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A ROLE OF A CATALYST IN CATALYTIC OZONATION PROCESS.

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ABSTRACT

Ozone is one of the important oxidants used in water and wastewater treatment processes. It is a very effective oxidative agent in both technologies, however, the drawbacks of the usage of ozone (compared with chlorine) is higher cost of its production. Therefore, at present, there is an emphasis on maximizing the effect of ozone introduced into the water. Ozone can react with impurities according to both molecular and radical mechanism. The main disadvantage of the ozonation, which runs according to the molecular mechanism is formation of compounds such as aldehydes and organic acids, that can not be further oxidized due to the fact that such compounds react with ozone very slowly. On the other hand, free radicals reactions are preferred processes both in the water and wastewater treatment technology.

The search of techniques promoting the production of free radicals is directed mainly on combinations of the ozonation along with another factors contributing to the radicals' formation. These processes are known under the general name of Advanced Oxidation Processes (or the AOPs). One of them is a combination of ozonation process with the process of catalysis. This technique is called catalytic ozonation, and it aims on both generating more free radicals, also in low pH, and on facilitating the attack of ozone on organic molecules adsorbed on the catalyst. The end result is to increase the degree of impurities removal, or to induce their destruction, that can not be done by classical ozonation. In the catalytic ozonation both homogeneous and heterogeneous catalysis processes are used. Ozonation catalysts are some metals, heavy metals ions, insoluble in water oxides of these metals.

The authors investigated an efficacy of manganese dioxide (MnO_2) as catalyst during a process of ozonation of chloronitrophenols (CNPs), chiefly 2-chloro-4-nitrophenol. Chloronitrophenols belong to a group of compounds called chlorinated nitroaromatic compounds (CNAs). CNAs are highly toxic chemicals which have many uses in agriculture worldwide, as fungicides, herbicides and pesticides. These chemicals have been classified into three major groups: chloronitrobenzenes, chloronitrophenols, and chloronitrobenzoates.

Manganese dioxide applicability, as the catalyst in a catalytic ozonation, was considered both as ozone decomposition accelerator as well as a CNP adsorbent. The influence of presence of MnO_2 on an ozone decomposition was investigated at pHs 4,5 and 7,0 however the ozone decomposition, for ozone only, was also investigated at pH=9.0. The ozone decomposition was observed at both pHs. The CNP destruction during catalytic ozonation on MnO_2 was investigated at pHs 4.5 and 7.0 only, because on pH=9.0 CNP destruction efficacy is high also during classic ozonation. The highest impact of MnO_2 presence on CNP destruction efficacy was observed at pH=4.5. Thus manganese dioxide seems to be an effective catalyst, both as ozone decomposition accelerator as well as significantly increase yield of chloronitrophenols destruction, chiefly at low pH. On the other hand however the mechanism, of CNP destruction, seems to run according to molecular mechanism.

Keywords: Ozone, catalytic ozonation, catalysts, manganese dioxide, chloronitrophenols

1. Introduction

Ozone is one of the oxidants used in water and wastewater treatment processes. It is a very effective oxidative agent in both technologies, however, the drawbacks of the usage of ozone (compared with chlorine) is higher cost of its production. Therefore, at present, there is an emphasis on maximizing the effect of ozone introduced into the water. Ozone can react with impurities in accordance to both molecular and radical mechanism. The main disadvantage of the ozonation according to the molecular mechanism is relatively high selectivity of the reactions and formation of compounds such as aldehydes and organic acids that can not be further oxidized due to the fact that such compounds react with ozone very slowly. On the other hand, reactions concerning the use of the free radicals, is preferred process both in the water and wastewater treatment technology.

The search of techniques promoting the production of free radicals is directed mainly on combinations of the ozonation along with another factors contributing to the radicals' formation. These processes are known under the general name of Advanced Oxidation Processes (or the AOPs). One of them is a combination of ozonation process with the process of catalysis. This technique is called catalytic ozonation, and it aims on both generating more free radicals, also at low pH, and/or on facilitating the attack of ozone on organic molecules adsorbed on the catalyst. However, it should be noted that there are reports describing an effective pollutants' destruction by catalytic ozonation without the involvement of free radicals. Therefore we search rather for the methods where the end result is the increased degree of pollutant removal, or its destruction, that cannot be done by classical (single) ozonation. In the catalytic ozonation both homogeneous and heterogeneous catalysis processes are used. Ozonation catalysts are some metals, heavy metals ions, and metal oxides. Both homogeneous and heterogeneous catalysis are reviewed by Nawrocki *et al.* [1-3]. For the heterogeneous catalytic ozonation metal oxides have been used (MnO_2, TiO_2, Al_2O_3, $FeOOH$, Fe_2O_3, CeO_2, NiO, Ni_2O_3, CuO, CoO , SnO_2, MgO) as well as metals (Cu, Ru, Pt, Co) on supports (SiO_2, Al_2O_3, TiO_2, CeO_2, activated carbon), metal ion substituted zeolites and activated carbon [1-3]. One of the possibilities is to use a catalyst, which contains the metal (element) able to change the valence state easily. Manganese seems to be one of such elements. There is quite a few papers concerning the use of MnO_2 as an ozonation catalyst, but there are also many contradictions in these works. In general the catalytic processes are possible if at least one of the cases is fulfilled [1-4]:

