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Study of the aromatic by-products formed from ozonation of anilines in aqueous solution

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Abstract

Aqueous solutions of aniline and *p*-chloroaniline were treated with ozone in order to study the reaction and oxidation by-products. Aniline solutions were ozonated at low and high pH, so as to compare both molecular and hydroxyl free radical mechanisms, respectively. The main identified aromatic by-products were nitrobenzene and azobenzene when the experiment was carried out at acid pH. Formation of nitrobenzene, azobenzene, azoxybenzene and 2-pyridine-carboxylic was observed when the ozonation was carried out at basic pH. *p*-Chloroaniline was treated with ozone only at high pH and the identified by-products were in accordance with those obtained in the ozonation of aniline: *p*-chloronitrobenzene, 4,4′-dichloroazobenzene and 4-chloro-2-pyridine-carboxylic acid. All the aromatic by-products found were less toxic than the raw materials. The pseudo-first-order constants in aniline concentration were calculated, whilst kinetic in *p*-chloroaniline concentration could not be adjusted to a first-order reaction. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ozone; Aniline; *p*-Chloroaniline; Ozonation by-products

1. Introduction

The ozonation of aniline and *p*-chloroaniline in aqueous solution is investigated in this study. These compounds were selected because they are frequently detected in many industrial wastewaters. Aniline is an important raw material used in the manufacturing of 4,4′-methylene bis(phenyl isocyanate) (MDI) and poly-MDI, which are intermediates for the production of urethanes [1]. Other principal applications of aniline include production of rubber accelerators and antioxidants to vulcanize rubber; the manufacture of intermediates for herbicides and other pesticides, especially fungicides; and the manufacture of dyes and pigments, especially azo. Aniline is also used to produce medicinals and pharmaceuticals, resins, varnishes, perfumes, shoe blacks, photographic chemicals (hydroquinone), explosives, petroleum refining chemicals, diphenylamine and phenolics [2–4]. *p*-Chloroaniline is used as an intermediate for pesticides, pharmaceuticals, pigments and dyes.

In previous works [5–9], we have studied the application of ozonation as a chemical treatment for industrial wastewaters. Aniline and *p*-chloroaniline were identified as the principal raw materials present in effluents derived from dye manufacturing and manufacturing of rubber vulcanization accelerators. Aniline is detected in high concentration in these wastewaters. Although it is not regulated by legislation, it is highly toxic to aquatic life and US Environmental Protection Agency (US EPA) has suggested an ambient limit in water of 262 μg/L, based on health effects [1]. *p*-Chloroaniline is a compound of interest because it is included in List II of European Union (EU) [10], as a compound which will be regulated by legislation in the future.

In this investigation, synthetic aqueous solutions of aniline and *p*-chloroaniline were treated with ozone with the aim of studying its application to industrial

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wastewaters containing aniline derivatives. The reaction of ozone with these compounds was investigated at different conditions. The aromatic by-products formed during and after the ozonation reaction were identified. Ozone reacts with organic compounds in water via two pathways: directly or indirectly. The molecule of ozone can remain as O_3 or it can decompose by a variety of mechanisms producing the hydroxyl free radical ($OH^\bullet$). Molecular ozone itself, being a weaker oxidizing agent than hydroxyl free radical, is a rather selective oxidant [11]. Some authors have investigated the by-products formed from the reaction of ozone with aniline. Depending on ozonation conditions, the attack of ozone is directed towards aromatic ring cleavage. Aliphatic aldehydes, ketones and acids, along with nitrates and ammonia can be found as final by-products [12,13]. Chan and Larson [14,15] described the next compounds as the main by-products formed after ozonation of anilines: nitrobenzene, nitrosobenzene, azobenzene, azoxybenzene, 4-amino-diphenylamine, benzidine and phenazine. Some condensation products, as well as amino-phenols, have been identified as intermediate by-products of the ozonation reaction [11].

