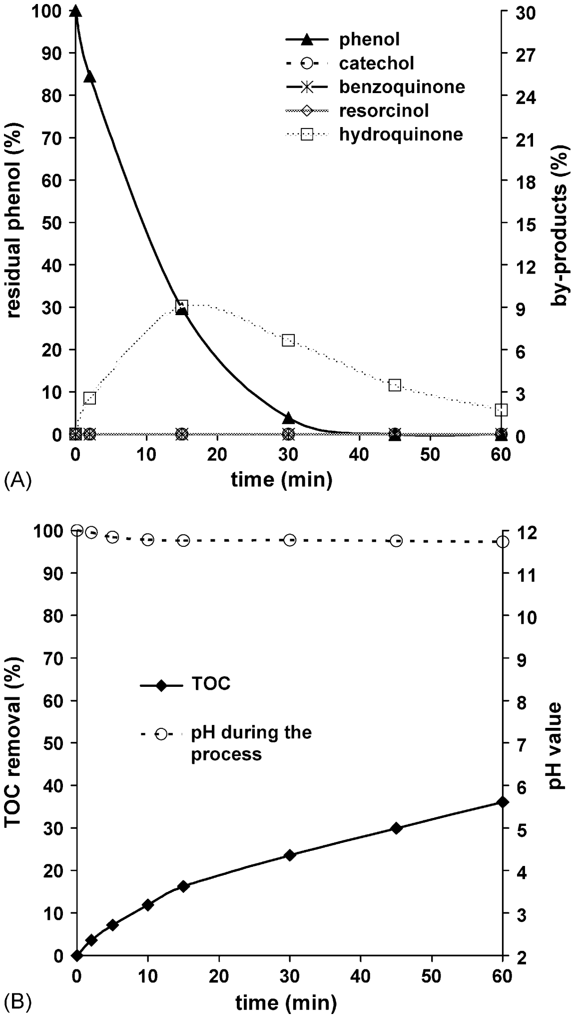

Fig. 7. Kinetics of phenol decomposition and its primary aromatic by-products formation/degradation (A) and phenol model solution mineralization alongside with pH (B) during a 1-h treatment by O_3 process (pH 12).

In Fig. 8 results of phenol decomposition (A) and the mineralization of phenol solution (B) during a 1-h treatment by O_3/H_2O_2 process (pH 11, 30 mM H_2O_2) are shown. Similarly like in case of O_3 process, complete phenol degradation was achieved after 45 min of treatment by O_3/H_2O_2 process. However, trend of the phenol curves (Figs. 7 and 8) indicate somewhat slower rate of phenol decay by O_3/H_2O_2 process. From Fig. 8(A) it can be seen among all monitored by-products; only catechol was detected, which was degraded after 30 min of treatment. As it was mentioned before, by phenol degradation, acidic by-products were formed which lowered pH during the treatment. In the case of O_3/H_2O_2 process, the inhibition of mineralization in comparison to O_3 process might be caused by the formed HAA as phenol oxidation by-products manifesting in a decrease of pH, from 11.0 to 6.9 (Fig. 8(B)). Although constant leveling off in TOC curve is demonstrated, further mineralization of phenol solution could be expected by an extension in treatment time over 60 min, but

