Trimethylamine oxidation by peroxydisulfate activated by Fe^{+2} or CuO. Risk of N-nitrosodimethylamine formation

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Abstract Methylamines i.e. monomethylamine, dimethylamine and trimethylamine are present in wastewater both as a result of organic matter degradation, as well as as originated from anthropogenic sources. Depending on both types of oxidant as well as oxidant/methylamine ratio, methylamines can be oxidized to nitrates and carbon dioxide. Such a reaction may be stopped at the stage of intermediates formation such as formic acid, formaldehyde, and nitrite. However, a probem occurs in case of a formation of another compound, namely N-nitrosodimethylamine (NDMA), which is considered to be strongly mutagenic and carcinogenic. NDMA can be formed as a result of reaction of strong oxidants with e.g., dimethyl or trimetylamine. On the other hand, strong oxidant called peroxydisulfate (PDS) is lately often considered as very useful oxidant. Before use, PDS, however, has to be activated. Several types of the activators were pointed out, among them the application of ions of some metals on lower valence (such as Fe^{+2}) or oxides of some metals (such as CuO) seems to be the most promising. An influence of activation method of PDS activation on PDS reactivity with trimethylamine was the basic subject of this study. Peroxydisulfate could be considered as 'safe' oxidant against trimethylamine presence in water. This means that PDS destroys TMA without NDMA formation. The relatively low destruction rate of TMA (less than 2%) shows, however, that remain part of TMA may act as NDMA precursor for subsequently applied disinfection agents like chloramines and ozone.

Keywords: Di/tri- methyl amines, oxidation, peroxydisulfate - PDS, NDMA

1. Introduction

Methylamines i.e., monomethylamine, dimethylamine and trimethylamine are present in wastewater both as a result of organic matter degradation as well as originated from several anthropogenic sources like discharge of sewages from pharmaceutical or tires manufacturing industries. Depending on both types of oxidant as well as oxidant/methylamine ratio, methylamines can be oxidized to nitrates and carbon dioxide. Such a reaction stopped on the stage of intermediates formation such as formic acid, formaldehyde and nitrite. These compounds are not considered as potentially hazardous ones. However, a problem occurs in case of a formation of other compound, namely N-nitrosodimethylamine (NDMA). This compound shows strong mutagenic and carcinogenic effects. NDMA can be formed as a result of reaction of strong oxidants such as chloramine (Mitch & Sedlak, 2002; Choi & Valentine, 2002), chlorine dioxide (Andrzejewski & Nawrocki, 2007), ozone (Andrzejewski & Nawrocki, 2007; Andrzejewski, 2008), or permanganate (Andrzejewski & Nawrocki, 2009) with dimethylamine presented in water. Moreover, NDMA may be also formed during ozone reaction with some compounds containing dimethylamine group (Oya, 2008). Trimethylamine may be considered as a part of above mentioned group and its reaction with ozone results in N-nitrosodimethylamine formation (Lee, 2007).

A mechanism of NDMA formation during mono- or di-chloramine reaction with DMA (or dimethylamine-containing compounds) is still a matter of deliberates, however, milestones of this reaction are out of any discussion. These milestones are:

- reaction of monochloramine with DMA or dichloramine with DMA, which results in 1,1-dimethyl hydrazine (UDMH) or chloro-dimethyl hydrazine (Cl-UDMH) formation.
- 1,1-dimethyl hydrazine (UDMH) or chloro-dimethyl hydrazine (Cl-UDMH) are oxidized to form NDMA. (Mitch & Sedlak, 2002; Choi & Valentine, 2002)

During these reactions, DMA served as a source of dimethylamine part of NDMA molecule, and the reaction seems to undergo according to molecular mechanism of reaction. However, radical mechanism are also considered.

So far, several mechanisms of NDMA formation during ozonation of DMA or dimethylamine containing compounds have been proposed. However recently, a formation of UDMH as an intermediate compound is

considered as the milestone of this mechanism. UDMH is subsequently oxidized to form NDMA; however, detailed mechanism of UDMH formation is still a matter of the dicusssion (Yang, 2009). Despite of discussion on details of NDMA formation mechanism (Yang, 2009; Andrzejewski, 2012), DMA served both as a source of dimethylamine part as well as nitrozo-part of NDMA molecule. Therefore, NDMA/DMA conversion rate is lower than in the case of chloramination of DMA containing water. The NDMA formation mechanism during ozonation of DMA containing water is fully considered as radical. Dimetyl amine containing compounds (including trimethyl amine) ozonation take place according to the mechanism of trimetyl amine conversion to dimethyl one, and subsequently the reaction similar to the ones described above (Lee, 2007).

