Application Of Advanced Oxidation Process Based on Ozone in Water Treatment

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Abstract. Wastewater treatment is an effective way to address water scarcity. Advanced oxidation processes (AOPs) are a wastewater treatment technology that is currently attracting a lot of attention, and it is a technology that uses physical or chemical pathways such as ozone, ultraviolet light, and the Fenton reaction to generate free radicals and then treats pathogens and organic pollutants by oxidation of the free radicals.Ozone is very strong oxidising agent and it has a powerful ability to break down wide range of organic and inorganic pollutants. However its usage in the wastewater treatment is still not very popular due to several drawbacks it posses, as it not possible to achieve the goal of wastewater treatment by ozone alone due to its mass transfer limitations, slow reaction rates, non specific for certain under low reaction rates pollutants select,may costs relatively higher thanother treatment processes etc. By combining ozone with H_2O_2, UV light, and catalysts, the efficiency of the wastewater treatment process will be increased because it will help make more hydroxyl radicals. This review discusses various ozone-based AOPs such as ozone/UV, ozone/hydrogen peroxide, and catalytic ozonation, focusing on their mechanisms and applications in wastewater treatment.

Keywords: Ozonation; advance oxidation process; wastewater.

1. Introduction

Increasing water scarcity is now a major problem in many regions due to the increased demand for water brought about by global population and economic growth. Effective treatment of wastewater has become a necessity for solving water resource problems.

Advanced oxidation processes (AOPs) are a set of technologies that produce hydroxyl radicals (·OH) with high oxidative potency for the purpose of disinfection and decomposition of hazardous organic substances, mainly in liquid media [1]. Advanced oxidation processes can be broadly classified into four categories: photocatalytic processes, Fenton reaction-based processes, ozone-based processes, and others, i.e., photocatalyst, Fenton's reagent, hydrogen peroxide and ozone are usually used to generate highly reactive hydroxyl radicals for wastewater treatment [2]. Ozone can be used for wastewater treatment through advanced oxidation processes as a strong oxidant to decompose a wide range of organic pollutants due to its high redox potential in water (2.07 volt, only after fluorine). In this paper, the mechanism and application of ozone-based advanced oxidation process for wastewater treatment will be introduced and summarised.

2. Ozone-based Advanced Oxidation Processes

Compounds in an aqueous solution are by two mechanisms of ozone:

Heterogeneous reactions of ozone with solute substances are generally considered direct reactions, especially when these involve ozone electrophilic, nucleophilic, or cycloaddition reactions.

(2) Instead, when ozone decomposes and solid and insoluble substances are generated or when efficient and not selective hydroxyl radicals are produced, reactions are almost ever considered quite “indirect” [3].

2.1. Principle of O3/UV Binding for the Removal of Organic Pollutants

The combination of ozone and ultraviolet (O_3/UV) light is a photochemical oxidation process carried out in the presence of visible or ultraviolet light. It is used as an efficient catalytic system to degrade difficult-to-degrade pollutants in wastewater. The process starts with photolysis of ozone and then O· reacts with water to produce hydroxyl radicals. O_3/UV has been rapidly developing due to its mild reaction conditions (ambient temperature, atmospheric pressure) and strong power.
Direct hydroxyl radicals' production process:

$$O_3 + UV \rightarrow O\cdot + O_2 \tag{1}$$

$$O\cdot + H_2O \rightarrow 2OH\cdot \tag{2}$$

$$2O\cdot + H_2 \rightarrow OH\cdot + OH\cdot \tag{3}$$

$$2OH\cdot \rightarrow H_2O_2 \tag{4}$$

Indirect hydroxyl radicals' production process:

$$O_3 + H_2O \rightarrow O_2 + H_2O_2 \tag{5}$$

$$H_2O_2 \rightarrow 2OH\cdot \tag{6}$$

2.2. Principle of O3 / H2O2 Binding for the Removal of Organic Pollutants

H_2O_2 is widely used as an oxidant for the removal of difficult-to-degrade pollutants in different industrial. The combination of O_3/H_2O_2 provides better removal of organic pollutants due to the ability of H_2O_2 to accelerate the decomposition of ozone through an electron transfer mechanism and the formation of hydroxyl radicals. The O_3/H_2O_2 process is also known as the process, which starts with the conversion of H_2O_2 to the anionic HO_2^-, and then the formation of the hydroperoxyl radicals by the reaction of O_3 and HO_2^-, which can react with ozone to promote the formation of hydroxyl radicals. HO_2^- and the ozone anion O_3^-, which can react with ozone to promote the formation.

