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Anaerobic-aerobic biodegradation of antibiotic wastewater

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ABSTRACT

The purpose is to improve the treatment effect on the antibiotics in the wastewater of livestock farms. The antibiotic wastewater from a livestock farm is taken as the research object. The wastewater from the livestock farm is sampled and analyzed through batch anaerobic biochemical degradation experiment and direct aerobic biochemical degradation experiment. Also, an anaerobic and aerobic biochemical test device is constructed in the laboratory to study the removal effect on the antibiotics in the wastewater based on anaerobic biochemical degradation and aerobic biochemical degradation technologies. The results show that the removal rate of antibiotics in the wastewater of the livestock farm by anaerobic biochemical degradation technology is only about 25%. The main reason is that sulfa mono methoxine (SMM) is difficult to be degraded by anaerobic degradation technology, and its concentration in the wastewater is more than 95%. And the degradation effect of anaerobic biochemical treatment on sulfonamide antibiotics is far less than that on lactam antibiotics. When the concentrates of sulfadiazine (SD), sulfamethoxazole (SMX), sulfamethazine (SMZ), and SMM (sulfamonomethoxypyrimidine) in the wastewater are high, the degradation effect of anaerobic sludge on the four is SMX > SD > SMZ > SMM. In the direct aerobic biochemical treatment, aerobic sludge has good degradation ability for sulfonamides and β-lactam antibiotics, and the overall removal rate of antibiotics in the wastewater can reach more than 80%. When the concentrates of SD, SMX, SMZ, and SMM in the wastewater are high, the degradation effect of aerobic sludge on the above four antibiotics in the direct aerobic treatment is SD > SMX > SMZ > SMM.

Keywords: Antibiotics; Anaerobic biochemical treatment; Aerobic biochemistry treatment; Degradation effect

1. Introduction

In recent years, with the rapid development of the livestock industry, the large amount of antibiotic wastewater discharged from the livestock industry becomes one of the important sources of antibiotic pollution. The most typical types of pollutants are sulfonamides and β-lactam antibiotics. However, the ability of current pollution control equipment to remove refractory pollutants like antibiotics on livestock farms is limited [1]. At the same time, people in the livestock industry often overuses antibiotics due to the turn of the season, temperature changes, and infectious diseases, which continuously aggravates the problem of antibiotic pollution in the environment. Antibiotics, as a substance that is difficult to be biodegraded, are easily attached everywhere in the ecological environment, resulting in antibiotic residues in the environment, and ultimately bringing great threats to the security of the environment. An appropriate amount of antibiotics can protect human health. But if they are beyond the normal standard in drinking water, antibiotics will not only cause food safety problems but also lead to the imbalance of gastrointestinal flora and other health problems [2,3].

Based on the above analysis, the antibiotic wastewater from a livestock farm is taken as the research object to explore the degradation effect of anaerobic and aerobic biological treatment technologies on the removal of antibiotics (especially sulfonamides and β-lactams antibiotics).

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The removal effects of anaerobic and aerobic biological treatment on antibiotics in the wastewater and the treatment effects of two tests on high-concentration antibiotic wastewater are mainly analyzed. The influence of hydraulic load and sludge concentration on removing antibiotics in the wastewater is mainly explored. The results of the anaerobic biodegradation test of antibiotic wastewater from the livestock farm show that the degradation effect of anaerobic biochemical treatment on removing antibiotics (especially SMM) is poor, and the overall removal rate is not more than 25%. The removal effect of antibiotics in the wastewater is not significantly correlated with the change of sludge concentration [4]. The degradation effect of sludge on the main antibiotics in the wastewater during anaerobic biochemical treatment is sulfamethoxazole (SMX) > SD (sulfadiazine) > SMZ (sulfamethazine) > SMM (sulfamonomethoxypyrimidine). The degradation effect of sludge on the above four antibiotics during direct aerobic treatment is SD > SMX > SMZ > SMM. This study improves the removal rate of antibiotics in the wastewater of livestock farms and provides a theoretical reference for the research on anaerobic and aerobic biochemical treatment technologies [5].

2. Method

2.1. Main chemical reagents

2.1.1. Main chemical reagents and their specifications

The main chemical reagents and their specifications required in this experiment are shown in Table 1.

Table 1
Main chemical reagents

Chemical reagents	Specification
H_2SO_4	94.0%–98.0%
HCI	35.0%–39.0%
NH_4CI	≥99.8%
Na_2HPO_4	AR
Na_2CO_3	≥99.8%
NaOH	≥96.5%
$HgSO_4$	≥98%
$K_2Cr_2O_7$	≥99.5%
Ag_2SO_4	≥98.0%
$K_2S_2O_8$	≥99.5%
NH_2HSO_3	AR, 99.5%
$C_6H_7NO_3S$	Reagent ACS
Urea	99.0%