On the other hand, strong oxidant called peroxydisulfate (PDS, also known as persulfate) is often considered as a very useful oxidant. A behavior of this oxidant is however different from other compounds such as ozone or chlorine. Prior to use of PDS, this compound has to be activated. Several types of activators were pointed out, but an application of ions of some metals on its lower valence (such as Fe^{+2}) (Anipsitakis & Dionysiou, 2003; Anipsitakis & Dionysiou, 2004) or oxides of some metals (such as CuO) (Zhang, 2014) seems to be the most promising. PDS activation with ions of some metals on its lower valence leads to the formation of very reactive sulfuric radicals (SO_4^{*-}) according to the following equation (Dionysiou, 2004):

$$S_2O_8^{2-} + Fe^{+2} \rightarrow SO_4^{*-} + SO_4^{2-} + Fe^{+3} \quad \text{(Eq.1.)}$$

On the other hand, PDS activation with oxides of some metals, mainly CuO, results with non-radical oxidation mechanism.

The reactivity of DMA with potassium monopersulfate (an analogue of peroxydisulfate) in the presence of nitrite, as a method of secondary nitrosamines synthesis, was considered by Zolfigol *et al*.(2001a, 2001b). These authors published several papers concerning highly effective method of the synthesis of secondary nitrosamines by catalytic nitrosation of secondary amines with strong acids or the salt (including potassium monopersulfate) and sodium nitrite, in heterogeneous conditions. Wet SiO_2 (50% w/w) was applied as a catalyst. The authors stressed the crucial role of wet SiO_2 (the nitrosation reaction did not occur in the absence of silica). All compounds successfully applied by Zolfigol *et al*. were strong oxidants. Unfortunately, the authors presented no data on pH of these reactions. On the other hand, authors pointed also the role of NO^+ as nitrosation agent, and nitrosation agent's carriers (IO_x^- where X= 3 or 4) as parts of in situ generated structure: ($NO^+O_x^-$). The nitrosation process, however, undergo successfully only at low pH (3 - 4).

As mentioned before, PDS activation with selected metal ions (including Fe^{+2}) leads to the formation of very reactive sulfuric radicals, which significantly increase the efficiency of destruction of micropollutants. However, on the other hand, two main drawbacks of this activation methods should be mentioned. Firstly, an activation efficacy is lower than 50% due to the formation of sulfuric ion, which is formed simultaneously to sulfuric radical (see Eq. 1.) Secondly, sulfuric radicals may react with chloride anions. Chloride ions are presented in all raw water and wastewater at the level of at least hundreds of milligrams per liter. The potentially danger radicals are formed as a result of the reaction among sulfuric radicals and chloride anions. Chlorine radical (Cl_2^{*-}) not only reduces pollutant degradation rate, but also leads to the formation of highly chlorinated products. Moreover, sulfate radicals may also oxidize bromide ions present in the water (Zhang, 2014). Brominated products are considered as more hazardous to the environment in comparison with its chlorinated analogs.

In contrast to the above-described PDS activation method, peroxydisulfate activation with metal oxides, chiefly CuO, leads to the formation of non-radical species, which are very effective oxidants. However, both the mechanism of PDS activation as well as an oxidation mechanism have not been fully recognized. Therefore, such activation method is considered as 'safe oxidation'.

Based on above-described data, peroxydisulfate seems to be unique oxidant to be applied due to possibility oxidation mechanism control by means of selecting of PDS activation method.

