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Review

Wet air oxidation for the decolorization of dye wastewater: An overview of the last two decades

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A B S T R A C T

Wet air oxidation (WAO), a liquid phase reaction between organic materials in water and oxygen, is one of the most economical and technologically viable advanced oxidation processes for wastewater treatment, particularly toxic and high organic content wastewater. WAO is the liquid phase oxidation of organics or oxidizable inorganic components at elevated temperatures (125–320 °C) and pressures (0.5–20 MPa) using gaseous oxygen (or air) as oxidant. In the past two decades, the WAO process was widely studied and applied in the treatment of dye wastewater. Compared to conventional WAO, catalytic WAO processes have higher efficiency and use moderate reaction conditions. The catalysts included homogenous and heterogeneous types. The key points that need to be solved are recycling of homogenous catalysts and better stability of heterogeneous catalysts. In the present review, the technological processes are first introduced, then some research history and hotspots of WAO research are presented, and finally, its application in the treatment of dye wastewater in the past two decades is summarized to reveal the impressive changes in modes, trends, and conditions used. The application includes model pollutant studies and wastewater tests.

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1. Introduction

Dye wastewater from the printing and dyeing industry is a major source of environmental contamination. Dyestuff, slurries, dyeing aids, acids and alkalis, and fibers and inorganic compounds are present in dye wastewater [1]. Generally, dye wastewater is characterized by a strong color, high pH, high chemical oxygen demand (COD), and low biodegradability [2]. Such wastewater is difficult to treat, especially with color removal, using conventional wastewater processes [3].

In a brief search in Scopus, many hits were obtained for the term "dye oxidation" (Fig. 1). The major peak for works on the wet air oxidation (WAO) process was in the 21st century. The present review first introduces the technology and process, and the research history and research hotspots of WAO. Its application in dye wastewater treatment is then described in detail. Major conclusions were obtained from the different procedures during the past decades, which strongly influenced the new trends and economic aspects of each time period. All these confirmed the sustainability of this process.

Recently, advanced oxidation processes (AOPs) have received attention as effective pretreatment processes for less biodegradable wastewater [4]. AOPs were first proposed by Glaze [5] in 1987. They were defined as near ambient temperature and pressure water treatment processes based on the generation of hydroxyl radicals (•OH) to initiate the oxidative

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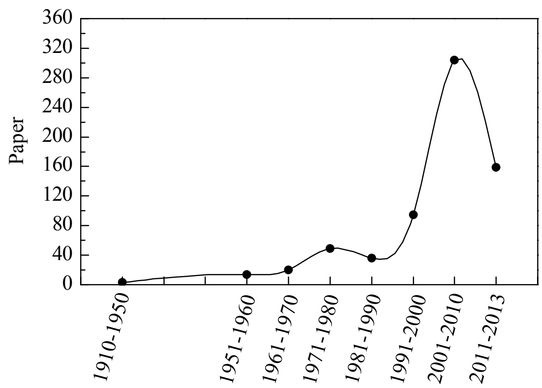

Fig. 1. Works published with the "dye oxidation" keyword (data search in Scopus).

destruction of organics [5]. •OH is a powerful, non-selective chemical oxidant, which reacts a million to a billion times faster than either ozone (O_3) or H_2O_2 (Table 1) [6].

AOPs can achieve the oxidative destruction of refractory compounds that conventional oxidation cannot. In addition, they have the potential to completely oxidize organic contaminants to CO_2, H_2O, and mineral salts. AOPs can also oxidize inorganic contaminants such as cyanides, sulfides, and nitrites [6]. Their advantages for the treatment of dye wastewater include fast reaction, complete treatment, and being pollution-free and of wide application.

WAO, which was established and developed by Zimmermann [7–10], is one of the most economical and technologically viable AOPs for wastewater treatment, particularly toxic and high organic content wastewater. The application range of each AOP is different and depends on the flow rate and organic content of the effluent [11]. Unlike other AOPs, WAO is suitable for high organic loads at high flow rates. Especially, WAO has great potential for treating effluents containing a high content of organic matter (about 10–100 g/L of COD) and/or toxic contaminants, for which a direct biological treatment is not feasible [12]. WAO is not only eco-friendly, but also economical compared to other AOPs that use harmful and expensive oxidants like O_3 and H_2O_2.

Table 1
Relative oxidation power of some oxidizing species with chlorine as the reference species [6].

Oxidation species	Oxidation power
Hydroxyl radical	2.05
Atomic oxygen	1.78
Ozone	1.52
Hydrogen peroxide	1.31
Permanganate	1.24
Chlorine	1.00

2. Technology and process

WAO is the liquid phase oxidation of organics or oxidizable inorganic components at elevated temperatures (125–320 °C) and pressures (0.5–20 MPa) using a gaseous source of oxygen (O_2 or air) as oxidant. The solubility of O_2 in aqueous solutions is greatly enhanced at elevated temperatures and pressures, which provide the strong driving force for oxidation. WAO has been demonstrated to oxidize organic compounds to CO_2 and other end products (carbon is oxidized to CO_2, nitrogen is converted to NH_3 and nitrate ions (NO_3^-), and halogen and sulfur are converted to inorganic forms). WAO is useful for the treatment of hazardous, toxic, and non-biodegradable waste streams. The process becomes self-sustaining when the feed COD is about 20000 mg/L [13].

Figure 2 shows a typical WAO treatment system. The wastewater is brought into the system using a high pressure pump. Air (or O_2) is added to the reactor using a compressor. Preheating may be necessary to raise the temperature of the wastewater. The feed temperature is adjusted to let the exothermic heat of reaction raise the mixture temperature to the

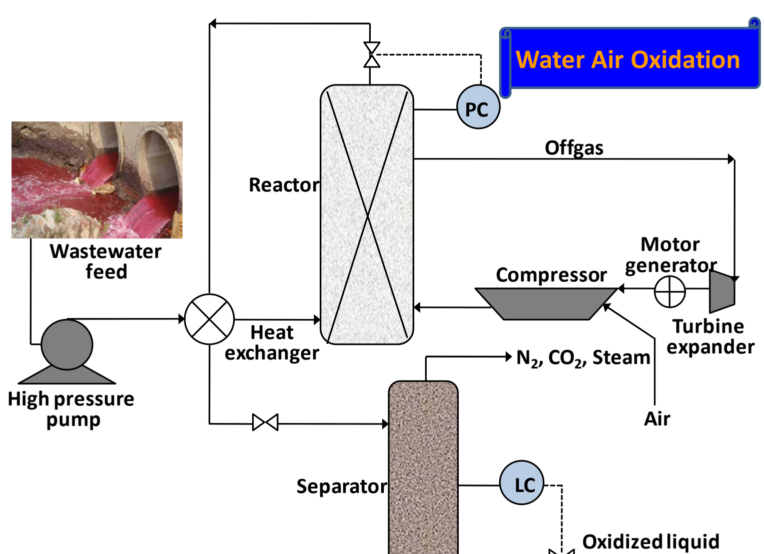

Fig. 2. Basic wet air oxidation plant flow sheet.

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