TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

MASS TRANSFER OF OZONE AND ITS DECAY IN SEMI-CONTINUOUS REACTOR: A CASE STUDY

OSOONI MASSITRANSPORT JA LAGUNEMINE POOLPERIOODILISES REAKTORIS

MASTER THESIS

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AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
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CONTENTS

PREFACE

This work was conducted at Tallinn University of Technology, school of engineering, Department of Materials and Environmental Technology.

I would like to thank my head supervisor of this master thesis Ph.D. Juri Bolobajev. I am grateful for his excellent guidance, support in the experimental and theoretical parts.

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Anna Setskaja

Ozonation, semi-continuous reactor, mass-transfer, chemisorption, master thesis.

List of abbreviations and symbols

Abbreviations	
AOP	advanced oxidation process
AOX	adsorbable organic halides
BC	bubble column
Bio	bio-oxidation
BOD	biochemical oxygen demand
CD	“corona” discharge (generator)
COD	chemical oxygen demand
CT	color threshold
DO	dissolved oxygen
DOC	dissolved organic carbon
GAC	granular activated carbon
M	micropollutant
MT	mechanical treatment
OD	oxygen demand
PTFE	polytetrafluoroethylene
R	reaction product
R	reaction tank (reactor)
S	scavenger
UV	ultraviolet
TBA	tert-butyl alcohol
TSS	total suspend solids

Symbols		**units**
A	specific volumetric area	m^{-1} (m^2m^{-3})
A	total bubble surface area	m^2
b	path length of cell	cm
C	concentration	$mg{\cdot}L^{-1}$
C^*	saturation concentration	$mg{\cdot}L^{-1}$
C_G	ozone concentration in gas phase (in reactor)	$mg{\cdot}L^{-1}$
C_{Go}	influent-gas concentration	$mg{\cdot}L^{-1}$
C_{Gi}	is ozone concentration in gas phase film	$mg{\cdot}L^{-1}$
C_{Ge}	effluent-gas concentration	$mg{\cdot}L^{-1}$
C_L	ozone concentration in liquid phase	$mg{\cdot}L^{-1}$
C_{Li}	is ozone concentration in liquid phase film	$mg{\cdot}L^{-1}$
D	diameter of a semi-continuous reactor	mm

f	coefficient of absorption 0.42	-
H_C	Henry’s Law constant	-
k	film mas transfer coefficient	$m \cdot s^{-1}$
k’	mass-transfer coefficient in case of chemisorption	$L \cdot (cm^2 \cdot min)^{-1}$
k	reaction rate constant, first or second order	s^{-1} or $M^{-1} \cdot s^{-1}$
k_D	mass-transfer coefficient, pseudo-first order (in this work)	s^{-1}
k_L	liquid-film mass transfer coefficient	$m \cdot s^{-1}$
k_La	liquid-phase volumetric mass-transfer coefficient	s^{-1}
n	reaction order	-
N	mass-transfer flux	$mg \cdot m^{-1} \cdot s^{-1}$
P	pressure	Pa
pK_a	dissociation constant	-
Q_G/Q_L	gas/liquid flow rate	$1\ s^{-1}$
r_L	ozone consumption rate in liquid phase	$mg \cdot L^{-1} \cdot s^{-1}$
R	ideal gas constant; R = 0.082	$atm \cdot (mol \cdot K)^{-1}$
$\tau = t$	time	s
T	temperature	°C
V_G/V_L	gas/liquid volume	mL
W	is molar flow rate by chemisorption	$mol \cdot min^{-1}$

Greek Alphabetic		**units**
δ	width of film	m
λ	wavelength	nm

INTRODUCTION

Ozone has been playing a crucial role in development of life on Earth. It is known that ozone layer absorbs the ultraviolet radiation of sunlight in stratosphere protecting therefore organisms from dangerous electromagnetic radiation. Moreover, ozone is attracted attention because of its strong oxidizing ability, which makes this compound especially important in environmental technologies. Continuous growth of human population has led to the increased demand in water use and reuse. Oxidative properties of ozone are successfully implemented in many industrial applications of water treatment, e.g. in pharmaceutical industry, organic synthesis and more importantly in the treatment of drinking water and wastewater.

Since ozone is very unstable compound, which is presented at normal conditions in gaseous state, it must be produced in-situ by a corresponding generator and directed into the reactor by means of a gas diffuser. The ozonation process is followed then by ozone dissolution in aqueous phase. Ozone can react in two different ways, i.e. either direct or indirect. The direct pathway undergoes predominantly at acidic conditions and involves reactions of ozone molecule (O_3) with substrate. The indirect pathway is known as purported advanced oxidation process (AOP) due involving the participation of hydroxyl radicals HO●. Indirect reactions predominate under alkaline conditions at pH values above 10.

Ozone technology is applicable in medium to large size water treatment plants and it is commonly used after secondary treatment. The main objectives of ozone applications are disinfection, odor control, improvement of organoleptic properties of water etc. In spite of its high capital costs, ozonation is widely used in Europe, e.g. in Tallinn drinking water production plant, because of its high ability of disinfection.

The general aim of the present study was to investigate the process of ozone mass-transfer (at pH=7) and decay in laboratory semi-continuous reactor. The ozone was generated by using “corona discharge” generator. This work helped to understand the behavior of ozone depending on several chemical and hydrodynamics properties, such as mass-transfer coefficient, the rate constant of ozone decay etc.

1 LITERATURE REVIEW

1.1 The process of ozonation

Ozone (O_3) is a relatively unstable molecule which consist of three atoms of oxygen. Although it represents only a tiny fraction of the atmosphere, ozone is crucial for life on Earth. The reason is that ozone layer filters out the sunlight with the wavelengths from about 200 to 315 nm protecting therefore the Earth's living organisms from the negative impact of high energy electromagnetic radiation [1]. In addition, ozone is characterized by its strong oxidizing power and the tendency to recombine to molecular oxygen (Eq. 1) [2].

$$O_3 \rightarrow 3O_2 \qquad (1)$$

Its oxidative properties are successfully used in many industrial applications such as drug industry, production of lubricants, organic synthesis etc. The most important sphere of ozone application that falls within the scope of present thesis is ozonation of drinking and waste waters.

As ozone is quite unstable compound, its production in industry undergoes directly on site of application. The water ozonation, whether it is applied as disinfection or wastewater treatment, is followed by ozone dissolution in water. That can be achieved by means of water bubbling with gas saturated with ozone.

Ozone can react in aqueous phase in two different ways, i.e. direct and indirect. Both ways are relevant, depending on modelling goals. These reaction pathways lead to different chemical reaction products and are controlled by different types of kinetics. Figure 1 gives an overview of two different processes, and their interaction [3].

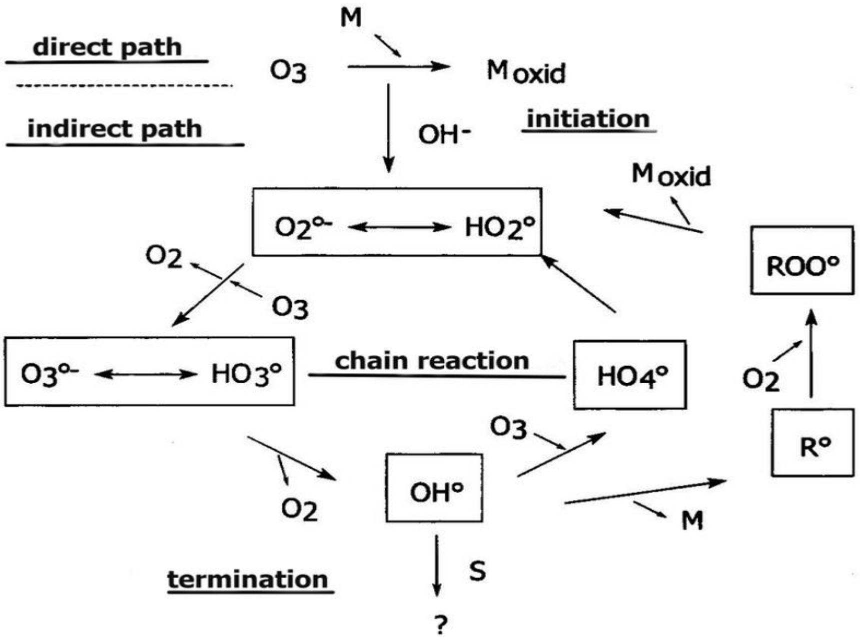


Figure 1. Mechanism of the direct and indirect ozonation pathways, where S- scavenger, R- reaction product, M- micropollutant [3].

1.1.1 Direct reactions

The direct oxidation (M + O_3) of substances by ozone is a selective reaction with slow reaction rate constants, which are typically in the range of 1.3 – 10^3 M^{-1} s^{-1}. The ozone molecule (O_3) reacts with the unsaturated bond due to its dipolar structure and leads to a splitting of the bond, the latter is based on the so-called Criegee mechanism (Figure 2). This mechanism was discovered in non-aqueous solutions [3].

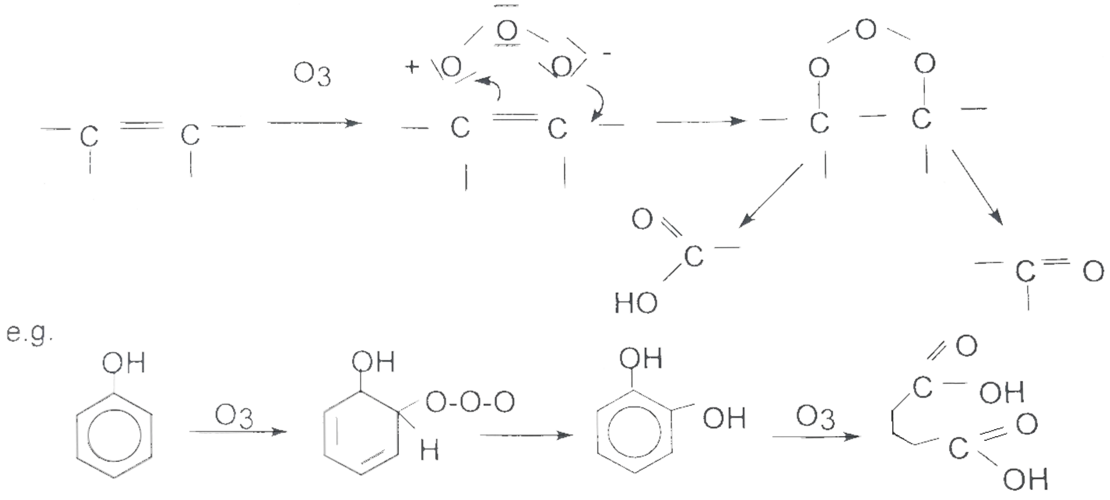


Figure 2. Feasible aqueous reactions of ethene and phenol with ozone [3].

Ozone reacts slowly with many types of water pollutants such as odour compounds, for example geosmin (compound with earthy flavour) or unactivated aromatics such as chlorinated benzenes. During ozonation process the reaction rate may be affected by certain types of aromatic compounds, because of electron supplying substituents such as the hydroxyl group in phenol. Without such substituent the rate of ozonation is much slower.

The direct pathways dominate when water matrix pH is under acidic conditions ($pH < 4$), whereas at pH values above 9-10 it changes to the indirect, or radical reaction pathway, which has undoubtedly more rapid reaction rates [3][4].

1.1.2 Indirect reactions (AOP)

Indirect reactions are referred to as purported advanced oxidation processes, as much as the indirect reaction pathways involves radicals. The first step in the series of reactions is a decay of ozone accelerated by initiators, e.g. hydroxyl groups. As a result, the secondary oxidants are formed such as hydroxyl radicals ($HO\bullet$). $HO\bullet$s play in AOP the general role as they are able to react very fast (reaction constant $k = 10^{8} – 10^{10}\ M^{-1}\ s^{-1}$) and nonselectively with organic substrate. Indirect pathway could be initiated by many compounds [5]. The present mechanism can be divided into three steps: initiation, radical chain and termination step [3].

The initiation step indicates the reaction between hydroxide ions and ozone that leads to the formation of one superoxide anion radical $O_2^-\bullet$ and hydroperoxyl radical $HO_2\bullet$ (Eq. 2).

$O_3 + HO^-\bullet \rightarrow O_2^-\bullet + HO_2\bullet \qquad k_1 = 70\ M^{-1}\ s^{-1}$ (2)

The hydroperoxyl radical is in an acid-base equilibrium (Eq. 3).

$HO_2\bullet \leftrightarrow O_2^-\bullet + H^+ \qquad pK_a = 4.8$ (3)

Secondly, the radical chain reactions occur (Eq. 4 – 6), where the ozonide radical $O_3^-\bullet$ is formed by the reaction between ozone and the superoxide anion radical $O_2^-\bullet$. $HO_3\bullet$ decomposes immediately into a $HO\bullet$ radical.

$O_3 + O_2^-\bullet \rightarrow O_3^-\bullet + O_2 \qquad k_2 = 1.6\ 10^{9}\ M^{-1}\ s^{-1}$ (4)

$HO_3\bullet \leftrightarrow O_3^-\bullet + H^+ \qquad pK_a = 6.2$ (5)

$HO_3\bullet \rightarrow HO\bullet + O_2$ $k_3 = 1.1 \times 10^8\ M^{-1}\ s^{-1}$ (6)

The interactions of HO• with ozone (Eq. 7 and 8) are based on the theoretical model presented by Hoigné 1982 [6].

$HO\bullet + O_3 \rightarrow HO_4\bullet$ $k_4 = 2.0 \times 10^9\ M^{-1}\ s^{-1}$ (7)

$HO_4\bullet \rightarrow O_2 + HO_2\bullet$ $k_5 = 2.8 \times 10^4\ M^{-1}\ s^{-1}$ (8)

The decay of $HO_4\bullet$ into oxygen and hydroperoxide radical (Eq. 8) instigate the chain reaction (Eq. 2). The chemical compounds which convert HO• into superoxide radicals $O_2^-\bullet$/ $HO_2\bullet$, act as chain carriers, the so-called promoters. Some of organic molecules (R) containing functional groups could react with HO• and form organic radicals R• (Eq. 9). Promoting thereby chain reactions (Eq. 10 – 12) [3].

$H_2R + HO\bullet \rightarrow HR\bullet + H_2O$ (9)

As a result, peroxyradicals ROO• are formed, which react further with $O_2^-\bullet$/ $HO_2\bullet$ eliminating them and so enter again into the chain reaction.

$HR\bullet + HO\bullet \rightarrow HRO_2\bullet$ (10)

$HRO_2\bullet \rightarrow R + HO_2\bullet$ (11)

$HRO_2\bullet \rightarrow RO + HO\bullet$ (12)

The decay of ozone, which can be initiated by the hydroxide ion, leads to a chain reaction and produces fast-reacting and non-selective HO• radicals. These radicals have a very short half-life, less than 10 µs at an initial concentration of 10^{-4} M. Being strong electrophiles HO• radicals react with the molecule sites with the highest electron density.

The process is terminated by the sequence of reactions, where either organic or inorganic substances react with HO• radicals to form secondary radicals (Eq. 13 – 14). As they do not produce $HO_2\bullet/O_2^-\bullet$, these radicals terminate the chain reaction and inhibit ozone decay [3].

