Sulfur mustard destruction using ozone, UV, hydrogen peroxide and their combination

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Abstract

Numerous methods are used for destruction of sulfur mustard. Oxidation is one of those methods. There have been only limited data concerning application of the advanced oxidation technologies (AOTs) for mustard destruction available before. In this study sulfur mustard oxidation rate depending on kind of the oxidative system and process parameters used was assessed using selected AOT. The following were selected for mustard oxidation: ozone (O_3), UV light (UV), hydrogen peroxide (H_2O_2); double systems: UV/O_3, UV/H_2O_2, and O_3/H_2O_2; a triple system: $O_3/H_2O_2/UV$ and Fenton reaction. Effectiveness of the selected AOT methods has been evaluated and the most suitable one for mustard destruction was chosen. Using ozone in various combinations with hydrogen peroxide and UV radiation mustard can be destroyed much quicker comparing to the classical oxidizers. Fast mustard oxidation (a few minutes) occurred in those systems where ozone alone was used, or in the following combinations: O_3/H_2O_2, O_3/UV and $O_3/H_2O_2/UV$. When those advanced oxidation technologies are used, mustard becomes destroyed mainly in course of the direct oxidation with ozone, and reactions of mustard with radicals formed due to ozone action play a secondary role. Rate of sulfur mustard oxidation in the above mentioned ozone-containing oxidative systems decreases with pH value increasing from 2 to 12. Only when pH value of reaction solutions is close to pH 5, mustard oxidation rate is minimal, probably due to "disappearance" of radicals participating in oxidation in this pH. Sulfur mustard can be most effectively destroyed using just ozone in pH 7. In that case mustard destruction rate is only slightly lower than the rate achieved in optimal conditions, and the system is the simplest.
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Keywords: Sulfur mustard decontamination; Advanced oxidation technologies; Ozone; Hydrogen peroxide; UV light; Fenton reaction; GC/AED analysis

1. Introduction

Two basic directions of studies on chemical warfare agents (CWA) destruction are noticeable in the scientific literature. Large scale CWA destruction methods are developed in the first trend of those studies [1]. This applies to CWA stored in warehouses and in chemical ammunition still possessed by various armies of the world [2,3]. The other direction of search for new CWA destruction methods results from the fact that there is still a possibility of contamination of various objects in course of the military [4,5] or terrorist [5,6] actions with chemical warfare.

CWA should be destroyed fast and completely, and products of their conversion should not be toxic [7,8]. Sulfur mustard decontamination, from the point of view of its course, is usu-

ally a complex and difficult process. It is quite common believe, that almost all effective mustard destructing agents will also be applicable for destruction of almost all CWA. In 2002 a very interesting review of organisational and technical aspects connected with large scale CWA destruction was published [9].

CWA can be rendered harmless with numerous methods. Part of those methods assumes that oxidation is an effective method of destruction. Studies on implementation of methods based on oxidation are carried out in many research centres [10–13]. Some of those centres have begun basic studies on application of the advanced oxidation processes (AOPs) for destruction of organic sulfur and phosphorus toxic substances [14–17].

The process of destruction of hazardous substances, including CWA, should produce non-hazardous substances, or at least substances less hazardous than the original ones. Applied methods should not cause introduction of secondary pollutants into the environment. Advanced oxidation technologies (AOTs) meet that requirements. The technologies use several

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AOP   advanced oxidation process
AOT   advanced oxidation technology
CWA   chemical warfare agents
GC/AED   gas chromatography/atomic emission detection
GC/MS   gas chromatography/mass spectrometry
HO^- hydroxyl anion
$HO^{\bullet}$ hydroxyl radical
H_2O_2 hydrogen peroxide
$HOO^{\bullet}$ hydroperoxide radical
HOO^- hydroperoxide anion
$O_2^{\bullet-}$ superoxide anion radical
O_3 ozone
ROS   reactive oxygen species
$t_{1/2}$ half-life time
UV   ultraviolet light

Fig. 1. Scheme of the reactor where mustard oxidation reaction studies were performed.

