

Chemical pretreatment of formaldehyde wastewater by selected Advanced Oxidation Processes (AOPs)

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Chemical oxidation processes: Fenton process and catalytic ozonation with Mn^{2+} ions were investigated for effectiveness of formaldehyde (FA) oxidation. The influence of operational variables — O_3 , H_2O_2 , Mn^{2+} and Fe^{2+} concentrations and reaction time were investigated. Researches were carried out on aqueous solution of FA, which concentration was 500 mg/l. Fenton process was investigated at pH 3 and catalytic ozonation at pH 7, 10 and 12. Results revealed that Fenton process was much more effective in FA degradation than catalytic ozonation with Mn^{2+} as a catalyst. The optimal H_2O_2/Fe^{2+} dosage for a Fenton process was 2000/1000 mg/l. COD and FA concentrations were reduced 59,6% and 79,5%. In case of catalytic ozonation with Mn^{2+} the effectiveness was much less and it was the biggest at pH 12 and Mn^{2+} dosage 25 mg/l where COD and FA concentration were reduced 14% and 38%. Therefore, Fenton process can be promising technology for FA wastewater pretreatment.

Topic description

Formaldehyde is widely used in the chemical industry including for the manufacture of phenol-formaldehyde and urea-formaldehyde resins and adhesives, dyes, plastics, explosives and pharmaceuticals. It is also used in hospitals, as a formalin solution (ca. 37% HCHO and 10% CH_3OH), for the preservation of biological preparations.

This aldehyde is toxic to living organisms, inhibiting the physiological activity of the cells by creating permanent connections with amino groups of proteins. Formaldehyde also causes DNA damage, mutations in microorganisms and mammalian cells, and therefore creates a carcinogenic risk.

Wastewater containing formaldehyde are toxic to microorganisms. When its concentration exceeds 300 mg/l, the biological treatment process is almost completely inhibited [1]. Therefore, a formaldehyde concentration must be significantly decreased before a biological wastewater treatment. It is possible to apply chemical oxidation for example Advanced Oxidation Processes (AOPs).

A number of publications on the chemical pretreatment of formaldehyde wastewater by AOPs is inconsiderable [2–11]. Most studies were performed on formaldehyde solutions prepared from formalin.

Composition of formaldehyde wastewater varies depending on the type of production. In the case of wastewater from the production of phenol-formaldehyde and urea-formaldehyde resins are mainly: formaldehyde, volatile phenols, volatile aromatic hydrocarbons (xylene), chloroform, trichloroethylene and from inorganic compounds mainly chlorides and ammonia nitrogen. This wastewater has very high COD values (even above 100000 mg O_2/l) and low BOD_5/COD ratio what means that their susceptibility for the biological treatment is weak.

AOPs processes, which have been examined for use in formaldehyde wastewater treatment were: Fenton's process, photo-Fenton's process, electro-Fenton's process, ozonation with the addition of H_2O_2 , catalytic ozonation and H_2O_2/UV process.

Especially interesting are catalytic ozonation processes with different catalyst. There are 2 kinds of catalysis — homogenous and heterogeneous.

Homogenous catalysts are metal ions, which added to the examined solution, cause ozone activation by its decomposition with hydroxyl radical production. These are transition metals ions such as: Fe^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Ag^+ , Cr^{3+} or Zn^{2+} . The nature of transition metal applied determines not only the reaction rate, but also selectivity and ozone consumption. Most of the above mentioned ions gave good effects in catalytic

ozonation of humic substances [12]. Mn^{2+} and Fe^{2+} ions were found to be effective catalysts of the ozonation of chlorinated benzene derivatives. A high decrease of examined compounds as well as COD and TOC were achieved [13].

