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Research on treatment of printing and dyeing wastewater by hybrid anaerobic baffled reactor

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ABSTRACT

The printing and dyeing wastewater was treated by a pilot-scale hybrid anaerobic baffled reactor (HABR) which was modified from general anaerobic baffled reactor by adding combined packing in the upper part of each compartment and inert carrier at the bottom of the reactor. The start-up of the reactor, the performance of HABR in treating printing and dyeing wastewater, and the transformation of sulfate and removal of bivalent sulfur in the treatment were investigated. The results showed that less time was taken during the start-up in comparison with the general one, and higher COD removal efficiency and sufficient color removal rate were also obtained in the HABR. When the hydraulic retention time was 12–13 h and the sludge return ratio was 0.3, the average COD and color removal rates were 47% and 56%, respectively. The anaerobic bacteria community in each compartment developed well because of available substrates and specific environmental conditions. The results also showed that high reduction rate of SO_4^{2-} was reached in the HABR, and the S^{2-} transformed from SO_4^{2-} could be removed by adding Fe^{2+} into the wastewater in order to reduce the inhibitory effect on the anaerobic bacteria and the odor.

Keywords: Hybrid anaerobic baffled reactor (HABR); Printing and dyeing wastewater; Combined packing; Inert carrier

1. Introduction

Industrial textile processes not only consume large quantity of water, but also produce a substantial amount of chemical pollutions. As effluents produced are relatively heavily colored, complicated, and contain high concentrations of salt, it is the most unfavorable one from the ecological point of view. The anaerobic treatment process, due to its capacity of hydrolysis, has the following advantages: (1) non-biodegradable organic compounds and chromophore groups can be replaced or disintegrated, or cracked into smaller molecules. (2) The biodegradability of the wastewater is improved. (3) The removal efficiency of chroma is higher. (4) There is no oxygen required, which cuts down the cost and energy requirements [1]. It is increasingly recognized as an advanced technology and widely used in the industrial wastewater treatment [2]. The anaerobic baffled reactor (ABR) was extensively used in the treatment of palm oil mill effluent wastewater [3], swine wastewater [4], pulp and paper mill black liquors [5], whisky distillery

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wastewater [6], landfill leachate [7],domestic wastewater [8], sulfate-containing wastewater [9], and soybean protein processing wastewater [10]. If the anaerobic treatment process is combined with the coagulation and the aerobic treatment, the printing and dyeing wastewater could be treated to meet the highest industry standards. ABR is a novel high efficient anaerobic reactor developed by McCarty and coworkers in 1980s and has several advantages over well-established systems such as the upflow anaerobic sludge blanket and the anaerobic filter [11], characterized by simple process, less investment and easy start-up. It well performs the thought of the advanced stage of phase separation wastewater treatment [12].

As a kind of anaerobic bioreactor with high efficiency in treating wastewater, ABR has a unique modular structure and a plug-flow-type flow pattern [13]. For the sake of the special character, each chamber can domesticate microbial communities adapted to the wastewater and the environmental conditions, and the distribution of microbial populations in the chamber is reasonable [14–18]. In addition, the up and down flow pattern makes the wastewater and sludge contacting completely, a strong shock load resistant as a result [11]. However, through engineering application and experimental research of ABR in treating the printing and dyeing wastewater, it was found that the height of sludge bed expansion in general ABR reactor chamber was restrained on the loss of sludge. Microbial biomass was less in the upper chamber space; therefore, the space utilization of the chamber was inefficient. Moreover, due to the poor biodegradability and low value of COD of printing and dyeing wastewater, it's hard to form granular sludge. Even if it is inoculated with granular sludge, it's vulnerable to be deflocculated during the operation. The formation of a large number of granular sludge as well as the full mixture of sludge and wastewater was important factors to ensure the high efficiency of the anaerobic treatment system [19], the mentioned cases made an effect on the efficiency of ABR. Accordingly, we had improved the general ABR to hybrid anaerobic baffled reactor (HABR). Liu Rongrong has explored the performance evaluation of HABR for treatment of PVA-containing desizing wastewater [20]. This study applied the developed HABR to treat dyeing wastewater containing sulfur and investigated the operating characteristics as well as the affecting factors.

