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A novel integrated ozone-SBR-ozone process for treatment of baker's yeast wastewater

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ABSTRACT

The wastewater which released from fermentation industries containing a high organic matter with a dark color is the major source of soil and aquatic pollution. The aim of this study was to evaluate an integrated ozonation and sequencing batch reactor (SBR) processes for the treatment of molasses wastewater. This study was conducted in three series (pre-ozonation, SBR, and post-ozonation) glass reactor. While pre- and post-ozonation reactors were operated with ozone doses from 0.1 to 1 g O_3/g COD, and for SBR, hydraulic detention times (HRT) of 12–60 h were used. Different pH from 7.5 to 11 was examined in the process. According to the results, pre-ozonation of baker's yeast wastewater with optimum operational conditions of ozone dose of 0.6 g O_3/g COD and pH 10.5, has removed 31.74% and 88.31% COD and color, respectively. In the SBR process, maximum COD removal rate (52%) was achieved during 36 h aeration time. Due to increasing readily biodegradable intermediate compounds in pre-ozonation step, the ratio of the BOD_5/COD was increased from 0.37 to 0.59 in the next biological reactor. In addition, optimum ozone concentration in post-ozonation step was obtained 0.5 g O_3/g COD. The overall removal efficiencies of COD and color in whole operational status for the combination process of ozone-SBR-ozone were obtained 80% and 88%, respectively. This process might be suitable for treating high strength baker's yeast wastewater in terms of COD and color removal.

Keywords: Baker's yeast wastewater; Ozonation; Sequencing batch reactor; Decoloration; Melanoidin

1. Introduction

The food industry is one of the contributors of wastewater pollution, which among them, the baker's yeasts industry could produce highly polluted wastewater [1,2]. Wastewater from yeast industry may contain dark color, high COD, high concentrations of nitrogen and sulfates and nonbiodegradable organic contaminants [3,4]. In addition, effluents of baker's yeasts might contain soluble materials such as organic acids, trimethylglycine, colored melanoidin, resins, gums, and other types of sugar and phenol, as well as suspended organics and variable concentrations of phosphorus [5,6]. Moreover, molasses in wastewater of yeast industry could contain 45%–50% sugar, 15%–20% nonsugar substances, 10%–15% ash (minerals), and around 20% water [7,8]. During yeast fermentation, sugar in molasses plays an important role as carbon and energy source; however, a major part of nonsugar substances in molasses may not usable by yeast; thus, it may enter unchanged to the yeast processing effluents [8,9].

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Furthermore, the chemicals which are added during fermentation (e.g., antifoams, propionic acids, brine, etc.), yeast metabolites, and residual yeast cells could appear in wastewaters as well [10]. Generally, wastewaters from molasses processing could consist of a large amount of colored substances giving dark brown color with high organic load to the effluents [11,12]. In fact, the main colored compounds are known as melanoidins which are high molecular weight amino-carbonyl compounds [5]. These compounds, due to their dark color and high content of complex organic substances are the main threat for the soil and aquatic ecosystem [5,7]. Melanoidins in water bodies could result in some problems such as reduction of sun light penetration, decreasing photosynthetic activity and dissolved oxygen concentration; in addition, in soil system could decrease soil alkalinity and seed germination [13]. Furthermore, melanoidin can react with metal ions and may affect on the biogeochemical cycle of many constituents in natural water [14–16]. When it released in water bodies, they could cause oxygen depletion and associated problems, and/or if released in soil they may reduce the soil alkalinity and manganese availability, inhibit seed germination and affect vegetation [6,17]. Although, biological treatment is often inexpensive and micro-organisms effectively eliminate industrial pollutants; however, unfortunately not all compounds are biodegradable, whereas many physical and chemical processes are just concentrate on the pollutants or transfer them from one medium to another (stripping from liquid to air) [18]. In addition, conventional anaerobic–aerobic treatment processes can accomplish the degradation of melanoidins only up to 6% or 7% [19]. Moreover, many researchers have tried to isolate microorganisms, which have the ability to decolorize melanoidins; although the ability of microorganisms to remove melanoidins from molasses wastewater is clear; however, their actual use of molasses wastewater treatment processes might be difficult from the viewpoints of the stability and maintenance of color removal activity [4].