Heterogeneous catalysts are metal oxides or metals/metals oxide on supports. Heterogeneous catalysts are more often applied than homogenous. The most commonly used metal oxides are: MnO_2 , TiO_2 and Al_2O_3 and metals/metals oxide on supports: $Cu-Al_2O_3$, $Cu-TiO_2$, $Ru-CeO_2$, $V-O/TiO_2$, $V-O/silica$ gel and TiO_2/Al_2O_3 , Fe_2O_3/Al_2O_3 . The catalytic activity of the above-mentioned catalysts is mainly based on the catalytic decomposition of ozone and the enhanced generation of hydroxyl radicals, which are strong oxidants. As can be seen in the case of heterogeneous catalytic ozonation processes there are still major research capabilities. They are related for example with the possibilities of mixing different metals oxides or application of different supports in the case of one metal oxide and testing of their catalytic activity. It is also possible to obtain the same catalyst in different conditions (eg. in different calcination temperature). It affects its structure and the surface area and thus its ability to catalysis.

Several studies concerning application of catalytic ozonation for the oxidation of different organic compounds were performed. However, only a very small part of them concerned formaldehyde.

TiO_2 was efficient in the oxalic acid degradation in water at acidic pH [14] and Al_2O_3 was effective in the decomposition of 2-chlorophenol at neutral pH [15].

Catalytic efficiency of MnO_2 has been proved for many organic compounds such as: atrazine [16], oxalic acid [17], pyruvic acid [18], propionic acid [19].

$Fe(III)/Al_2O_3/O_3$ system was effective in phenol and its ozonation by-products removal from water. A significant decrease of TOC was obtained [20]. TiO_2/Al_2O_3 calcinated at $500^\circ C$ gave good results in the degradation of humic substances [21]. Al_2O_3 , TiO_2/Al_2O_3 and Fe_2O_3/Al_2O_3 were active in the degradation of oxalic acid, chloroethanol and chlorophenol in water. The modification of the Al_2O_3 surface both with TiO_2 and Al_2O_3 resulted in significant increase of oxidation efficiency (with exception of oxalic acid) than bare Al_2O_3 [22].

The literature report on application of various AOPs processes to formaldehyde oxidation, also catalytic oxidation is presented below. They were mainly carried out on an aqueous solution of formaldehyde, prepared from formalin.

Kajitvichyanukul et al. [2] studied Fenton, photo-Fenton and H_2O_2/UV processes. The study was conducted in an aqueous solution containing 10000 mg/l of formaldehyde and 252,8 mg/l of methanol. These authors achieved 90% and 94% decrease of HCHO

concentration in a Fenton and a photo-Fenton's process respectively. In the case of two-stage process: Fenton and photo-Fenton similar results to the photo-Fenton's process were obtained. The optimal reaction parameters were as follows: pH 2,6, reaction time 80 min, 22768 mg/l H_2O_2 , 3735 mg/l Fe^{2+} . In all these cases decrease of TOC value after 120 min of process were detected (approximately 45% in the photo-Fenton's process and about 25% in the Fenton's process.)

In H_2O_2/UV process after 240 min complete formaldehyde oxidation were achieved. However, no decrease of toxicity of compounds present in examined solution was found. The TOC value before and after 240 min of reaction was differ by less than 5%. It indicates that oxidation of HCHO was incomplete and HCOOH was generated.

These same authors [3] examined also formaldehyde oxidation in a photo-Fenton's process with simultaneous control of changes in methanol concentration. Examined solution of HCHO and optimal reaction conditions were the same as in previous work [2]. Concentrations of formaldehyde and methanol decreased by 94% and 78% respectively.

Do and Chen [4] studied electro-Fenton's process using anodized graphite as a cathode. The study was conducted in an aqueous solution of formaldehyde at initial concentration of 514 mg/l. H_2O_2 was generated at the cathode and Fe^{3+} was added as a reactant. 99% decrease of formaldehyde concentration was obtained. The optimum conditions were as follows: pH 13, current density 0,75 mA/cm², temperature $45^\circ C$, oxygen flow of 2 cm³/s.

Above mentioned authors [5] also examined the electro-Fenton's process in which as a cathode was used unanodized graphite. Aqueous solution of formaldehyde was studied. The process was conducted in conditions such as in [4] with the exception of current density which was 0,5 mA/cm². In such conditions a decrease of formaldehyde concentration from initial 1000 mg/l to 1 mg/l was obtained.