Aniline was treated with ozone at low and high pH, comparing both molecular ozone and hydroxyl free radical mechanisms, respectively. *p*-Chloroaniline was treated with ozone only at high pH, due to the best results obtained from ozonation of aniline at the same conditions.

2. Materials and methods

2.1. Preparation of solutions

Aniline and *p*-chloroaniline solutions were prepared from pure standards (Merck and Riedel-de-Haën, respectively, 99% of purity) in Milli-Q® water, previously purified by means of methylene chloride extraction, with the objective of eliminating possible impurities. The concentration of aniline and *p*-chloroaniline solutions was 1 and 3.5 mM, respectively.

2.2. Ozonation

A Fischer Model 501 Ozonizer was used for the production of ozone. The ozone stream was continuously introduced in the sample through a porous sparger as microbubbles at the bottom of the ozone contactor. The surplus ozone was stored in two bubblers containing 250 mL of 2% KI solution. According to the apparatus calibration curve and through the titration of the solutions in the bubblers using sodium thiosulphate and starch as indicator [16], the medium dosage of ozone consumed was calculated for all the experiments.

Samples of 50 mL were taken at different time steps during the ozonation reaction for the determination of the different compounds. Ozonation of aniline was carried out at two different pH values: pH 2 (by adding 6 N H_2SO_4) and pH 8. In the latter case, pH was controlled with a phosphate buffer and monitored during the experiment to assure that it was held approximately constant. The ozonation of *p*-chloroaniline solution was carried out at pH 8 with phosphate buffer. The ozonation conditions are summarized in Table 1.

2.3. Analytical methods

The aromatic compounds were determined by means of a liquid–liquid extraction of the aqueous samples with methylene chloride and subsequent concentration of the extracts (US EPA Method 625 [16]).

A Varian 3300 Gas Chromatograph connected with an ITD FinniganMAT 800 Mass Spectrometer was used for identifying the compounds. The chromatographic conditions were the following: Column: DB-5 (J&W Scientific); injection volume: 2 μL in splitless (0.8 min.); injection temperature: 250°C; carrier gas: helium (30 cm/s) and temperature programme: 60(1)-4-280(15). The identification of the compounds was carried out by National Institute of Standards and Technology (NIST). Library searching and the main substances were verified by comparison with reference standards.

Table 1
Ozonation conditions of the solutions

Conditions	Aniline		*p*-Chloroaniline
Initial concentration (mM)	1	1	3.5
Initial volume of sample (mL)	1000	1000	1000
Final volume of sample (mL)	750	750	750
Ozonation pH	2	8 (phosphate buffer)	8 (phosphate buffer)
Flow rate of ozone (mg/min)	12	12	10.4
Ozonation time (min)	25	25	25
Medium ozone consumed (mg/L)	305	348	274
Mole O_3 consumed/mole compound	6.3	7.2	1.6

A HP5890 Gas Chromatograph equipped with flame ionization detector (FID) was used for quantifying the representative substances (aniline, *p*-chloroaniline, nitrobenzene and *p*-chloronitrobenzene). The chromatographic conditions were the following: Column: DB-WAX (J&W Scientific); injection volume: 2 μL in splitless (0.8 min.); injection temperature: 300°C; carrier gas: helium (30 cm/s); auxiliary gas: nitrogen and temperature programme: 60(1)-25-120(3)-4-250(5). Semi-quantitative estimation via GC/MS was used to quantify some compounds of which no reference standards were available. Both GC/FID quantification and semi-quantitative estimation were done taking into account the variation of volume due to sample collection.