factors simultaneously, such as ozone, hydrogen peroxide and UV radiation. Various combinations of those factors are used: UV/O_3, UV/H_2O_2, O_3/H_2O_2, $O_3/H_2O_2/UV$. This group of methods includes also reactions realized using the Fenton reagent, composed of hydrogen peroxide and iron(II) cations. The use of Fenton's reagent to remove less-biodegradable organics in wastewater is relatively attractive due to the fact that iron is an abundant and non-toxic element, and because hydrogen peroxide is easy to handle and can be broken down to environmentally benign products. The Fenton's process is able to destroy phenols, chlorinated phenols and herbicides in water media, as well as reduce chemical oxygen demand in municipal waste [18]. If H_2O_2 is added to an aqueous system containing an organic substrate and ferrous ions in a strong acid medium some complex redox reactions will occur. The hydroxyl radical generated would attack the organic substrate RH like the unsaturated molecule [19].

All advanced oxidation technologies have one thing in common: when certain factors interfere with each other, reactive oxygen species (ROSs) are formed. ROS originating from the advanced oxidation processes are characterised by high reactivity, and majority of them—by high effectiveness towards numerous groups of organic compounds [20]. During the last decade the studies on AOP application for destruction of organic pollution from both waste and drinking water have been largely intensified [21].

The simplest way to destroy mustard gas would be to oxidize it with easily available and relatively cheap atmospheric oxygen. However, atmospheric oxygen oxidizes mustard very slowly, and it is necessary to use catalysts to increase rate of that reaction. Mustard can be oxidized with hydrogen peroxide, but to speed the reaction up proper catalysts should be used as well. That is why numerous research centres look for catalysts for oxidation with oxygen or hydrogen peroxide [22–24]. Some research centres work on photochemical method of oxidation of sulfides, as mustard simulations [25].
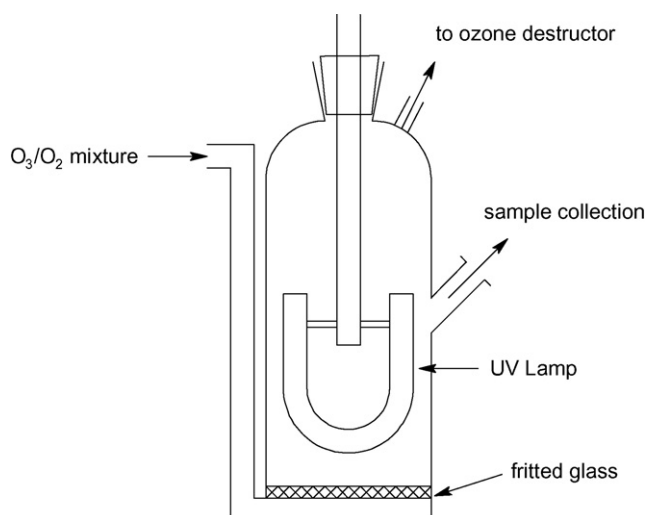
The aim of this study was to determine sulfur mustard oxidation rate depending on kind of the oxidizing system and physical and chemical parameters of the process. The following have been chosen for studying the mustard oxidation rate: O_3 (ozonolysis), UV (photolysis), H_2O_2 (reaction with a classic oxidizer—hydrogen peroxide); double systems: UV/O_3, UV/H_2O_2 and O_3/H_2O_2; and a triple system: $O_3/H_2O_2/UV$, and the Fenton system.

Further aim of the study was to compare effectiveness of all the studied methods of advanced oxidation and choosing the best one (or ones) for mustard gas destruction.

2. Equipment, reagents and study methodology

2.1. Equipment

Mustard gas oxidation was performed in a glass photochemical reactor, structure of which allows simultaneous or separate usage of ozone and UV radiation as oxidizing agents. The reactor of 0.6 L capacity is schematically presented in Fig. 1.

Ozone generator OEM-15 from Ozone Advanced Systems (Munka Ljungby, Sweden) was used for ozonization. Ozone was produced of oxygen passed through a set of column dryers; the dryers were equipped with molecular sieves 5A and 10A and silica gel. A 6 W power mercury discharge lamp (produced against order by the Laboratory of Discharge Lamps in the Institute of Electro-engineering, Warsaw, Poland) was used as a UV radiation source.

Analyses were performed with a gas chromatograph HP 6890 with the atom emission detector HP G2350A from Hewlett-Packard. Equipment operation and data storage was realized with a Chemstation HP 35920A software.