The aim of this research was an investigation of an influence of PDS activation method on trimethylamine destruction during peroxydisulfate oxidation. Amount of formic acid (formed as the result of methyl groups oxidation) and nitrate (formed as the result of nitrogen in amine groups oxidation), would be the indicators of DMA degradation. On the other hand, the concentration of sulfate, origin from PDS decomposition, would serve as an indirect indicator of PDS degradation. Changes in sulfate concentration would be compared to the changes in, continuously measured, red-ox potential of the reaction mixture, which also serves as an indirect indicator of PDS degradation. Amount of NDMA, if it forms during these reactions, would be considered as a risk factor of NDMA formation versus PDS activation mode. Thus we decided to evaluate an influence of the activation method of PDS activation on PDS reactivity with trimethylamine. PDS concentration in water may be determined by means of derivatization technique prior to absorption measurement at 352 nm. (Chenju, 2008). The authors of this paper decided to apply two indirect methods for searching changes of PDS concentration during the oxidation process: a determination of sulfate concentration (one of molecule of PDS finally generates two molecules of sulfate ions) and red-ox measurement.

2. Materials and methods

2.1. Reagents

- high purity water (Millipore).
- Trimethyl amine (TMA) solution (Fluka, 60% solution in water)
- pH adjustments i.e. H_2SO_4 (>95%, Fluka) or NaOH (>98%, Fluka) as diluted solutions
- Potassium peroxydisulfate (Fluka >99%)
- CuO prepared by means of two hours $CuCO_3$ (98% Fluka) calcination at temperature of 320°C.

- $FeSO_4$ (source of ferrous ions) was prepared from pure iron (>95%, Fluka) as the result of metal Fe reaction with solution of sulfuric acid (>95%, Fluka).

2.2. Experimental procedure

TMA oxidation with potassium peroxydisultate activated with Fe^{+2} ion or CuO were carried out. Experiments were conducted on deionized model water spiked with TMA. The model water was prepared by an addition of pure TMA solution into high purity water (Millipore). Solution pH was adjusted by the addition of H_2SO_4 or NaOH in the pH of 5.8. This pH was pointed by Zhang et. al. as the optimum value for CuO activation of PDS (Zhang, 2014). No buffers were added to the reaction mixtures. PH of reaction mixture were, however, checked twice, namely at the stage of TMA solution before PDS addition and after one hour of the reaction. Buffers like phosphate one, is suspected of its influence on reactions of sulfuric radical (SO_4^{*-}), formed as the result of PDS activation with ferrous ion (Zhang, 2014). Subsequently PDS and the activators were added. Sequences of PDS and activators addition depended on the type of activator applied. In the experiments for which CuO was used as the activation agent, CuO was added first and then subsequently PDS was added, contrary to ferrous ion activation, where PDS was added as the first one. Concentrations of the main reagents varied in the range of 0.205–0.41 mML^{-1} for TMA and 0.41–0.62 mML^{-1} for PDS. Peroxydisulfate was activated with addition of Fe^{+2} ions (added as $FeSO_4$) or CuO. Fe^{+2} ions were added as a dry solid. Copper oxide was added also as a dry solid, to reach the concentration of 2,5 mML^{-1}.

The Fe_2O_3 or CuO suspensions (the first generated as the result of Fe^{+2} ion oxidation, the second one previously added to the reaction mixture), were removed by the filtration. The influence of several parameters, such as pH, molar ratio of TMA/PDS, PDS concentration and contact time of TMA/PDS, on the formation of NDMA, TMA and PDS degradation products (formic acid, nitrite, nitrate and sulfate) were tested. The red-ox potential of reaction mixtures were also controlled. The following correlations were examined:

- the correlation between changes of the concentrations of NDMA, PDS, nitrite, nitrate, sulfate and formic acid vs. PDS/TMA contact time,
- the correlation between changes of the concentrations of sulfate and the changes of red-ox potential vs. PDS/TMA contact time.

In general, one of the four possible scenarios of reaction pathways of above described experiments could occurs:

1) NDMA is formed, independently of activation method applied. Conclusion: PDS could be considered as a ‘dangerous’ oxidant against presence of TMA in treated water, independently of an activation method applied;
2) NDMA is formed during application of one of activation techniques. Conclusion: PDS could be considered as a ‘dangerous’ oxidant against presence of TMA in treated water, only in case of application of one of activation methods i.e. according to molecular or radical mechanism of reaction;
3) No NDMA is formed, independently of activation method applied, but TMA degradation products are formed. Conclusion: PDS could be considered as a ‘safe’ oxidant against presence of TMA in treated water, independently of an activation method applied. Moreover, an application of the subsequent, second, oxidant should significantly decrease NDMA formation potential or even eliminate it;
4) No NDMA is formed, independently of activation method applied, and TMA degradation products are not formed. Conclusion: PDS could be considered as a ‘safe’ oxidant against presence of TMA in treated water, independently of an activation method applied. However, an application of the subsequent (second) oxidant does not decrease NDMA formation potential of the second oxidant.