2.1.2. Wastewater required for the test

The wastewater in this study is discharged by a livestock farm. The wastewater is mainly composed of the urine of the livestock and the water used to wash the shelters of livestock. The wastewater is separated from the solid waste by a solid-liquid separation device and then mixed with the manure of the livestock. After it is fermented, the mixture is used for farmland as an organic fertilizer [6]. About 40% of the wastewater from the primary sedimentation tank is put into the anaerobic digestion tank (about 55 d) and discharged to the storage pool after anaerobic biochemical treatment. There are some defects in the structure of the anaerobic digestion tank of this farm, and it is impossible to treat all the wastewater here. Therefore, about 60% of the wastewater is directly put into the storage pool without anaerobic digestion (about 90 d) and then mixed with a certain amount of river water for farmland irrigation [7]. In this study, three sampling points are selected at the inlet of the anaerobic digestion tank, the outlet of the anaerobic digestion tank, and the outlet of the storage pool, as shown in Fig. 1.

2.1.3. Experimental method

2.1.3.1. Anaerobic biological treatment technology

The volume of the reaction bottle selected for anaerobic biochemical degradation is 1L, and the main material of the bottle is organic glass, as shown in Fig. 2. The mouth of the reaction bottle is sealed with a wooden plug. The water sample is sucked out or injected by a syringe, and the biogas produced during the anaerobic biochemical process is discharged into the air through a water-tight seal bottle [8]. The sludge required for anaerobic biochemical degradation is obtained by Upflow Anaerobic Sludge Bed (UASB) of an enterprise. During the experiment, the anaerobic bottle is placed in a constant temperature box, which maintains a rotating speed of 160 rpm and a temperature of 35°C ± 2°C. This experiment is conducted intermittently, with 24-h as a cycle, including a 22-h oscillating reaction and a 2-h settlement. In the experiment, the time of suction and injection of the water sample is very short, so it could be ignored. The load and hydraulic retention time (HRT) of the wastewater are controlled by changing the amount of water sucked out and injected. In the initial stage of the experiment, the inoculated sludge is domesticated by increasing the influent load, so that it can adapt to the wastewater from the farm [9]. The anaerobic test is divided into four stages, and the influent conditions of each stage are shown in Table 2.

2.1.3.2. Aerobic biological treatment method

Sequencing Batch Reactor (SBR) is used for aerobic biological treatment. Four reactors are needed in this experiment, and the volume of each reactor is 5 L. The sludge needed in the experiment is taken from the aeration tank of

Table 2
Operating conditions for the anaerobic treatment of the wastewater of a livestock farm

Stages	1	2	3	4
Time (d)	1–25	26–46	47–65	66–220
Water intake (L/d)	0.15	0.20	0.25	0.3
HRT (d)	10.5	8.5	5.5	3.4
MLSS (g/L)	15.8			

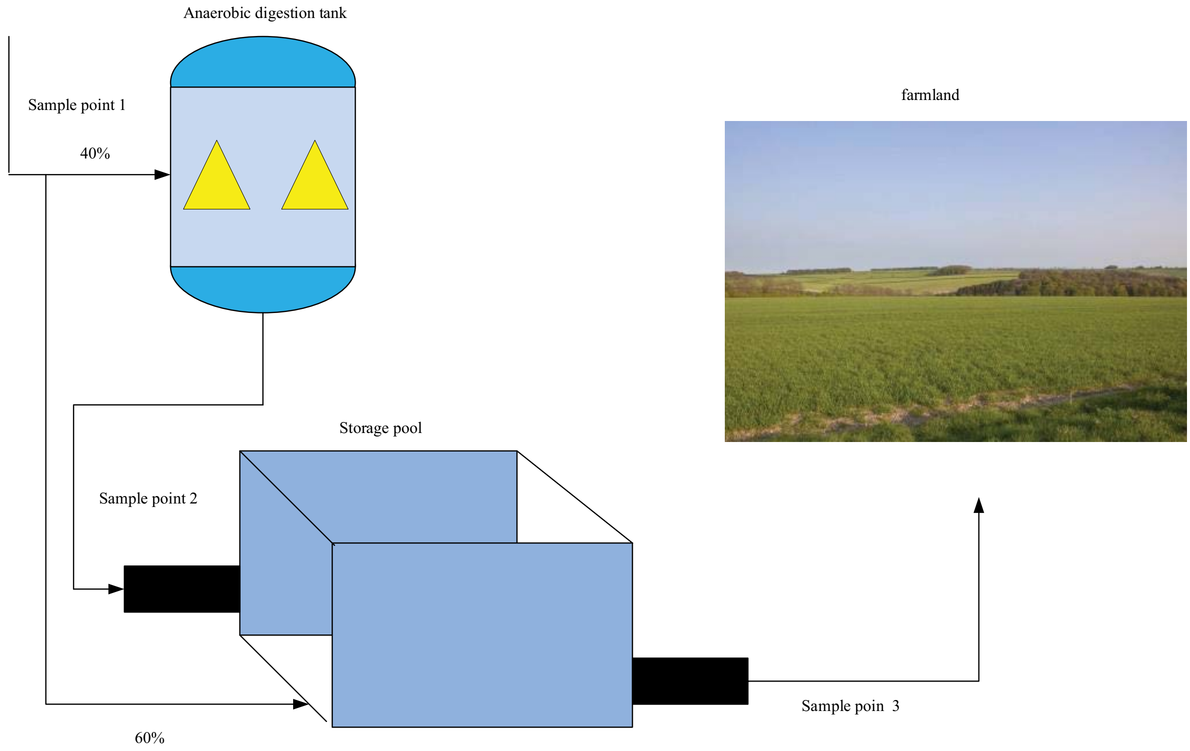

Fig. 1. Treatment process of the wastewater of a livestock farm.