Do and Yeah [6] studied the electro-Fenton's process involving the generation of oxidizers on both electrodes (ClO^- at anode and H_2O_2 at cathode). The research were carried out in an aqueous solution of formaldehyde at initial concentration of 3000 mg/l — anolite and 1500 mg/l — catholite. The optimum process conditions were as follows: for a catholite: pH 13, temperature $45^\circ C$, current density 0,75 mA/cm², volume of examined solution 250 ml, stirring rate 600 rpm; for anolite: current density 41 mA/cm², volume of examined solution 120 ml, other parameters such as the catholite. A charge for both electrodes was 1800 C. In these conditions decrease of formaldehyde concentration by 93% and 62% was achieved for catholite and anolite respectively.

Murphy et al. [7] investigated a Fenton-like process, where instead of Fe^{2+} ions were used Fe^{3+} ions (as FeCl_3). Experiments were conducted in an aqueous formaldehyde solution at initial concentration of 500 mg/l. 95% formaldehyde concentration decrease was obtained after 90 min of reaction at 25°C. The molar ratio of H_2O_2 : HCHO was 6:1.

Parisheva et al. [8] studied the ozonation process at acidic and alkaline pH with the addition of H_2O_2 . Experiments were carried out in an aqueous solution, which initial HCHO concentration was 100 mg/l. In an acidic medium (pH 3,5) with the addition of 0,1 and 0,01 mol/l H_2O_2 concentration of formaldehyde decreased by 99% and 90% respectively. When ozone was used alone (pH 3,5) percentage was only 58%. In an alkaline medium (pH 10) with the same additives of H_2O_2 , HCHO concentration reduced by 89% and 87% respectively. When only ozone was applied the efficiency was only 34% (pH 10).

Parisheva et al. [9] also carried out a research on catalytic ozonation. The study was conducted in an aqueous solution of HCHO — initial concentration 100 mg/l. When the mixture of MnO_2 and MoO_3 in weight ratio 5:1 was applied (10 g/l MnO_2 and 2 g/l MoO_3) at pH 10, 88% decrease of HCHO concentration was obtained. No catalytic effect was found for pure MoO_3 .

Moussavi et al. [10] studied the catalytic oxidation where MgO nanocrystals were used as a catalyst. MgO nanocrystal powder was prepared by calcinating a $\text{Mg}(\text{NO}_3)_2$ solution. The $\text{Mg}(\text{NO}_3)_2$ solution was first dried at 100°C. The remaining material was calcinated in air at 500°C for 2h, producing the final MgO nanocrystals. Experiments were conducted in an aqueous formaldehyde solution at initial concentration of 7000 mg/l. The authors achieved a decrease in the concentration of HCHO and COD by 79% and 66% respectively. The effluent was post-treated in SBR system, which completely removed HCHO and removed 98% of COD (to a lower than 60 mg/l O_2). The optimum conditions were found to be: a pH of 8, 5 g/l of MgO powder, 3060 mg/l H_2O_2 , reaction time 120 min and 0,153 g/l/min O_3 . The changes of methanol concentration during a process was not investigated. Simultaneously, at the same conditions, catalytic ozonation with TiO_2 (anatase) was investigated. Results revealed only 18% decrease of HCHO concentration in this process. It indicates that the MgO in this case is a much better catalyst.

Christoskova and Stoyanova [11] investigated the catalytic decomposition of HCHO and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$. As a catalyst was used nickel oxide ($\text{Ni}_x(\text{OH})_y\text{O}_z \cdot m\text{H}_2\text{O}$). When it comes to HCHO researches were conducted in an aqueous solution of formaldehyde at initial

concentration of 30000 mg/l. 90% of the oxidation of HCHO was obtained. HCOOH as a by-product was detected. The process was carried out under the following conditions: pH 7, temperature 298 K, catalyst dose 2 g/l, reaction time 150 min. Oxygen from the air was used as an oxidizer. Solution was saturated with oxygen for 30 min before catalyst addition and it was continued in order to maintain a constant concentration of dissolved oxygen during the entire experiment.