2. Materials and methods

2.1. ABR and HABR configuration

The ABR was made of PVC except for the opposite side of PE board in order to observe the sludge bed better. The whole reactor is rectangular shaped with L × B × H dimensions of 4,000 × 500 × 3,000 mm and effective volume of 6,000 L. The ABR consisted of five chambers (CH1#–CH5#) connected in series as shown in Fig. 1. Each individual chamber was divided by a baffle plate into two compartments, i.e. upper room and lower room with a width ratio of 3:1 except CH1#. The bottom portion of baffle plate inclined at 45˚ to en courage water and sludge completely mixing in the upper room. The area of five upper rooms was distributed rationally to make the velocity ratio of upflow to be 1:1:0.87:0.87:0.62, which would help the sludge to sink at the end of reactor, avoiding sludge running off. Wastewater was distributed into the reactor evenly through the perforated pipe in the bottom of CH1# and ran out in the CH5#. Three sampling ports were set up in every chamber from top to bottom, for collecting water and sludge samples.

The improved HABR's configuration is shown in Fig. 2. The improved features are as follows: (1) forming a filler layer in upside of the chamber with combination ring packing of 1/3 volume of which would increase the capacity utilization; (2) adding modified rubber particles of 0.5–1 mm diameter as an inert carrier in the lower part of first four chamber benefit the formation and preservation of granular sludge; (3) fortifying sludge return device to make supplement to the loss of front grid room's sludge as well as increasing the flow rate and improving the degree of sludge mixed with wastewater.

2.2. Wastewater source and composition

Textile wastewater samples used for the entire study were taken from a regulating pond of a large knitting and dyeing factory in Dongguan, Guangdong. Because of the company production using reactive

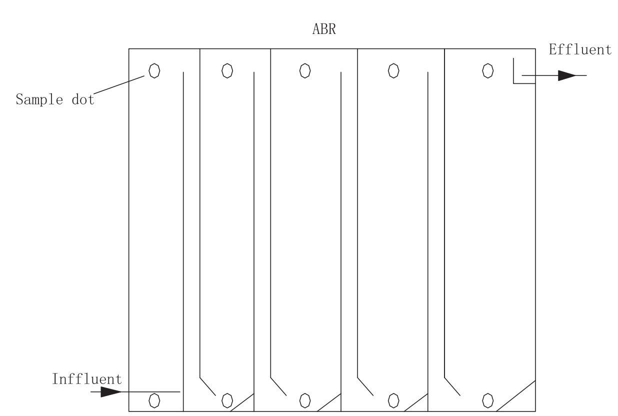

Fig. 1. Schematic diagram of ABR.

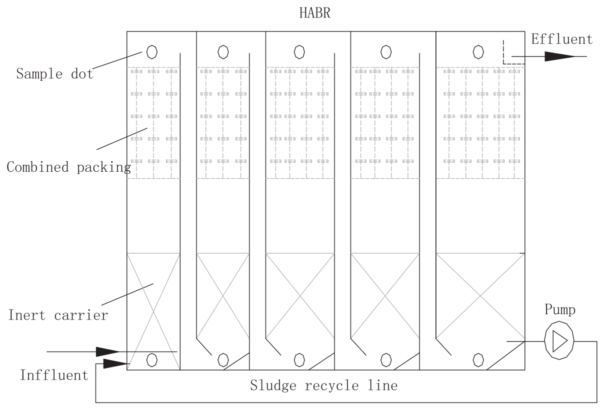

Fig. 2. Schematic diagram of HABR.

dyes, sulfur dyes, and sodium sulfate, sulfate content in the wastewater was high. The wastewater quality is shown in Table 1.

