Study on the composition of resistant organics in winery wastewater and their degradation technique

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Abstract. Winery wastewater contains a large number of resistant organic compounds, and the residual effluent COD is high after common biological treatment processes, which is hard to meet the increasingly rigorous wastewater discharge standard in China. Two techniques, Fenton oxidation and Fenton oxidation + SBR processes, were applied to treat winery wastewater in this study, and Gas Chromatography (GC) was used to analyze the resistant organic compounds in the effluent. The results indicated that resistant organic compounds in winery wastewater are mainly composed of long chain alkanoic acids, polyphenols, macromolecular esters and alcohols, and the combination treatment of Fenton + SBR process could eliminate COD effectively, and only 0.43% COD left in the effluent compared to the raw winery wastewater. Fenton pre-oxidation not only can oxidize the resistant organics directly, but also can improve the biodegradability of winery wastewater, and the effluent COD meets 60 mg/L standard. The combination of Fenton pre-oxidation and SBR aerobic treatment is the optimal process treating winery wastewater.

1. Introduction

Winery wastewater mainly comes from pressed liquor of grape processing and discharge liquor of vinasse in the stage of fermentation and brewing. The wastewater has higher COD (5000-12800 mg/L), lower pH (3-4) and lower concentrations of N, P [1,2]. Studies have shown that winery wastewater mainly contains saccharides, organic acids, polyphenols and esters [3,4]. Among them, saccharides and low molecular organic acids account for more than 97%. These compounds are easily biodegradable, and they can be effectively removed through anaerobic and aerobic treatment [5,6]. However, the research has shown that winery wastewater still contains a large number of resistant organic compounds. Although these kinds of compounds only account for about 1.3% of total COD in wastewater, they are multitudinous and have complex structure. Common biological treatment processes are difficult to biodegrade these substances, and the effluent quality cannot meet the new discharge standard.

In recent years, advanced oxidation technique has been adopted to preprocess winery wastewater [7-9]. The results have shown that advanced oxidation can remove 30-50% COD, improving the biodegradability of wastewater. However, COD in the effluent is still high and it is hard to meet the increasingly rigorous wastewater discharge standard in China.

As a result, it is necessary to analyze the composition of resistant organic compounds in winery
wastewater and explore the optimal treatment process to increase the degradation efficiency of resistant organics. Fenton oxidation and Fenton oxidation + SBR treatment processes were adopted in this study to treat winery wastewater, and GC was used to analyze the composition of resistant compounds in each stage of the process. By analyzing the variation of resistant compounds in the treatment process, the efficiency of Fenton oxidation and (or) SBR technique on winery wastewater treatment was explored in order to seek the optimal treatment technique and increase the treatment efficiency of winery wastewater.

2. Materials and methods

2.1. Wastewater

Wastewater taken from regulating pond of Qingdao winery factory wastewater treatment plant was used in the experiment. The average water quality parameters in the raw winery wastewater are as follows: COD is 12136 (±35) mg/L, SS is 1524 (±8) mg/L, pH is 3.6 (±0.2) and chrominance is 3058 (±12).

2.2. Experimental methods

2.2.1. Fenton oxidation. 300 mL winery wastewater was added to 500 mL conical flask, and then Fe$^{2+}$ and H$_2$O$_2$ was put into the flask according to the molar ratio m(H$_2$O$_2$): m(Fe$^{2+}$)=1 [10]. HCl is used to adjust pH to 3. After reacting 3 min at the speed of 120 r/min, NaOH was added to adjust pH to 8. The supernatant was sampled to be detected.

2.2.2. Fenton oxidation + SBR treatment. SBR process was simulated respectively by taking 3 beakers of 5 L volume. Sludge obtained from the aerobic pond of wastewater treatment station in Qingdao winery factory was inoculated at a concentration of 3000 mg/L. DO was maintained about 4 mg/L with the aeration device and an online detector. Effluent oxidized by Fenton reagent was added to the SBR with the ratio of 20% (v/v). Aeration of 40 hours and precipitation of 2 hours is defined as 1 period. After 10 periods, samples from the effluent were filtered and then analyzed.

2.3. Analytic method

2.3.1. Wastewater parameter. COD and chrominance was detected by potassium dichromate colorimetric method and dilution multiple method respectively [11], pH was examined by Hanna pH measuring apparatus.

