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Influence of chloride concentration on the formation of AOX in UV oxidative system

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Abstract

In this study, the effects of chloride ion concentration and pH on UV oxidation treatment were examined. Acetone and sodium dodecyl sulfate (ABS) were used as organic substances. The treatment efficiencies of these chemicals by UV/H_2O_2 oxidation using a laboratory scale UV-free surface reactor (UV-FSR) with or without Cl^- addition at different pH values was compared. Results of this study indicated that Cl^- concentration and the chemical structure of the substances are more decisive than pH in the oxidation process. There was no AOX at the start of the experiments but as a result of oxidation a de novo synthesis of AOX was observed, and these $AOX_{de\ novo}$ compounds were destroyed during the treatment. Treatment was followed by TOC and AOX measurements. Approximately 98% and 95% TOC removal efficiencies were obtained for the treatment of acetone and ABS containing wastewaters, respectively.
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1. Introduction

Adsorbable organic halogens (AOX) is a measure for halogenated compounds and is an important parameter for the characterization of industrial wastewaters. A large number of AOX causing substances show a significant eco-toxicity [1].

Sewage water legislation in Germany provides very strict regulations for the discharge of AOX containing wastewaters [1]. Those wastewaters often cause technical and financial problems for specific industries [2]. It is well known that, chlorination of drinking water or swimming pool water causes unwanted formation of chloroform and other halogenated derivatives such as chloramines. Another source of AOX in wastewater is created by the application of chlorous budget cleaners (chloramine T, chloramine BARS, sodium hypochlorite, chloric lime) [3]. Addition of chlorine to water produces hypochlorite by the following reaction [4]:

$$Cl_2 + 3H_2O \rightleftarrows OCl^- + Cl^- + 2H_3O^+$$

Chlorine addition can be formulated in a simplified manner as follows:

$$Cl_2 + RHC{=}CHR \rightarrow RHCCl{-}C^+HR + Cl^-$$
$$Cl^- + RHCCl{-}C^+HR \rightarrow RHCCl{-}CClHR \qquad (2)$$

In the last decade, the so-called "advanced oxidation processes" (AOPs) have been proposed for the waste-free degradation of toxic pollutants in industrial wastewaters. Several AOP methods are based on the combination of classical oxidants such as H_2O_2 or O_3 with UV irradiation with or without catalizers. In these processes, extremely reactive hydroxyl radicals are primarily generated and these are able to oxidize and destroy most of the wastewater constituents, including halogenated organic compounds [5].

Many industrial wastewaters such as tannery and dye manufacturing wastewaters have extraordinarily high chloride ion concentrations due to extensive use of sodium chloride. High Cl^- concentrations may cause serious corrosive problems with reactor components consisting of stainless steel. Dissolved chloride ions react rapidly with hydroxyl radicals ($^\bullet OH$) as described

by the following equations [6].

$$\bullet OH + Cl^- \rightarrow \bullet ClOH^- \tag{3}$$

$$ClOH^- + H^+ \rightarrow Cl\bullet + H_2O \tag{4}$$

$\bullet ClOH^-$ can decompose to yield chlorine atoms. Chlorine atoms can add to C=C– double bonds of the compounds present during advanced oxidation processes (AOP) treatment, generating chlorinated hydrocarbons (Eq. (5)), and leading to an undesirable increase of the global parameter AOX [6].

$$Cl\bullet + R_2C=CR_2 \rightarrow R_2ClC\bullet - CR_2$$
$$\rightarrow \text{chlorohydrocarbons (formation of AOX)} \tag{5}$$
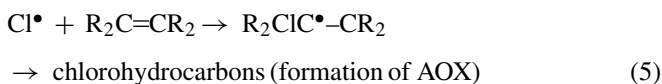
Some researchers have reported the effect of chloride ion concentration on the efficiency of AOP at a constant pH value, while some others have reported the effect of pH in the absence of chloride ions. For example, chloride ion was reported to inhibit the decomposition of dichlorvos insecticides [7] and 2,4-dichlorophenol [8] in the Fenton process, which produces $\bullet OH$ efficiently under acidic pH conditions. In addition, chloride ion was also found to inhibit color removal, oxidation of tetrachloroethylene (PCE), and mineralization of natural organic matter in processes where TiO_2 [9], O_3/H_2O_2 [10] or sonolysis/O_3 [11] were used. Gurol and Akata [12] used a Cl^- as $\bullet OH$ trap to determine the primary quantum yield in ozone photolysis.