3. Results and discussion

3.1. Study of the ozonation reaction

Fig. 1 shows the evolution in aniline and *p*-chloroaniline concentration during ozonation reaction. As it is observed in the figure, the elimination of aniline is more effective at pH 8 than at pH 2, for a similar amount of ozone consumed (100% and 80% of elimination, respectively, after 25 min of treatment). It was observed that the pH value remained constant when ozonation was carried out at pH 2. The reaction at acid pH is dominated by the action of molecular ozone whereas at pH 8, the amino group of aniline enhances the ozone decomposition in hydroxyl radicals by releasing superoxide anion radical ($O_2^{\bullet -}$). In addition, the amino group of aniline at acid pH remains as its protonated form (pKa = 4.6), which is an electron-withdrawing group. As a result of this, the electrophilic attack by molecular ozone at acid pH is slower than $OH^{\bullet}$ mechanism at basic pH. From these results, the pseudo-first-order constant in aniline concentration was calculated for both experiments: K' (pH = 2) = $9.8 \times 10^{-4}\,s^{-1}$ and K' (high pH) = $3.5 \times 10^{-3}\,s^{-1}$. As it was expected, the rate constant for the hydroxyl free radical mechanism is higher than the one corresponding to the molecular mechanism.

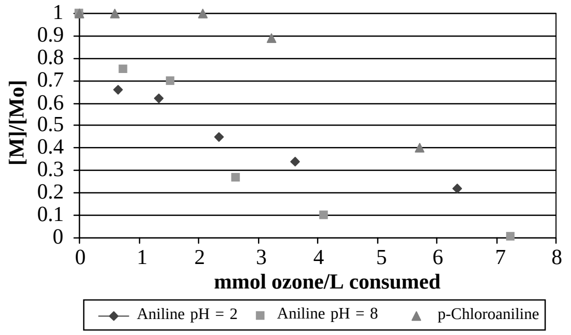


Fig. 1. The evolution of aniline and *p*-chloroaniline concentration during ozonation reaction (M_0(aniline) = 1 mM and M_0(*p*-chloroaniline) = 3.5 mM).

In Fig. 1, it can be seen that the decrease in *p*-chloroaniline concentration is produced in final steps of the reaction, and after the complete treatment 60% of the compound is eliminated. *p*-Chloroaniline degradation is produced by an hydroxyl radical mechanism, enhanced by the amino group of the molecule at pH = 8 (pKa = 3.98). However, kinetic in *p*-chloroaniline concentration cannot be adjusted to a first-order reaction.

3.2. Study of the by-products formed

The by-products formed after complete ozonation of aniline in both experiments and *p*-chloroaniline are shown in Table 2. The main by-products formed after ozonation of aniline at low pH were nitrobenzene and azobenzene, and the evolution of formation of these by-products is shown in Fig. 2. In the reaction of ozone with aniline at high pH, in addition to nitrobenzene and

Table 2
Final by-products identified after ozonation of aniline and *p*-chloroaniline solutions

Compound	Identified by-product	Final concentration (mM) O_3 pH = 2	Final concentration (mM) O_3 pH = 8
Aniline (1 mM)	Nitrobenzene	1.6×10^{-2}	1.1×10^{-2}
	Azobenzene	8.2×10^{-5}	9.6×10^{-4}
	Azoxybenzene	n.d.	5.4×10^{-4}
	2-Pyridine-carboxylic acid	n.d.	3.1×10^{-3}
p-Chloroaniline (3.5 mM)	*p*-Chloronitrobenzene	—	1.2×10^{-2}
	4,4′-Dichloro-azobenzene	—	4.7×10^{-1}
	n,n′-Dichloro-azobenzene	—	8.4×10^{-2}
	4-Chloro-2-pyridine-carboxylic acid	—	1.2×10^{-2}

n.d.: not detected.

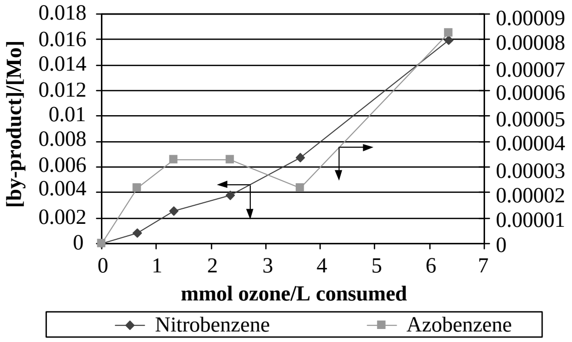


Fig. 2. The evolution of formation of by-products during ozonation of aniline at acid pH.