2.3.2. Composition of resistant compounds. The effluent from each process is analyzed by Gas Chromatography (GC, Agilent) equipped with a separation column (6890A/5975C, 30 m × 0.25 mm×0.25 μm, Agilent) which temperature is kept stable at 100°C for 4 min and then increased to 325°C with a 20°C/min heating rate, maintaining 3 min. Helium is used as the carrier gas, and flow rate and diversion ratio are set to 1 mL/min and 20:1, respectively. The temperature of Gas Chromatography is enhanced from initial 100°C to 250°C with an 8°C/min of heating rate, and then increased to 325°C with a 20°C/min heating rate, keeping 3 min. EI source which temperature is 170°C is selected as detector and the corresponding energy is 70 ev. The scan time is 30 min. NIST library is adopted to analyze intermediates in this experiment [12].

2.3.3. Quality control. Each experiment was done in triplicate. Considering the influence of various complicated organics on the measuring results of GC, manual integral was adopted to determine the intensity of different organic compounds.

3. Results and analysis
3.1. Composition of resistant compounds in winery wastewater

Previous research has indicated the major compounds in winery wastewater are saccharides (maltose, fructose) and alcohol compounds, and they account for above 95% of COD in wastewater [3,10]. These compounds are biodegraded easily and here they are not discussed in this paper. GC is adopted in the experiment to detect resistant compounds in the raw winery wastewater which are hard to be removed biologically. The results are shown in figure 1.

![Figure 1. GC spectrum of raw winery wastewater.](image)

It is notable from figure 1 that the composition of winery wastewater is extremely complex. There are 3 types of compounds detected in raw winery wastewater: (1) straight-chain alkanes and alkanoic acids such as lactic acid, lauric acid, myristic acid, cetane, etc; (2) polyphenols, such as resveratrol, phthalic acid, dibutyl phthalate, sterol, etc; (3) other substances, such as glycerin, benzene, phenyl naphthylamine, etc.

The resistant organic compounds in raw winery wastewater generally come from two sources: (1) natural ingredients in grape flesh, skins, and seeds; (2) the additives in winery production process. Because some additives are not natural compounds, the resistant organics in winery wastewater is strongly related to the grape types and the processing technology. Although these compounds are in low concentration (usually about 0.5 to 10 mg/L), their contribution to COD in winery wastewater are usually in the range of 100-300 mg/L. Because they are hard to be biodegraded, the effluent quality after biological treatment is usually influenced by these compounds.

Table 1 shows the composition of resistant organic compounds in raw winery wastewater. The intensity of Adipic acid (2-ethyl) dihexyl ester and dibutyl phthalate are the highest among the resistant organics, 4287475 and 6709488 respectively, and the intensity of other compounds ranged from 289868 (lactic acid) to 2145001 (palmitic acid), which is much lower than the two above mentioned. In order to compare the removal efficiency of Fenton oxidation and Fenton + SBR treatment, the organic compounds in the effluent were also analyzed.

| No. | Retention Time (min) | Name       | Intensity (a.u.) | No. | Retention Time (min) | Name       | Intensity (a.u.) |
|-----|---------------------|------------|-----------------|-----|---------------------|------------|-----------------|
| 1   | 6.921               | lactic acid| 289868          | 11  | 21.643              | dibutyl phthalate | 4287475        |
3.2. Treatment effects of two different process

3.2.1. Fenton oxidation process. GC spectrum of winery wastewater after Fenton oxidation is shown in figure 2. The intensity of Adipic acid (2-ethyl) dihexyl ester and dibutyl phthalate decreased to 61855 and 78075 respectively, and only 0.9% and 1.8% remained in the effluent, indicating Fenton oxidation process is very effective to remove some of the resistant organics in winery wastewater. Furthermore, nearly all compounds detected in raw winery wastewater have been removed to some extent with the exception of lactic acid, whose intensity increased from 289868 to 899767. These results indicated that after Fenton oxidation, most of the resistant compounds were removed. To further explore the removal extent of resistant compounds in winery wastewater, SBR process was designed following Fenton oxidation, and the degradation efficiency of different compounds was analyzed.

![Figure 2. GC spectrum of winery wastewater after Fenton oxidation.](image)

3.2.2. Fenton oxidation + SBR process. The GC spectrum of Fenton oxidation + SBR treatment is presented in figure 3. The intensity of Adipic acid (2-ethyl) dihexyl ester and dibutyl phthalate was further reduced to 50569 and 47716 respectively, and only 0.8% and 1.1% left in the effluent.
compared to the raw winery wastewater.

