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Color removal of distillery wastewater by ozonation in the absence and presence of immobilized iron oxide catalyst

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Abstract

Ozone is a strong oxidant, which can oxidize both biodegradable and non-biodegradable organics. The main objective of this study was to use iron oxide as a heterogeneous catalyst to enhance the ozone oxidation process. The wastewater used in this study was distillery wastewater, which was diluted 20 times before use. The diluted distillery wastewater was fed continuously in a downflow direction in an ozonation column. The iron oxide catalyst was coated on 10.3 mm diameter alumina balls (5.5 m^2/g specific surface area) by using $Fe(NO_3)_3$ as a precursor. The prepared catalyst was in the form of ferric oxide, and its loading was 0.07%. From the experimental results of both with and without the iron oxide catalyst, an increase in hydraulic retention time resulted in an increase in the treatment efficiencies of both chemical oxygen demand (COD) and color reduction, since the residence time of ozone increased. When the ozone mass flow rate increased, both COD and color reduction increased, resulting from an increase in the hydroxyl radical available in the system. The ozonation system with the iron oxide catalyst gave the highest efficiency in both COD and color removals because the hydroxyl free radical generated from the catalyst is more reactive than the ozone molecule itself.

Keywords: Ozonation; Catalytic ozonation; Organic oxidation; Color removal; Iron oxide

1. Introduction

In the sugar-cane production process, molasses is obtained as the main by-product. It is normally used as a raw material for the commercial production of yeast and ethanol because of its low price. Environmental problems in molasses fermentation factories are mainly related to the production of a large amount of highly polluted and brown colored organic substance-containing effluent. Such effluent is usually subjected to anaerobic digestion for removing organic matter and producing biogas, which can be successfully used as a fuel substitute to produce steam for the fermentation process. After the anaerobic digestion, aerobic treatment is needed to meet the effluent standards. However, most of the colored compounds are still present, because of their non-biodegradability, in the treated distillery wastewater with almost the same dark brown color as that before treatment. The colored compounds present in molasses and distillery wastewater are brown nitrogenous high-molecular-weight polymers known as melanoidins [1,2]. The formation of melanoidins results from a set of consecutive and parallel chemical reactions taking place between amino compounds and carbohydrates (known as the Maillard reaction [3–5]), which takes place during sugar processing. Conventional anaerobic–aerobic treatment processes can accomplish only up to 6–7% degradation of melanoidins [2,6]. An intensive review of the biological approaches for the treatment of distillery wastewater derived from sugar-cane molasses pointed out the persistence of the unaccepted dark brown color after the combined anaerobic and aerobic treatment [7]. The color pretreatment step using coagulation or oxidation was found to be infeasible for a large quantity of this colored wastewater. Even though several microbial decolorization methods using bacteria and fungi show effectiveness in melanoidins breakdown, they are not practical because of the need for a high dilution ratio for optimum activity. A study on the color removal from distillery wastewater after the combined anaerobic and aerobic treatment processes was done using *Aspergillus* species isolated from the soil located in a distillery plant. The studied biological system was operated on a fill-and-draw basis with the feed containing a biological oxygen demand (BOD) of 100 mg/l. A color removal of 70%, the highest, was

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achieved at the beginning of operation, but the process efficiency deteriorated over time because of the loss of microbial activity [8]. Other treatment processes, such as combined electron-beam and coagulation [9], membrane-based nanofiltration [10], combined enzymatic hydrolysis and aerobic biological oxidation [11], electrocoagulation and electrofenton [12], and activated carbon adsorption [13], have also been used for the treatment of distillery wastewater; however, their difficulty in system setup, high investment and operation costs, and complexity of system operations are reasonably the main drawbacks for applying to such a purpose. Therefore, it is necessary to study alternative treatment processes to efficiently remove non-biodegradable organic compounds and the color in distillery wastewater.

