

Study on the Treatment of Tannery Wastewater by Bio-Zeolite Reactor

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Abstract: This article investigated the removal efficiency of ammonium and COD by biological-zeolite at different influent mode and different hydraulic retention time (HRT) after start-up successfully. The results showed that the removal of pollutants at upflow mode was better than that of downflow mode that ammonium removal and COD removal rate could reach 95% and 85% respectively and ammonium concentration in worked water was less than 15mg/L; Ion exchange was the major contributor to ammonium removal at both influent modes and the average ion exchange rate was 76.15%, while downflow mode obviously strengthened nitrification by the average nitrification rate was 25.29%; The removal efficiency of COD by activated sludge and reaction column could reach the same effect that removal rate was higher than 80%; The removal efficiency of ammonium was over 75% in the reaction column and it even could reach 92% on the condition that HRT was 10h, and it had a good effect on the removal of ammonium in real tannery wastewater that the removal rate could reach 84.3%.

Keywords: ammonium, COD, upflow, downflow, hydraulic retention time(HRT)

1. Introduction

In recent years, the high concentration of ammonium in tannery wastewater has gradually aroused people's attention, the ammonium was mainly discharged from liming and deliming process, where lots of ammonium salt and enzyme were used, besides, the proteolysis of hide during degreasing, deliming and bating process brought organic nitrogen into wastewater, and they were transformed into ammonium later, which made the treatment of ammonium more difficult^[1].

The concept of "biological-zeolite" (bio-zeolite) was proposed by Tsuno Hiroshi in 1994^[2], as well as a bio-zeolite reactor, and it was then the deamination by bio-zeolite got gradual attention. The deamination by bio-zeolite combined the selective adsorption of zeolite with biological nitrification and denitrification, enhancing the performance and efficiency of biological deamination^[3]. The removal effect of COD and ammonium by bio-zeolite under different influent modes and hydraulic retention time (HRT) was studied on the basis of earlier successful start-up, in order to provide data for practical tannery wastewater treatment.

2. Experimental device and method

2.1. Experimental device

The experimental bio-zeolite reactor is made from plexiglass and its effective volume is 6L. There are five

sampling ports, with distance of 15cm between each other, marked 1# to 5# sequentially from top to bottom, and sampling port 5# was 25cm from the bottom. The vessel was filled with zeolites sized at 3-5cm, with smooth pebbles as the supporting layer, as was shown in Figure 1.

2.2. Experimental method

After the earlier successful start-up of bio-zeolite reactor, the ammonium and COD removal efficiencies, at upflow and downflow modes were investigated respectively. The mechanism of ammonium removal by bio-zeolite was analysed, and the effect of hydraulic retention time (HRT) was also studied. During the experiment, COD was measured with standard reflux method, and the concentration of ammonium, nitrite

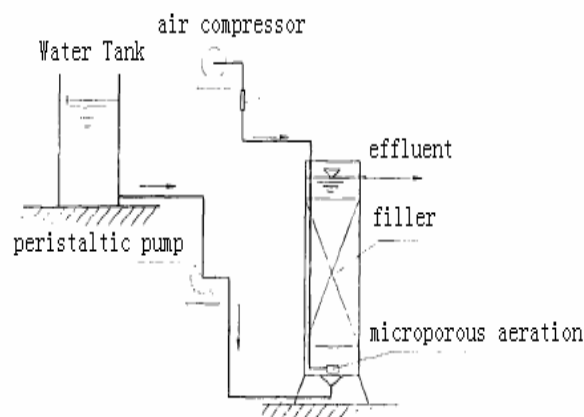


Fig.1 Experimental device

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nitrogen, and nitrate nitrogen was determined by distillation titration, N-(1-naphthyl)-ethylene diamine spectrophotometry and Phenol disulfonic acid spectrophotometry.

3. Experimental results and discussion

3.1. Removal effect and discussion of pollutants at different influent modes

3.1.1. Removal rate of COD and ammonium at two influent modes

The removal rates of COD and ammonium at both influent modes were studied, as shown in Figure 2 and Figure 3. The COD removal efficiency at upflow mode was better than that of downflow mode. The COD removal rate was higher than 70% at both modes, with highest at 85%. As to ammonium, the removal efficiency at upflow mode was about 95% at best, and the ammonium concentration of treated water was lower than 15 mg/L, which was better than that of downflow mode. Literature^[4] showed that when at upflow mode, the zeolites were in microdilancy, leaving wide space among them, and so the larger particles in wastewater would easily get through the filter layer instead of block up. The frequent collisions and friction of zeolites was conducive to the metabolism of the biofilm, resulting in better treatment efficiency. TIAN Wen-hua etc^[5] carried out a pilot-scale study on the sewage treatment by biological aerated filter and the experimental results showed that the COD and ammonia nitrogen removal efficiency could reach 73.9% and 88.4% respectively under the optimal condition of hydraulic loading. Different influent mode had a certain impact on the removal efficiency when under different conditions of influent water quality, process parameters and types of reactor. For the high concentration of ammonium in simulated tannery wastewater, there might be differences in the maturity of biofilms and the upflow mode had a larger capacity of buffering load, and so it got higher removal efficiency than that of downflow.