Melanoidins can also be removed by physicochemical treatments [4,5]. These methods require high reagent dosages and could generate a large amount of sludge. In addition, biological treatments with certain bacteria and fungi have also been applied, leading to lower color removal efficiencies [20,21]. Main problems in treatment of baker's yeast wastewater could be high COD, high color, odor in the effluent as well as high amount of excess sludge generated in the wastewater treatment processes [4]. If more purification of yeast wastewater is needed, biological processes can be integrated with other advanced oxidation processes (AOPs) [13,22,23]. Among these AOPs, ozone has proven as a powerful oxidizing agent which its oxidizing ability is because of nascent oxygen atoms and hydroxyl radicals [12]. It reacts, directly or indirectly, with complex compounds, through breaking them into simpler and smaller molecules [12]. Ozone is in fact effective in reducing color compared with COD [12,24]. However, biological treatment alone cannot remove enough of the color, surfactants and resistant COD fraction to direct discharge of the wastewater to the environment. Therefore, to achieve this goal, certain other steps, such as ozonation or AOPs, are still required. Ozone is one of the most attractive options, because it is a very strong oxidant that reacts promptly, either as molecular ozone or radically, through hydroxyl radical produced by ozone decomposing in water. In addition, no solid residue is produced. Hence, ozone is widely used as a final treatment step or as a pre-treatment [25].

The biological treatment and chemical oxidation are used as an integrated process and not separately or sequentially, the effectiveness of the two methods, rather than the additive, is synergistic. This will lead to a more effective use of chemical oxidants along with strong and sustainable biological treatment because the effects of toxic and inhibitory compounds in bioreactors are reduced. Also, in the pre-ozonation, the chemical oxidation of organic compounds causes the color as well as heavy organic compounds to break down and the oxidation of organic matter is subsequently easily carried out at the biological treatment stage (SBR), and ultimately, in the post-ozonation step, with the complete oxidation of the wastewater, its color and COD are reduced.

Advantages of application of ozonation in treatment of yeast production wastewater could be removal of toxicity, destruction of organic matters, and enhancement of the biodegradability of recalcitrant compounds in the effluent [26]. In addition, ozone as pre-treatment has been used to improve subsequent biodegradation. Moreover, ozonation can also increase the biodegradability of previously biologically treated wastewaters [24,27]. Since no comprehensive study has been carried out about COD removal as well as color removal in the baker's yeast wastewater using combined ozone and sequencing batch reactor (SBR) process, it was necessary to conduct a research in this regard. The aim of this study was to investigate the integrated ozonation and application of SBR (as biological process) to evaluate the oxidation and biological processes for COD and color removal in the baker's yeast wastewater.

2. Materials and methods

2.1. Sample preparation

Raw wastewater samples were taken from outlet points of separators 1 and 2 of baker's yeast factory in Kermanshah city, located in the west of Iran. The average effluent flow rate of this factory was between 350 and 400 m^3/d. The collected wastewater samples were mixed with a ratio of 2:1 of separator 1 to 2, respectively. Characteristics of the raw wastewater are shown in Table 1.

2.2. Pilot setup

This experimental study was carried out in three stages including pre-ozonation, aerobic oxidation (SBR), and the final ozonation using a pilot. The pilot was consisted of a glass ozone reactor for pre- and post-ozonation (with a height of 110 cm and efficient volume of 1.35 L), glass SBR reactor (with an efficient volume of 5 L), ozone generator (provided by OzoneAb Co., Iran) with a capacity of 20 g/h and O_2 supplier (Model LFY-I-5F-W) with a capacity of 5 L/min. The ozone generator has produced ozone by the corona discharge method and then cooled with water. To prevent any reaction between ozone and other substances, all paths of ozone were provided from glass substrates and silicon. A schematic diagram of the bench scale pilot plant units is shown in Fig. 1.

