

## Increasing the biodegradability of rocket fuel polluted groundwater by means of chemical oxidation processes

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**Abstract.** Highly toxic residues of rocket fuel have been detected in the groundwater of an abandoned military missile base in north-west Estonia. The growth of indigenous rocket fuel-degrading bacteria in the polluted groundwater is strongly inhibited by a high concentration of pollutants in the groundwater. Two chemical oxidation processes, ozonation and catalytic wet oxidation (CWO), were studied for the treatment of such groundwater. The ozonation experiments were carried out in a wetted-wall column and the CWO experiments were conducted in an autoclave in the presence of granulated activated carbon. The ozone–water contact column operated at laboratory temperature whilst in CWO the operational variables ranged as follows: temperature from 413 to 446 K, oxygen pressure from 0.4 to 1 MPa. Both processes degraded the primary rocket fuel pollutant (dimethylanilines) and increased biodegradability. The solution remaining after ozonation and CWO contained mainly organic acids. Despite the formation of refractory compounds, the residual water can be treated in bioprocesses without complications because organic acids are easily biodegradable.

**Key words:** 2,4-dimethylaniline, ozonation, catalytic wet oxidation, biodegradability.

### INTRODUCTION

Groundwater polluted with rocket fuel residues can be found at the sites of former Soviet military missile bases because of spills of the organic part of the liquid two-component (nitric acid and organic liquid) missile fuel. The organic component of the fuel consists of triethylamine (50 wt%) and various isomers of dimethylaniline (45 wt%).

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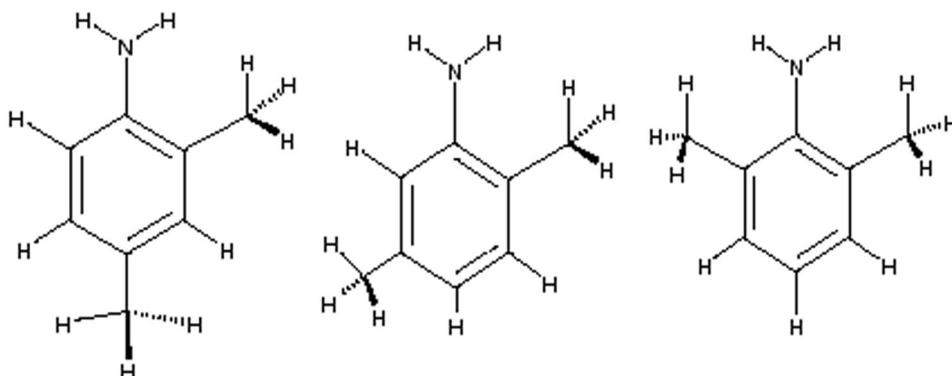
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According to environmental analyses from an abandoned Soviet missile base at Keila-Joa (north-west Estonia), the groundwater is polluted and contains components that originate from missile fuel – dimethylanilines up to  $210 \text{ g/m}^3$  and triethylamine up to  $125 \text{ g/m}^3$  [1]. Similar contamination of groundwater can be found at former military bases in Barta and Tasi, West Latvia [2]. As triethylamine is an easily volatile component this work focuses on the degradation of dimethylanilines, which are the main toxic components from missile fuel. Chemical oxidation was applied for the treatment.

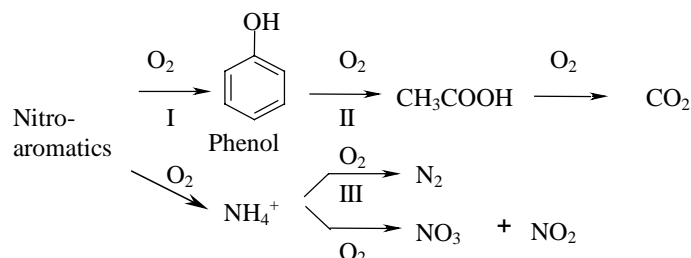
Dimethylanilines are extremely toxic, carcinogenic, and mutagenic compounds. Typically, dimethylanilines are a mixture of isomers in which the 2,4-, 2,5-, and 2,6-isomers are dominant. Molecular structures of the isomers are presented in Fig. 1. Dimethylanilines are relatively soluble, mobile, and persistent in groundwater [3]. Based on the effects observed in animals, it is likely that dimethylanilines can be absorbed through human skin in sufficient amounts to cause dangerous methemoglobinemia even at concentrations as low as  $2 \text{ g/m}^3$  [4, pp. II-208]. There is a high risk that groundwater polluted with carcinogenic dimethylanilines may contaminate drinking water wells, with resultant impacts on human health.

