Ozonation as a method for industrial wastewaters purification

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Abstract. *The article briefly provides information on the chemical properties of ozone and the use of ozone technologies to remove organic (aromatic compounds, oil products, dyes) and inorganic (cyanide ions, heavy metal ions) pollutants from wastewater. The prospects for the use of ozone in various combinations with other activators of the purification processes are noted.*

Keywords: *ozone, waste water, treatment*

Introduction

Ozonation is a widely used method of deep purification of water from a large number of organic and inorganic biologically difficultly oxidized compounds. Ozone can also be used to decolorize effluents, remove suspended solids and colloids, oxidize complex organo-mineral complexes, toxic ions, organic micro-contaminants, and as a disinfectant.

Among the areas of ozone use in wastewater treatment, the main ones are the local treatment of individual wastewaters from toxic substances; deep post-treatment after biological structures (reduction of odors, color COD, BOD); post-treatment after physical and chemical treatment (coagulation flotation); intensification of biological treatment; disinfection.

Ozone is one of the most powerful oxidizing agents. Its redox potentials in acidic and alkaline environments are

$O_3 + 2H_2O + 2e = O_2 + 2OH^-$ $\quad E_o = +1{,}246$ V

For comparison, the redox potentials (*Eo*) of commonly used oxidants are: +2.075 V for persulfate; +1.70 V for iodic acid and permanganate; +1.76 V for hydrogen peroxide in an acidic environment; +1.63 V for hypochlorite; +1.359 V - for chlorine. Fluorine +2.87 V has a higher potential [1].

Ozone is also a powerful disinfectant. It destroys bacteria (*colibacteria*, *staphylococcus*, *salmonella*) and bacterial spores (*brevibacteiumspores*); destroys viruses (HBsAg, HAAg, PVI, HIV, influenza virus, hepatitis A virus); kills fungal parasites (*aspergillusversicolor*, *penicillium*, *aspergillusniger, fusariumoxysporumf.sp.melonogea, fusariumoxysporumf.sp. lycopersici, candida bacteria*); destroys unicellular parasites [2].

In the last 20 years, the fields of application of ozone have expanded greatly. The development of ozone technologies is facilitated by the unlimited raw material resource (air, oxygen) as well as the ecological purity of this reagent, since the final product of ozone decomposition is oxygen, and the ozonation products are not carcinogenic substances and do not pollute the environment, as is the case with oxidation, for example, with chlorine. During ozonation of aromatic pollutants, C_1-C_2- carboxylic acids are formed as products, which are actively utilized by microorganisms, as they enter the cycles of their metabolism.

The disadvantages of the ozonation process include, mainly, the high cost of ozone, the need to use corrosion-resistant materials for equipment, the toxicity of ozone (MPC in the air is 0.0001 mg/l) [3].

Being a strong oxidizing agent, ozone actively interacts with almost all components of wastewater, however, the rate and mechanism of the reaction depend on the nature of the reagent and the conditions of the reaction. The oxidizing properties of ozone in water can be manifested in direct oxidation reactions, and oxidation by radicals formed during the decomposition of ozone.

The diagram shows the mechanism of ozone decomposition in water [4]:

$H_2O \leftrightarrow H^{+} + OH^{-}$

$O_3 + H_2O \longrightarrow 2OH^{\cdot\bullet} + O_2$ $\quad k_2 = 1.1\times10^{-4}$(l/mol.s)

$O_3 + OH^{-} \longrightarrow O_2^{-\cdot} + HO_2{}^{\cdot\,-\bullet}$ $\quad k_3 = 70$ (l/mol.s)

$O_3 + OH^{\cdot\,\bullet} \longrightarrow O_2 + HO_2{}^{\cdot\,-\bullet} \rightarrow O_2^{-\bullet} + H^{+}$

$O_3 + HO_2{}^{\cdot\,\bullet} \rightarrow 2\,O_2 + OH^{\cdot\bullet}$ $\quad k_5 = 1.6\times10^{9}$ (l/mol.s)

$2\,HO_2{}^{\cdot} \longrightarrow O_2 + H_2O_2$

The rate of decomposition of ozone in water depends on the pH of the medium. The rate constant of ozone decomposition increases by two orders of magnitude from $2.3\times10^{4}s^{-}$ to $1.6\times10^{6}s^{-}$ when the pH of the medium changes from 1 to 8.[3,6,7] With an increase in pH, the concentration of reactive radicals ($OH^{\bullet}$, $HO_2^{\bullet}$, $O_2^{-\bullet}$) increases, the rate of oxidative destruction of organic pollutants increases significantly. However, it should be borne in mind that the products of reactions involving molecular ozone and radicals can differ significantly. This makes it necessary to discriminate between radical and molecular reactions, as well as to determine the conditions corresponding to a particular mechanism.