2.2. Reagents and solutions

Sulfur mustard was prepared in this laboratory in the 1990s and stored in a sealed glass ampoule; its purity (99.8%) was

now checked by GC/MS. *Warning: mustard is a potent vesicant and must be handled in a closed system or in a hood with good ventilation.*

Mustard oxidation was carried out in buffered aqueous solutions. Mustard solutions were prepared by mixing of 10 μL mustard with 100 mL of the Britton–Robinson buffer solutions, pH: 2, 5, 7, 9, 12. Aqueous hydrogen peroxide solutions, pH 2, 5, 7, 9 and 12, were prepared by mixing aqueous 30% H_2O_2 (Chempur, Piekary Śląskie, Poland) with appropriate Britton–Robinson buffer solutions. Britton–Robinson buffers were prepared in a usual way, i.e. by mixing a solution of 0.04 mol L^{-1} phosphoric acid, 0.04 mol L^{-1} acetic acid, and 0.04 mol L^{-1} boric acid with the appropriate amount of 0.2 mol L^{-1} sodium hydroxide solution [26]. Chemicals for the preparation of the Britton–Robinson buffers were obtained from POCH Gliwice, Poland. Reagent-grade dichloromethane (POCH, Gliwice) was used to extract mustard oxidation products from reaction mixtures. The dichloromethane solutions obtained by extraction were dried over anhydrous magnesium sulfate (POCH, Gliwice).

Hydrogen peroxide solutions in the following concentrations: 10^{-4}, 10^{-3}, 5×10^{-3}, 10^{-2}, 5×10^{-2}, 10^{-1} mol L^{-1} were used in the designed advanced oxidation systems (except for the Fenton reaction). In the Fenton reaction, reagent-grade iron(II) sulfate heptahydrate (Chempur, Piekary Śląskie) in form of 5×10^{-3}, 10^{-2}, 5×10^{-2}, 10^{-1} mol L^{-1} aqueous solutions was used as a catalyst. Hydrogen peroxide solutions in 0.049; 0.098; 0.47; 0.89; 1.63 and 3.27 mol L^{-1} concentrations were also used in the Fenton reaction. pH regulation in this reaction system was realized by addition of 10% sulfuric acid solution of the analytical grade (POCH, Gliwice).

2.3. Study methodology

2.3.1. The course of oxidation reaction with ozone

For all the mustard oxidation studies for which ozone was used, the volume rate of ozone–oxygen mixture flow was 1.5 L/min. Ozone concentration in water was maintained between 1 and 2 mg L^{-1} and was assayed with an indigo [27] and iodometric method [28].

2.3.2. Solution preparation, sampling and preparing samples for analysis

Samples were collected from the reactor and prepared for chromatographic analysis with liquid–liquid extraction. After a definite reaction time a 3 mL sample of the reaction mixture was collected from the reactor using a syringe connected to a Teflon hose dipped in the reacting solution. The collected sample was transferred into a tube containing 50 μL of aqueous solution of 1 mol L^{-1} thiosulfate. Thiosulfate caused decomposition of ozone dissolved in the collected sample and prevented its further oxidation. After a whole series of samples was collected this way, exactly 2 mL of the solution was pipetted from each tube and transferred to a tube with a screwed cap pre-filled with 2 mL of methylene chloride. Tubes were closed and shaken for 15 s and left until phase separation. Then, the lower phase containing dichloromethane was transferred with a syringe to the

next tube and dried with anhydrous magnesium sulfate. Dried dichloromethane solution was decanted into the last tube. One microliter of the solution was collected from the last tube and injected into the gas chromatograph. The procedure was repeated for three experiments at particular conditions and the results are mean values.

2.3.3. Chromatographic analysis

Chromatographic conditions: cavity and transfer line temperature was 270 °C, injector temperature: 260 °C, stream splitter 10:1, helium was a carrier gas, with a flow rate of 2 mL/min. The following reaction gases were used: hydrogen, oxygen and the methane–nitrogen (1:9) mixture. For the analysis of sulfur mustard and its decomposition products an HP-5 capillary column was used, 30 m long and 0.25 mm in internal diameter, provided with a (5:95, w/w) diphenyl-dimethyl-polysiloxane film, 0.25 μm thick.