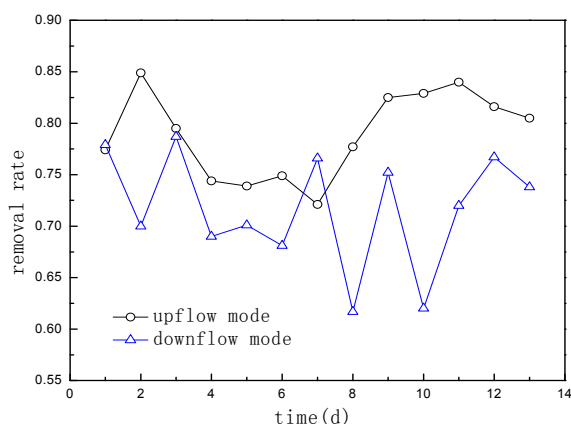


Fig.2 The COD removal rate at two influent modes

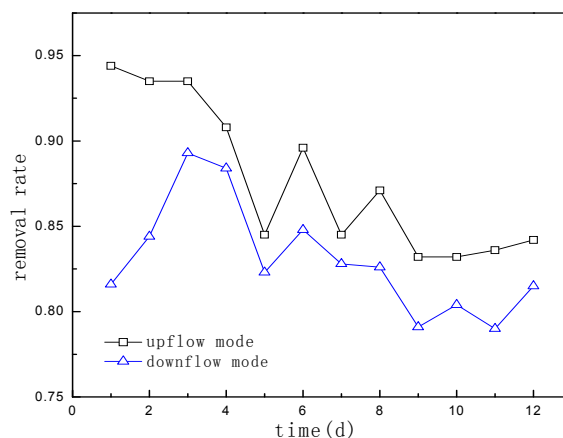


Fig.3 The ammonium removal rate at two influent modes

3.1.2 Changes of ammonium and nitrite concentration at upflow mode

In this part of experiment, the ammonium and nitrite concentration of five sampling ports were determined under upflow mode, which could reflect the biological nitrification more directly in different part of reactor. When the ammonium concentration of influent was about 200mg/L, the ammonium concentration of effluent was less than 30mg/L and the removal efficiency could reach 85% in 5# sampling port. The adsorption of zeolite was the major contributor to the removal of ammonium and biological nitrification was not obvious with the nitrite concentration 4mg/L. Ammonium concentration decreased gradually along the way while nitrite concentration increased which could reach the highest port in 3# sampling port in the eighth day, which indicated that the biofilm of 3# was mature and it played a better nitrification. The entire process of denitrification was not obvious in 1# sampling port probably because of its high nitrite concentration.

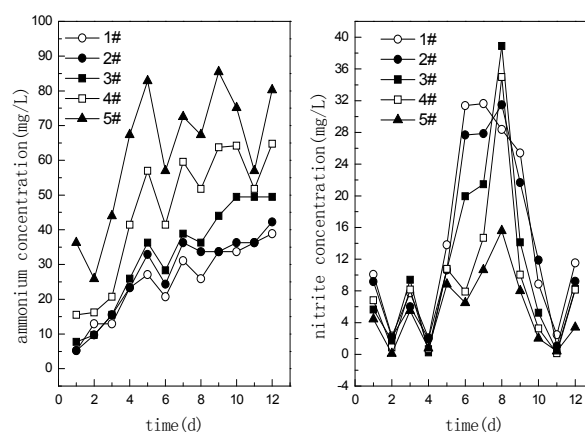


Fig.4 The ammonium and nitrite concentration of five sampling ports

3.1.3 Analysis of removal mechanism of ammonium at two influent modes

Literature^[6] showed that the removal of $\text{NH}_3\text{-N}$ by zeolite involved two types of reactions that were ion exchange and nitrification. The increase of $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ concentration represented the part that $\text{NH}_4\text{-N}$ removed by nitrification; The decrease of total inorganic nitrogen (the sum of $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$) represented the part removed by ion exchange. The removal efficiency of ammonium under two influent modes was compared and experimental results were shown in Figure 5. The results showed that ion exchange was the major part in the removal of ammonium under two influent modes and the average ion exchange rate was 76.15% at upflow mode while the average nitrification rate could reach 25.29% because of strengthened nitrification by downflow mode, therefore it was good to take upflow mode in the initial biofilm formation because ion exchange was the main part in removal of ammonium, while it was good to take downflow mode as the biofilm was gradually mature, and ammonium from water phase could be nitrated directly by nitrifying bacteria within the biofilm, which could enhance the effect of nitrification.