Some researchers carried out experiments to examine the effects of Cl^- on the photocatalytic degradation of Methylene Blue, and Orange II in aqueous TiO_2 suspensions under UV light illumination [13]. They found that the high chloride concentration adversely affected the degradation rate of the dyes. In another study, the toxicological effect of disinfections using sodium hypochlorite on aquatic organisms, and its contribution to AOX formation in hospital wastewater were investigated [14]. The same workers found that low chloride concentrations corresponded to low concentrations of AOX, and the high chloride concentrations generated high AOX and high toxicity on *D. magna*.

As can be seen, in the literature there are no significant publications concerning the amount of AOX formation, or elimination in wastewaters containing different amounts of chloride ions when UV/H_2O_2 treatment is applied.

Today most of the UV/H_2O_2 photoreactors used for industrial wastewater treatment are equipped with submerged UV-radiators—a rather disadvantageous design, which originates from the sterilization technique for clear effluents. If high loaded wastewaters are treated with submerged radiators, dirty coatings on the surface of the UV-radiator quartz cover tubes cause considerable reduction of the effectiveness of the UV/H_2O_2 process. In order to overcome this problem, in cooperation with industry, a completely new reactor type for UV wet oxidation was developed at the University of Stuttgart, namely, the UV-free surface reactor (UV-FSR), and was used in this work. In contrast to the commonly used UV-reactors with submerged radiators the new concept is marked out by the position of the UV radiator, which is a few centimeters above the surface of the wastewater.

The main goal during the UV-FSR development was simplification of the entire technique to obtain a low price, robust, and user-friendly reactor. The aim was to operate the UV-FSR with a single push-button, and to be able to replace the UV radiator or the UV reflectors with a few simple manipulations. The UV-FSR is completely air cooled and equipped with 10 cm UV medium pressure radiators with a specific power of approximately 170 W/cm. The electrical equipment consists of a newly developed power semiconductor unit without transformers.

The main objectives of this study were to observe the effect of chloride ion concentration, and pH on AOX$_{\text{de novo}}$ formation using this recently developed UV-free surface reactor (UV-FSR) and to determine the degradation efficiency of acetone and ABS under these conditions.

2. Materials and methods

2.1. Materials

Acetone (C_3H_6O) and ABS (sodium dodecyl sulfate) ($C_{18}H_{29}SO_3Na$) were obtained form Merck Chemical Company. Concentration of each substance was 1000 mg/l in the synthetic wastewaters, and the COD values were calculated theoretically. In this study, only one concentration of hydrogen peroxide was applied. The hydrogen peroxide (H_2O_2) (50%, w/w) dosage was based on the stoichiometric ratio with respect to COD. This was calculated assuming complete oxidation of COD as follows:

$$1\,g\,COD = 1\,g\,O_2 = 0.03125\,mol\,O_2 = 0.0625\,mol\,H_2O_2$$

The COD, TOC and H_2O_2 equivalents corresponding to 1000 mg/l of acetone or ABS are given in Table 1.

During the experiments, pH was kept constant at pH 3, 7 or 10 with the addition of either 25% H_2SO_4 or 33% NaOH depending on the experimental conditions. NaCl was used as a Cl^- source and purchased from Merck. The experiments were continued until all H_2O_2 was consumed, and reactions times were 4 and 5 h for acetone and ABS, respectively.

2.2. UV-FSR reactor

The reactor used in this work is a bowl-shaped, laboratory-scale, 10 l glass reactor with 300 mm diameter and 140 mm depth (Fig. 1). It is gold coated on the outside to prevent emission of light from the reactor. Gold coating was used for its inert and durable nature. The reactor is equipped with a cooling jacket,

Table 1
COD, TOC and H_2O_2 equivalents for acetone and ABS

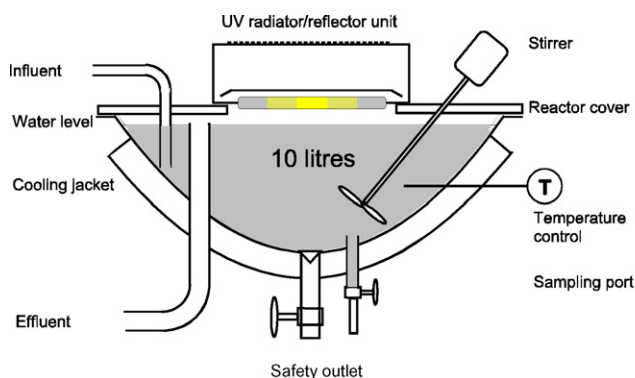| Organic substances (1000 mg/l)	COD equivalent (mg/l)	TOC equivalent (mg/l)	H_2O_2 equivalent (mg/l)	H_2O_2 dose (ml/10 l)
Acetone	2204	620	4686	78
ABS	2342	621	4979	83

Density of H_2O_2 (50%) = 1.195 g/ml.

