

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 ($5.5 \text{ m}^2/\text{g}$ specific surface area) by using $\text{Fe}(\text{NO}_3)_3$ 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.

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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 poly-

mers 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 $5.5 \text{ m}^2/\text{g}$, were soaked in a 300-ml solution containing 100 g of $\text{Fe}(\text{NO}_3)_3$ 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 α radiation ($\lambda = 1.5406 \text{ \AA}$) 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

Table 1
Characteristics of distillery wastewater, so-called slop, obtained from an alcoholic drink-producing factory in Thailand which uses sugar-cane molasses

Parameter	Value
pH	5.7
COD (g/l)	106.5
BOD (g/l)	31.6
Total solid (g/l)	78.3
Suspended solid (g/l)	4.0
Dissolved solid (g/l)	74.3
Total nitrogen (g/l)	1.9
K ⁺ (g/l)	13.3
P (g/l)	0.3
SO ₄ ²⁻ (g/l)	2.4
Ca ²⁺ (g/l)	0.7

distillery wastewater was diluted by distilled water by 20 times before use in order to simulate the treated effluent from the biological treatment system, which generally can reduce only COD and BOD, but not the color. Since the raw distillery slop has a dark brown color, the high dilution (by 20 times) used in this study was to make it possible for color analysis by spectroscopy.

2.3. Experimental setup and procedure

Fig. 1 illustrates the experimental set-up of the catalytic ozonation unit used in this study. The studied system consisted of an ozone generator, a reaction column, an ozone-measuring device, a feed system, and an ozone destructor. The ozone generator (Ozone Generator, OG 20) has a maximum ozone generation rate of 20 g/h. At a maximum input power of 1144 W, the unit can produce 100 g O₃/m³ with a maximum oxygen intake of 200 l/h. The reaction column had a total volume of 1.5 l with an inside diameter of 5 cm and a height of 80 cm. The working

liquid volume was maintained at either 600 or 680 ml. A sintered glass plate having pore sizes of 14–60 μm was located at the column bottom to generate fine bubbles of ozone gas rising through the solution. An ozone measuring unit (Ozone Generator, UG 40) was used to measure ozone concentrations using UV absorption at 200–300 nm. The outlet gas from the reaction column was passed into the ozone destructor in order to decompose the excess ozone to molecular oxygen before being discharged into the atmosphere.

The studied wastewater was fed into the ozonation column at the top in the range of 30–100 ml/min, countercurrent with the fed ozone, with a constant flow rate controlled by using a peristaltic pump. The liquid volume of the ozonation column was kept constant at 680 ml, and the volume of the alumina balls with and without the studied catalyst coating packed in the reaction column was about 500 ml. By measuring the liquid drainage from the column, the holding liquid volume in the reaction column (in the voidage of the packed alumina balls and above the packed alumina balls) was about 370 ml, which was used to calculate hydraulic retention time (HRT). The calculated value of the porosity of the alumina balls in this column is approximately 18%.

2.4. Measurement and analysis

The color of the wastewater samples before and after the ozonation step was measured by a UV–vis spectrophotometer (Shimadzu, UV2550). A sample was first centrifuged at 10,000 rpm for 15 min. The absorbance of the supernatant was measured at an optimum wavelength of 475 nm [30,31]. The percentage of color removal was calculated from the difference in absorbance values before and after treatment. The concentration of both biodegradable and non-biodegradable organic