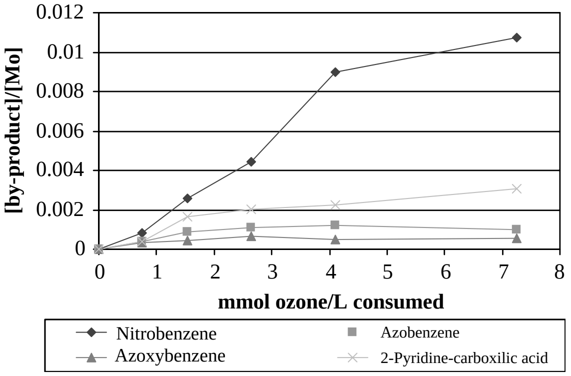


Fig. 3. The evolution of formation of by-products during ozonation of aniline at basic pH.

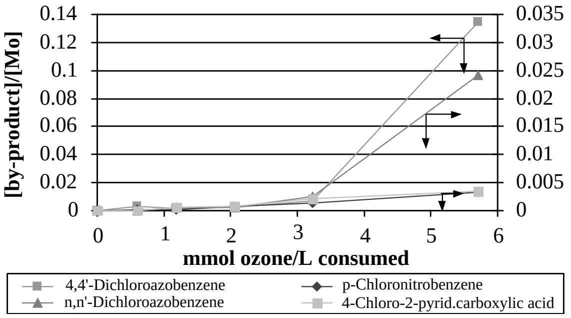


Fig. 4. The evolution of formation of by-products during ozonation of *p*-chloroaniline at basic pH.

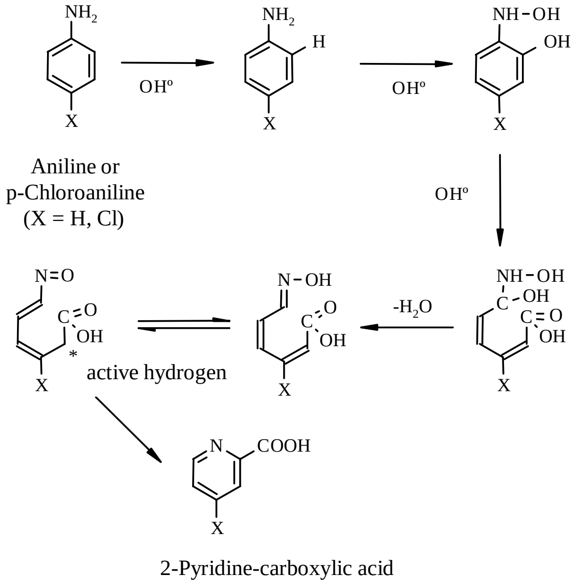


Fig. 5. The proposed mechanism for the formation of 2-pyridine-carboxylic acid from ozonation of anilines.

azobenzene, azoxybenzene and 2-pyridine-carboxylic acid were found (Fig. 3). Nitrobenzene, which was formed by oxidation of aniline, was the majority by-product identified in both experiments, and it was detected in higher concentration at acid conditions. Mainly azobenzene is formed in final steps of the reaction at pH 2, while at pH 8, it reaches a maximum of concentration (mole ozone consumed/mole initial aniline = 4.1), and then it begins to be eliminated. At basic pH, $OH^{\bullet}$ radicals are nonselective in their action on organic matter and can degrade the azobenzene formed. However, final concentration of azobenzene after 25 min of treatment is much higher when the experiment is carried out at basic pH. The evolution of the formation of azoxybenzene is similar to azobenzene, although it is only detected when the ozonation is carried out at pH 8. The compounds identified as by-products of aniline ozonation are in accordance with those reported by Chan and Larson [14,15], who describe the formation mechanisms of azobezene and azoxybenzene from the reaction of ozone with aniline. However, no reference has been found about the formation of 2-pyridine-carboxylic acid.

