

The Feasibility of AOPs and an SBR for Treating Wastewater from Polyurethane Manufacturing

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Abstract

We studied the feasibility of two advanced oxidation processes (AOPs), including the Fenton and ozonation processes, and a conventional sequence batch reactor (SBR) for treating wastewater from polyurethane manufacturing. The results showed that the SBR achieved a COD removal rate of 93.3% when the influent COD concentration was 1,600 mg·L⁻¹, which was 22.1 and 522.1% higher than the best results by the Fenton (H₂O₂/COD = 0.0623 mM·g⁻¹ and Fe²⁺/COD = 0.0102 mM·g⁻¹) and ozonation (1 g·L⁻¹, 45 min) processes. A COD removal rate of 90.6% for SBR was achieved after an aeration time of 12 h, and the COD degradation rate was similar to that of a zero-order reaction. A study of the SBR drivers suggested that air stripping and self-volatilization contributed to the higher COD removal rates obtained in this process. This study shows that a single SBR is practical for treating small amounts of polyurethane manufacturing wastewater, and that it had a higher ability to remove COD and resist feeding load shock than the other methods tested. But the potential risks of volatile organic compounds (VOCs) stripping out during the aeration process should be of concern.

Keywords: polyurethane manufacturing wastewater, AOPs, Fenton process, ozonation, SBR

Introduction

As a kind of organic polymer material, polyurethane is widely used to manufacture, among other products, foam plastics, adhesives, and coatings. During the polyurethane manufacturing extraction and evaporation process, a small amount (0.5-1 m³·d⁻¹) of low-boiling-point alcohol ester wastewater, with a complex composition and a high chemical oxygen demand (COD, up to 15,000 mg·L⁻¹), is produced. The wastewater also has low total nitrogen (TN, less than 70 mg·L⁻¹) and total phosphorus (TP, less than 0.5 mg·L⁻¹), and nutrient concentrations that are very imbalanced. If discharged directly without any treatment, this kind of wastewater will certainly have an impact on the

receiving water, and will cause problems to the surrounding environment and may also be a threat to human health.

To date, there has been little research about how to deal with complex organic wastewater like this. Typical studies on treating polyester wastewater have mainly focused on using combined processes so that the wastewater meets the discharge standards. For example, Jun Zheng [1] used an 'up-flow anaerobic sludge blanket (UASB)-hydrolytic acidification-biological aerated filter (BAF) process' to treat a kind of polyester wastewater, the COD concentration of which was 10,000-12,000 mg·L⁻¹. After an esterification reaction, the effluent COD decreased to below 150 mg·L⁻¹. Aijun Tian [2] achieved a COD removal rate of 98.7% by applying a 'steam extracting-anaerobic-biological contact oxidation-air flotation process' to treat a polyester wastewater with a COD concentration of between 25,000 and 30,000 mg·L⁻¹. Because of the long procedure involved, the

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Table 1. Characteristics of raw water and sludge.

Item	pH	COD [mg·L ⁻¹]	BOD ₅ [mg·L ⁻¹]	TN [mg·L ⁻¹]	TP [mg·L ⁻¹]	MLSS [mg·L ⁻¹]
Raw water	7.01	14,160	1,790	68.50	0.40	/
Inoculum	8.28	/	/	/	/	10,260

combined processes require significant upfront investment, which, when combined with high operation costs, are uneconomical for treating small quantities of wastewater. An SBR therefore seemed to be a useful method to treat this kind of wastewater, because of its high buffering ability to resist load shock, a greater possibility to automate the process, the shorter technological process, lower construction and operation costs, and higher security during operation. It was also noticed that advanced oxidation processes (including the Fenton process, ozonation, electrochemical oxidation, and others) may be useful alternatives for strong wastes of limited volume, owing to their ability to directly mineralize organics or raise the BOD₅/COD ratio of industrial wastewater with high COD concentrations and avoid a complicated treatment sequence [3]. For example, Nora San Sebastián Martínez [4] used the Fenton process as a pre-treatment method to deal with pharmaceutical wastewater whose COD concentration was up to 36,200 mg·L⁻¹, and achieved a 56.4% COD removal rate using 3M hydrogen peroxide and 0.3 M ferrous iron. Donglei Wu [5] used ozonation to treat wastewater from the bamboo industry and the results indicated that, when the ozone concentration was 52.5 mg·L⁻¹ and the ozonation time was 25 min, the removal rates of color, COD, and total organic carbon (TOC) in 1 L raw water were 95, 56, and 40%, respectively. However, to date the Fenton process and ozonation technology have not been used to treat polyurethane wastewater.

