

Study on the Effect of Iron-carbon Filler on Simultaneous Nitrogen and Phosphorus Removal During Short-cut Nitrification and Denitrification

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Iron-carbon filler is added to the short-cut nitrification and denitrification biological reactor (A/O/A) to evaluate the pollutant removal effect. The results show that under the condition of pH=7.8-8.7 and DO=3-5mg/L in oxic unit, the nitrite could be accumulated quickly and the rate of accumulation could reach more than 45%. Meantime, the average removal rate of NH₄⁺-N, COD, TP could reach 92%, 88.6% and 90.5% respectively under steady working condition. By comparison, without adding iron-carbon filler, the average removal rate of NH₄⁺-N, COD, TP are 86.3%, 79.5% and 80.1% respectively. This technology indicates new directions for urban wastewater nitrogen and phosphorus removal process.

1. Introduction

In the course of wastewater treatment process, we would often confront the issue of nitrogen and phosphorus removal. For simultaneous nitrogen and phosphorus removal, there would be some confusions such as different sludge age, the carbon resource, etc, which make the process of simultaneous nitrogen and phosphorus removal unsteady and inefficient (Yang, et al, 2010; Hai et al, 2015; Wang et al, 2015). As one of the required mineral nutrient substance for microbial growth, iron element plays the positive role in helping plants to grow, and thereby can apparently improve the wastewater treatment effect.

Catalytic iron could consume part of dissolved oxygen in wastewater and create the more anaerobic environment, and thereby improve the phosphorus removal effect of dephosphorization bacteria. Zero-valent iron (ZVI) is accessory factor to some enzyme e.g. decarboxylase. Iron ion plays an important role in aerobic respiration of microorganism. Meantime, iron ion is one of the best chemical catalyst and has the invigorating effect on membranal permeability.

Currently, micro-electrolysis has been widely applied in treatment of various wastewaters for its easy operation, low cost and good treatment efficiency (Zhou, et al, 2013). Activated carbon (AC) has exceptionally high surface area (ranges from 500 to 1500 m²/g) and well-developed internal microporosity (Rivera-Utrilla et al, 2011), so it is an ideal cathodic material for microelectrolysis. When ZVI (anode) and AC (cathode) are mixed and contacted with each other, numerous microscopic galvanic cells are formed spontaneously between these two electrodes, and simultaneous occurrences of redox reactions on the surface of a large number of electrodes can result in significant electron flow in micro-electrolysis system. Because the electric energy is converted from chemical energy of ZVI, micro-electrolysis is much less expensive than conventional electrolysis with an external power supply. The half-cell reactions can be represented as (Lai et al, 2012) There are two common situations for iron element in aqueous solution; under the weak acidity, iron is corroded and generates hydrogen, see Eq(1). While under the weak alkalinity, iron absorbs oxygen, see Eq(2).



Under the condition of aeration, the corrosion of iron will accelerate. In addition, iron is endowed with electrochemical property, which could make macromolecule break up into macromolecule midbody.

To our best knowledge, there has been no study that investigated the effects of ZVI-AC micro-electrolysis (hereafter named "iron-carbon") on simultaneous nitrogen and phosphorus removal during short-cut nitrification and denitrification till date. Hence, this work was carried out to assess the performance of iron-carbon filler on the nitrite accumulation, COD removal, nitrogen and phosphorus removal in the course of short-cut nitrification and denitrification.

2. Materials and methods

2.1 Experimental setup and process

The experimental setup and process are shown in Figure 1. The raw water is from domestic wastewater in one community. Iron-carbon filler is added into oxic unit, the treatment capacity of this system is 10L/h.

