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Xylidine-polluted groundwater purification. Ozonation and catalytic wet oxidation

Janek Reinik[a,b*] and Juha Kallas[c]

[a] Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[b] National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia
[c] Department of Chemical Technology, Lappeenranta University of Technology, P.O. Box 20, FIN-53851 Lappeenranta, Finland

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Abstract. This paper discusses the removal of xylidines from polluted waters by means of chemical oxidation methods. Xylidines, persistent compounds of rocket fuel, have been detected in high concentrations in groundwater in the areas of former Soviet missile bases. To treat such groundwater, two chemical processes, ozonation and catalytic wet oxidation, were studied. The kinetics of degradation of 2,4-xylidine by ozonation was investigated in a wetted-wall column. A laboratory-scale ozone–water contact column was designed and a steady-state wetted wall reactor model was developed. The ozonation model with the estimated parameters showed good agreement between predicted and experimental data. The estimated reaction rate coefficients could be used for the design of a bubble ozonation column for xylidine-polluted groundwater treatment. The developed model and experimental set-up can be used in the future to estimate the kinetic parameters of ozonation reactions involving other similar compounds. Catalytic wet oxidation was carried out in a stirred batch autoclave in the presence of granulated activated carbon. 2,4-Xylidine was concentrated on the surface of the granulated activated carbon and then oxidized at different temperatures (140–170 °C) and oxygen partial pressures (4–10 atm). The GAC type catalyst was active enough for 2,4-xylidine oxidation, but not for the oxidation of the formed organic acids. Degradation of organic acids needs severer conditions. Both chemical oxidation processes could be used as a pre-treatment before biological treatment. The results of this paper can be used to design two chemical processes for purification of xylidine polluted water.

Key words: 2,4-xylidine, ozonation, wetted wall column, catalytic wet oxidation, mathematical modelling, reaction kinetics.

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[*] Corresponding author, jreinik@kbfi.ee

INTRODUCTION

Xylidine-polluted groundwater can be found in the sites of former Soviet military missile bases due to spills of a xylidine-based missile fuel – samine. The fuel consists of triethylamine (50 wt%) and xylidines or dimethylanilines (45 wt%) [1]. The precise composition of the rocket fuel can be found in the literature [2]. Similar contamination of groundwater occurs at former military bases in Barta and Tasi, West Latvia [3]. Triethylamine is an easily volatile component and therefore we focused on the treatment of xylidines, the main unvolatile toxic components of samine.

Xylidines are toxic and mutagenic compounds. Typically, xylidines are a mixture of isomers in which the 2,4-, 2,5-, and 2,6-isomers are dominant. Molecular structures of isomers are presented in Fig. 1. They are relatively soluble, mobile, and persistent in groundwater [4]. Based on the effects seen in animals, it is likely that xylidine can be absorbed through skin in sufficient amounts to cause dangerous methemoglobinemia [5]. The maximally allowable concentration of aromatic amines (including xylidines) in drinking groundwater is 0.1 μg/L [6].

Several investigations have been carried out on the purification of water contaminated with aromatic amines, including xylidines. Some of them are presented in our previous study [7].

Among physical wasterwater treatment methods, adsorption on granulated activated carbon (GAC) has been the most common treatment because of its simplicity, effectiveness, and relatively low price. The method is largely used in the purification of groundwater [8, 9] from organic pollutants. Despite the fact that adsorption gives a good purification effect, the pollution is not totally eliminated but only transferred from one medium to another. Rising costs, particularly those associated with the disposal of used GAC, are raising the competitiveness of chemical oxidation methods.

The main target of this study was to investigate the feasibility of the treatment of xylidine-polluted groundwater by means of chemical methods and to develop

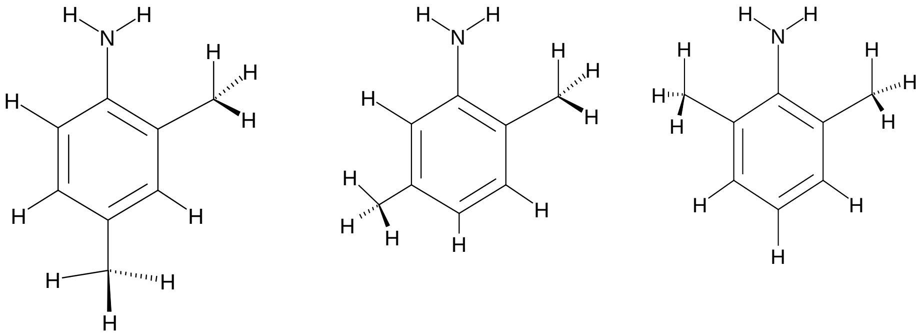

Fig. 1. The molecular structures of 2,4-, 2,5-, and 2,6-dimethylaniline.

a theoretical basis for the design of the treatment processes. To achieve the target, two processes were experimentally studied and mathematically modelled: ozonation and catalytic wet oxidation (CWO) using GAC as a catalyst.

The reaction rate coefficients of 2,4-xylidine ozonation are not available in the literature. In order to design an ozone reactor for 2,4-xylidine destruction on a rational basis, these kinetic parameters must be evaluated from the laboratory experiments.

Another target was to evaluate the reaction kinetics of CWO in the presence of GAC. The CWO process could be used as a regeneration unit in the integrated adsorption process. The pollutant is concentrated on the surface of GAC and then degraded in the wet oxidation unit.