In general, the rate of biodegradation of contaminated water decreases with increasing molecular weight, making aromatic amines persistent to biodegradation. Studies on the biodegradability of nitroaromatics, such as trinitrotoluene, have indicated that anaerobic biodegradation is not possible [5].

A relatively high number ( $4 \times 10^6 \text{ CFU/mL}$ ) of indigenous rocket fuel-degrading bacteria have been found in the polluted groundwater from the abandoned Keila-Joa missile base, but bacterial growth is strongly inhibited by a high concentration of pollutants in the groundwater [1]. This inhibition was alleviated after at least two-fold dilution with pure water. Photocatalytic oxidation of the polluted groundwater increased biodegradability (BOD/COD ratio). However, the toxicity of the UV-treated groundwater increased nearly three times. The formation of toxic intermediates is one of the concerns in photo-



**Fig. 1.** The molecular structures of 2,4-, 2,5-, and 2,6-dimethylaniline.



**Fig. 2.** General pathway of the degradation of nitroaromatics by chemical oxidation.

oxidation technology. In the course of two weeks of aerobic incubation, the primary aromatic amines were degraded to a residual concentration of 6–10 g/m<sup>3</sup>. Removal of primary aromatic amines was not accompanied by simultaneous reduction of toxicity, which started to decrease only after the amine concentration decreased to its lowest level of 6–10 g/m<sup>3</sup>.

With the help of chemical oxidation it is possible to decrease the concentration of toxic components beyond detection limits and increase their biodegradability. At the first stage of oxidation the anilines are probably converted into nitro-aromatic compounds. The different steps of the chemical oxidation of nitro-aromatics involved in the process is summarized in Fig. 2 [6].

It clearly appears that acetic acid and ammonia are the most refractory compounds to oxidation. Both of these compounds are easily biodegradable. Two chemical oxidation processes, ozonation and catalytic wet oxidation (CWO), were studied.

## MATERIALS AND METHODS

All the experiments were carried out on a model solution consisting of 2,4-dimethylaniline (2,4-DMA) and distilled water. The 98% pure 2,4-DMA solution was obtained from MERCK-Schuchardt (Germany).

### Ozonation

Ozonation experiments were carried out in a wetted-wall reactor [7]. The wetted-wall reactor is well suited to reaction kinetics research because of the precisely known mass transfer area and absence of foaming [8].

Ozonation kinetics and mass transfer experiments were carried out at room temperature (293 K). The operation mode of the reactor was countercurrent. To achieve a complete film distribution, the reactor was washed before runs with a NaOH solution and rinsed with distilled water. The polluted water was fed into the top of the reactor with a PVC pipeline (Ø 10 mm) using a peristaltic pump. Ozone was generated from pressured air by a laboratory ozone generator

**Table 1.** Experimentally parameters in ozonation experiments

Variable	Notation	Unit	Range
Solution pH	PH	–	3.34–7.52
Liquid residence time	$t$	s	4.6–12.6
Liquid flow rate	$Q_L$	m <sup>3</sup> /s	$0.7–3.0 \times 10^{-6}$
Gas flow rate	$Q_G$	m <sup>3</sup> /s	$2–3.5 \times 10^{-5}$
2,4-Dimethylaniline concentrations	$c_{L,in,2,4-DMA}$	g/m <sup>3</sup>	54–200
	$c_{L,out,2,4-DMA}$	g/m <sup>3</sup>	45–182
Ozone concentrations	$c_{G,in,O_3}$	g/m <sup>3</sup>	16.3–19.6
	$c_{G,out,O_3}$	g/m <sup>3</sup>	9.6–20.3
Biodegradability in	BOD <sub>7</sub> /COD <sub>in</sub>	–	0–0.01
Biodegradability out	BOD <sub>7</sub> /COD <sub>out</sub>	–	0.05–0.26

(*Trailigaz* “Labo 10”). The ozone–air mixture was fed into the system through a fluoroplast pipe (Ø 10 mm) from the bottom of the reactor. Sampling was carried out while the system was at a steady state. The ozone concentration was measured at the inlet and outlet of the gas phase. The liquid phase concentration of the 2,4-DMA, biological and chemical oxygen demand (BOD and COD), and pH were measured inside the feed tank and at the outlet of the liquid. During the liquid phase sampling the air was bubbled through the sample bottle to desorb the residual ozone from the water sample. The volumetric flow rate of the gas feed was measured with a rotameter. The experimentally observed parameters varied in the range presented in Table 1.