Table 1
Characteristics of the raw wastewater of local baker's yeast factory

Parameter	Values
TSS, mg/L	31,000 ± 550
TDS, mg/L	24,000 ± 350
COD	20,700 ± 220
NO_2, mg/L	27 ± 2
NO_3, mg/L	625 ± 15
SO_4^{2-}, mg/L	3,000 ± 10
Ammonia-N, mg/L	140 ± 5
Turbidity, NTU	26,000 ± 450
PO_4^{3-}, mg/L	74 ± 5
BOD_5, mg/L	8,000 ± 50
Color, mg Pt-Co/L	27,900 ± 55
pH	6.9 ± 1

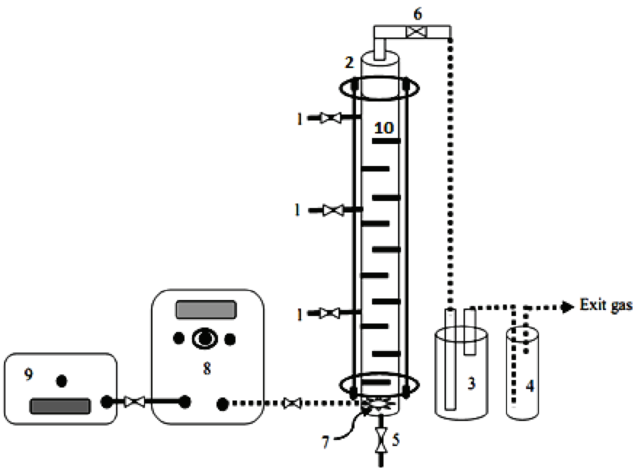

Fig. 1. Schematic of pilot for ozonation. 1, Sampling port; 2, ozonation reactor; 3, ozone gas collection jar; 4, Cariolite; 5, wash valve; 6, sir valve; 7, diffused glass; 8, ozone generator; 9, pressure air compressor; and 10, baffle for ozone caption.

2.3. Pre-ozonation

To find out the optimum pH in the pre-ozonation stage, ozonation was carried out in different ranges of pH (e.g., 7.5, 8.5, 9, 10, 10.5, and 11) and different ozone concentrations (e.g., 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1 g O_3/g COD). pH adjustment of samples was done using H_2SO_4 and NaOH 0.5 N. All experiments in this stage were repeated twice. Each ozonation cycle lasted 70 min and samples for measurement of pH, color, and COD were collected every 7 min. In each cycle 1.350 L of the baker's wastewater was used and in each sampling period, 10 mL specimen was taken. Before sampling, all glasswares were thoroughly washed with detergent and twice with deionized water and to neutralize free radicals and to prevent hydroxyl reaction, one droplet of sodium thiosulfate 1 N was added and then the pH of samples was adjusted around 7–7.5 using NaOH 20%. After that, the samples were filtered using paper filter with a pore diameter of 0.45 μm. Before each experiment, ozone generator was calibrated. The main objective of this phase was to determine the appropriate pH as a catalyst for the hydroxyl free radical production and required ozone to remove color and COD from the baker's yeast wastewater.

2.4. Biological treatment (SBR)

To setup the biological stage, 4 L of ozonated wastewater in the first stage were mixed with about 1 L of returning activated sludge from the local wastewater treatment plant as a microbial seed. After different long time aeration of SBR reactor (12, 24, 36, 48, and 60 h), the mixed liquor was left to be settled for 1.5 h, and then 1.5 L of the supernatant was conducted to the final ozonation. Adaptation period was done in 13–15 d and total operation time of SBR process was longed 35 d.

2.5. Final ozonation

For further removal of color and COD in the effluent, final ozonation stage (like pre-ozonation) was considered in this research. After optimizing the operating conditions for each step of the processes, in order to obtain the overall combined process efficiency of ozone-SBR-ozone, taking into account optimal conditions of each stage, the overall process optimization was done in triplicate and by calculating the removal efficiency for whole process using Eq. (1):

$$\text{Removal efficiency (\%)} = (C_0 - C)/C_0 * 100 \quad (1)$$

where C_0 is the color or COD inlet to process; C is the color or COD outlet from the process.