$HO\bullet + CO_3^{2-} \rightarrow OH^- + CO_3^-\bullet$ $k_6 = 4.2 \times 10^8\ M^{-1}\ s^{-1}$ (13)

$HO\bullet + HCO_3^- \rightarrow OH^- + HCO_3\bullet$ $k_7 = 1.5 \times 10^7\ M^{-1}\ s^{-1}$ (14)

There is another pathway that terminates the chain reaction (eq. 15):

$HO\bullet + HO_2\bullet + H^+ \rightarrow O_2 + H_2O$ $k_8 = 3.7 \times 10^{10}\ M^{-1}\ s^{-1}$ (15)

The combination of the Eq. 2 – 8 indicate that three ozone molecules can produce two HO• radicals.

$3\ O_3 + OH^- + H^+ \rightarrow 2\ HO\bullet + 4\ O_2$ (16)

Many of chemical compounds can initiate, promote or terminate the chain reactions. Some examples of these compounds are given in Table 1 [3].

Table 1. Typical initiators, promoters and scavengers for decomposition of ozone in water matrix [3].

Initiator	Promoter	Inhibitor
OH^-	humic acid	HCO_3^-/CO_3^{2-}
H_2O_2/HO_2^-	aryl-R	PO_3^{4-}
Fe^{2+}	primary and secondary alcohols	humic acid alkyl-R tert-butyl alcohol (TBA)

Staehelin and Hoigné (1985) studies show that phosphate, which reacts slowly with HO•, can also act as an efficient scavenger when used in concentrations typically found in buffer solutions (50 mM).

The action of humic acid is ambivalent, it can react as inhibitor or promoter, depending on its concentration. The tert-butyl alcohol is often used to supress the chain reactions. The moderators can be used during ozonation for the stabilization of ozonation process [3].

1.2 Ozonation of wastewater and drinking water

1.2.1 Ozonation of wastewater

Wastewater treatment technologies are used for municipal and industrial wastewaters in order to reduce the toxicity and the concentration of pollutants prior to discharge in the natural environment. The wastewater contains a high range of COD, BOD, TSS levels and other contaminants i.e. microorganisms, pharmaceuticals, glycol, amines, alcohols, complex proteins, aldehydes, etc. This includes water from industries such as textile, food industry, pharmaceutical industry, paper & pulp, cosmetic and other production facilities. Some examples of typical variation of microorganisms in untreated wastewater are given in the Table 2 [7][8].

Table 2. Infectious agents potentially present in untreated domestic wastewater [7].

Organism	Disease Caused
Bacteria	
Escherichia coli (enterotoxigenic)	Gastroenteritis
Salmonella typhi	Typhoid fever
Salmonella (=2,100 serotypes)	Salmonellosis
Shigella	Shigellosis (bacillary dysentery)
Vibrio cholerae	Cholera
Protozoa	
Balantidium coli	Balantidiasis
Cryptosporidium pavrum	Cryptosporidiosis
Entamoeba histolytica	Amebiasis (amoebic dysentery)
Giardia Lamblia	Giardiasis
Helminths	
Ascaris lumbricoides	Ascariasis
T. solium	Taeniasis
Trichuris trichiura	Trichuriasis
Viruses	
*Enteroviruses (*72 types, e.g., polio, echo, coxsackie)	Gastroenteritis, heart anomalies, meningitis
Hepatitis A virus	Infectious hepatitis
Norwalk agent	Gastroenteritis
Rotavirus	Gastroenteritis

The chemical oxygen demand (COD) is a measure of water/wastewater quality. That evaluates chemically oxidizable substances. COD concentrations are higher than that of BOD in wastewater. Typical COD range in wastewater is 200-40 000 mg·L^{-1}, whereas values of COD in domestic wastewaters varies in the range between 100-450 mg·L^{-1}.

Fig. 3 gives an overview about the destruction of target pollutants by direct or indirect reactions [8][9].

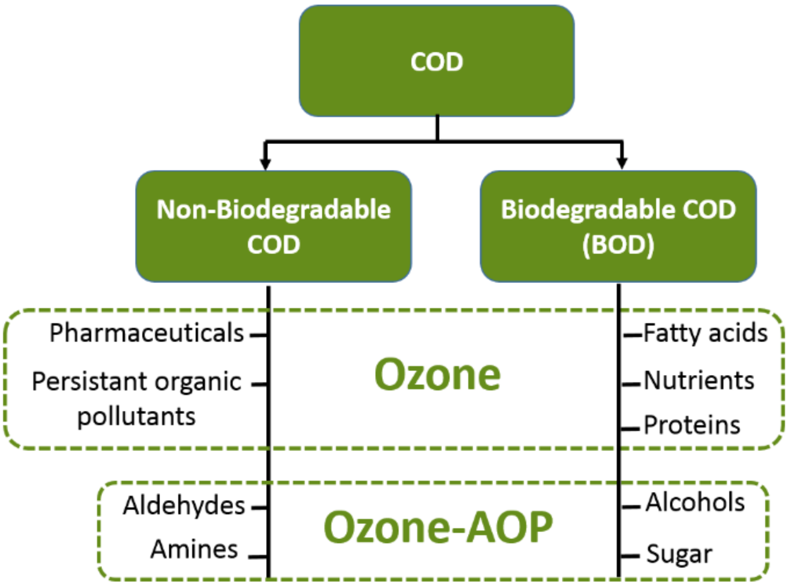


Figure 3. The treatment of COD with ozonation, where ozone - direct reaction and ozone-AOP - indirect [9].

Applicability

Ozone disinfection is applicable in medium and large size plants. It is commonly used after secondary treatment. One of the main objectives (besides disinfection, taste, colour) of using ozone in wastewater treatment is odour control.

Water treatment technologies based on ozone is widely used in Europe. The reason is that the ozonation can demonstrate higher levels of disinfection comparing to some other methods (i.e. chlorine, UV etc.). However, the capital costs as well as maintenance expenses are higher than in case of other alternatives. Ozone is therefore used infrequently only in cases, where alternatives are not effective.

The treatment with ozone can reduce BOD/COD, turbidity, colour and it also increase the DO level. The mechanisms of disinfection include the following processes: distraction of the cell wall (direct oxidation); reaction of radicals; degradation of the constituents of the nucleic acids and breakage of carbon-nitrogen bonds leading to depolymerization. The rate of treatment during ozonation depends on the susceptibility of the target organisms, contact time and concentration of ozone. Typical block diagram of ozonation technology is shown in Figure 4. This system consists of feed gas preparation, ozone generation, ozone contacting with wastewater and disintegration of emissions [7][9].

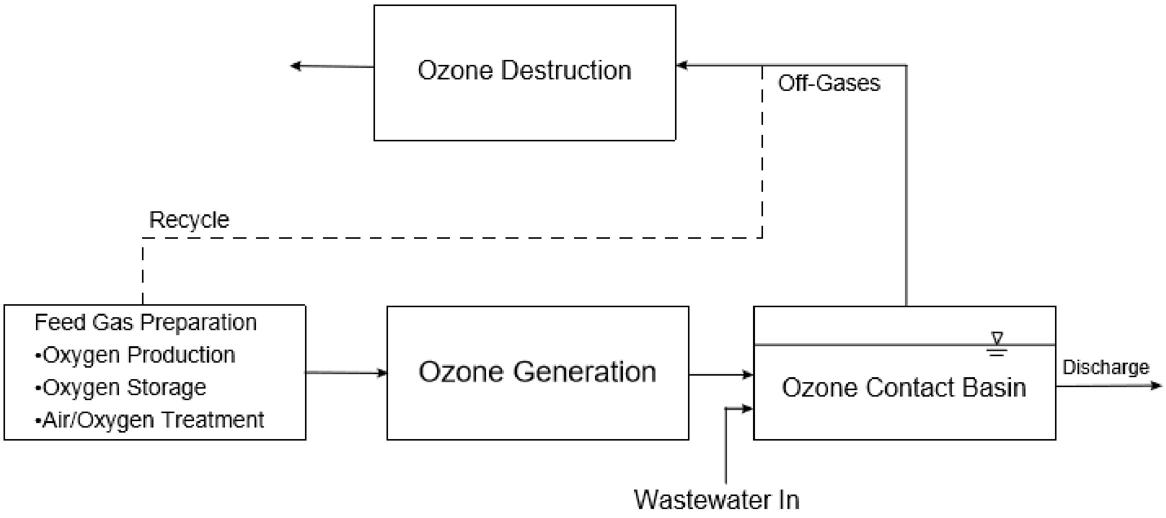


Figure 4. The ozonation block flow process diagram [7].

The combinations of ozonation are commonly used to achieve the required treatment goals for maximization of mineralization level. These combinations can be done with UV-radiation, hydrogen peroxide, bio-oxidation, chlorine and many others. It depends on the bio-chemical parameters of drinking water or wastewater properties and considerations in terms of profitability.

For example, the wastewater collected in textile factories located in Lodz, Poland, was studied by Technical University of Lodz (Institute of Knitting Technology and Techniques Institute of Applied Radiation Chemistry), year 2003. The main objective of the study was decolouration of real textile wastewater with an advanced oxidation process including ozonation. The study was conducted with 16 different samples of wastewaters taken from knitting plants in Lodz [10].

Figure 5 shows the time (h) dependence of colour threshold level (%). As seen, the degree of purification depends directly on the exposure time. In this case, the combination of ozone and gamma irradiation are more successful option. The complex application of ozone and ionizing radiation contribute to an increase in the concentration of oxidizing agents in the aqueous solutions, including reactive HO• radicals, due to reactions between the products of radiolysis and ozone decomposition.

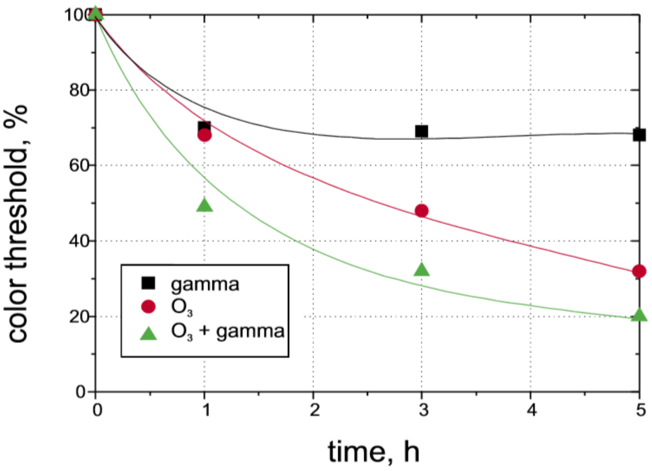


Figure 5. The changes comparison of the colour threshold (CT) number in dyehouse wastewater nr. 6 by gamma irradiation, ozonation and gamma irradiation with ozonation [10].

The study demonstrated the higher efficiency of decolouration and higher decomposition efficacy of organic contaminants. Besides that, the synergetic effect was observed, which allows to significantly decrease the dose of ozone and radiation and as a consequence to reduce the time of wastewater treatment. The results depend on the type and concentrations of contaminants and applied doses of radiation and ozone. For achieving more than 90% water decolouration (at CT=500, which is high), were required ozone doses from 145 to 725 $mg \cdot dm^{-3}$ and radiation doses varied from 1.2 to 6.0 kGy, respectively. More detailed data is given in Table 3. For the wastewater with colour threshold from 25 to 100 (with less intensive colour) at the same doses, total decolouration was reached [10].

Table 3. Decolouration of wastewater by ozonation with gamma radiation [10].

Dyehouse wastewater	Treatment time	Ozone dose	Radiation dose	Reaction	Specific colour	Colour threshold
	h	mg $O_3 \cdot dm^{-3}$	kGy	pH	description	
Nr 6	0	0	0	8.4	Blue	500
	1	145	1.2	7.2	Blue	250
	3	435	3.6	7.3	Yellow green	50
	5	725	6.0	7.3	Light yellow	25

1.2.2 Ozonation of drinking water

Drinking water (potable water) is a water with certain parameters, which are regulated by law, that is safe to drink or to use for food preparation. The treatment of drinking water depends directly on its source and on its properties, full scale plants are usually using chlorination and advanced oxidation processes, including ozonation.

Figure 6 demonstrates the process of drinking water treatment that uses ozonation [11]. First of all, raw water from lake is being pumped into the plant where the preliminary mechanical treatment takes place in order to remove seaweed, plankton and larger debris by using grids and microfilters. The first grid also stops the fish from getting into the plant. Therefore, a large part of pollutants removed from lake is discharged into the sewer.

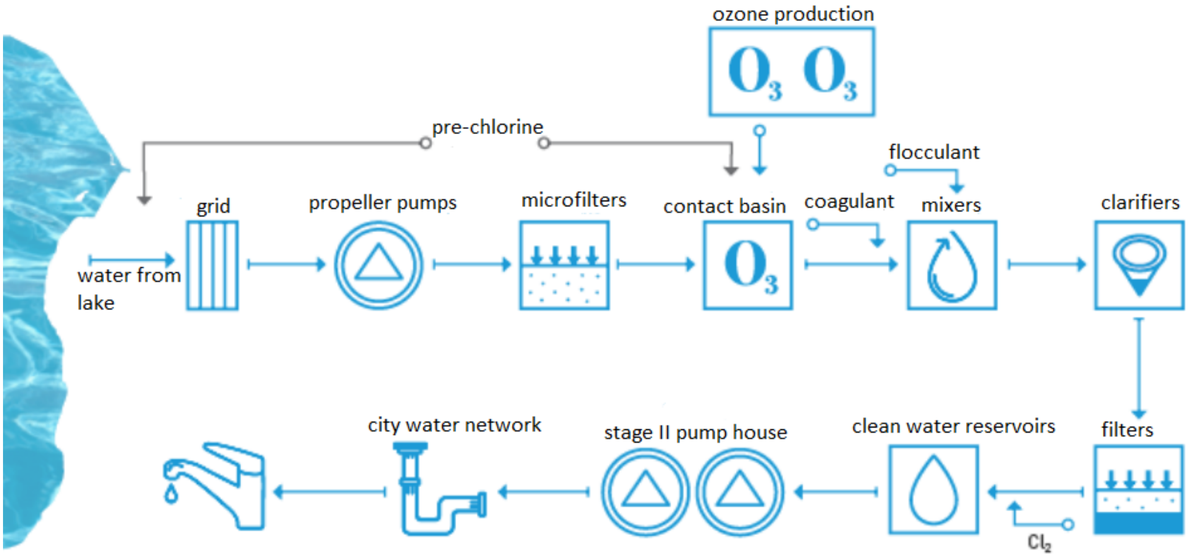


Figure 6. The block flow diagram of drinking water treatment in Tallinn [11].

The next step is chemical treatment, which consists of ozonation and coagulation. The main objective of ozonation is to kill microorganisms and viruses by radicals and to oxidize chemical compounds. Thereafter special water treatment chemicals such as coagulant are added into water. The coagulant concentrates around particles, making them larger and heavier (formed in flakes). As a consequence, the resultant flocs are precipitated to the bottom of the basin by way of gravitation force and then flushed into a sewer. The dual layered sand filters are used further for removing of fine particles that were not eliminated from water using coagulation.