It was observed that the pH of the solution decreased during the ozonation (by about 1 unit) indicating that organic acids were formed in the degradation process. The colour of the liquid changed from colourless to slightly yellowish at the outlet. The HPLC analyses showed the appearance and decay of 18 peaks. These peaks represent the ring cleavage and final acidic products, which was confirmed by the growth of biodegradability in tests. In addition to oxalic acid, the analyses showed the formation of propionic, formic, and acetic acids during the ozonation.

### Catalytic wet oxidation

In the study of CWO, the influence of reaction conditions, namely temperature and oxygen partial pressure, were evaluated. The CWO experiments were carried out in a 0.3 L autoclave equipped with a temperature controller [9]. Before the experiment, the reactor and sampling tube were cleaned with distilled water. The cold reactor was then charged with 100 g of wet granulated activated carbon (GAC) saturated with 2,4-DMA solution and 0.1 dm<sup>3</sup> of residual liquid from the adsorption process. The reactor was then sealed and heated to the appropriate test temperature and agitated at a stirrer speed of 900 rpm. Impeller rotation was set to eliminate any external mass transfer resistance. Thermal equilibrium was achieved in about 1 h after the desired temperature was entered

**Table 2.** Experimental conditions of the CWO experiments

Parameter	Notation	Unit	Range
Temperature	T	K	428–448
Total pressure	$P_{TOT}$	MPa	1.0–1.5
Oxygen partial pressure	$p_{O_2}$	MPa	0.4–1.0
2,4-Dimethylaniline concentration in liquid in 0-sample	$c_{L,in,2,4-DMA}$ ( $t = 0$ min)	$g/m^3$	159–900
2,4-Dimethylaniline concentration in liquid in final sample	$c_{L,2,4-DMA}$ ( $t = 120$ min)	$g/m^3$	0–0.45
GAC concentration	$c_{GAC}$	$kg_{dry}/m^3$	265
TOC in 0-sample	TOC ( $t = 0$ )	$g\ C/m^3$	140–700
BOD <sub>5</sub> in 0-sample	BOD <sub>5</sub> ( $t = 0$ )	$g/m^3$	53–500
TOC in final sample	TOC ( $t = 120$ min)	$g\ C/m^3$	150–256
BOD <sub>5</sub> in final sample	BOD <sub>5</sub> ( $t = 120$ min)	$g/m^3$	304–870

into the temperature controller and the 0-sample ( $5 \times 10^{-3} \text{ dm}^3$ ) was then taken by opening the liquid sampling valve. Then the oxygen inlet valve was opened and the oxygen pressure was adjusted to the desired level, and timing started immediately. Samples were taken throughout the run to assess the dependence of the reaction rate on the 2,4-DMA concentration after 10, 30, 60, and 120 min by closing the O<sub>2</sub>-inlet valve and opening the liquid sampling valve. After sampling, the sample valve was closed and the O<sub>2</sub>-valve was re-opened, which flushed the sample tube at the same time. The conditions of the CWO experiments are presented in Table 2. The values of the concentrations of the 0-samples mean the values after the preheating period.

### Analysis

The 2,4-DMA concentration in the liquid phase was determined by a High Performance Liquid Chromatograph (Hewlett-Packard HP1100 series with UV and RI detectors) analyser with a 15 cm YMC-Pack Pro C18 column. In the analyses MERCK LiChrosolv® HPLC grade methanol and analysis grade (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> were used. Ozone concentration in the gas phase was measured using a spectrophotometer (*Unicam Helios Beta*). COD was measured with the Hach standard method [10a] using a Portable Datalogging Spectrophotometer Hach DR/2010 at a wavelength of 605 nm. BOD<sub>7</sub> and BOD<sub>5</sub> were measured with a standard method [10b], using a Marvet Junior dissolved oxygen meter. The total organic carbon (TOC) content in the CWO experiments was analysed with a Shimadzu Total Organic Carbon Analyzer TOC-5050A. The pH of the inlet and outlet liquid was measured using a *Vernier* PH-BTA pH sensor.

