RESEARCH ARTICLE

Performance study of activated carbon reinforced internal circulation reactor for high-salt organic production wastewater treatment

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When the biological method is used to treat organic wastewater with high salinity, the large amount of salt has a strong inhibitory effect on microbial growth. Therefore, traditional biological and physical-chemical treatment technologies are difficult to meet the standards for treating high-salinity organic wastewater. There is an urgent need to study how to strengthen the biological treatment process for the treatment of high-salt production wastewater. This study investigated the effect of activated carbon biofortification anaerobic reactor with coconut shell granular activated carbon. The study found that the optimal dosage of activated carbon was 6 g/L. The results demonstrated that mixing 2 g/L activated carbon with activated sludge before entering the wastewater treatment had a stronger treatment effect than making activated carbon and wastewater entering the reactor at the same time to contact sludge. The treatment effect of the internal circulation (IC) system with granular activated carbon under the optimized dosage and method was better than that of the IC system that was not reinforced with activated carbon with the removal rate increased by 4-10%. Activated carbon enhanced IC reactor had higher resistance to organic load impact and better chroma removal ability. These results provided reference for the treatment of similar high-salinity organic industrial wastewater.

Keywords: activated carbon biofortification anaerobic reactor; IC reactor; fatty acid high-salt organic wastewater.

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Introduction

Many chemical and pharmaceutical companies produce large amounts of high-salinity and high-concentration organic wastewater during the production process. The salt-containing organic wastewater has large discharge, high content of toxic, and harmful organic matter, thus posing a great threat to the environment. The treatment technology for high-salinity organic wastewater holds an important place in wastewater treatment. As a low-cost biotechnology, anaerobic biochemical treatment technology can stably and efficiently remove pollutants under high organic load. However, when this method is applied to treat organic wastewater with high salinity, the large amount of salt has a strong inhibitory effect on microbial growth, which makes the processing efficiency being reduced and the application of the traditional biological processing being limited. Therefore, it is an urgent need to develop a more efficient, economical, and applicable treatment technology for the high-salinity organic wastewater.

Currently, the most reported anaerobic reactors mainly include upflowed anaerobic sludge bed reactor (UASB) [1, 2], anaerobic fluidized bed anaerobic composite reactor, expanded granular sludge bed reactor (EGSB) [3, 4], and internal circulation reactor (IC) [5, 6]. The activated carbon reinforced aerobic process for activated sludge has been successfully used in many engineering practices and achieved good results such as petrochemical wastewater treatment [7, 8]. However, there are few studies on its application in anaerobic reactors [9-11], especially in the IC reactor [12-15].

This study used hypersaline fatty acid wastewater to explore the effect of activated carbon on the start-up of IC anaerobic reactors and the treatment performance for high-salt and high-concentration organic wastewater [16-19], and, in addition, to observe whether activated carbon could promote the formation of anaerobic granular sludge [20, 21]. Based on the water quality characteristics of high salt and high-concentration organic matter, this study focused on the role of activated carbon reinforced IC reactors in the treatment of hypersaline fatty acid wastewater. A comparative study was conducted to investigate the effect of adding activated carbon on the biological treatment system and its mechanism. The results of this study would provide a reference scheme and basis for the design of bio-reinforced anaerobic treatment process for high salt organic wastewater.

Materials and Methods

Activated carbons

Three (3) types of powder activated carbons including coal powdered carbon (P1), wood powdered carbon (P2), and coconut shell powdered carbon (P3) (Hanyan, Guangzhou, Guangdong, China) and 3 types of granular activated carbons including coal-based granular carbon (G1), wooden granular carbon (G2), and coconut shell granular carbon (G3) (Huairen Huanyu Purification Material Co., Lt, Tianjin, China) were employed in this study. All activated carbons were dried in an XMT-152A oven (Shanghai Yuejin Medical Equipment Factory, Shanghai, China) at 105°C and stored in a drying dish.

Preparation of simulated wastewater

The simulated wastewater experiment device mainly consisted of an anaerobic reactor (a simulated beaker) and a DK-98-IIA thermostatic magnetic stirring water bath (Tianjin Tester Instrument Co., LTD, Tianjin, China). The reaction temperature was set as 35±5°C. The artificial test water was prepared by mixing glucose with water, and then, adding urea and potassium dihydrogen phosphate to adjust the ratio of chemical oxygen demand, total nitrogen, and total phosphoru (COD:N:P) to 500:5:1. The trace elements including Ca^{2+}, Mg^{2+}, Fe^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} were added simultaneously. Meanwhile, $NaHCO_3$ was added to the water to adjust the pH of the solution in the range of 6.5~7.5. The ratios of glucose were changed by dissolving it in different amounts of Na_2SO_4 to form raw wastewater with different salt contents.

Seeding sludge

The anaerobic biological filtered granular sludge from the sewage treatment plant of Jinshawan Industrial Park, Hukou, Jiujiang, Jiangxi, China was used as the seeding sludge. The seeding sludge was dark brown color with the volatile suspended solids (VSS) concentration of 44.7 g/L, and the total suspended solids (TSS) concentration of 59.4 g/L. Before seeding, the sludge particles were screened and washed, and then rinsed and activated with artificial water with the COD concentration of about 22,000 mg/L and the SO_4^{2-} concentration of about 8,000 mg/L. The amount of seeding sludge in the IC reactor was 16 L.

Selection of activated carbon

200 mL of activated sludge that had been cultured with the simulated wastewater for one week was mixed with each type of activated carbon in a 500 mL beaker, respectively. After stirring evenly, more wastewater was added to an effective volume of 400 mL to make the concentration of activated carbon in each beaker 2 g/L. After standing for 2 h, the upper clear layer of each beaker was drained, and the wastewater was added to the volume to 400 mL in each beaker again, making the mixed liquid suspended solids (MLSS) in the beaker reaching 20,000 mg/L. During the experiment, the COD concentration of wastewater was within the range of 12,000-15,000 mg/L, and the reaction temperature was controlled at 35±5℃ in DK-98-IIA water bath (Tianjin Tester Instrument Co., LTD, Tianjin, China). The contents in each beaker was stirred and shaken well, and the water samples taken from each beaker were passed through a 0.45 µm microporous membrane to determine the COD content of the filtrate. The experiment lasted for a total of 10 days. Then, the relationship between different types of activated carbon and COD removal rate was obtained and analyzed.

The COD, salinity (SO_4^{2-}), pH, volatile fatty acid (VFA), and the temperatures of the influent and effluent of the reactor were continuously measured every day. The flow rate of inlet water and circulation amount were recorded in each stage every other day. Microbial community structure, morphology of the sludge, and chromaticity were also analyzed. The COD was measured by using potassium dichromate method. VFA was measured by using titration method. The concentration of suspended solids (SS) sludge and salt content were measured by using gravimetric method. pH was determined by using acidimeter. Microbial community structure was determined by using high-throughput sequencing. Chromaticity was measured by applying dilution times method.