One of the other methods of concentrated formaldehyde wastewater treatment is adding to them Na_2SO_3 . It causes a formation of complex compound of formaldehyde with sulfate(IV), which is well-biodegradable by microorganisms. In order to gain good effect it is necessary to add sulfide(IV) in an amount corresponding to the concentration of formaldehyde in wastewater [1].

Researches Methodology

Tests were conducted in an aqueous solution of formaldehyde prepared from formalin (37% HCHO and 10% of CH_3OH) which concentration was 500 mg/l. Fenton process was carried out in a beaker with a capacity of 1 l. Solution in a beaker was slowly stirred all the times with a magnetic stirrer. Catalytic ozonation was carried out in a cylindrical reactor with a 80 mm diameter and sample volume of 1 l. As a source of ozone was used laboratory ozone generator of Wedeco Company — type BMT/LAB802N with a capacity of 250 g/ Nm^3 . Ozone remaining after the reaction was burned in a Bunsen burner. As a catalysts was used MnSO_4 solution which concentration was 1 cm^3 = 10 mg Mn^{2+} . Solution of catalysts was added using a pipette after pH correction to 7, 10 or 12 by means of 1M and 0,1M NaOH. FA was determined using a method of titration with sulphate sodium(IV) [23]. COD was determined according to ISO 6060 and ISO 15705 (miniaturized method). These marks were made after removing the residual hydrogen peroxide by catalase. Catalase solution was prepared by diluting a commercial solution of catalase (Sigma-Aldrich) with a volume of 2,941 ml (23,000 U/mg of protein, 34 mg of protein/ml) of distilled water to 50 ml. Thus obtained solution with a concentration 45997,24 U/ml. Knowing that 1 U of catalase at 20°C decomposes 1 mmol of H_2O_2 for 1 min, the volume of a dilute solution of catalase required to decompose the remaining H_2O_2 was calculated. In practice it was used in two-, three-fold excess due to unfavorable environmental conditions. Complete removal of H_2O_2 was confirmed iodometrically. Remaining after the reaction H_2O_2 was determined iodometrically as well.

The course of study and the results

Fenton process

Extensive research on the aqueous solution with a concentration of FA from 468 to 540 mg/l and COD from 657 to 756 mg/l O₂ were conducted in previous work [25]. In these studies, the following dosages H₂O₂/Fe²⁺: 1000/250, 1000/500, 1500/500, 1500/750, 2000/1000 and 2500/1000 mg/l were examined. For each of the tested doses were done two series of tests and the results were averaged. All tests were carried out at pH 3.0. Preliminary trials have shown that FA oxidation process occurs rapidly after addition of reagents. Therefore, the first measurement was performed after 1 min, measured from the addition of all reagents (it took about 20 seconds). To check that the reason for the rapid disappearance of FA is not its trimerisation, occurring at pH 3.0 or under the influence of Fe²⁺ ions, after 1 min were analyzed the effect of the process

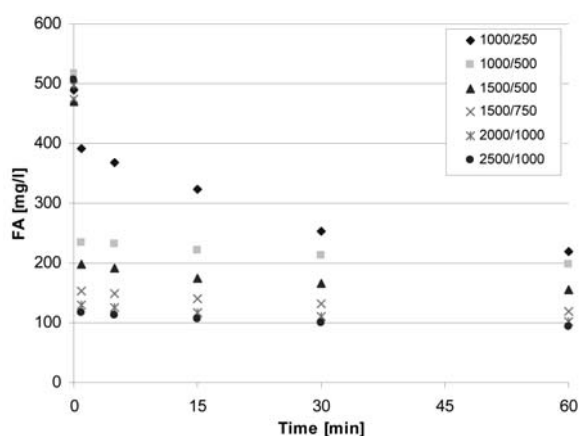


Fig. 1. Removal of FA from aqueous solution in the Fenton process — FA concentration change over time for different H₂O₂/Fe²⁺ dosages [mg/l].