Ozonation

Ozonation is a well-established technology capable of destroying a wide range of organic molecules, including toxic organics. Ozone is a very reactive and powerful oxidizing agent ($E^0 = 2.07$ V) compared to other oxidizing agents, such as chlorine (1.36 V) and H_2O_2 (1.78 V) [10]. A considerable disadvantage of ozone can be high production costs. Moreover, high capital cost of the ozonation unit makes ozonation technologies best suited to large-scale applications [11].

The reaction between ozone and aromatics includes the insertion of oxygen into the benzene ring, which results in the breaking of the double bonds. The opening of the benzene ring usually requires 1–2 moles of ozone per mole of aromatics [12].

Aromatic amines decompose to several by-products during ozonation (e.g., nitrobenzene and azobenzene, acetic and formic acid) [13–15] before mineralization. Most of the reaction products are biodegradable and less toxic than the reactants.

The kinetic parameters for reactions between xylidines and ozone are not available in the literature. In order to design a larger-scale ozone contactor (e.g., a bubble column, stirred tank reactor, etc.) for the treatment of polluted groundwater, the reaction rate coefficients should be known. In the present work, a wetted-wall reactor was used for evaluating the kinetic parameters of the reaction. The wetted-wall reactor provides an advantage in reaction kinetics research because of its precisely known mass transfer area and absence of foaming. However, a wetted-wall reactor can be used for fast reactions only; otherwise the contact time is too short for sufficient concentration changes to be observed. The coefficients of the ozonation reaction rate for aromatic amines show adequate values [16, 17] in order for the above-mentioned reactor system to be used.

A steady-state mathematical model that takes into account the mass transfer between phases, the reaction between ozone and xylidine, xylidine vaporization, the enhancement of the mass transfer due to the reaction between ozone and xylidine, and the stoichiometric ratio of the consumed ozone to the reacted xylidine was developed for the wetted-wall reactor.

The developed model and experimental set-up can be used in the future for the estimation of the kinetic parameters of reactions involving other similar compounds. The estimated rate coefficients could be used for the design of bubble ozonation columns. The values of the volumetric ozone mass-transfer coefficient can be easily obtained from the oxygen mass transfer data [18].

Catalytic wet oxidation

Among the treatments of nitrogen-containing organic compounds in water, wet air oxidation (WAO) appears as one of the most promising [19]. The idea of the wet oxidation process is to enhance contact between molecular oxygen and the organic matter to be oxidized [20]. Nevertheless, in order to obtain high conversions for pollutants, the non-catalytic techniques need severe operating conditions in terms of temperature and pressure. The CWO process with molecular oxygen using GAC at mild conditions (temperature below 200 °C, pressure below 15 atm) reduces significantly the severity of the wet oxidation process and constitutes an economically attractive pretreatment step for non-biodegradable aqueous pollution due to its low capital and operating costs [21].

The CWO process can be carried out in a tubular packed-bed reactor operating in the trickle flow regime using air oxygen as an oxidant. In these conditions, chlorinated and nitroaromatic compounds (e.g. phenol) are oxidized over a solid catalyst in a three-phase system under mild conditions of oxygen partial pressure (6–12 atm) and temperature (120–160 °C) [22]. The activated carbon has been demonstrated to have catalytic effect on the wet oxidation of phenols. The oxidation can be carried out even in mild conditions of air pressure (4.7 atm) and temperature (40 °C) with 48% of phenol conversion [23].

The different steps of the reaction mechanism of the wet oxidation of nitroaromatics involved in the process can be summarized as shown in Fig. 2 [24].

It clearly appears that acetic acid and ammonia are the most refractory compounds. Both oxides and supported noble metals can be used in the CWO of organic compounds. However, catalysts active in steps I and II could be different

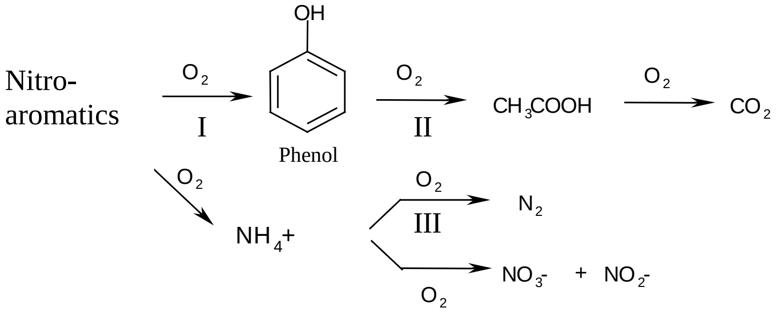

Fig. 2. General pathway of degradation of nitroaromatics by wet oxidation.

from those that are active and selective to N_2 in step III. The end products are very resistant to total oxidation even under severe conditions and their oxidation to carbon dioxide is usually the rate-limiting step [25]. A reaction mechanism similar to the nitroaromatics oxidation scheme (Fig. 2) is supposed to take place in the 2,4-xylidine degradation process; the first step for xylidine oxidation is probably just the formation of nitroaromatics.

EXPERIMENTAL PART

Chemical oxidation methods, such as ozonation and catalytic wet oxidation in the presence of GAC, were studied experimentally. The following chapter gives a brief overview of the experimental part of the study.

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

Ozonation

The ozonation kinetics and mass transfer experiments were carried out on a wetted-wall reactor (Fig. 3). The height of the wetted-wall ozonation column (a glass tube) was 1 m and its inner diameter was 0.015 m. The column was carefully set in a vertical position and was equipped with special sections prior to the gas and liquid inlets and outlets in order to maintain a stable annular flow. The use of the glass tube made it possible to observe the complete wetting of the inner wall.