At the end of treatment process, chlorine is added in small quantities for to maintain the quality of water in the city network. The diagram of tap water treatment is sowed on Figure 6 [11].

In recent years, ozonation has been increasingly used for several reasons. The wide application of chlorine for water treatment has led to the appearance of chlorine resistant bacteria, which pose a severe danger to health. W. Ding, W. Jin, S. Cao et al. [12] have published the research of ozone disinfection of chlorine resistant bacteria in drinking water. The study explored the physiological-biochemical specification and pH, temperature, turbidity influence. Ozonation was used to inspect the destruction of bacteria and spores. The samples (raw water) were collected from municipal drinking water treatment plant in China.

In raw water such bacteria as Bacillus alvei, Bacillus cereus, Lysinibacillus fusiformis were detected. These strains are considered to be chlorine resistant. Spores have strong thermostability and resistance to ordinary disinfectants. Ozone concentration was certain by spectrophotometry with potassium indigo trisulfonate [12]. The concentration of ozone in water can be definite by the decolouration of indigo trisulfonate ($\lambda = 600$ nm). The reaction is very fast, selective and stoichiometric. The indigo molecule has one C=C double bond which react with ozone and with a very high reaction rate. The system is easy, one mole ozone decolorates one mole of aqueous indigo trisulfonate at pH> 4 [3].

Bacteria were wand shaped and about 3-5 μm, whilst spores were 1-2 μm long. Ozone doses were selected as follows, 1 $mg \cdot L^{-1}$, 2 $mg \cdot L^{-1}$,3 $mg \cdot L^{-1}$. Each sample was treated for 4 min. At dosage of 1.5 $mg \cdot L^{-1}$, ozone resistance of bacteria was lower than of spores and more than 99.9% of spores were disrupted by increasing ozone concentration and exposure time. The results of research showed that ozone disinfection is hopeful approach for chlorine resistant bacteria and spores’ destruction in drinking water [12].

1.2.3 Advantages and disadvantages of ozonation

The ozonation as any other method has its own peculiar properties and naturally has its pros and cons. One of the most important advantage is high effectivity in destroying viruses and bacteria in comparison with chlorine (it is important to calculate the dosage and influence time). Secondly, the ozonation process apply a short contact time and don’t have harmful residuals because ozone decomposes rapidly. In addition, ozone is generated onsite and this resolve safety problems related with shipping and handling. Equally important is that treatment by ozonation elevates the dissolved oxygen aggregation (DO) of the effluent, it can obviate the need of reaeration.

The main disadvantages of this method lies in the complexity of ozonation technology. Ozonation is a more sophisticated technology than UV disinfection or chlorine, it needs more complicated equipment and contacting systems. Also, the cost can be comparatively high in capital and in power intensiveness. Furthermore, it is not economically viable for wastewater with high COD and total organic carbon (TOC), biochemical oxygen demand (BOD), suspended solids (SS). Insofar as ozone is very reactive, corrosion resistant material such as stainless steel is required. Being a strong oxidant ozone is very toxic as well [7].

1.3 Combination of ozone with other water treatment methods

As it has been already mentioned here, ozone combination with other technologies is widely used. Thereby, a higher degree of purification can be achieved. It is also important solution for economical standpoint. In order to compose the treatment scheme, the origin and properties of water must be considered. The process of drinking and wastewater treating differs with a various stages. For example, for municipal or industrial water treatment an activated sludge process (anaerobic or aerobic bio-oxidation) is often used.

1.3.1 Combination of ozonation with bio-oxidation

Activated sludge process is very widely used in wastewater treatment and is applicable to waste waters with a large range of concentrations. Bio-oxidation can be used to treat wastewater with biodegradable chemical oxygen demand (COD), from 50 to 10000 $mg \cdot L^{-1}$. Herewith, anaerobic bioreactors are often more effective than aerobic. In activated sludge process the appropriate microorganisms are of high importance. For example, Fungi, Acinebacte, Bacillus, Arthobacter, Flexibacter etc. are using organic pollutants for vital activity, thereby pollutants are converted into a biomass, carbon dioxide or to other harmless form. In the activated sludge process, sewage is mingled with 20 to 50 % of its returned activated sludge volume. The mixture in the aeration tank are called mixed liquor. Then the blend enters to aeration tank with large quantity of air. The mixed liquor enters settling tank, where the flocculent masses are removed from sewage. The general chemical reactions are as follows (Eq. 17 - 19) [13][14]:

Oxidation

$$Organic\ matter + O_2 + bacteria \rightarrow CO_2 + H_2O + NH_3 + other\ end\ products + energy \qquad (17)$$

Synthesis

$$Organic\ matter + O_2 + bacteria + energy \rightarrow New\ microbial\ cell\ tissue\ (C_5H_7NO_2) \qquad (18)$$

Endogenous respiration

$$New\ microbial\ cell\ tissue + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O + energy \qquad (19)$$

The combination of bio-oxidation and ozonation is used in full-scale applications to treat such industrial wastewaters, e.g. textile, pulp and paper. These sources are commonly considered as complex, because its often contains a higher degree of pollution (COD, BOD, heavy metals, pharmaceuticals, pesticide etc.) compared to that of municipal water. Usually, the effluent from plants is directed to the water, which necessitates the effluent ranges on COD below 200 mg·L^{-1}, toxicity factor to fish lower than 2 and an AOX level 500 µg·L^{-1} [3]. Due to aforesaid, the ozonation process is ordinarily operated between two biological treatment (Bio-O_3-Bio). In the first stage, all easily biodegradable organic compounds are removed. The biological stage can also decrease nitrate, nitrite and ammonium concentrations by way nitrification and denitrification. In this scheme, ozone is used to oxidize substances in order to increase their biodegradability in the following biological stage. The main advantage of this combination is that secondary waste is not produced, as if the O_3-Bio process steps were replaced by granular activated carbon treatment.

Due to the high potential of ozone for decolouration, its application in the textile industry has gained particular attention in the last decade. Several full-scale plants are already in operation. In addition to the main purpose of removing residual non-biodegradable dyes from waste streams, ozone is able to degrade the surfactants reducing the concentration of DOC. The high rate of total DOC removal (for example > 80 %) can be very expensive for smaller applications. For example, one of the largest full-scale applications of ozonation in wastewater treatment industry is located in Germany at BASF Schwarzheide GmbH, where the ozone generator of 15 kg O_3 h^{-1} efficiency is installed. The wastewater is collected from manufacture of polyurethane foams. The treatment of this highly toxic wastewater is accomplished by aforementioned Bio – O_3 – Bio system. The main purpose is to remove recalcitrant and toxic nitroaromatic compounds, so that the level of COD content would less than 4 % [3].

To achieve better result with a minimum cost, the combination of ozone and biological treatment should be optimized economically and technically. Figure 7 shows schematic view of a typical wastewater treatment application in pulp and paper industry with tertiary stage of using ozonation and biofilter. The system consists of primary treatment with mechanical part, secondary treatment with activated sludge basin and tertiary treatment represents a chemical and biochemical oxidation (ozonation + biofiltration) with a partial distillation and post filtration.

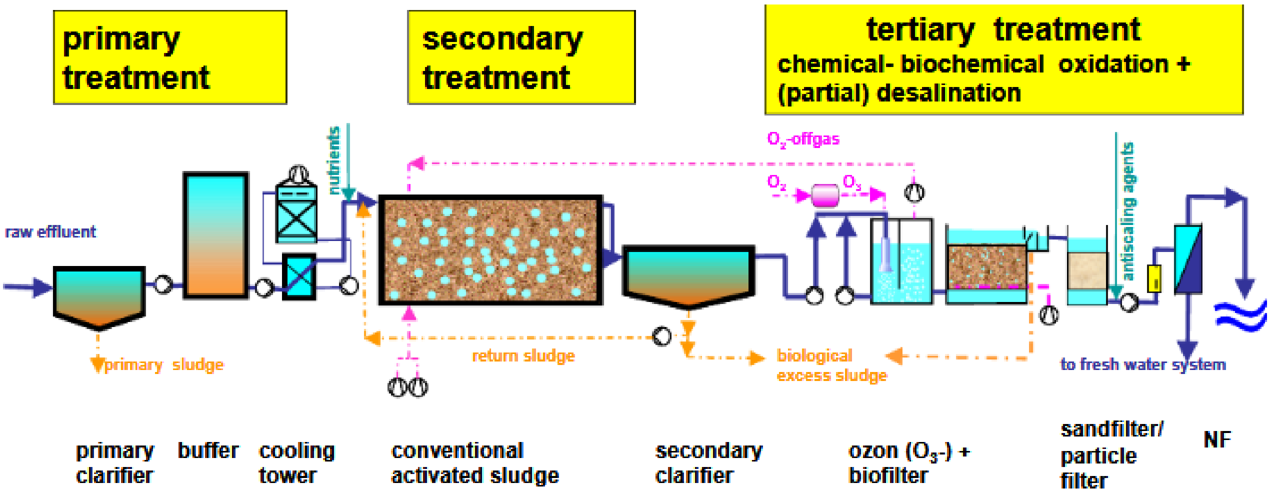


Figure 7. The scheme of a papermill wastewater treatment plant with ozonation combination with bio-oxidation [15].

To get the best possible results with lowest ozone dose it is important to investigate the oxidation process in the gas-liquid interface.

1.3.2 Combination of ozonation with granular activated carbon (GAC) filtration

The drinking water treatment with mere ozone is not effective for the removal of recalcitrant pollutants, particularly micropollutants. The Amsterdam Water Supply introduced new concept for the treatment of surface water (of Rhine River), which include regular pre-treatment by coagulation, sedimentation and fast sand filtration, then followed by slow sand filtration and a reverse osmosis or ozonation, GAC filtration, slow sand filtration and reverse osmosis. The general emphasis is placed on combination GAC (granular activated carbon) with ozonation. The system combines chemical oxidation, adsorption and biological oxidation in activated carbon filters. The full-scale drinking water application at the Leiduin (1995), Amsterdam uses the following processes: coagulation, sedimentation, rapid sand filtration, dune infiltration, aeration, rapid sand filtration, ozonation, softening, GAC, slow sand filtration (Figure 8.) [16].

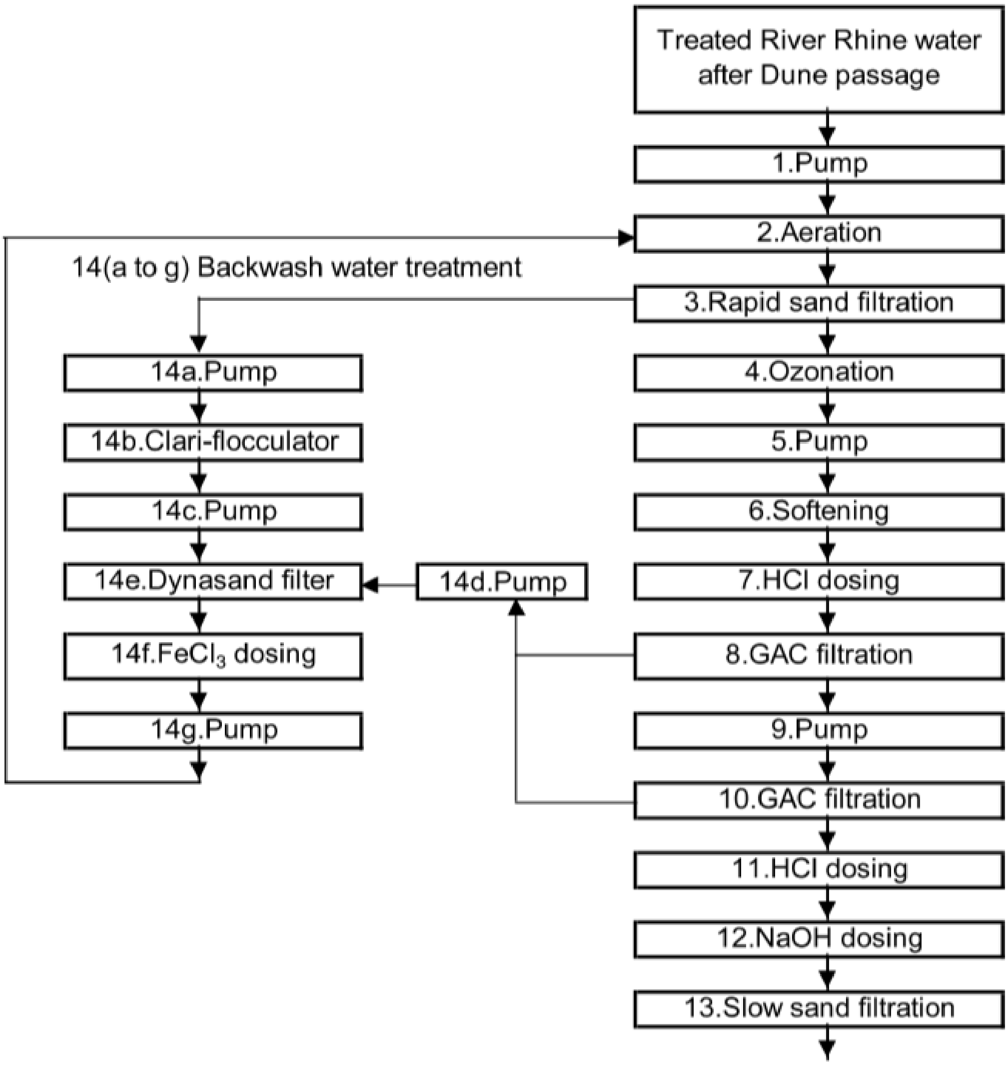


Figure 8. The flow chart of Leiduin drinking water treatment plant [17].

In the Amsterdam Water Supply, ozonation has a multifunctional role, which considers the oxidation of pesticides and other organic compounds, disinfection and the improvement of pollutants removal by granular activated carbon filtration.

The GAC filtration includes two primary processes, i.e. adsorption and biodegradation by bacteria. Activated carbon consists of appropriate carbonic material such as coal, wood or coconut shells, peat, bitumen or lignite with determined pore structure. The adsorption capacity of granular activated carbon depends on its surface structure and internal surface area (ranging from 500 to 1500 $m^2 \cdot g^{-1}$). CaO concentration in material (can increase pH of water due to $Ca(OH)_2$ extrication) and the initial chemisorption of oxygen are the general characteristics, which needs to be considered during GAC filtering start-up.

At the beginning of the operation the activated carbon filters produce anaerobic effluent. After about week O_2 concentration in GAC filter effluent is approaching the concentration of filter influent. The mass transfer of a micropollutant occurred within a GAC particle is divided into three parts as follows, bulk diffusion (mass transfer by flow of water), film diffusion (external mass transfer) and surface or pore diffusion (internal mass transfer). Since the water intake undergoes from the river, a research was conducted about impact of ozonation and GAC filtration technology on pesticides (atrazine) degradation. The aim of E. Orlandini et., al [16] was to relate oxidation of atrazine and formation of secondary compounds to the ozone applied dose and to designate GAC adsorption capacity for these substances. The ozonation was expected to improve removing of pesticides with GAC filtration and also oxidation of background organic matter (BOM) attended in filter influent.