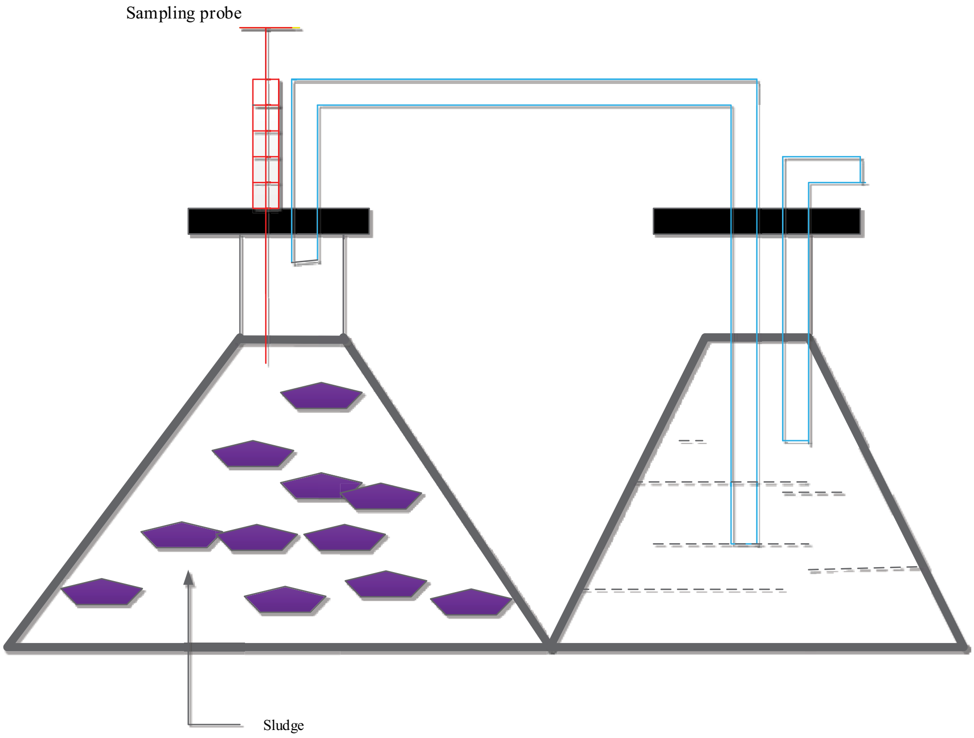

Fig. 2. Anaerobic test device.

a water purification plant. During the experiment, the dissolved oxygen concentration in the SBR tank is controlled to be 1.8–4.5 mg/L, the pH dimension is 7.0 ± 0.5, and the experimental temperature is room temperature. The period of this experiment is also 24 h, of which 21 h are used for aeration reaction and 3 h for static precipitation. Like anaerobic biochemical degradation, due to the short time spent at the inlet and outlet in the experiment, it can be ignored. The aerobic biological treatment experiment includes six stages in a complete test cycle, as shown in Table 3.

3. Results and discussion

3.1. Treatment effect of the wastewater based on anaerobic biochemical treatment

3.1.1. Removal effect of anaerobic biochemical treatment on antibiotics

Anaerobic biochemical treatment technology has the advantages of great treatment capacity and low energy consumption, which makes it widely used in the treatment of antibiotic wastewater [10]. The wastewater from livestock farms usually contains high concentrations of antibiotics and has good biodegradability. At present, most livestock farms have anaerobic biochemical treatment systems for wastewater. In the study, the change rule of degradation effect of new pollutants like antibiotics in the wastewater during anaerobic degradation is explored, the degradation effect of anaerobic treatment technology on antibiotics and other pollutants through intermittent anaerobic experiments is investigated. Due to the limitation of equipment in different experimental stages, it is impossible to accurately measure the antibiotics in the wastewater. All the data of antibiotics in this experiment are obtained in the final stage, namely in the fourth experimental stage [11,12].