As mentioned, even though a biological process is by far the most effective method to treat organic-containing wastewater in terms of the lowest treatment cost, a number of organic compounds are not easily biodegraded and still produce a color problem. Chemical oxidation can then be more suitably employed to effectively oxidize these refractory organics. Ozone is a strong oxidant and is widely used as a disinfectant in producing drinking water. An ozone molecule, which consists of three atoms of oxygen, is soluble in water and is readily available to instantly react with any organic compounds present in water. Ozone can be produced by passing air or oxygen through a dielectric barrier discharge or silent electric discharge under a high voltage of 9–15 kV [14]. Unfortunately, ozone itself is unstable and can decompose quickly to molecular oxygen in a gaseous system. As a result, ozone cannot be held or transported a long distance, and it must be produced for immediate use. In an aqueous system, ozone can decompose to form several free radicals, including $OH^{\bullet}$ (hydroxyl), $HO_3^{\bullet}$, $HO_4^{\bullet}$, and O_2^- (superoxide) [15]. The hydroxyl radical is the most powerful form among the free radicals of ozone in reacting with organic compounds.

Ozone has been successfully used in a vast number of applications ranging from producing drinking water to treating wastewater, as well as in many chemical industrial systems such as pulp and paper processing. Chemical oxidation with ozone, or the ozonation process, is particularly attractive for wastewater treatment because ozone can destroy most hazardous organic contaminants, such as dyes, phenolic compounds, pesticides, organochlorides, and ammonium compounds [16–21]. Even though the ozonation process seems to be a promising technology for the treatment of molasses-derived wastewater, only a few studies have been done on the ozonation of effluents from molasses-based industries [22–25]. In most of the studies, synthetic solutions or very diluted wastewater was treated by ozone [3,26].

A major drawback of ozonation processes is the high operation cost caused by the installation of an expensive ozone generation unit and the cost of electricity. To reduce the costs accompanying the use of ozone, the efficiency of the ozonation process has to be maximized by combining it with other technologies. To our best knowledge, the use of ozone coupled with effective mobilized/immobilized heterogeneous catalysts with low cost and non-toxicity for the treatment of wastewater has seldom been reported [27–29].

This study has investigated the application of a combination of ozonation and an immobilized heterogeneous catalyst for the oxidative color removal of highly polluted distillery wastewater from a whisky production plant, which uses sugar-cane molasses as the raw material. The main objective of this work was to optimize various operating parameters of the catalytic ozonation system to obtain maximum efficiency in color removal. Iron oxide was selected as the catalyst in this study since it is non-toxic and cost-effective.

2. Experimental

2.1. Catalyst preparation and characterization

Alumina balls were used as the support media to be coated with the iron oxide catalyst. Alumina balls, having an average diameter of 10.3 mm and a low specific surface area of 5.5 m^2/g, were soaked in a 300-ml solution containing 100 g of $Fe(NO_3)_3$ for 15 min and were subsequently dried at 105 °C. The dried alumina balls were then soaked and dried again a few more times. Finally, the dried alumina balls were calcined at 500 °C for 3 h to convert the ferric nitrate into ferric oxide (Fe_2O_3). The BET (Brunauer–Emmett–Teller) specific surface areas of the alumina balls without and with the deposited catalyst were measured by a surface area analyzer (Quantachrom, Autosorb-1) using nitrogen adsorption analysis. The iron content of the catalyst coated on the alumina balls was determined by an atomic absorption spectrometer (Varian, SpectrAA 300). The crystalline phases of both fresh (as-prepared) and spent (after-ozonation) Fe_2O_3 catalysts scraped from the alumina balls were investigated by an X-ray diffractometer (Avance, D8) equipped with a Cu tube for generating Cu kα radiation (λ = 1.5406 Å) at a generator voltage and current of 40 kV and 30 mA, respectively.

2.2. Wastewater characteristics

The wastewater used in this study was distillery wastewater, so-called slop, from a whisky production plant in Thailand, which uses sugar-cane molasses as the raw material. The studied wastewater had a dark brown color and contained very high concentrations of organic and inorganic compounds. The dark brown color results from melanoidin compounds generated from the polymerization reaction during the sugar-producing process. These melanoidin compounds ordinarily have very high molecular weights and negative charges, and they always exist in colloidal form. The characteristics of the distillery wastewater are shown in detail in Table 1. The wastewater not only had very high chemical oxygen demand (COD) and biological oxygen demand values of 106,500 and 31,600 mg/l, respectively, but also contained high levels of various minerals. Since a typical biological treatment system for distillery wastewater consists of two steps, anaerobic and subsequent aerobic operations, the distillery wastewater is first diluted by 2–3 times before passing through an anaerobic tank in order to reduce the toxicity of both potassium and sulfate. After that, the anaerobic effluent is combined with other diluted wastewater, and this combined wastewater is further treated aerobically. Hence in this study, the