Determination of the optimal amount and dosing of activated carbon

The optimal amount of selected activated carbon was determined by mixing 200 mL of activated sludge with 200 mL of wastewater in a 500 mL conical bottle to bring the MLSS to 20,000 mg/L. The different concentrations of selected activated carbon were tested at 2 g/L, 4 g/L, 6 g/L, and 10 g/L, respectively, with 0 g/L as the control. The concentration of wastewater was in the range of 12,000-22,000 mg/L and the temperature of the water bath was set at 35±5℃. The solution was shaken gently and then placed at rest for 2 h. The upper layer of each reaction was removed, and the wastewater was added to replenish the volume to 400 mL. The samples taken from each reaction were passed through a 0.45 µm microporous filter membrane and the COD contents of the filtrate were determined. The experiment was conducted for 16 days. The relationship between the COD removal rate and the concentration of activated carbon was analyzed and expressed as reactor effective volume.

Determination of the dosing method of activated carbon

Four reactions were set for this investigation. Briefly, 200 mL of activated sludge were placed in 3 beakers with only No.1, beaker adding coconut shell granular carbon. An additional beaker No.4 was only activated carbon added. Except for the No.2 beaker that the activated carbon was added with the wastewater at the same time, the other three beakers were all added with the wastewater. Additional wastewater was added to bring the total volume to 400 mL. After standing for 2 h, the upper clear sample of each beaker was drained, and the samples were replenished to 400 mL with wastewater, making the MLSS in the beakers reach 20,000 mg/L. During the test, the COD concentration of wastewater was in the range of 4,000-12,000 mg/L, and the temperature of the water bath was controlled at 35±5°C. The solutions were shaken slightly, and the samples taken from each beaker were passed through a 0.45 µm microporous membrane to determine the COD content of the filtrate. The experiment lasted for a total of 4 days. The relationship between different dosing methods and COD removal rate was obtained and analyzed.

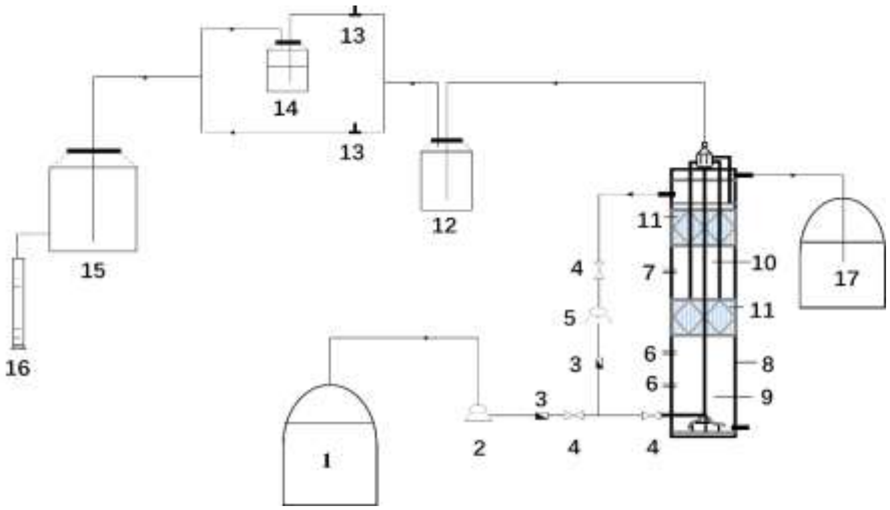

Figure 1. Flow chart of combined experimental device of IC reactor. (Note: 1. inlet bucket; 2. inlet pump; 3. rotor flowmeter; 4. control valve; 5. reflux pump; 6. sampling port; 7. feed port; 8. insulation material; 9. the first reaction zone; 10. the second reaction zone; 11. three-phase separator; 12. water sealed bottle; 13. valve; 14. CO_2 absorption bottle; 15. Markov bottle; 16. graduated cylinder; 17. outlet bucket).

Dynamic study of activated carbon enhanced IC reactor for the treatment of high salt fatty acid wastewater

(1) Customized IC reactor

The IC reactor was customized made of plexiglass in cylindrical shape with a volume of 38 L by Ruyi Organic Glass Products Factory, Wuhan, Hubei, China. The flow chart of IC reactor was shown in Figure 1. The reaction temperature was controlled at 35±5°C. The experimental water was prepared in the inlet bucket, and then passed through the inlet pump, rotameter, and control valve to reach the bottom of the V-shaped inlet of the reactor. The return pipe was in the sludge settlement area of the reactor, under the three-phase separator, and 45 cm away from the outlet pipe. The return water passed through the return pump and rotameter, mixed with new water in the water inlet pipe, and entered the reactor. The reactor was connected with a constant temperature water bath heating device. The surface of the reactor was covered by insulation material to insulate the reactor. The effluent from the reactor flew into the outlet bucket. According to its quality, the effluent would be either discarded or used to reconfigure the experimental water. Water-sealed bottle in the gas collection device was used to stabilize the voltage and ensure the stability of the three-phase separator. After the gas passed Water-sealed bottle, it would pass the CO_2 absorption bottle, Mariotte or Markov bottle, and measuring cylinder to measure the methane gas output. It could also skip the CO_2 absorption bottle and directly passed to Markov bottle and measuring cylinder to measure the total gas production. The inner diameter of the column in the IC reaction zone was 200 mm with a thickness of 10 mm and the total height of 1.2 m. The IC reaction zone was divided into upper and lower parts. The upper part was the first reaction zone, while the lower part was the second reaction zone. There were 4 sample holes with an inner diameter of 10 mm and 3 feed holes with an inner diameter of 50 mm on two sides of the reactor, respectively.

(2) Domestication of salt-tolerant sludge

The seeding anaerobic granular sludge should account for about 2/5 to 3/5 of the volume of the reactor. 10 kg of glucose was mixed with a ton of sludge and were added at the same time. In addition, urea and sodium dihydrogen phosphate were added at 1/20 and 1/100 of glucose amount, respectively. Before the test, the salt-tolerant activated sludge was cultivated and domesticated with the raw water of wastewater with 22,000 mg/L of COD and 8,000 mg/L of sulfate ion collected from the biochemical regulating tank of the enterprise for 9 days. The sodium bicarbonate was used to adjust the pH. The soaking water was changed every two days. After the seeding sludge basically adapted to the quality of the wastewater, it was fed into the reactor with the concentration within the range of 20,000 - 40,000 mg/L. A certain amount of Na_2SO_4 and the wastewater collected by the biochemical adjustment tank of the enterprise were used to prepare raw water with a salt content of 8,000 mg/L.