The removal effect of antibiotics in the anaerobic treatment of the wastewater is shown in Figs. 3 and 4. The data in the figures are measured 120 d later after the anaerobic treatment. Fig. 3 shows that the antibiotic concentration in the wastewater at the outlet and inlet of the anaerobic reactor is very close, that is, the antibiotic concentration changes little after the anaerobic treatment, and it is only about 3%, as shown in Fig. 4. This may attribute to the weak degradation ability of anaerobic microorganisms

Table 3
Operating conditions for the aerobic treatment of the wastewater of a livestock farm

Stages	1	2	3	4	5	6
Time (d)	1–30	31–56	57–95	96–145	146–205	206–246
Water intake (L/d)	1.8	0.5	0.5	0.8	1.2	1.8
HRT (d)	3.5	17.0	17.0	11.0	6.0	3.5
MLSS (g/L)	3.2–3.8	3.8–4.2	3.8–5.2	4.3–6.5	5.0–7.0	5.8–7.4

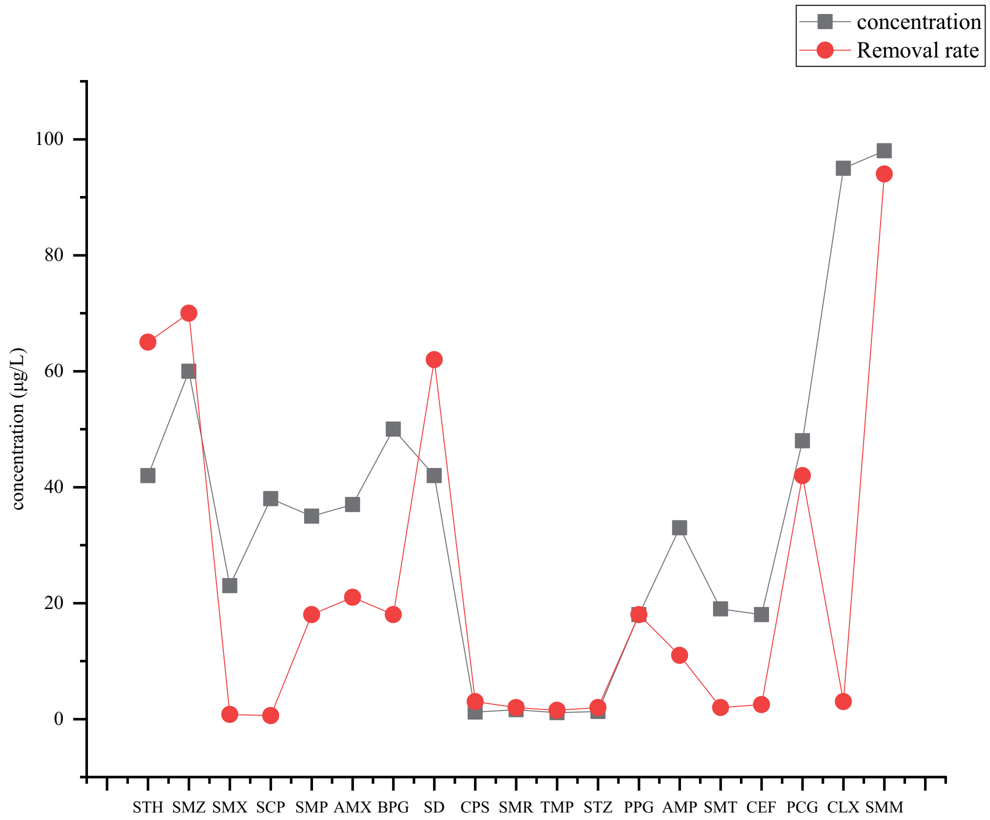

Fig. 3. Degradation effect of the anaerobic biochemical treatment on antibiotic wastewater from livestock farms (a).

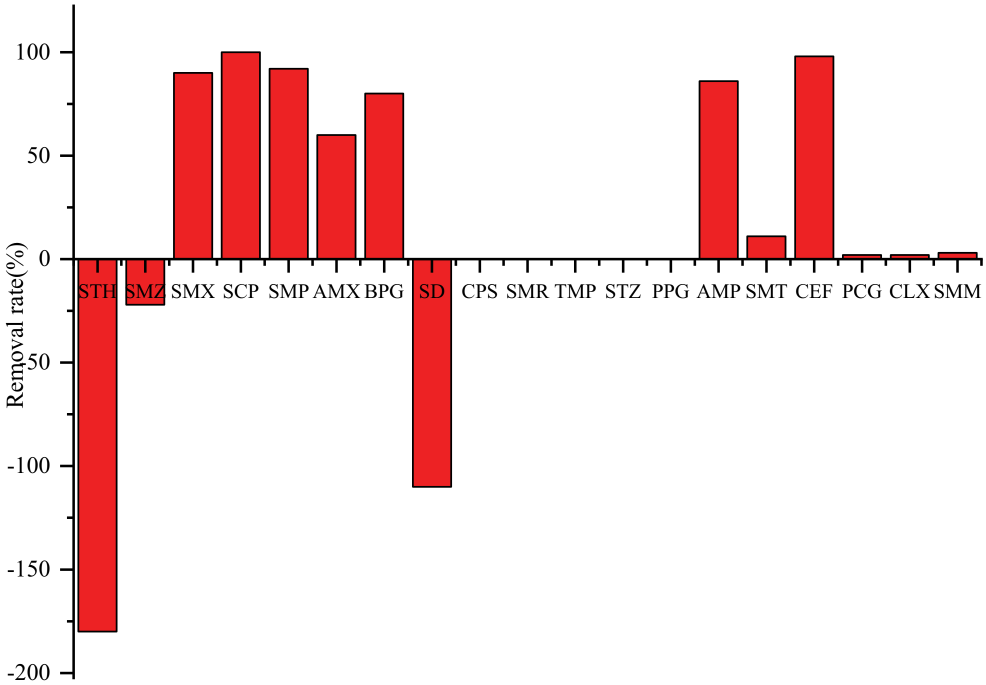

Fig. 4. Degradation effect of the anaerobic biochemical treatment on antibiotic wastewater from livestock farms (b).