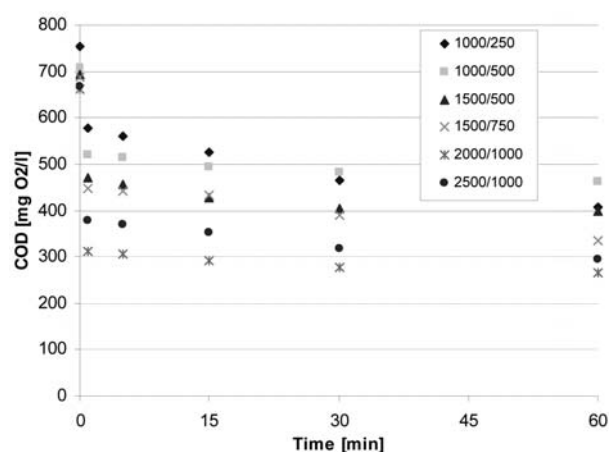


Fig. 2. Removal of FA from aqueous solution in the Fenton process — change of the COD value over time for different H₂O₂/Fe²⁺ dosages [mg/l].

without the addition of H₂O₂ and the effect of oxidation by H₂O₂ at pH 3.0 and subsequent neutralization. In both cases, the concentration of FA has not changed. Results of studies on the effect of Fenton's process are shown in Fig. 1–2. That rapid decrease in the concentration of formaldehyde during 1 min was varied from 20 to 76%, depending on the dosage of the reactants. FA concentration significantly decreased in a very short time, accompanied by smaller but significant decrease in COD values. After a very short time, the further decrease in the concentration of FA was much slower. After 15 min the FA concentration decreased by 64–78% and after 60 min of 74–82% depending on the dosage of the reactants.

Similar results were obtained for H₂O₂/Fe(II) dosages: 1500/750, 2000/1000 and 2500/1000 mg/l. The 2500/1000 dosage gave the best results. However, the difference of results was small, particularly at dosages of 2000/1000 and 2500/1000 mg/l. The other tested doses gave worse results.

Catalytic ozonation with Mn²⁺ ions

Tests were conducted in an aqueous solution with FA concentration from 490 to 510 mg/l and COD from 719 to 759 mg/l O₂. Examined pH was 7, 10 and 12, because ozonation take place at neutral and at high pH. Reaction time was always 60 min. Longer time of reaction gave only slightly better results (difference was less than 5%) that's why process was not continued. Concentration of ozone was ranging from 220 to 250 mg/l. During experiment various dosages of the catalyst — Mn²⁺ ions (as MnSO₄ solution) were examined. The following dosages of Mn²⁺ were examined: 5, 10, 20, 50 and 100 mg/l at pH 7, 50 and 100 mg/l at pH 10 and 25 and 50 mg/l at pH 12. For each of the tested doses were done two series of tests and the results were averaged. The best results were obtained at pH 12 for a dose of 25 mg/l Mn²⁺. However, the effectiveness of the process was small — the concentration of FA after 60 min decreased 38% and COD only 14%. For the rest of dosages at all examined pH values the effectiveness of the FA decomposition was worse. Results of studies on the effect of catalytic ozonation with Mn²⁺ ions are shown in Fig. 3–8.

Results discussion and conclusions

The presented results indicate that much more effective among examined processes was Fenton's process. The nature of changes in the concentration of FA in this case is somewhat different than for similar studies conducted by other authors. In studies on aqueous solution of FA rapid decrease of FA concentration after 1 min was observed. The reason for this apparent discrepancy

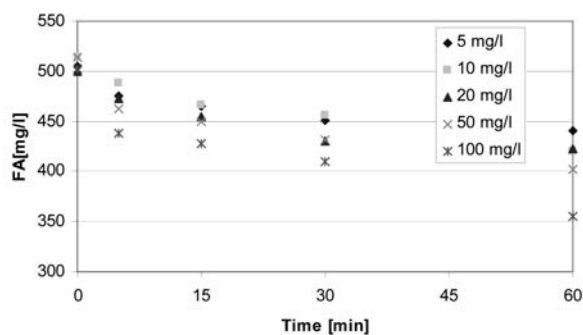


Fig. 3. Removal of FA from aqueous solution in the process of catalytic ozonation with Mn^{2+} ions at pH 7 — FA concentration change over time for different Mn^{2+} dosages [mg/l].