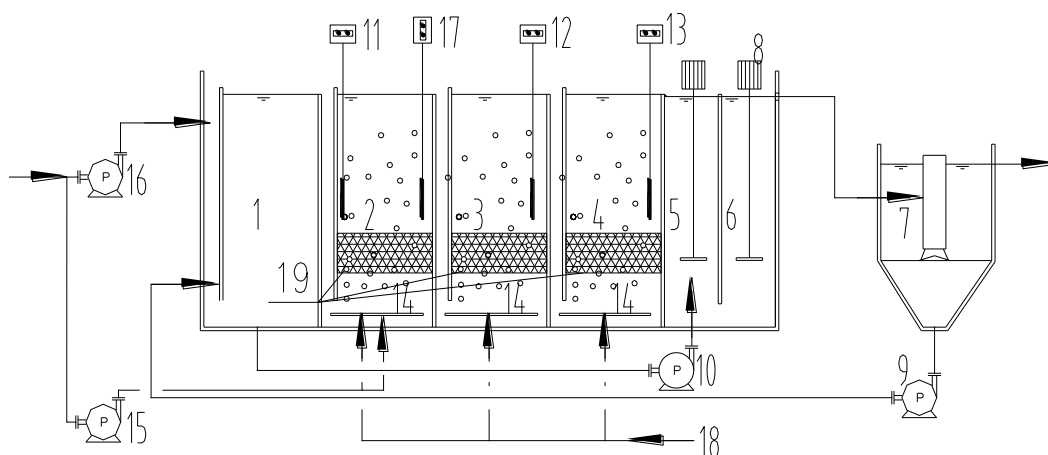


Figure 1: Process flow diagram of Anaerobic-Oxic -Anoxic simultaneous nitrification and denitrifying dephosphatation (1-anaerobic unit; 2,3,4-oxic unit; 5,6-anoxic unit; 7-sedimentation tank; 8-mixing device; 9-sludge reflux pump; 10-effluent pump for anaerobic unit; 11,12,13-DO control device; 14-aerating device; 15-bypass feed pump; 16-feed pump; 17-pH online monitoring device; 18-air/oxygen; 19-iron-carbon filler).

The advantages of this system are: a) part of raw water is shunted to oxic unit, which increase the concentration of dissociated ammonia and thereby promote the growth of nitrite bacteria in oxic unit; b) divided-flow feeding can extend the retention time of wastewater in anaerobic unit, which is helpful to phosphorus release sufficiently; c) part of the effluent from anaerobic unit after sufficient phosphorus release is shunted to anoxic unit. In such case, taken nitrite as electron acceptor, phosphorus can be accumulated easily.

The optimum pH for nitrite bacteria and nitrate bacteria is different. When pH is approximately 7.9, the optimal accumulation effect of nitrite is achieved. In the experiment, the pH was adjusted and controlled within 7.8-8.7 by means of adding NaOH solution, then NH₄Cl solution was added to control the concentration at the level of 60mg/L.

The chosen iron-carbon filler in the experiment is heliciform shape with the length of ca. 50 cm, which is mainly composed of zero-valent iron and carbon element. Before feeding into oxic unit, iron-carbon filler was immersed into 10% hydrochloric acid in order for activation and striping. After striping, the filler was cleaned by deionized water.

The mixed liquor inside of the reactor remains weakly-alkaline because in the weakly-alkaline environment, iron can generate Fe(OH)₂. Iron-corrosion leads to increasing of pH, which results in increasing of dissociated ammonia. This reaction is helpful for the growth of nitrite bacteria, and thereby makes the nitrite accumulate steadily and quickly.

2.2 Analytical methods

Samples were collected periodically from the system to determine of COD, TP, $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$. COD, TP, $\text{NH}_4^+\text{-N}$, nitrite were determined in accordance with standard methods (AHPA et al., 1998) integrated with domestic standard methods. DO and pH values were determined daily with a pH meter and a DO meter (HACH, Loveland, Colorado, USA). Determination procedures for the following indicators were referenced from the literature: COD, dichromate method (GB11914-89); ultraviolet spectrophotometry (HJ/T 346-2007); $\text{NO}_2^-\text{-N}$, spectrophotometric method (GB 7493-87); $\text{NH}_4^+\text{-N}$, Nessler's reagent spectrophotometry (HJ 535-2009); TP, ammonium molybdate spectrophotometric method .