Fig. 1. Schematic sketch of the 10 l UV-FSR.

influent inlet, safety outlet, a sampling port, temperature control equipment and, a stirrer. The UV-FSR is a completely mixed reactor, mixing is obtained with a mechanical stirrer having a Teflon coated blade. The UV irradiation source (10 cm) is a 170 W/cm (UVH 100 26 S1) air-cooled medium pressure mercury UV radiator (0.3 kW UVC-power = 18–20% of the plug) encased in a quartz tube and it was purchased from UV Technique Mayer Ltd., Bleichenbach, Germany.

2.3. Experimental procedure and analytical methods

For a standard reaction run, 10 l of aqueous solution was used. As a first step in this study it was necessary to remove the free chlorine present in the tap water to study the effects of free chlorine on the photo-degradation of organic substances. Prior to each experiment, the feed tank was filled with hot tap water (60–70 °C) and the free chlorine in tap water was removed overnight by aeration. It was observed that the elimination of free chlorine by this method was successful. Dechlorinated water was pumped into the UV-FSR reactor and following the adjustment of Acetone (C_3H_6O) or ABS ($C_{18}H_{29}SO_3Na$) concentration in the solution, the required amount of sulphuric acid or sodium hydroxide was added to obtain the desired pH in the solution where needed. The pH of the solutions was not buffered; therefore, during experiments, pH was always controlled with a pH control system (a pH meter, a controller and a dosing pump) located within the reactor, and kept constant. Each substance was treated in the presence of 1000 mg/l Cl$^-$, 10,000 mg/l Cl$^-$ or without Cl$^-$ at pH 3, 7 and 10. In the batch experiments, all of the required H_2O_2 was added into the reactor at the beginning of the test run. The time at which the ultraviolet lamp was turned on was considered time zero. Then, a stopwatch was started and samples were taken at predetermined time intervals to be analysed for TOC, AOX and H_2O_2. Samples were taken at beginning of the experiments and after 6, 18, 30, 60 min and 4 or 5 h until the H_2O_2 had completely disappeared. Because large volumes are necessary, samples were not taken during 1–4 or 1–5 h of the experiments. The samples were analysed immediately to avoid further reaction. It is possible that VOCs could be produced during the oxidation; to prevent the VOCs escape from the reactor the temperature of the solution was kept constant at 30 ± 2 °C throughout all the experiments.

AOX was determined in a TOX analyser (TOX-10 $\sum$, Abimed, Düsseldorf, Germany) after enrichment on activated carbon [15]. TOC measurements were carried out by using a Jena Type Multi NC 3000 TOC Analyzer equipped with an auto sampler. H_2O_2 concentration was measured according to German Standard Methods [16].

3. Results and discussion

The first step was to determine the effect of chloride concentration on the process. Therefore, experiments were carried out at three different chloride ion concentrations (without Cl$^-$, or in the presence of 1000 mg/l Cl$^-$ or 10,000 mg/l Cl$^-$) at a constant initial acetone concentration of 1000 mg/l and a hydrogen peroxide concentration of 4686 mg/l (1 × stoichiometric). Under these conditions the amount of H_2O_2 (78 ml/10 l) concentration was nearly zero after 4 h batch treatment. There was no AOX at the beginning of the experiments, but AOX appeared and increased after 6–18 min in the presence of Cl$^-$ ions. After 4 h of batch treatment, this newly formed (AOX$_{de\ novo}$) was decomposed. The maximum AOX$_{de\ novo}$ production was obtained in the presence of 10,000 mg/l Cl$^-$, whereas no AOX production occured when Cl$^-$ was not added (Fig. 2a). Vollmuth et al. [17] as well as other authors [18] have already observed the formation of AOX during UV oxidation.