2.3. Seed and sludge domestication

Seed sludge in the HABR was from the factory's original hydrolysis acidification pool. The volume of seed sludge took up about 1/2 of the reactor (with volume of wet sludge) with sludge concentration of 18 gVSS/L and VSS/TSS ratio 0.56. The start-up could be facilitated by adding the nutrient solution to the reactors after seed sludge had inoculated. The composition of the nutrient solution was as follows (concentrations of the constituents were given in brackets as mg/L): glucose (600), ammonium chloride, and sodium dihydrogen phosphate (in accordance with COD:N:P = 200:5:1), trace elements (1). Then, start up the internal circulation pump to stir sludge and keep circulating for 5 d. Stop stirring for one hour a day to make the sludge settled. Then a certain amount of supernatant fluid was took out and pumped into the equivalent of printing and dyeing wastewater instead and add nutrition. Keep the same operation of ABR reactor. After 10 d of adaptation period with nutrient solution and textile wastewater, the loose and hydrolyzed sludge was changed to be better settled. Then take the fixed influent concentration, gradually shorten the retention time [21–23] to start up the HABR and ABR systems.

The flow of printing and dyeing wastewater was increased from 120 to 400 L/h (through six runs as follows: 120, 150, 180, 240, 300, and 400 L/h, whose retention times range from 50 h to 15). Influent and effluent COD concentration in each run was monitored to ensure that steady COD remove ratio was achieved to enter to the next run.

2.4. Test procedure

The ABR reactor system was started to operate with real textile wastewater since the reactors had been previously used to treat with simulated textile wastewater steadily. The reactor system was operated under different flow rates in order to investigate the effect of hydraulic retention time (HRT) and sludge reflux ratio on the grid operating characteristics. Since the temperature of textile wastewater was high and kept in 28–35℃, no temperature control measures would be taken. Samples were collected once a day from the inlet and the outlet to analyze the overall treating efficiency of the reactor while using the sampling from the sampling ports to check the performance of the individual chambers. The operating characteristic of the reactor was defined by the color and COD removals, SS and VSS concentrations, dissolved oxygen and pH. All the parameters were estimated with standard methods.

3. Results and discussion

3.1. The start-up of reactors

The acclimatization curves of the start-up period of HABR and ABR are shown in Fig. 3.

In the early stage of start-up, COD removal efficiency of HABR and ABR both rose slowly in similar patterns. As granular sludge is gradually formed in the HABR and biofilm colonization, COD removal rate increased significantly after 40 d. At about the 75th day, 48% COD was removed at a HRT of 25 h. When shortened the HRT sequentially, it could be found that the reactor would recover quickly if negative impact was exerted on. Moreover, the resistance to load capacity is strengthened while COD removal efficiency decreased. We can make a conclusion that the reactor was successfully started up at 75 d when

Table 1
Water quality of wastewater

Wastewater quality	pH	COD_{Cr} (mg/L)	BOD_5 (mg/L)	SS (mg/L)	Chroma	S^{2-} (mg/L)	SO_4^{2-} (mg/L)
Numerical value	8.5–9.5	500–600	150–180	200–300	600–800	20–30	400–500

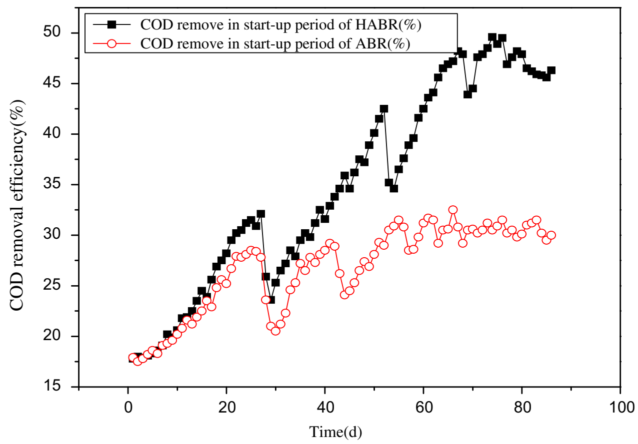

Fig. 3. Removal efficiency of COD in start-up period of HABR and ABR.