## RESULTS AND DISCUSSION

### Ozonation

The rate (mol/s) of the reaction between 2,4-DMA and ozone can be expressed with a second-order rate equation as follows:

$$R = m \cdot k \cdot c_{O_3} \cdot c_{2,4-DMA}, \quad (1)$$

where  $k$  is the reaction rate constant ( $m^3/(mol\ s)$ ),  $c$  is the concentration ( $mol/m^3$ ), and  $m$  is the stoichiometric coefficient ( $mol\ O_3/mol\ 2,4-DMA$ );  $m = 1$  for 2,4-DMA. The kinetic parameters for 2,4-DMA ozonation were estimated in a previous work by the authors [7] and are listed in Table 3.

The outlet concentration of 2,4-DMA depends on several variables including ozone concentration, liquid residence time, and gas flow rate (see Table 4).

Figure 3 shows the trend in biodegradability during ozonation: the greater the relative destruction of 2,4-DMA, the greater the increase in biodegradability.

From Fig. 3 the increase in the BOD/COD ratio can be estimated with a certain reservation. The simplified 2,4-DMA ozonation reaction scheme could be assumed to be as follows:



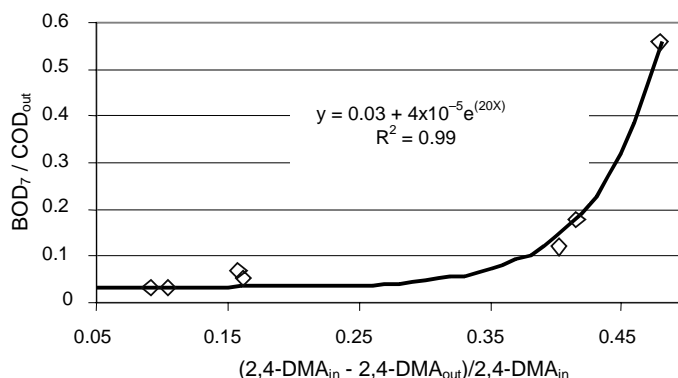
The last reaction ( $k_2$ ) is slow for ozonation,  $k_2 \ll k_1$ , and it is followed by minor changes in COD during ozonation. As  $COD_{TOT}$  is measured and  $COD_{TOT} = COD_{2,4-DMA} + BOD$ , it means that  $COD_{TOT}$  is decreasing together with the

**Table 3.** The estimated kinetic parameters of 2,4-dimethylaniline ozonation

Kinetic parameter	Unit	Value
$k$	$m^3\ (mol\ s)$	$5.65 \times 10^6$
$m$	$mol\ O_3/mol\ 2,4-DMA$	3.04

**Table 4.** Experimental results of 2,4-DMA ozonation

Liquid flow, $m^3/s \times 10^5$	Gas flow, $m^3/s \times 10^5$	$c(O_3)$ , $g/m^3$	$c(DMA)$ , $g/m^3$	BOD <sub>7</sub> / COD	$c(O_3)$ , $g/m^3$	$c(DMA)$ , $g/m^3$	BOD <sub>7</sub> / COD
IN					OUT		
0.07	3.5	16.3	53.9	0	15.7	28.6	0.56
0.07	2.3	18.8	73.0	0	17.6	42.6	0.18
0.28	2.3	19.6	73.0	0	17.1	61.5	0.07
0.07	2.3	18.1	103	0.02	17.0	61.5	0.12
0.28	2.3	18.4	103	0.02	15.2	86.4	0.05
0.28	2.0	13.3	200	0.07	9.6	182	0.03
0.28	2.2	15.7	202	0.06	10.3	181	0.03



**Fig. 3.** Dependence between 2,4-DMA consumption and biodegradability at the outlet of the ozone contactor.

decreasing concentration of 2,4-DMA whilst BOD is increasing. The trend line in Fig. 3 can be used for the prediction of the behaviour of biodegradability in dependence on the 2,4-DMA concentration at the outlet.

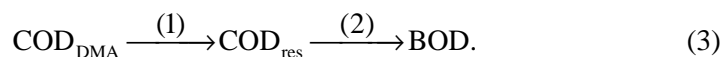
From Table 3 it follows after recalculation of the stoichiometric coefficient  $m$  into mass units that  $1.4 \times 10^{-3}$  g of ozone is needed to reduce 2,4-DMA concentration by 1 g/m<sup>3</sup>. Figure 3 shows that biodegradability is related to the relative concentration decrease of 2,4-DMA. When the desired BOD/COD ratio is fixed, the ozone needed per 1 L of polluted water can be evaluated on the basis of reaction stoichiometry and the curve from Fig. 3.

