

Oxidative decomposition of benzoic acid in the presence of metal ionic catalysts

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Abstract. Catalytic ozonation as one of the advanced oxidation processes gives a wide range of opportunities for the enhancement of the degradation of resistant compounds. The efficiency of catalytic ozonation with homogeneous (containing dissolved ions of Fe^{2+} , Mn^{2+} , Cu^{2+} , Ni^{2+} , Mo^{6+}) and heterogeneous (Fe_2O_3 , MnO_2 , Ni_2O_3 , CuO , Al_2O_3 , MoO_3 , TiO_2) catalysts and non-accompanied ozonation was compared for the degradation of benzoic acid (BA). A combination of ozonation and the Fenton reagent was found to be quite effective for BA. Although a slight acceleration was followed in the catalytic ozonation of BA, a significant improvement in the COD removal was observed. The current study proved that catalytic ozonation may be efficient for the degradation of resistant compounds but the performance of catalysts in ozonation is quite sensitive towards treatment conditions and the compound.

Key words: catalytic ozonation, benzoic acid (BA), Fenton treatment, homogeneous catalysts, heterogeneous catalysts.

INTRODUCTION

Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, BA) and sodium benzoate are used to preserve silage for cattle and various food products (oyster sauce, fruit juices, salads, baked goods, cheeses, etc.). Benzoic acid can be prepared by the oxidation of toluene, benzyl alcohol, benzaldehyde, and cinnamic acid [1]. Thus, it is one of the possible aromatic contaminants in the effluents of organic synthesis. Only a few publications were found about BA removal from water by oxidation. Masten & Davies [2] concluded that in the case of ozonation the initial attack of the ozone molecule was usually at the activated meta-position to the electron-withdrawing group ($-\text{COOH}$). Ikemizu [3] studied the photooxidation of BA in

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combination with H₂O₂, expecting that the hydroxylation of the aromatic ring by [•]OH radicals would compete with the decarbonylation or decarboxylation of BA. He also identified hydroxybenzoic acids, phenol, and benzene as reaction intermediates, which, contrary to the common practice at the oxidation processes, were found to be more reactive than BA itself towards the [•]OH radicals. Mokrini et al. [4] studied pure photolysis, ozonation, and advanced oxidation (O₃/UV, O₃/H₂O₂, O₃/H₂O₂/UV) of phenol and BA at acidic pH. After 60 min of treatment they achieved the following removal degrees for the BA with the initial concentration of 0.8 mol/L depending on the oxidation system: UV – 23.5%, ozone – 49.7%, O₃/UV – 55.4%, and O₃/H₂O₂/UV – 97.2%. These results show that simple ozonation of BA proceeds during a certain time interval with a moderate degradation degree. A significant increase in the removal degree of BA when ozone is combined with hydrogen peroxide and UV radiation indicates the dominating role of [•]OH radicals in the oxidation process. However, an improvement of the oxidation rate of BA can also be expected when catalytic ozonation is applied.

The present study was undertaken to compare the treatment efficiency of non-accompanied ozonation and catalytic ozonation of BA with homogeneous (containing ions of Fe²⁺, Mn²⁺, Cu²⁺, Ni²⁺, Mo⁶⁺) and heterogeneous (Fe₂O₃, MnO₂, Ni₂O₃, CuO, MoO₃, Al₂O₃, TiO₂) catalysts. Additionally, the decrease of the COD of BA solutions during ozonation was investigated.

METHODS

The chemicals used were of analytical grade purchased from Aldrich Co. The samples were prepared dissolving the tested compound in twice-distilled water. The initial concentration of BA was 1.0 mM. The amount of catalysts added was 1 g/L for heterogeneous catalysts (solid oxides: Fe₂O₃, MnO₂, Ni₂O₃, CuO, Al₂O₃, MoO₃, and TiO₂) and 0.1 mM for homogeneous ones (metallic ions: Fe²⁺, Mn²⁺, Cu²⁺, Ni²⁺, and Mo⁶⁺). All experiments were carried out at 20 ± 1 °C.

The ozonation experiments were carried out in a bubble column with a volume of 0.8 L. The inlet and outlet concentrations of ozone in the gas phase were measured spectrophotometrically (λ = 258 nm). The concentration of ozone in the liquid phase was measured using the indigo method [5]. The volume of fresh solution placed into the reactor was 0.7 L. Ozone was produced from oxygen in a laboratory ozone generator and bubbled through the aqueous solution of BA. In the ozonation experiments the ozone concentration in the feed-gas was kept at 12.0 ± 0.5 mg/L. The initial pH value was adjusted to 3.0 to keep the dissolved ozone in a molecular form. The gas flow rate was kept at 1.0 L/min.