the sludge was matured. At this time, the organisms covered the granular inert negative carriers in the HABR. The larger particles formed the biofilm while the smaller ones whose size was 0.5–3 mm were acted as a core for the formation of granular sludge. The color of sludge in the chambers changed from off-white to black successively and the amount of sludge in the CH1# and CH2# was larger than other chambers. This phenomenon may be because that most of the organic was degraded by the previous chambers, while the remaining COD could no longer met the growth needs of the subsequent chambers. At the same time, some small sludge was driven out of sludge bed due to the upflow and stopped by the upper filler wire Villeneuve. Micro-organisms immediately secreted extracellular material, which was absorbed by PVA filament, forming a 2–3 mm biofilm on the surface of the combination filler.

On the other hand, ABR reactor has no need of forming biofilm, or colonization, it could achieve stable operating conditions in 60 d, which means a successful startup. Comparing to HABR, COD removal rate of ABR was lower (about 30%).There was no granular sludge but black flocculent sludge existed.

3.2. Effect of HRT on COD and color removals in HABR and ABR

HRT is one of the most important parameters for anaerobic reaction and a key factor in ABR treatment effects, or directly determines the investment in engineering applications [24]. The reactor systems were operated during every 7th day under steady-state conditions in order to investigate the effect of HRT on COD and color removals. The result is shown in Fig. 4. 45.8% of COD removal ratio was obtained in the HABR at a HRT of 12 h while that in ABR's was 27.6%. As the HRT increased from 6 to 20 h, the COD removal efficiencies increased to 49.2 and 30% for the HABR and the ABR, respectively. The COD removal efficiencies increased as the HRT increased. However, the COD removal rate showed a slow growth when HRT was more than 12 h. This result could be explained by the following two reasons: (1) the longer the HRT was, the lower speed of the upflow in the chamber, which would reduce the mixture degree of the sludge and wastewater,thereby affecting the processing efficiency; (2) some substances in the textile wastewater have poor biodegradability, and even a number of big dye molecules had been decomposed into small molecules through a period of anaerobic treatment,they were hard to be treated with anaerobic microbial degradation continually. HABR had higher color removal efficiency too. The color removal of the HABR was up to 51% while the ABR's was 40.5%. It can be explained that the reactive dye molecules belong to heterocyclic compounds, which contain polycyclic aromatic hydrocarbons. The anaerobic micro-organisms, especially hydrolysis acidification bacteria, have the advantage on easy-to-induced acidification and a diverse open loop enzymes system. It is making a guarantee for anaerobic acidification of aromatic hydrocarbons and heterocyclic,and making them easy to open loop cracking and successfully getting degradation through biochemical reaction. The open loop cracking damages the reactive dye and color groups so as to reduce the wastewater chroma.

The results showed that HABR being improved not only made up for the sludge formation in the up chamber, but also promoted granular sludge preserva-

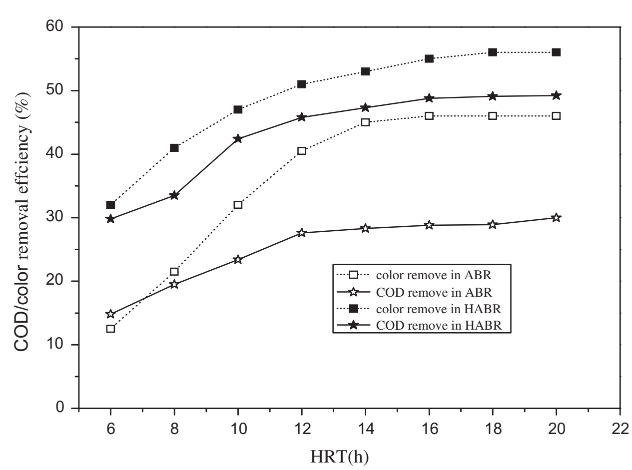

Fig. 4. Effect of HRT on COD and color removal efficiencies in HABR and ABR.

tion, thus promoted reactor treating efficiency, shortened the required HRT, and saved engineering investment. The longer the HRT, the more waste of energy will be generated. At the same time, the longer the HRT, the volume of the reactor has to be constructed larger, leading to more construction investment. Considering the economic and other factors, for dealing with reactive dye-based printing and dyeing wastewater, HRT of HABR was appropriate for 12–13 h.