- the ozone adsorption occurs on the surface of the catalyst and that results in formation of highly reactive radicals, (including hydroxyl radicals),
- adsorption of pollutant molecule on a catalyst' surface facilitates the attack of ozone on the molecule.
- both processes occur.

Proposed mechanism description is however frequently rather based on speculations of the authors than on the hard experimental data [1-3].

The investigations on mechanism of classic and catalytic ozonation of chloronitrophenols were the aim of this research.

2. Materials and methods
2.1. Reagents and reaction solutions

All chemicals used, obtained from Fluka, were of reagent grade or analytical grade, when available, and were used without further purification. Stock solutions were prepared in high quality pure deionized water (Millipore). Reaction solutions were prepared by spiking of high quality pure deionized water (Millipore) with 2-chloro-4-nitrophenol (2CNP).

Tert-Butyl alcohol (*t*BuOH, >99.8%) was used as a hydroxyl radical scavenger in some experiments. The pure water samples spiked with CNP were buffered, before oxidation, at desired pH by adding borax buffer solutions. The pH of reaction solutions was adjusted using aqueous solutions of H_3BO_3 and NaOH to maintain pH at levels of 4.5 and 7. Manganese dioxide (MnO_2), as the catalyst, was added in some experiments. Manganese dioxide was manufactured *in-situ* by means of reduction of potassium permanganate with sodium sulfite. Obtained MnO_2 suspension was twice washed with deionized water and subsequently

concentrated by sedimentation. MnO_2 were added, in some experiments, to reaction solution as concentrated sediment (2CNP destruction) or as dried powder (ozone decomposition).

2.2. Experimental procedures
2.2.1. Ozone decomposition
The experiments on ozone decomposition were carried out at room temperature (20 $^{\circ}$C) in a batch mode. The glass reactor was filled with buffered high purity water and was saturated with ozone up to reach ozone concentration between $1.7 \div 1,8$ mg O_3 L^{-1}. In some experiments dry MnO_2 was added to ozone saturated water. Concentration of ozone was measured according to indigo method. Samples of the ozone solution were collected after 0, 2, 5, 10, 15, 20, 25 and 30 minutes

2.2.2. 2CNP ozonation
The ozonation of 2CNP experiments were carried out at room temperature (20 $^{\circ}$C) in a semi-continuous mode. 1000 ml of model solution was transferred to the contact column and continuously treated with ozone for 20 min. MnO_2 were added, in some experiments, to reaction solution as concentrated sediment. Ozone was generated from pure oxygen and introduced to the reactor through a ceramic sparger. Total doses of ozone were fixed on the level of to 14 mg O_3 L^{-1} while O_3/CNP ratio equals 0.2 - 0.21 (M/M). Only during selected experiments 2CNP dose were significantly decreased, which results with O_3/CNP ratio of 1.2. pH of the buffered 2CNP solution ranged from 4.5 to 7.0. Samples of the reaction solution were collected at 0, 5, 10, 15 and 20 minutes during time of ozonation and subsequently, after ozonation cease, at 30, 40, 50 and 60 minutes and quenched with 0.025 M Na_2SO_3 (>98%, Fluka) in order to dissipate any residual ozone.

2.2.3. An influence of 2CNP adsorption on the surface of MnO_2.
Due to evaluation of an influence of 2CNP adsorption on the surface of MnO_2, a concentrated manganese dioxide suspension was added to 2CNP solution. The 2CNP concentration in solution was determined according to the same procedure as for ozonation samples collection.