(3) Startup period

Activate carbon was added to the IC reactor according to the above selected dosing scheme. In order to facilitate the comparison of the effect of activated carbon addition to the IC reactor, the reactor startup program was almost the same as that without activated carbon addition of the IC reactor experiment. The experiments were divided into phases I to VI and lasted from April 2 to May 31, 2021, for a total of 60 days with each phase lasted for 10 days except for 12 days in the phase IV and phase VI, and 6 days in the phase V. The hydraulic retention time (HRT) remained at 38 hr. Flow remained at 1 L/h. The reactor was started up with the influent SO_2^{4-} concentration at 2,000 mg/L and maintained the COD:SO_2^{4-} mass ratio at 2.8:1. The influent SO_2^{4-} concentration gradually increased from 2,000 to 2,700, 4,000, and 4,800 mg/L in phases I, II, III, and IV, respectively, and then maintained at 4,800 mg/L from phases V-VI. The organic loading rate (OLR) gradually increased from 3.47 to 4.74, 6.95, and 8.34 kg COD (m^3d). Corresponding steps recorded as I, II, III, and IV, and then maintained 9.17 mg/L from phases V-VI.

Results and discussion

Selection of activated carbon types

Some studies have revealed that the adsorption performance of nutshell charcoal and wood charcoal is better than coal-based charcoal [1]. The comparison of the adsorption characteristics of the six activated carbons (all of them are 300 mesh) in this study was shown in Table 1.

In general, activated carbon with a large specific surface area has a large adsorption capacity. The results showed that P2 and P3 powder activated carbons demonstrated stronger adsorption capacity than that of others (Table 1). However, sometimes the specific surface areas of two types of activated carbons are the same, but the adsorption capacities are very different, which is mainly due to the different factors such as the pore structure and pore size of the activated carbon [1]. The pore size of activated carbon should be adapted to the radius of adsorbent molecules for better adsorption. Previous studies have pointed out that adsorption is the easiest when the diameter of the adsorbate is smaller than the pore size [1]. The adsorption capacity of activated carbon for a certain adsorbate is determined by the pore size distribution of activated carbon and the molecular mass of the adsorbate. In this study, the pore diameters of the six activated carbons were ranked as P1 < P2 < P3 < G1 < G2 < G3. The test water was high-salt fatty acid production wastewater with macromolecular organic matter. Thus, coconut shell granular activated carbon with developed pores was considered suitable. Due to the large pore size, the migration speed of organic matter inside the activated carbon was accelerated, which was suitable for the characteristics of short adsorption time in the application of activated carbon. In addition, from the scanning electron microscope (SEM) images of the six types of activated carbon, the pore distribution of G3 coconut shell granular activated carbon was uniform, which was more suitable for retaining large molecules of organic matter. Although the particle size of activated carbon has little effect on the adsorption capacity, it has a certain effect on the adsorption rate. In the liquid phase adsorption, the internal diffusion process of carbon is the main factor affecting the adsorption rate, and the particle size is required to be small. However, in practical applications, too small powder activated carbon particle size will cause an increase in the amount of floating carbon when dosing. The particle size of the six types of activated carbons were ranked as G3 > G2 > G1 > P3 > P2 > P1. It was recommended to use granular

Table 1. Characteristic parameters of activated carbons.

Activated carbon types	Coal powder (P1)	Wood powder (P2)	Coconut shell powder (P3)	Coal granules (G1)	Wood columnar granules (G2)	Coconut shell columnar granules (G3)
Specific surface area (BET m^2/g)	563	900	1000	400	453	865
Pore size (nm)	3.7	3.9	3.8	4.3	4.5	4.8
Iodine adsorption value (mg/g)	550	980	1050	200	400	900
Particle size (mm)	1.3	1.5	1.8	2.0	2.1	2.3

Note: The data came from the manufacturer's instructions.

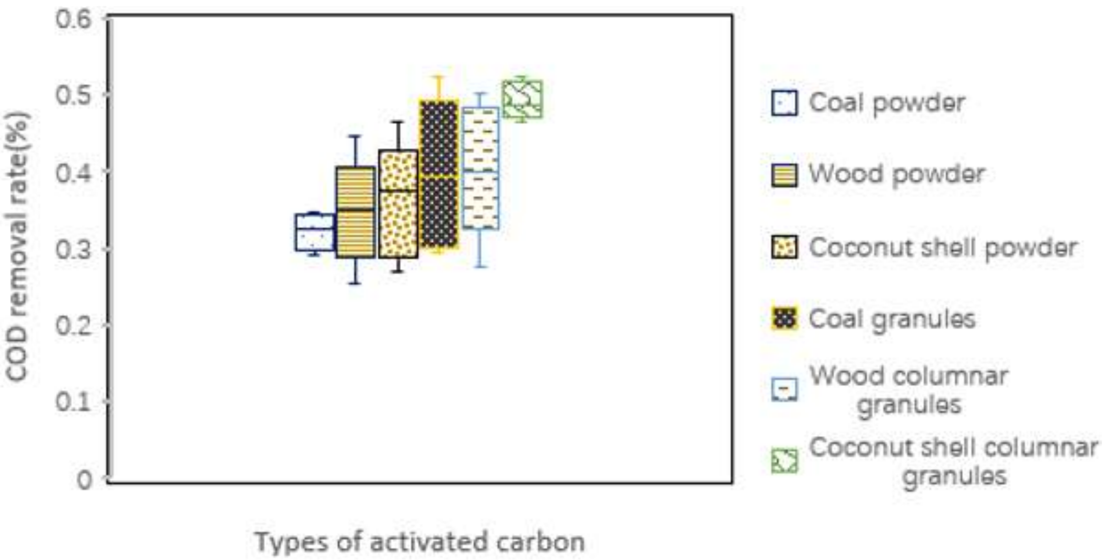

Figure 2. Comparison of anaerobic bio-enhancement effects of different activated carbons.

activated carbon. The enhanced treatment effects of six different activated carbons on anaerobic biological treatment were shown in Figure 2. The removal rate of COD by granular activated carbon was 43.3% that was higher than that of powder activated carbon (35.3%). Among the granular activated carbons, coconut shell granular activated carbon demonstrated the best performance, and the removal rate of COD reached 52.4%. Comparing the SEM analysis of different activated carbons used in this study, granular activated carbon displayed a well-developed pore structure, a large specific surface area, and strong surface adsorption performance, which was conducive to the retention of activated sludge microorganisms. Through the results of this study, coconut shell granular activated carbon (G3) was suitable for the treatment of this type of wastewater because of its moderate particle size, large specific surface area, pore-volume, large pore size, and strong adsorption capacity. On the other hand, 300 mesh coconut shell powder activated carbon was used as the dosing filler for anaerobic bio-enhancement.

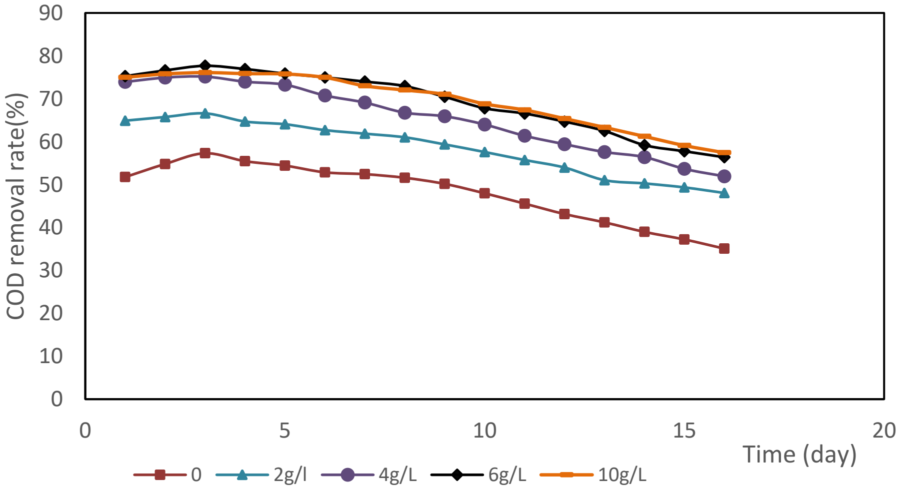

Figure 3. Effect of activated carbon dosage on COD removal rate.