3.1.4 Changes of dissolved oxygen(DO) concentration at different influent mode

Nitrification is a typical aerobic reaction while denitrification is the anaerobic reaction, therefore the level of dissolved oxygen concentration has an important influence on the pollutant removal effect. Dissolved oxygen of each sampling port was monitored regularly under different influent mode, and the results were shown in Figure 6. At upflow mode, dissolved oxygen concentration increased from 5# to 1# and the reactor was in different gradients of dissolved oxygen, which is conducive to the conduct of nitrification and denitrification. Under downflow mode, dissolved oxygen

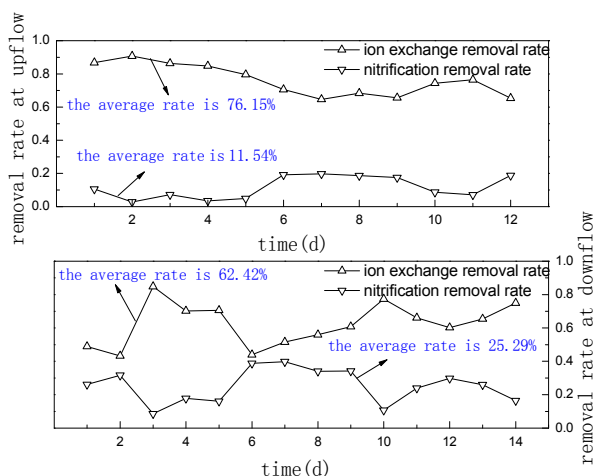


Fig.5 The ammonium removal efficiency under two influent modes

concentration of 3#,4# and 5# were over 2mg/L, which nitrification could be carried out smoothly, while nitrite and nitrate concentration were much higher in worked water and dissolved oxygen concentration of 1# and 2# was about 0.5~1.5mg/L, and the upflow mode was changed that a portion of effluent was returned to the influent. Nitrification and denitrification could be strengthened on the condition of lack of much oxygen. Dissolved oxygen was over 2mg/L of each sampling port after returning, which could provide a suitable condition for the nitrification, and denitrification could be strengthened by anoxic area in biofilm.

3.2 Result and discussion of the removal efficiency at different HRT

The removal efficiency of COD and ammonium by activated sludge and reaction column was studied at different hydraulic retention time, as shown in Figure 7. The results showed that the COD removal efficiency was over 70% by activated sludge and reaction column and even reached the similar effect on the condition that HRT was 8h. The average ammonium removal rate by reaction column was over 75% which was better than that activated sludge probably because reaction column had a better capacity of buffering load. The removal rate of ammonium could reach 92% with HRT 10h and then the rate decreased. The comparison of the COD and ammonium removal rate with HRT 10h in the reaction column implied that the removal efficiency of