The Fenton reaction was also carried out at pH = 3.0, which is considered optimal for the Fenton treatment. The degradation rate of BA in the aqueous solution during the Fenton treatment was examined under batch conditions. A standard procedure was that 100 mL of fresh BA solution was treated in the cylindrical glass reactor with magnetic stirring. Different concentrations of H₂O₂

(from 2.0 to 8 mM) and the catalyst Fe^{2+} (from 0.2 to 0.8 mM) were used. Thus, the molar ratio of the oxidant to BA was 10:1. The reaction was stopped by the addition of 10% aqueous solution of Na_2SO_3 .

The progress in the degradation of BA was followed with a high performance liquid chromatograph (Millichrom, Nauchpribor, USSR) equipped with a UV-spectrophotometer (190–360 nm). A reverse phase column 2×64 mm was packed with $5 \mu\text{m}$ Separon C18 (Chemapol, Czechoslovakia). The isocratic method with a solvent mixture of 55% acetonitrile and 0.2% acetic acid in water with a flow rate of $100 \mu\text{L}/\text{min}$ was applied. The chemical oxygen demand (COD) was determined by the closed reflux titrimetric method according to [6].

RESULTS AND DISCUSSION

Catalytic ozonation of BA

Ozonation of BA followed mainly the first order kinetics. The pseudo-first order reaction rate constant in non-accompanied ozonation was $1.22 \times 10^{-3} \text{ s}^{-1}$. No substantial enhancement of BA degradation was attained with heterogeneous catalysts (Table 1, Fig. 1). Among heterogeneous catalysts, Al_2O_3 definitely retarded the ozonation of BA, whereas slight acceleration was observed for Fe_2O_3 , TiO_2 , MoO_3 , and MnO_2 (the enhancement factor varied from 1.15 to 1.3). However, the acceleration was observed mainly at an early stage of the ozonation process, and after 45 min of ozonation the amount of BA degraded was quite similar for all systems except the ozonation with Al_2O_3 addition. As to the homogeneous catalysts, manganese and nickel in the ionic form did not influence the degradation rate of BA. However, an acceleration was observed in the presence of Mo^{6+} , Fe^{2+} , and Cu^{2+} (the enhancement factor was 1.2, 1.25 and 1.5, respectively; Table 2). Thus, among the catalysts studied, copper in ionic form was found to be the most effective for the degradation of BA.

Table 1. Pseudo-first order reaction rate constants (k_1) and squared correlation coefficients (R^2) for the degradation of BA with heterogeneous catalysts

	No catalyst	MnO_2	Fe_2O_3	Ni_2O_3	MoO_3	CuO	Al_2O_3	TiO_2
$k_1 \times 10^{-4} \text{ s}^{-1}$	12.2	13.7	16.3	12.5	14.7	14.4	7.8	14.7
R^2	0.964	0.989	0.991	0.992	0.978	0.985	0.994	0.994

Table 2. Pseudo-first order reaction rate constants (k_1) and squared correlation coefficients (R^2) for the degradation of BA with homogeneous catalysts

	No catalyst	Mn^{2+}	Ni^{2+}	Mo^{6+}	Fe^{2+}	Cu^{2+}
$k_1 \times 10^{-4} \text{ s}^{-1}$	12.2	11.5	12.5	14.8	15.4	18.2
R^2	0.964	0.994	0.993	0.995	0.956	0.997

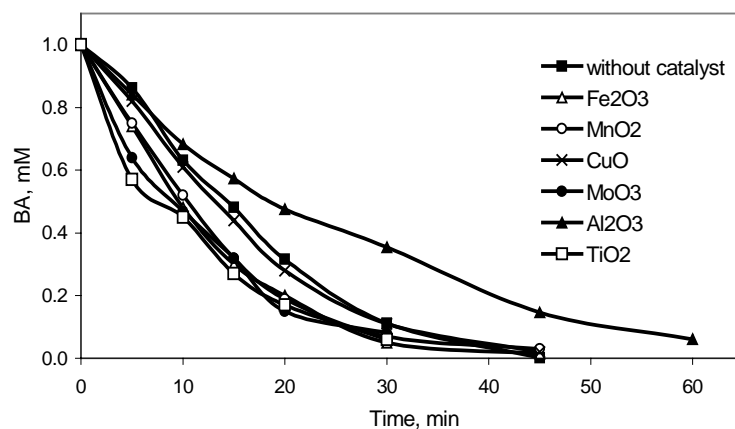


Fig. 1. Catalytic ozonation of benzoic acid (BA) at pH 3.0 with heterogeneous catalysts.

Fenton treatment and ozonation combined with the Fenton treatment

In addition to the ozonation experiments, three tests with the Fenton reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) were carried out to find the optimum concentrations and ratio of the reagents. According to the literature data the optimum ratio of hydrogen peroxide and iron is in the range from 10:1 to 13:1, and the pH may be from 3.0 to 5.5 [7].