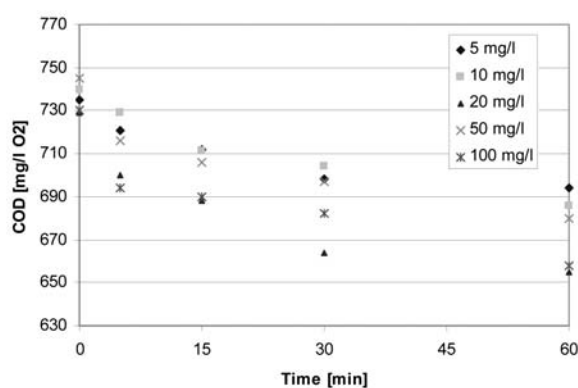


Fig. 4. Removal of FA from aqueous solution in the process of catalytic ozonation with Mn^{2+} ions at pH 7 — change of the COD value over time for different Mn^{2+} dosages [mg/l].

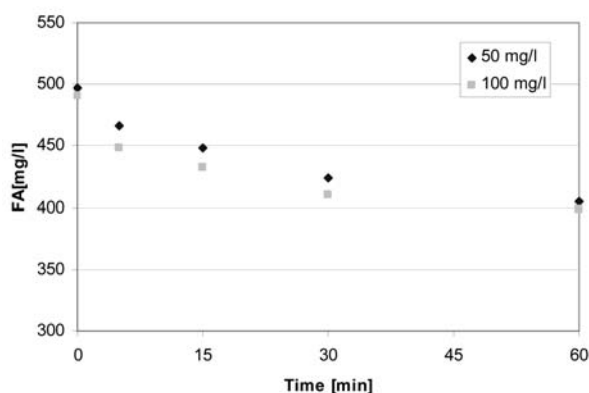
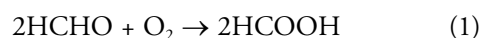


Fig. 5. Removal of FA from aqueous solution in the process of catalytic ozonation with Mn^{2+} ions at pH 10 — FA concentration change over time for different Mn^{2+} dosages [mg/l].

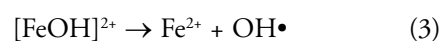
between the results of own research results and other authors is probably that they have not studied the changes in FA and COD concentration after such a short time [2, 7]. Obtained in these studies, the final result of removing the FA is slightly worse than the effect obtained by other authors [2, 7]. This may be due to the fact that

the authors conducted research on FA aqueous solution whose concentration was 20-fold higher than in the present study [2]. These authors also studied as a sole the effect of the addition of methanol and had accounted it in the overall result of the FA decomposition process. Methanol is oxidized to FA, so the actual decline in FA concentration is higher. In other works changes in the concentration of methanol have not been studied, which could also affect a difference in the results.

Obtained results show that Fenton process initially take place very quickly, after which its rate drops significantly. It can be caused by formic acid which is direct product of the oxidation of FA:



HCOOH is a carboxylic acid. In the absence of carboxylic acids the reproduction of Fe^{2+} ions proceeds according to the following reaction:



Formed HCOOH creates a complex compound of iron(III) — $[Fe(CH_3CO)_6]^{3+}$, making it difficult to reduce Fe(III) to Fe(II) and Fe^{2+} ions reproduction. As a result less hydroxyl radicals are formed in a solution. This factors probably contribute to the diminishing speed of the process. For this reason, the study was conducted only for 60 min, because at longer reaction times the effectiveness of the process was only a few percent higher regardless the dosage of H_2O_2/Fe^{2+} .

