

THE EXTREMELY HIGH STABILITY OF CARBOFURAN PESTICIDE IN ACIDIC MEDIA

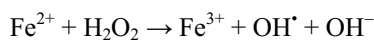
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Environment friendly iron catalysts were applied in the decomposition reactions of some toxic compounds like phenol, methomyl and carbofuran pesticide. The applied catalytic processes belong to photo-Fenton reactions. Heterogeneous iron catalysts showed significant activity in phenol and methomyl conversion, however, these catalysts were completely inactive in destruction of carbofuran molecule, even in the catalytic reaction promoted with UV light at high temperature.

KEYWORDS: Heterogeneous photo-Fenton reaction, phenol, methomyl, carbofuran, destruction

INTRODUCTION

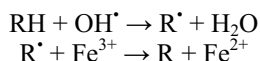
Water pollution problem is a major issue of environmental protection. Photocatalytic oxidation processes can degrade organic compounds at low and medium concentration being almost free of secondary pollution (1). These chemical processes, known as advanced oxidation processes (AOP), are methods for the generation of highly reactive intermediates, above all the hydroxyl radical, which is able to oxidize almost all organic pollutants (2). The classical procedure consists of addition of hydrogen peroxide to a solution or suspension in the presence of iron ions. The reaction involves a number of steps, the most important being (3):



The combination of iron and other metal ions (4) with hydrogen peroxide in acidic media is an efficient source of hydroxyl radicals which in the process of photo-Fenton reaction are added to aromatic, heterocyclic rings, as well as to the unsaturated compounds of alkenes or alkynes (3).

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The proposed degradation scheme of phenol via identified di-, tri- and tetrahydroxybenzene, etc. is given in (5). Hydroxyl radicals can also abstract a hydrogen atom, initiating a radical chain reaction (3):



Natural water and wastewater are usually very complex systems and contain a variety of organic and inorganic substances. In this work, the destruction of the molecules of frequently used pesticides as methomyl and carbofuran is given. The results are completed with our previously obtained data concerning catalytic wet peroxide phenol conversion (6,7). Phenol (IUPAC name Hydroxybenzene) belongs to weak acids. Its solubility in water is 67 g/litre at 16°C. Phenol appears very often in waste waters of crude oil refineries, petrochemical, dye and lacquer industries. Methomyl (IUPAC name S-methyl N-[(methyl-carbamoyl)oxy] thioacetimidate) is often used as an effective insecticide. However, it is a very toxic and hazardous pesticide. Its solubility in water is 57.9 g/L at 25°C. Methomyl is stable in water for 30 days at pH=5-7, and at temperatures up to 140°C. When exposed to sunlight at ambient temperature it is stable for 120 days (8). Methomyl has a low sorption affinity to soils and can easily cause both ground- and surface-water contamination (9). Carbofuran (IUPAC name 2, [3-dihydro-2, [2-dimethyl-benzofuran-7-yl methylcarbamate) belongs to commonly used insecticides, and is also a toxic and hazardous material. Its solubility in water is 351 mg/L at 25°C. Carbofuran is stable in acidic and neutral, and unstable in alkaline media. It decomposes over 150°C (10). The structural formulas of the investigated toxic materials are shown in Figure 1.

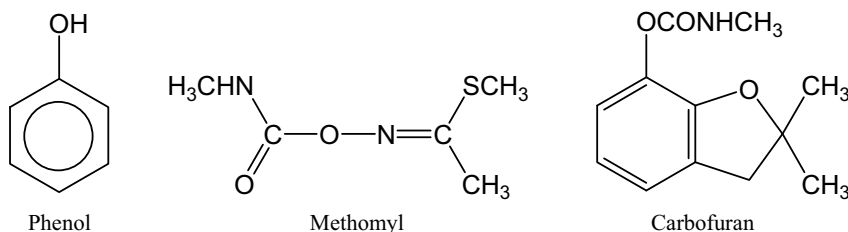


Fig.1. Structural formulas of the investigated toxic materials

Degradation of carbofuran by using ozone, UV radiation, and homogeneous AOPs was studied by Benitez *et al.* (11). The most effective process in removing carbofuran was the homogeneous photo-Fenton system. These results encouraged us to do the experiments with two heterogeneous iron catalysts under the Fenton reaction conditions.