2.6. Analyses

The pH was measured using digital pH meter (Model Metrohm, pH Lab 827, Germany). Color was determined according to method 8027 with colorimeter device (DR/2000, HACH, Germany) at a wavelength of 550 nm and COD was tested based on method number 5220C using digestion reactor (Model DRB200, HACH, Germany) [28]. The residual ozone concentration in the mixture was measured using indigo colorimetric method (No. 4500-O_3). All chemicals used in this experiment were obtained from Merck Company (Germany).

3. Results and discussion

3.1. Pre-ozonation

In this step, the effect of ozonation versus pH for COD and color removal was studied. Pre-ozonation was conducted with various ozone doses in the range of 0.1–1 g O_3/g COD and pH range of 7.5–11. According to an S/N ratio analysis using the Taguchi methodology, optimum pH and ozone dose were achieved in 10.5 and 0.6 g O_3/g COD, respectively (Figs. 2 and 3).

While in pH of 7.5 and 8.5 no changes were seen in the COD amount reduction. The color removal rate increased with increasing of pH from 7.5 to 9.5, in pH = 10, COD and color reduction rate were decreased (Fig. 1). In addition, by raising pH to 10, an increasing trend were observed in COD

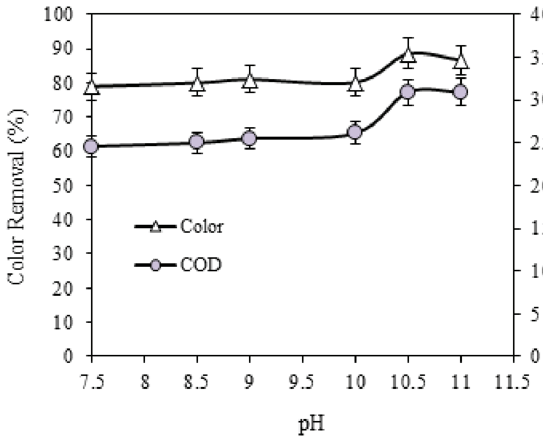

Fig. 2. Effect of pH on COD and color removal of baker's yeast wastewater in pre-ozonation process.

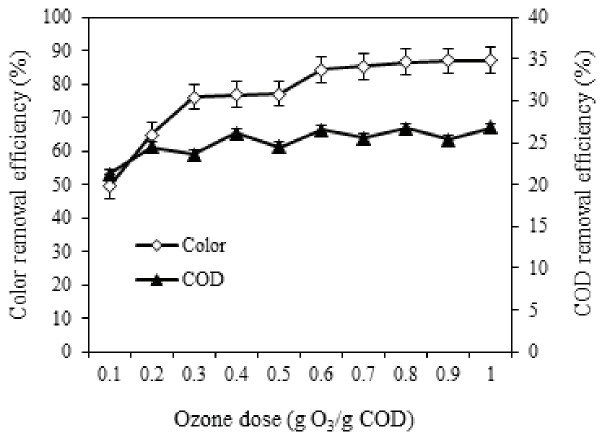

Fig. 3. Effect of applied of ozone concentration on COD and color removal (optimum pH = 10.5).

and color reduction and this reduction reached to its maximum amount in pH = 10.5. But as the pH increased to 11, a decreasing trend in COD and color were occurred. Thus, the optimum pH for reduction of COD and color was 10.5.

According to Fig. 3, with increasing of ozone dose from 0.1 to 0.3 g O_3/g COD, the COD reduction rate was increased. The color removal rate was also increased with increasing of ozone dose from 0.1 to 1 g/g. However, when the ozone dose increased to 0.5 g/g, the COD was not decreased. In fact, with increasing of ozone dose up to 0.8 g/g, the COD and color reduction were not remarkable. Only in an ozone dose of 1 g/g, a minor increasing in COD and color removal were occurred, but this dose of ozone is not recommended due to economical aspects. Thus, the optimum ozone dose of 0.6 g/g COD was determined for maximum COD and color removal in the pre-ozonation process.

The highest rates of COD and color removal in optimal conditions of ozone concentrations at different pH are shown in Fig. 4. In this condition, COD and color were removed about 31.74% and 88.31%, respectively.