In an attempt to find an efficient way to treat the small quantities of low-boiling-point alcohol ester water generated in the polyurethane manufacturing industry, in this study we examined the performance of the Fenton, ozonation, and SBR methods for treating polyurethane wastewater. Furthermore, R. A. Caffaro-Filho [6, 7] had observed that toxicity of polyester manufacturing industry wastewater was largely attributed to volatile organic compounds (VOCs) and that removing VOCs from polyester manufacturing wastewater could reduce toxicity toward unacclimated active sludge biomass. Besides, during aeration treatment of polyester manufacturing wastewater, most of the removal of VOCs was caused by air stripping. As such, we examined the SBR mechanisms to show the effects of air stripping and self-volatilization during the SBR process.

Materials and Methods

Substrates and Inoculums

Raw water used in this study was collected from a polyurethane factory in Beijing. Raw water contained low-boiling-point alcohols (including ethylene glycol, diethyl-

ene glycol, neopentyl glycol, etc.) that were not completely reacted, and low-boiling-point esters and other byproducts from condensation reaction. Raw water was preserved in a freezer at 4°C. We used aerobic sludge from the wastewater treatment plant of the Beijing Municipal Research Institute of Environmental Protection as the initial inoculum. Before commencing this study, the characteristics of the substrates and inoculums were analyzed, and results are shown in Table 1.

Reactors and Operation

Fenton Process

The Fenton process was carried out in a 250 mL glass beaker with a working volume of 100 mL. The reaction system was magnetically stirred to ensure complete homogeneity during the reaction. The pH of the reaction system was first adjusted to 3.00±0.02 [8]. Different concentrations of hydrogen peroxide (H₂O₂) (w/v, 30%) and ferrous iron (Fe²⁺) were then added according to Table 2, and the reaction time was 10 min. There were three parallels for each factor. After reaction, 20% sodium hydroxide on a mass concentration basis was added into the system so as to precipitate the Fe²⁺ and decompose the residual H₂O₂ (pH > 10) [9]. The samples were then centrifuged at 2,200×g for 5 min and the supernatant was collected to determine the COD concentration.

We evaluated the effects of different concentrations of hydrogen peroxide (H₂O₂) and ferrous iron (Fe²⁺) on COD removal rates by converting the usage dose of H₂O₂ and Fe²⁺ into molecular dose per gram COD-treated.

Ozonation

The ozonation system was composed of a 500 mL measuring cylinder coupled with an ozone generator 3S-A10 (Tongligaoke, Beijing, China). The measuring cylinder was used as the reactor and had a working volume of 250 mL. The average production of ozone was around 1 g·L⁻¹ and was distributed to the wastewater by an air diffuser to improve the capacity for ozone absorption. We evaluated the COD removal rates under different oxidation times.

SBR

The aerobic sludge was acclimated using a square reactor (210×190×310 mm) with a working volume of 8 L before the SBR experiment commenced. The reactor was equipped with an air pump and an air diffuser to keep dissolved oxygen (DO) levels of the system between 2 and 4 mg·L⁻¹.

Table 2. Results of the Fenton process.

Samples	H ₂ O ₂ [mL]	FeSO ₄ ·7H ₂ O [g]	H ₂ O ₂ [mM·g ⁻¹] (COD)	Fe ²⁺ [mM·g ⁻¹] (COD)	H ₂ O ₂ /FeSO ₄ ·7H ₂ O	Effluent COD [mg·L ⁻¹]	Removal rate of COD/%
1#	0.25	0.10	0.0016	0.0003	6.13	14,283±203	-0.9±1.4
2#	0.50	0.10	0.0031	0.0003	12.26	14,866±104	-5.0±0.7
3#	1.00	0.25	0.0062	0.0006	9.81	14,725±175	-4.0±1.2
4#	2.00	0.25	0.0125	0.0006	19.62	13,108±264	7.4±1.9
5#	2.00	1.00	0.0125	0.0025	4.91	11,458±212	19.1±1.5
6#	5.00	1.00	0.0312	0.0025	12.26	11,533±152	18.5±1.1
7#	5.00	4.00	0.0312	0.0102	3.07	5,666±119	60.0±0.8
8#	10.00	4.00	0.0623	0.0102	6.13	3,336±141	76.4±1.0

The equivalent H₂O₂ and FeSO₄·7H₂O were measured according to the following equations:

(A) H₂O₂ [mM·g⁻¹] (COD) = V×30%/M(H₂O₂)/(v×C);

(B) Fe²⁺ [mM·g⁻¹] (COD) = m/M(FeSO₄·7H₂O)/(v×C)

...where V stands for volume of H₂O₂ used, m stands for weight of FeSO₄·7H₂O used, M stands for molar mass of the two chemicals, v stands for volume of tested raw water, and C stands for the initial COD concentration of the tested raw polyurethane wastewater.