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{7}$$

$$HO2- + O3 \rightarrow HO2\cdot + O3\cdot- \tag{8}$$

$$O3\cdot- + H+ \rightarrow HO3\cdot- \tag{9}$$

$$HO3\cdot- \rightarrow O2 + OH\cdot \tag{10}$$

The total reaction process is:

$$2O_3 + H_2O_2 \rightarrow 2OH\cdot + 3O_2 \tag{11}$$

The reaction rate of the above process depends on the initial concentration of O_3/H_2O_2. However, excess H_2O_2 reacts with hydroxyl radicals and instead reduces the concentration of hydroxyl radicals, making the removal of organic matter less efficient.

$$OH\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O \tag{12}$$

2.3. Catalytic Ozonation

Catalytic ozonation uses a catalyst to enhance the decomposition of ozone to produce hydroxyl radicals. The catalytic ozone process is divided into homogeneous and heterogeneous catalytic ozone processes, where ozone decomposition is by transition metal ions and solid catalysts, respectively, which accelerates ozone decomposition and the formation of hydroxyl radicals.

2.3.1 Homogeneous catalytic ozonation

Homogeneous catalysis usually uses metal ions as catalysts, such as divalent manganese ions and trivalent iron ions. For homogeneous catalysis, there are generally two ways to promote the degradation of organic matter: (1) the metal ions themselves can promote ozonolysis and the generation of hydroxyl radicals, thus enhancing the oxidation of organic pollutants; and (2) the metal ions and the organic molecules bind to form a complex, which can be oxidised by ozone or OH·.

Homogeneous catalysis did not significantly increase the removal rate for trace organic pollutants (TrOCs). There was no significant increase in the removal rate. Therefore, the degradation mechanism of organic matter during homogeneous catalytic ozonation is not fully understood, except for the possible influence of experimental conditions. In addition, the addition of metal ions to wastewater causes secondary pollution and is a major impediment to the diffusion of the technology. Therefore, non-homogeneous catalysis by solid catalysts has recently received more attention [4].

2.3.2 Heterogeneous catalytic ozonation

Catalysts used in ozone catalysis include solid metal catalysts, metal oxide catalysts, catalysts loaded on carriers, and other catalysts. The reaction mechanism that happens in noble non-homogeneous catalysis is because of the reactivity of the metal oxide solid catalyst due to high number of unpaired electrons in transition metal oxide which rise the electron transfer tendency which reduces the activation energy for ozone. Iron oxides and manganese oxides are the most common examples for these catalysts [2].

Catalysts used for ozone catalysis include solid metal catalysts, metal oxide catalysts, catalysts loaded on carriers and other catalysts. The mechanism of non-homogeneous catalysis using solid catalysts is mainly due to the fact that the reactive electronic structure of the metal oxides allows an increased probability of electron transfer between the catalyst and the target compound, thus reducing the activation energy of ozone. Iron oxides and manganese oxides are the most widely used among them [2].

There are three steps involved in the mechanism of O3/non-homogeneous catalysis. Based on the interaction of the catalyst with ozone and organic compounds, the catalyst is classified as an adsorbent first because the surface charge of the catalyst is due to the presence of different functional groups.ozone or polar organic compounds can be adsorbed on its surface. In this way, the organic matter can react with ozone on the surface of the catalyst. Secondly, the catalyst can promote the decomposition and formation of ozone, thus increasing the removal rate of organic matter. Thirdly, catalysts can react with adsorbed compounds, for example by forming surface complexes, which can then be reacted by ozone or hydroxyl radicals [4].

3. Influencing Factors in Ozone-based AOPs

In ozone-based advanced oxidation processes, factors affecting the reaction process include water temperature, water pressure, catalyst type and concentration, pH, and ozone gas concentration.