The second step was to determine the effect of pH on the process. Therefore, experiments were carried out at three different pHs: acidic (pH 3), neutral (pH 7) and basic (pH 10). During batch treatment studies of acetone, the maximum AOX formation rate was observed in the presence of 10,000 mg/l Cl$^-$ at pH 10, whereas Glaze and Kang [10] reported that the rate of oxidation of PCE is barely affected by the addition of chloride at pH 8.4–8.5, where the $^\bullet$HOCl$^-$ tends to dissociate back and release $^\bullet$OH.

In all the studies, TOC values (620 mg/l) decreased to almost zero after 4 h of batch treatment (Fig. 2b).

The effects of pH and chloride ion concentration on the TOC removal efficiencies for acetone are given in Table 2 as a function of irradiation time. TOC removal efficiencies are between 93% and 100% after 4 h of batch treatment, whereas after 1 h of oxidation, TOC removal efficiencies are between 70% and 85% and the maximum treatment efficiency is obtained at pH 7 and without chloride addition. It is possible to say that increasing chloride ion concentration has some adverse effect on TOC degradation at pH 7. Although Seiss et al. [19] found that different pH values and chloride concentrations affect TOC removal efficiencies greatly; in our studies, it has been found that this is not true under all the reaction conditions.

The other substance investigated in this study was ABS. The initial ABS concentration was 1000 mg/l and the hydrogen peroxide concentration used was 4979 mg/l (1 × stoichiometric). The concentration of H_2O_2 (83 ml/10 l) was almost zero after 5 h of batch treatment of ABS. Although there was no AOX at the beginning of the experiments, it formed and increased after 18–30 min of oxidation in the presence of 1000 mg/l Cl$^-$ or 10,000 mg/l Cl$^-$ (Fig. 3a). After 5 h of oxidation, the AOX$_{de\ novo}$ produced was degraded again as Ormad et al. [20] have observed.
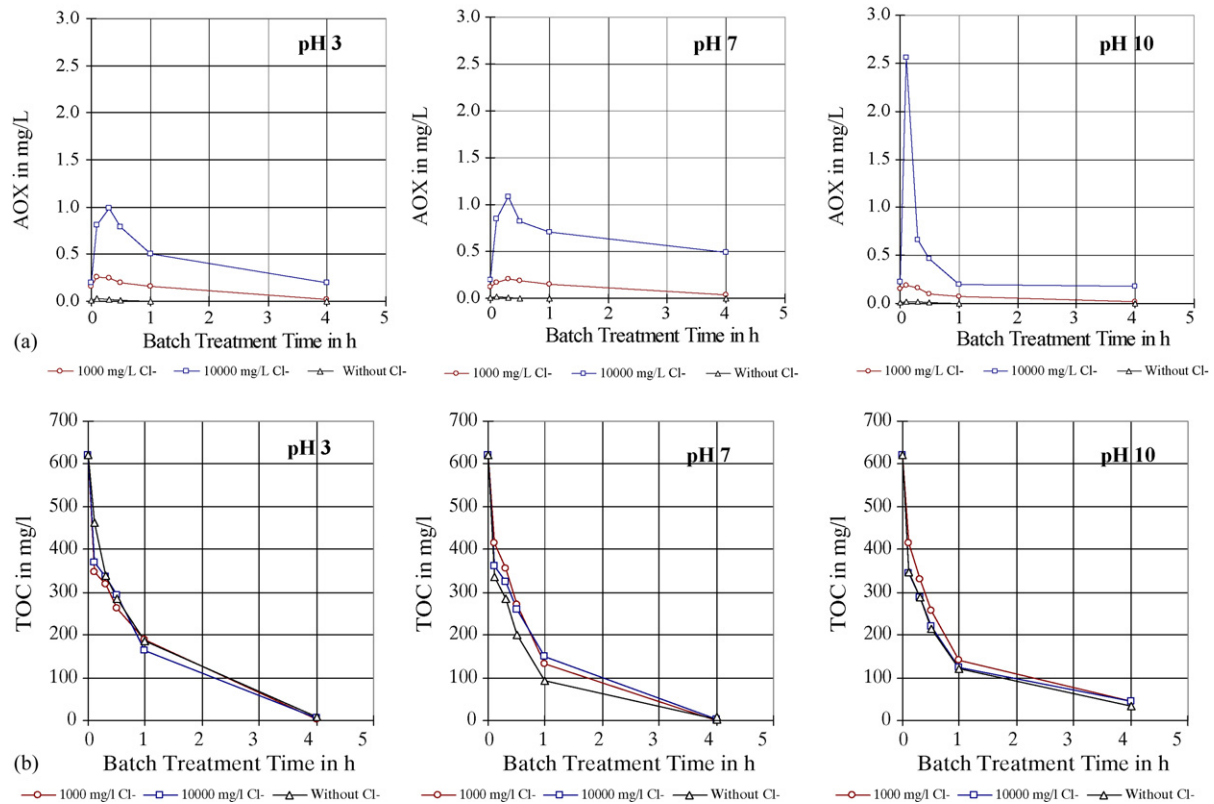
Fig. 2. (a) AOX formation (and decomposition) in the treatment of acetone and (b) TOC removal in the treatment of acetone.

