APPLICATION OF OZONATION TO INTENSIFY NITRIFICATION AND DENITRIFICATION PROCESSES

VYUŽITÍ OZONIZACE K INTENZIFIKACI NITRIFIKAČNÍCH A DENITRIFIKAČNÍCH PROCESŮ

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Abstract

Nitrogen and phosphorus belong to most important biogenic macro elements and both are required for the growth of microorganisms. Sewage waste waters and industrial waste waters from nitrogen production are important sources of organic and inorganic nitrogen compounds in water. Surface water predominantly contains nitrogen in a form of ammonium cations (NH_4^+). This knowledge could be used in waste water treatment. The paper deals with a potential application of ozonation in waste water treatment to treat waste water polluted with excessive amounts of organic compounds, primarily containing nitrogen and its subsequent co-application with advanced oxidation processes (AOPs).

Abstrakt

Dusík a fosfor patří mezi nejdůležitější makrobiogenní prvky, které jsou nezbytné pro rozvoj mikroorganismů. Významným zdrojem organických i anorganických sloučenin dusíku ve vodách jsou splaškové odpadní vody a průmyslové odpadní vody z výroby dusíkatých látek. V povrchové vodě se většina amoniaku nachází ve formě amonných kationtů, NH_4^+. Tohoto poznatku lze využít v procesu čištění odpadních vod. Článek je zaměřen na možné využití procesu ozonizace při úpravě a čištění vod znečištěných nadměrným množstvím organických látek obsahujících zejména dusík dusíkatých látek a jeho následné aplikaci v kombinaci s jinými oxidačními procesy (AOP).

Key words: ozone, ozonation, advanced oxidation processes (AOPs), nitrification, denitrification, waste water treatment plant (WWTP)

1 INTRODUCTION

People have long considered water as nature's gift which does not cost much. Having an unlimited supply of water at one's disposal results in the loss of its value. However, water reserves are not endless. Its consumption is closely connected with population growth, higher living standards and development of industry and agriculture.

Ozone is a molecule composed of three oxygen atoms (O_3). From the practical point of view, it is important that ozone is a very reactive form of oxygen. Its oxidation properties and capacity to form unstable ozonides adding ozone to the double bond of organic compounds are brought forward. It belongs to strongest oxidizers and this capacity is used in numerous industrial branches (e.g. chemical, textile industries, etc.), including waste water treatment. Nowadays a lot of publications about ozonation exist, but there are still new findings which make ozonation more convenient than classic water treatment technologies. Watching all the parameters and the efficiency of ozonation process is required for its successful application. High efficiency of oxidation, leading (based on conditions) to complete mineralization of organic compounds (even those difficult to degrade) into carbon dioxide and water, is one of the strengths of ozonation. Therefore, it is the case of wasteless technology, not separation. An interesting application of ozonation, which is also unique as for its performance, has recently been installed in a chemical plant where it successfully helps to minimize specific waste water pollution.

The mechanisms of ozone behaviour in water under the presence of organic compounds are considerably complex and may be affected by a number of parameters and modifications of technological procedures.

The majority of ozonation methods are still in the stage of testing in order to determine their top efficiency in the elimination of pollution as well as to keep the economic costs of operation as low as possible.

2 OZONATION

The first continuous use of ozone in water management is associated with the end of the 19th century when ozone was used to disinfect drinking water. This way it belongs among oldest disinfectants. Recently, ozone gas gained a lot of attention thanks to its oxidation properties which rank ozone among strongest oxidizers ever. Therefore, ozonation is a preferred method both in treating drinking water and waste water. This trend is also enhanced by stricter legal requirements in both the mentioned fields.

In waste water treatment, possible applications of ozone can be specified as follows:

- to reduce values of COD, AOX,
- to decolorize and deodorize waste water,
- to target a defined pollutant (pesticides, phenols, etc.),
- to improve biodegradability of waste water,
- to disinfect waste water.