The analysis was carried out using a temperature program: column heating up from the temperature of 80–220 °C with a constant rate of 10 °C/min and maintaining the final temperature for 5 min.

2.3.4. Reaction rate determination

Mustard oxidation rate in the individual oxidation systems was determined with a mustard half-life $t_{1/2}$, that is the time in which mustard concentration dropped to the half of the initial value. For this purpose the percentage rate of mustard in the reaction mixture comparing to the initial content was determined based on the results of chromatographic analysis. Then, mustard quantity in the reaction environment relationship curves to the time of oxidation reaction was drawn. Time passed until mustard concentration drops to the half of the initial value was obtained from the equation of the curve based on the measurement points.

3. Results and discussion

Sulfur mustard oxidation was realized with single oxidizers: O_3, H_2O_2, UV and their double systems: O_3/UV, UV/H_2O_2, O_3/H_2O_2 and a triple system: (O_3/UV/H_2O_2). Fenton reaction was also used with hydrogen peroxide and Fe^{2+} cations as catalyst.

3.1. Mustard oxidation rate in the Fenton reaction

Sulfur mustard oxidation rate in the Fenton reaction was studied by changing the value of:

- pH of the oxidizing solution;
- hydrogen peroxide concentration;
- iron(II) cations concentration in solution.

3.1.1. Influence of the pH value of the solution

To optimize the pH value the initial hydrogen peroxide concentration of 0.098 mol L^{-1} was chosen, and the iron(II) cation concentration of 10^{-2} mol L^{-1}. In those conditions it became clear that the Fenton reaction with mustard takes the highest
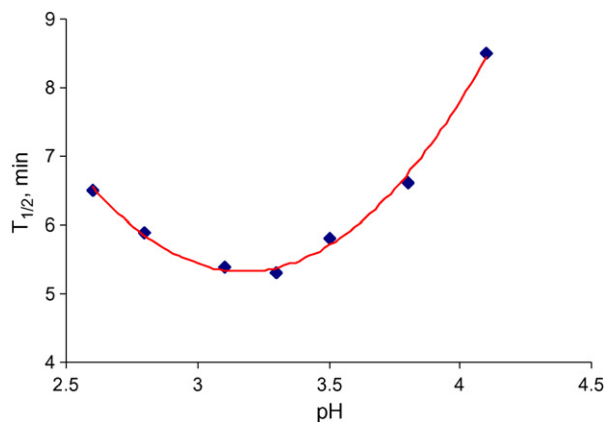
Fig. 2. Relationship between the mustard half-life and pH of the Fenton reaction environment.

rate in solutions with pH value close to 3.3 (Fig. 2.). The pH value of 3.3 was applied for the further tests as an optimal one.

3.1.2. Influence of hydrogen peroxide concentration and iron(II) cations concentration

To study the influence of iron(II) concentration on mustard oxidation rate the following iron(II) concentrations were applied: 5×10^{-3}, 10^{-2}, 5×10^{-2}, 10^{-1} mol L^{-1} and seven various concentrations of hydrogen peroxide within the range 0.0098–3.266 mol L^{-1}. A matrix of 28 measurement points was obtained this way (Fig. 3). On this basis it was found that mustard oxidation rate is the highest in the system of the following parameters: hydrogen peroxide concentration -0.89 mol L^{-1}, iron(II) concentration -5×10^{-2} mol L^{-1}.

3.2. Rate of mustard oxidation with ozone

The tests were performed for buffered aqueous solutions with pH of 2, 5, 7, 9, and 12. Based on the results obtained it was found that the rate of mustard oxidation is the highest in solutions with
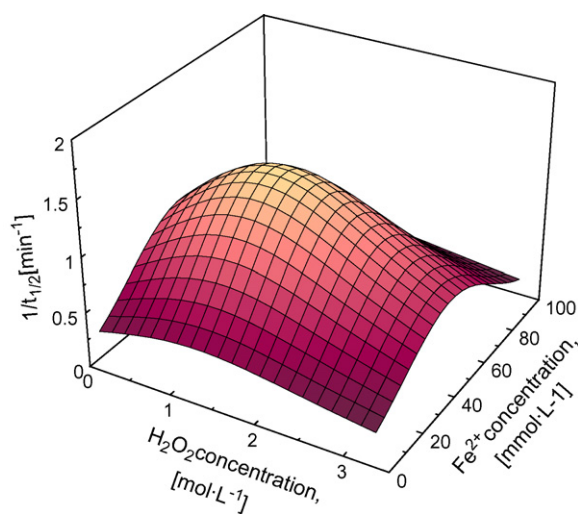

Fig. 3. Spatial relationship of mustard oxidation rate, expressed as $1/t_{1/2}$, and H_2O_2 and Fe^{2+} concentration, obtained as a result of the process condition optimization.