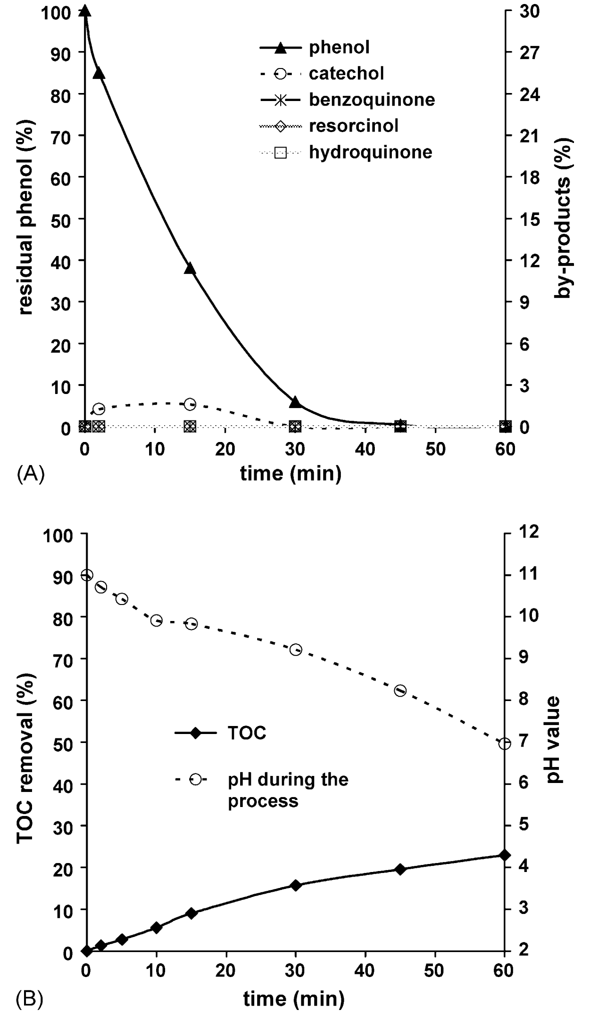

Fig. 8. Kinetics of phenol decomposition and its primary aromatic by-products formation/degradation (A) and phenol model solution mineralization alongside with pH (B) during a 1-h treatment by O_3/H_2O_2 process (pH 11, 30 mM H_2O_2).

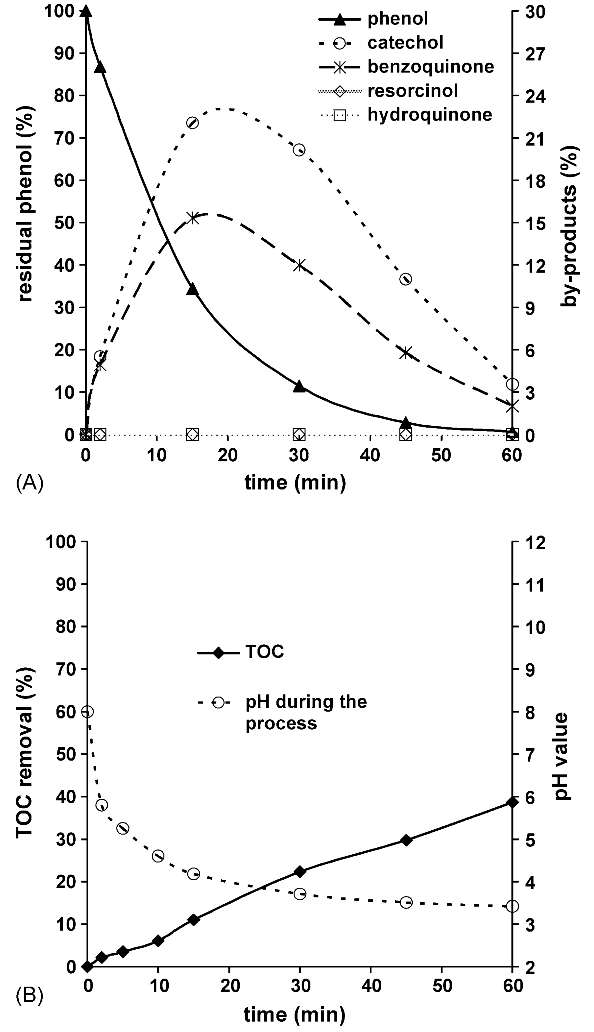

Fig. 9. Kinetics of phenol decomposition and its primary aromatic by-products formation/degradation (A) and phenol model solution mineralization alongside with pH (B) during a 1-h treatment by UV/H_2O_2 process (pH 8, 90 mM H_2O_2).

the consumption of added H_2O_2 as a system limitation should be kept in mind.

Almost complete phenol, 99.4%, was degraded within 60 min of treatment by UV/H_2O_2 process (pH 8, 90 mM H_2O_2) (Fig. 8(A)). Unlike to the previously described processes, the significantly higher concentration of catechol and benzoquinone were detected during the treatment of phenol solution by UV/H_2O_2 process. In comparison to O_3 process (Fig. 7(A)), a significantly smaller discrepancy at each time point between the amount of degraded phenol and the produced aromatic by-products, and on the other side the mineralized part of phenol solution, indicate that the formation of aliphatic organic acids occurred mainly over degradation of formed aromatic by-products than directly from phenol degradation. From Fig. 4(B) it can be observed that initial acid conditions did not favor the mineralization of phenol solution. However, mineralization process was not inhibited by the drop of pH during the treatment process when phenol as a parent compound was already mostly transformed to its by-products (Fig. 9(B)). Similarly like in previous cases, further mineralization could be considered even after 60 min of treatment time. However, UV/H_2O_2 system is even more limited with H_2O_2 consumption than O_3/H_2O_2, due to the lower mineralization efficiency of UV light itself in comparison to O_3 (Fig. 2) [19].