Ozonation experiments were carried out at room temperature (20 °C). The operation mode of the reactor was countercurrent. To achieve a complete film distribution, the reactor was washed with a NaOH solution and rinsed with distilled water before runs. Polluted water was fed into the top of the reactor with the help of a peristaltic pump. Ozone was generated from pressured air by a laboratory ozone generator (*Trailigaz* "Labo 10"). The ozone–air mixture was fed into the system through a fluoroplast pipe from the bottom of the reactor. Sampling was carried out while the system was at a steady state. The liquid phase concentration of the 2,4-xylidine was measured inside the feed tank and at the outlet of the liquid. The ozone concentration was measured at the inlet and outlet of the gas phase. In mass transfer experiments (no reaction), the ozone concentration was measured additionally in a liquid effluent. The volumetric flow rate of the gas feed was measured by a rotameter. The pH was measured for all the samples before and after ozonation. The main values of the experimental parameters as well as experimental results are presented in [26]. The experimentally observed parameters varied in a range presented in Table 1.

It was observed that the pH of the solution decreased during the ozonation (by about 1 unit), indicating that in the degradation process acids are formed. The

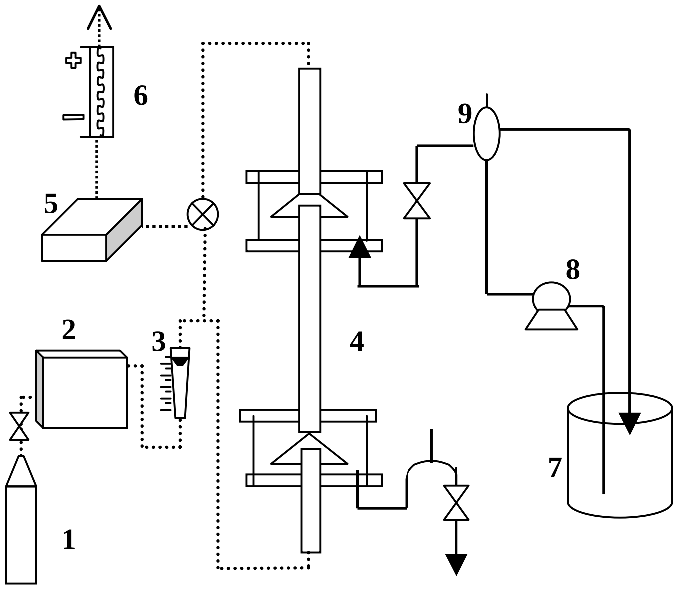

Fig. 3. Schematic diagram of the wetted-wall reactor system. 1 – pressurized air cylinder, 2 – ozone generator, 3 – rotameter, 4 – wetted-wall reactor, 5 – spectrophotometer, 6 – ozone destructor, 7 – feed storage tank, 8 – peristaltic pump, 9 – overflow.

Table 1. Experimentally observed variables

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	L/min	0.04–0.18
Gas flow rate	Q_G	L/min	1.2–2.1
2,4-Xylidine concentration	c_{Lin}^{xyl}, c_{Lout}^{xyl}	mg/L	54–200, 45–182
Ozone concentration	$c_{Lin}^{O_3}$, $c_{Gout}^{O_3}$	mg/L	13.2–22.7, 9.6–20.3
Biodegradability in	BOD_7/COD_{in}	–	0–0.01
Biodegradability out	BOD_7/COD_{out}	–	0.05–0.26

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 present the ring-cleavage and final acidic products, which was confirmed by the biodegradability growth in tests. In addition to oxalic acid, the analysis showed the formation of propionic, formic, and acetic acids during the ozonation.

Catalytic wet oxidation

In the study of CWO the influence of the reaction conditions, viz. temperature and oxygen partial pressure, were evaluated. The CWO experiments were carried out in 0.3 L *Parr Series 4561 Mini Reactor* equipped with *Series 4840 Temperature Controller* (made in the USA). A scheme of the reactor system is presented in Fig. 4. The conditions of the CWO experiments are presented in Table 2.

In the CWO experiments, the commercial Granulated Acicated Carbon GAC NORIT RB 1 (made in The Netherlands) was used in adsorption and as the catalyst. High purity compressed oxygen was used as the oxidant (AGA-Finland).

Before the experiments, the reactor and sampling tube were cleaned with distilled water. The cold reactor was then charged with 100 g of 2,4-xylidine saturated wet GAC and 100 mL of residual liquid solution from adsorption experiments. The adsorption isoterms, xylidine diffusion coefficient in GAC

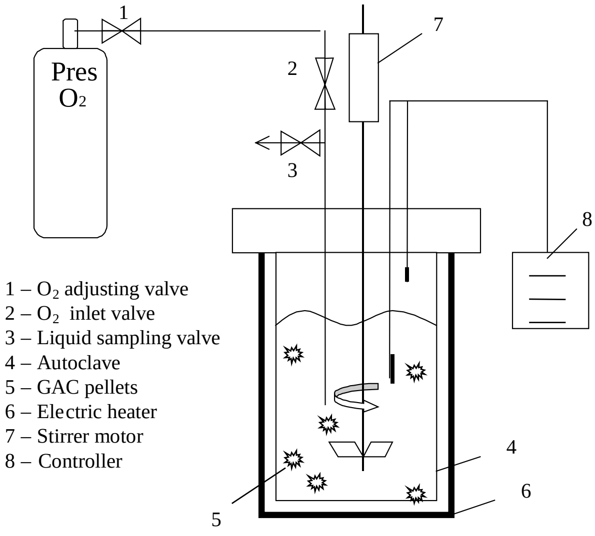

Fig. 4. Catalytic wet oxidation reactor system.