EXPERIMENTS

Synthesis of catalysts

AlFe-pillared clay catalyst (PILC): The purified parent bentonite clay (Šipovo, Republic Srpska), Ca-type, was used for PILC catalyst preparation. The raw bentonite clay

was dried (105°C), milled and sieved ($\leq 63 \mu\text{m}$). Hydro-separation procedure (JUS U.B1.018, 1980) was used to separate the grain size $\leq 2 \mu\text{m}$, expecting to increase the montmorillonite fraction as confirmed by XRD analysis (7).

Pillaring solution (iron and aluminium nitrate solution with molar ratio Fe/Al = 1) was prepared by slow adding of the base (0.2 M NaOH) to the mixed metal nitrate solution under constant stirring (OH/metal molar ratio equal 2), and aging afterwards overnight at room temperature. The 1 mass% clay water suspension was doped by pillaring agent drop-wise under constant stirring, following by overnight aging at room temperature. Filtered and washed samples were air-dried, first at ambient temperature and afterwards at 105°C for 4 hours. The isothermal calcination at 300°C was performed in static air for 2 hours. One gram pillared montmorillonite catalyst contains 5 mmol (iron + aluminium) cations. The applied physico-chemical methods for catalyst characterization are given elsewhere (7).

Fe-ZSM-5 catalyst: Another catalyst used for wet peroxide oxidation of phenol and both carbamates (methomyl and carbofuran) was a commercial ZSM-5 zeolite-supported Fe catalyst. According to Kögel et al. (12), this catalyst is obtained by solid-state ion exchange of NH_4^+ ions of commercial ZSM-5 zeolite with Fe^{2+} ions. The applied zeolite catalyst was produced by ALSI-PENTA Zeolithe GmbH, Schwandorf, Germany (13).

Homogeneous iron catalyst: The third catalyst used in this work was the iron ions obtained by direct dissolution of an appropriate quantity of iron salt, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (methomyl and carbofuran conversion) and $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (carbofuran conversion) in the reaction solution.

Characterization of samples

The applied physico-chemical methods for catalyst characterization are given elsewhere (7, 14).

Catalysts activity measurements

Phenol and carbamates oxidation were carried out at room temperature in a glass batch reactor at constant pH = 3.5-4.0. A volume of 100 cm^3 of water solution with the defined concentration of pollutant was placed into the reactor, together with 2.0 cm^3 0.1 M H_2O_2 and 0.1 or 0.5 g of an appropriate powdered catalyst (Fe-ZSM-5 or AlFe-pillared clay). The reaction was carried out under vigorous stirring and at constant airflow 30-35 cm^3/min , and under halogen lamp light. The catalyst testing of carbofuran conversion was carried out at both ambient and elevated temperature (85°C), and illuminating the reaction solution with UV light (Philips, 15 W).

Pollutant content in the reaction solution was followed using a Pharmaspec UV-1700, Shimadzu spectrophotometer, with a 1-cm quartz cell. Absorbances at 240 nm, 275 nm and 510 nm were followed in case of methomyl, carbofuran and phenol, respectively. The reaction was followed in time-on-stream after 1, 2, 3 and 4 hours, and corresponding conversion was determined as $X (\%) = (A_0 - A_t) \times 100 / A_0$, where A_0 is the absorbance of the solution at the beginning of catalytic reaction, and A_t is the absorbance of the solution in the measurement time, t.