In Fig. 10 kinetics of phenol degradation (A) and mineralization of phenol solution (B) by UV/O_3 process (pH 11) are presented. Phenol decay is rather fast, the complete removal is obtained within 30 min of treatment time. As by-products, resorcinol and benzoquinone were detected in low concentrations (Fig. 10(A)). Again, formation of acidic by-products caused the significant lowering of pH, from 11.0 to 6.5. Formed aromatic by-products in very low concentrations indicate that the most of acidic by-products was formed directly from phenol. It can be assumed that the pronounced inhibition of mineralization efficiency, occurred after 15 min of treatment time, is due to the strong lowering of pH, from 10.0 to 8.0, in period between 15 and 30 min of process. This can be connected with the results presented in Fig. 5, where the drop in mineralization efficiency in pH range between 8 and 11 can be observed. From the linear trend of TOC curve after 30 min of treatment time, and taking into account constant ozone feed rate and UV irradiation, the

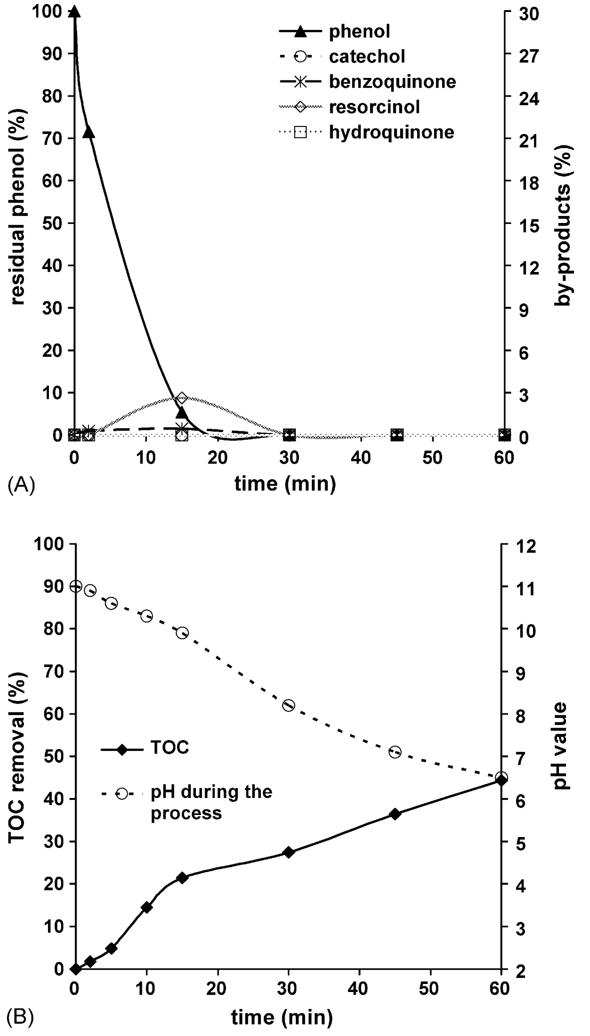

Fig. 10. Kinetics of phenol decomposition and its primary aromatic by-products formation/degradation (A) and phenol model solution mineralization alongside with pH (B) during a 1-h treatment by UV/O_3 process (pH 11).

continuation of mineralization process could be expected, but the negative influence of acidic conditions on the process effectiveness should also be considered.

Finally, kinetics of phenol decomposition and mineralization of phenol solution by UV/H_2O_2/O_3 process (pH 7, 10 mM H_2O_2) are shown in Fig. 11(A) and (B), respectively. Like in the case of UV/O_3 process (Fig. 10), the complete phenol decay was achieved within 30 min of treatment (Fig. 11(A)). In the same treatment period the formation of catechol, benzoquinone and hydroquinone was detected and they were subsequently completely degraded. Among investigated systems, UV/H_2O_2/O_3 demonstrated the highest mineralization efficiency for the treatment of phenol solution. Within 60 min, 58.0% of TOC was removed. Linear trend of TOC curve can be observed through entire treatment time interval. Generally, such system behavior could be considered as zero order kinetics [42]. This can be explained with the fact that ozone is continuously introduced into the reaction mixture and constantly irradiated. Major source of OH radicals, H_2O_2, is continuously consumed during the process, but alongside added amount, the additional H_2O_2 can be generated mainly through ozone photolysis. Therefore, overall higher mineralization extent could be presumed even after 60 min of treatment time.