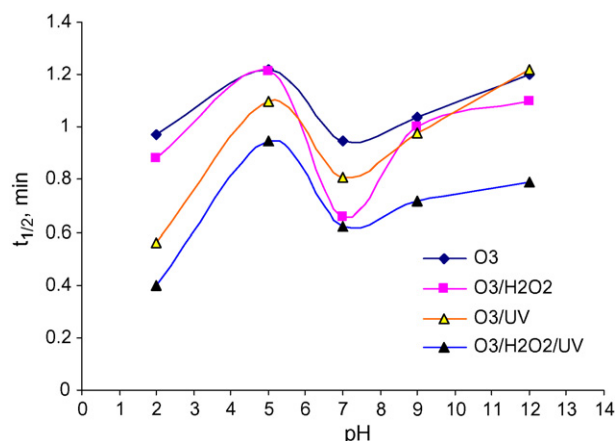
Fig. 4. Relationship between mustard half-life and pH value of the solution for the AOT in which ozone was used. Hydrogen peroxide concentration was 5×10^{-3} mol L^{-1}.

pH close to neutral. Relatively fast mustard oxidation takes place in acid solutions with pH close to 2. This relationship is presented in Fig. 4.

3.3. Mustard oxidation rate in the O_3/H_2O_2 system

Mustard oxidation rate in the O_3/H_2O_2 system was studied changing the following process parameters: hydrogen peroxide concentration and pH value of the buffered solution.

3.3.1. Influence of hydrogen peroxide concentration

All buffer solutions had the same pH of 7 while testing the H_2O_2 influence in the oxidizing system of O_3/H_2O_2 on mustard oxidation. Only hydrogen peroxide concentration in the buffer solution was variable. Oxidation rate was the highest in hydrogen peroxide solution with concentration of 10^{-3} mol L^{-1}. Increasing the H_2O_2 concentration caused decrease in oxidation rate, and when H_2O_2 of 1 mol L^{-1} concentration the oxidation rate was lower than rate of oxidation with ozone without H_2O_2 addition (Fig. 5). This last case can be described as "inhibition" of the mustard ozonization process by H_2O_2.
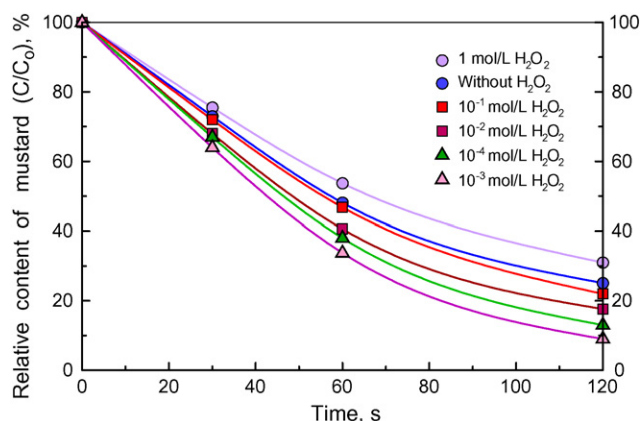

Fig. 5. The course of mustard oxidation process in the O_3/H_2O_2 system with various hydrogen peroxide concentrations; pH 7.

3.3.2. pH influence

When testing the influence of pH in the oxidizing system O_3/H_2O_2 on mustard oxidation rate, hydrogen peroxide concentration in all the buffer solutions was the same, 10^{-3} mol L^{-1}. Only pH value of the buffer solution was variable.

Sulfur mustard oxidation rate in the O_3/H_2O_2 system was the highest in neutral solutions. The process of mustard oxidation in this system is much slower both in acid and alkaline solutions (Fig. 4). It was found, however, that just like in case of oxidation with ozone alone, significant acidification of the environment increases oxidation rate.