The COD, TP and $\text{NH}_4^+\text{-N}$ removal efficiency and catalytic selectivity to N_2 were calculated as:

$$\text{COD removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (3)$$

$$\text{Nitrate removal efficiency (\%)} = \frac{C'_0 - C'_t}{C'_0} \times 100\% \quad (4)$$

$$\text{Nitrite removal efficiency (\%)} = \frac{C''_0 - C''_t}{C''_0} \times 100\% \quad (5)$$

$$\text{TP removal efficiency (\%)} = \frac{C'''_0 - C'''_t}{C'''_0} \times 100\% \quad (6)$$

where C_0 is the initial concentration of COD in wastewater (mg/L), C_t is the COD concentration (mg/L) at time t (min) ; C'_0 is the initial concentration of nitrate in wastewater (mg/L), C'_t is the nitrate concentration (mg/L) at time t (min); C''_0 is the initial concentration of nitrite in wastewater (mg/L), C''_t is the nitrite concentration (mg/L) at time t (min) ; C'''_0 is the initial concentration of TP in wastewater (mg/L), C'''_t is the TP concentration (mg/L) at time t (min) .

3. Results and discussions

In the beginning of the experiment, the metal carrier bed was added in the middle of oxic unit, and air was fed from bottom. Afterwards, the aeration type was changed. Aeration device was installed inside of filler, which can avoid uneven aeration thus make sludge black under anaerobic condition. In such case, the system became steadier. Under steady working condition, pollutant removal effects were studied.

3.1 COD removal

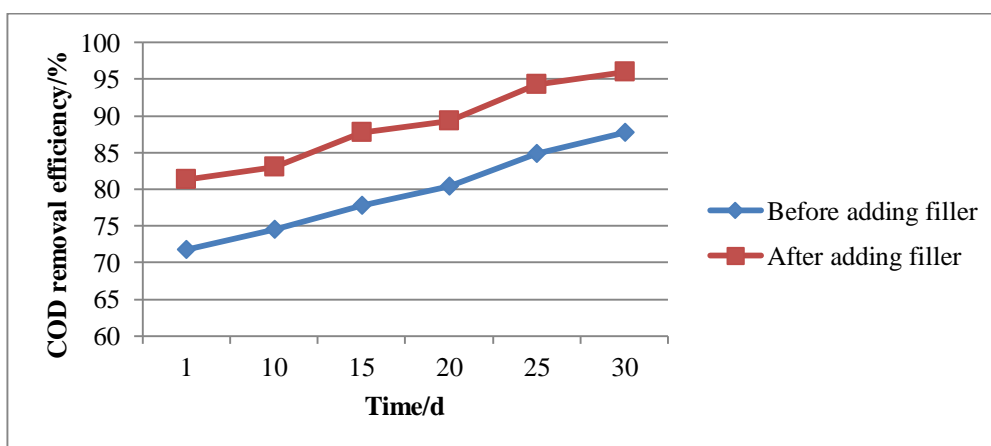


Figure 2: Effect of iron-carbon filler on COD removal.

Figure 2 shows the change of COD removal after adding iron-carbon filler compared with previous non-filler. From the figure, we can know that adding filler have a profound impact on the COD removal for the wastewater treatment. It's clear to see that before adding filler, the COD removal efficiency remains the upward trend and reaches the peak of about 87% at the 30d. The average COD removal efficiency is 79.5%. while after adding filler, the COD removal efficiency improved obviously. At the first day, the removal reaches approximately 82% that increases by 10% compared with that before adding the filler. And then the removal goes up steadily until reaches 96% at the 30d. The COD removal efficiency is 88.6% averagely.