Table 2. Experimental conditions of the CWO experiments

Variable	Notation	Unit	Range
Temperature	T	ºC	140–170
Total pressure	P^{TOT}	atm	10–15
Oxygen partial pressure	P^{O2}	atm	4–10
2,4-Xylidine concentration	c^{Xyl}	g/L	8–11
GAC concentration	c^{GAC}	g_{dry}/L	265

pores, and breakthrough curves are presented in [7]. The reactor was then sealed and heated to the appropriate test temperature and agitated at 900 rpm stirrer speed. Impeller rotation was set to eliminate any external mass transfer resistance. The thermal equilibrium was achieved in about 1 h after the desired temperature was entered into the temperature controller and the zero sample (5 mL) was taken by opening the liquid sampling valve. Then the oxygen inlet valve was opened and the oxygen pressure was adjusted to a desired level. The stopwatch was immediately started. Samples were taken throughout the run to assess the dependence of the reaction rate on 2,4-xylidine concentration after 10, 30, 60, and 120 min by closing the the O_2-inlet valve and opening the liquid sampling valve. After sampling, the sample valve was closed and the O_2-valve was re-opened, which flushed the sample tube at the same time.

Analysis

The 2,4-xylidine concentration in the liquid phase was determined by a High Performance Liquid Chromatorgaph (Hewlett-Packard HP1100 series with UV and RI detectors) analyser. Analyses used MERCK LiChrosolv® HPLC grade methanol, analytical grade $(NH_4)H_2PO_4$ and $(NH_4)_2HPO_4$, and a 15 cm YMC-Pack Pro C18 column and method from YMC Co, Ltd (Japan). The ozone concentration in the gas phase was measured using a spectrophotometer (*Unicam Helios Beta*) and iodometrically in the liquid phase [27]. The pH of the inlet and outlet liquids was measured using a *Vernier* PH-BTA pH sensor. In addition, the COD was measured with the Hach standard method [28a], using a Portable Datalogging Spectrophotometer Hach DR/2010 at wavelength 605 nm. BOD_7 was measured with a standard method [28b], using a Marvet Junior dissolved oxygen meter.

In CWO the total organic carbon (TOC) content was analysed by Shimadzu Total Organic Carbon Analyzer TOC-5050A.

MODELLING: RESULTS AND DISCUSSION

Ozonation

A steady-state wetted wall reactor model was developed taking into account the mass transfer between the phases (*N*), the reaction between ozone and 2,4-xylidine (*R*), the 2,4-xylidine vaporization, as well as the stoichiometric ratio of the consumed ozone to the reacted 2,4-xylidine. The enhancement of the ozone mass transfer, ϕ^{O_3}, due to the reaction between ozone and 2,4-xylidine was calculated in the model using an equation based on the second-order reaction kinetics [29]. The model was based on countercurrently connected and perfectly mixed mass transfer stages (Fig. 5).

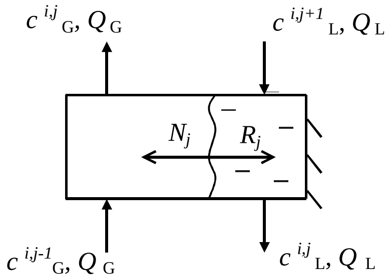

Fig. 5. Modelling block of the *j*th stage of the mass transfer stage. c_L and c_G are the liquid and gas phase concentrations and Q_L and Q_G are the liquid and gas flow rates.

The mass balances for the *i*th ($i = 1$ for ozone and $i = 2$ for 2,4-xylidine) component in the *j*th stage are:

$$Q_\mathrm{L}(c_\mathrm{L}^{i,j+1} - c_\mathrm{L}^{i,j}) + \left[k_\mathrm{L}^{i} a \phi^{i} \left(\frac{c_\mathrm{G}^{i,j}}{H^{i}} - c_\mathrm{L}^{j} \right) - m^{i} k c_\mathrm{L}^{\mathrm{O_3}} c_\mathrm{L}^{\mathrm{xyl}} \right] F h_\mathrm{L} l = 0 \tag{1}$$

for the liquid phase and

$$Q_\mathrm{G}(c_\mathrm{G}^{i,j-1} - c_\mathrm{G}^{i,j}) - k_\mathrm{L}^{i} a \phi^{i} \left(\frac{c_\mathrm{G}^{i,j}}{H^{i}} - c_\mathrm{L}^{i,j} \right) F h_\mathrm{L} l = 0 \tag{2}$$

for the gas phase, where F is the cross-sectional area of the reactor, l is the height of the stage ($l = L/n = 0.1$ m, where L is the total length of the reactor and n is the number of stages), H^{i} is Henry's dimensionless coefficient calculated for ozone according to IOA [30] ($H^{\mathrm{O_3}} = 4.12$ at 20 °C) and for 2,4-xylidine obtained from the literature ($H^{\mathrm{xyl}} = 0.27$ [31]). The stiochiometric coefficient and enhancement factor for 2,4-xylidine are equal to one ($m^{\mathrm{xyl}} = 1$ and $\phi^{\mathrm{xyl}} = 1$). The mass-transfer coefficient for 2,4-xylidine, $k_\mathrm{L}^{\mathrm{xyl}}$, was calculated using the equation based on the penetration mass transfer theory in dilute solutions [32] and for ozone was estimated experimentally (Eq. 6) from the ozone mass-transfer experiments (no reaction).