The concentration of atrazine in Rhine River pre-treated water was 3 $\mu g \cdot L^{-1}$. The study showed that ozonation results in partial oxidation of atrazine was about 25 %, 45 % and 65 % with applied ozone doses 0.5 $mg \cdot L^{-1}$, 1.0 $mg \cdot L^{-1}$ and 1.5 $mg \cdot L^{-1}$. Desethylatrazine and desisopropilatrazine amide (products of atrazine degradation) are formed with ozone doses up to 4 $mg \cdot L^{-1}$. These by-products are less absorbable but more biodegradable in comparison with atrazine. The quantity of atrazine in the top of GAC filters 0.35 m and in the entire 1.1 m was 3.5 g and 7.4 g (non-ozonated influent), whereas atrazine removal with included ozonation technology makes up to 4.8 g and 8.9 g [16].

Ozonation allowed to remove about 40 % in the top of GAC and for the whole depth was removed about 20 % more than with non-ozonated influent. As a consequence, the ozonation technology improves atrazine removal by GAC filtration due to effect of ozone inducted oxidation. Also, an oxidation of background organic matter took place. As a result, the combination of ozonation with GAC allows less frequent regeneration of carbon filters. The regeneration of GAC filters is quite expensive, so ozonation process can lead to substantial savings [16].

1.3.3 Combination of ozonation and UV

The combination of ozonation and UV-radiation technology is referred to as advanced oxidation processes due to emergence of radicals. This process is initiated by the photolysis of ozone and its photodecomposition leads to hydrogen peroxide radicals. The maximum radiation output of UV lamps for an effective ozone photolysis can be at 254 nm. The chemical reaction can be:

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \qquad (20)$$

Thus, there is three ways to produce •OH radicals and to oxidize the micropollutants for successive reactions. These are ozone, hydrogen peroxide and ultraviolet radiation (UV). The photolysis takes place if pollutant absorbs due to UV-radiation. At ambient temperature and pH between 5 - 10 direct oxidation by hydrogen peroxide is negligible, if any. [3].

This kind of system can be used for example for swimming pool water treatment. Chlorine is most widely used for maintaining swimming pool water quality. However, chlorine reacts unceasingly with dissolved organic matter and produce chlorinated organics, which can be harmful for pool users. UV-radiation technology is broadly used for chloramines removal (prevalent group of disinfection by-products), although chloro-organic disinfection by-products often increase upon post chlorination. Ozonation can be used for elimination of this problem [18].

Were conducted batch experiments with water samples from swimming pool (hot water pool in Gladsaxe municipal pool). Since, ozone and chlorine have a similar reactivity, ozonation was used after UV treatment for reduction of by-products formation (Figure 9). The system consists of filtration, UV-radiation, ozonation and chlorination. The UV system is placed on a side stream recirculation, followed by ozone dosing point and a small reaction tank (with 1-2 min and then returning to the recirculation flow). Most part of by-products concentrations decreased during repeated treatments. It was found that disinfection by-products (formed by post-ozone chlorination) was removed by photolysis. Research shows that repeated treatments with UV-radiation and ozone improve water quality as result of continuous UV and ozone combination [18].

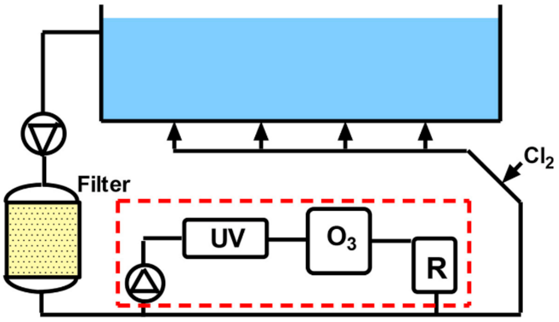


Figure 9. Schematic of the swimming pool treatment system, where R is reaction tank [18].

The Y. Bustos, M. Vaca and other authors conducted the research towards municipal wastewater treatment by continuous UV-radiation and ozone system as disinfection alternatives for wastewater treatment plant located at the Autonomous Metropolitan

University in Mexico City. The destruction of faecal and total coliforms was estimated. Different ozone dosages from 3 to 40 $mg_{O3}·L^{-1}$ and UV-radiation fluencies from 8.5 to 12 $mJ·cm^2$ (254 nm) were tested, at pH values from 5 to 9. Best results were reached with ozone concentrations about 20 $mg_{O3}·min^{-1}$, 72% and 78% were removed of faecal and total coliforms. At the same dosage was also removed 36% of organic matter (COD). The poorest inactiavation of bacteria was observed at pH 7 in both, ozonation and UV-radiation. The UV disinfection demonstrated a high destruction of bacteria, over 80%. Faecal coliforms were less influenced by the energy fluency increment, compared with total coliforms. The plant was designed to treat the wastewater at the rate of up to 1 $L·s^{-1}$ of, treatment consists of coagulation - flocculation step, followed by sedimentation and filtration step (Figure 10) [19].

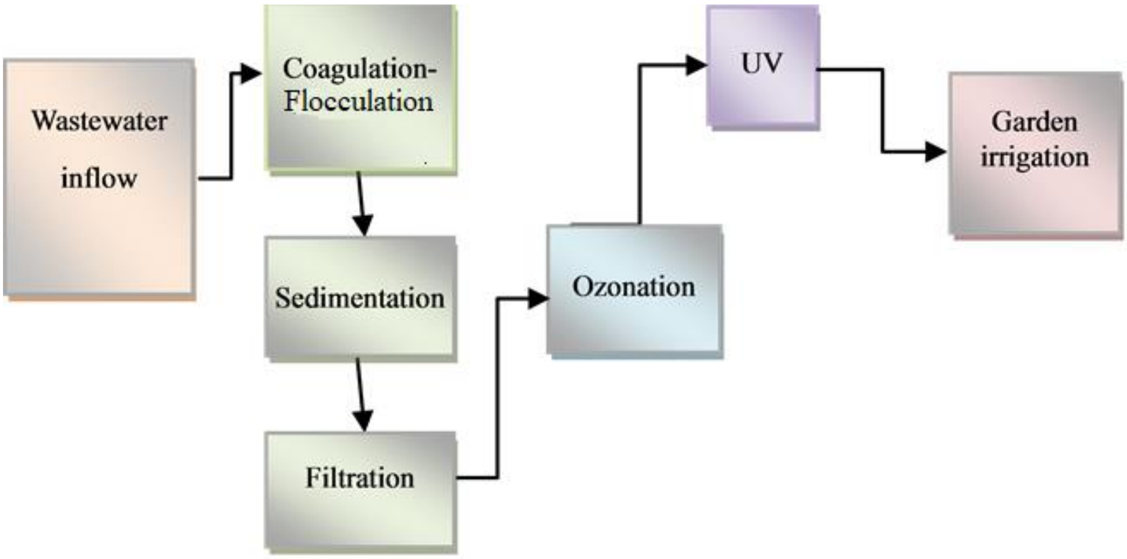


Figure 10. Schematic of wastewater treatment plant from Autonomous Metropolitan University [19].

1.3.4 Combination of ozonation with hydrogen peroxide

The anion HO_2^- promote a reaction between ozone and hydrogen peroxide. This method belongs to the advanced oxidation process. The reaction rate of peroxone system depends on the concentration of primary oxidants.

The reaction between ozone and undissociated hydrogen peroxide is insignificant (Eq. 23). Oxidation in peroxone system undergoes by the two pathways, direct oxidation by ozone and indirect oxidation by radicals (decomposition of ozone). The reaction proceeds mostly by way of indirect reactions (i.e. radicals) and two ozone molecules produces two hydroxyl radicals (Eq. 24). H_2O_2 or UV-radiation contribute to the decomposition of ozone and increases the HO● concentration. After addition of hydrogen peroxide, the production of hydroxyl radicals is 1.0 mole HO● per mole of ozone. Peroxone can oxidize saturated organics and produce such by-products as aldehydes, ketones, peroxides, biodegradable organics and bromate ions [3][20].

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \qquad (21)$$

$$HO_2^- + O_3 \rightarrow HO_2^{\circ} + O_3^{\circ-} \qquad (22)$$

$$H_2O_2 + O_3 \rightarrow H_2O + 2\,O_2 \qquad k < 10^{-2}\ M^{-1}\cdot s^{-1} \qquad (23)$$

$$H_2O_2 + 2O_3 \rightarrow 2\,OH^{\circ} + 3\,O_2 \qquad (24)$$

In 1995, the Los Angeles Department of Water and Power conducted a pilot testing during 16 months and operated 454,249 $L\cdot h^{-1}$ full scale pilot plant. Ground water contained 447 $mg\cdot L^{-1}$ trichloroethylene and 163 $mg\cdot L^{-1}$ tetrachloroethylene, used ozone doses was 0.5 to 0.6 $mg\cdot L^{-1}$ [20].

Experiments showed that for virus and bacteria inactivation, long contact time and high hydrogen peroxide concentrations are required. The peroxone is widely used for the improvement of water taste and odour, oxidation of synthetic organic compounds, degradation of herbicides, pesticides and volatile organics. The main difference between peroxone and ozone treatment of water lies on the oxidation pathways. Both act in a different way reacting with water and, thereby influence the disinfection effectiveness. Table 6 summarizes differences in drinking water treatment. In the combination of ozone with hydrogen peroxide there are two major effects, which might increase the oxidation efficiency, e.g. by conversation of ozone to hydroxyl radicals and by improvement of ozone transfer into liquid phase (ozone reaction rates increase). For the efficient operation ozone should be added first to obtain colour removal. Then hydrogen peroxide has to be added for the initiation of oxidation by radicals [3][20]. Table 4 shows differences between ozonation and peroxone technologies.

The research was conducted by R. Rosal [21], Department of Chemical Engineering of Universidad de Alcala, Spain, about oxidation of dissolved organic matter (of a sewage) by peroxone. Among the main objectives was the improvement of the wastewater reuse. The samples of wastewater were collected during one year. The removal of dissolved organic matter reinforced by adding hydrogen peroxide periodically (under pH 8.0). In less than one hour almost complete mineralization was reached. In the absence of hydrogen peroxide (only ozonation), the removal of TOC (total organic carbon) was less than 35%. The specific rate of reactions was high during the first part, and then decreased drastically after ca 5-15 minutes. The moles of total organic carbon removed per mole of ozone were in the range between 9.2-17.7 $mg_{O_3} \cdot mg_{(TOC)}^{-1}$. It was determined at maximum ozone efficiency (in the first 10 minutes).

Table 4. The comparison between peroxone and ozonation [20].

Process	Ozonation	Peroxone
Ozone decomposition rate	"Normal" decomposition producing hydroxyl radical as an intermediate product	Accelerated ozone decomposition increases the hydroxyl radical concentration above that of ozone alone
Ozone residual	5-10 minutes	Very short lived due to rapid reaction
Oxidation path	Usually direct aqueous molecular ozone oxidation	Primarily hydroxyl radical oxidation
Ability to oxidize iron and manganese	Excellent	Less effective
Ability to oxidize taste and odour compounds	Variable	Good, hydroxyl radical more reactive than ozone
Ability to oxidize chlorinated organics	Poor	Good, hydroxyl radical more reactive than ozone
Disinfection ability	Excellent	Good, but systems can only receive CT credit if they have a measurable ozone residual
Ability to detect residual for disinfection monitoring	Good	Poor, cannot calculate CT value for disinfection credit

1.3.5 Combination of ozonation with photocatalysis

Photocatalytic ozonation is categorized as more expensive technology comparing to that of conventional combinations such as ozone/GAC, Peroxone etc. The main objective of this oxidation method is disruption of recalcitrant organic compound for improving biological degradability. Generally, target compounds for photocatalytic ozonation are pharmaceuticals, detergents, surfactants, organic herbicides, dyes, pesticides, saturated aliphatic carboxylic acids, aromatic and aliphatic organohalogens and nitroaromatics. The technology of ozonation combination with photocatalysis relates to advanced oxidation process.

The presence of photocatalysts in ozonation process can significantly change oxidation process. The photocatalytic mechanisms are initiated by photoexciting surface of photocatalyst with UV and visible radiation, which provides energy and as consequence generates photoactivated electron-hole pairs (Eq. 25). At the same time, ozone molecules can be absorbed on the photocatalyst surface due to three different ways: physical adsorption, formation of feeble hydrogen bonds with hydroxyl groups, and molecular dissociative adsorption into Lewis acid (chemical species with empty orbital) sites (Eq. 26). The active oxygen radicals react with H_2O molecules to generate hydroxyl radicals (Eq. 34). Molecules of hydrogen peroxide and ozone can also absorb wavelengths shorter than 300 nm, generating hydroxyl radicals and active oxidising reagents (Eq. 27 and 28). In ozone decomposition chain reactions is produced hydrogen peroxide as intermediate (Eq. 38-40). The photogenerated electrons on the photocatalyst surface (Eq. 25) reacts with adsorbed molecules of ozone and oxygen as electron acceptors (Eq. 29 and 30). Generated hydrogen peroxide can react with photoexcited electrons on the photocatalyst surface and as a result, hydroxyl radicals are formed (Eq. 31). The photogenerated holes (Eq. 1) are supposed to react directly with pollutant molecules adsorbed on the photocatalyst surface (Eq. 32 and 33). Assumed to that, were generated in reactive intermediates in the photocatalytic ozonation medium such species as oxygen radicals (O·), superoxide and ozonide radical anions ($\cdot O_2^-$ and $\cdot O_3^-$). These oxidative species can also potentially oxidize pollutants directly or by produced (via chain reactions, Eq. 34-44) hydroxyl radicals. Besides, such water contaminants as amines, phenols and humic substances are supposed to act as instigators for ozone decomposition ozonide radical anions and further hydroxyl radicals, which increase the decay of these pollutants [22].

There are three possible ways for degradation of contaminants by hydroxyl radicals: electron transfer, radical addition and hydrogen disposal. Initial reactions with photocatalysts, ozone and irradiation [22]:

$$Photocatalyst + hv \rightarrow Photocatalyst + e^- + h^+ \tag{25}$$

$$O_3 + Photocatalyst\ (active\ surface) \rightarrow O \cdot + O_2 \tag{26}$$

$$O_3 + hv \rightarrow O \cdot + O_2 \tag{27}$$

$$H_2O_2 + hv \rightarrow 2HO \cdot \tag{28}$$

Feasible reactions between photogenerated electron (e^-) and the surface of photocatalyst:

$$O_{2(ads)} + e^- \rightarrow \cdot O_2^- \tag{29}$$

$$O_{2(ads)} + e^- \rightarrow \cdot O_3^- \tag{30}$$

$$H_2O_{2(ads)} + e^- \rightarrow HO \cdot + HO^- \tag{31}$$

Feasible reactions between photogenerated holes (h^+) and the surface of photocatalyst:

$$Pollutant_{(ads)} + h^+ \rightarrow [Pollutant]^+_{(ads)} \rightarrow CO_x, NO_x, SO_x, etc. \quad (32)$$

$$H_2O_{(ads)} + h^+ \rightarrow HO \cdot + H^+ \ (pH < 7) \ or \ OH^-_{(ads)} + h^+ \rightarrow HO \cdot (pH > 7) \quad (33)$$

Feasible subsequent chain reactions in the oxidation medium:

$$O \cdot + H_2O \rightarrow 2HO \cdot \quad (34)$$

$$\cdot O_2^- + H^+ \leftrightarrow HO_2 \cdot \quad (35)$$

$$\cdot O_3^- + H^+ \leftrightarrow HO_3 \cdot \quad (36)$$

$$HO_3 \cdot \rightarrow O_2 + HO \cdot \quad (37)$$

$$O_3 + OH^- \rightarrow \cdot O_2^- + HO_2 \cdot \quad (38)$$

$$O_3 + HO \cdot \leftrightarrow HO_4 \cdot \rightarrow O_2 + HO_2 \cdot \quad (39)$$

$$2HO_2 \cdot \rightarrow H_2O_2 + O_2 \quad (40)$$

$$H_2O_2 + \cdot O_2^- \rightarrow HO \cdot + OH^- + O_2 \quad (41)$$

$$O_3 + HO_2 \cdot \rightarrow 2O_2 + HO \cdot \quad (42)$$

$$O_3 + \cdot O_2^- \rightarrow \cdot O_3^- + O_2 \quad (43)$$

$$O_3 + H_2O_2 \rightarrow HO \cdot + HO_2 \cdot + O_2 \quad (44)$$

The electron can be trapped by ozone to produce a hydroxyl radical (Eq. 30, 36, 37), whereas three electrons were needful for the generation of one hydroxyl radical when oxygen behave as the electron acceptor (Eq. 29, 35, 39, 40).