RESULTS AND DISCUSSION

The resulting catalysts' activities are listed in Table 1. All applied catalysts, homogeneous and heterogeneous, showed significant activity in phenol and methomyl conversion. At lower phenol concentration (0.5×10^{-6} mol/L) both homogeneous and zeolite-iron catalyst, Fe-ZSM-5, yielded a 100 % phenol conversion after only 1 hour of the reaction. At ten times higher phenol content (5.3×10^{-6} mol/L), however, the total phenol conversion was achieved only with homogeneous iron catalyst, while the conversion with Fe-ZSM-5 catalyst dropped to only 46 %. AlFe-PILC catalyst show significantly lower catalyst activity in phenol conversion comparing to the homogeneous iron catalyst and heterogeneous zeolite supported iron catalyst. The phenol conversion was 49% at lower and only 9% at higher phenol concentration of the starting solution. Besides, a saturation phenomenon was observed in the presence of pillared interlayered clay catalyst: the phenol conversion after 4 hours was the same as it was after only one hour.

Table 1. Kinetics of phenol, methomyl and carbofuran conversion in %, on different unsupported and supported iron catalysts

Catalyst	Cat.load [#]	Substrate	C ₀ , mol/L	1 h	2 h	3 h	4 h
Fe ³⁺ (nitrate)	505	Phenol	0.5×10^{-6}	100	-	-	-
Fe ³⁺ (nitrate)	505	Phenol	5.3×10^{-6}	100	-	-	-
AlFe-PILC	500	Phenol	0.5×10^{-6}	49	-	-	49
AlFe-PILC	500	Phenol	5.3×10^{-6}	9	-	-	9
Fe-ZSM-5	500	Phenol	0.5×10^{-6}	100	-	-	-
Fe-ZSM-5	500	Phenol	5.3×10^{-6}	46	-	-	-
AlFe-PILC	500	Methomyl	1.0×10^{-4}	29.1	47.4	48.9	57.3
Fe-ZSM-5	100	Methomyl	1.0×10^{-4}	82.2	85.7	91.9	96.4
Fe ³⁺ (nitrate)	505	Carbofuran	1.0×10^{-4}	0	0	0	0
AlFe-PILC	500	Carbofuran	1.0×10^{-4}	0	0	0	0
Fe-ZSM-5	500	Carbofuran	1.0×10^{-4}	0	0	0	0

[#]Catalyst loading: mg/100 cm³ substrate

Fe-ZSM-5 catalyst was significantly more active comparing to the AlFe-PILC catalyst in methomyl conversion, too. This catalyst was more active even at lower catalyst loading. Catalyst loading of AlFe-PILC five times of Fe-ZSM-5 catalyst converts only 57.3% of phenol, comparing to 96.4% conversion for Fe-ZSM-5 catalyst. However, both applied catalysts showed no activity in the carbofuran conversion (Figures 2-4), even at an elevated temperature, 85°C.

Similar results were obtained by investigating photocatalytic degradation of carbofuran using semiconductor oxides (15). The rate of degradation increased with increase in pH from 4 to 7. Since the p*H*_{zpc} (zero point of charge) of TiO₂ is 6.8, the surface of the catalyst is protonated and positive below 6.8. Again, at such pH values, carbofuran might also be protonated at the carbonyl oxygen. Such protonation might result in electrostatic repulsion between the catalyst and carbofuran, and could reduce both adsorption and degradation rate.

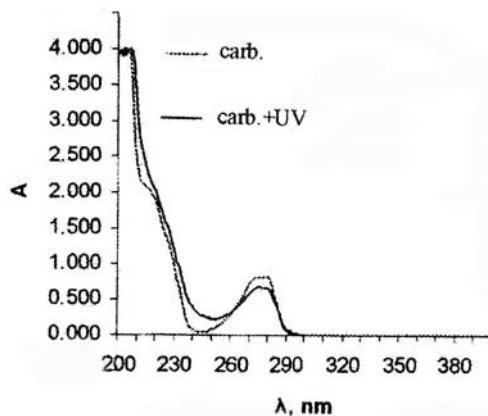


Fig.2. Absorbance of carbofuran solution in the absence and presence of UV light (ambient temperature, after 4 hours of irradiation)