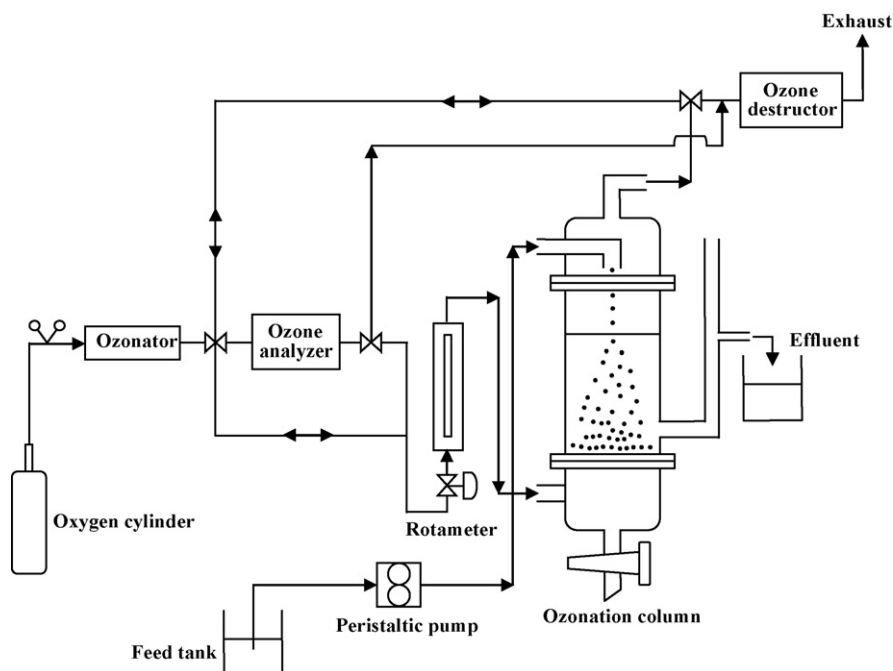


Fig. 1. Schematic of the catalytic ozonation unit.

Table 2
Characteristics of alumina balls and ferric oxide catalyst used in this study

Material	Characteristics	Value
Uncoated alumina balls	Range of ball diameter (mm)	9.8–11.0
	Average ball diameter (mm)	10.3
	Specific surface area (m ² /g)	5.5
	Crystal form	α -Al ₂ O ₃
Coated alumina balls	Fe content (based on dried weight of alumina balls)	0.07%

compounds was analyzed by a chemical oxygen demand analyzer and a spectrophotometer (Hach, DR/2000) at a wavelength of 600 nm.

After the feed solution was fed into the reaction column and the ozone generator was turned on, the effluent was collected for the analysis of COD and color when the system reached steady state. The steady-state condition was justified when the organic concentration and color of the effluent were invariant with time. To obtain reliable data, at least 5 samples of the effluent and feed were taken, and the averaged values of the experimental data were used to assess the process performance of the studied unit. All experimental runs were conducted at room temperature (25–27 °C).

3. Results and discussion

3.1. Catalyst characterization results

Table 2 shows the characteristics of both support media with and without the deposited catalyst used in this study. The alumina balls had an average diameter of 10.3 mm and a specific surface area of 5.5 m²/g. From the analysis results, the catalyst loading was 0.07% Fe, which was in the form of ferric oxide (Fe₂O₃). The crystalline phases of both fresh and spent catalysts verified by XRD are shown in Fig. 2. Both catalysts show the dominant γ -Fe₂O₃ peaks at $2\theta = 33.2^\circ, 35.7^\circ, 41.0^\circ, 49.6^\circ, 54.2^\circ,$ and 57.8° , which correspond to (3 0 0), (3 1 1), (3 2 1), (4 2 0), (5 1 1), and (5 2 0) crystalline planes, respectively [32]. The phase change of the Fe₂O₃ catalyst could not be experimentally observed,

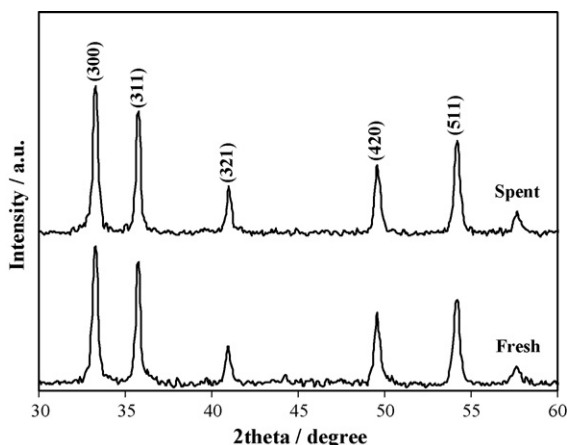


Fig. 2. XRD patterns of fresh and spent Fe₂O₃ catalysts scraped from alumina balls.

indicating that the catalyst is potentially stable under the strong oxidizing condition of the ozonation system.