3.3. Effect of the sludge return ratio on COD and color removals in HABR

In the HABR, the rising flow velocity of the printing and dyeing wastewater in the front chambers was relatively higher than the latter ones. Actually, due to the low rising flow velocity in the last chamber, the condition was in favor of the sedimentation of sludge when compared with the front ones, the sludge loss was less. Moreover, sludge return device was fixed in HABR in order to make up for the sludge loss in the front chambers. Sludge return was also more beneficial to improving the rising flow velocity of water, enhancing the expansion height of sludge bed, and promoting the mixture of wastewater and sludge at the same HRT. The reactor system was operated with fixed flow when the HRT was 12 h in order to investigate the effect of sludge return ratio on COD and color removals. The result is shown in Fig. 5. Increasing in return ratio caused increasing in COD and color removal efficiencies while the return ratio was in the range of 0.0–0.3. As the return ratio is too high (more than 0.3), it would make the rising flow velocity too fast to settle sludge down; then, the biofilm and sludge in the chambers would be washed out. Hence, it would bring an adverse effect on treating efficiency of the reactor, which was reflected by fast decreasing of the COD and color removal efficiencies.

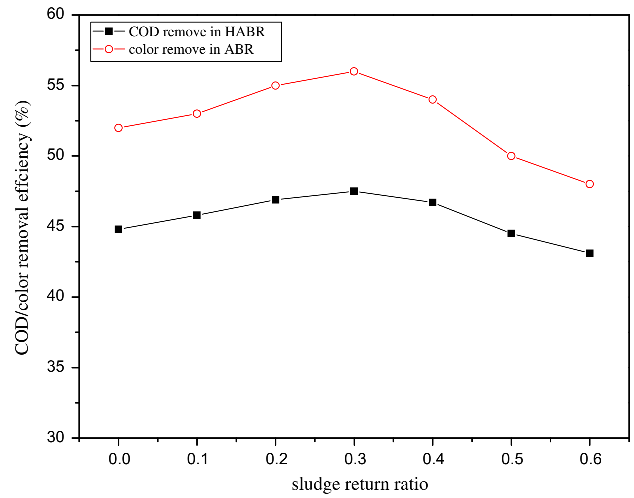

Fig. 5. Effect of sludge return ratio on COD and color removal efficiencies in HABR.

3.4. Analysis of operating performance of different chambers in HABR

Biofacies with significant interpopulation combining ability and good frictional distribution are important characteristics and advantages of anaerobic baffle reactor. The reactor system was operated with different HRT in order to investigate the effect of HRT on the changes of pH and COD and color removals which would reflect the biofacies and the pollutions frictional distribution in the textile wastewater treatment by HABR indirectly. The results are shown in Figs. 6 and 7.

The average pH of the effluent in each chamber would reflect the degree of acidification of the chamber [20,22]. The macromolecular organic compounds were decomposed into a large number of small molecules and organic acids under the activity of dominated hydrolytic acidification bacteria in the reactor. As a result, pH decreased quickly. As the HRT increased more than 12 h, the pH of the effluent gradually rose in the latter chamber. It could be conjectured that methanogenesis in the latter chambers become advantageous gradually. Methane bacteria made use of the acid produced in anterior chambers to carry out gas production reactions, thereby consuming organic acids. When the HRT wan shorter (HRT was 6 h), pH in each chamber decreased gradually. The whole reactor was in hydrolytic acidification phase. According to Fig. 7, color was mostly removed