The liquid hold-up, h_L, is calculated from the following equation:

$$h_\mathrm{L} = \frac{\pi d \delta}{F}, \tag{3}$$

where d is the column's inner diameter, F is the cross-sectional area, and the liquid film thickness for the laminar flow, δ, is obtained from the following equation [33]:

$$\delta = \sqrt[3]{\frac{3 \mu \Gamma}{g \rho^{2}}}, \tag{4}$$

where Γ is the liquid mass flow rate per wetted perimeter, μ is the liquid dynamic viscosity, ρ is the liquid density, and g is the gravitational acceleration.

Parameter estimation

The developed mathematical model was coupled with the parameter estimation program [34]. First, the ozone mass-transfer coefficient, $k_\mathrm{L}^{\mathrm{O}_3}$, for the wetted wall column was estimated from the pure water–ozone mass-transfer experiments (self-decomposition of ozone was ignored). The objective function was used to minimize the differences between the observed and predicted ozone concentrations as follows:

$$\Phi = \sum_{l=1}^{N} (c_{\mathrm{Lout},l}^{\mathrm{O}_3,\mathrm{calc}} - c_{\mathrm{Lout},l}^{\mathrm{O}_3,\exp})^2 + \sum_{l=1}^{N} (c_{\mathrm{Gout},l}^{\mathrm{O}_3,\mathrm{calc}} - c_{\mathrm{Gout},l}^{\mathrm{O}_3,\exp})^2, \tag{5}$$

where N is the number of observations.

The dependence of $k_\mathrm{L}^{\mathrm{O}_3}$ [m/s] on the liquid flow rate Γ in the laminar-wavy film flow range (0.01–0.09 kg/m s) in the wetted-wall reactor resulted in the following relation with the estimated parameters e and p:

$$k_\mathrm{L}^{\mathrm{O}_3} = e\Gamma^p = 0.44310^{-4}\, \Gamma^{0.411}. \tag{6}$$

The reaction rate and the stoichiometric coefficient for ozone (k^{O_3} and m^{O_3}) were estimated from the experimentally measured concentrations of $c_{\mathrm{Lout}}^{\mathrm{xyl}}$ and $c_{\mathrm{Gout}}^{\mathrm{O}_3}$, obtained from the experiments. The sum of the residual squares

$$\Phi = \sum_{l=1}^{N} (c_{\mathrm{Lout},l}^{\mathrm{xyl},\mathrm{calc}} - c_{\mathrm{Lout},l}^{\mathrm{xyl},\exp})^2 + \sum_{l=1}^{N} (c_{\mathrm{Gout},l}^{\mathrm{O}_3,\mathrm{calc}} - c_{\mathrm{Gout},l}^{\mathrm{O}_3,\exp})^2, \tag{7}$$

was minimized in the estimation. The quality of the data fitting was checked with the degree of explanation, R^2, defined as follows:

$$R^2 = 1 - \frac{\sum_{l=1}^{N} \sum_{i=1}^{2} (c_{l,i}^{\exp} - c_{l,i}^{\mathrm{calc}})^2}{\sum_{l=1}^{N} \sum_{i=1}^{2} (c_{l,i}^{\exp} - c_{l,i}^{\mathrm{mean}})^2}. \tag{8}$$

The estimated parameters, 95% confidence limits, and the degree of explanation, R^2, are presented in Table 3.

The elaborated steady-state wetted-wall ozonation reactor model was able to describe the evolution of the pollutant and ozone concentrations in the liquid and gas phases along the reactor length coordinate in various conditions, as presented in Fig. 6.

The model for the wetted-wall reactor showed a good agreement when validated against experimental data (see Fig. 7).

Table 3. Estimated parameters of 2,4-xylidine ozonation

Parameter	Unit	Value	95% confidence limits		R^2
			Lower	Upper	
e		4.43×10^{-4}	1.61×10^{-5}	7.25×10^{-5}	0.994
p		0.411	0.287	0.429	
k^{O_3}	L/(mol s)	0.316×10^{5}	1.67×10^{3}	4.65×10^{3}	0.961
m^{O_3}	mol/mol	2.45	1.74	3.16	

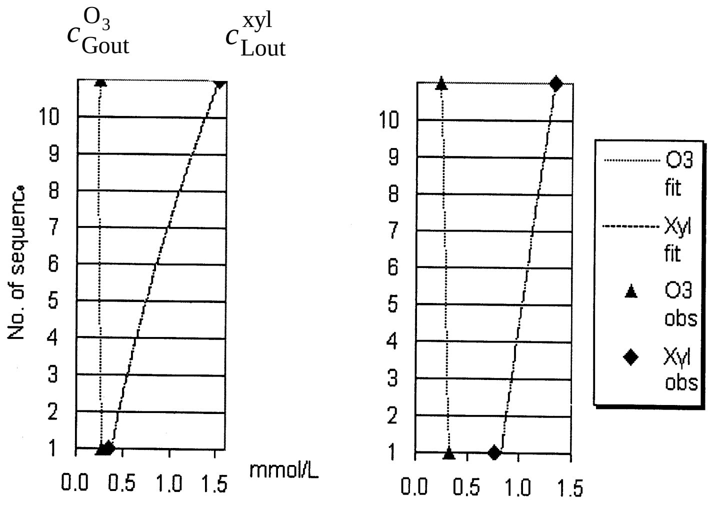

Fig. 6. Concentration profiles of two runs.