3.2. Removal efficiencies of ozonation system without packing media

3.2.1. Effect of operating time

The results of the ozonation system can be explained in that the COD parameter represents organic compounds in the distillery slop while the color parameter includes only melanoidins, which is hardly degraded by ozone. The operating time to reach the steady states of the continuous ozonation system was first investigated. Fig. 3 shows the effect of operating time on COD and color removal efficiencies. From the results, the system reached steady state much faster (shorter than 10 min) in terms of COD removal than in terms of color removal (longer than 20 min). It can be implied that an operating time of 20 min is essentially sufficient for the operation to reach steady state. Therefore, to ensure that the experimental data were obtained under steady-state conditions, an operating time of 20 min was selected to start collecting the first wastewater sample from the system for COD and color analysis.

3.2.2. Effect of input power of ozone generator

The effect of the input power of the ozone generator was studied in the range of 572–1150 W, while maintaining other parameters at constant. When the input power of an ozone generator increases, the rate of ozone produced increases accordingly. There are two possible ways to increase the amount of ozone generation in the system: an increase in the input power and an increase in the feed flow rate of oxygen. The effect of the input power of the ozone generator is shown in Fig. 4. As the input power increased from 572 to 860 W, both COD and color removal efficiencies increased, indicating that organic compounds present in the wastewater were increasingly degraded. This can be attributed to a greater amount of ozone available

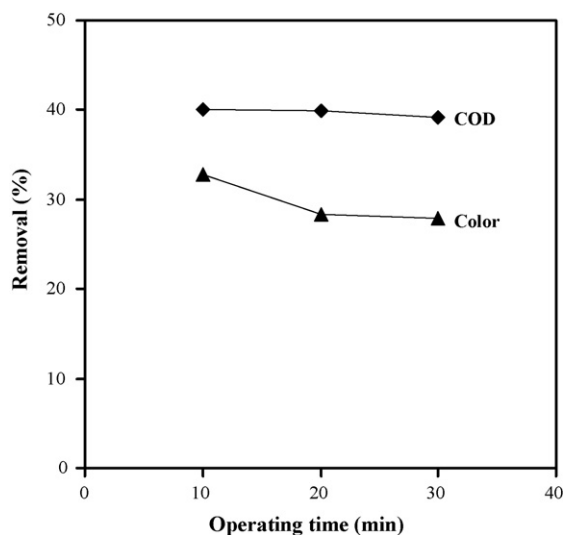


Fig. 3. Effect of operating time on COD and color removal efficiencies (flow rate of ozone = 15 l/h (0.5 g O₃/h); flow rate of slop = 75 ml/min; reaction volume = 600 ml; input power of ozone generator = 572 W).

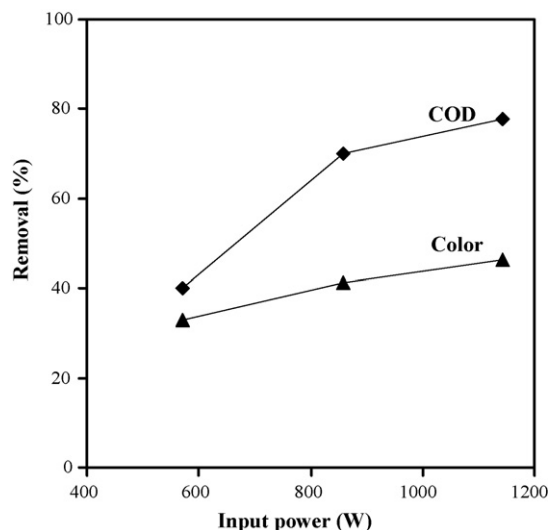


Fig. 4. Effect of input power of ozone generator on COD and color removal efficiencies (flow rate of ozone = 15 l/h (0.5 g O₃/h); flow rate of slop = 75 ml/min; reaction volume = 600 ml).