Temperature and ozone consumption are also important parameters that should be considered when optimizing the water treatment process. Taking into account that the solubility of ozone in water decreases with increasing temperature, it is advisable to carry out ozonation at a low temperature (20-50°C) [4].

Removal of aromatic compounds

Ozone effectively oxidizes phenols and aromatic hydrocarbons. Table 1 shows data indicating the dynamics of the removal of phenol and cresols from alkaline aqueous solutions depending on the ozone consumption.

Table 1. The content of phenol and o-, m-cresol, depending on the consumption of ozone. Initial concentration of phenols 100 mg/l, (pH=12) [5].

Phenol		*o*-Cresol		*m*-Cresol	
Ozone consumption, mg/l	Phenol content, mg/l	Ozone consumption, mg/l	Content of o-Cresol, mg/l	Ozone consumption, mg/l	Content of m-Cresol, mg/l
0	96	0	99	0	99
54	47	49	46	57	41
110	12	100	11	110	2,7
180	0,4	150	1,7	150	0,4
220	0,2	200	0,0	200	
260	0,1	240	0,1	260	

Ozonation of phenols in an alkaline medium leads to their deep and rapid oxidation, which is associated with the predominance of radical processes under these conditions. $OH^{\bullet}$ radicals do not react selectively with aromatic compounds, causing a variety of reactions - hydroxylation, decarboxylation, depolymerization, etc.

The rate constants of reactions of organic compounds with the participation of $OH^{\bullet}$ radicals are in the range of 10^6 - 10^9 l/mol×s, which is much higher than the corresponding rate constants of reactions for molecular ozone [6]. For comparison, Table 2 shows the rate constants of reactions in an acidic medium of molecular ozone with compounds that are the main components of PPI wastewater [6, 7].

One of the main problems of PPI wastewater treatment is the presence of organochlorine compounds formed at the stage of pulp bleaching. Chlorine can be present both in the aromatic nucleus and in the side chain of the phenylpropane unit of lignin. The presence of chlorine, an electron-withdrawing substituent in the aromatic structure of lignin and its degradation products, increases the stability of the aromatic ring in ozone oxidation reactions.

Table 2. Rate constants of reactions of molecular ozone with phenols and intermediate products of ozonation [6, 7].

Compound	*k*, l/mol×s.	Compound	*k*, l/mol×s.
Lignosulfonate Na	3×10^5	2.3-dichlorophenol	$< 2.0\times10^3$
Phenol	3.0×10^3	2.4-dichlorophenol	$< 1.5\times10^3$
Guaiacol	$>5.1\times10^5$	2.4.5-trichlorophenol	$< 3.0\times10^3$

Veratrol	1.5×10^4	Muconic acid	1.6×10^4
Veratric alcohol	3.0×10^4	Maleic acid	1×10^3
Veratric aldehyde	4.0×10^3	Formic acid	< 3
Veratric acid	5.6×10^3	Glyoxalic acid	0.2
2-chlorophenol	1.1×10^3	Oxalic acid	$< 4\times10^{-2}$
4-chlorophenol	6.0×10^2	Acetic acid	3.0×10^{-5}

Polyaromatic hydrocarbons (PAHs) are relatively poorly soluble in water. The solubility of PAHs in water increases in the presence of benzene, oil and oil products, detergents, etc. The more of these substances are in the effluent, the more toxic and carcinogenic PAHs can be dissolved in water. Under the action of ozone, PAHs are easily oxidized with the formation of quinones or dicarboxylic acids, which is preceded by the breaking of the double bond of the phenanthrene type. Side chain oxidation and more complex intramolecular oxidation are also possible [8].

Substitution, oxidation and addition reactions more readily enter less stable hydrocarbons. Therefore, acenes or hydrocarbons containing acene structures are more reactive than phenes (phenanthrene type structures) with the same number of rings, or hydrocarbons containing phenic structures [8]. The ozone reaction rate increases in the series benzene→naphthalene→anthracene [6].