3. Results and discussion
3.1. Ozone decomposition
Results of investigations on ozone decomposition of ozone alone and in the presence of manganese dioxide are shown in Fig 1.
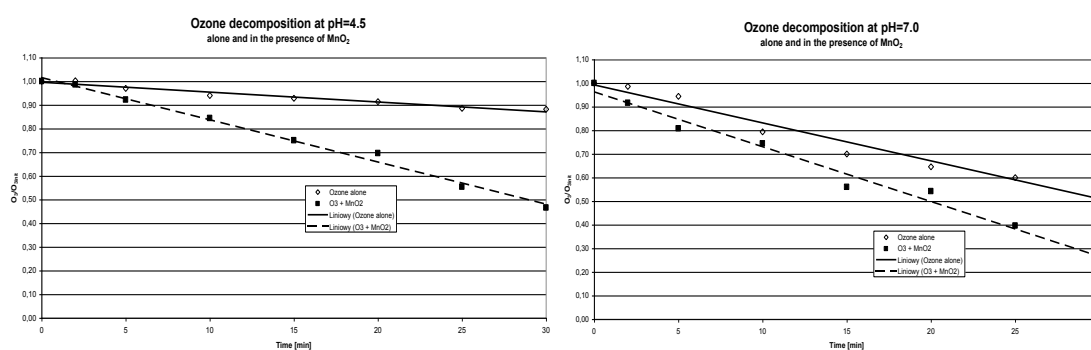

Figure1: Decomposition of ozone alone and in the presence of MnO_2 suspension at pH=4.5 (a left fig.) and at pH=7.0 (a right fig.).

As it shown in Fig.1. ozone decomposition runs faster at higher pH (it is obvious: the higher concentration of hydroxyl groups occurs at the higher pH). Moreover faster ozone decomposition runs in the presence of MnO_2 suspension, for both pHs, than for classic ozonations however observed effect is more distinct for lower pH.

3.2. 2CNP degradation
3.2.1. Ozone degradation during classic and catalytic ozonation.
The degradation of 2CNP was examined during classic and catalytic ozonation. Results obtained at pH equals to 4.5 is shown in Fig.2.
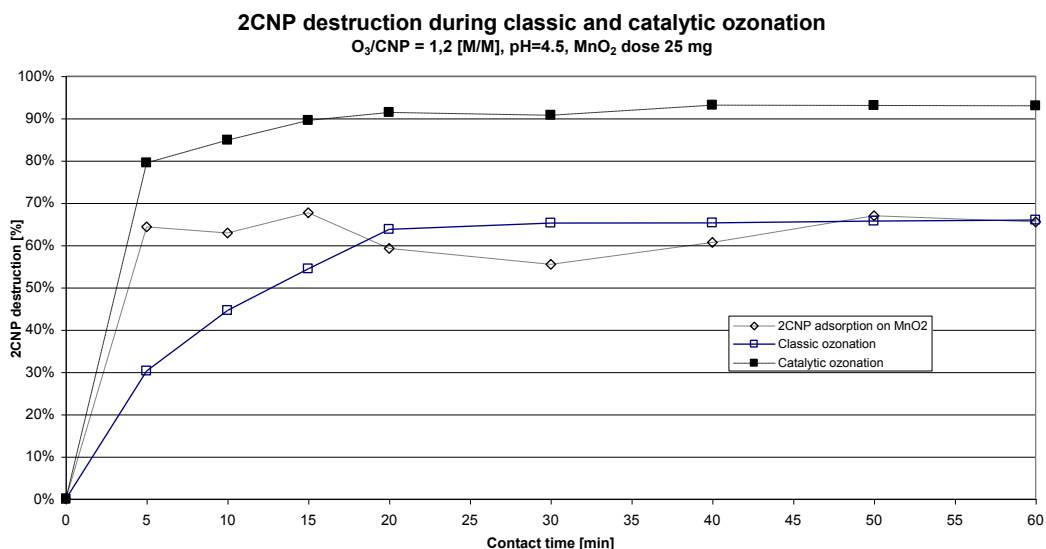

2CNP destruction during classic and catalytic ozonation
$O_3/CNP = 1,2 [M/M], pH=4.5, MnO_2$ dose 25 mg

Figure 2: The degradation of 2CNP during classic and catalytic ozonation at pH 4.5.

At pH=4.5 an influence of MnO_2 presence on 2CNP degradation is considerable. 2CNP adsorption at the level of app. 60%, however makes evaluation of 'net' catalytic effect difficult.