The synergistic effects of ozonation and photocatalysis combination have been perceptible in different cases, because of intensive formation of highly oxidative and non-selective chemical agents (hydroxyl radicals) in the oxidizing medium of photocatalytic oxidation [22].

2 MATERIALS AND METHODS

2.1 Reagents and chemicals

All chemicals used (potassium dihydrogen phosphate (KH_2PO_4, Lachner, purity 99%), dipotassium hydrogen phosphate (K_2HPO_4, Lachner, purity 99%), potassium indigo trisuplhonate ($C_{16}H_7N_2O_{11}S_3K_3$), sodium sulphite (Na_2SO_3, purity 98%), iodine solution (I_2, 0.1 g-ekv, FIXANAL), sodium thiosulfate ($Na_2S_2O_3$, 99%)) were of analytical grade. All aqueous solutions were prepared with bidistilled water.

2.2 Reactor assembly

In this study, a semi-continuous reactor was used (Figure 11). The ozonation was studied by means of bubbling the ozone-air mixture through the water solution. All the experiments were carried out at ambient conditions, i.e. $T=20\text{-}22^{\circ}C$ and $P=1$ atm. The particular emphasis was placed on the reactor assembly. The materials were selected based on their ability to resist the corrosive properties of ozone, i.e. the reactor was made from the glass, all the piping and junctions were made from PTFE, or glass.

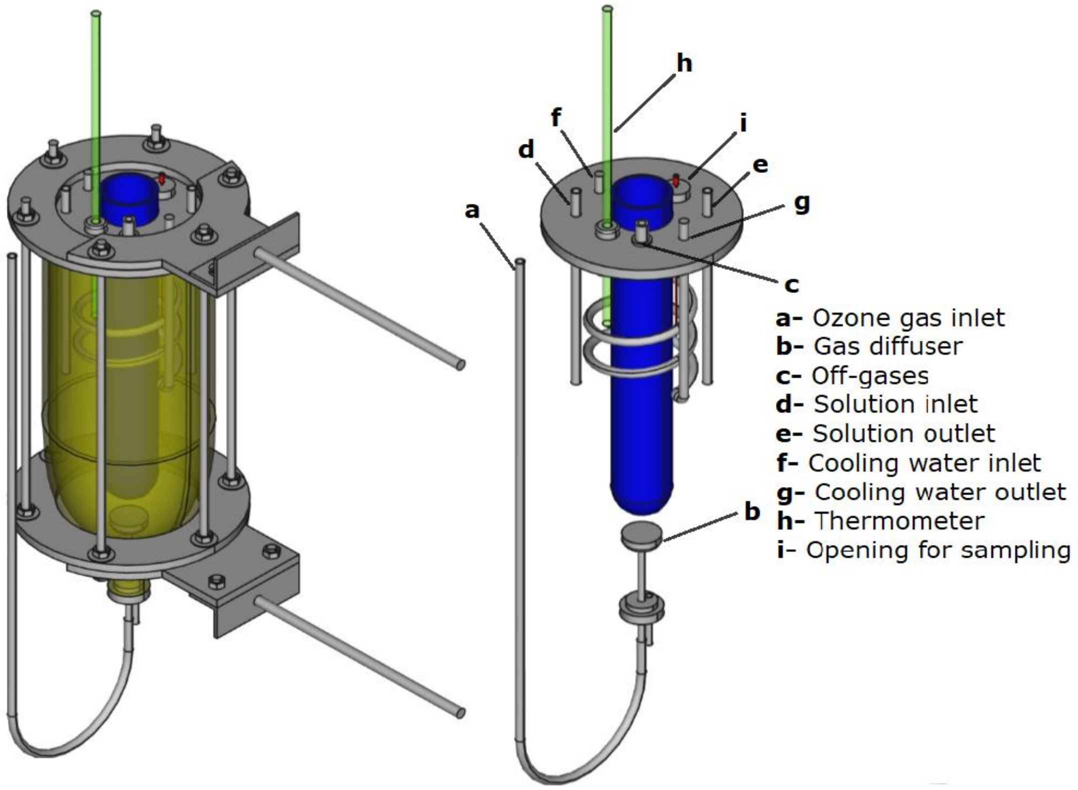
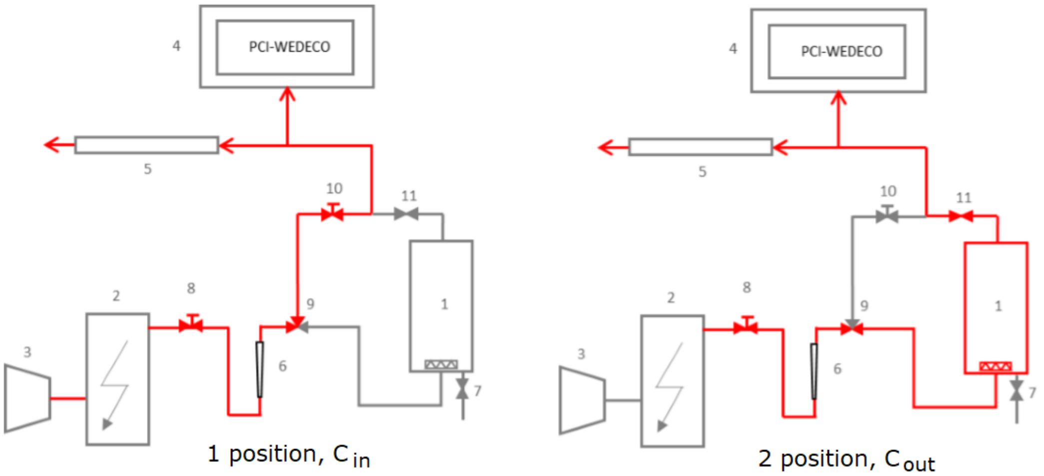


Figure 11. Semi-continuous glass reactor.

The reactor was topped with a PTFE lid, which was sealed with silicone in order to prevent any leaks of ozone. The glass diffuser and the drain tube were mounted to the bottom of the reactor. The cap was attached to the drain tube to prevent leakage. The top of the reactor was equipped with thermometer, sampling port, tubing for mixing of the solution, ozone exhaust, the port for samples withdrawal. The sampling hole was threaded and covered with a cap with a stainless-steel needle for sampling with a syringe. All openings were sealed with teflon sleeves and slilicone to prevent the leakage. The reactor assembly is tightened with a metal frame and mounted to a tripod for sealing and stability. During the experiments, the volume of investigated solution was selected approximately ¾ of the reactor height, which corresponds to the volume of 600 ml. The temperature is controlled using a mercury thermometer. The temperature is regulated using spiral-cooler integrated into the reactor assembly. In addition, the present reactor assembly was equipped quartz tube for the experiments on photo-assisted ozonation.

2.2.1 Gas-distribution system

Reactor gas -distribution system is shown in figure 12. The ozone-air mixture was generated using ozone generator (A2ZS-10GLAB) and fed through a diffuser to the reactor (2 position). Gas flowrate was adjusted by means of a rotameter (6) and, if necessary, balanced between two gas channels using valves (8 and 10).



1 position, C_{in}

2 position, C_{out}

Figure 12. Gas-distribution system. 1- semi-continuous reactor; 2- ozone generator; 3- compressor; 4- ozone analyzer in gaseous phase; 5- degradation column of ozone exhaust; 6- rotameter; 7, 11- taps; 8,10- valves; 9- three-channel valve.

The reactor operates in two positions (Figure 12), red lines show the gas flow outlines in their respective positions. The gas flow is switched to different positions with a three-channel valve (9). In the first position, gas mixture is transferred directly to the analyser (4) for determination of the concentration of produced ozone (C_{in}). In the second position, gas stream is directed to the reactor, where the water is treated with ozone. A diffuser is used to ensure better contact between the liquid and gas phases. Gas stream from the reactor enters the ozone analyzer (4). In this way, the residual ozone after water treatment (C_{out}) is measured.

2.2.2 The type of ozone generator

Due to instability of ozone it must be generated in-situ. Ozone was generated by A2ZS-10GLAB ozone generator, which produce up to 10 g/h of ozone at the power of 190W. Generator uses a fan-cooled Corona Discharge (CD) tube to generate ozone from either oxygen, or dried air.

The Corona Discharge technology is operating by passing dried air or pure oxygen through an electrical field. The electrical discharge causes the split of oxygen molecules, which bind to another oxygen molecule to form ozone (O_3). Conventionally accepted technologies can be divided into: low frequency (50 to 100 Hz), medium frequency (100 to 1000 Hz) and high frequency (>1000 Hz). In full-scale applications, ozone is normally generated by medium frequency (200-650 Hz) and high voltage systems (8,500 to 10,000 V). In lab-scale applications generators are working at high frequency and low voltage (230 to 380 V). As the process of ozone synthesis produces heat, a cooling system is required. The present ozone generator is air-cooled. The electricity is diffused over dielectric surface, making "corona discharge" (Figure 13). Oxygen molecules are passed between electrodes made from dielectrics (anode and cathode). As a result, the ozone is formed. Correct air preparation is very important in corona discharge systems. The feeding gas must be dry and free of impurities. The presence of humidity during ozone generation may cause the formation of nitric acid. Nitric acid is corrosive to internal parts of generator [23][24][25].

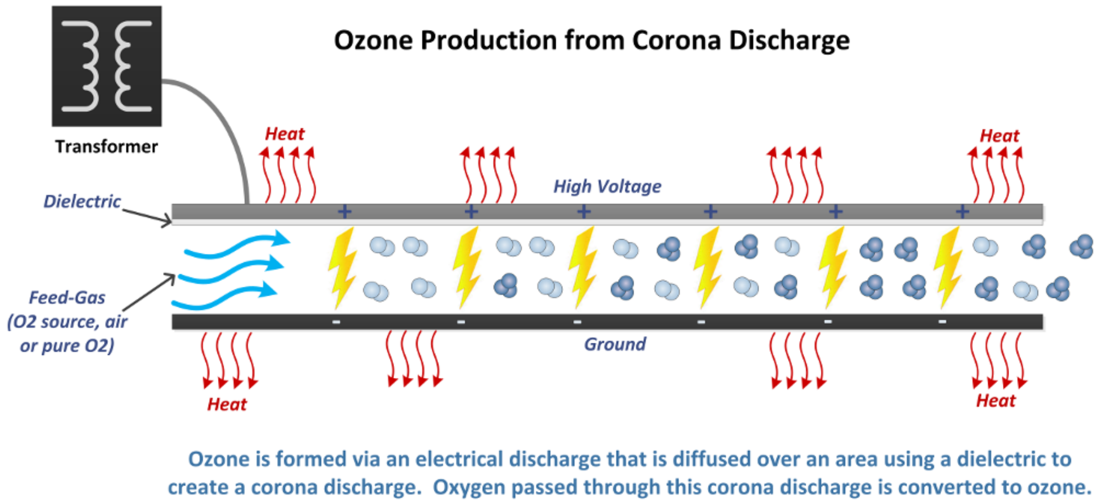


Figure 13. Ozone production from Corona Discharge generator [25].

2.3 Analytical methods

2.3.1 Ozone analyzer in gaseous phase

PCI-WEDECO gas analyzer determines photometrically the ozone concentration in the ultraviolet spectrum. The unit measures the concentration by comparing the UV absorption of the sample with the zero gas (Figure 14), where no ozone is present. Depending on the position of the solenoid valve (3), zero or sample gas is forced through the solenoid to the gas cuvette (4).

The intensity of the UV light traversing the sample chamber is attenuated according to Beer’s law. The ratio of the intensities is determined, and the results processed by the microcomputer to determine the ozone concentration and display it on the digital readout.

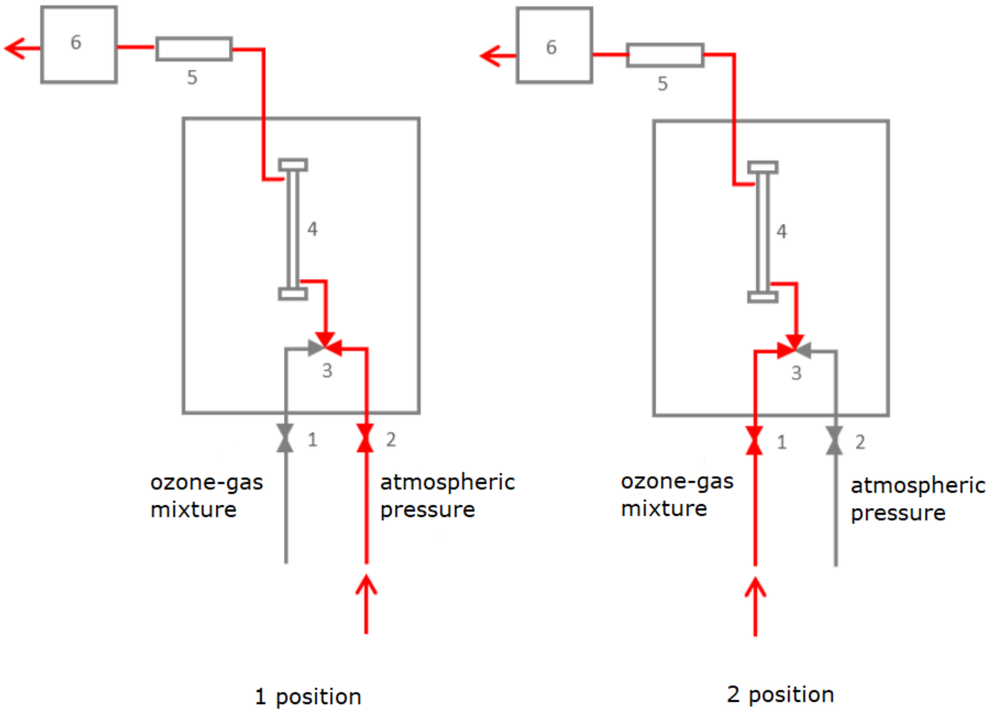


Figure 14. PCI-WEDECO gas analyzer simplified scheme. 1,2- gas inlet valves; 3- three-channel automatic valve; 4- optical measuring cell; 5- ozone decomposition column; 6- vacuum pump.