There is a lack of information on the carboxylic acids oxidative treatment. Some parallels may only be drawn with the salicylic acid Fenton treatment [8]. In this study it was established that the optimum pH was 3.5 to have the maximum concentration of $\cdot\text{OH}$ radicals and, to have the stable reaction conditions, the ratio of hydrogen peroxide and iron must be 5:1 or higher. A very high reaction rate constant of salicylic acid decomposition obtained in that study, $2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, is typical of radical reactions.

Our experiments with different hydrogen peroxide and iron catalyst concentrations showed that if the initial concentration of H_2O_2 reached 10 mM, the BA decomposition was fast and it took only some minutes to obtain the 90% conversion degree. Figure 2 shows the curves of BA Fenton treatment. It can be seen that the concentrations $[\text{Fe}^{2+}]_0 = 0.2 \text{ mM}$ and $[\text{H}_2\text{O}_2]_0 = 2 \text{ mM}$ are too low for total decomposition of BA. However, at the concentrations $[\text{Fe}^{2+}]_0 = 0.8 \text{ mM}$ and $[\text{H}_2\text{O}_2]_0 = 8 \text{ mM}$ the reaction is very fast (during 7 min BA was totally decomposed), but the economic side of this treatment is quite questionable. To keep the operation costs down, 4–5 mM of H_2O_2 and ten times less iron concentrations will be enough. On the basis of experiments we consider the concentrations $[\text{Fe}^{2+}]_0 = 0.4 \text{ mM}$ and $[\text{H}_2\text{O}_2]_0 = 4 \text{ mM}$ as optimum for BA removal from the solution.

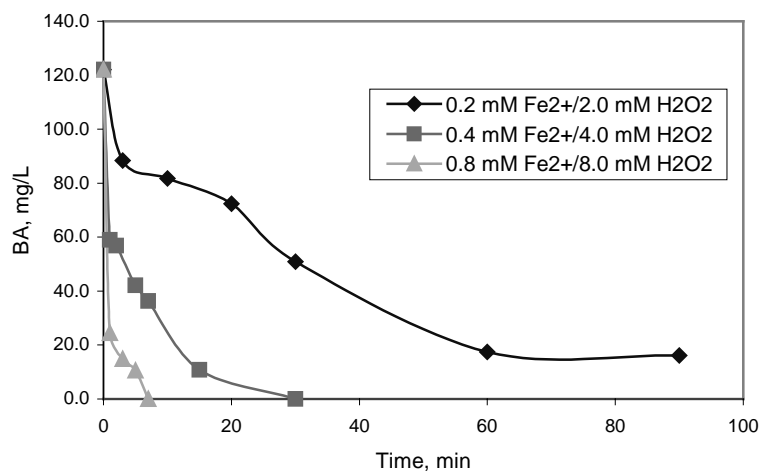


Fig. 2. Fenton treatment of benzoic acid (BA) at different concentrations of reagents.

There is some evidence that the advanced oxidation processes based on the combination of ozonation and the Fenton reagent may enhance the degradation of organics [9]. Therefore, such combination was applied in the present study for the degradation of BA (Fig. 3). The results presented in Fig. 4 indicate that such combination enhanced the degradation of BA as compared with non-accompanied ozonation and catalytic ozonation with homogeneous Fe²⁺ (the enhancement factor 1.6–1.8). There was no substantial difference in the degradation rate of BA in the presence of used peroxide (1.0 mM and 2.5 mM) and iron (0.1 and 0.25 mM).

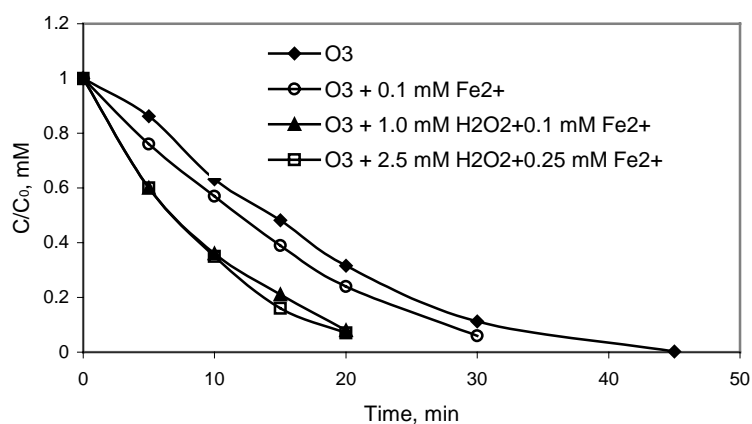


Fig. 3. Degradation curves of benzoic acid (BA) for ozonation combined with the Fenton reagent.