3.2.2. An influence of TBA presence on 2CNP degradation: ozonation mechanism examination
The degradation of 2CNP were examined also in an absence and a presence of TBA a radical scavenger. Results obtained during 2CNP ozonation in an absence and a presence of TBA at pHs 4.5 and 7.0 is shown in Fig.3.
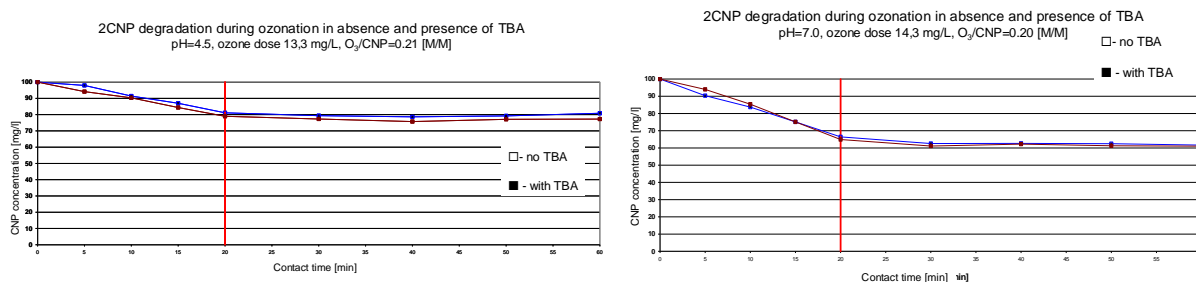

2CNP degradation during ozonation in absence and presence of TBA
pH=4.5, ozone dose 13,3 mg/L, $O_3/CNP=0.21 [M/M]$

2CNP degradation during ozonation in absence and presence of TBA
pH=7.0, ozone dose 14,3 mg/L, $O_3/CNP=0.20 [M/M]$

Figure 3: 2CNP classic ozonation in an absence and a presence of TBA at pHs 4.5 (left fig.) and 7.0 (right fig.).

No significant differences were observed between yields of 2CNP destruction in the presence and in the absence of TBA , independently of reaction pH.

3.2.3. An influence of TBA presence on 2CNP degradation during catalytic ozonation
The degradation of 2CNP were examined also during catalytic ozonation (with MnO_2 addition) in an absence and a presence of TBA a radical scavenger. Results obtained during 2CNP catalytic ozonation in an absence and a presence of TBA at pH 7.0 is shown in Fig.4
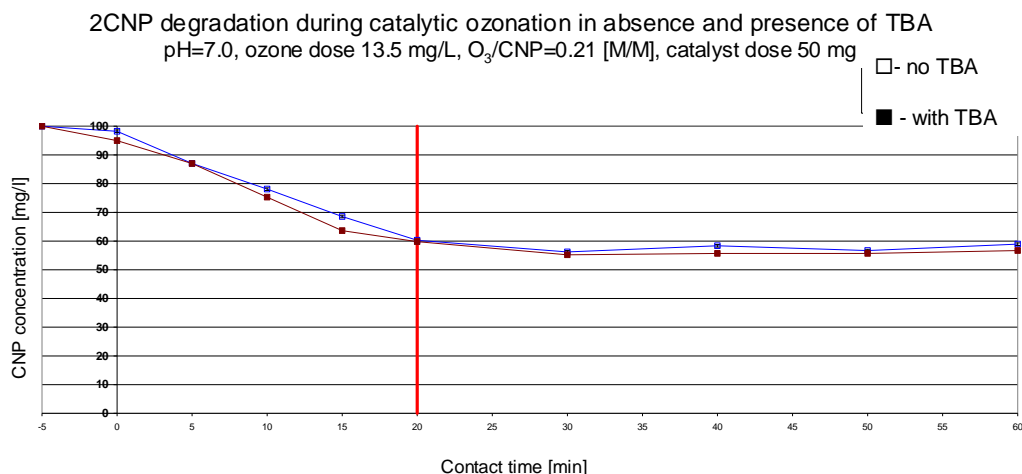
2CNP degradation during catalytic ozonation in absence and presence of TBA
pH=7.0, ozone dose 13.5 mg/L, O_3/CNP=0.21 [M/M], catalyst dose 50 mg

□ - no TBA
■ - with TBA

Figure 4: 2CNP catalytic ozonation in an absence and a presence of TBA at pH 7.0

No significant differences were observed between yields of 2CNP destruction in the presence and in the absence of TBA also during catalytic ozonation. The efficacy of 2CNP destruction in presence of MnO_2 slightly increases at pH=7.0 (see Fig.6 and right part of fig. 5) but significantly at pH=4.5 (see fig. 4)

4. Conclusions

1. Manganese dioxide presence distinctly accelerates ozone decomposition.
2. The presence of manganese dioxide increases the efficacy of 2CNP destruction, chiefly at low pH
3. Despite of conditions favorable to radical mechanism a process of 2CNP destruction runs according to molecular mechanism.

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