for SMM. However, SMM is a class of antibiotics with the highest proportion in the wastewater of livestock farms [13]. Therefore, the ability of anaerobic treatment technology to remove antibiotics in wastewater (especially the wastewater with high concentrations of antibiotics) is limited because antibiotics have some functional groups that are difficult to be degraded, like aromatic rings and double bonds [14,15].

Figs. 3 and 4 show that the degradation effect of the anaerobic biochemical treatment on β-lactam pollutants is very good, while the degradation effect on sulfonamide antibiotics is poor. The degradation rate of lactam pollutants is about 70%, and that of sulfonamide antibiotics is about 2%. Compared with sulfonamide antibiotics, β-lactam antibiotics are more easily degraded by anaerobic biochemical treatment [16]. In addition, it is found that the removal rates of some antibiotics (SD, SMZ, and STH) are negative. This may be because the concentration of these substances at the inlet of the reactor is higher than that at the outlet after anaerobic reactor treatment, which is consistent with the actual detection of the inlet and outlet of the anaerobic digestion tank in the livestock farm [17,18].

3.1.2. Degradation effect of anaerobic sludge on high concentration antibiotics

Livestock farms will increase the amount of antibiotic use and other drugs for livestock because of weather changes, the turn of the season, and infectious diseases among livestock, which directly leads to a significant increase of antibiotics in the wastewater. Therefore, it is necessary to explore the degradation effect of anaerobic sludge on the wastewater with plenty of antibiotics. In this experiment, the degradation effect of aerobic sludge on four types of antibiotics in the wastewater is analyzed [19]. The four types of antibiotics are SD, SMX, SMZ, and SMM respectively, and injected into the wastewater at 250 μg/L. Then, the aerobic degradation test is carried out on the wastewater injected with antibiotics. The degradation effect of anaerobic sludge on the above four types of antibiotics is shown in Fig. 5.

Fig. 5 shows that the concentrations of SD and SMZ at the outlet of the anaerobic reactor will continue to decrease with the extension of the experimental time and the continuous injection of the above four types of antibiotics, which indicates that the degradation effect of the anaerobic sludge on SD and SMZ is strengthened with the extension of the experimental time. In addition, the concentration of SMX at the outlet of the reactor is low except for day 202, which further shows that anaerobic sludge is easy to degrade SMX, which is also related to the strong adsorption capacity of anaerobic sludge for SMX. Fig. 5 shows that SMM is most difficult to be degraded by anaerobic sludge. During 135–202 d, the concentrations of SD, SMZ, SMX, and SMM at the outlet of the reactor are 59.1, 76.6, 5.6 and 341.9 μg/L, respectively, and the corresponding removal rates of the antibiotics are about 76.4%, 69.4%, 97.8%, and 23.8%, respectively. Therefore, it can be concluded that the degradation effect of anaerobic sludge on the above four antibiotics is SMX > SD > SMZ > SMM. The total removal rate of the four types of antibiotics is 50%–69%, with an average rate of about 59.7%. Obviously, after a certain concentration of SD, SMZ, SMX, and SMM are added to the wastewater, the removal rate of anaerobic biochemical treatment for antibiotics is far better than that of anaerobic biochemical treatment without antibiotics. This is mainly due to the following two reasons. On the one hand, the effect of anaerobic biochemical treatment is better when the concentration of antibiotics at the inlet is relatively high. On the other hand, except for SMM, the degradation