At the same time, the intensity of lactic acid reduced to 82033 after SBR treatment, indicating 90.9% has been removed by SBR process. Although the intensity of lactic acid has increased after Fenton oxidation, the total removal efficiency of Fenton +SBR reached 71.7%. Overall, after Fenton +SBR process, the intensity of the resistant organics in raw winery wastewater decreased significantly, from 61.5% to 99.2% respectively (data not shown). From these results, it appears that Fenton oxidation can decrease the intensity of most of the resistant organics in raw winery wastewater. Although the intensity of a very few organics might increase in the process, the subsequent SBR process can degrade these compounds efficiently. Mosteo et al [13] employed Fenton + activated sludge process to treat winery wastewater, the results showed that more than 90% COD was removed, which coincided with the experimental results in this paper.

4. Discussion

4.1. Influence of resistant organic compounds on the effluent quality of winery wastewater

Polyphenols in winery wastewater are the main source of residual COD and chrominance, and studies have shown that the higher concentration of polyphenols in wastewater results in the less activity of microorganisms [14]. The relationship between polyphenols concentration and COD removal efficiency during biological treatment is shown in figure 4. It can be observed that when the concentration of polyphenols is varied from 13.1 and 247.0 mg/L, the COD removal efficiency decreased from 95% to 85% [1,14]. Neither aerobic nor anaerobic treatment of winery wastewater solely can meet the COD standard of 60 mg/L [15-17].

Fenton oxidation and Fenton + SBR process was adopted in the study to treat winery wastewater, respectively. Resveratrol is one of the polyphenols substance tested in the effluent of each process, and its intensity decreased from 572400 to 909901 after Fenton oxidation with the removal efficiency of 84.1%. Then the effluent was treated with SBR, and SBR could remove extra 32.0% COD. Overall, the combination of Fenton + SBR process could eliminate resveratrol effectively, and only 10.8% resveratrol left in the effluent compared to the influent.

The variation of COD in each treatment process was measured in the study. It is found COD removal efficiency after Fenton oxidation was 89.68%, and after SBR treatment, another 95.87% COD was removed. The combination treatment process of Fenton + SBR could make effluent COD less than the discharge standard 60 mg/L.

Figure 3. GC spectrum of winery wastewater by Fenton oxidation + SBR treatment.
4.2. Analysis of Fenton oxidation + SBR process

It is indicated that Fenton oxidation + SBR treatment can remove most of the resistant organics in winery wastewater, and no intermediate products appeared in the effluent (figure 3). The total areas of all peaks in Fenton oxidation + SBR treatment is less than these in the raw winery wastewater, which means that the removal ability of hybrid process is strong.

As no intermediate compounds emerged in the effluent after Fenton oxidation + SBR treatment, it indicates that the intermediate products produced by Fenton pre-oxidation are easily biodegraded by SBR treatment. The results in this experiment show that Fenton pre-oxidation can not only oxidize the resistant organics directly, but can also improve the biodegradability of winery wastewater, which is of great significance for the deep purification of wastewater and their reuse [18-20].

Fenton oxidation occurs under pH 3, where high activity •OH is produced by ferrous ions intensifying H₂O₂. The raw winery wastewater is usually highly acidic, with pH of approximately 3-4 [21]. Considering that the pH requirement of Fenton oxidation is consistent with that in the raw winery wastewater, pH adjustment is not needed during treating winery wastewater by Fenton oxidation.

When Fenton oxidation completed, near-neutral pH would be achieved because a large number of organic acids were oxidized and decomposed during the oxidation process. Hence, Fenton oxidation process greatly reduced the running costs of pH adjustment. Therefore, the combination of Fenton pre-oxidation and SBR aerobic treatment can be regarded as the optimal process treating winery wastewater.

5. Conclusions

Straight-chain alkanes, alkanoic acids and polyphenols are the main components in raw winery wastewater. Fenton oxidation could remove 89.68% COD, and SBR process could eliminate another 95.87% COD in winery wastewater. The combination of Fenton pre-oxidation and SBR aerobic treatment are the optimal process treating winery wastewater, and the effluent COD could meet 60 mg/L discharge standard.

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