Henry's law determines the solubility of ozone in water. Optimal conditions of pH, temperature, pressure, relative humidity, and airflow are factors that affect ozone solubility. Other factors such as conductivity and the amount of organic matter in solution also affect the effectiveness of ozone application in liquid media [5].

4. Applications in Water Treatment

A fundamental treatment step in many areas of the water treatment industry (including drinking water supply and industrial wastewater treatment) is the disinfection and decontamination of water through the use of agents. Ozone, as a strong oxidant, can decompose a wide range of organic pollutants for wastewater treatment due to its high redox potential in water (2.07 eV, second only to fluorine). However, due to the limitations of using ozone such as mass transfer limitations, selectivity to certain pollutants, slow reaction rate, and relatively high cost, ozone-based advanced oxidation processes are more commonly noticed and applied [6]. The treatment effect can be greatly improved by using an advanced oxidation process. The oxidation process destroys pollutants by generating chemical reactions. AOP is effective in detoxifying various industrial, pharmaceutical products, pesticides and organics.

Chhaya V summarised the wastewater from different industrial sources and the treatment parameters and efficiencies of AOP processes used by them, as shown in table 1, from which it can be seen that AOP can be used to flexibly change the parameters in the treatment of a wide range of wastewaters including tannery wastewater, petrochemical wastewaters, textile dyeing and printing and other wastewaters.

Table 1. Ozone-based AOP for wastewater treatment

Wastewater	Catalyst/Process	Processing efficiency	Reaction condition
Hospital wastewater	O_3+ hydrogen peroxide	100% cytostatic compound removed	55.3 g/m^3 of O_3; Reaction for 20 min; pH 8
Pesticide wastewater	TiO_2/O_3/UV	Malathion and parathion were degraded up to 99%.	1.5 mg/L of O_3; Reaction for 30 min; pH 9
Petrochemical wastewater	O_3	Removal of 37% DOC	10 mg/L of O_3; Reaction for 4 min
Piggery wastewater	O_3	Liquid light transmission increased by 50	1.1 mg/L of O_3
Pharmaceutical wastewater	O_3/TiO2/UV-A	Removal of 100% diclofenac and 90% TOC	1.5 g/L of TiO_2; 1 mg/L of O_3; pH 7
Petrochemical wastewater	Fe^{++}-BAF	Removal of 68.37% TSS	0.08 mmol/L of Fe^{++} dose; 25 mg/L of O_3
Textile dyeing wastewater	Carbon aerogel supported cobalt oxide	Removal of 80% COD	3 g of catalyst; 2.2 mg/min of O_3 dose; T 24°C
Textile wastewater	Copper oxide with carbon aerogel as carrier	Removal of 46% COD	–
Pesticide wastewater	MgO/CNT/Graphite composite	–	–
Pesticide wastewater (Atrizine)	Iron filings	Removal of 86.6% TOC	–
Municipal wastewater	Iron Shaving (FeO)	1.36 times more effective in removing COD than O_3	–
Coking wastewater	Fe shaving	78% of TOCs and 85.2% of contaminants with molecular weights between 10 and 20 KDa were removed.	–

5. Conclusion

Ozonated water treatment technologies are receiving increasing attention, but there are a number of barriers to their further diffusion, including the generation of bromate by-products and production and operating costs. This paper describes various ozone AOP processes and principles, including O_3/UV, O_3/H_2O_2, and catalytic ozone, and their applications for treating contaminants in wastewater, and discusses the factors that influence ozone AOP processes. The essence of ozone based AOP technology is to promote the generation of more oxidising and less selective hydroxyl radicals by coupling them with substances such as UV, H_2O_2 or catalysts. It has great potential for application in wastewater treatment, effectively treating difficult-to-degrade pollutants in a variety of industrial wastewaters, such as medical and tannery wastewaters. However, further research is needed as the technology may have drawbacks such as high treatment cost, secondary pollution and lack of widespread practical industrial applications. Future research could focus on further optimising the process parameters, applying the combined advanced oxidation process and carrying out studies in practical industrial wastewater treatment, so as to improve the treatment efficiency and capacity of the technology, reduce the energy consumption and cost, and promote the practical application of the technology for treatment through further investigations and experiments.

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