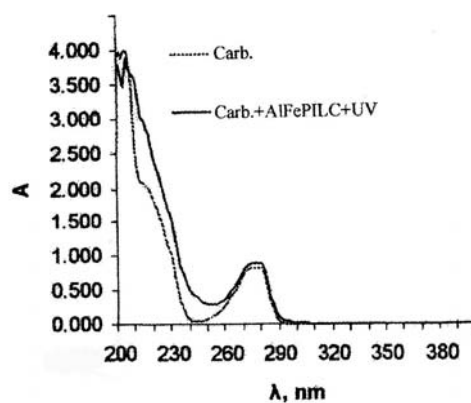


Fig.3. Absorbance of carbofuran solution in the absence and presence of AlFe-PILC catalyst and UV light (ambient temperature, after 4 hours of irradiation)

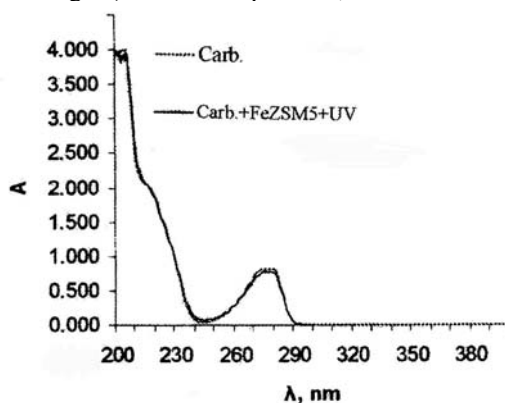


Fig.4. Absorbance of carbofuran solution in the absence and presence of Fe-ZSM-5 catalyst and UV light (ambient temperature, after 4 hours of irradiation)

The reason for extremely different ability for catalytic destruction of carbofuran in acidic media comparing to the same of methomyl and phenol might be connected to the different oxidation stability of these pollutants. The oxidation of sulphides, methomyl molecule, is fairly and virtually every imaginable oxidizing agent, strong and weak can accomplish this reaction (16). Phenol oxidation is also a fairly and easy reaction. During phenol oxidation, several different reactive intermediates can be formed. The initial products are reactive themselves; phenoxy radicals and the final reaction products arise after several stages (17). However, the formation of the phenoxy radical in the carbofuran molecule is not possible, because the H atom in the OH group on the phenol molecule is substituted with $-\text{CONHCH}_3$. Besides, carbofuran stability can be explained by its geometrically closed structure, comparing to the open structure of methomyl and phenol. The real explanation of carbofuran stability demands further detailed theoretical and experimental investigation.

CONCLUSIONS

Homogeneous and heterogeneous iron catalysts were applied for phenol, methomyl and carbofuran decomposition in acidic aqueous media. The applied catalysts decompose phenol and methomyl successfully in photo-Fenton reaction. However, these catalysts were inactive for carbofuran degradation. The high chemical stability of carbofuran could be explained by its electronic structure but this claim requires further theoretical and experimental investigations.

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ЕКСТРЕМНО ВИСОКА СТАБИЛНОСТ ПЕСТИЦИДА КАРБОФУРАНА У КИСЕЛОЈ СРЕДИНИ

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Изучавана је фото-каталитичка разградња фенола, метомила и карбофурана у присуству катализатора на бази гвожђа. Примењени катализатори су показали знатну каталитичку активност у реакцијама разградње фенола и метомила, међутим били су потпуно инертни у реакцији разградње карбофурана. Неактивност примењених катализатора у реакцији разградње карбофурана може да се тумачи затвореном стабилном електронском структуром молекула карбофурана. Ова претпоставка међутим треба да се потврди детаљним теоријским и експерименталним истраживањима.

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