Table 3. Result of the blank experiments.

Item	Initial COD [mg·L ⁻¹]	COD after 12 h aeration [mg·L ⁻¹]	Removal rate of COD [%]
B1	805	700	13.0%
	828	727	12.2%
	788	693	12.1%
B2	809	780	3.6%
	821	793	3.4%
	817	787	3.7%

SBR operation conditions were as follows: 0.25 h for filling, 21.5 h for aeration-reaction, 1.5 h for settling, 0.25 h for decanting, and 0.5 h for resting. The water filling ratio was 3/8. Inoculum sludge was added at a rate of 3,500 mg·L⁻¹ (based on MLSS), while raw water was diluted with tap water. The water was prepared by adding nitrogen (KNO₃) and phosphorus (KH₂PO₄) at a COD:N:P ratio of 200:5:1. The COD concentration of the prepared water was raised from 400 to 1,600 mg·L⁻¹ at a rate of 200 mg·L⁻¹·d⁻¹. We measured the pH and COD every day, while sludge volume (SV), MLSS, and other indexes were measured after assimilation. The effects of aeration time (0, 2, 4, 6, 8, 12, 16, 24 h) and sedimentation time (0, 30 min, 1 h, 1 h 30 min, 2 h) on the removal rate of the SBR system were evaluated at a feeding load of 1,600 mg·L⁻¹. Each factor was conducted in triplicate.

Analysis Methods

pH was measured with a TS-100 pH meter (SUNTEX, Taiwan). COD was measured by an ORION AQ4001

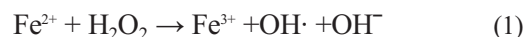
COD165 COD analyzer (Thermo Scientific, USA). BOD₅, MLSS, and other indexes were measured using standard methods (APHA/AWWA/WEF1996).

Results and Discussion

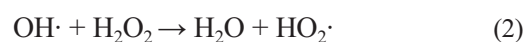
Fenton Process

The effects of different concentrations and ratios of H₂O₂ and Fe²⁺ on COD removal rates are shown in Table 2

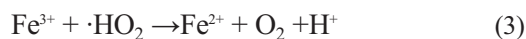
It was assumed that as the H₂O₂/COD and Fe²⁺/COD molar ratios increased, more hydroxyl radicals would be available to degrade organic matter based on the reaction equation of the Fenton process by Walling [10].



As can be seen in Table 2, the COD removal rate increased as the amount of H₂O₂ and Fe²⁺ increased, which may be caused by greater generation of hydroxyl radicals. When the H₂O₂/COD ratio was between 0.0016 and 0.0062 mM·g⁻¹ and the Fe²⁺/COD ratio was 0.0003-0.0006 mM·g⁻¹, the raw water COD concentration increased slightly. However, the COD removal rate changed dramatically when the H₂O₂/COD and Fe²⁺/COD ratios were each increased to between 0.125 and 0.0623 mM·g⁻¹ and 0.0025 and 0.0102 mM·g⁻¹, respectively. COD removal reached 76.4% when H₂O₂/COD was 0.0623 mM·g⁻¹ and Fe²⁺/COD was 0.0102 mM·g⁻¹. We also noticed that when the Fe²⁺ concentration was constant (1#, 2#, 5#, and 6#), the effects of H₂O₂ increases were negative. This may be because of OH scavenging, as shown by reaction (2) [11].



However, the opposite result was obtained when the H_2O_2 concentration was much higher than that of Fe^{2+} , which may be attributable to ferric iron reduction to ferrous iron by $HO_2\cdot$, and the generation of $OH\cdot$ through reaction (3) [11] and reaction (1).