in the system with increasing input power, resulting in a higher capability of oxidizing organic compounds. Nevertheless, when the input power was further increased from 860 to 1150 W, the removal efficiencies of organics and color increased only slightly. This is probably because the remaining fraction of the organic compounds in the wastewater is hard to oxidize. Therefore, it is not practical to apply excessive input power in the ozonation system.

3.2.3. Effect of mass flow rate of ozone

To determine the effect of mass flow rate of ozone, the ozone generator was operated at a constant input power of 572 W while the oxygen feed flow rate was varied. The ozone concentration in the outlet stream was analyzed and used to calculate the mass flow rate of ozone. The effect of mass flow rate of ozone is given in Fig. 5. The experimental results clearly reveal that both organic and color removal efficiencies were drastically improved with increasing the mass flow rate of ozone from 0.3 to 0.5 g/h. However, a further increase in the mass flow rate of ozone from 0.5 to 1 g/h had an insignificant effect on the removal efficiencies. The results obtained were in the same trend as that for the case of increasing the input power of the ozone generator. This can also be explained in a similar manner in that the mass flow rate of ozone up to 0.5 g/h was sufficient to provide enough ozone molecules to the system for effectively oxidizing the existing organic compounds. At a very high ozone mass flow rate, the degradable fraction of the organic compound in the distillery slop decreases, resulting in the remaining fraction containing more non-degradable organics.

3.2.4. Effect of flow rate of slop

The flow rate of the slop is another parameter that considerably affects the system efficiency. Fig. 6 shows the effect of the flow rate of slop on both COD and color removal efficiencies. With increasing the flow rate of slop from 30 to 100 ml/min, the COD and color removal efficiencies tended to decrease. This is

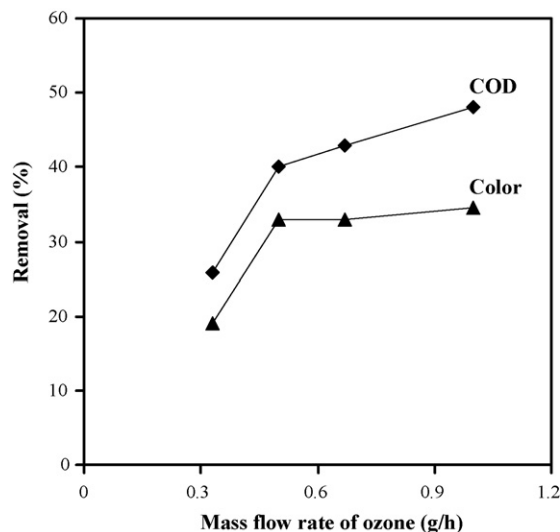


Fig. 5. Effect of mass flow rate of ozone on COD and color removal efficiencies (flow rate of slop = 75 ml/min; reaction volume = 600 ml; input power of ozone generator = 572 W).

due to the decrement in contact time between the ozone and the organic compounds present in the slop in order for them to react with each other, causing decreased capability of organic compound oxidation. In other words, an increase in the flow rate of the slop simply means a greater amount of organic compounds present in the system and a shorter contact time or a shorter reaction time with the ozone. With decreasing feed flow rate, the remaining portion of the inert organic molecules increases, resulting in lower removal efficiencies.