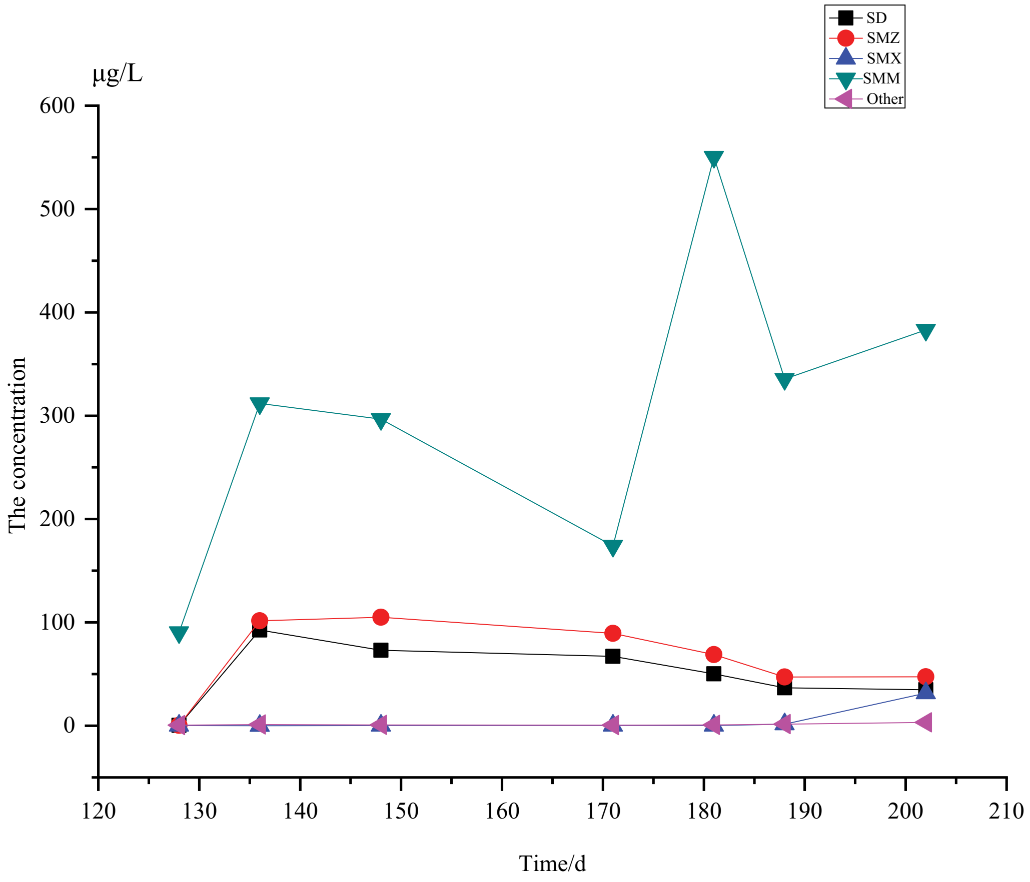

Fig. 5. Degradation effect of anaerobic sludge on the antibiotics with a high concentration

effect of anaerobic biochemical treatment on the other three types of antibiotics (SD, SMZ, and SMX) is good. In the anaerobic treatment without adding antibiotics to the wastewater, SMM is difficult to be degraded because its concentration in the wastewater is more than 95% [20,21].

3.2. Treatment effect of the wastewater based on direct aerobic biochemical treatment

3.2.1. Removal effect of direct aerobic treatment on antibiotics

According to the above analysis, the removal effect of anaerobic biochemical treatment on the antibiotics in the wastewater is very poor, and the removal rate is only about 25%. Therefore, the removal effect of aerobic biological treatment on the antibiotics in the wastewater is studied in this section.

The wastewater from a livestock farm is treated by direct aerobic treatment technology, and the degradation effect on the antibiotics is shown in Figs. 6 and 7. Fig. 6 shows that in each stage of the experiment, the removal rate of antibiotics by direct aerobic treatment is more than 80%. During the whole experiment, the daily volumes of the wastewater needed to be treated are 500, 1,000, and 1,500 mL, respectively. The average concentrations of antibiotics at the outlet are 7.5, 11.8, and 32.6 μg/L, respectively. The overall concentrations of sulfonamide antibiotics are 7.6, 11.5, and 32.8 μg/L, respectively. The total concentrations of β-lactam antibiotics are 0,478 and 930 μg/L, respectively. The concentration of antibiotics at the outlet of the SBR system will increase with the increase of water intake. Fig. 7 shows that the direct aerobic biochemical treatment has a good effect on the removal of β-lactam and sulfonamide antibiotics, and can achieve a higher removal rate of antibiotics. And the removal rate of antibiotics in the wastewater after direct aerobic treatment exceeds 75%, but the total concentration of antibiotics at the outlet is low.

3.2.2. Degradation effect of aerobic sludge on the wastewater with a high concentration of antibiotics

Livestock farms will increase the use of antibiotics and other drugs for livestock due to weather changes, the turn of the season, and sudden infectious diseases, which directly leads to a significant increase of antibiotics in wastewater. Therefore, the degradation effect of aerobic sludge on the wastewater with a high concentration of antibiotics is explored [22]. In this experiment, the degradation effect of aerobic sludge for the wastewater with a high concentration of four types of antibiotics is analyzed. The four types of antibiotics are SD, SMX, SMZ, and SMM. The above antibiotics are injected into the wastewater at 250 μg/L, and then the aerobic degradation test is carried out on the wastewater injected with antibiotics. The degradation effect on each type of antibiotics is shown in Fig. 8.