2.3. Analytical methods

2.3.1. NDMA and formic acid analytics

The principal aim of the study was to find out whether NDMA is formed as a reaction product of PDS with trimethylamine. The GC–MS technique, preceded by liquid–liquid extraction of post-reaction mixture with dichloromethane was chosen for the identification of NDMA. This technique, though useful for qualitative purposes, was not fast enough to be used for quantitative ones. For that reason for the quantitative analysis of nitrosamines, slightly modified ion-exclusion chromatography with UV-Vis detection was applied. The quantitative method, i.e., HPLC-IEC-UV-Vis allows to determine NDMA at the level of 0.07 uM/L. This technique enabled also the analysis of other byproducts, such as formic acid. methods: GC–MS and HPLC–IE–UV have been described in our previous papers (Andrzejewski, 2005).

2.3.2. Analysis of nitrate, nitrite and sulfate ions

The presence of nitrate, nitrite and sulfate ions (the byproduct of DMA oxidation or PDS decomposition) in the reaction mixture were determined by means of ion chromatography (IC).

Chromatographic conditions

The eluent was composed of 1.0 mM $NaHCO_3$ and 3.5 mM Na_2CO_3. The eluent flow rate was 0.8 $mL \cdot min^{-1}$. The column pressure and temperature were set up at 9.8 MPa and 45°C, respectively. The suppressor was automatically regenerated by 20 mM H_2SO_4. The instrument was equilibrated for 30 minutes prior to use. The instrument was calibrated with standard solution after minimizing the baseline drift. Blank solutions deionized distilled water were tested for anionic impurities before analysis.

Dependencies between the peak area and the compound concentration were determined as a result of a

chromatographic analysis of samples with added multi-anion standard solution. Based on these dependencies, the calibration graphs were prepared. Calibration curve was constructed using standard solutions in the range of 1.00 $mg \cdot L^{-1}$ - 5 $mg \cdot L^{-1}$ for NO_2^-, NO_3^-, 5.00 $mg \cdot L^{-1}$ - 25.00 $mg \cdot L^{-1}$ for Cl^{-1} and 10.00 – 50.00 $mg \cdot L^{-1}$ for SO_4^{2-} using five concentration levels. A simple solution at each concentration level was injected in triplicate. The calibration plots were approximated by the equation $y = ax + b$, where y is the peak area, x is the concentration of determination compound ($mg \cdot L^{-1}$), and a and b are model parameters. Good correlation coefficients, higher than 0,9990, were obtained. The following parameters: relative standard deviation (RSD), limit of detection (3×SD), upper limit of the linear range of calibration (UL), were calculated for all ions. The RSD values for all the investigated ions were below 2.5%, and the LODs were 0.50, 0.19, 0.11, 0.09 $mg \cdot L^{-1}$, respectively, for Cl^-, NO_2^-, NO_3^-, SO_4^{2-}.

2.3.3. Red-ox potential measurement

Red-ox potential measurement, as a tool for investigation of process of pollutants destruction with PDS was proposed by Waclawek et. al. (Wacławek, 2016). Authors of presented paper automatically recorded red-ox potential, with 1 sec. intervals, during all the time of experiments, i.e., 60 min. Checking of correlations of dynamics, of the red-ox potential changes, with changes of sulfates concentration were the aims of these tests. Moreover, dynamics of the red-ox potential changes vs. PDS activation techniques were also investigated.

2.4. Apparatus

2.4.1. NDMA and formic acid.

These two compound (i.e. NDMA and HCOOH) were analyzed simultaneously by means of HPLC-Ion Exclusion-UV-VIS technique with wavelengths 230 nm and 210 nm respectively using Waters 2690 HPLC coupled with Waters 2487 dual wave detector.