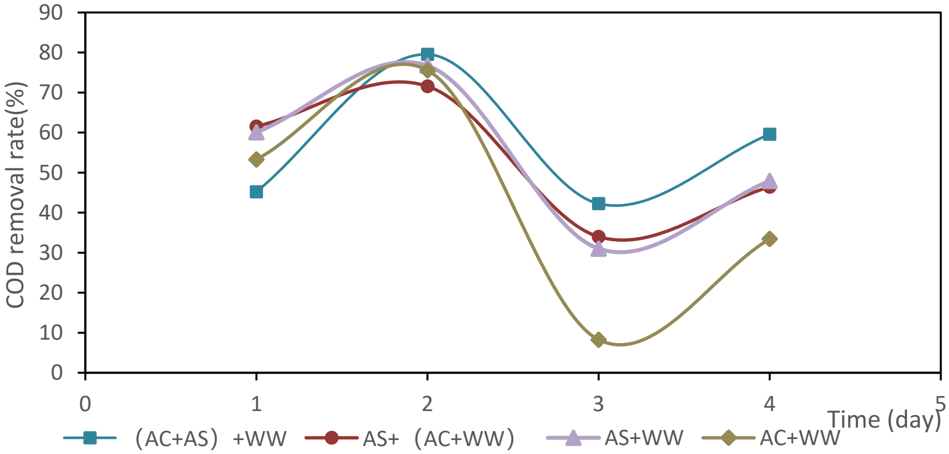

Figure 4. Relationship between different dosing methods of activated carbon and COD removal rate.

Determination of the optimal dosage of activated carbon

Under different activated carbon dosages that were calculated by the effective volume of the reactor, the COD removal rate of each group was shown in Figure 3. The removal effect of COD was poor when activated carbon was not added, which was only about 50%. As the reaction progressed, due to the deterioration of sludge activity and other reasons, the removal rate gradually decreased, and was only 35% when reached the end of the reaction. However, on the first day after the addition of activated carbon, when the activated carbon concentration was 2 g/L and 4 g/L, the removal rate was 65% and 74%, respectively. Each additional 2 g/L of activated carbon could increase the removal rate by about 10%. When the activated carbon concentration was greater than 6 g/L, a continuous increase of the dosage of activated carbon would not lead to an increase in the removal rate anymore. The increase in the removal rate was not proportional to the increase of the concentration of granular activated carbon, indicating that the difficult-to-

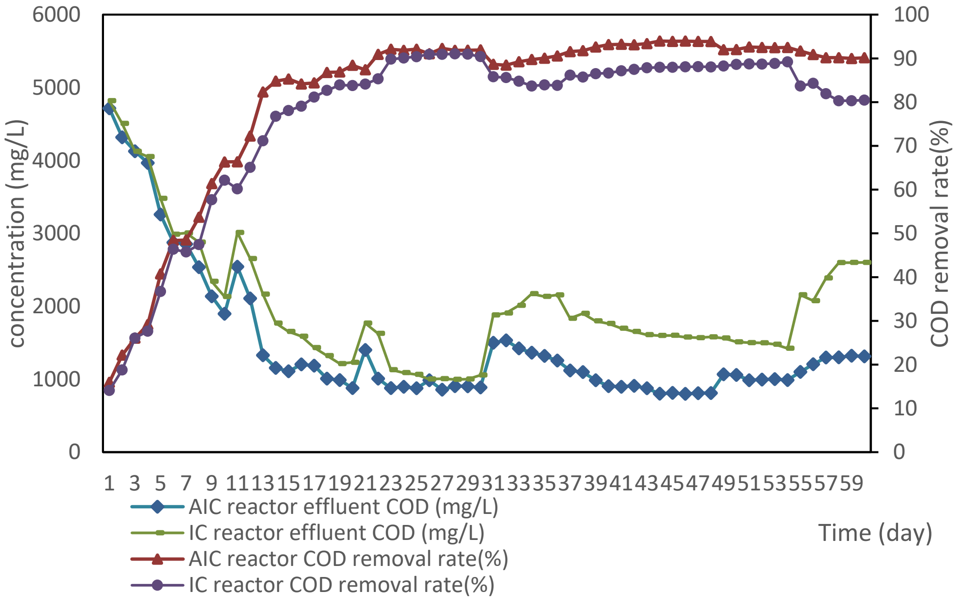

Figure 5. Comparison of COD removal rate in IC reactor with or without activated carbon.

degrade organic matter in the wastewater could not be completely removed by increasing the concentration of activated carbon. After a period of reaction, the adsorption of activated carbon gradually reached its saturation, and the adsorption capacity was getting worse and worse. The results of this study indicated that the dosage of activated carbon was 6 g/L.

Determination of the best dosing method of activated carbon

The experimental results found that the method of mixing activated carbon with activated sludge before entering the wastewater (referred to as (AC+AS) + WW) demonstrated a higher COD removal rate than the method of adding activated carbon and wastewater together to the activated sludge (referred to as AS + (AC + WW)) (Figure 4). The pre-mixing of activated carbon and activated sludge was conducive to the adhesion of activated sludge microorganisms to the activated carbon pores. In contrast, mixing activated carbon and wastewater first might cause the pollutant molecules of the wastewater to fill the pores of the activated carbon, which affected the adsorption of the microorganisms during the anaerobic reaction. Therefore, mixing the activated carbon and the sludge first was selected as the dosing method. In the actual operation of the anaerobic reactor, a part of activated carbon and sludge were mixed evenly before the water was fed. In the later stage, part of the activated carbon could also be supplemented to enter the reactor along with the wastewater. In this study, the COD removal effects of the conventional sludge injection (AS + WW) and the reactor with only 300 mesh granular activated carbon (pure adsorption method) (AC + WW) were also compared (Figure 4). The overall COD removal effects were ranked as (AC + AS) + WW > AS + (AC + WW) > AS + WW > AC + WW. The results showed that the COD removal rate of (AC + AS) + WW method could reach 56%, which was about 3% higher than the average COD removal rate of AS + WW method. Based on the comprehensive analysis of the mechanism of (AC + AS) + WW anaerobic intensification process, the following findings were concluded [22-25]: (1) The removal effect of pollutants in wastewater was not a simple addition of activated carbon adsorption and biodegradation effects but exceeded the sum of the biodegradation effects of both methods. Activated carbon adsorption and biodegradation