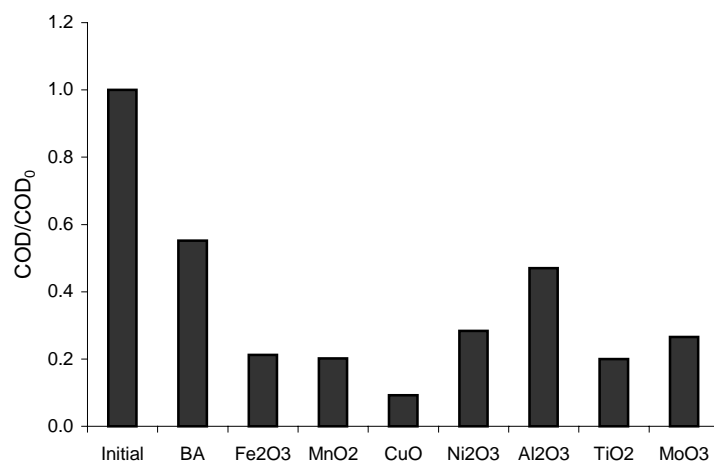


Fig. 4. The COD removal after 1 h of ozonation of benzoic acid (BA).

Improvement of COD removal by catalytic ozonation

The catalytic ozonation improved the COD removal relatively to the non-accompanied ozonation (Fig. 4). Although only a slight acceleration of BA degradation was observed in the catalytic ozonation, the removal of COD was significantly enhanced by addition of catalysts. An improvement of COD removal was observed in both homogeneous and heterogeneous catalytic ozonation at all stages of the degradation including the early stage. The improvement of COD removal observed in the catalytic ozonation testified to the ability of catalysts to enhance the degradation of oxidation intermediates.

CONCLUSIONS

Only a slight acceleration of the degradation rate of BA was observed in the catalytic ozonation in the presence of Fe₂O₃, MoO₃, and MnO₂, whereas other catalysts did not accelerate BA degradation at all. Nevertheless, a significant improvement in the COD removal was observed in the catalytic ozonation of BA. The improvement of COD removal testified to the ability of catalysts to enhance the degradation of intermediates. Catalytic ozonation as one option of the advanced oxidation processes gives a wide range of opportunities to enhance the degradation of resistant compounds. However, as the theory and practice for catalytic ozonation have not yet been developed sufficiently, the performance of catalysts in ozonation is quite sensitive to treatment conditions as well as to the compound and, therefore, is not easily predicted.

The Fenton treatment and ozonation combined with the Fenton treatment are other options to remove BA. On the basis of experiments the concentrations [Fe²⁺]₀ = 0.4 mM and [H₂O₂]₀ = 4 mM can be considered optimum for the

removal of BA from the solution. Combination of ozonation and the Fenton treatment enhanced the degradation of BA as compared with non-accompanied ozonation and catalytic ozonation with homogeneous Fe^{2+} by a factor of 1.6–1.8.

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Bensoehappe oksüdeeriv lagundamine metall-ioonsete katalüsaatorite juuresolekul

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Katalüütiline osoonimine kui üks täiustatud oksüdatsiooni protsesse pakub laialdasi võimalusi püsivate saasteainete lagundamiseks. Võrreldi homogeenseid (Fe^{2+} , Mn^{2+} , Cu^{2+} , Ni^{2+} , Mo^{6+} ioonid) ja heterogeenseid (Fe_2O_3 , MnO_2 , Ni_2O_3 , CuO , Al_2O_3 , MoO_3 , TiO_2 oksiidid) katalüsaatoreid bensoehappe (BH) oksüdeerival lagundamisel. Ehkki tavalise osoonimisega võrreldes saavutati BH katalüütilisel osoonimisel ainult vähene BH lagunemise reaktsiooni kiirenemine Fe_2O_3 ,

MoO₃ ja MnO₂ juuresolekul, oli katalüsaatorite mõju lahuse keemilise hapnikutarviduse (KHT) vähenemisele väga oluline. See tõestab katalüsaatorite võimet kiirendada oluliselt esmase reaktsiooni vaheproduktide edasist lagunemist. Osoonimise ja Fentoni reagenti (Fe²⁺/H₂O₂) kombinatsioon osutus BH lagundamisel kõige efektiivsemaks. BH lagunemine kiirenes 1,6–1,8 korda, võrreldes tavalise osoonimise ja katalüütilise osoonimisega Fe²⁺ ionide juuresolekul. Kuna katalüütiliste protsesside teoreetilised alused on senini veel täielikult välja töötamata, on katalüsaatorite käitumine protsessi tingimuste suhtes väga tundlik ning raskesti etteaimatav.