3.4. Rate of mustard oxidation in the O_3/UV system, depending on the pH value

Mustard oxidation rate in the O_3/UV system was tested by changing the pH value of the buffered solution. Synergic conjugation of the oxidizing factors: ozone and UV irradiation caused increase of oxidation rate. According to Fig. 4 mustard oxidation in the O_3/UV system, depending on the pH value, has a similar course to oxidation with ozone alone. In the alkali environment, starting from the pH 7 a systematic decrease in oxidation rate is noted. In acid environment, the oxidation rate first decreases with pH decrease, and after passing the pH value of 5 it starts to increase again.

3.5. Mustard oxidation rate in the H_2O_2/UV system

Mustard oxidation rate was tested by changing the hydrogen peroxide concentration and pH value of the solution where the oxidation was taking place.

3.5.1. Influence of hydrogen peroxide concentration

Influence of H_2O_2 concentration on mustard destruction rate was tested with constant pH of the reaction environment equal 7. For this purpose the following hydrogen peroxide concentrations were selected: 0, 10^{-4}, 10^{-3}, 5×10^{-3}, 10^{-2}, 5×10^{-2}, 10^{-1} mol L^{-1}. Fig. 6 presents kinetic curves of mustard destruction in the UV/H_2O_2 system, for various initial concentrations of hydrogen peroxide, and Fig. 7 presents the mustard half-life
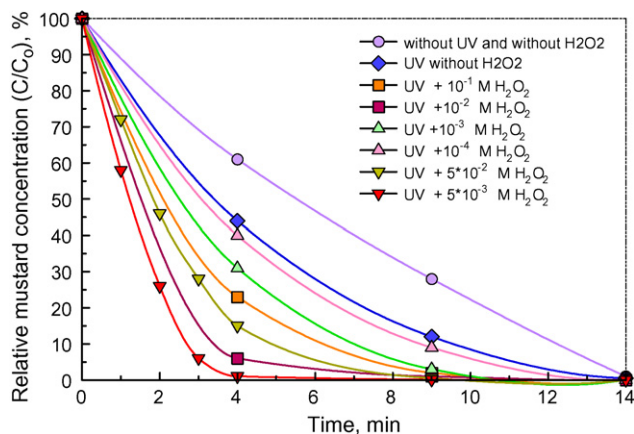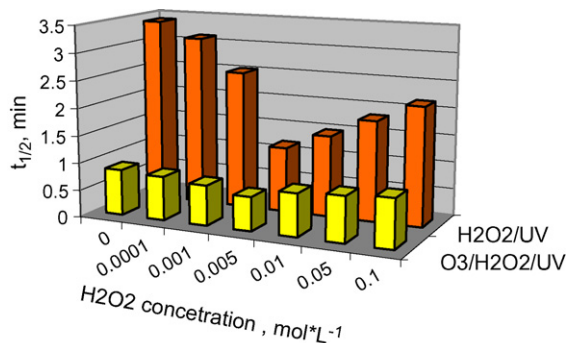

Fig. 7. Influence of H_2O_2 concentration on mustard half-life in the UV/H_2O_2, and UV/H_2O_2/O_3 systems. pH of the solution was 7.

determined based on those curves. Increasing hydrogen peroxide concentration from 0 to 5×10^{-3} mol L^{-1} caused increase of mustard oxidation rate (Fig. 7). Rate of mustard destruction in the H_2O_2/UV system decreased with increase of hydrogen peroxide concentration above 5×10^{-3} mol L^{-1}.

3.5.2. pH influence in the UV/H_2O_2 system

pH influence on mustard destruction process rate was tested with constant H_2O_2 concentration of 5×10^{-3} mol L^{-1}. During these tests it was found that in the oxidizing system H_2O_2/UV the reaction rate is generally higher for acid solutions comparing to alkali ones (Fig. 8). In alkali solutions the reaction rate decreases in a linear manner with increasing pH, and in acid solutions the rate reaches its local minimum close to the pH value of 5.