Thus, we may conclude that when Fe^{2+} remains constant, increases in H_2O_2 may result in increased COD removal rates. This agrees with the findings of Piyawat Tanvanit [12], who treated explosive-contaminated wastewater, and Jian Wei [13], from his study of dry-spun acrylic fiber manufacturing wastewater. Moreover, it is commonly accepted that chemical coagulation is the main wastewater treatment mechanism when H_2O_2 exceeds Fe^{2+} , while chemical oxidation is the main mechanism when Fe^{2+} exceeds H_2O_2 [11]. Based on this theory, chemical oxidation was the principle mechanism of COD removal in this study, since all the samples reacted when the $H_2O_2/FeSO_4 \cdot 7H_2O$ molar ratio was greater than one. We also noticed that the COD removal rate was highest with the highest reagent dose in this study. Since the color of the Fenton system increased with reagent dose, the reagent dose was not increased, as the dark color in the system would have caused problems for the processing unit, resulting in extra costs. Hence, the highest COD removal rate of raw water during the Fenton process was 76.4%.

Ozonation

By generating high oxidation potential hydroxyl radicals, the Fenton process was able to decompose organic matter. Compared with the Fenton process, ozonation can oxidize organisms directly, in addition to generating hydroxyl radicals, which make it an attractive way to deal with this kind of wastewater.

Changes in COD in the ozonation system with oxidation time are presented in Fig. 1.

pH decreased with ozonation time. This may be caused by breakdown products such as organic acids formed during ozonation [14]. However, COD concentrations did not change significantly under different ozonation times, and

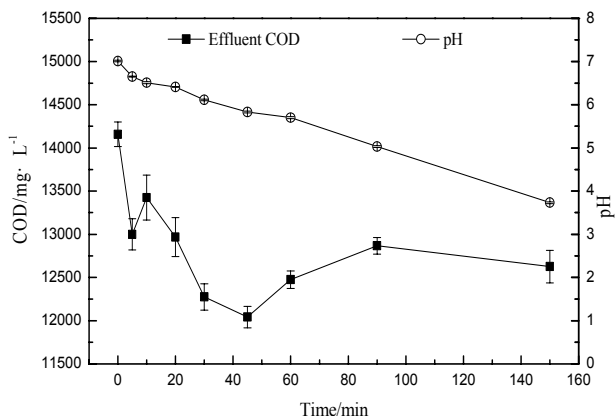


Fig. 1. Results of the ozonation experiment.

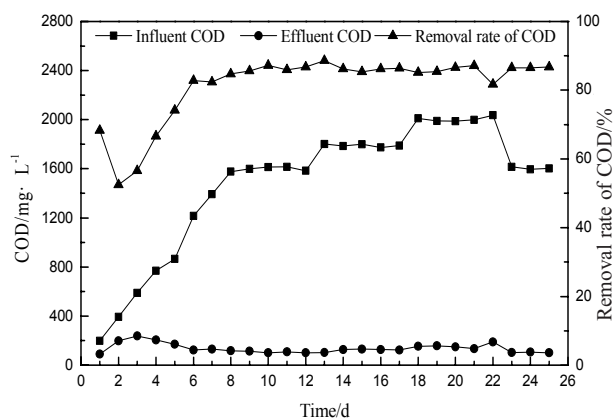


Fig. 2. Results during the starting stage of SBR.

the removal rate was below 20%. The highest COD removal rate (15.0%) was obtained 45 min after ozonation. Comparison shows that the best results for treating this kind of wastewater by ozonation are much worse than the results for the Fenton process. Ozonation is good at treating large molecular weight organic matter while the performance drops when dealing with small molecular weights [15]. In this experiment, raw water was composed of small molecular weight alcohol and esters.

SBR

Starting Stage of SBR

Influent water was prepared according to the experimental design, and effluent COD and pH were measured. The results from the initial stage of the SBR process are shown in Fig. 2.

As shown in Fig. 2, the COD removal rate initially decreased and then gradually increased. When the SBR system reached a steady state, the COD removal rate of the system fluctuated around 93.0%. When the COD of the prepared wastewater increased from 1,800 to 2,000 $mg \cdot L^{-1}$, the effluent COD was around 150 $mg \cdot L^{-1}$. Although the COD removal rate was maintained, the effluent struggled to meet the secondary standard ($COD \leq 120 mg/L$) for integrated wastewater discharges (GB 8978-1996, China). When the COD of the prepared wastewater was 1,600 $mg \cdot L^{-1}$, effluent COD met the above standard. After running the experiment for 5 days at 2,000 $mg \cdot L^{-1}$, the influent COD was reduced to 1,600 $mg \cdot L^{-1}$, and the experiment was continued at this level for a further 3 days so as to accomplish the acclimation stage. After acclimation, the MLSS concentration in the SBR system was increased to 4,260 $mg \cdot L^{-1}$.