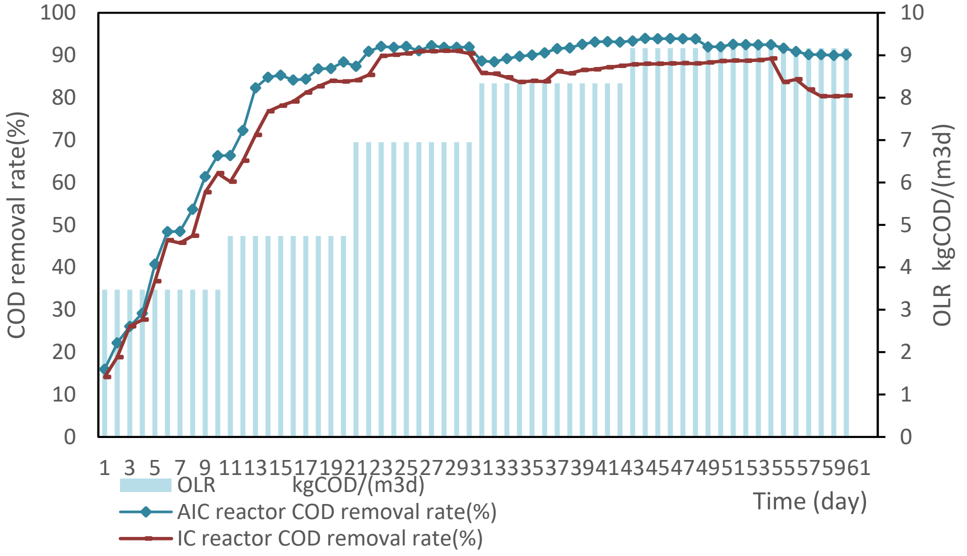

Figure 6. Relationship between COD removal efficiency and organic load in IC reactors.

had mutually promoting effects. (2) The granular activated carbon in the anaerobic system created a good living environment for the metabolism of microorganisms. Due to its huge surface area and strong adsorption effect, the activated carbon could effectively adsorb the pollutants in the wastewater and improve the degradation effect of the pollutants.

Dynamic experimental study of activated carbon enhanced IC reactor for the treatment of high salt fatty acid wastewater

(1) COD removal rate

Figure 5 showed the effluent COD concentration and COD treatment efficiency of the IC reactor after activated carbon reinforcement. The COD treatment efficiency was over 90% after 22 days of startup. Compared with the condition without adding activated carbon reinforcement, the COD treatment efficiency of the IC reactor reinforced with activated carbon was slightly higher. The relationship between COD removal efficiency and organic load in the IC reactor with or without activated carbon was shown in Figure 6. In the first stage, the influent COD concentration of the reactor was controlled within the range of 5,500 mg/L. By adjusting the influent peristaltic pump, the organic load of the influent was maintained at 3.47 kg COD/(m^3·d). At this time, the reactor had gone through the adaptation stage of 11 days. During this period, the sludge in the reactor gradually formed a stable biological structure, the microbial biomass in the reactor gradually increased, and the treatment efficiency of COD gradually improved. The highest COD treatment efficiency of the IC reactor with activated carbon was 66.33%, which was increased by 50.38% from the highest treatment efficiency of 15.95% at the initial start-up period. The highest COD treatment efficiency of the IC reactor without activated carbon was 62.16%, which was increased by 48.06% from the highest treatment efficiency of 14.10% at the initial start-up period. At this stage, the COD removal efficiency increased significantly, and the COD removal efficiency of the IC reactor with activated carbon reinforcement (AIC reactor) was slightly higher than that of the IC reactor by 1.5 to 6.26%. In the second stage, the influent COD concentration was increased by 7,500 mg/L, and the organic load of the influent was increased to 4.74 kg COD/(m^3·d). The AIC reactor showed a certain degree of tolerance under the impact of increased organic load. The COD removal efficiency continued to increase and stabilized at about 87% in the later period. The increase in

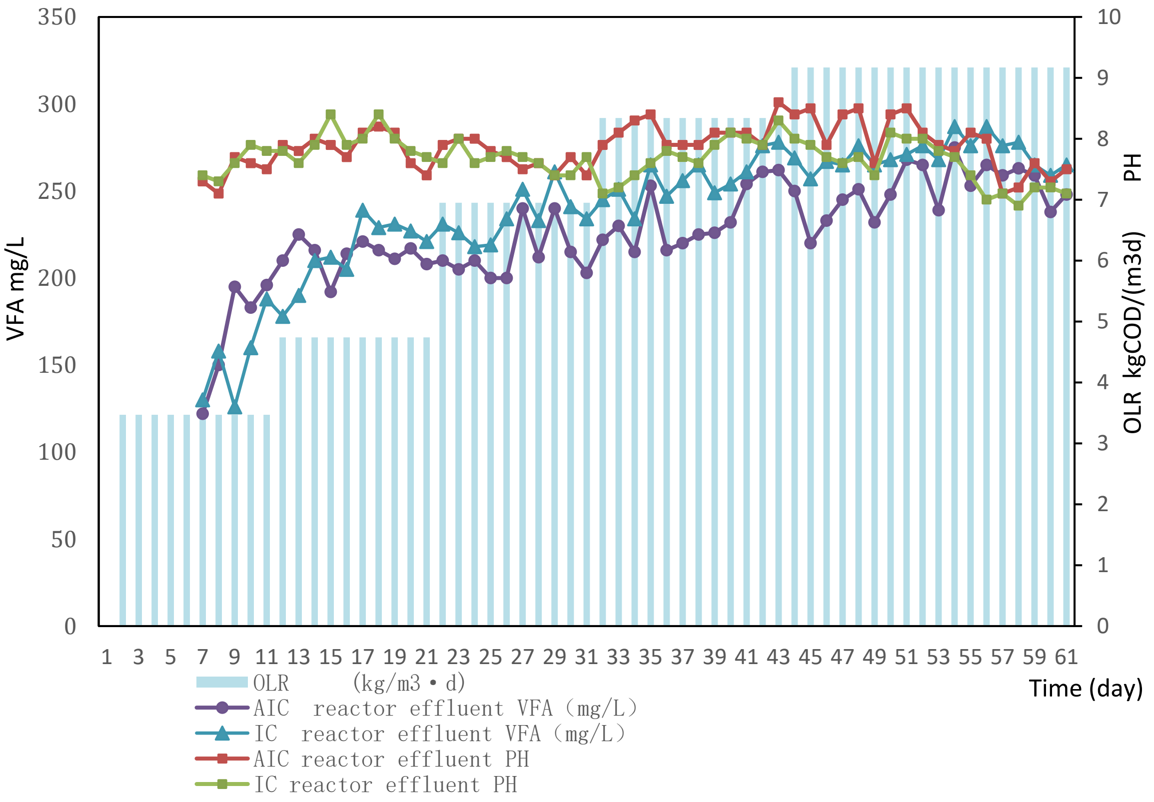

Figure 7. VFA and pH changes of IC reactor with or without activated carbon.