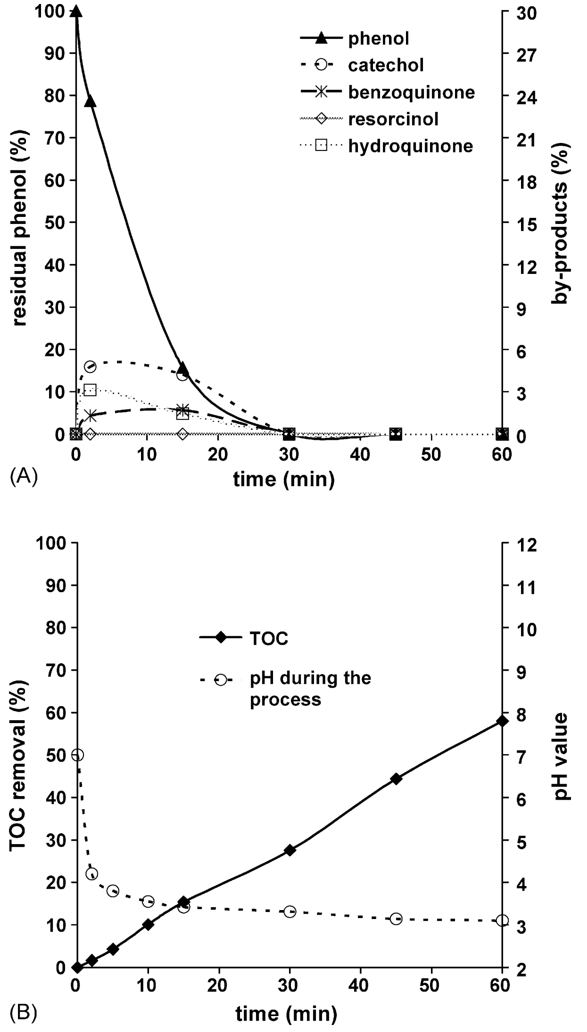

Fig. 11. Kinetics of phenol decomposition and its primary aromatic by-products formation/degradation (A) and phenol model solution mineralization alongside with pH (B) during a 1-h treatment by UV/O_3/H_2O_2 process (pH 7, 10 mM H_2O_2).

According to the fact that different by-products of phenol degradation by applied process were detected and presented in Figs. 7–11(A), it can be concluded that degradation of phenol occurs throughout different oxidation pathways.

Among investigated AOPs, UV/H_2O_2/O_3 process with maximal phenol and TOC removal at above established operating conditions is considered to be the most eco-effective. Thereafter, the cost-effectiveness for each applied process was estimated. Processes were compared according to their pseudo first order rate constant of phenol removal, calculated by linear regression (Fig. 12). The highest calculated rate constant for phenol degradation, $k_{\mathrm{UV/O_3}} = 0.1936\,\mathrm{min}^{-1}$, was obtained for UV/$O_3$ process. Other rate constants for studied processes are significantly lower than that of UV/O_3 process, and they followed decreasing order: $k_{\mathrm{UV/H_2O_2/O_3}} > k_{\mathrm{O_3}} > k_{\mathrm{O_3/H_2O_2}} > k_{\mathrm{UV/H_2O_2}}$. Pseudo first order rate constants and half-life time, $t_{1/2}$, present

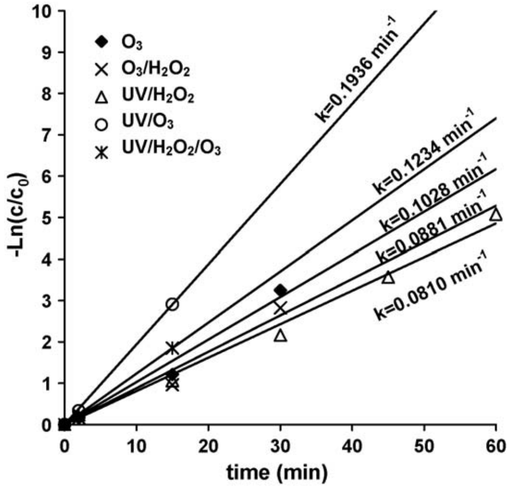

Fig. 12. Graphical estimation of pseudo first order rates of phenol degradation by studied AOPs.