Optimization of the SBR Operating Parameters

Comparison of the three systems (Fenton, ozonation, and SBR) clearly shows that the SBR system achieved the highest COD removal rate. The average COD removal rate of the SBR system was 21.1 and 522.1% higher than those achieved by the Fenton and ozonation processes,

respectively. The aeration and sedimentation times for the SBR system were optimized so as to shorten the reaction times without decreasing the efficiency of the system. The results are shown in Fig. 3. Since the filling ratio was 3/8, COD was first diluted by the remaining water in the system, which made the COD of the mixed liquor in the SBR system lower than that of the prepared liquor, and the initial COD concentration referred to here was that for the mixed liquor.

COD dropped sharply from 779 to 73 mg·L⁻¹ during aeration in the first 12 h and reached a removal rate of 90.6%. Extending the aeration time from 12 to 24 h led to continued gradual decreases in COD. Generally, it was assumed that, during the aeration phase, the degradation process should be subjected to the first order kinetics equation shown (4), where *S* represented degradable COD (mg·L⁻¹), *t* represented aeration time (h), *X* represented MLSS (mg·L⁻¹) and *K* represented degradation rate constant for COD (L·(mg·h)⁻¹). We assumed that the degradation profile would show an exponential decay curve [16]. Judging from the figure above, this was not the case for this study.

$$-ds/dt = KXS \tag{4}$$

However, when aeration time was set as the *x*-axis and the COD concentration in the SBR system was set as the *y*-axis, it was interesting to find that there was a good fit between the COD concentration and aeration time ($y = 771.27 - 58.21x$, correlation coefficient $R^2 = 0.9990$). This suggests that, during the first 12 h of aeration, there was no interaction between the degradation rate of COD and the initial COD, since dy/dx was equal to -58.21 and the relationship was similar to that of a zero-order reaction.

Sludge performance was characterized by SV. Sedimentation time was optimized by measuring the percentage volume of sludge and effluent COD.

There was no significant difference in the COD concentrations under different sedimentation times. The coefficient of variation (CV) was 1.2%, which was within an acceptable range. Meanwhile, SV changed under different sedimentation times, which suggests that this is a feasible way to decant water during sedimentation as long as a certain water and sludge buffer volume is maintained.

SBR Mechanisms

For biological treatments, especially those with active sludge, mechanisms are normally understood to be a complex combination of physical, chemical, and biochemical reactions that include initial absorption of organic pollutants and metabolism of microorganisms. However, for polyurethane wastewater containing low-boiling-point alcohol and esters, the effects of air stripping and self-volatilization should also be considered. To confirm this hypothesis, we used two simple blank experiments. In experiment B1, inoculum sludge was displaced by tap water while other parameters remained the same as for the sludge acclimation phase. Experiment B2 was exactly the same as B1, except that it was aerated. The COD concentrations of the systems were measured after 12 h. The two blank tests were repeated three times and the results are shown in Table 3.

Results show that both air stripping and volatilization contributed to COD removal in polyurethane manufacturing wastewater. The contribution of self-volatilization was less than 3.6%, while almost 10.0% of COD was removed by air stripping. These results suggest that the effects of air stripping should not be ignored in the SBR system. It was demonstrated by R.A Caffaro-Filho that aeration during wastewater biotreatment processes mainly strips VOCs from the wastewater to the atmosphere and would then reduce the toxicity of the wastewater and achieved better performance of the activated sludge treatment process [7]. So the air stripping self-volatilization effect may contribute to the high COD removal rate achieved by SBR and further improvement of SBR apparatus, and risk assessments should be of concern with regard to air pollution control.