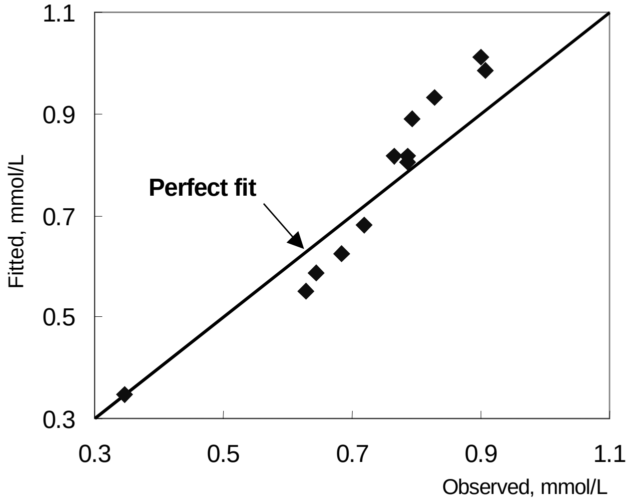

Fig. 7. Calculated versus observed 2,4-xylidine effluent concentration in the liquid phase.

Kinetic models for catalytic wet oxidation

Several completely different sets of kinetic models have been reported for CWO [35]. In this study the reaction was modelled in terms of the Langmuir–Hinshelwood kinetic model and with the power law kinetics (second-order kinetic model). It can be noted that both models predict satisfactory 2,4-xylidine degradation in the CWO process. HPLC analysis showed the formation and decay of several intermediate compounds. The exact concentrations of these species were not measured and the CWO models were developed without intermediates.

Langmuir–Hinshelwood model

The Langmuir–Hinshelwood kinetic model for CWO reaction is theoretically most justified. It assumes an irreversible surface reaction between the absorbed reactants (2,4-xylidine and oxygen). The reaction rate of xylidine is a function of the concentrations of the reacting species on the surface of the GAC. The surface reaction of chemisorbed 2,4-xylidine and oxygen is rate controlling as follows [36]:

$$\frac{dc^{\mathrm{xyl}}}{dt} = -k\frac{K^{\mathrm{xyl}}c^{\mathrm{xyl}}\sqrt{K^{\mathrm{O_2}}c^{\mathrm{O_2}}}}{\left(1 + K^{\mathrm{xyl}}c^{\mathrm{xyl}} + \sqrt{K^{\mathrm{O_2}}c^{\mathrm{O_2}}}\right)^2}, \qquad (9)$$

where k is the reaction rate coefficient, and K^{xyl} and $K^{\mathrm{O_2}}$ are the adsorption coefficients of 2,4-xylidine and oxygen, respectively.

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

$$K = K_0 e^{-\frac{\Delta H}{RT}}, \qquad (10)$$

where K_0 is the pre-exponential factor and ΔH is the heat of adsorption.

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

$$k = k_0 e^{-\frac{E_\mathrm{a}}{RT}}, \qquad (11)$$

where k_0 is the pre-exponential factor and E_a is the activation energy.

The oxygen concentration in the liquid phase was calculated using the following oxygen solubility equation [37]:

$$c^{\mathrm{O_2}} = p^{\mathrm{O_2}} e^{\frac{0.046T^2 + 203.357T\ln\left(\frac{T}{298}\right) - (299.378 + 0.092T)(T - 298) - 20.591\cdot 10^3}{8.3144T}}, \qquad (12)$$

where $p^{\mathrm{O_2}}$ is the oxygen partial pressure.

In the optimization routine, the oxygen adsorption coefficient parameters, $K_0^{O_2}$ and ΔH^{O_2}, as well as the pre-exponential factor, k_0, and activation energy, E_a, for the Langmuir–Hinshelwood kinetic model (Eq. 9) were estimated. The values of parameters in the 2,4-xylidine adsorption coefficient (Eq. 10) in the temperature range of 415–450 K were separately estimated from the mass balances at the end of the pre-heating period before oxygen was added.

Power-rate law model

The simplest rate equation that would adequately fit the experimental data is the power-rate law model. The reaction kinetics is presented formally through a direct oxidation reaction in the liquid phase, including oxygen and 2,4-xylidine concentrations in the liquid phase. The rate of reaction is given by [38]:

$$\frac{dc_{\text{xyl}}}{dt} = -k(c^{\text{xyl}})^x (c^{O_2})^y, \tag{13}$$

where k is the reaction rate constant, c^{xyl} and c^{O_2} are the concentrations of 2,4-xylidine and dissolved oxygen in the liquid phase, and superscripts x and y are reaction orders.

This model is entirely empirical, and it does not take into account the adsorption on the catalyst surface in the heterogeneous CWO, which are included in Eq. 9. The equation is correct for the wet oxidation without catalyst. In the parameter estimation routine, the pre-exponential factor, k_0, activation energy, E_a, and reaction orders x and y were estimated.

Parameter estimation

The two models were implemented so that it was easy to link the model into the optimization algorithm of the *Flowbat* program framework [34]. The Davidson optimization routine was used for parameter estimation. All the parameters except K_0^{xyl} and ΔH^{xyl} were evaluated simultaneously.