2.4.2. Inorganic ions: nitrite, nitrate and sulfate

The employed ion chromatography system was a LC-20 ADSP Shimadzu equipment with a CDD-10Avp conductometric detector, DGU-20A5R degasser, CTO-20AC oven column with a 25µL injection loop and Shodex SI 52 4E analytical column. The system was controlled by a CBM-20A communication bus module with LabSolution software. During the analysis, the Continuous Anion Regeneration System — CARS (SeQuant, Sweden) was used.

2.4.3. Red-ox potential

Multifunction meter CX-505 equipped with red-ox electrode Aqua Medic Red-Ox/ORP coupled with data acquisition system based on ASUS G74S computer

3. Results and Discussion

3.1. NDMA formation

No traces of NDMA were found into post-reaction mixtures of trimethylamine and peroxydisulfate activated by iron ions (Fe^{+2}) or copper oxide (CuO). Thus the first conclusion can be formed: PDS could be considered as a 'safe' oxidant against presence of TMA in treated water, independently of an activation method applied.

3.2. Presence of nitrate, nitrite and sulfate ions in post-reaction mixture

No traces of nitrite (as product of TMA destruction) were found into post-reaction mixtures of trimethylamine and peroxydisulfate activated both by iron ions (Fe^{+2}) as well as copper oxide (CuO). The changes of amounts of sulfate ions (as product of PDS destruction) and nitrate (as product of TMA destruction) vs. PDS activation methods were shown in Figures 1 and 2. These changes were presented as SO_4^{-2}/PDS ratio [M/M %] and NO_3^-/TMA ratio [M/M %] and vs. reaction time.

Results clearly show that both Fe^{+2} as well as CuO activated PDS, which underwent as the result of the activation. (See Fig.1). PDS destruction, measured as increase of SO_4^{-2}/PDS [M/M %] ratio, strongly depends on mode of PDS activation. Ferrous ion activation of PDS results with 200% conversion PDS to SO_4^{2-} ions. It means that the total decomposition of peroxydisufate occurred, because decomposition of one molecule of PDS results in the formation of two molecules of sulfate ions. An activation of PDS by CuO also results in it conversion to sulfate ions. However, this value was definitely lower and does not exceed 50%. It means that only 25% of PDS was finally destructed during this process.

Differences were observed for nitrate formation as the result of TMA oxidation (see Fig.2). No nitrate formation was observed during Fe^{+2} ion activated PDS reaction with TMA, contrary to the CuO activated PDS, for which the nitrate formation was observed. The amount of nitrate, which was formed during this reaction, was very low and did not exceed 2 % calculated as NO_3^-/TMA ratio [M/M %]

One interesting phenomena was also observed. The destruction of TMA, during its oxidation with CuO activated PDS, measured as an increase of NO_3^-/TMA ratio, seems to undergo initially vigorously, while since the fifth minute of the reaction, the plateau is observed.

Figure. 1. Sulfate ions formation during PDS degradation vs. PDS activation mode

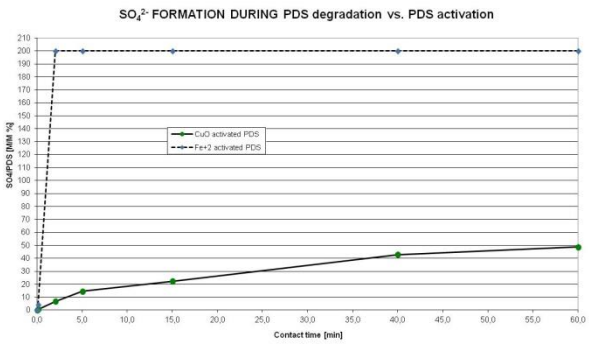
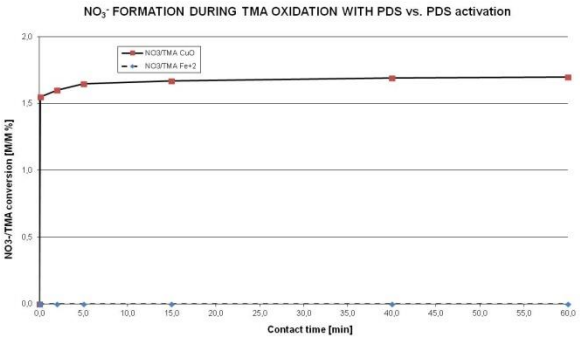


Figure. 2. Nitrate ions formation during TMA oxidation vs. PDS activation mode



3.3. Presence of formic acid in post-reaction mixture

Formation of formic acid was observed only as the result of TMA oxidation with CuO activated PDS. An amount of HCOOH, measured as a quotient of HCOOH/TMA [M/M %], is low as NO_3^-/TMA ratio and does not exceed a half of percent. The dynamics of this process is, however, similar to the one observed for nitrate (initially vigorously and subsequently plateau).