Evaluation of Three Methods

Efficiency and economy should be well balanced when treating small amounts of polyurethane wastewater. Out of the three methods, the ozonation process was excluded because of its low COD removal efficiency ($\leq 15.0\%$) from wastewater and the high investment needed for the ozone

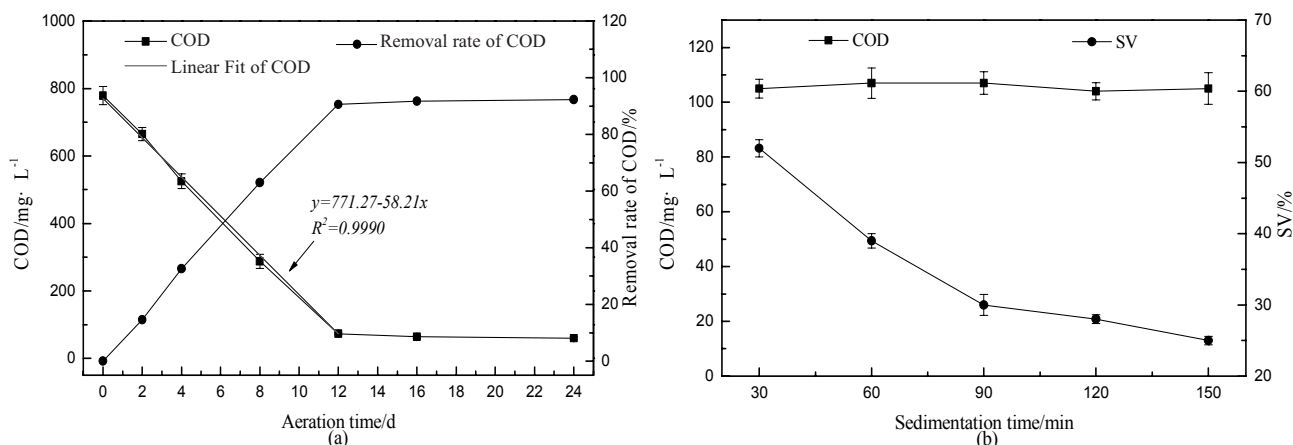


Fig. 3. Effect of aeration time and sedimentation time on SBR system.

generator, its operation, and maintenance. While the results from the Fenton process appear satisfactory (76.4%), there are still several defects. First, the Fenton process is based on a chemical reaction and is much more violent than a biological method, which may result in potential threats during operation. Second, the reagents used for the Fenton process were corrosive, which resulted in higher apparatus and pipe maintenance. Moreover, the effluent from the Fenton process needed further treatment to decompose the remaining hydrogen peroxide and precipitated ferrous irons, which resulted in a large amount of sludge and a cost for additional alkaline usage. The biological SBR method was superior to the Fenton and ozonation processes, not only because of its high COD removal ability but also because of, among other factors, its high buffering ability that allows it to resist load shock, the greater possibility to automate the process, the shorter technological process, and lower construction and operational costs. But the potential risks of VOCs stripping out during the aeration process should be of concern with regard to air pollution and health threat control.

Conclusions

Three methods, including the Fenton process, ozonation, and SBR, were used to reduce the COD concentration of low-boiling-point alcohol ester wastewater generated during the extraction and evaporation processes of the polyurethane manufacturing industry. An average COD removal rate of 93.3% was obtained by the SBR system when the influent COD concentration was diluted to about 1,600 mg·L⁻¹, while the highest COD removal rates achieved by the Fenton and ozonation processes were 76.4% (when the H₂O₂/COD ratio was 0.0623 mM·g⁻¹ and Fe²⁺ was 0.0102 mM·g⁻¹) and 15.0% (when the average ozone production was 1 g·h⁻¹ and the ozonation time was 45 min), respectively. The operation parameters of the SBR system were optimized (when the influent COD concentration was 1,600 mg·L⁻¹ and the MLSS concentration was around 4,260 mg·L⁻¹), and results showed that the aeration time was 12 h, a COD removal rate of 90.6% was achieved, while increasing the aeration time from 12 to 24 h did not significantly improve SBR efficiency. Also, with a sedimentation time of between 60 and 90 min, the SV was reduced to below 40% without any significant difference in COD removal rate. Air stripping and self-volatilization contributed to 3.6% and about 10.0% COD removal in the SBR system. Treating this kind of wastewater with an SBR system could ensure that the effluent meets its emission standards. Compared with the other two chemical methods, the SBR method may be a practical method to treat polyurethane wastewater because of the high COD removal rate, simplicity, and operational flexibility. However, considering how air-stripping and volatilization contributed to the removal of COD in the SBR system, which may result in toxic and mutagenic compounds stripped into the environment, the feasibility of SBR should be further assessed and possible improvements to the system should be considered. All in all, the results from this study provide useful

information on methods available for treating small amounts of polyurethane wastewater and equipment development.

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