3.5.3. pH influence in the aqueous solutions exposed to UV light

Mustard destruction rate upon exposure to UV radiation was studied for the buffered aqueous solutions with pH values of 2, 5, 7, 9, and 12. Based on the results obtained, present in Fig. 8, it was found that the mustard disappearance process was the fastest in the solution with pH 7. Both in the acid and alkaline solutions, mustard decomposition rate was low. Mustard disappearance rate under influence of UV radiation in these solutions was just slightly higher than its hydrolysis.

Fig. 6. Course of mustard oxidation process in the H_2O_2/UV system in the selected hydrogen peroxide concentrations, pH 7.
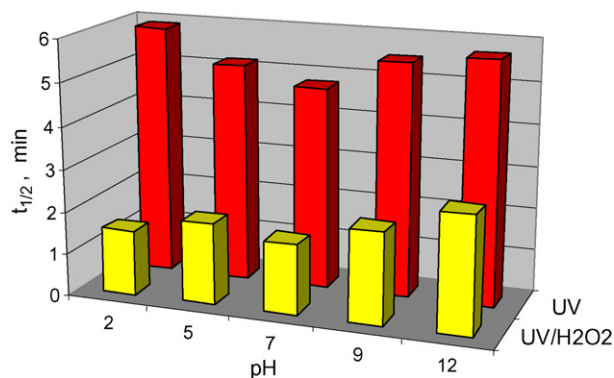

Fig. 8. Relationship between mustard half-life under influence of UV light and pH value of the reaction environment.
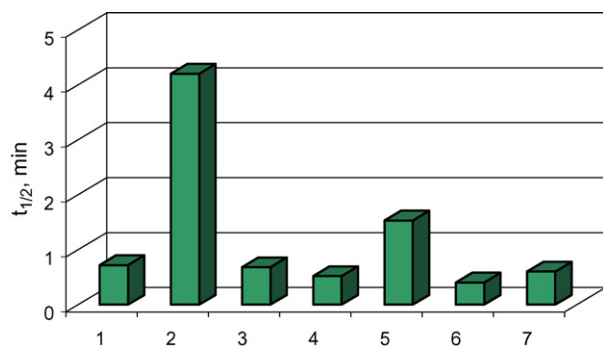
Fig. 9. Mustard destruction effectiveness in the applied advanced oxidation systems, presented as a relationship between mustard half-life and kind of the applied system. Oxidizing systems, in the individually optimised conditions: (1) O_3 (pH 2); (2) UV (pH 7); (3) O_3/H_2O_2 (pH 7, $[H_2O_2] = 10^{-3} \, mol \, L^{-1}$); (4) O_3/UV (pH 2); (5) H_2O_2/UV (pH 2, $[H_2O_2] = 5 \times 10^{-3} \, mol \, L^{-1}$); (6) $O_3/H_2O_2/UV$ (pH 2, $[H_2O_2] = 5 \times 10^{-3} \, mol \, L^{-1}$); (7) Fenton system (pH 3.3; $[H_2O_2] = 0.89 \, mol \, L^{-1}$, $[Fe^{2+}] = 5 \times 10^{-2} \, mol \, L^{-1}$).

3.6. Mustard oxidation rate in the $O_3/H_2O_2/UV$ system

Mustard oxidation rate in the $O_3/H_2O_2/UV$ system was tested changing hydrogen peroxide concentration and pH value of the solution.

3.6.1. Influence of hydrogen peroxide concentration

Influence of H_2O_2 concentration on mustard half-life was tested in the buffered solution of pH 7 (Fig. 7). Hydrogen peroxide concentration of $5 \times 10^{-3} \, mol \, L^{-1}$ proved to be optimal for the given oxidative system.

3.6.2. pH influence

Sulfur mustard oxidation rate was tested in the oxidizing system $O_3/H_2O_2/UV$ for the reaction environment of pH equal 2, 5, 7, 9 and 12 (Fig. 4). Hydrogen peroxide concentration in all tested solutions was $5 \times 10^{-3} \, mol \, L^{-1}$.

Mustard oxidation rate is the highest in highly acidic solution (pH 2), moderate in neutral and alkaline solutions, and the rate was the lowest with the pH value close to 5.

4. Discussion and conclusions

Based on the performed tests it is possible to compare mustard half-lives in the studied systems, taking the optimised parameters of the oxidation process into account. This comparison is present in Fig. 9.