Information on ozonation costs is available in the literature [11]: 20–24 kWh energy is needed for the production of 1 kg of O<sub>3</sub> from air. Energy is also needed to mix air and water; this takes about 50% (e.g. 10–12 kWh) of the ozone generation energy [12]. Currently, the approximate energy costs are EUR 0.1 for 1 kWh, thus energy costs for ozonation are 0.3–0.36 EUR/kgO<sub>3</sub>. The cost of 1 mg/m<sup>3</sup> reduction of 2,4-DMA by ozonation is EUR 0.36–0.43.

### Catalytic wet oxidation

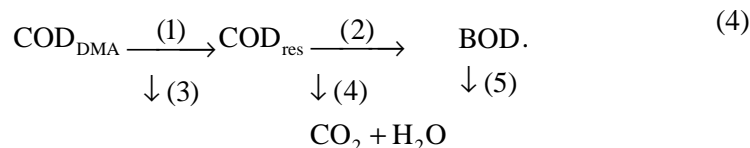
In the CWO experiments the 2,4-DMA was first adsorbed on the surface of GAC and the saturated GAC was then placed into the CWO reactor (0.3-dm<sup>3</sup> autoclave). The variables changed during the experiments were temperature and oxygen partial pressure.

The CWO reaction could be divided into two phases: preheating and oxidation. A simplified reaction scheme for the preheating stage can be written as follows:



During preheating TOC does not change but as BOD increases, also the biodegradability increases.

A simplified reaction scheme for the oxidation phase can be described with the following equation:



Reactions (3), (4), and (5) are the major reactions where TOC decreases with  $\text{CO}_2$  formation. BOD is formed from  $\text{COD}_{\text{res}}$  (2) and destroyed by reaction (5).  $\text{COD}_{\text{res}} = \text{COD}_{\text{TOT}} - \text{COD}_{\text{DMA}}$  is formed from 2,4-DMA (reaction (1)) and decreased by reaction (3), and  $\text{COD}_{\text{TOT}}$  includes BOD. To follow the BOD/COD behaviour in such a complicated system is too cumbersome; however, BOD/TOC shows clearly that some biodegradable organics are formed already during the preheating stage and BOD/TOC increases significantly during CWO. As all reaction rate coefficients are increasing with temperature and competition between reactions takes place, there is no clear trend of BOD/TOC with increasing temperature.

The 2,4-DMA wet oxidation kinetics is described by the Langmuir–Hinshelwood kinetic model equation [9]:

$$\frac{dc_{2,4\text{-DMA}}}{dt} = -k \frac{K_{2,4\text{-DMA}} c_{2,4\text{-DMA}} \sqrt{K_{\text{O}_2} c_{\text{O}_2}}}{(1 + K_{2,4\text{-DMA}} c_{2,4\text{-DMA}} + \sqrt{K_{\text{O}_2} c_{\text{O}_2}})}, \quad (5)$$

where  $k$  is the reaction rate coefficient ( $\text{m}^3/\text{mol s}$ ), and  $K_{2,4\text{-DMA}}$  and  $K_{\text{O}_2}$  are the adsorption coefficients of 2,4-DMA and oxygen ( $\text{m}^3/\text{mol}$ ), respectively.

The dependence of the adsorption coefficient on higher temperatures is presented by the van't Hoff equation as follows:

$$K = K_0 e^{-\frac{\Delta H}{RT}}, \quad (6)$$

where  $K_0$  is the pre-exponential factor,  $\Delta H$  is the heat of adsorption,  $R$  is the ideal gas constant, and  $T$  is the temperature.

The temperature dependence of the reaction rate coefficient,  $k$ , is determined by the Arrhenius equation:

$$k = k_0 e^{-\frac{E_a}{RT}}, \quad (7)$$

where  $k_0$  is the pre-exponential factor and  $E_a$  is the activation energy. The estimation routine for CWO kinetic parameters is presented in a previous work by the authors [9] and the values are listed in Table 5.