The main by-product formed after ozonation of *p*-chloroaniline was 4,4′-dichloroazobenzene. Other compounds detected were an isomer of 4,4′-dichloroazobenzene, *p*-chloronitrobenzene and 4-chloro-2-pyridine-carboxylic acid. These compounds are in accordance with the results obtained in the ozonation of aniline in similar conditions, although the corresponding chlorinated azoxybenzene has not been detected. The evolution of the concentration of by-products identified during the reaction between *p*-chloroaniline and ozone is shown in Fig. 4.

As it can be seen, *p*-chloronitrobenzene and 4-chloro-2-pyridine-carboxylic acid are continuously formed during the reaction, whilst azobenzene derivatives are generated at final steps, in accordance with the major degradation of *p*-chloroaniline. Although during the first steps of the reaction, elimination of *p*-chloroaniline is rather small in Fig. 1, by-products are being generated in minor concentration. As in the case of aniline ozonation, the corresponding chlorinated pyridine-carboxylic acid is detected as by-product.

The reaction mechanism proposed for the formation of the pyridine-carboxylic acid from ozonation of anilines could be the following: as a first step, the hydroxylated compound in 2-position is formed. Although this intermediate has not been detected, the by-product is generated only at basic conditions, where the hydroxyl free radicals are more predominant than molecular ozone. After the opening of the aromatic ring, the nitroso- intermediate ($-N=O$) is formed, as a final result of the reaction between ozone and the amino group. The nitroso compound can react with an active hydrogen of the molecule, yielding an imine ($-C=N-$) [17], which in this case leads to the formation of the pyridine-carboxylic acid after a rearrangement of the molecule (Fig. 5).

Although aniline in water is subject to bio- and photodegradation, it is a toxic substance to aquatic life and it must be eliminated of wastewaters before being released to the aquatic environment. Besides, aniline can be subjected to adsorption to sediment and humic materials; this fact can extend the persistence of aniline in the aquatic environment. A half-life for aniline of 2.3 days has been reported in an industrial river [18,19]. *p*-Chloroaniline, being a less toxic compound than aniline, is highly toxic by ingestion, inhalation and skin contact [4,20]. The results of this study show that ozonation is very effective in removing anilines in water. In order to determine if ozonation is applicable to effluents containing aniline derivatives, the toxicity of new by-products and their effect on the environment has been studied. Some toxicity parameters corresponding to raw materials and final ozonation by-products are shown in Tables 3 and 4.

The more representative toxicity parameters for aniline found in published bibliography, are presented in Table 3. Other authors have reported toxicity parameters of nitrobenzene (the majority by-product), however, fewer data have been found about toxicity of azobenzene and azoxybenzene, and no toxicity data of 2-pyridine-carboxylic acid have been published. Comparing toxicity data, it can be concluded that ozonation by-products of aniline are less toxic than the raw material.

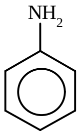
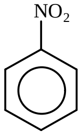
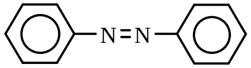
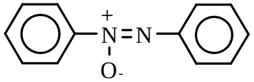
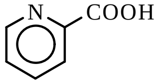
Among the by-products formed, the most interesting compound is nitrobenzene: it is included in the Priority Pollutant List [30] and there is an effluent limitation of US EPA applicable to the process wastewater discharges containing nitrobenzene resulting from the manufacture of organic chemicals, plastics and synthetic fibers [31]. These effluent limitations are the following: direct discharge point sources that use end-of-pipe biological treatment: 68 μg/L (maximum for 1 day) and 27 μg/L (maximum for monthly average) (EPA 40CFR, Part 414, Subpart I); direct discharge point sources that do not use end-of-pipe biological treatment: 6402 μg/L (maximum for 1 day) and 2237 μg/L (maximum for monthly average) (EPA 40CFR, Part 414, Subpart J); indirect discharge point sources: 6402 μg/L (maximum for 1 day) and 2237 μg/L (maximum for monthly average) (EPA 40CFR, Part 414, Subpart K). Although nitrobenzene is regulated in some wastewaters by USA legislation, available information indicates that it is moderately toxic to aquatic life and less toxic than aniline. Besides, nitrobenzene is subject to bio- and photodegradation in water; small amounts also adsorb to sediment or volatilize from the surface. The half-life of nitrobenzene in model waste stabilization ponds was measured at 3.8 days; 89.5% of the added chemical was degraded, 4.9% volatilized, 2.3% adsorbed to sediment, 2.3% was lost in effluent and 1% remained [19]. The half-life of nitrobenzene in aquatic environments has been estimated at 0.3 days [26].