On the basis of the 2,4-xylidine decay, the apparent activation energies and pre-exponential constants were determined for the reactions of the CWO and the WAO, with and without catalyst, using a parameter estimation program. The objective function was

$$\Phi = \sum_{l=1}^{N} (c_l^{\text{xyl,calc}} - c_l^{\text{xyl,exp}})^2, \tag{14}$$

where N is the total number of observations.

The results of the parameter estimation of the power-rate law and Langmuir–Hinshelwood kinetic model kinetics are presented in Tables 4 and 5.

Table 4. Estimated parameters for catalytic wet oxidation

Parameter	Unit	Value	Model
			Langmuir–Hinshelwood, Eq. 9
k_0	mol/min	5.72×10^3	Eq. 11
E_a	kJ/mol	31.3	Eq. 11
$K_0^{O_2}$	m^3/mol	8.8×10^{-3}	Eq. 10
ΔH^{O_2}	kJ/mol	−13.2	Eq. 10
K_0^{xyl}	m^3/mol	3.45×10^{-3}	Eq. 10
ΔH^{xyl}	kJ/mol	−18.1	Eq. 10
			Power-rate model, Eq. 13
k_0	mol/min	80.3	Eq. 11
E_a	kJ/mol	5.59	Eq. 11
x	–	1.01	Eq. 13
y	–	1.00	Eq. 13

Table 5. Estimated parameters for wet air oxidation (experiments without catalyst)

Parameter	Unit	Value	Model
			Power-rate model, Eq. 13
k_0	1/min	1.18	Eq. 11
E_a	kJ/mol	20.3	Eq. 11

As can be seen from Table 4, the reaction between 2,4-xylidine and oxygen is formally a typical second-order reaction, first-order in respect to both reactants. In WAO experiments, the oxygen partial pressure was kept constant and the oxidation reaction was first-order in respect to 2,4-xylidine.

A satisfactory fit was achieved with both the CWO models when validated against experimental data. The effect of temperature on the 2,4-xylidine degradation under constant oxygen pressure, $p^{O_2} = 5$ atm, is presented in Fig. 8 and the effect of oxygen partial pressure under constant temperature, $T = 430$ K, is presented in Fig. 9. Predictions for the WAO without catalyst in Fig. 8 were calculated from the power-law kinetic model (Eq. 13) and for the CWO, from the Langmuir–Hinshelwood kinetic model (Eq. 9). Predictions for the CWO by the power-law are presented in [39].

Catalytic wet oxidation under operating conditions completely oxidized 2,4-xylidine. The TOC degradation was significant but not 100% complete. The TOC reduction was incomplete because the 2,4-xylidine degradation pathway involves side reactions that lead to the formation of stable acids. The HPLC analysis indicated that over 20 intermediates were formed. Some of the organic compounds, such as propionic and formic acids, were determined throughout the analysis.

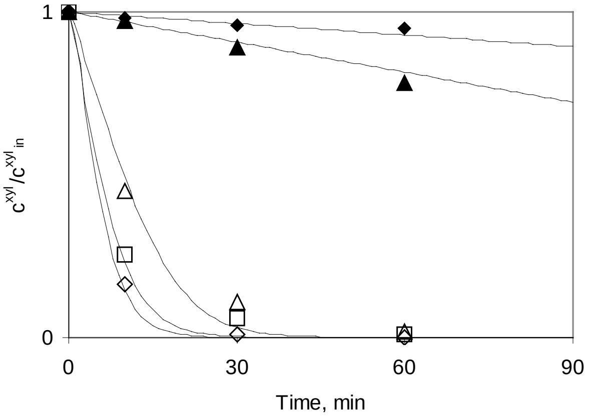

Fig. 8. Measured normalized 2,4-xylidine concentration plotted versus reaction time for three temperatures (◇ – 450 K, □ – 430 K, and △ – 415 K) at p_{O2} = 5 atm. Symbols denote experimental data and lines denote prediction from the kinetic model. Filled symbols denote experiments without GAC for two temperatures (◆ – 415 K and ▲ – 450 K) with predictions with lines.

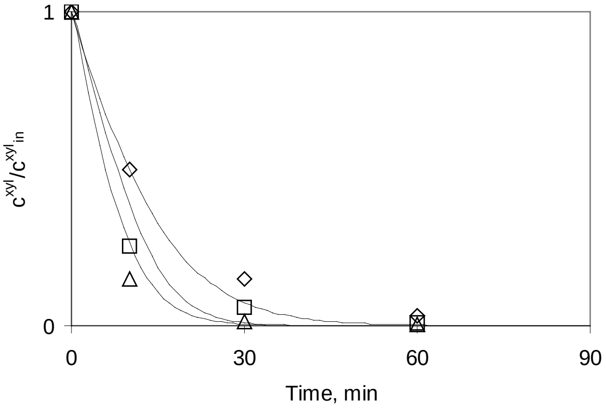

Fig. 9. Measured normalized 2,4-xylidine concentration plotted versus reaction time for three oxygen partial pressures (△ – 4 atm, □ – 5 atm, and ◇ – 10 atm) at 430 K. Symbols denote experimental data and lines denote prediction from the kinetic model.

COMPARISON OF TREATMENT METHODS

Ozonation gives a good effect in destructing xylidines but complete mineralization is not feasible. The same concerns the CWO process because organic acids, which are formed throughout the oxidation process, are resistant to wet oxidation. In addition the ozonation process is feasible for large-scale applications whilst adsorption onto GAC with subsequent CWO can be economically used for small-scale purification plants.