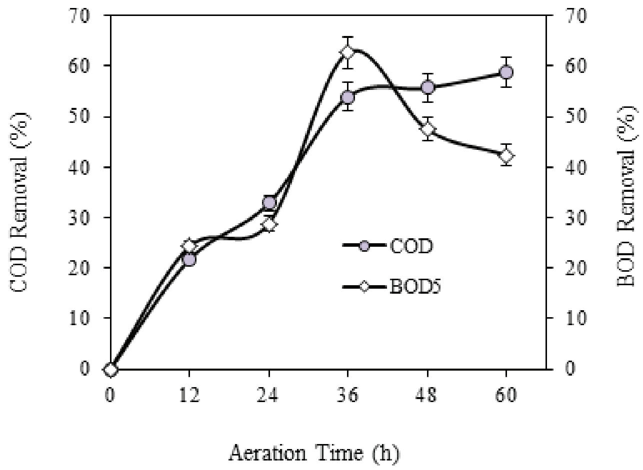

Fig. 4. Effect of HRT in SBR process on BOD_5 and COD removal efficiency.

Some studies have indicated that effectiveness of ozone under alkaline conditions is more than acidic conditions [29,30]. In this research, ozonation process was optimized at pH = 10.5 and this led to increase of BOD_5/COD from 0.37 to 0.56 at the following biological process. In addition, Battimelli et al. [26] applied simultaneous biological degradation and ozonation for molasses wastewater treatment and found out 33% increase in biodegradability rate with using of 0.5 g O_3/g COD [26]. In our research, the optimum dose of ozone was 0.6 g O_3/g COD and an increase in biodegradability index of 75% was observed.

3.2. SBR process

After pre-ozonation, ozonated wastewater was conducted to the SBR process. At this stage, different aeration times (12–60 h) were examined on removal rate of BOD_5 and COD (Fig. 4).

As it is shown, with increasing aeration time from 12 to 36 h, an increased trend was seen in BOD_5 and COD removal rates due to readily increasing biodegradable intermediate compounds [26]. Therefore, due to economical aspects, aeration time of 36 h in the SBR was determined as an optimized time, and in this condition BOD_5 and COD were removed 63% and 53%, respectively.

To investigate the effect of aeration time on BOD_5, COD and color removal in the SBR process, the Pearson correlation coefficient was used. According to this analysis, correlation coefficient for BOD_5, COD, and color were –0.764, –0.947, and 0.798, respectively (Table 2). It means that the parameters of BOD_5 and COD were decreased with increasing of time and there was a significant relationship between them (P value < 0.05). But the color was not decreased with increasing of time. Mohan et al. investigated the SBR system with aeration time of 23 h for treating of industrial wastewater with different organic loading rates of 800, 1,700, and 3,500 mg/L and they resulted COD removal rate of 66%, 47%, and 25%, respectively [31]. Sirianuntapiboon et al. [27] studied 10 times diluted molasses wastewater treatment using SBR and reported BOD_5 and COD removed about 82% and 65%, respectively.

3.3. Post-ozonation

For further removal of COD and color, the SBR effluent was directly transferred to final ozonation step. With regard to pre-ozonation stage and the optimum ozone dose which obtained from this step (0.6 g O_3/g COD), the ozonation of final effluent was conducted with an ozone dose of 0.5–4 g O_3/g COD and an optimal ozone dosage of 0.5 g O_3/g COD showed more removal efficiency in COD and color. The effect of ozone dose of color and COD removal efficiency in post-ozonation stage is depicted in Fig. 5.

According to the results (Fig. 5), maximum removal efficiency of 36.6% and 55% for COD and color was obtained, respectively. Based on Sangave et al.'s study [18], for distillery wastewater treatment using combined processes (ozonation–aerobic oxidation–ozonation), COD and color reduction were achieved maximum 79% with compared to only 35% COD reduction for nonozonated samples over the treatment times. Post-ozonation process that was used for biologically treated baker's yeast effluent by Blonskaja et al. [5] resulted as COD reduction by 30%–49%, with consumed ozone dosage of 1.2–2.5 g O_3/g COD removed. While in this research with improving of operational conditions and performing pre-ozonation, COD was removed about two times more than the Blonskaja et al.'s study (80%) with a total ozone dose of 1.1 g O_3/g COD (sum of pre- and post-ozonation).

