

Advanced Oxidation and Microbial Treatment of Distillery Effluents: Recent Advances and Future Perspectives

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Abstract

Distillery industries generate large volumes of high-strength wastewater, commonly known as spent wash, which is characterized by intense dark colour, high Chemical Oxygen Demand (COD), high Biological Oxygen Demand (BOD), and the presence of complex organic compounds such as melanoidins and phenolic substances. These recalcitrant compounds are resistant to conventional treatment processes and pose significant environmental challenges when discharged untreated. Various physical, chemical, and biological methods have been explored; however, individual treatment approaches often show limited efficiency in complete mineralization and toxicity reduction. This paper examines the potential of radiation-based advanced oxidation processes as an effective pretreatment method for distillery wastewater. Ionizing radiation generates highly reactive species, particularly hydroxyl radicals, which degrade complex organic molecules into simpler and more biodegradable intermediates. The improved biodegradability of irradiated effluent enhances the performance of subsequent microbial treatment processes. The paper further discusses the role of selected microorganisms and microbial consortia in mineralizing intermediate degradation products into environmentally benign end products. The integration of radiation pretreatment with biological treatment is highlighted as a promising, sustainable, and efficient strategy for distillery wastewater management. The challenges, advantages, and future research directions for large-scale application of this combined approach are also addressed.

Keywords: Distillery wastewater, Ionizing radiation, advanced oxidation process, Radiation pretreatment, Microbial degradation, integrated treatment system.

1. Introduction

There has been a growing trend toward more development of the agro-industrial sector (i.e., agriculture and Industry combined) particularly with distillery Industries (alcohol). The combined development of both agriculture and industrialization has been associated with increasing environmental issues related to the amount of highly contaminated

wastewater that is generated. This type of wastewater or effluent is referred to as spent wash; the characteristics of this wastewater make it extremely complex and difficult to treat: the high organic load, the acidity, and the dark brown/black colour resulting from the very high number of large molecular weight polymers (melanoidins) are all characteristics that

contribute to the complexity of processing it. In India, the sugar cane molasses-based alcohol distilleries generate 12–17 m³ waste water/m³ ethyl alcohol produced. This waste water is commonly known as distillery waste water (DWW), distillery spent wash (DSW). The distillery spent wash is dark brown in colour and has very high chemical oxygen demand (COD = 60–200 kg/m³) and biochemical oxygen demand (BOD = 50–75 kg/m³). The dark brown colour is imparted by the pigment called “melanoidin” which is refractory in nature to the biological treatment (Parmesh Kumar Chaudhari et al., 2007). The discharge of such highly contaminated industrial wastewater directly to surface water bodies (i.e., rivers, lakes, etc.) without any type of treatment will result in significant decreases in dissolved oxygen levels, significant disturbances to the aquatic ecosystem, and significant contamination of the groundwater supply. In addition, the phenols and metals that are present in the spent wash also result in spent wash being toxic, therefore limiting the ability of the receiving water body to self-purify, which represents a significant risk to both human health and environmental health. There has been an extended period of exploration into possible means having distillery effluents treated; thus, there still does not exist an adequate paradigm for the treatment of this type of wastewater. Treatment options that have existed for many years using both biological methodology (anaerobic digestion or the activated sludge method) will be ineffective for the treatment of distillery effluents due to the existence of recalcitrant organic material that not only is toxic to microorganisms but that also will cause microorganisms to not fully mineralize and color and thus provide a low level of mineralization through the biological treatment process. Wastewater not only has an adverse effect on the environment, but it also presents serious health hazards to people. 80 % of diseases and 50 % of child deaths worldwide are related to poor water quality (Rushikesh et al., 2024). Furthermore, treatment options that have existed for many years using traditional forms of physical-chemical methodology (coagulation or adsorption) will primarily only be transferring pollutants from one form to another and would not be physically (or chemically) removing them from the environment

(Kyere-Yeboah et al., 2023) [1]