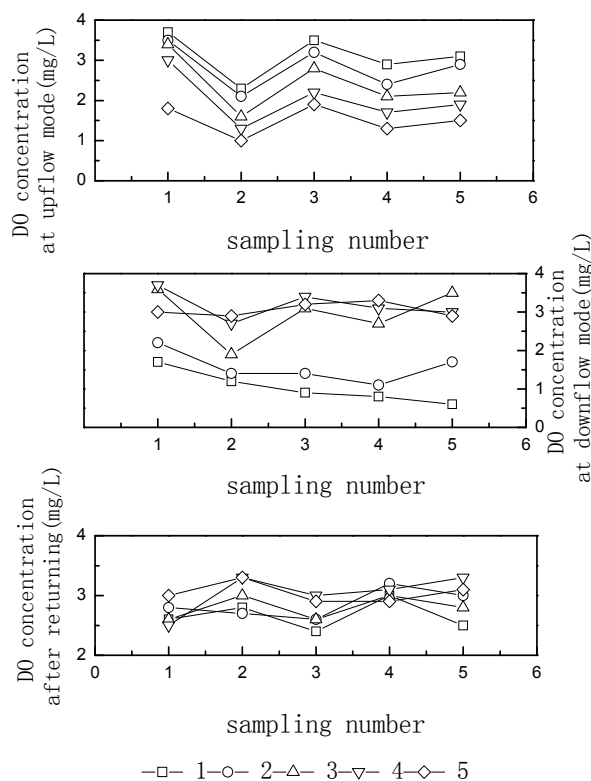


Fig.6 DO concentration under different influent mode

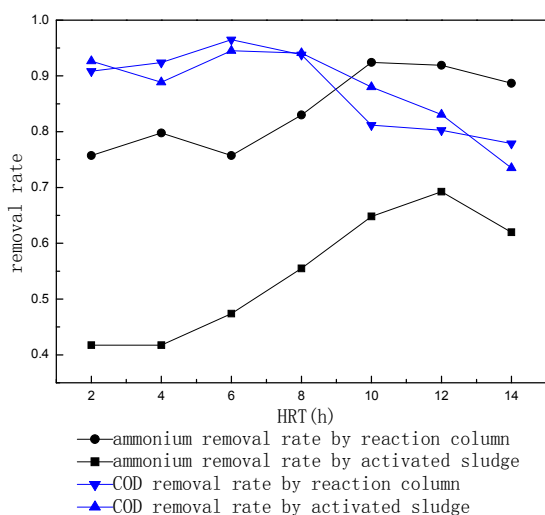


Fig.7 The ammonium and COD removal rate at different HRT

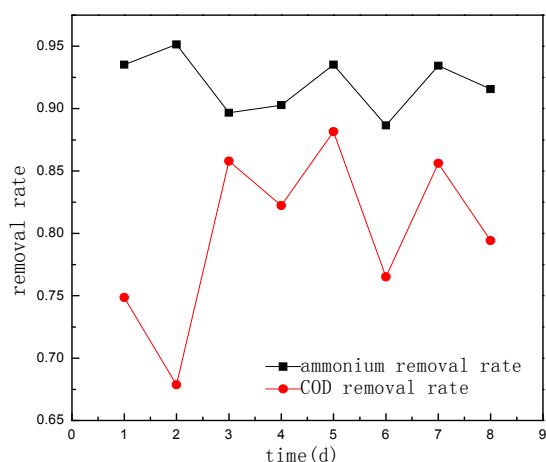


Fig.8 The ammonium and COD removal rate with HRT 10h

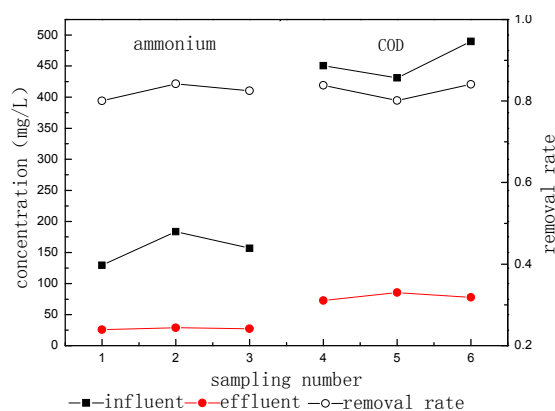


Fig.9 The ammonium and COD removal rate by reaction column in real tannery wastewater

ammonium was more stable and the removal rate of ammonium was about 90%, as shown in Figure 9.

3.3 Result and discussion of the removal efficiency of real tannery wastewater in the reaction column

The removal efficiency of ammonium and COD in the real tannery wastewater was investigated after a stable operation of reaction column, as shown is Figure 9. The results indicated that the removal efficiency of ammonium and COD by reaction column could reach 84.3% and 84.1% with influent concentration 183mg/L and 490mg/L respectively.

4. Conclusions

The experimental result of this paper could lead to the following conclusion:

(1) The COD removal efficiency at upflow mode was over 70% and even could reach 85% and the removal efficiency of ammonium at upflow mode was better than that of downflow mode, and the removal rate could reach 95% and ammonium concentration in worked water was less than 15mg/L.

(2) The ion exchange was the major part in removing ammonium under two influent modes. The mean ion exchange rate was 76.15% and the average nitrification rate was 25.29% because of strengthened nitrification by downflow mode.

(3) The COD removal efficiency by activated sludge and reaction column was over 70% and two methods had a similar effect on COD with HRT 8h. The average ammonium removal rate by reaction column was over 75% and the rate could reach 92% with HRT 10h, and the removal effect of ammonium of the real tannery wastewater by reaction column was 84.3%.

5. Acknowledgment

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