From a comparison between the effect of flow rates of ozone (Fig. 5) and the effect of flow rates of the slop (Fig. 6), it is obvious that the increase in the COD removal efficiency with doubling the ozone concentration is significantly lower than that with decreasing the slop concentration by two times. This clarifies that the feed flow rate of the slop plays a much more

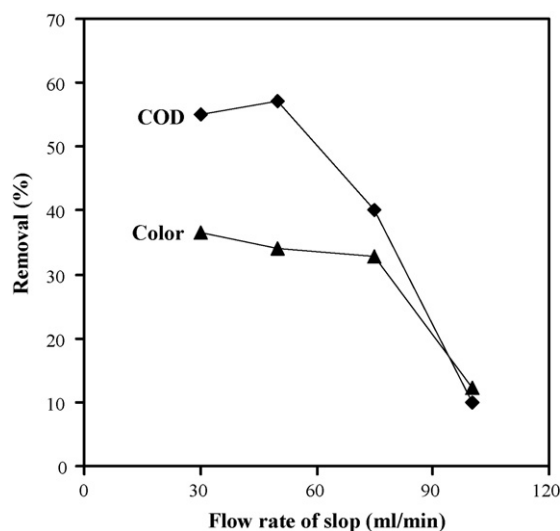


Fig. 6. Effect of flow rate of slop on COD and color removal efficiencies (flow rate of ozone = 15 l/h (0.5 g O₃/h); reaction volume = 600 ml; input power of ozone generator = 572 W).

important role in the COD removal efficiency than the ozone concentration. For the case of color removal, both the feed flow rate and the ozone concentration exhibited similar trends.

3.3. Removal efficiencies of ozonation system with packed alumina balls and Fe₂O₃-coated alumina balls

For each experimental run, it was found that the ozonation system packed with alumina balls reached steady state after 20 min, which was similar to that of the system without the packing media. Hence, effluent samples were taken after 30 min of operation for analysis. In this study, the hydraulic retention time is calculated based on the liquid holding volume.

3.3.1. Effect of pure alumina balls

Fig. 7(a) (solid lines) illustrates the removal efficiency of COD as a function of HRT and the flow rate of ozone. For a given ozone mass flow rate, an increase in hydraulic retention time resulted in increasing COD removal. This is because there is a longer reaction time as the HRT increases. For a given HRT,

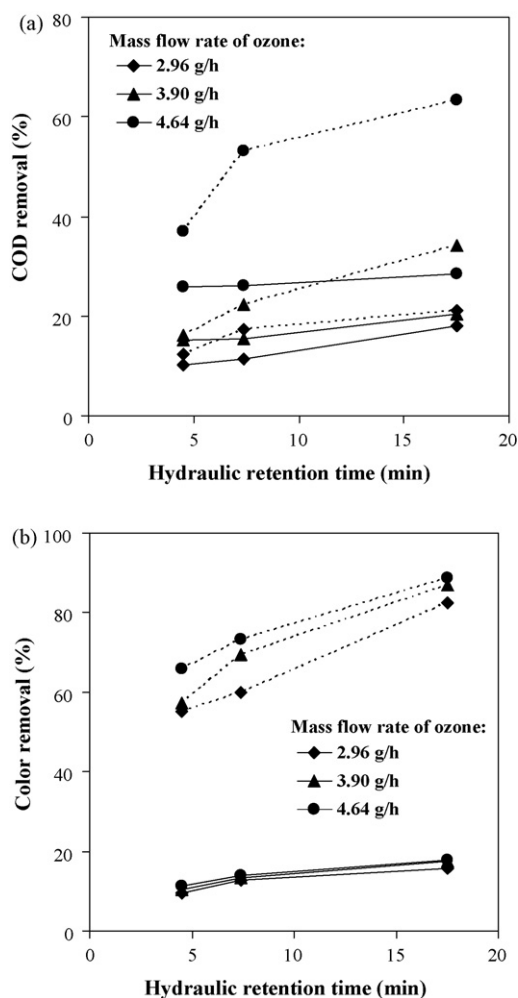


Fig. 7. Effect of hydraulic retention time on (a) COD and (b) color removal efficiencies at different mass flow rates of ozone with packed alumina balls (solid lines) and Fe₂O₃-coated alumina balls (dotted lines) (column volume = 680 ml; packing media volume = 500 ml; input power of ozone generator = 572 W).