2.1 Ozone O_3

Ozone is a natural gas forming through the breakage of a two-atom oxygen molecule $3O_2 = 2O_3$. This may occur naturally during a storm or UV radiation from the sun. Ozone is also formed by using technological procedures such as high-voltage electric discharge in air or UV tubes.

Under normal conditions, ozone is a gas which is rather unstable, with a significantly acrid odour, slightly bluish colour and it is insoluble in water. It has strong oxidation effects. Oxidation by ozone takes place according to the equation (2–1):

$$O_3 + 2\,H^+ + 2\,e^- = O_2 + H_2O \qquad E0 = 1.65\ V \qquad (2 - 1)$$

Dissolved ozone decomposes in water spontaneously. The rate of decomposition depends on the temperature and pH. Ozone is a much stronger oxidizer than chlorine and thus also has a high germicidal efficiency. Ozone degrades humic substances, dyes and phenols. Due to the action of ozone, hard biodegradable compounds break into simpler ones, bio-accessible molecules that decompose completely when exposed for a long time. Compared to chlorine, ozone does not produce any further harmful products. However, its disadvantage can be seen in worse solubility in water, which requires larger reactor volumes and more complex facilities for its dosage into the treated water.

Specifically, ozone is used in the treatment of waste water from the textile and chemical industries, in oxidation of phenol waste water. Ozonation is often applied as the final purification stage of water (biological treatment) as concurrently with oxidation of residual organic compounds, the discharge gets sanitized. [4] As an unstable gas, ozone must be generated onsite. A wide range of contactors (liquid – gas) are used to transport ozone into water under a concurrent chemical reaction. Mostly, ozone is made from oxygen-containing gases in ozone generators functioning on the base of a silent electric discharge. The gas may be air, oxygen from an oxygen tank (LOX), or oxygen produced onsite by means of oxygen generators (PSA).

Ozone may react with substances by means of two mechanisms, direct and indirect ones. The two different mechanisms lead to diverse products and each of them has own kinetics. Fig. 1 shows the paths of direct and indirect reaction of ozone with substances and their mutual interactions.

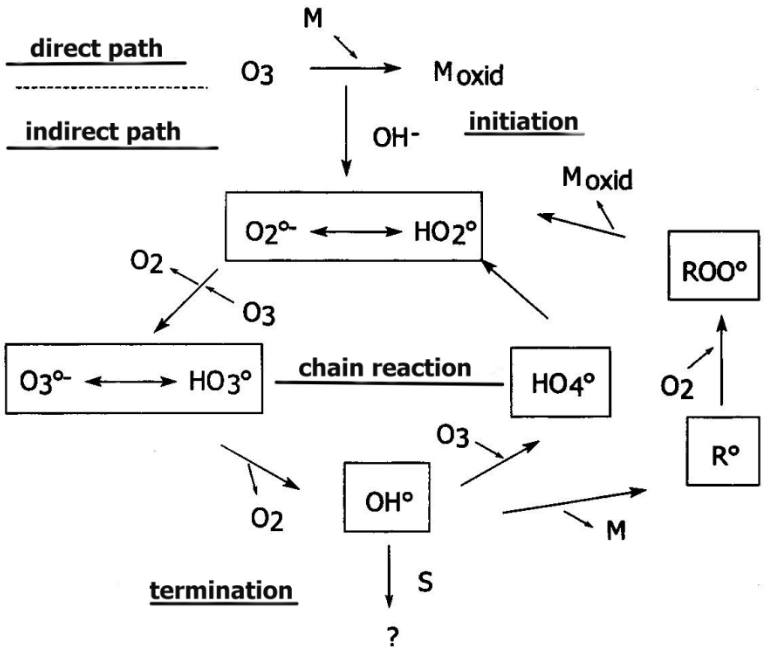

Fig. 1 Mechanism of direct and indirect ozonation, S: inhibitors of chemical reactions (Scavengers), R: radicals (reaction products), M: micro pollutant