2.3.2 Determination of dissolved ozone in aqueous phase

Ozone concentration was determined using indigo colorimetric method. It is based on reaction between indigo reagent and ozone, where the decolorization of indigo trisulfonate occurs in acidic conditions. The decrease in light absorption is proportional to the concentration of ozone in aqueous phase. The indigo method has high selectivity towards ozone and replaces other existing methods based on the measurement of total oxidants. Light absorption was measured at the wavelength λ= 600 using spectrophotometer (Heλios β, Thermo Corp.). The indigo reagent solution was prepared in acidic phosphate buffer.

To a 500 mL volumetric flask ca. 250 mL of distilled water and 0.5 mL of concentrated phosphoric acid were added. Mixture was stirred and 385 mg of potassium indigo trisulfonate ($C_{16}H_7N_2O_{11}S_3K_3$) was dissolved and the resultant solution was diluted to the mark with distilled water.

To a 500 mL volumetric flask 50 mL of indigo stock solution, 5 g of sodium dihydrogen phosphate (NaH_2PO_4), and 3.5 mL of concentrated phosphoric acid were added, and the resultant mixture was diluted to the mark. Ozone concentration was calculated from Equation 45.

Calculations for spectrophotometric procedure:

$$mg\frac{O_3}{L} = \frac{100 \times \Delta A}{f \times b \times V}, \tag{45}$$

where ΔA is difference in absorbance between sample and blank; b is path length of cell (cm); V is volume of sample (mL) and f is extinction coefficient, 0.42 [26].

2.3.3 Determination of oxygen in aqueous phase

All the experiments were conducted at the similar conditions to that of ozonation. First, water was purged using nitrogen in order to remove the dissolved oxygen from aqueous phase. The temperature of water and atmosphere pressure were 23°C and 101.325 kPa, respectively.

Oxygen concentration was determined by voltammetry using dissolved oxygen meter (SevenGo Pro, Mettler Toledo). Voltammetry is an electrochemical technique, where an electrode with varying potential is used and corresponding current is measured. The determination of dissolved oxygen in water was accomplished using Clark´s electrode. The principle of measuring is based on the method of amperometry, where electric current is proportional to the concentration of analyte (reactant). The Clark´s electrode is used for dissolved O_2 measurement in small concentrations. The tip of the cathode is coated with Au, which is less susceptible to contamination than Pt upon adsorption of particles from the test solution. The microelectrode has 5 μm opening at the base and inside of it is a 10 to 40 μm long plug of silicone rubber, which is permeable to oxygen. Oxygen diffuses in the electrode through the rubber and is reduced (Eq. 46) at the gold tip on the silver wire, which is maintained at -0.75 V with respect to the Ag│AgCl reference electrode [27]:

Pt│Au cathode: $$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{46}$$

Ag│AgCl anode: $$4Ag + 4Cl^- \rightarrow 4AgCl + 4e^- \tag{47}$$

The calibration of Clark's electrode was accomplished by saturation of distilled water with oxygen by way of bubbling the air through the water. In this way, the electrode was calibrated to the maximum concentration of oxygen in water at known temperature. The electrode was zeroed in 2M Na_2SO_3, where the concentration of oxygen was close to zero.

2.3.4 Chemisorption

The process of chemisorption allowed to determine the interfacial surface area. Chemisorption of oxygen in sulphite solutions was used for the determination of mass-transfer characteristics. In this chemical system, oxygen reacts with SO_3^- forming sulphate according to the reaction eq. 48.

$$O_2 + 2SO_3^{2-} \rightarrow 2SO_4^{2-} \tag{48}$$

This reaction is considered as relatively slow, but it can be catalysed by a number of metal ions including Co or Cu. Co is more preferable as its catalytic property is more reproducible [28]. Therefore, 6 mL of 0.1M Co(II) solution was added into 600 mL SO_3^{2-} solution before the chemisorption experiments. That corresponds to 0,001 Co(II) solution in the reactor. The oxidation of sulphite is considered to be second-order by oxygen and zero-order dependent on sulphite.

Therefore, the chemisorption experiments were conducted by means of absorption of air oxygen in sulphite solution at ambient pressure and temperature so that this chemical system conforms to a fast pseudo-second-order reaction. Air was bubbled through the reactor filled with 600 mL of 20 gL^{-1} sulphite solution at the same flow rate as it was in ozonation experiments. After adjusting the flow rate of gas, it was directed to the reactor, where gas-liquid dispersion achieved the hydrodynamic steady-state conditions. The aqueous samples were withdrawn using syringe and the concentration of residual SO_3^{2-} was determined by means of iodometric titration (Eq. 49).

$$C_{SO_3^{2-}} = \frac{N_{I_2} \cdot V_{I_2} - N_{(S_2O_3^{2-})} \cdot V_{(S_2O_3^{2-})}}{V_{sample} \cdot 2} \tag{49}$$

N_{I_2} – concentration of iodine, N

V_{I_2} – volume of iodine solution, mL

$N_{(S_2O_3^{2-})}$ - concentration of thiosulphate solution, N

$V_{(S_2O_3^{2-})}$ - volume of thiosulphate solution, mL

As with absorption of gases, the molar flow rate in chemisorption depends on concentration gradient (eq. 50)

$$W_{O_2} = k'A(C^* - C) \tag{50}$$

where W_{O_2} is molar flow rate by chemisorption, mol·min^{-1};

k′ is the mass-transfer coefficient of chemisorption;

A is the contact surface between liquid and gaseous phases;

C^* - C is the concentration gradient.

For the determination of unknown contact surface, the chemisorption was conducted with and without bubbling of oxygen through the reactor, Scenario1 and Scenario 2, respectively. In the absence of bubbling, air gets contact with aqueous phase at the top of the reactor. The contact surface becomes equal to cross-sectional area of the reactor at the point of contact between two phases.

Considering zero-order kinetics the molar flow rate is constant and can be calculated from the corresponding concentration of residual sulphite as follows (Eq. 51).

$$W_{O_2} = \frac{V_L \cdot \Delta C_{SO_3^{2-}}}{\Delta t \cdot 2} \tag{51}$$

V_L is the total volume of solution in the reactor

Δt is specified time interval

$\Delta C_{SO_3^{2-}}$ is concentrations difference in some specified time interval

2 - corresponds to stoichiometric ratio of reaction eq. 48

The mass-transfer coefficient of chemisorption can be found from Scenario 2 (Eq. 52), where contact surface is known (A_{ref} = 47.9 cm^2). As the concentration of oxygen in sulphite solution is close to zero because of the rapid reaction between sulphite and O_2, the concentration gradient C^* - C is simplified to C^*, where C^* is the concentration of oxygen at equilibrium (Eq. 52).

$$k' = \frac{W_2}{A_{ref} \cdot C_{O_2}^*} \tag{52}$$

The equilibrium concentration of oxygen was found through Eq. 53 and 54. Equation 54 considers the ionic strength of sulphite solution used.

$$C_{O_2}^* = \frac{P_{O_2}}{mRT} \tag{53}$$

$$m = \frac{m_{O_2}}{1-(K_G+K^-z^+ + K^+z^-)C^{0.75}} \tag{54}$$

Where P_{O_2} – partial pressure of oxygen in air; P_{O_2}=0.21 atm

R – ideal gas constant; R = 0.082 atm·(mol·K)$^{-1}$;

m_{O_2} – constant of equilibrium in pure water (m_{O_2}= 31.06);

m – constant of equilibrium in saline solution;

C – concentration of Na_2SO_3 in solution;

Correction factors K_G, K^+, K^-, z^+, z^- are 0.08, 0.16, 0.20, 1, and 2, respectively [29][30].

The contact surface of studied bubble column can be found using the sequence of Eq. 55-58.

$$A = \frac{W_1}{k\prime \cdot \Delta C^*_{average}} \tag{55}$$

$$\Delta C^*_{average} = \frac{C^*_{in} - C^*_{out}}{\ln\left(\frac{C^*_{in}}{C^*_{out}}\right)} \tag{56}$$

, or $\Delta C_{average} = \frac{C^*_{in} + C^*_{out}}{2}$ if $\frac{C^*_{in}}{C^*_{out}} < 2$ (57)

$$C^*_{in} = \frac{C^{air}_{in}}{m} = \frac{P_{O_2}}{mRT}; \qquad C^*_{out} = \frac{C^{air}_{out}}{m}; \quad C^{air}_{out} = C^{air}_{in} - \frac{W_1}{Q_{air}} \tag{58}$$

3 RESULTS AND DISCUSSION

3.1 Absorption of ozone in water matrix

3.1.1 The scheme of mass balance of studied reactor

The behaviour of ozone in aqueous phase plays an important role in the oxidation of water pollutants. Undoubtedly, the understanding of this process deserves special attention and the knowledge obtained in laboratory study will help in making the corresponding decisions on pilot- and/or full-scale applications.

The way by which ozone is distributed between gaseous and liquid phases in reactors is determined generally by the type of reactor and its hydrodynamics properties. Bubble columns (BC) and stirred-tank reactors (STR) are the most frequently used types of reactors in laboratory ozonation experiments. STRs are generally assumed to be perfectly mixed reactors with respect to the liquid phase, whereas this applies to BC only when the ratio of height (H) to diameter (D) is small (H/D ≤ 10) [31]. In the present study, a bubble column-type reactor was used with the H/D value of 7,5 (where H=200 mm and D=36,5 mm). Therefore, the present reactor could be considered as perfectly mixed reactor. The mass balance for ozone distribution in the system is schematically described in Figure 15.

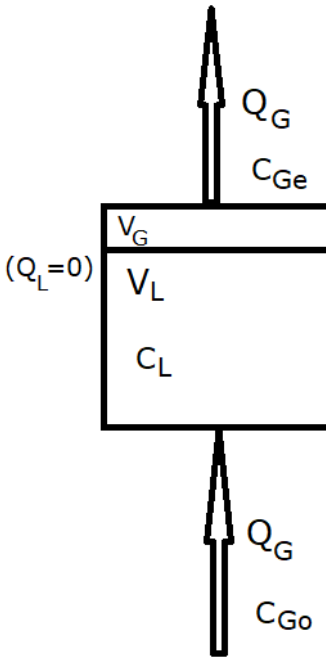


Figure 15. Schematic sketch of studied semi-continuous reactor and general operating parameters for ozone mass balances. C_{Go} is influent-gas concentration; C_{Ge} is effluent-gas concentration; V_L is liquid volume; and T, P is ambient temperature and pressure.

Ozone-containing gas mixture is directed into aqueous solution at the flow rate of Q_G with the concentration of ozone in gas phase C_{G_0}. During the ozonation, ozone containing gas mixture contacts with the liquid phase in the reactor. As a result, liquid phase is saturated with ozone according to Henry’s law, which describes the solubility of gases in the liquid phase. The ozone transfer from phase interface into either liquid, or aqueous phases is based on the equation of hydrodynamics and convective diffusion. To simplify the model of mass transfer, Lewis and Whitman (1924) proposed a two-film or two-resistance theory (the total resistance to mass transfer is the sum of the resistances in each phase). It is assumed that fixed or laminar layers are formed on both sides of the contact surface (Fig. 16). They separate the contact surface from the corresponding phase core. The driving force of mass transfer is the concentration difference of ozone between two phases. The molar flux into liquid phase N (Eq. 59) is proportional to the concentration gradient and it can be characterized with a constant of proportionality k_L, linear concentration gradient [23].

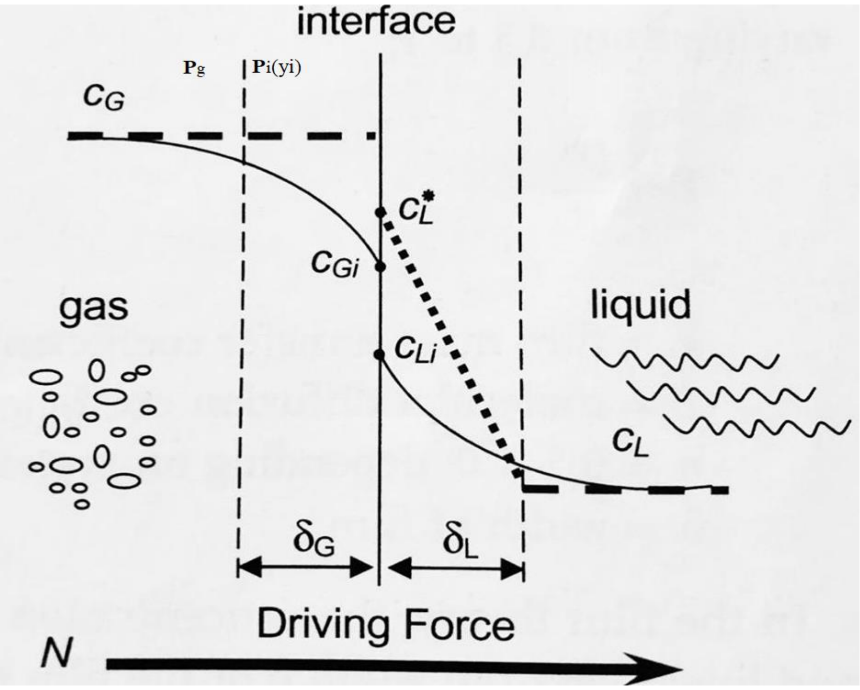


Figure 16. Schematic illustration of Two-film theory. P_g is a partial pressure of ozone in the gas; $P_i(y_i)$ is a partial pressure of ozone in the film (laminar zone of the gas phase); N is molar flux; C_G is ozone concentration in gas phase; C_{Gi} is ozone concentration in gas phase film; C_{Li} is ozone concentration in liquid phase film; C_L is concentration of ozone in the liquid; C_L^* is ozone equilibrium concentration in liquid phase; δ_G and δ_L are film widths of gas and liquid phases, respectively [23].

$$N = k_L(C_{Li} - C_L) \qquad (59)$$

k_L- liquid film mass transfer coefficient

Hereinafter, it is more preferable to operate with the mass transfer flux, which is expressed as the mass flow rate per volume unit (Eq. 60)

$$m = N \cdot \frac{A}{V_L} \cdot MW = k_L a (C_L^* - C_L) \qquad (60)$$

where volumetric interfacial area a is defined as transfer surface area per volume of liquid; MW – molecular weight of ozone; V_L is volume of liquid; and $k_L a$ is mass transfer coefficient per volume; C_L^* is ozone concentration at saturation condition.