The overall optimization of the combination process of ozone-SBR-ozone for removal of COD and color was carried out by considering the optimal conditions of each step with triplicate repetition and calculation of standard deviation as per Table 3. For this purpose, optimal conditions for pre-ozonation, SBR, and post-ozonation processes were considered 0.6 g O_3/g COD, 36 h, and 0.5 g O_3/g COD, respectively. In combination process used in this study, COD decreased from 20,000 to 4,000 mg/L (removal efficiency 80%) and color reduced from 27,000 to 3,150 mg/L (removal efficiency 88%).

Overall removal efficiencies for COD and color removal in ozone-SBR-ozone process (this study) of baker's yeast wastewater are shown in Table 3.

Costs of wastewater treatment, depending on several variables such as plant size, process type, energy consumption, etc. But in this study and beyond the effect of these variables, treatment costs as obtained based on the calculation for the treatment site in pilot scale was 1,300–1,400 \$/m^3.

Table 2
Statistical analysis results for COD and BOD_5 in SBR process

Parameters	COD	BOD_5	Color
Pearson correlation coefficient	–0.947	–0.764	0.798
P value	0.05	0.05	0.05

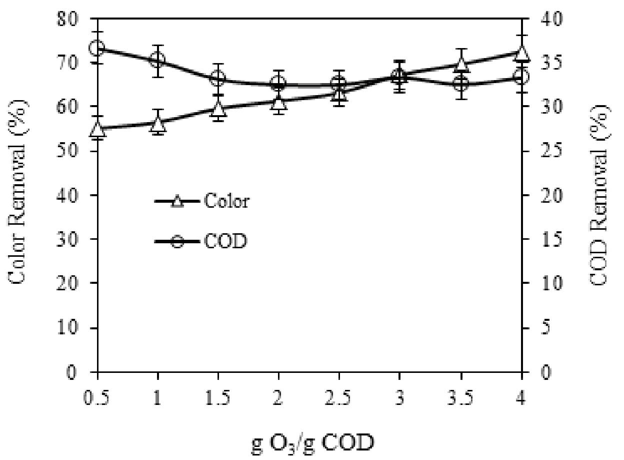

Fig. 5. Effect of ozone dose on COD and color removal in post-ozonation process.

4. Conclusions

This study showed that in the presence of hydroxide ions by hydroxyl radical reactions in the pre-ozonation process for the baker's yeast wastewater, the optimum pH was 10.5. The optimum dose of ozone for COD and color removal in the baker's yeast wastewater treatment in pre-ozonation stage was also obtained as 0.6 g O_3/g COD. Therefore, application of pre-ozonation can be optimized by biological process in the term of COD removal efficiency. Moreover, in this research, with applying of an integrated system comprising ozone-SBR-ozone process for treatment of the highly polluted baker's yeast wastewater, we could remove COD and color about 80% and 88%, respectively. Therefore, one of the strength points of this study was using of raw baker's wastewater without dilution (compared with other studies with using of diluted samples). Thus, the integrated chemical–biological process for the treatment of baker's yeast

Table 3
Overall efficiencies of COD and color removal in ozone-SBR-ozone process for baker's yeast wastewater treatment

Items	COD		Color	
	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)
Raw wastewater	20,600 ± 563	–	27,170 ± 1,730	–
Pre-ozonation	14,000 ± 130	31.39 ± 1.25	3,180 ± 267	88 ± 0.33
SBR process	6,450 ± 208	54.36 ± 1.05	7,020 ± 176	NM[a]
Post-ozonation	4,100 ± 100	36.42 ± 0.5	3,150 ± 50	55.12 ± 0.42
Overall removal rate	–	80.1 ± 0.06	–	88.20 ± 0.24

[a]NM: not measured.

wastewater, containing high organic and soluble color contaminations, can be applied successfully for COD and color removal.

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