3 MATERIAL AND METHODS

3.1 Incorporation of ozone in the ozonation process

Ozone is one of the strongest oxidizers and it contributes to break chemical compounds in waste water to make them more biodegradable. For this reason, ozonation technology has been incorporated into the waste water treatment system in a chemical plant. Ozone is generated by means of an electric discharge in an ozone generator from gaseous oxygen. Heat is liberated during the reaction which must be removed from the system by cooling. Oxygen is supplied from the Messer storage unit. Oxygen concentrations are kept at about 99.5 vol%. The maximum ozone generator output is 5 kg O_3/h. The sum of the set dosage for ozonation (the first and the second steps) must not exceed 5 kg O_3/h. The maximum ozone dosage for the individual steps is 5 kg O3/h. The own ozone dosage for the individual steps is determined based on laboratory analyses (especially in regular monitoring of COD, BOD, SS, nitrites, nitrates, ammonia, pH) by the head of the WWTP technological line.

3.2 Basic data of the waste water treatment plant

The WWTP is designed to be able to ensure, with a sufficient reserve of capacity, the treatment of waste water arising from production (Tabs 1, 2).

Input parameters:

- Average daily quantity of waste water 1560 m /d
- Maximum daily quantity of waste water 1920 m /d
- Maximum hourly supply 80 m /d
- Average daily pollution CODCr 3600 kg/d
- Average daily pollution BOD5 1740 kg/d (corresponds to 29000 EP*)

* EP – equivalent person

Tab. 1 Quantity of waste water

Parameter	Unit	OPWW*	NAWW**	mix
Q_{24}	m^3/d	360	1200	1560
Q_v	m^3/d	15	50	65
Q_{min}	m^3/d	8	25	33
Q_{max}	m^3/d	20	60	80

where:

*OPWW – organically polluted waste water

**NAWW – neutralized acidic waste water

Tab. 2 Quality of influent waste water

Parameter	OPWW*		NAWW**		mix	
	mg/l	kg/d	mg/l	kg/d	mg/l	kg/d
COD_{Cr}	7000	2520	900	1080	238	360
BOD5	4000	1140	250	300	115	170
SS	50	18	0	0	12	18
$N\text{-}NH_4$	70	25.2	117	140	106	1652

where:

*OPWW – organically polluted waste water

**NAWW – neutralized acidic waste water

Mean quantity of WW in WWTP 35 m^3/h, out of which 22 m^3/h is NAWW

Total volume of activation 5357 m^3

Total contact time **153 h**

Contact time for the 1st stage is 62 h

Contact time for the 2nd stage is 54 h

Sludge age is not calculated in WWTP, decantation is executed based on SS analysis results.

Suspended solids (SS) are at the level 3.5 – 6.0 g/l

Ozone generator output (max.) 5 kg O_3/h

3.3 Brief description of technology

Waste water (WW) in Fig. 2 flows into an equalization tank (two equalization tanks) which serves to balance the inflow peaks and to homogenize the influent waste water. From here, the homogenized waste water is pumped into the reaction tank I, upstream which ozone is dosed into the waste water. Having reacted with ozone, the water flows into the ripening tank, from where it is pumped into the activated sludge tank. There, through a biological process, the majority of organic pollution is degraded by means of activated sludge, and nitrogen is eliminated through the process of nitrification and denitrification. The mixture of water and activated sludge flows down into the secondary settling tank I where the treated water is separated from the activated sludge which returns into the activated sludge tank. Via main ozonation, the settled water flows down into the reaction tank II and later into the ripening tank. The path follows through the denitrification tank, nitrification tank and the secondary settling tank II. The returnable sludge is pumped back into the denitrification tank by means of one of the returnable sludge pumps l. The purified waste water is discharged into an effluent or the Central Waste Water Plant in Ostrava for final treatment. The surplus sludge is stabilized in the sludge tank, from where it is pumped with a screw pump for dewatering in a centrifuge. The preparation of a flocculant in a flocculation station makes part of the sludge management.