Considering the reactivity of ozone in water, the mass balance of its absorption in water becomes the following mathematical description (Eq. 61) [3][23]:

$$\frac{dC_L}{dt} = k_L a \cdot (C_L^* - C_L) - r_L \qquad (61)$$

r_L- the rate of ozone decay in liquid phase

The decay of ozone follows first-order reaction [3]. Thus, the final mass balance becomes the corresponding form (Eq. 62).

$$\frac{dC_L}{dt} = k_L a \cdot (C_L^* - C_L) - k_D C_L \qquad (62)$$

k_D- decomposition constant of ozone in liquid phase

The differential equation (Eq. 62) should be solved in the concentration and time ranges of C_0 to C and t_0 to t, respectively. The resultant equation (63) predicts the ozone absorption path in water.

$$ln\left[1 - \frac{C_L(k_L a + k_D)}{k_L a \cdot C_L^*}\right] = -t(k_L a + k_D) \qquad (63)$$

The concentration of ozone at saturation point (C_L^*) can be found using Henry's law (Eq. 64)

$$C_L^* = \frac{C_G}{H_C} \qquad (64)$$

For the prediction of ozone absorption in water several parameters need to be found. These are as follows: specific surface area (a), mass-transfer coefficient ($k_L a$), ozone decay rate constant (k_D). Thus, the following discussion will be dedicated for the determination of these parameters and final comparison of the model to that of experimental data.

3.1.2 Specific contact area

The semi-continuous glass reactor belongs to a two-phase systems. It consist of the gas phase (containing ozone) and the liquid phase, where ozone must be transferred for a chemical reaction to occur. The ozonation depends noticeably on ozone concentration in gas phase and the ozone mass transfer rate, which depends on the ozone distribution in the fluid phase (through diffuser). To increase the ozone mass transfer rate the interfacial area must be increased by decreasing the size of the gas bubbles dispersed in the liquid. Also, the time of bubbles residence must be increased. The important parameters for reactor are total volume, and the gas-liquid interfacial contact area (a, m^{-1} or $m^2 \cdot m^{-3}$), which can be defined as Eq. 65 [23]:

$$a = \frac{A}{V_L} \tag{65}$$

Where A is contact surface of liquid and gas, and V_L is volume of liquid.

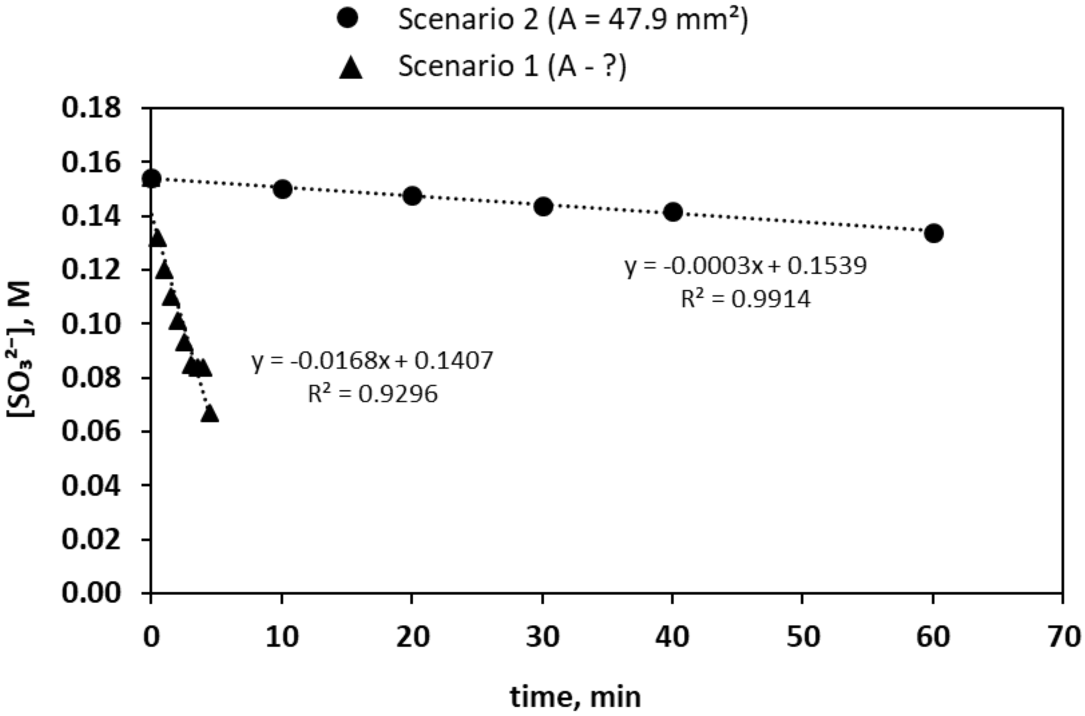


Figure 17. Concentration profiles of sulphide during chemisorption experiments. Scenario 1 and Scenario 2 correspond to the experiment with and without air bubbling, respectively.

The theory of gas absorption accompanied by chemical reaction (chemisorption) has been widely used for the determination of specific interfacial area in various gas-liquid contactors [28]. The reaction between SO_3^{2-} and O_2 is convenient to use, because sulphide oxidation has been determined to be zero-order dependent on sulphide ($n = 0$). As can be observed, straight lines were fitted through the experimental data (Fig. 17).

The list of necessary parameters obtained for the calculation of contact surface area is given in Table 5. As a result, the contact surface of studied bubble column was found to be A = 3744 cm^2, which corresponds to the specific contact area (a = 624 m^2m^{-3}). This value is considered to be relatively high due to the small size of the laboratory reactor and correspondingly high gas flow rate (Q = 2.5 $L \cdot min^{-1}$).

Table 5. General intermediate parameters of chemisorption

Parameter	**Value**	**Corresponding equation in text**
Molar flow rates W_1 and W_2, $mol \cdot min^{-1}$	$6.53 \cdot 10^{-3}$ and $9.60 \cdot 10^{-5}$	$W = k'A(C^* - C)$
Equilibrium oxygen concentration in sulphite $C^*_{O_2}$, $mol \cdot L^{-1}$	$2.38 \cdot 10^{-4}$	$C^*_{O_2} = \frac{P_{O_2}}{mRT}$
Mass-transfer coefficient (k'), $L \cdot (cm^2 \cdot min)^{-1}$	$8.42 \cdot 10^{-3}$	$k' = \frac{W_2}{A_{ref} \cdot C^*_{O_2}}$
Average concentration gradient $\Delta C^*_{average}$, $mol \cdot L^{-1}$	$2.03 \cdot 10^{-4}$	$\Delta C^*_{average} = \frac{C^*_{in} - C^*_{out}}{\ln\left(\frac{C^*_{in}}{C^*_{out}}\right)}$

3.1.3 Indirect determination of k_La based on oxygen transfer measurement

Indirect determination of the ozone mass transfer coefficient k_La is based on the oxygen transfer measurements. It can be calculated using oxygen mass-transfer coefficient $k_La_{O_2}$ and a ratio of the diffusion coefficients (Eq. 66).

$$k_L a_{O_3} = \left(\frac{D_{O_3}}{D_{O_2}}\right)^n k_L a_{O_2} = 0.867 \cdot k_L a_{O_2} \tag{66}$$

Where D_{O_2} is the oxygen diffusion coefficient and $k_L a_{O_2}$ is the oxygen mass transfer coefficient. n varies from 0.5 to 1 depending on hydrodynamic conditions in the reactor. For ozonation in bubble columns, n is generally assumed to be 1.0. Diffusion coefficients are valid for the system "gas/(clean) water" at T = 20 °C [3][13]. $k_L a_{O_3}$ can be easily found using experimentally determined diffusion coefficients for ozone $D_{O_3} = 1.76 \cdot 10^{-9}$ m^2s^{-1} and [32] oxygen $D_{O_2} = 2.03 \cdot 10^{-9}$ m^2s^{-1} [33]. Figure 18 demonstrates the saturation of water with oxygen in aqueous phase.

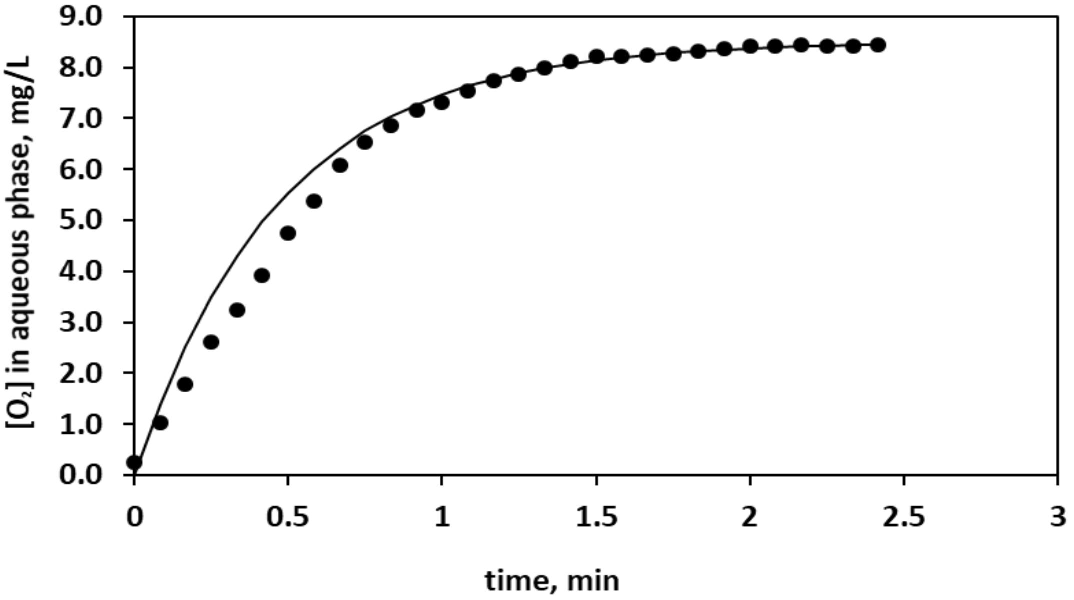


Figure 18. Concentration of dissolved oxygen during saturation.

The difference between saturation with ozone and air is that oxygen does not decompose in liquid as ozone does. Thus, the oxygen concentration in the reactor will increase according to the Equation 67.

$$\frac{dC_{O_2}}{dt} = k_L a_{O_2}(C^*_{O_2} - C_{O_2}) \tag{67}$$

$C^*_{O_2}$- maximum dissolved oxygen concentration at saturation conditions

C_{O_2}- oxygen concentration in aqueous phase

$k_L a_{O_2}$- mass-transfer coefficient

The mass transfer coefficient can be found from the experimental data using the method of linearization. That is obtained from partial solution of differential equation (67) in the concentration and time ranges of $C_{O_2(0)}$ to C_{O_2} and t_0 to t, respectively. The left part of Eq. 68 could be solved by the method of variable substitution (Eq. 69). The resultant solution has the form expressed by Eq. 70.

$$\int \frac{dC_{O_2}}{k_L a_{O_2}(C^*_{O_2} - C_{O_2})} = \int dt \tag{68}$$

$$U = k_L a_{O_2}\left(C^*_{O_2} - C_{O_2}\right) \tag{69}$$

$$-\frac{1}{k_L a_{O_2}} \cdot ln\left[k_L a_{O_2}(C^*_{O_2} - C_{O_2})\right] = t + const \tag{70}$$

Constant from Eq. 71 is to be found with respect to the conditions, where $C_{O_2} = C_{O_2(0)}$ and and t = t_0 (Eq. 72). Thus, the resultant linearized form (Eq. 72) allows to find $k_L a_{O_2}$.

$$-\frac{1}{k_L a_{O_2}} \cdot ln\left(k_L a_{O_2} \cdot C^*_{O_2}\right) = const \tag{71}$$

$$-ln\left(1 - \frac{C^*_{O_2}}{C_{O_2}}\right) = k_L a_{O_2} \cdot t \tag{72}$$

$C^*_{O_2}$ is obtained from Henry’s law. At the temperature of T = 23°C and normal atmospheric pressure the maximum dissolved oxygen concentration is $C^*_{O_2}$= 8.5 mg·L^{-1}.

The regression analysis (Fig. 19) confirmed that the experimental data fits to the linearized model with high probability (R^2 = 0.9895). The volumetric mass transfer coefficient for oxygen ($k_L a_{O_2}$) was found to be 2.107 min^{-1}. This parameter allows to calculate the mass-transfer coefficient for ozone ($k_L a_{O_3}$ = 1.83 min^{-1} or 0.0305 s^{-1}) using Eq. 66. Detected mass-transfer coefficient of ozone shows that the saturation with O_3 in studied reactor was very fast. The mass-transfer rate of ozone in bubble columns depends on energy introduced by ozone-air mixture flow rate and internal recirculation. For comparison, in simple bubble columns $k_L a_{O_3}$ values can range of 0.005 – 0.01 s^{-1} [34] or for impinging-jet reactors 0.01 - 0.1 s^{-1} [35] or 0.07 – 0.70 s^{-1} [36][37].

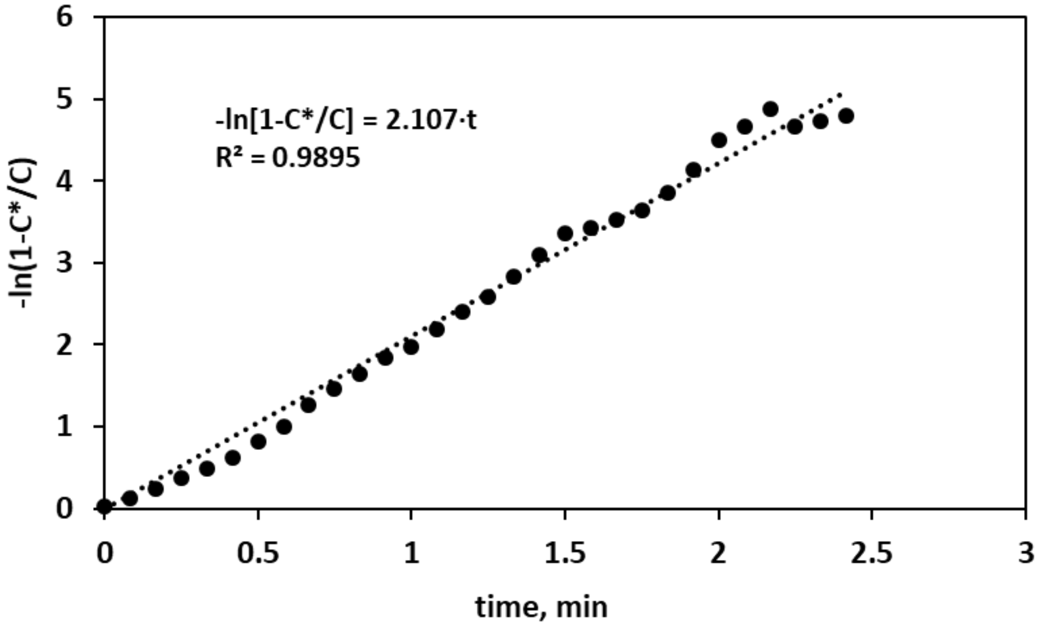


Figure 19. The determination of a liquid phase volumetric mass transfer coefficient.

3.1.4 The decay of ozone in aqueous phase

The reaction rate constant k_D for ozone decomposition can be determined by experimental data based on the ozone decay in liquid phase. The ozone concentration in the solution is reduced by its spontaneous decomposition in aqueous solution (Fig. 20). The latter occurs as a slow chain process that can be described by one of two different mechanisms proposed by Hoigné-Staehelin-Bader or Gordon-Tomiyasu-Fukutomi [4]. In both cases, many reactive intermediates are formed due to decay of ozone. This means that both direct and indirect reactions occur during ozonation.