COD removal efficiency of the AIC reactor was slightly higher than that of the IC reactor. The COD removal efficiency of the IC reactor was stabilized at about 83% in the later stage. In the third stage, the influent COD concentration was increased to 11,000 mg/L, and the influent organic load was increased to 6.95 kg COD/(m^3·d). The COD treatment efficiency of the AIC reactor increased from 87.4% to 91.83%, and the COD removal efficiency of the IC reactor increased from 84.1% to 90.1%. Afterwards, the COD removal efficiency stabilized at around 92% and 90%, respectively. In the fourth stage, the influent COD concentration was increased to 13,200 mg/L, and the influent organic load was increased to 8.34 kg COD/(m^3·d). At this time, the reactor showed a slight fluctuating decline. Both the AIC reactor and the IC reactor showed a small reduction in COD treatment efficiency. The COD treatment efficiency of the AIC reactor dropped from 91.93% to 88.64%, and the COD removal efficiency of the IC reactor dropped from 90.39% to 85.78%. However, after 5 days of fluctuations, the COD treatment efficiency of the AIC reactor gradually stabilized, and no further decline was observed. Afterwards, the COD removal efficiency stabilized at around 93.1% and 87.5%, respectively. In the fifth and sixth stages, the influent COD concentration was stable at 13,200 mg/L, and the influent organic load was increased to 9.17 kg COD/(m^3·d). Both the AIC reactor and the IC reactor showed reductions in COD treatment efficiency. The COD treatment efficiency of the AIC reactor dropped from 93.37% to the lowest value of 90.13%, while the treatment efficiency of the IC reactor decreased from 87.83% to the lowest value of 80.45%. The reduction in the COD treatment efficiency of the AIC reactor was smaller than that of the IC reactor, and finally stabilized at 90%. Thus, the AIC reactor had higher treatment efficiency than the IC reactor. In this stage, the highest treatment efficiency of the AIC reactor was 94%, and the highest treatment efficiency of the IC reactor was 89%.

Analysis of VFA value change

When the organic load increased from 3.47 kg COD/(m^3·d) to 9.17 kg COD/(m^3·d), the concentration change of the liquid end-product VFA during the operation phase of the IC reactor with activated carbon and the unenhanced IC reactor was observed (Figure 7). During this period, the influent organic load of the reactor was increased in five stages, and the total volatile acid concentration in the effluent of the reactor decreased from 265 mg/L to 248 mg/L. Compared to the AIC reactor, the IC reactor had lower acid production. In addition, when the organic load of the IC reactor was 9.17 kg COD/(m^3·d), the acid-base balance performance of the microorganisms in the reactor was lost, indicating that the unenhanced IC reactor had poor performance in treating high-salt fatty acid wastewater. The acid production efficiency and acid-base balance ability of microorganisms of the unenhanced IC were worse than that of the activated carbon-enhanced IC reactor.

Analysis of pH change

In the process of increasing the organic load of the influent water, due to the acid-base balance ability of the microbial flora in the reactor, the pH value appeared to decrease and then recovered rapidly under the impact of the increase in organic load and remained within a relatively stable fluctuation range (Figure 7). Both the AIC reactor and the IC reactor could maintain a relatively stable pH before acidification. When the organic load was 8 kg COD/(m^3·d), the PH changes of both the AIC reactor and IC reactor were relatively stable. The pH value of the AIC reactor was stable between 7.4-8.6, which was less different from that of the IC reactor. Under the impact of increased organic load, the equilibrium pH value of the IC reactor decreased faster, indicating that the microorganisms in the AIC reactor were more resistant to the impact of the organic load than those in the IC reactor. When the AIC reactor and the IC reactor had an organic load of 9.17 kg COD/(m^3·d), the pH fluctuated greatly and gradually decreased, indicating that the AIC reactor and the IC reactor were in a high-load operation state, and the pH balance system was under a lot of pressure. At the same time, the pH values of both reactors dropped rapidly below 8.5, indicating that the reactor was overloaded, and acidification occurred in the reactor. In contrast, the pH value of the AIC reactor decreased much slower than that of the IC reactor, indicating that the microbial community of the AIC reactor was more stable than that of the IC reactor.

Analysis of chromaticity removal effect

The chromaticity removal effects of the AIC system and IC system were shown in Figure 8. The test wastewater was brownish, and the IC reactor could remove the chromaticity to a certain extent. At the beginning of the reaction, the chromaticity of the influent water was about 100 times. Although measures were taken to protect the wastewater from light and keep it sealed with a lid, the color of the wastewater continued to increase as the test progressed, and the color of the influent water increased about 150 times in the late stage of the test. The system had almost no removal effect on the chromaticity of the influent. In the first 21 days of the test, the chromaticity of the influent was less than 151 times. The biochemical aeration accelerated the deepening of the wastewater chromaticity. From day 22 to day 40, the chromaticity of the influent water was around 140 times, and the removal rate of chromaticity by the system was below 34%, while, from day 41 to day 60, the chromaticity of the influent water was around 150 times, and the removal rate of chromaticity by the system dropped to below 36.4%. In contrast, after the granular activated carbon was added to the AIC reactor, the activated carbon adsorbed a large amount of auxochrome groups and chromogenic groups in the wastewater, which significantly reduced the chromaticity of the effluent. As the initial granular active carbon (GAC) dosage was large, the chromaticity of the reactor effluent dropped rapidly to below 40 times, and the removal rate reached about 70%.

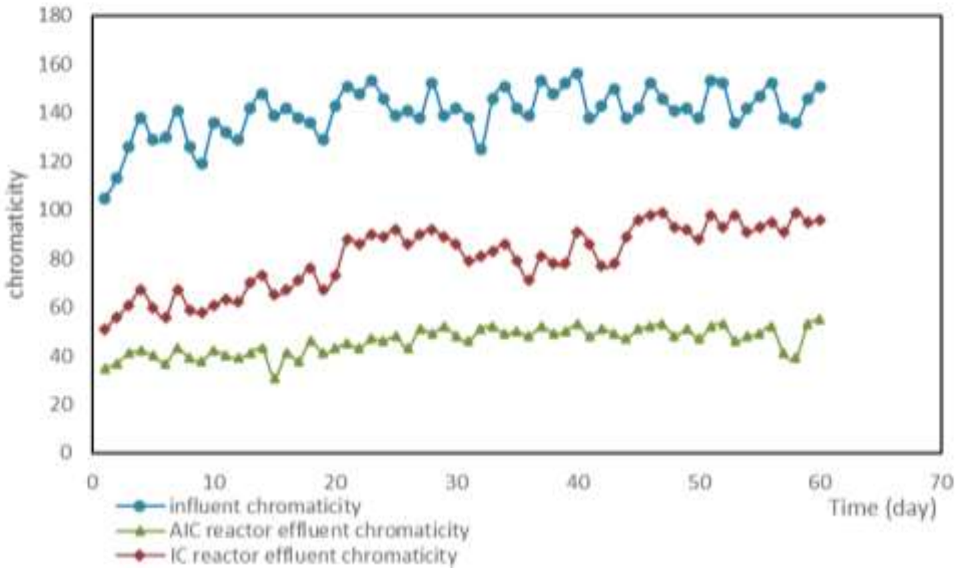

Figure 8. Chromaticity change of IC reactor with or without activated carbon.