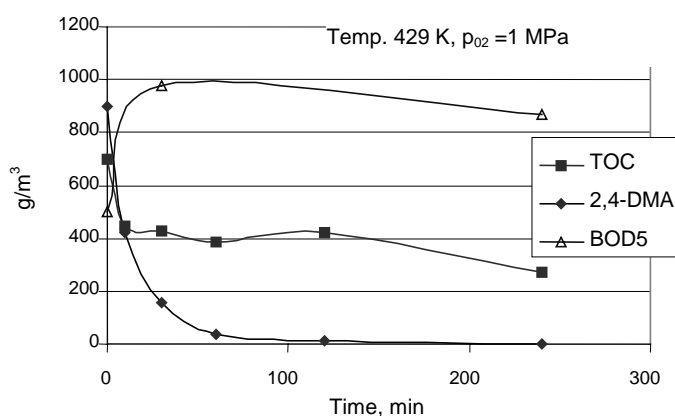


**Table 5.** Estimated kinetic parameters for the CWO of 2,4-DMA

Kinetic parameter	Unit	Value
$k_0$	mol/s	95
$E_a$	kJ/mol	31.3
$K_{0,O_2}$	$m^3/mol$	$8.8 \times 10^{-3}$
$\Delta H_{O_2}$	kJ/mol	-13.2
$K_{0,2,4-DMA}$	$m^3/mol$	$3.45 \times 10^{-3}$
$\Delta H_{0,2,4-DMA}$	kJ/mol	-18.1

During the preheating stage of CWO, the 2,4-DMA/TOC ratio slightly decreased to 0.87 whilst TOC remained constant. The changes in the 2,4-DMA concentration during CWO (after  $t = 0$ ) could be calculated with Eq. (5).

An example of concentration changes during CWO is presented in Fig. 4. The concentration of xyldine is decreasing rapidly, at the same time TOC decreases as part of the organic carbon is destroyed. BOD increases at the beginning of the oxidation period as organic acids are formed, and during the later stage of the process the BOD destruction is slightly faster than its formation (reaction scheme, Eq. (4)). As to changes of biodegradability, the BOD/TOC ratio increases at the beginning of the process and decreases with the reduction of organic acids during the final stage of oxidation. The maximum value of BOD/TOC was about 3 during this experiment and it decreased to 2.5 after 2 h CWO, which is the typical duration of CWO. A relatively high BOD/TOC ratio was reached within 1 h and during this time nearly all 2,4-DMA was destroyed, making the water easily biodegradable. The same trends were observed in CWO with lower and higher temperatures and with lower and higher oxygen partial pressures.

**Fig. 4.** Concentration profiles during the 2,4-DMA CWO reaction.

**Table 6.** Experimental results of 2,4-DMA CWO

$T$ , K	$p_{O_2}$ , MPa	$c_{\text{liq},2,4\text{-DMA}}$ , g/m <sup>3</sup>		BOD <sub>5</sub> /TOC, g O <sub>2</sub> /g C	
		$t = 0$ min	$t = 120$ min	$t = 0$ min	$t = 120$ min
413	0.6	268	0	1.04	2.14
429	0.4	328	0.45	1.07	3.50
429	0.6	159	0	1.13	2.27
429	1.0	900	0.2	0.72	3.60
439	0.6	359	0	0.70	1.21
448	0.8	178	0	0.31	2.11

Biodegradability is presented here as the ratio of BOD<sub>5</sub>/TOC. The initial 2,4-DMA concentration in the liquid and biodegradability are determined from the 0-sample after thermal equilibrium is reached and the outlet concentrations represent the concentrations at time = 120 min. Some results of CWO are presented in Table 6.

## CONCLUSIONS

Chemical oxidation gives a good tool for increasing the biodegradability of aqueous solutions with subsequent detoxification. Both ozonation and catalytic wet oxidation were effective in destroying the dimethylanilines but complete mineralization is not feasible because of the formation of organic acids that are resistant to oxidation.

Ozonation of 2,4-DMA in an aqueous solution was carried out in a wetted-wall column. A wetted-wall reactor is well suited to reaction kinetics research because of its fixed mass transfer area. As the mass transfer area is specified, it is easier to separate the influence of ozone mass transfer and reaction rate from each other.

Catalytic wet oxidation with GAC as a catalyst at mild conditions (temperature below 473 K, total pressure below 1.5 MPa) was also experimentally studied. The GAC type catalyst is active enough to oxidize 2,4-DMA molecules. The 2,4-DMA was almost completely oxidized in the CWO reactor within an hour; however, the intermediates such as ring cleavage by-products and organic acids, which are formed throughout the oxidation process, are resistant to degradation.