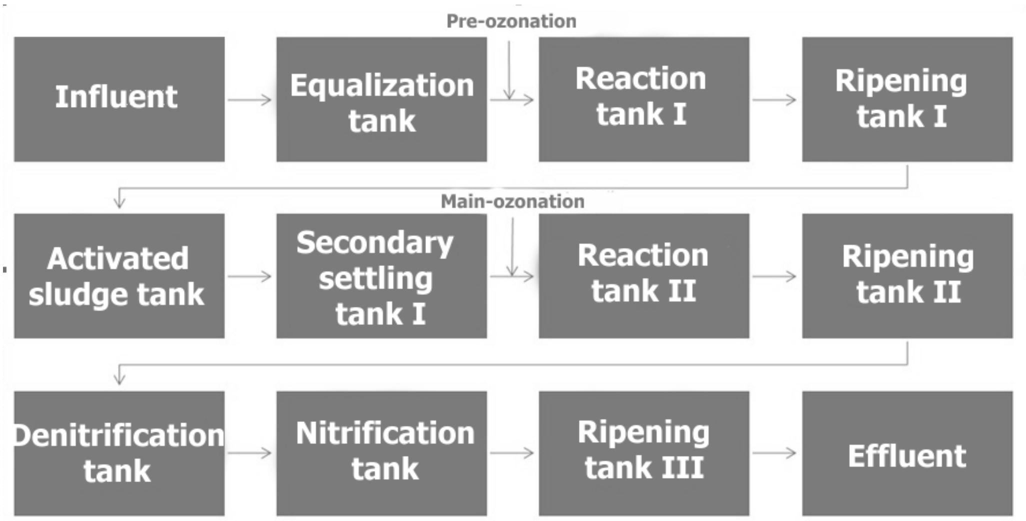

Fig. 2 Scheme of ozonation process

4 RESEARCH METHODOLOGY

The chemical plant produces various organic and nitrogenous chemicals (aniline, cyclohexylamine, dicyclohexylamine, diethyl oxalate, nitrobenzene, etc.) and the waste water arising from production thus requires treatment. There were diverse pilot tests performed on WWTP models (anaerobic/aerobic), and it was discovered that nitrification and denitrification do not occur without prior breakage of chemical substances. Therefore, ozonation has been incorporated into the WWTP concept.

During test operation, it is crucial to identify an optimum ozone dosage both for the primary and the secondary treatment stages in order to comply with the limits stipulated by Government Regulation 23/2001 Coll., amending Government Regulation 61/2003 Coll., on Emission standards of pollution indicators for surface and waste water. At the same time, economic requirements for facility operation must be met.

Experiments focused on monitoring the ozonation process under laboratory conditions where the major work objective is to identify a suitable and optimal dosage of ozone in the process of biological waste water treatment in the WWTP. Two experiments were carried out; one of them tested the waste water treatment with added O_3 and the other tested the treatment without added O_3. The ozone dosage was executed directly in a biological waste water treatment plant (BWWTP) by means of an ozone generator. The dosage is determined by a BWWTP technical worker. Thanks to this, the effect of treatment efficiency of the ozone dosage was assessed. Measurements were carried out by means of batch tests where the effect of the ozone dosage manifested itself faster than in larger volumes in WWTPs. Monitoring was executed in graduated vessels of 3 l, into which 2 l of activated sludge and 600 ml of waste water were dosed. According to the relevant order, ozone was batched in the volume from 0 g/m3 to 50 g/m^3. Ozone was batched directly into the waste water in the WWTP by means of ozone generators. The ozone dosage altered in the course of research in order to identify the optimum dosage, i.e. the ideal proportion between the treatment efficiency and the total costs of ozoniser operation.

The own research is grounded on the observation of ammoniated nitrogen using a spectrophotometric method during three days. On the first day, measurements took place every two hours; next, other measurements took place after 24 and 48 hours. The identified values are plotted in an ammonia kinetic curve (Fig. 3).