The predominant mechanism is strongly influenced by pH of process. At acidic conditions direct reactions (molecular ozone) are predominant, whereas at alkaline conditions indirect reactions (hydroxyl radicals) dominate [23]. The determination of k_D value gives an opportunity to calculate a half-life of ozone (t), which refers directly to ozone decay. At low pH (<4) values a half-life time of ozone is longer in comparison to higher pH values [27].

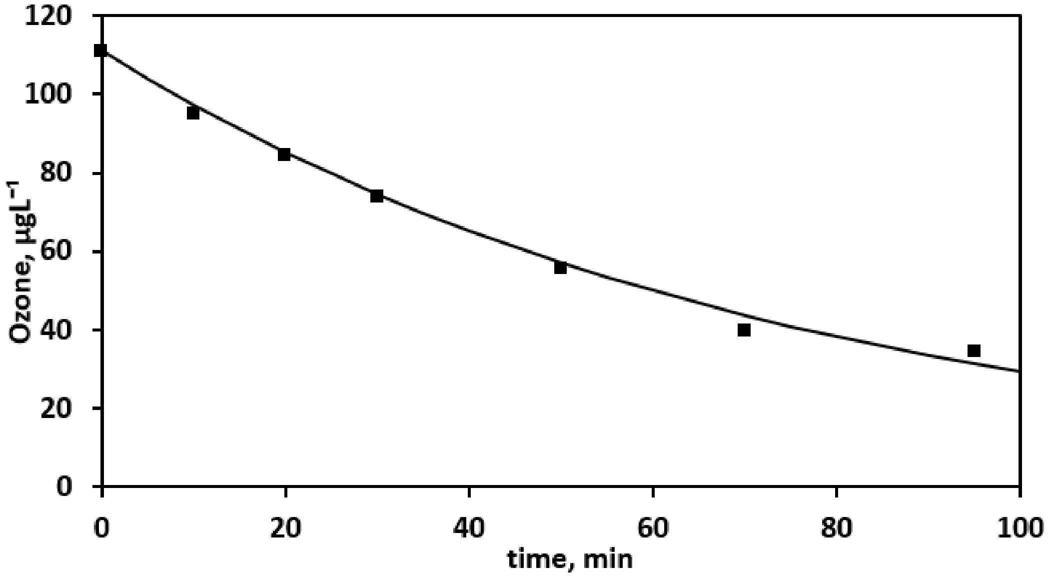


Figure 20. The decay of ozone in aqueous phase.

Ozone decomposition rate is not naturally first-order reaction (reaction rate order is between 1 and 2)[27], but the measurement of accurate order of reaction can be problematic. Ozone can react directly and indirectly (ozone molecules and hydroxyl radicals). To calculate the total reaction rate constant (k_D) the direct and indirect reaction rates as well as concentrations must be known [23]. Therefore the ozone reaction rate can be approximated to a pseudo-first-order reaction rate kinetics (Eq. 73), where k_D (at pH ~7 dominate direct reactions) is pseudo-first-order reaction rate constant. The constant k_D was calculated by the integration of differential equation (73) in the range from $C_{O_3} = C_{O_{3_0}}$ at t=t$_0$ to $C_{O_3} = C_{O_3}$ at t=t, obtaining the equation (74).

$$\frac{dC_{O_3}}{dt} = -k_D \cdot C_{O_3} \tag{73}$$

$$\ln\left(\frac{C_{O_{3_0}}}{C_{O_3}}\right) = k_D \cdot t \tag{74}$$

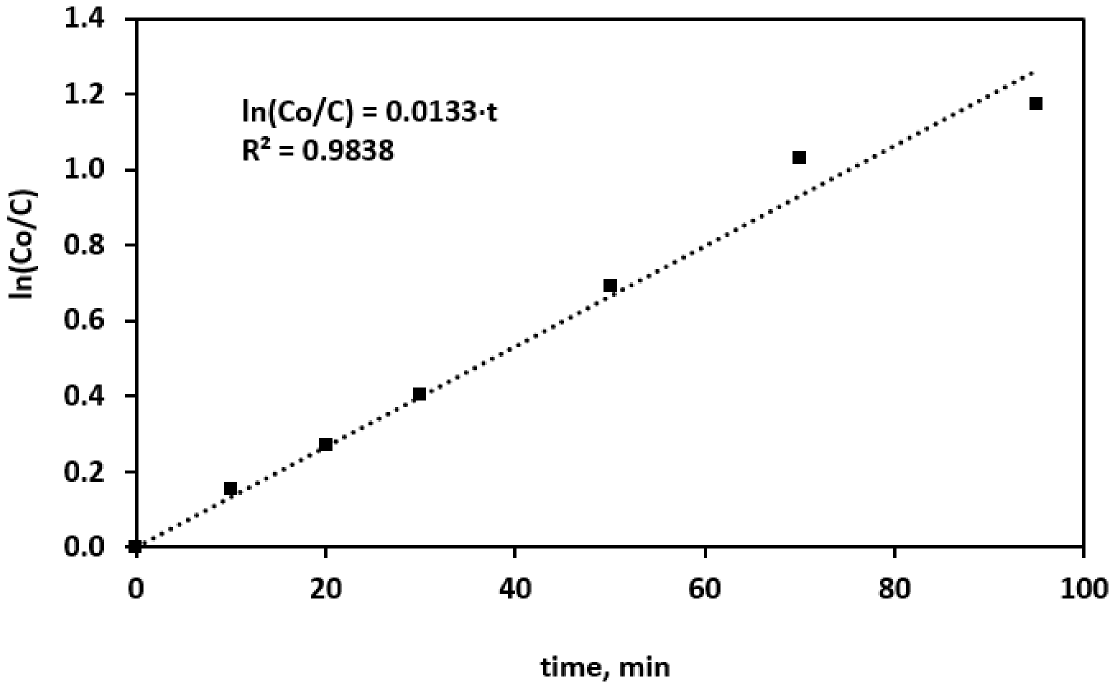


Figure 21. Determination of the reaction rate constant for ozone decomposition.

The fitting of the experimental data to Eq. 74 gives reaction rate constant k_D. The regression analysis (Fig. 21) shows that the experimental data correspond to the linear model, and the reaction rate constant for ozone decomposition (k_D) was found to be 0.0133 min^{-1}, or $2.22 \cdot 10^{-4}$ s^{-1} (not significant). k_D allows to calculate a half-life time of ozone (52 min).

3.1.5 Fitting of the experimental data into ozone absorption model

All the necessary parameters (Table 6) found in this study can be checked by fitting of the data to the ozone absorption model. Ozone concentration dependency on time (Eq. 89) was found from eq. 63. Ozone concentration path (with different ozone-gas mixture flow rates) is shown in Figure 22, which demonstrates very fast saturation of ozone in the studied reactor.

The maximum ozone concentrations were achieved within first 1-2 minutes of experiments.

Table 6. Summary table of studied parameters

Parameter, unit	**Value**
Specific surface area (a), m^2m^{-3}	624
Mass-transfer coefficient (k_La), s^{-1}	$3.05 \cdot 10^{-2}$
Ozone decay rate constant (k_D), s^{-1}	$2.22 \cdot 10^{-4}$

$$1 - \frac{C_L(k_La+k_D)}{k_La \cdot C_L^*} = e^{-t(k_La+k_D)} \quad (75)$$

$$C_L = \frac{k_La \cdot C_L^*\left[1-e^{-t(k_La+k_D)}\right]}{k_La+k_D} \quad (76)$$

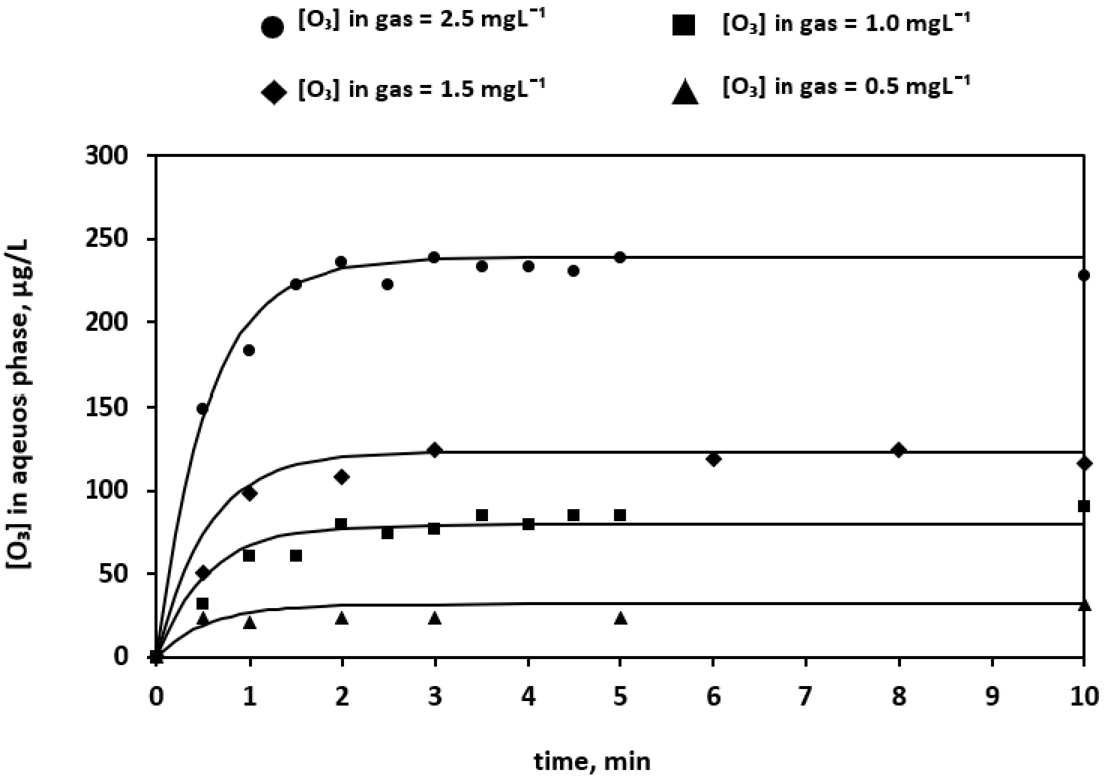


Figure 22. The ozone concentration in aqueous phase dependency of time.

SUMMARY

Ozonation is successfully used in several industrial applications of environmental technologies. The advantages of ozonation process include high effectivity in killing viruses and bacteria, short contact time, the possibility of generation onsite, which solves several issues related to shipping and handling of chemicals.

This study was aimed to the determination of ozone mass-transfer in the semi-continuous reactor its decay in aqueous phase. The understanding of this process is necessary in the subsequent modelling of oxidation processes by means of ozone. With respect to this study the following conclusions were reached:

1. The saturation of water with ozone depends on volumetric interfacial surface area (a). In this study (a) was found to be 624 m^2m^{-3}, which is relatively high for the bubbled columns. This was due to the small size of the laboratory reactor and correspondingly high gas flow rate (Q = 2.5 $L\cdot min^{-1}$).
2. Ozone mass-transfer coefficient $k_L a_{O_3}$ (1.83 min^{-1} or $3.05\cdot10^{-2}$ s^{-1}) was determined by indirect measurement through the oxygen mass-transfer. This value is somewhat higher than that found in literature (0.005 – 0.01 s^{-1}) [24]. Again, the obvious reason was the enormously high gas flow rate. As a result, the obtained $k_L a_{O_3}$ characterizes very fast saturation of ozone in the reactor. The equilibrium concentrations were achieved within 1 - 2 minutes of saturation.
3. The reaction rate constant k_D for ozone decomposition was determined by experimental data based on the ozone decay in liquid phase. The ozone decay reaction rate constant k_D was found to be 0.0133 min^{-1} (not significant) and indicates its slow decomposition. The studied parameter (k_D) together with $k_L a_{O_3}$ allowed to predict the overall course of ozone absorption kinetics in aqueous phase. Using k_D half-life time of ozone is 52 min.

RESÜMEE

Osoonimistehnoloogia rakendamine joogi- ja reovee puhastamiseks on väga oluline. Vee tarbimise kasv nii olme kui kui tööstuslikkus valdkonnas on tinginud vajaduse reovett võimalikult tõhusalt puhastada edasiseks taaskasutamiseks. Osooni oksüdeerimisvõimalusi rakendatakse edukalt nii tööstuses kui ka keskonnatehnoloogia valdkonnas. Osoonimise põhilisteks eelisteks on kõrge efektiivsus bakterite ja viiruste hävitamisel; lühike–kontaktaeg; osooni kiire lagunemise tõttu ei esine töödeldud vees kahjulike ühendeid; gaasi genereerimine toimub kohapeal, mistõttu lahendatakse mitmeid ohutusprobleeme, mis on seotud transpordiga ja käitlemisega.

Tehtud katsed võimaldasid määrata osooni massiläbikande ja selle lagunemise (pH = 7 juures ning keskkonna temperatuuri T = 20 - 22°C ja rõhu P = 1 atm juures) uuritavas reaktoris. Antud teadmised aitasid mõista osooni käitumist poolperioodilises reaktoris. Katsetes kasutatud kontaktori tüüp on sisuliselt mullkolonnik. Reaktoris võib töödelda korraga V_L = 0,6 L vett. Reaktori kõrguse ja läbimõõdu suhe on H/D = 7.5. Osooni-õhu segu sattub reaktori sisse difuusori kaudu, mille tagajärjel tekkivad väiksed mullid. See tagab kontakti kahe faasi vahel ning moodustab kahefaasilise süsteemi pidevat segunemist. Antud magistritöö uuringutes jõuti järgmistele järeldustele:

1. Osooni massiläbikande kiirus sõltub otseselt faaside pindadevahelisest kokkupuute pindalast (a). Kemosorptsiooni eksperimendist on leitud, et (a) väärtuseks on 624 m^2m^{-3}, mis vastab väga kõrgele väärtusele. Antud parameeter näitab, et reaktoris esineb suur hulk väga väikeste diameetritega mullikesi, mis suurendab ka faasidevahelise kokkupuute pindala (Q = 2.5 $L\cdot min^{-1}$).

2. Osooni massiläbikanne konstant $k_La_{O_3}$ (1.83 min^{-1} või $3.05\cdot10^{-2}$ s^{-1}) oli leitud kaudsel meetodil, mis põhineb hapniku läbikande koefitsiendi $k_La_{O_2}$ (2.107 min^{-1}) määramisel. Võrreldes teiste kirjanduses esitatud $k_La_{O_3}$ väärtustega (0.005 – 0.01 s^{-1}) [24], käesolev koefitsient on kõrge ning iseloomustab väga kiiret küllastumist. Antud reaktoris kestis veefaasi osooniga küllastumine 1 – 2 minutit.

3. Käesolevas töös määrati kindlaks pseudo-esimest järku osooni lagunemiskiiruse konstanti k_D, mille väärtus on k_D = 0.0133 min^{-1}. Antud parameeter võimaldab leida lisaks osooni poolestusaja, mille suuruseks saadi 52 min.

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LIST OF FIGURES

LIST OF TABLES