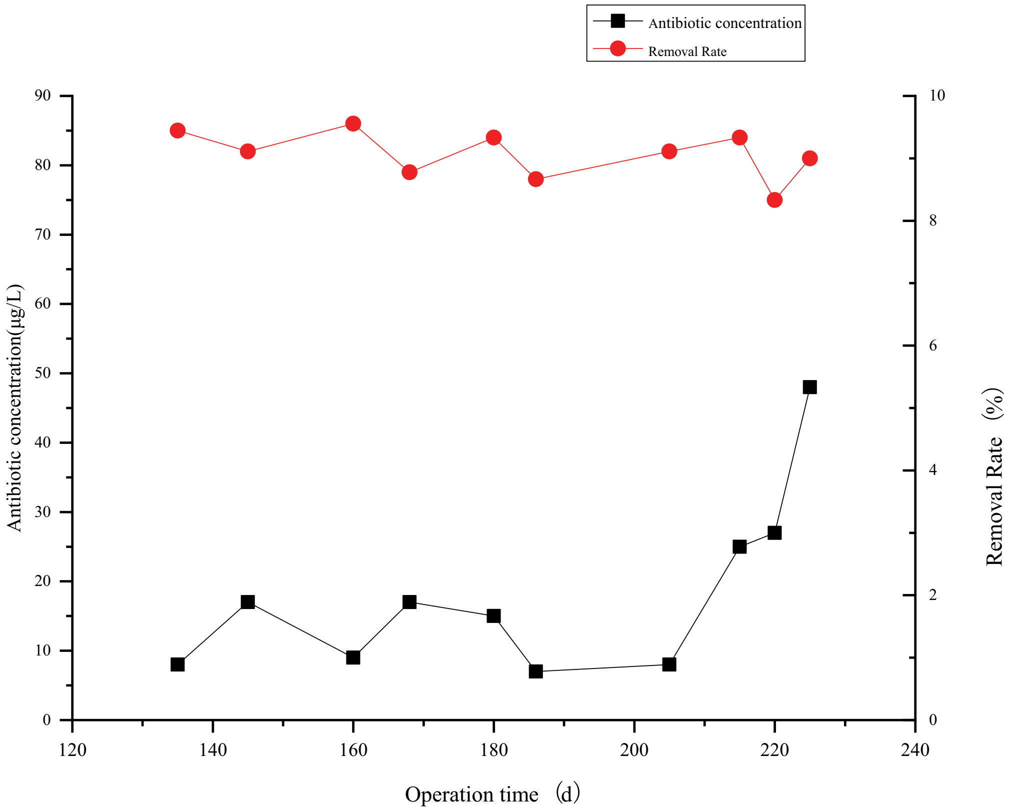

Fig. 6. Effect of aerobic biochemical treatment on antibiotics in the wastewater from a livestock farm (a).

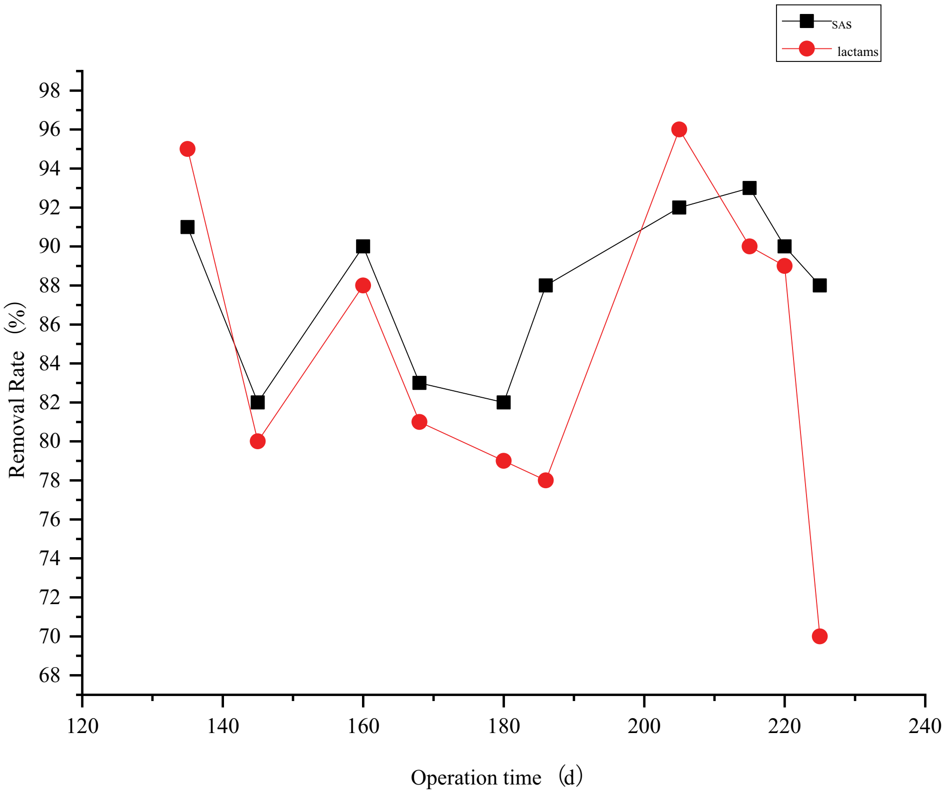

Fig. 7. Effect of aerobic biochemical treatment on antibiotics in the wastewater from a livestock farm (b).