Table 2
Effect of pH and chloride ion concentration on TOC removal efficiencies in the treatment of acetone with UV/H$_2$O$_2$

Time (h)	pH 3[a]			pH 7[a]			pH 10[a]		
	1000 mg/l Cl$^-$	10,000 mg/l Cl$^-$	Without Cl$^-$	1000 mg/l Cl$^-$	10,000 mg/l Cl$^-$	Without Cl$^-$	1000 mg/l Cl$^-$	10,000 mg/l C$^-$	Without Cl$^-$
0.1	44	40	25	33	42	46	33	44	44
0.3	49	46	46	43	47	54	47	54	54
0.5	58	53	54	56	58	68	58	64	65
1	70	74	70	79	76	85	77	80	80
4	100	99	99	100	99	100	93	93	95

[a] TOC removal efficiency (%).

During the treatment experiments of ABS, the greatest amount of AOX production was observed in the presence of 10,000 mg/l Cl$^-$ at all the pH values used (Fig. 3a). AOX formation during the oxidation of ABS is higher than AOX formation during the oxidation of acetone. It can be assumed that the amount of AOX formed is affected by the molecular structure of the substances. During oxidation the aromatic ring could be decomposed and bind more chloride than the linear chain structure.

The TOC concentration of synthetic wastewater containing ABS was 621 mg/l. The curves for the degradation of TOC were not the same at the three different Cl$^-$ concentrations

Table 3
Effect of pH and chloride ion concentration on TOC removal efficiencies in the treatment of ABS with UV/H$_2$O$_2$

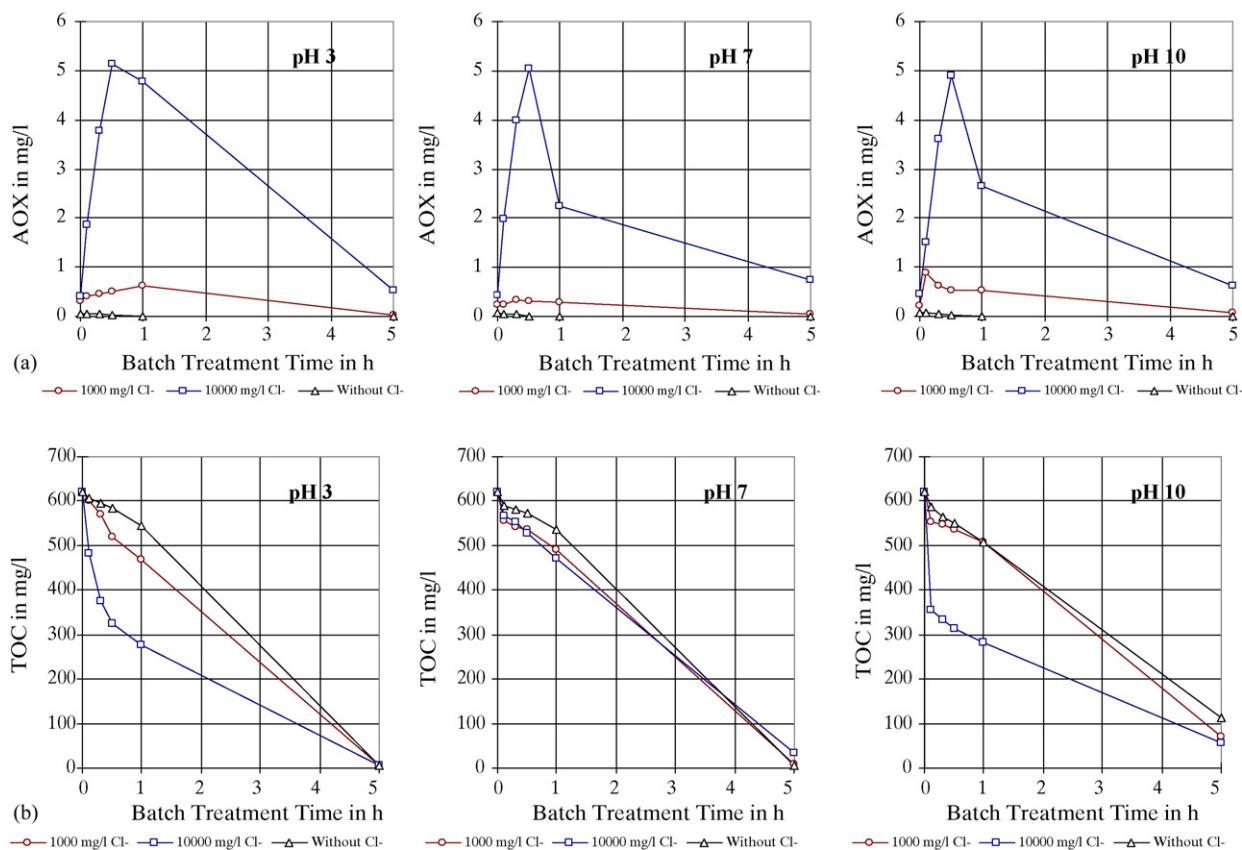| Time (h)	pH 3[a]			pH 7[a]			pH 10[a]		
	1000 mg/l Cl$^-$	10,000 mg/l Cl$^-$	Without Cl$^-$	1000 mg/l Cl$^-$	10,000 mg/l Cl$^-$	Without Cl$^-$	1000 mg/l Cl$^-$	10,000 mg/l Cl$^-$	Without Cl$^-$
0.1	3	22	2	11	8	5	11	43	5
0.3	8	39	4	13	11	6	12	46	9
0.5	16	48	6	14	15	8	14	50	12
1	24	55	12	21	24	14	18	55	18
5	99	99	99	99	94	99	88	91	82