Table 1
Cost of reagents used in applied processes (costs are given in euros and the values are valid for Croatian market)

Reagent	Basis	Cost (EUR)
H_2O_2, 30%	1 L	31.324
O_2, >99.9%	100 L	0.188
Electricity	1 kWh	0.134

global parameters including all the phenomena involved in the studied process, thus allowing the overall comparison between the different AOPs [16]. In order to evaluate the treatment costs of proposed processes costs of used reagents valid for Croatian market were taken into account (Table 1). Values of $t_{1/2}$ and $t_{3/4}$, times required to decrease phenol concentration to half and quarter the amount present before reaction, respectively, are given in Table 2. When the values of $t_{3/4}$ are equal to $t_{1/2} \times 2$, it is possible to conclude that reactions obey first order rate constants [16], which is mostly the case in our experimental conditions tested.

As discussed earlier, complete phenol was degraded during a 1-h treatment by all investigated AOPs with an exception of UV/H_2O_2 where 99.4% of phenol was removed. However, from Table 2 it can be seen that less than 30 min of treatment was required for total phenol decay by both UV/O_3 and UV/H_2O_2/O_3 processes, producing costs of 0.032 and 0.048 EUR, respectively. On the other hand, partial mineralization of phenol solution was achieved in all cases. The overall highest mineralization extent was achieved by UV/H_2O_2/O_3 process with corresponding cost of 1.41 EUR g^{-1}. This calculated treatment cost expressed as € per gram of removed organic matter for UV/H_2O_2/O_3 process is around 10% higher than that for the cheapest O_3 process which yielded with more than 20% lower mineralization effectiveness. Moreover, required strong basic conditions i.e. adjustment of initial pH to 12 as well as necessary conditioning of treated effluent additionally disfavors O_3 process. Therefore, it was concluded that among all investigated processes treatment of phenol model wastewater by UV/H_2O_2/O_3 process is the most cost-effective. However, it should be emphasized that these evaluation of operating costs has been made on the basis of laboratory scale investigations. The overall costs are represented by the sum of capital, operating and maintenance costs. For a full-scale system these costs will, besides the nature and the concentration of pollutants, strongly depend on the flow rate of the effluent and the configuration of the reactor [43].

4. Conclusion

In this comparative investigation the different ozone- and/or UV-based processes, O_3, O_3/H_2O_2, UV/H_2O_2, UV/O_3 and UV/H_2O_2/O_3, were applied for phenol minimization in model wastewater. From the fact that different by-products of phenol degradation by applied process were detected, it was concluded that degradation of phenol occurs throughout different oxidation pathways. Complete phenol removal was achieved by all applied processes at the best operating conditions determined for each process in investigated ranges of selected varied process parameters, with an exception of UV/H_2O_2 where 99.4% of phenol was removed within a 1 h treatment. UV/H_2O_2/O_3 process (pH 7, $c(H_2O_2) = 10$ mM) was shown to be the most eco-effective with 100% of phenol removal within 30 min of treatment, and 58.0% of TOC removal after a 1-h treatment. On the other hand, the most cost-effective, i.e. the cheapest with respect to the mineralized part of solution, was found to be O_3 process (pH 12) with the corresponding cost of 1.34 EUR g^{-1}. But, concerning lower mineralization efficiency and additional costs for strong conditioning of solution before and after the treatment, O_3 process is disfavored in comparison to UV/H_2O_2/O_3 process with corresponding cost of 1.41 EUR g^{-1}. Therefore, due to its eco and cost effectiveness UV/H_2O_2/O_3 process is proposed as the most suitable for minimization of phenol wastewater among investigated ozone- and/or UV-based processes.

Table 2
Cost evaluation for all applied processes (processes conducted in laboratory scale)

Process	k (min^{-1})	$t_{1/2}$ (min)	$t_{3/4}$ (min)	t_{max} (min)	Costs for phenol decay (EUR)			Final TOC removal (%)	Cost (EUR g^{-1})
					50%	75%	Maximum		
O_3	0.1028	9.3	16.8	<45.0	0.007	0.013	0.035	36.1	1.34
O_3/H_2O_2	0.0881	11.3	20.3	<45.0	0.058	0.065	0.084	23.0	4.27
UV/H_2O_2	0.0810	10.3	19.3	60.0	0.149	0.152	0.163	38.7	4.33
UV/O_3	0.1936	5.5	10.0	<30.0	0.006	0.011	0.032	44.3	1.48
UV/H_2O_2/O_3	0.1234	7.0	12.3	<30.0	0.024	0.029	0.048	58.0	1.41

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