3.4. Changes of red-ox potential during experiment

Red-ox potential increased independently to activation method applied. The results are shown on Fig. 3.

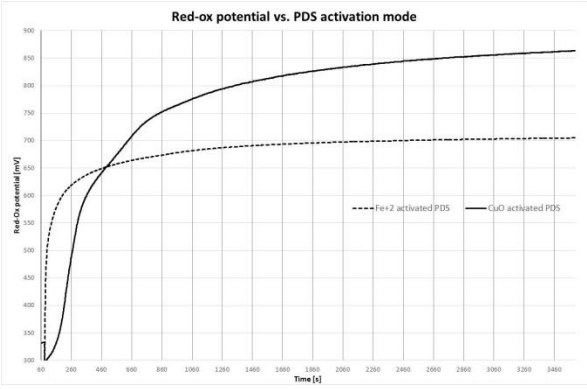


Figure 3. Red-ox potential changes vs. PDS activation mode (Fe^{+2} or CuO)

Dynamism of the processes depends on activation method applied, i.e., the one based on Fe^{+2} or CuO. Applying ferrous ions as activation agent resulted in rapid increase of red-ox potential from 300 mV to app. 525 mV during a few seconds. Next, dynamics of the process significantly decreased up to 460 sec and reaches red-ox potential of 650 mV. From this point, red-ox potential increases very slowly, in practice linearly, from 650 mV to 700 mV during the last period of experiment (3140 seconds, i.e., app. for 52 mins). In contrast to the results obtained for Fe^{+2} ions activated PDS, dynamics changes in the red-ox potential during peroxydisulfate activation with CuO is different. During the first period of the experiment, the increase of red-ox potential is vigorous, however dynamics of its changes is slower, comparing to the one observed for Fe^{+2} ion activated PDS. Moreover, no 'turning point' on red-ox potential vs. time curve may be indicated; the red-ox potential just increases slower and slower with growing time of experiment. The final value of red-ox potential was, however, significantly higher and reached app. 860 mV.

4. SUMMARY

Reactivity of PDS with trimethylamine strongly depends on the PDS activator applied. Ferrous-ions-activated PDS does not react with TMA, at least under the observed experimental conditions. It seems that very active sulfuric radicals do not oxidize trimethylamine, despite of total PDS decomposition. On the other hand, CuO-activated PDS reacts with TMA, despite of definitely lower, compare to ferrous ions PDS activation, PDS decomposition rate. Contrary to the radical mechanism of ferrous ion activation PDS, CuO-activated PDS reacts according to the molecular mechanism (Zhang, 2014). However, the TMA decomposition rate, measured as nitrate and formic acid formation is low.

Differences in reactivity of PDS with TMA, as the result of activation mode, cannot be attributed to different values of final red-ox potentials (860 mV vs. 700 mV), because both nitrate and formic acid are formed during the first few minutes of the process (see Fig. 2). During that time the red-ox potential of the reaction mixture is higher for Fe^{+2} activated PDS. It seems that type of oxidation mechanism is responsible for the difference in PDS reactivity with TMA.

5. CONCLUSIONS

1. Reactivity of PDS with trimethylamine strongly depends on PDS activator applied.

2. Trimethylamine was oxidized by peroxydisulfate to form its oxidation products, i.e., nitrate and formic acid only, in case CuO is applied as PDS activation agent.

3. Independently to PDS activation methods, no NDMA is formed during these reactions.

4. Both techniques, i.e., the determination of sulfate concentration and red-ox measurement, applied for the determination of kinetics of PDS degradation, show differencies in PDS degradation vs. activation methods. These techniques may be applied as simple substitutes of the direct method of an evaluation of PDS degradation rate.