Removal of oil products

Ozonation is the most effective way to remove oil products from wastewater. The use of ozone does not lead to the formation of toxic products. The process includes a direct reaction of molecular ozone and reactions involving the resulting $OH^{\bullet}$ - radicals.

When ozonizing water containing oil products at a concentration of 1 mg/l, which is about 10 times higher than their odor threshold, complete deodorization of water was observed as a result of 3-5 minutes treatment with a dose of ozone of 3 mg/l [9]. In the case of increased concentrations of oil products in water, it is necessary to increase the dose of ozone, which is not always economically feasible, therefore, ozonation must be used in combination with other methods, for example, chemical clarification, filtration, and adsorption. This allows you to bring the efficiency of water purification up to 99%.

Removing dyes

Ozone is successfully used for the destruction of dyes. Since dyes are unsaturated compounds, they are easily oxidized by ozone. Ozonation is an effective method of wastewater treatment in the textile industry, especially in combination with biological treatment [10].

It is shown that ozonation in an alkaline medium (pH 13) with preliminary and subsequent sedimentation is the most effective for the treatment of wastewater generated during dyeing of fabric with vat, cold and direct dyes. For wastewater generated by sulfur dyeing, the greatest bleaching effect is achieved when it is settled and subsequently ozonized in an acidic environment. Studies have shown that, depending on the type of dye used, the duration of ozonation of wastewater in the textile industry should be 3–15 min at an oxidant dose of 30–60 mg/l [10].

Removal of inorganic contaminants

Ozone is also successfully used to neutralize inorganic pollutants, for example, cyanides [11]. The amount of cyanide in the wastewater of electroplating workshops varies within a wide range from 2 - 30 mg/l to 150 - 300 mg/l. Ozonation in an alkaline medium with the participation of OH radicals under conditions of ozone decomposition (pH 10-11) leads to the formation of less toxic cyanates, which are then oxidized by ozone to CO_2 and H_2O:

$CN^- + O_3 \rightarrow CNO^- + O_2$

$2CNO^- + 3O_3 + 2OH^- \rightarrow 2(CO_3)^{2-} + N_2 + 3O_2 + H_2O$.

The ozone consumption per 1 mg of cyanide ions corresponds to the stoichiometric ratio of the reaction and is practically 2.0-2.1 mg/l.

During ozonation, simple cyanides are oxidized faster, more difficult - complex metal-bound ($[Fe(CN)_6]^{4-}$, $[Ag(CN)_2]^-$). Complex cyanides exhibit different activities: copper and nickel cyanides are the easiest to oxidize, since their ions catalyze the reaction. The oxidation rates of complex cyanides of silver and cadmium are approximately the same as those of simple cyanides. Zinc cyanide interacts worse with ozone. The decomposition of very stable complexes of iron or gold under normal conditions is insignificant [12].

With the help of ozone, one can also purify water from iron ions and remove manganese ions [11, 13]. Oxidation by ozone of Fe^{2+} and Mn^{2+} ions in an alkaline medium proceeds with the formation of insoluble oxides and hydroxides Fe^{3+} and Mn^{4+}.

Conclusion

Despite the fact that the electrosynthesis of ozone was discovered more than 130 years ago, only in the last few decades has tangible technical progress been made towards the practical use of ozone. The use of the latest advances in ozone synthesis technology has dramatically improved the efficiency and reliability of ozone generators.

An obstacle to the widespread use of ozonation in various industries was the significant energy consumption for ozone synthesis. However, at present, in our country and abroad, new generation ozonizers are produced with high efficiency of ozone synthesis and low energy consumption. Improving the designs of ozonizers, the use of new dielectric materials (enamel, aluminum oxide, ceramics), a decrease in the thickness of the dielectric barrier, a decrease in the size of the discharge gap, an increase in the frequency of the supply voltage, the use of oxygen instead of air as a working gas, make it possible to obtain high concentrations of ozone with low energy consumption. This enables widespread use of ozone technologies.

In addition, the use of modern advanced oxidation process, combining ozone with hydrogen peroxide, transition metal salts, titanium oxide, UV and ultrasonic irradiation, electrochemical processes, can significantly increase the efficiency of oxidation at lower ozone consumption.

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