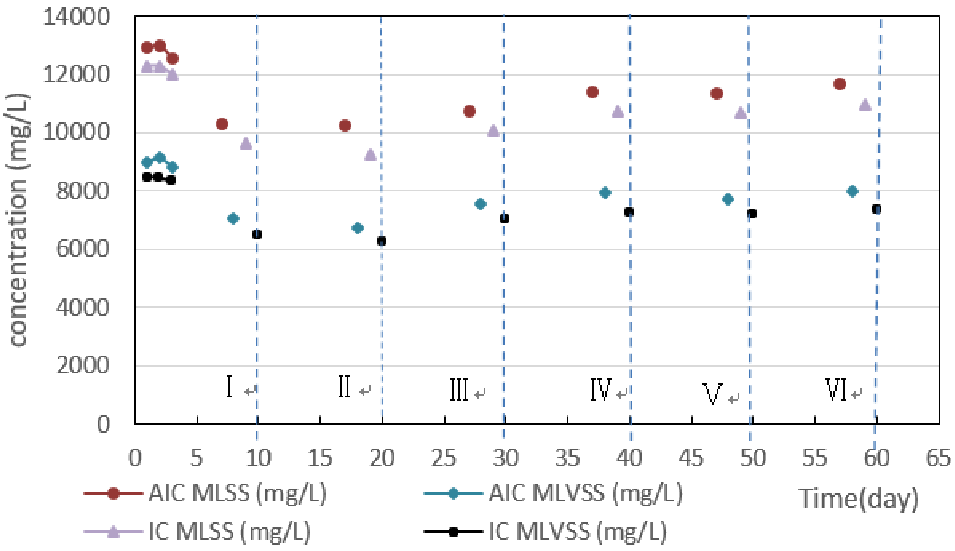

Figure 9. Changes in biomass of IC reaction system with or without activated carbon.

As the AIC system continued to run, part of the adsorption capacity of GAC was occupied by easily adsorbed and hard-to-biodegrade substances, and it was difficult to regenerate all of them, thus the removal rate of effluent chromaticity decreased. Due to the continuous replenishment of GAC, the effluent chromaticity of the AIC reactor could still be maintained at about 40-60 times. After the 10th day of operation, the chromaticity removal rate of the AIC system was basically stable in the range of 63.5-71.3%.

The influence of activated sludge properties

The concentration of suspended solids (MLSS) in the system was composed of biomass (A/S) and activated carbon (GAC). The line graph in Figure 9 showed the changes of the total amount of activated carbon sludge with time of the AIC system and the IC system. Due to the poor quality

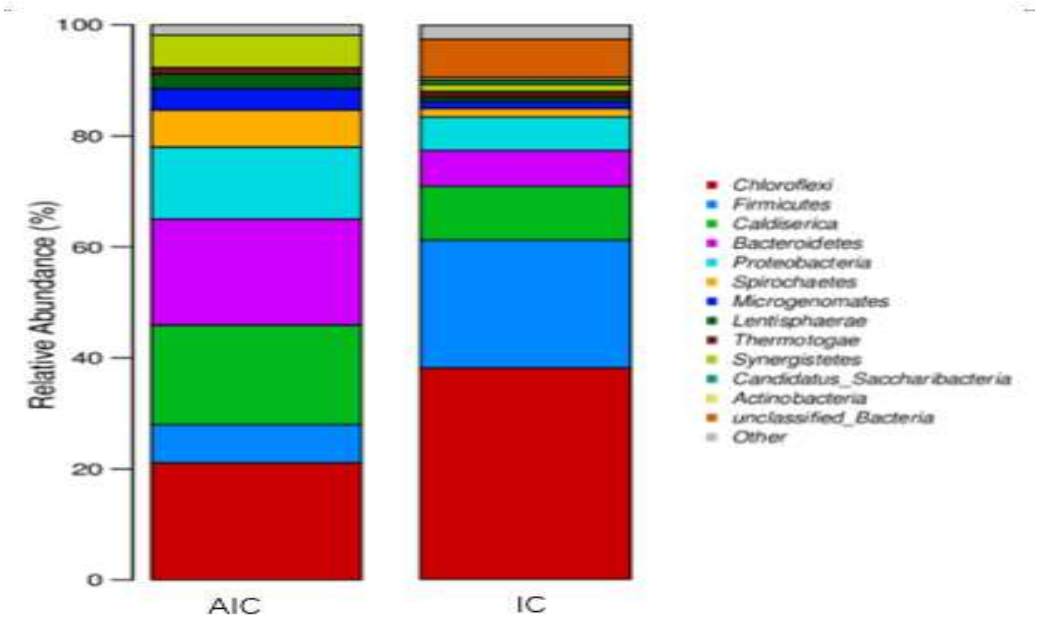

Figure 10. Comparison of relative abundance of microbial community structure in IC reactor with or without activated carbon.

of the wastewater, the biomass in both systems did not increase significantly. During the test period, the sludge was discharged every phase. When the reactor was started, due to the lack of nutrients in the wastewater system and the high salinity of the influent water, the microbial growth environment deteriorated, and the biomass of the system dropped sharply. At the end of stage I, the MLSS of the system dropped to 9,933 mg/L. After that, the microorganisms in the AIC system gradually adapted to the environment and maintained stable at about 10,022 mg/L in stage II. There was almost no increase in biomass. In the first four weeks, the biomass of the IC system remained stable, and then it increased slowly after the end of stage IV. After stage IV, the biomass basically remained at about 11,000 mg/L without a significant increase. Throughout the experimental period, the biomass in the AIC system was always higher than that in the IC system. Due to the addition of activated carbon, the AIC system's adaptability to adverse environments was improved, which could reduce biodegradable carbon source reduction factors and always maintain high biomass. The biomass of the IC system was partially lost due to other reasons such as the discharge of remaining sludge and the loss of effluent sludge. At the end of the test, the MLSS content in the IC system was 7,346 mg/L.

Comparison of microbial community structure and function changes between AIC and IC systems

At the end of the 60th day, the activated sludge in the reactor was taken for microbial community structure analysis. Figure 10 showed a histogram of the relative abundance of activated sludge microbial community structure in the AIC and IC reactors. The results demonstrated that *Chloroflexi* was reduced after the addition of activated carbon. In addition, the proportion of *Proteobacteria*, which could play a sulfate reduction effect in a more acidic environment, was not high in both reactors, but it was slightly higher in the AIC reactor than that in the IC reactor. In the reactor, *Chloroflexi* was still the dominant one. Since the sulfate concentration in the final stage VI of the AIC reactor was 4,800 mg/L, *Proteobacteria* in activated sludge, which could play a role in sulfate reduction in a more acidic environment, were more abundant in the

AIC reactor than that in the IC reactor, which had been impacted by 22,000 mg/L sulfate concentration. Thus, *Proteobacteria* maintained the reactor removal rate of the AIC reactor [26].