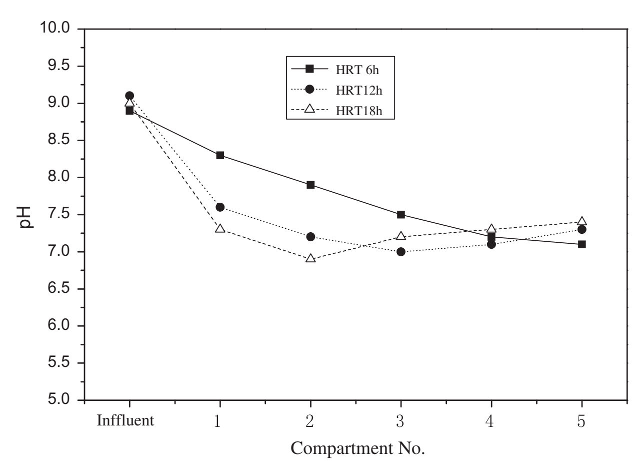

Fig. 6. Variation of pH in each compartment at different HRT.

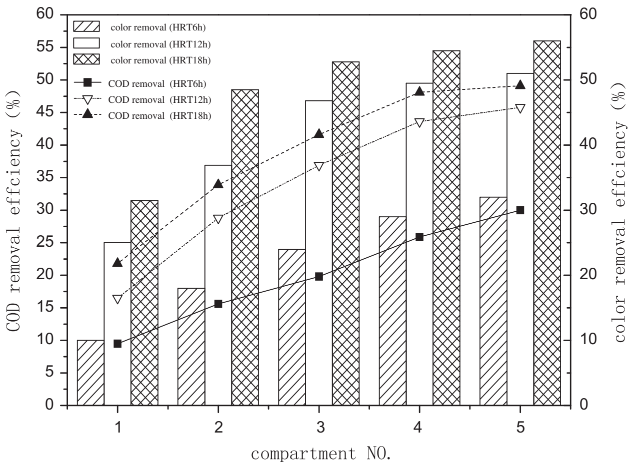

Fig. 7. Variation of COD and color removal efficiencies in each chamber at different HRT.

in the anterior chambers while the HRT increased gradually. There is barely efficiency of the latter chambers. The reason was that microbial populations suitable for the relevant grew better in longer HRT. Hydrolysis acidification bacteria, which could be achieved to decolorization, were mainly in the anterior chambers. COD removal was the same situation as the color removal. Most easily degradable material was absorbed by sludge in the anterior chambers and removed by hydrolysis acidification bacteria and a small group of acetic-metabolizing filamentous methanogens. The HRT has a strong impact on the treatment of textile wastewater by HABR, which has been proved by the effect of each chamber's operation. It is necessary to keep enough HRT for the growth of methanogens and the better work of HABR.

3.5. Transformation and control of sulfur on the treatment of textile wastewater by HABR

There is a lot of sulfate in the textile wastewater, and the influent concentration of SO_4^{2-} in this study was in the range of 400–500 mg/L. In anaerobic treatment of organic wastewater containing sulfate, SO_4^{2-} will be reduced by SRB to form a mass of S^{2-}, HS^-, and H_2S. These substances will not only produce odor, but also have a certain degree of inhibition and toxicity action for anaerobic micro-organisms such as acid-producing bacteria, methanogens, SRB, and aerobic micro-organisms. Thus, the efficiency of anaerobic treatment and the following aerobic biochemical will decline. Operating conditions of HABR treating sulfate-containing textile wastewater were as follows: the influent concentration of COD was 500–600 mg/L; COD and SO_4^{2-} ratio (mass concentration ratio) 1.0–1.5; HRT 12 h; sludge reflux ratio 0.3. The results showed that the reduction rate of sulfate could be greater than 60%, the concentration of S^{2-} in the water was 100–120 mg/L. At the same time, there was heavy smell around the HABR reactor, which indicated that a substantial amount of H_2S escaped. Therefore, it was necessary to control S^{2-}. Fe^{2+} can react with S^{2-} in the wastewater to generate FeS, thereby reducing the concentration of S^{2-} in the water. The reaction can weaken the negative feedback of S^{2-} and promote the anaerobic reaction. Adding ferrous salt into the reactor to make the S^{2-} which was produced in the anaerobic process be removed continually.