[a] TOC removal efficiency (%).

Fig. 3. (a) AOX formation (and decomposition) in the treatment of ABS and (b) TOC removal in the treatment of ABS.

(0, 1000, and 10,000 mg/l) but after 5 h of batch treatment the TOC concentrations were reduced to 6 mg/l in all of the cases (Fig. 3b).

The effect of different pH values and chloride concentration on TOC removal efficiencies for ABS is given in Table 3 as a function of irradiation time. The maximum TOC degradation efficiencies were obtained at pH 3 and 10 with the addition of 10,000 mg/l Cl^- after 1 h oxidation. While TOC removal efficiency is between 12% and 55% after 1 h oxidation, it is 82–99% after 5 h batch treatment. Whereas, linear alkylbenzene sulfonate (LAS) was degraded by Tabrizi et al. [21] using UV/H_2O_2; they degraded 100 mg/l LAS with 720 mg/l H_2O_2 in 2 h and they obtained 95% degradation efficiency of LAS. Under alkali conditions, we find that TOC removal efficiencies are lower than in acidic or neutral conditions after 5 h treatment. Our study also shows that chloride ion concentration does not have an appreciable effect on the TOC removal efficiency. Liao et al. [22] also have stated that pH is much more effective than chloride ion concentration during oxidation processes.

4. Conclusions

This study reveals the role played by various chloride ion concentrations in the AOX formation at different pHs during UV/H_2O_2 oxidation. Regarding the experimental studies, during batch treatment of acetone, the maximum AOX formation rate was observed with 10,000 mg/l Cl^- at pH 10, and approxi-

mately 99% TOC removal efficiency was obtained. For the batch treatment of ABS, the maximum AOX production rate occurred with 10,000 mg/l Cl^- at pH 3 and 99% TOC removal efficiency was achieved.

According to other studies, pH is an important parameter for oxidation processes, but in our work, results showed that the Cl^- concentration in the water and the chemical structure of the substances are more important than the pH of the water for AOX$_{de\ novo}$ production. During the batch experiments, a de novo synthesis of AOX was observed very intensively due to the high chloride content of the wastewaters. This may imply that OH-radicals oxidize some chloride ions to form chlorine, which further reacts with organic compounds so that AOX$_{de\ novo}$ is produced; eventually, these AOX compounds are destroyed.

The advantages of the UV-FSR process as an oxidative pretreatment step over other photochemical treatment processes include reduced reaction times for complete mineralization, economics, efficiency; especially, if aromatic compounds are to be destroyed, easy handling method, because no specific technical equipment is necessary, and harmless process products, and no dirty coating on the surface of UV radiator.

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