Despite the formation of refractory compounds, the oxidation processes increase the biodegradability of the aqueous solution because these intermediate products and organic acids are more biodegradable than 2,4-DMA. A combination of chemical oxidation (ozonation, CWO) and biological treatment could be successfully used for treating rocket fuel polluted groundwater.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. Rozkov, A., Vassiljeva, I., Kurvet, M., Kahru, A., Preis, S., Kharchenko, A., Krichevskaya, M., Liiv, M., Käär, A. & Vilu, R. Laboratory study of bioremediation of rocket fuel-polluted groundwater. *Water Res.*, 1999, **33**, 1303–1313.
2. Avontis, J., Kokars, V., Malers, I., Valtere, S., Whittaker, H., Cooper, D. & Whittaker, R. Contamination and environmental remediation of former missile sites near Liepaja. *Crit. Rev. Anal. Chem.*, 1998, **28**, 97–100.
3. Pereira, W. E., Rostad, C. E. & Garbarino, J. R. Groundwater contamination by organic bases derived from coal tar wastes. *Environ. Toxicol. Chem.*, 1983, **2**, 283–294.
4. Gosselin, R. E., Smith, R. P. & Hodge, H. C. *Clinical Toxicology of Commercial Products*. 5th edn., Williams & Wilkins, Baltimore, 1984.
5. Coates, J. D. & Anderson, R. T. Emerging techniques for anaerobic bioremediation of contaminated environments. *Trends Biotechnol.*, 2000, **18**, 408–412.
6. Oliviero, L., Barbier, J., Jr. & Duprez, D. Wet air oxidation of nitrogen-containing organic compounds and ammonia in aqueous media. *Appl. Cat. B: Envir.*, 2003, **40**, 163–184.
7. Reinik, J., Jakobsson, K. & Kallas, J. 2,4-Xylidine degradation with ozonation: mass transfer and reaction kinetics. *Ozone Sci. Eng.*, 2004, **26**, 1–11.
8. Kallas, J., Huuskonen, M., Kamenev, S., Munter, R. & Viirja, A. Ozonation and AOP parameter estimation from countercurrent film absorber data. *Ozone Sci. Eng.*, 1995, **17**, 527–550.
9. Kallas, J. & Reinik, J. Xylidine-polluted groundwater purification. Ozonation and catalytic wet oxidation. *Proc. Estonian Acad. Sci. Chem.*, 2004, **53**, 97–115.
10. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC, (a) no. 5220, (b) no. 5210, 1995.
11. Gottschalk, C., Libra, J. A. & Saupe, A. *Ozonation of Water and Waste Water*. Wiley-VCH, Germany, 2000.
12. Langlais, B., Reckhow, D. A. & Brink, D. R. *Ozone in Water Treatment: Application and Engineering*. Lewis Publishers, Michigan, 1991.

## Raketikütusega reostatud põhjavee biolagundatavuse suurendamine keemilise oksüdatsiooni meetoditega

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Äärmiselt mürgiseid raketikütusejääke on leitud Loode-Eestis paiknenud endise raketibaasi põhjavees. Vees leiduva raketikütust lagundava bakteri kasv on tugevalt inhibeeritud reoainete kõrge kontsentratsiooni tõttu. Põhjavee puhastamiseks on uuritud kaht keemilise oksüdatsiooni meetodit – osoneerimist ja katalüütilist märghapendust. Osoneerimiskatsed on teostatud toatemperatuuril läbivoolu-kelmereaktoris, samal ajal kui katalüütilise märghapenduse reaktsioo-

nid on läbi viidud autoklaavis granuleeritud aktiivsöe juuresolekul (temperatuur 413–446 K, hapniku osarõhk 0,4–1 Mpa). Mõlemad protsessid vähendavad peamiste reoainete (dimetüülaniliinide) kontsentratsiooni ja suurendavad vee bioloogilist hapnikutarvidust. Vaatamata jääkainetele puhastatud vees (peamiselt orgaanilised happed), võib keemiliselt puhastatud vee komplikatsioonideta suunata bioloogilisse puhastusseadmesse, kuna orgaanilised happed on kergesti biolagunevad. Järelikult sobivad mõlemad keemilised meetodid eelpuhastusprotsessiks enne bioloogilist puhastust.