2. Method

The alternative forms of radiolysis are comparable to those of conventional radiolysis methods. In addition, the methodology developed draws upon the mechanistic data and knowledge gained from these radiolysis and plasma studies. In addition to using plasma for the final mineralization of the effluent, our methodology also relies on ionizing radiation to serve as a pre-treatment. This pre-treatment will be used to improve the effluent for the eventual microbial digestion of the effluent to maximize both the cost-effectiveness and environmental safety of the final effluent. To resolve the inherent impediments related to conventional remediation methods associated with spent wash, we present an integrated treatment paradigm that synergizes a radiation-based advanced oxidation pre-treatment with microbial degradation processes downstream of pre-treatment. Within this sequential framework, we have intentionally utilized the total (non-selective) oxidative capability of hydroxyl radicals to degrade the complex polymer materials found within the effluent (spent wash), in order to allow for subsequent biological mineralization of the effluent's biochemical potential.

2.1. Characterization and Preparation of the Effluent

The first step within the treatment paradigm is the complete physical and chemical characterization of the raw distillery wastewater (spent wash). High-strength spent wash will undergo baseline analysis of Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Organic Carbon (TOC), and colour intensity (determined by the absorbance of specific wavelengths associated with melanoidins). Because ionizing radiation generates free radicals whose reactivity may be endangered by the presence of excessive suspended solid matter, a pre-filtration or low-speed centrifugation step will take place prior to irradiation. To ensure optimal delivery of radiation energy to dissolved recalcitrant organic compounds as opposed to inert macroscopic debris, this theoretical pre-screening of particulate matter reduces turbidity. pH is continuously monitored; however, one advantage of using ionizing radiation compared with Fenton-based AOPs is that they do not require rigid pH control (Jagdevi et al.,

2020) [2].

2.2. Radiation-Induced Advanced Oxidation Pre-treatment

The main physical-chemical intervention is the bombardment of pre-filtered wastewater with ionizing radiation (i.e., using a hypothetical high-energy electron beam accelerator or a gamma ray source). The interaction of high-energy radiation with water induces water radiolysis, resulting in a cascade of very reactive transient species. The most important of these species is the hydroxyl radical (OH•), an extremely powerful and non-selective oxidant. Also, similar to the flux mechanics associated with remote plasma generation sources, hydroxyl radicals aggressively attack the electron-rich aromatic rings of melanoidins and phenolic toxins. The fast oxidation of the reaction will begin breaking down large long-chain heavily conjugated biopolymers into smaller-size low-molecular weight components, such as aliphatic acids and aldehydes. The intent of this process is not to produce complete minerals from the biopolymers, because that would take too much energy, but to convert non-biodegradable materials to biodegradable materials, thus shifting the BOD/COD ratio in a very favorable direction. The biopolymers after the rapid breakup will enter a biological reactor with acclimated microorganisms, where the ongoing metabolism will continue to mineralize and refine the low-molecular-weight products formed from the original biopolymers into products that can be safely discharged. This means that the partially oxidized, intermediate-rich effluent must be bioprocessed within a biological reactor that contains a microbial consortium with potentially enhanced populations of selected bacteria (e.g. *Pseudomonas* or *Bacillus* spp.) that are known to survive high levels of oxidative stress and are metabolically suited to converting short-chain carboxylic acids into acceptable end products, such as carbon dioxide, water, and microbial biomass. After being bioprocessed, the effluent will have little to no residual organic load left and will passively de-mineralize. Eventually, all of the remaining components of the effluent will either settle or be removed in a final polishing step to ensure that the discharged effluent meets applicable regulatory standards before being released to the environment Shown in Figure 1.

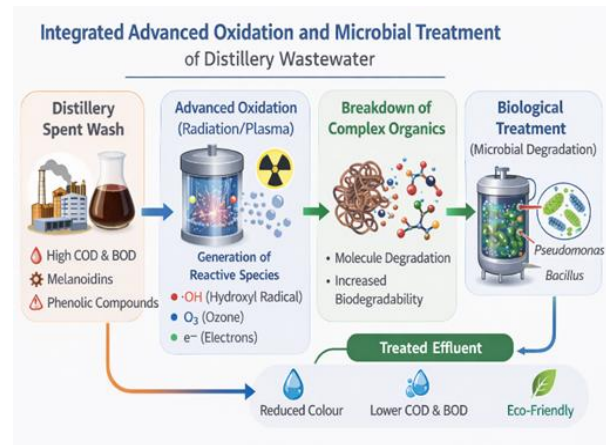


Figure 1 Conceptual Schematic of Integrated Advanced Oxidation and Microbial Treatment for Distillery Wastewater

The spent wash from the distillery containing high levels of COD, BOD, melanoidins, and phenolic compounds is subjected to advanced oxidation process technology. In the advanced oxidation process, highly reactive species are generated that degrade the complex organic matter. The degraded wastewater is then subjected to microbial degradation by *Pseudomonas* and *Bacillus* species [3].