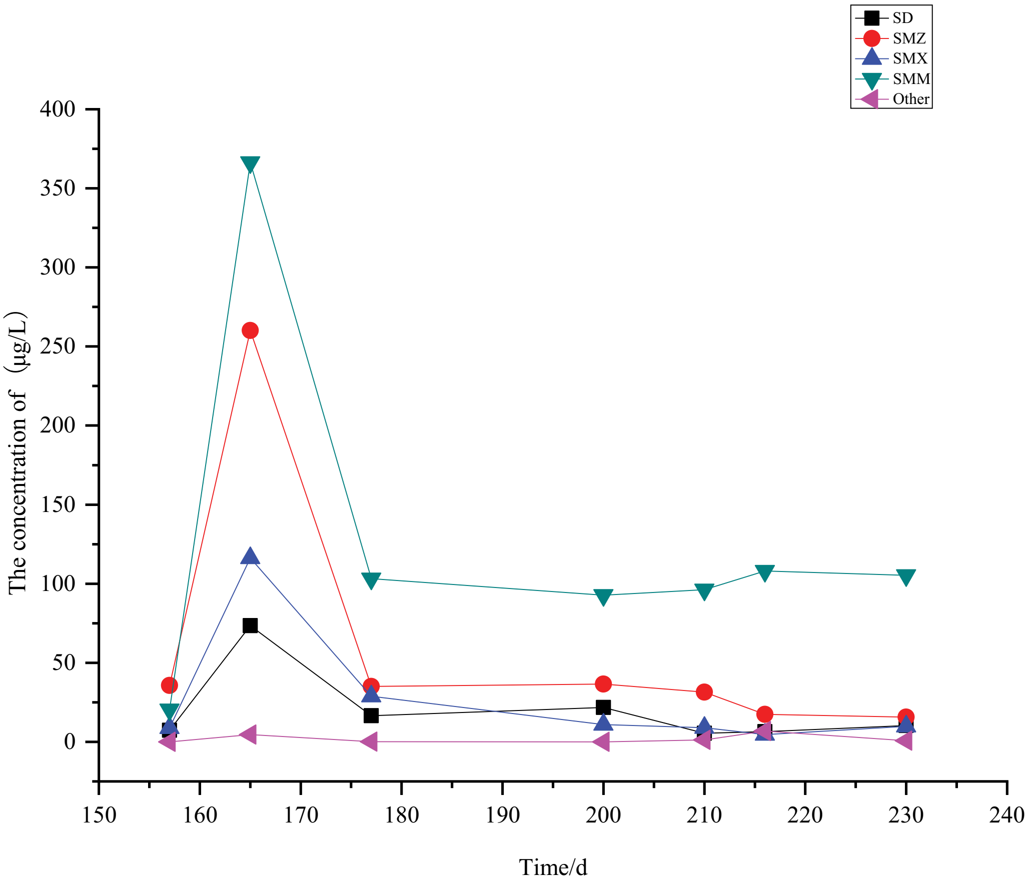

Fig. 8. Effect of aerobic sludge on the antibiotics in the wastewater of a livestock farm.

Fig. 8 shows that when the above four types of antibiotics are continuously injected into the inlet of the aerobic reactor, their concentrations at the outlet of the reactor begin to decrease from day 165. After the reaction is stable, the average concentrations of SD, SMX, SMZ, and SMM at the outlet of the reactor are 11, 8.5, 25.2, and 100.6 μg/L, respectively. It can be concluded that the removal effect of aerobic sludge on the four types of antibiotics is SD > SMX > SMZ > SMM.

4. Conclusions

The degradation effect on antibiotics in the wastewater of a livestock farm is studied by batch anaerobic biochemical treatment test and SBR direct aerobic biochemical treatment test. And the degradation effect on the wastewater with a high concentration of antibiotics under two different tests is studied. The results show that the removal effect on the antibiotics in the wastewater of a livestock farm by anaerobic biochemical treatment is very poor, only about 25%. The main reason is that the content of SMM in the wastewater is more than 95%. When the concentrations of SD, SMX, SMZ, and SMM in the wastewater are high, the degradation effect of anaerobic sludge is SMX > SD > SMZ > SMM. In the direct aerobic biochemical treatment process, aerobic sludge has good degradation ability for removing sulfonamides and β-lactam antibiotics, and the overall removal rate of antibiotics in the wastewater can reach more than 80%. When the concentrations of SD, SMX, SMZ, and SMM in the wastewater are high, the degradation effect of aerobic sludge on the above four types of antibiotics by the direct aerobic treatment is SD > SMX > SMZ > SMM.

The degradation effect of anaerobic and aerobic biochemical treatment on antibiotics in the wastewater is studied at room temperature. The temperature of the wastewater discharged from livestock farms is generally very low in winter. Therefore, the follow-up study will try to test the degradation effect of anaerobic and aerobic biochemical treatment on antibiotics in the wastewater of livestock farms at different temperatures, so that the influence of the types and quantity of antibiotics in the wastewater on the removal effect is explored, and the degradation effect of anaerobic and direct aerobic biochemical treatment on antibiotics in low temperature is studied.

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