The system was operated with different addition of Fe^{2+} in order to investigate its effect on the S^{2-} concentration in the effluent and the efficiency of anaerobic treatment. The result was showed in Fig. 8. Increased addition of Fe^{2+} in the reactor caused that the effluent concentration of S^{2-} decreased and COD removal increased up to 50%. It was due to the reducing of soluble sulfide weakened the inhibition on anaerobic micro-organisms. As a result, the sulfate reduction rate increased, so did the COD removal efficiency. Sulfur has little inhibitory effect on anaerobic micro-organisms when the concentration of S^{2-} in the effluent is less than 70 mg/L. Long-term operation showed that the small sediment of FeS could be easily removed from HABR reactor with the water. The sediment could also be removed by following coagulation-sedimentation process. Additionally, regular discharge anaerobic sludge to reduce sludge mineralization was a way to ensure normal operation.

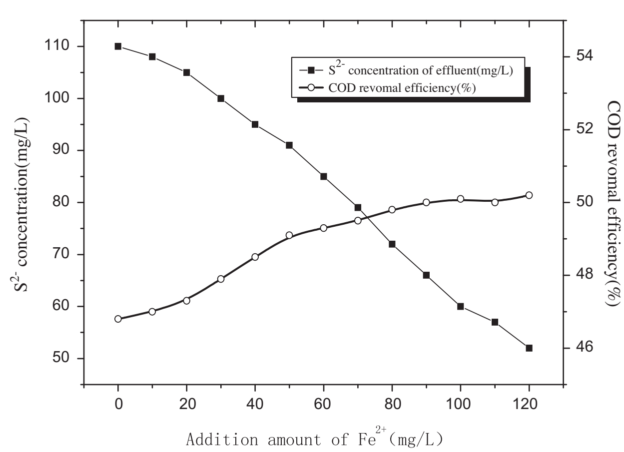

Fig. 8. Effect of dosage of Fe^{2+} on S^{2-} concentration in effluent and COD removal efficiency.

4. Conclusions

(1) The pilot-scale HABR was modified from general ABR by adding combined packing in the upper part of each chamber and inert carrier at the bottom of the reactor enhanced the reactor's space utilization, promoted the granular sludge formation and preservation, and improved the performance of the reactor effectively.

(2) With the increase of HRT, the COD and color removal efficiencies increased in the treatment of printing and dyeing wastewater by HABR. When the HRT was 12–13 h, COD and color removal rates were up to 45 and 50%. For economic considerations, the HRT of the treatment of printing and dyeing wastewater by HABR was most suitable at 12–13 h.

(3) The sludge return could compensate for the sludge loss in first chambers of reactor and increase the rising flow velocity. An appropriate sludge reflux ratio can improve the treatment efficiency of printing and dyeing wastewater. In this study, when the HRT was 12 h, and reflux ratio 0.3, COD and color removal rate were up to 47 and 56%, respectively.

(4) The operation of each chamber showed that the anaerobic bacteria in each chamber formed a good community structure on its available substrates and specific environmental conditions. Acid reaction occurred in the front-end of reactor where the easily degradable macromolecules were hydrolyzed. Organic acids had been degraded by methanogenic microbes in backgrid rooms.

(5) The sulfate conversion efficiency is high in HABR reactor, forming a large amount of S^{2-} and H_2S. S^{2-} could be reduced by adding Fe^{2+}, then, odor and the inhibitory effect of S^{2-} on anaerobic micro-organisms reduced. The treatment efficiency improved as a result.

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