3. Proposed Treatment Outcomes & Discussion

3.1. Proposed Treatment Outcomes

3.1.1. Improvement of Biodegradability after Radiation Pretreatment

The application of the advanced oxidation process using ionizing radiation like UV radiation to enhance the biodegradability of the wastewater through photolysis is likely to generate highly active species that will react with complex organic polymers such as melanoidins and phenolic structures. These polymers are likely to degrade into smaller molecular weight organic compounds. As intensity of UV light increase the rate of photolysis of H₂O₂ increase. Optimum value of UV 400-450 nm after that rate of degradation reduced. Value of UV intensity should be $\lambda < 450$ nm. (Jagdevi et al., 2020) Consequently, the BOD/COD ratio of the wastewater will improve. This will enhance the suitability of the wastewater for subsequent biological treatment steps.

3.1.2. Degradation of Recalcitrant Organic Pollutants

The application of the advanced oxidation process using ionizing radiation is likely to enhance the

degradation of recalcitrant organic pollutants present in the wastewater. The radiolysis process is likely to generate active species that will degrade the aromatic rings present in the recalcitrant organic pollutants.

3.1.3. Enhanced Microbial Degradation Efficiency

After the oxidative treatment of wastewater, it is expected that the wastewater will undergo efficient microbial degradation in the biological reactor. Microorganisms such as *Pseudomonas* and *Bacillus* species have the potential to degrade low molecular weight organic acids and aldehydes produced during the oxidation process. It may also degrade the organic matter in the wastewater to simple compounds such as carbon dioxide, water, and biomass [4].

3.1.4. Reduction of Color and Organic Load

Distillery wastewater contains high intensity of dark color due to the presence of melanoidins and other chromophoric compounds. Oxidizing free radicals generated during the radiolysis and plasma treatment of wastewater are expected to break the conjugated double bonds responsible for the color of the wastewater, leading to a significant reduction in color intensity and total organic carbon.

3.1.5. Efficiency of the Integrated Treatment System

The integration of advanced oxidation processes and biological processes in wastewater treatment is expected to increase efficiency. This is due to the fact that, in the oxidation process, wastewater is easily broken down. This is further broken down in the biological process (Fouad et al., 2021) [5-6]

3.2. Discussion

The increase in biodegradability after radiation pre-treatment can be explained in terms of the high reactive nature of the free radicals produced during radiolysis. These free radicals have shown high efficiency in degrading complex organic compounds, including melanoidins and phenolic compounds. This has also been shown in the degradation of recalcitrant organic pollutants, which can be broken down in the presence of reactive oxidative species. The reactive oxidative species can cleave aromatic rings and chromophoric structures in complex organic compounds. This is due to the decrease in toxicity and increase in concentration of readily available organic matter in wastewater. For instance, microorganisms

such as *Pseudomonas* and *Bacillus* spp. are known to degrade organic matter effectively. These microorganisms are able to degrade low molecular weight organic matter resulting from oxidation processes. This has been recognized as a promising approach to wastewater treatment from industrial sources. The decrease in color and organic matter is related to the degradation of chromophoric groups present in melanoidin compounds. Oxidative radicals generated in plasma-based systems are effective in degrading organic matter with color and total organic carbon content in wastewater (Moses Adondua Abah et al., 2025) Lastly, the combination of oxidation processes and biological treatment provides an integrated system that consists of fast chemical degradation and subsequent biological mineralization. Research on new oxidation processes and catalytic oxidation processes has proven that they are effective in the removal of recalcitrant pollutants from industrial wastewater

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