Before CWO, the pollutant is adsorbed on the surface of GAC as the first step (see breaktrough curves in [7]). In the second step of CWO, the 2,4-xylidine is oxidized in the presence of dissolved oxygen and the GAC acts as a catalyst. In our experiments, the 2,4-xylidine was almost completely oxidized in the CWO reactor within an hour at relatively mild temperatures (140–175 °C) and oxygen partial pressures (4–10 atm). Non-catalytic wet oxidation was not so effective for 2,4-xylidine removal.

It must still be born in mind that in the study a model solution was used in laboratory experiments and the kinetic parameters were estimated for the xylidines–distilled water system and therefore before real groundwater purification additional laboratory experiments must be carried out with *in situ* water, taking into account the deviations due to the water quality (additional organics, pH, etc.).

CONCLUSIONS

Xylidines are carcinogenic compounds originating from missile fuel and are dominating in polluted groundwater in the areas of abandoned Soviet missile bases in Eastern Europe. Two chemical methods for xylidine-polluted water purification were studied – ozonation and catalytic wet oxidation.

Ozonation of 2,4-xylidine in aqueous solution was carried out on a wetted-wall column. A laboratory-scale ozone contactor was designed and a steady-state wetted-wall reactor model was developed. The model was based on counter-currently connected and perfectly mixed mass transfer stages. It was possible to describe the changes of the pollutant and ozone concentrations along the reactor length coordinate in various conditions. The mathematical model elaborated for the wetted-wall reactor was observed to be in good agreement with the experimental data – the degree of explanation exceeded 96% for both the ozone mass transfer and the 2,4-xylidine ozonation data.

The developed wetted-wall reactor model is suitable for the investigation of ozonation kinetics for other organic compounds with similar nature. It is easy to include the intermediates into the reaction scheme, as the equation system for each stage of the ozonation column is solved numerically.

The catalytic wet oxidation with GAC as a catalyst at mild conditions (temperature below 200 °C, total pressure below 15 bar) was experimentally studied. The 2,4-xylidine was adsorbed on the surface of the GAC and then degraded in the wet oxidation unit. The GAC type catalyst is active enough for 2,4-xylidine oxidation. The 2,4-xylidine was almost completely oxidized in the CWO reactor within an hour, while the intermediates such as ring cleavage by-products and organic acids, which are formed throughout the oxidation process, are resistant to degradation. The non-catalytic wet oxidation did not degrade 2,4-xylidine at mild conditions and needs severer conditions.

Two kinetic models for predicting 2,4-xylidine degradation in the catalytic wet oxidation were studied. The Langmuir–Hinshelwood and the power-rate law kinetic models were both based on 2,4-xylidine decay. A satisfactory fit was achieved with both when validated against experimental data. The Langmuir–Hinshelwood kinetic model should be used in the reactor design as it has solid theoretical foundation.

In order to obtain more exact results, for the modelling of 2,4-xylidine degradation advanced CWO kinetic models that take into account the formation of intermediate products and their adsorption and desorption should be used. These intermediate products should be identified and quantitatively measured during the experiment. In this study only some of these intermediates were analytically identified (formic, acidic, and propionic acids).

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

This study gives a mathematical tool and rate coefficients for designing two chemical methods for xylidine-polluted groundwater purification: ozonation in a bubble column and adsorption onto GAC NORIT RB1 in a packed bed reactor with a subsequent catalytic wet oxidation in the presence of GAC. The results and models developed can be used to design a purification process when only one contaminant is present. The same approach can also be used for real water containing many compounds if they are presented through one lumped parameter, such as COD, BOD, TOC, etc.

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Ksülidiiniga reostatud põhjavee puhastamine. Osoneerimine ja katalüütiline märghapendus

Janek Reinik ja Juha Kallas

On uuritud kantserogeense ksülidiiniga reostatud vee puhastamist osoneerimise ja katalüütilise märghapenduse meetoditega. Niimoodi saastunud põhjavett leidub endistes Nõukogude armee raketibaasides. Ksülidiini lagundamise kineetikat uuriti osoneerimisel läbivoolu kelmereaktoris ja koostati matemaatiline mudel. Mudeliga hinnati reaktsiooni ja massiülekande kiirust. Hinnatud kineetiliste parameetrite alusel arvutatud reaktorist väljuvad kontsentratsioonid sobisid hästi katseliselt määratutega. Antud katseseadet ja mudelit saab kasutada teiste samalaadsete ainete osoneerimise kineetika uurimiseks. Ksülidiini osoneerimise kiiruskonstante on võimalik kasutada barbotaažkolonni projekteerimisel. Keemilistest puhastusmeetoditest uuriti aktiivsöe pinnale kontsentreeritud ksülidiini oksüdeerimist vees hapniku juuresolekul – katalüütiline märghapendus – erinevatel temperatuuridel (140–170 °C) ja hapniku osarõhkudel (4–10 atm) perioodilises reaktoris. Aktiivsüsi katalüüsis protsessi ja sellest piisas 2,4-ksülidiini lagundamiseks, kuid ei olnud efektiivne tekkivate orgaaniliste hapete oksüdeerimiseks. Protsessi kasutamine küllastunud granuleeritud aktiivsöe täielikuks regenereerimiseks nõuab karmimaid tingimusi. Märghapenduse modelleerimiseks töötati välja reaktsiooni kineetikat kirjeldavad mudelid.