Conclusion

This study screened the different types of activated carbon and found that the coconut shell granular activated carbon had a more suitable and more uniform pore structure and particle size, and a stronger COD removal rate. The optimal dosage of activated carbon was 6 g/L. In terms of the dosing method, mixing a certain amount of activated carbon with activated sludge before entering the wastewater treatment had a stronger treatment effect than making activated carbon and wastewater enter the reactor at the same time to contact sludge. The reaction was conducted for 60 days after adding preferred activated carbon to the IC reactor through the optimal addition method. During operation, the influent water was increased from 5,500 mg/L to 13,200 mg/L, and the processing load was increased from 3.47 to 9.17 kg COD/(m^3·d). The treatment effect of the IC system with granular activated carbon under the optimized dosage and method was better than that of the IC system without reinforced with activated carbon. The addition of activated carbon during the start-up stage could strengthen the IC reactor, thereby accelerating the start-up of the IC reactor and making the operation more stable. During stable operation, the maximum removal rate of the system was 93.94%, and the average removal rate was 91.63%. Compared to the system without activated carbon enhancement, the sludge particle size was larger, and the removal rate was increased by 4-10%. IC reactor with activated carbon reinforcement had higher resistance to organic load impact.

References

1. Lettinga G, van Velsen AFM, Hobma SW, de Zeeuw W, Klapwijk A. 1980. Use of the upflow sludge blanket (USB) reactor concept for biological wastewater treatment, especially for anaerobic treatment. Biotechnol Bioeng. 22(4):699-734.
2. Gaur RZ, Khan AA, Lew B, Diamantis V, Kazmi AA. 2017. Performance of full-scale UASB reactors treating low or medium strength municipal wastewater. Environ Process. 4(1):137-146.
3. Kato MT, Field JA, Lettinga G. 1997. The anaerobic treatment of low strength wastewater in UASB and EGSB reactors. Water Sci Technol. 36(6-7):375-382.
4. Kato MT, Rebac S, Lettinga G. 1999. Anaerobic treatment of 1ow- strength brewery wastewater in expanded granular sludge bed reactor. Appl Biochem Biotechnol. 76:15-32.
5. Habets LHA. 1999. Introduction of the IC reactors in the paper industry. Technical Report, PAQUES WATER SYSTEMS B.V., the Netherlands.
6. Xu F, Miao HF, Huang ZX, Ren HY, Zhao MX, Ruan WQ. 2013. Performance and dynamic characteristics of microbial communities in an internal circulation reactor for treating brewery wastewater. Environ Technol. 34(20):2881-2888.
7. Wu W, Zhang L, Chen Y, Liu WJ, Tu Y, Zhou J. 2014. Interaction between activated carbon and microorganisms in PACT process. Can J Chem Eng. 92:1340-1345.
8. Li M. 2013. Treatment of comprehensive chemical industrial wastewater using a PAC-AS process. Master Dissertation, Tianjin University.
9. Xiao ZL. 2019. Activation and operation of UASB reactor for treatment of kitchen waste strengthened by granular activated carbon. Master Dissertation, Northeast Forestry University. ·
10. Yan WW, Zhang L, Wijaya SM, Zhou Y. 2020. Unveiling the role of activated carbon on hydrolysis process in anaerobic digestion. Bioresource Technol. 296:122366.
11. Zhe K, Li L, Xue Y, Yang M, Li YY. 2019. Challenges and prospects for the anaerobic treatment of chemical-industrial organic wastewater: A review. J Clean Prod. 231:913-927.
12. Lu XQ, Zhen GY, Estrada AL, Chen M, Ni JL, Hojo T, *et al*. 2015. Operation performance and granule characterization of upflow anaerobic sludge blanket (UASB) reactor treating wastewater with starch as the sole carbon source. Bioresource Technol. 180:264-273.
13. Luo G. 2017. Treatment of sulfate-rich organic wastewater by internal circulation (IC) anaerobic reactor. Master Dissertation, Nanjing University.
14. Guo K, Shang Y, Gao B, Xu X, Lu S, Qi Q. 2018. Study on the treatment of soybean protein wastewater by a pilot-scale IC-A/O coupling reactor. Chem Eng J. 343:189-197.
15. Wang T, Huang Z, Ruan W, Zhao M, Shao Y, Miao H. 2018. Insights into sludge granulation during anaerobic treatment of high-strength leachate via a full-scale IC reactor with external circulation system. J Environ Sci. 64:227-234.
16. Zhou JT. 2018. COD removal of COD from high salinity wastewater using physical adsorption, chemical oxidation and biological process. Master Dissertation. Dalian University of Technology.
17. Zhao YY, Zhuang XM, Ahmad S, Sung S, Ni SQ. 2020. Biotreatment of high-salinity wastewater: Current methods and future directions. World J Microb Biot. 36:37.

18. Ng KK, Shi XQ, Ong SL, Lin CF, Ng HY. 2016. An innovative of aerobic bio-entrapped salt marsh sediment membrane reactor for the treatment of high-saline pharmaceutical wastewater. Chem Eng J. 295:317-325.
19. Yilmaz T, Erdirencelebi D, Berktay A. 2012. Effect of COD/SO_4^{2-} ratio on anaerobic treatment of landfill leachate during the start-up period. Environ Technol. 33(3):313-320.
20. Wei YJ, Ji M, Li GY, Qin FF. 2012. Enhancement of stability of aerobic granules by powdered activated carbon addition. J Tianjin Uni. 45(3):247-253.
21. Jia W, Dong HR, Zeng GM. 2018. Application of zeolite in removing salinity/sodicity from wastewater: A review of mechanisms, challenges and opportunities. J Clean Prod. 197:1435-1446.
22. Fang RY. 2019. Research on biochemical treatment of printing and dyeing wastewater strengthened by resuscitation-promotion. Master Dissertation, Zhejiang University.
23. Macova M, Escher BI, Reungoat J, Carswell S, Lee Chue K, Keller J, *et al*. 2010. Monitoring the biological activity of micropollutants during advanced wastewater treatment with ozonation and activated carbon filtration. Water Res. 44(2):477-492.
24. Reungoat J, Escher BI, Macova M, Argaud FX, Gernjak W, Keller J. 2012. Ozonation and biological activated carbon filtration of wastewater treatment plant effluents. Water Res. 46(3):863-872.
25. Ferro OA, Contreras EM, Zaritzky NE. 2011. Effects of combining biological treatment and activated carbon on hexavalent chromium reduction. Bioresource Technol. 102(3):2495-2502.
26. Biswal BK, Wang B, Tang CJ, Chen GH, Wu D. 2020. Elucidating the effect of mixing technologies on dynamics of microbial communities and their correlations with granular sludge properties in a high-rate sulfidogenic anaerobic bioreactor for saline wastewater treatment. Bioresource Technol. 297:122397.