Among the studied oxidizing systems, the mustard oxidation reaction rate was the highest in the triple system ($O_3/H_2O_2/UV$). Relatively fast mustard oxidation occurred in those systems where ozone was used (both as a sole factor and in the following systems: O_3/H_2O_2, O_3/UV and $O_3/H_2O_2/UV$). For all the a/m systems mustard half-lives in the reaction mixtures were similar. This tendency is shown in Fig. 9.

pH of the reaction environment has significant influence on the mustard oxidation rate. Fig. 4 presents relationship between mustard half-life and pH value of the solution for the oxidizing systems containing O_3. Usually, when O_3 is present in the

system—pH 2 is optimal. Only for the O_3/H_2O_2 system the pH 7 is optimal. Generally, oxidation rate is high in highly acidic and neutral solutions, and it is the lowest in solutions with pH value close to 5. In the alkaline solutions the reaction rate decreases with increase of pH of the solution. This means that mustard becomes destructed mainly in a direct reaction with ozone, and radical reactions play only a secondary role in this case. This conclusion is in line with reference data [20,21,29] regarding AOP application.

Presence of the $t_{1/2} = f(pH)$ function extreme with pH 5, characterised by low oxidation rate, can be explained with presence of the dismutation phenomenon (decay through disproportionation) of the superoxide anion radical and hydroxyl radical. Reference data show [30], that resultant dismutation rate for the $HO^\bullet_2/O_2^{\bullet-}$ radical system is the highest for the pH value between 4.5 and 5.5.

In the H_2O_2/UV system in alkaline environment, rate of mustard photolysis decreases with increase of pH value above 7 (Fig. 8). This is probably due to the fact that in alkaline environments rate of the reaction between the formed, highly reactive $HO^\bullet$ radicals and the dissociated form of hydrogen peroxide is quite high:

$$HO^\bullet + HOO^- \rightarrow H_2O + O_2^{\bullet-} \qquad (k = 7.5 \times 10^9 \, L \, mol^{-1} \, s^{-1})$$

Significant decay of the reactive radical leads to decrease of organic compounds destruction rate (including mustard), that is consistent with reference data [31]. Decrease of hydroxyl radical concentration negatively influencing the process rate and occurring in environments with pH < 10 is much slower, for in this pH range the hydroxyl radicals are scavenged via the process much slower than before:

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO^\bullet_2 \qquad (k = 2.7 \times 10^7 \, L \, mol^{-1} \, s^{-1})$$
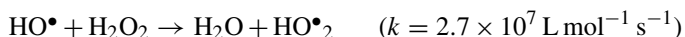
therefore their reaction with mustard is faster in this pH range.

5. Conclusions

- Using ozone in various combinations with hydrogen peroxide and UV radiation it is possible to destroy mustard in much shorter time comparing to classical oxidizers.
- Relatively fast mustard oxidation occurred in those systems where ozone was used (both for ozone alone and in the following systems: O_3/H_2O_2, O_3/UV and $O_3/H_2O_2/UV$). For all the systems, mustard half-lives in the reaction mixtures are similar.
- Mustard oxidation rate is the highest for solution pH 2, in those cases when the oxidizing system contains ozone alone or when ozone is supported by UV radiation, and when ozone is supported simultaneously by UV and H_2O_2.
- In the advanced oxidation systems in which ozone is the oxidizing factor (O_3/H_2O_2, O_3/UV, $O_3/H_2O_2/UV$ and O_3 alone)—mustard is destroyed mainly in course of the reaction of direct oxidation with ozone, and reactions of mustard with radicals generated by ozone play just a secondary role.
- Sulfur mustards oxidation in the following systems: O_3, O_3/H_2O_2, O_3/UV and $O_3/H_2O_2/UV$ is largely dependent on pH. Oxidation rate is high for very low pH values and for pH

value of approximately 7. Low oxidation rate for pH 5 is probably due to the fact that with those pH values hydroxyl radicals become effectively dismutated under influence of superoxide anion radicals.

- Sulfur mustard can be most easily destroyed using ozone alone in neutral environment with pH value of 7. In this case mustard destruction rate is just slightly lower than the rate achieved in optimal conditions, and the system is the simplest of all and it is convenient for practical applications.

Acknowledgements

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