4.1 Calculation of sludge load

The sludge load is calculated according to the formula:

$$B_x = \frac{V_1 \cdot COD}{V_2 \cdot SS}$$

where:

V_1 is the quantity of added water and V_2 is the vessel volume, or the sludge dosage. B_x (COD) = 0.08 kg/kg.d, quantity of suspended solids, SS = 4.67 g/l and chemical oxygen demand equals 1.293 g/l. The quantity of the added waste water V_1 was calculated from the equation:

$$V_1 = \frac{0.08 \cdot 4.67 \cdot 2}{1.293} = 0.577\ l/d$$

4.2 Analysis methodology – ammoniated nitrogen

Ammoniated nitrogen occurs in all types of water. Its determination belongs among most common water tests. For its direct determination, spectrophotometric methods are the most frequent methods, from which the conventional photometric method using Nessler's reagent is the oldest and most widespread and which was also applied in the measurements herein.

4.3 Spectrophotometric determination of ammonia using Nessler's reagent

Two drops of Seignette salt was added to 50 ml of the sample or a diluted sample and stirred. Next, 1 ml of the Nessler's reagent was added and the mixture stirred. After 10 minutes, absorbance at 425 nm wavelength was measured. The weight concentration of ammoniated nitrogen in the sample was determined in the sample from the calibration curve allowing for the sample dilution.

5 RESULTS

The laboratory measurements identified that the current suitable ozone dosage is 30 g/m3. The dosage may range from 25 to 50 g/m3, but the expected optimal dosage shall be between 25 and 20 g/m3. The ozone dosage depends on the BWWTP technology and mainly on the quantity and character of waste water influent into the WWTP.

Tabs 3, 4, 5 below show the measured values during batch tests:

Tab. 3 Input waste water parameters

Input water parameters	Value	Unit
sampling time	8:15	h
weather	sunny	
COD	519	mg/l
BOD_5	103.8	mg/l
SS sludge:	9.07	g/l
WW ($N\text{-}NH_4$)	67	mg/l
WW withO_3 ($N\text{-}NH_4$)	49	mg/l
Sludge ($N\text{-}NH_4$)	16	mg/l
Ozone dosage	**30**	**g/m^3**

Tab. 3 gives the basic input waste water parameters that must be observed during each determination of ammoniated nitrogen.

Tab. 4 Values of pH and temperature waste waters with and without ozone

Phase	Sludge pH	O_3 + sludge pH	Sludge temperature	O_3 + sludge temperature
Initial	7.78	7.87	22.6	22.9
Final	6.8	7.2	20.5	20.7

It is clear from Tab. 4 that the differences in pH and temperature of waste water with/without ozone are negligible and thus are only of a reference value.

Tab. 5 Ammoniated nitrogen concentration drop in waste water

$N\text{-}NH_4$	Unit	t = 0 h	t = 2 h	t = 4 h	t = 6 h	t = 8 h	t = 24	t = 48 h
O_3 + sludge	mg/l	17.1	2.4	2.6	2.84	2.7	2.36	2.3
sludge	mg/l	17	11.9	2.5	2.96	2.84	2.2	2.2

Tab. 5 demonstrates a drop in concentration of ammoniated nitrogen. In ozonated waste water, the ozone efficiency manifested already after 2 h when the concentration of ammoniated nitrogen decreased to 2.4 mg/l.

Next, the concentration values of ammoniated nitrogen dropped in 4, 6 and 8 hours. To double-check, measurements were also executed after 24 and 48 hours which confirmed the concentration drop in ammoniated nitrogen. The ozonation efficiency was thus confirmed. In waste water treatment without the ozonation step at time of 2 h, the concentration of ammoniated nitrogen decreased to 11.9 mg/l. Fig. 3 shows the graphic representation of the ammoniated nitrogen concentration drop.