Catalytic ozonation with Mn^{2+} ions was much less effective than the Fenton process. It was chosen, because of high effectiveness for the decomposition of humic substances in water [12] and also due to nontoxicity of manganese. Poor effectiveness in case of formaldehyde was probably caused by its simple structure and resistance for oxidation in spite of its high redox potential. In alkaline solution FA can create difficult oxidizable FA polymers [24] what also can be reason for weak effectiveness of the process.

For both examined processes decrease in COD value was much less than decrease of FA concentration. This fact suggest that FA in both processes oxidized mainly to formic acid, which is direct product of FA oxidation. Further oxidation of HCOOH to carbon dioxide and water proceeded much worse.

The effect obtained in the Fenton process can be considered as good as it can be used in pretreatment of formaldehyde wastewater before its biological treatment. However, it is necessary to remember about removing of hydrogen peroxide remaining after the reaction, because it is toxic to bacteria. It can be achieved for example by

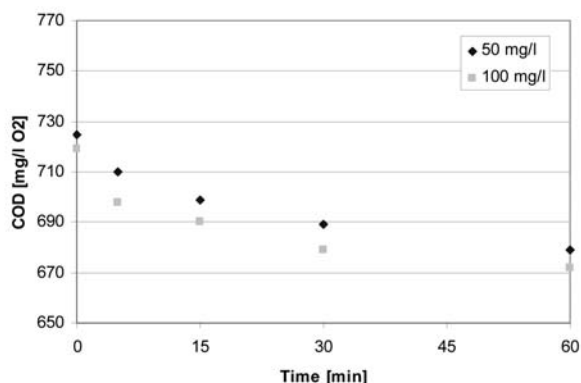


Fig. 6. Removal of FA from aqueous solution in the process of catalytic ozonation with Mn²⁺ ions at pH 10 — change of the COD value over time for different Mn²⁺ dosages [mg/l].

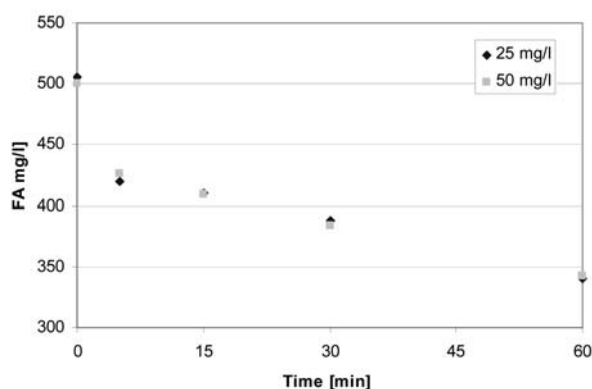


Fig. 7. Removal of FA from aqueous solution in the process of catalytic ozonation with Mn²⁺ ions at pH 12 — FA concentration change over time for different Mn²⁺ dosages [mg/l].

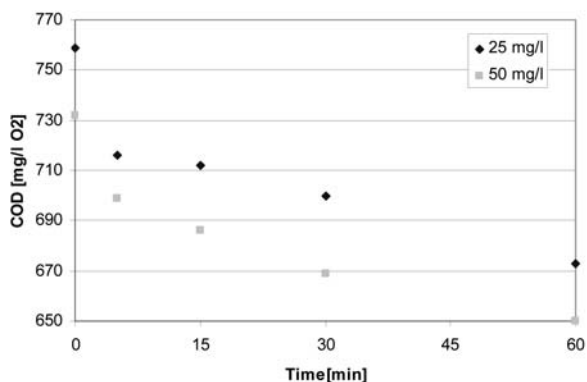


Fig. 8. Removal of FA from aqueous solution in the process of catalytic ozonation with Mn²⁺ ions at pH 12 — change of the COD value over time for different Mn²⁺ dosages [mg/l].

mixing the wastewater after Fenton process with municipal wastewater which contains easily oxidizable organic substances or the addition of Na₂SO₃ to the wastewater after the Fenton process (stoichiometric amount or slight excess which makes with FA complex

compound which is susceptible for biological decomposition [1]).

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