The toxicity parameters for *p*-chloroaniline and its ozonation by-products are presented in Table 4. No toxicity data have been found for 4,4′-dichloroazobenzene and 4-chloro-2-pyridine-carboxylic acid. Although both *p*-chloroaniline and *p*-chloronitrobenzene are included in List II of UE, comparing LD_{50} data it can be concluded that *p*-chloronitrobenzene is less toxic than *p*-chloroaniline.

4. Conclusions

1. Ozonation is very effective in removing aniline and *p*-chloroaniline in aqueous solutions. Ozonation reaction of aniline follows a first-order kinetic, with the pseudo-first-order constants $K' = 9.8 \times 10^{-4}\,s^{-1}$ (low pH) and $K' = 3.5 \times 10^{-3}\,s^{-1}$ (high pH). The ozonation reaction of aqueous solutions of *p*-chloroaniline and ozone at basic pH cannot be adjusted to first-order kinetics in our conditions.
2. Nitrobenzene is the majority by-product formed after ozonation of aniline at acid pH. The selective reaction of molecular ozone with aniline at acid pH leads to the oxidation of amino group to nitro group. Azobenzene is also detected in minor concentration.
3. The indirect reaction of ozone with aniline at basic pH, in addition to nitrobenzene and azobenzene, leads to the formation of azoxybenzene and 2-pyridine-carboxylic acid.
4. It is recommended to ozonize aniline solutions at basic pH. Although a greater number of aromatic by-products are generated, nitrobenzene, which is

Table 3
Toxicity parameters for aniline and its ozonation by-products

	Aniline	Ozonation by-products			
		Nitrobenzene	Azobenzene	Azoxybenzene	2-Pyridine-carboxylic acid
Chemical formula	C_6H_7N	$C_6H_5NO_2$	$C_{12}H_{10}N_2$	$C_{12}H_{10}N_2O$	$C_6H_5NO_2$
Structural formula					
CAS RN	62-53-3	98-95-3	103-33-3	495-48-7	98-98-6
Molecular mass	93.1	123.1	182.2	198.2	123.1
Acute toxicity parameters					
LD_{50} (orl-rat) (mg/kg)	250	640	1000	620	n.a.
LD_{50} (orl-mus) (mg/kg)	464	n.a.	n.a.	515	n.a.
LD_{50} (ipr-rat) (mg/kg)	420	640	n.a.	n.a.	n.a.
LD_{50} (ipr-mus) (mg/kg)	492	n.a.	500	n.a.	n.a.
LD_{50} (skn-rat) (mg/kg)	1400	2100	n.a.	n.a.	n.a.
LD_{50} (skn-rbt) (mg/kg)	820	n.a.	n.a.	1090	n.a.
LDL_0 (orl-rbt) (mg/kg)	500	700	n.a.	n.a.	n.a.
LDL_0 (orl-cat) (mg/kg)	100	2000	n.a.	n.a.	n.a.
LDL_0 (scu-rbt) (mg/kg)	1000	n.a.	n.a.	250	n.a.
LDL_0 (ivn-dog) (mg/kg)	200	150	n.a.	n.a.	n.a.
LDL_0 (unr-man) (mg/kg)	150	35	n.a.	n.a.	n.a.
Toxicity to aquatic organisms					
TLm96 (ppm)	100–10	100–10	n.a.	n.a.	n.a.
LC_{50}(96) (mg/L) Zebrafish	32–53	112.5	n.a.	n.a.	n.a.
LC_{50}(48) (mg/L) Medaka	165	20	n.a.	n.a.	n.a.
LC_{50}(48) (mg/L) Fathead minnow	65	156	n.a.	n.a.	n.a.
LC_{50}(48) (mg/L) Golden orfe	61–78	60–89	n.a.	n.a.	n.a.