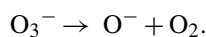
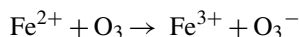
an increase in the mass flow rate of ozone also increased COD removal. The results showed that the ozone dosage affected the COD removal more than the hydraulic retention time did. Similar results were obtained for color removal, as shown in Fig. 7(b) (solid lines), but the removal efficiency occurred to a less significant degree. These results can be explained in that an increase in ozone dosage provides more active species to oxidize the organic compounds, resulting in increasing both COD and color removal.

3.3.2. Effect of Fe₂O₃-coated alumina balls

In these experimental runs, the same amount of alumina balls coated with Fe₂O₃ was packed in the reaction column as in the uncoated balls experiment. As can be seen from Fig. 7(a) (dotted lines) and (b) (dotted lines), an increase in either HRT or ozone mass flow rate increases almost monotonically both the COD and color removal efficiencies. The results show that a significant effect of ozone dosage on COD reduction was obtained as compared to an increase in HRT. Interestingly, an increase in HRT enhanced color removal even greater than an increase in ozone dosage. The results clearly reveal that the presence of the Fe₂O₃ catalyst greatly improves by about 6 times the catalytic activity of the ozone for the color removal in the studied wastewater. By extrapolation, one can remove the color completely by using the Fe₂O₃ catalyst with ozone at a very high HRT of around 30 min.

3.3.3. Comparison of removal efficiencies

The packing media is responsible for providing more surface area for the ozonation reaction and a longer retention time of ozone bubbles in the column. As can be comparatively seen from Fig. 7 for the case of the column packed with pure alumina balls, an increase in hydraulic retention time seems to only slightly affect the removal of both COD and color. Interestingly, significant increases in both COD and color removal were achieved when the Fe₂O₃/Al₂O₃ catalyst was applied. These results can be explained in that the Fe₂O₃ catalyst is responsible for producing hydroxyl free radicals from the ozone, which are a very reactive species for organic compound oxidation, i.e. more reactive than ozone itself. The formation of active species from ozone by the Fe₂O₃ catalyst is shown in the following equations [33–35]:



Interestingly, after running the experiments several times, the alumina balls were found to be still covered with the Fe₂O₃ layer with a low rate of Fe₂O₃ detachment. According to the XRD results as mentioned above, the catalyst is still in the form of Fe₂O₃ and does not form Fe(OH)₃ precipitating out with organics, causing the COD and color reduction. Moreover, the effluent pH, after passing through the ozonation column, did not change significantly, implying that the formation of hydroxyl free radicals proposed above is mainly

responsible for the color removal. The role of Fe_2O_3 and the optimum loading of Fe_2O_3 are currently being investigated in order to obtain a better understanding of the process and to optimize it. This finding will lead to further investigations in applying such an effective Fe_2O_3 catalyst for the enhancement of other chemical oxidation reactions, especially for non-biodegradable organics, which are classified as hazardous compounds.

4. Conclusions

For the ozonation system without the packing media, it was found that ozone could effectively treat distillery wastewater to remove both COD and color. The treatment efficiencies of both COD and color removals increased with increasing either the input power of the ozone generator or the ozone mass flow rate. For the ozonation system with the packing media, the COD and color removal efficiencies increased with increasing either the hydraulic retention time or the ozone dosage. In the presence of the Fe_2O_3 catalyst, ozone became more effective in reducing both COD and color since the catalyst is responsible for enhancing the formation of hydroxyl free radicals, which are very reactive for organic compound oxidation. Therefore, the combination of ozone and the Fe_2O_3 catalyst is recommended for treating wastewater in order to achieve an efficient treating system, especially to remove the color of the distillery wastewater, because of its cost-effectiveness and non-toxicity.

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