4. Peroxydisulfate could be considered as partly 'safe' oxidant against trimethylamine presence in water. This means that PDS reaction with TMA (if occurs), does not lead to NDMA formation. The relatively low destruction rate of TMA (less than 2%) shows however, that remaining part of TMA may serve as NDMA precursor for subsequently applied disinfection agents like chloramines or ozone.

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References

1. Mitch W.A., Sedlak D.L. (2002), Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination, *Environmental Science and Technology*, **36**, 588-595
2. Choi J., Valentine R.L. (2002), Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloroamine : a new disinfection by-product, *Water Research*, **36**,817-824
3. Andrzejewski P., Nawrocki J. (2007), N-nitrosodimethylamine formation during treatment with strong oxidants of dimethylamine containing water, *Water Science and Technology*, **56**, 125–131.
4. Andrzejewski P., Kasprzyk-Hordern B., Nawrocki J. (2008) N-nitrosodimethylamine (NDMA) formation during ozonation of dimethylamine-containing waters, *Water Research*, **42**, 863-870
5. Andrzejewski P., Nawrocki J., (2009), N-nitrosodimethylamine (NDMA) as a product of potassium permanganate reaction with aqueous solutions of dimethylamine (DMA), *Water Research*, **43**, 1219-1228
6. Oya M., Kosaka K., Asami M., Kunikane S. (2008), Formation of N-nitrosodimethylamine (NDMA) by ozonation of dyes and related compounds, *Chemosphere*, **73**, 1724–1730
7. Lee C., Schmidt C., Yoon J., von Gunten U. (2007), Oxidation of N-Nitrosodimethylamine (NDMA) precursors with ozone and chlorine dioxide: Kinetics and effect on NDMA formation potential, *Environmental Science and Technology*, **41**, 2056-2063
8. Yang L., Chen Z., Shen J., Xu Z., Liang H., Tian J., Ben Y., Zhai X., Shi W., Li G. (2009), Reinvestigation of the Nitrosamine-Formation Mechanism during Ozonation, *Environmental Science and Technology*, **43**, 5481–5487
9. Andrzejewski P., Fijołek L., Nawrocki J. (2012), An influence of hypothetical products of dimethylamine ozonation on N-nitrosodimethylamine formation, *Journal of Hazardous Materials*, **229**, 340-345 doi: 10.1016/j.jhazmat.2012.06.009
10. Anipsitakis G.P., Dionysiou D.D., (2003), Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt, *Environ. Sci. Technol.*, **37** (20), 4790-4797
11. Anipsitakis G.P., Dionysiou, D.D., (2004), Radical Generation by the Interaction of Transition Metals with Common Oxidants. *Environ. Sci. Technol.*, **38** (13), 3705-3712
12. Zhang T., Chen Y., Wang Y., Le Roux J., Yang Y., Croué J-P. (2014), Efficient Peroxydisulfate Activation Process Not Relying on Sulfate Radical Generation for Water Pollutant Degradation, *Environ. Sci. Technol.*, **48**, 5868−5875
13. Zolfigol, M.A., Choghamarani, A.G., Shirini, F., Keypour, H., Salehzadeh, S. (2001), Chemoselective N-nitrosation of secondary amines under mild and heterogeneous conditions. *Synthetic Communication* **31**, 359–365
14. Zolfigol, M.A., Bagherzadeh, M., Choghamarani, A.G., Keypour, H., Salehzadeh, S. (2001), N-nitrosation of secondary amines under mild and heterogeneous conditions. *Synthetic Communication*, **31**, 1161–1166
15. Liang, Ch., Chiu-Fen H., Nihar M., Kurakalva, R.M. (2008), A rapid spectrophotometric determination of persulfate anion in ISCO, *Chemosphere* **73**, 1540–1543
16. Andrzejewski P., Kasprzyk-Hordern B., Nawrocki J. (2005), The hazard of N-nitrosodimethylamine (NDMA) formation during water disinfection with strong oxidants. *Desalination*, **176**, 37-45.
17. Wacławek S., Antoš V., Hrabák P., Černík M., Elliott D. (2016), Remediation of hexachlorocyclohexanes by electrochemically activated persulfates, *Environ Sci Pollut Res*, **23,** 765–773 DOI 10.1007/s11356-015-5312-y