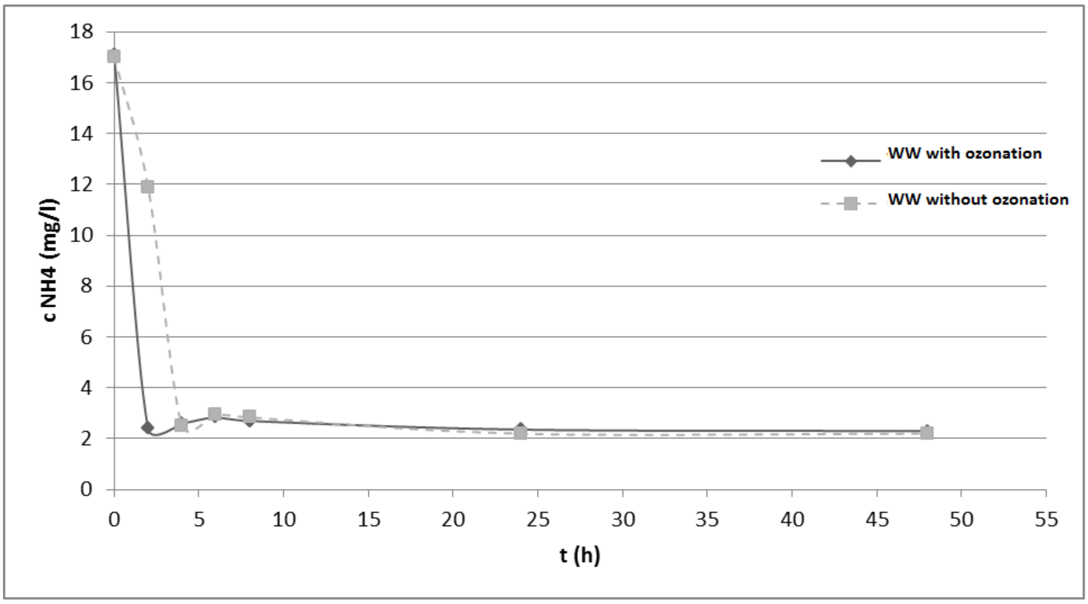

Fig. 3 Graphic representation of ammoniated nitrogen concentration drop in waste water

6 DISCUSSION

Fig. 3 shows the ammoniated concentration drop at the time of 0 to 48 h, both in waste water with and without ozonation. It implies that when treating waste water with ozonation, the effect is apparent already during main ozonation after 2 hours. Measurements are most important during the first day when most prominent ammoniated nitrogen concentration drops occur too. To double-check, measurements are repeated after 24 and 48 hours. If there is no drop in the concentration of ammoniated nitrogen, this is mainly due to a technical failure in the chemical plant or excess quantity of waste water or due to activated sludge. In future, there is a great potential in the qualitative determination of original bacterial consortium of the activated sludge.

Based on a one-year operation in the chemical plant, it may be stated that ozonation has been an appropriately selected type of oxidation dealing with the issue of waste water treatment.

7 CONCLUSION

The work describes potential incorporation of ozonation into an industrial waste water treatment process focusing on organic compounds, especially hard degradable compounds containing nitrogen. Thanks to its strong oxidation and disinfectant properties, ozone has a great potential not only in waste water treatment, but also in other water technology branches. Joint application of ozonation may help in the processes of nitrification and subsequent denitrification as described herein. Treatment time could be reduced by half with the use of ozonation technology.

In ozonation control, the economics of the operation is an important aspect as it is crucial to empirically determine and test an optimal ozone dosage, which shall permit to achieve required results at reasonable costs. The effluent treated waste water complies with all emission limits set by an integrated permit for waste water discharge.

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RESUMÉ

Cílem této práce bylo popsat možné způsoby zapojení ozonizace do procesu čištění průmyslových odpadních vod se zaměřením na organické látky, zejména na těžce odbouratelné látky obsahujících dusík. Ozon má díky svým silným oxidačním a dezinfekčním vlastnostem velký potenciál nejen pro použití při čištění odpadních vod, ale také i v dalších odvětvích technologie vody.

Důležitým hlediskem prořízení chodu ozonizace je ekonomika provozu, kdy je třeba empiricky stanovit a odzkoušet optimální dávku ozonu, což umožní dosáhnout potřebných výsledků za rozumnou cenu. Vyčištěné odpadní vody, které se vypouští do recipientu, splňují všechny emisní limity, stanovené integrovaným povolením pro vypouštění odpadních vod.