Carcinogenicity	Probable human carcinogen	Probable human carcinogen	Not classifiable as a human carcinogen	n.a.	n.a.
Test of genotoxicity	Positive	Negative	n.a.	n.a.	n.a.
Ambient limit in water (μg/L)	262	n.a.			
Proposed limit for protection of aquatic life (fresh water) (μg/L)		27,000 (acute toxicity)			
Proposed limit for protection of aquatic life (salt water) (μg/L)		6680 (acute toxicity)			
Proposed limit for protection of human health (μg/L)		19,800 (toxic effect)			
Compound included in list (water quality)		Priority pollutant list (US EPA)			

Sources: Budavari et al. [2]; Clansky [21]; Lewis and Tatken [22]; Sax [23]; Sittig [24]; USEPA [18,25–27] and Verschueren [28].

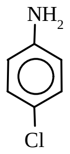
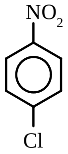
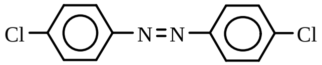
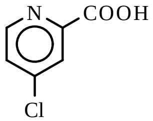
LD_{50}: lethal dose 50% kill
LDL_0: lowest published lethal dose
TLm96: threshold limit (96 h)
LC_{50}: lethal concentration 50 percent kill

ipr: intraperitoneal
ivn: intravenous
orl: oral
scu: subcutaneous
skn: skin
unr: unregistered

mus: mouse
rbt: rabbit

n.a.: not available

Table 4
Toxicity parameters for *p*-chloroaniline and its ozonation by-products

	p-Chloroaniline	Ozonation by-products		
		p-Chloronitrobenzene	4,4′-Dichloroazobenzene	4-Chloro-2-pyridine carboxylic acid
Chemical formula	C_6H_6ClN	$C_6H_4ClNO_2$	$C_{12}H_8Cl_2N_2$	$C_6H_4ClNO_2$
Structural formula				
CAS RN	106-47-8	100-00-5	1602-00-2	n.a.
Molecular mass	127.57	157.56	251.1	157.56
Acute toxicity parameters				
LD_{50} (orl-rat) (mg/kg)	310	420	n.a.	n.a.
LD_{50} (orl-mus) (mg/kg)	100	650	n.a.	n.a.
LD_{50} (ipr-rat) (mg/kg)	420	420	n.a.	n.a.
LD_{50} (skn-rat) (mg/kg)	3200	16,000	n.a.	n.a.
Toxicity to aquatic organisms				
TLm96 (ppm)	1000–100	1000–100	n.a.	n.a.
Compound included in list (water quality)	List II (EU)	List II (EU)		
Water quality criteria (μg/L) (EU proposed)	10	10		

Sources: Budavari et al. [2]; Clansky [21]; Lewis and Tatken [22]; Sax [23]; Sittig [24]; Verschueren, [28] and Bro-Rasmussen [29].

LD_{50}: lethal dose 50% kill
TLm96: threshold limit (96 h)
n.a.: not available

ipr: intraperitoneal
orl: oral
skn: skin
mus: mouse

regulated by US EPA, is detected in minor concentration.

5. The main by-products identified after complete reaction of ozone and *p*-chloroaniline are dichloroazobenzene derivatives. Other by-products detected in minor concentration are *p*-chloronitrobenzene and 4-chloro-2-pyridine-carboxylic acid.
6. In general, the aromatic by-products formed after ozonation of aniline and *p*-chloroaniline are less toxic to aquatic environment than the raw materials.

Acknowledgements

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