3.2 Nitrogen removal

Nitrification is the microbiological oxidation of $\text{NH}_4^+\text{-N}$ to $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$. Because of its oxygen demand and toxicity to aquatic macroorganisms, $\text{NH}_4^+\text{-N}$ removal is a mandated process for some wastewaters. In addition, wastewater treatment that involves denitrification of $\text{NO}_3^-\text{-N}$ frequently requires nitrification to convert the input $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$ (Eckenfelder, 2000). The denitrification rate will depend on the biodegradability of the organics in the wastewater and the concentration of active biomass under aeration similar to the aerobic process. This, in turn, is related to both the SRT or F/M and the presence of inert solid in the sludge. As the F/M increase, the concentration of active biomass and the rate of denitrification increase (Rittmann and MaCarty, 2001). Figure 3 shows the change of nitrogen removal. Before adding filler, the average $\text{NH}_4^+\text{-N}$ removal efficiency is 86.3% and reaches the peak of roughly 90% at the 30d. After adding filler, the $\text{NH}_4^+\text{-N}$ removal efficiency increases rapidly from 86% at the first day to about 96% at the 30d. The average $\text{NH}_4^+\text{-N}$ removal efficiency after adding filler is 92%. It increases by 5.7%.

According to the principle analysis of nitrogen removal, the removal of nitrogen is due to the co-effect of physical, chemical and biological reaction. But the primary factor is microbial nitrification and denitrification.

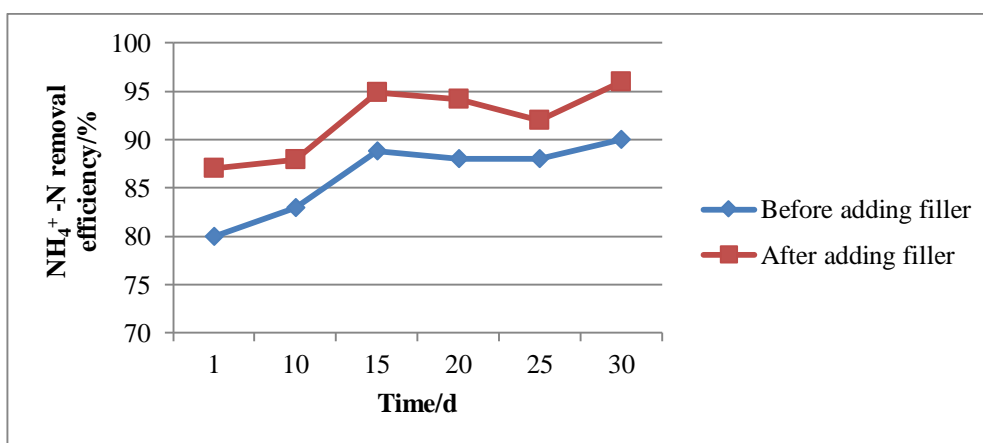


Figure 3: Effect of iron-carbon filler on $\text{NH}_4^+\text{-N}$ removal

Figure 4 shows the accumulation rate of nitrite in the section of oxic unit. It's obvious to see that the nitrite accumulation rate improves significantly after adding filler. Before adding filler, the nitrite accumulation rate maintains the same level (about 31.3%). However, after adding the filler, the rate rises greatly from 40% at the first day to 50% at the 30d. The average accumulation rate of nitrite. The rate after adding filler is 31.3% and 45% increased by 13.7%.

Analysis from the removal theory, traditional nitrification, which means oxidation of ammonia to nitrite and nitrate in turn by ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) respectively, is not the only way of nitrogen removing. In recent years, more and more studies showed short-cut nitrification (SCN) was achieved in reactors (Peng and Zhu, 2006; Yang and Yang, 2011). In SCN, ammonia is oxidized into nitrite by AOB without further transformation into nitrate by NOB, which causes nitrite accumulation. Nitrite can be directly changed into dinitrogen gas through denitrification, such as the SHARON (single reactor high activity ammonia removal over nitrite) process (Hellinga et al., 1998). Nitrite accumulated through SCN, together with ammonia, can also be converted into dinitrogen gas under anoxic conditions by anammox bacteria, such as the OLAND (oxygen limited autotrophic nitrification denitrification) process (Kuai and Verstraete, 1999).

In this A/O/A reactor, adding the filler, the nitrite accumulation rate remains a higher level, compared with that of before adding the filler. Therefore, from the experimental results, we can assume that the short-cut nitrification may occur in this stable system, which tends to increase the nitrite concentration in the wastewater. Therefore, the addition of iron-carbon filler is conducive to make nitrite accumulating.

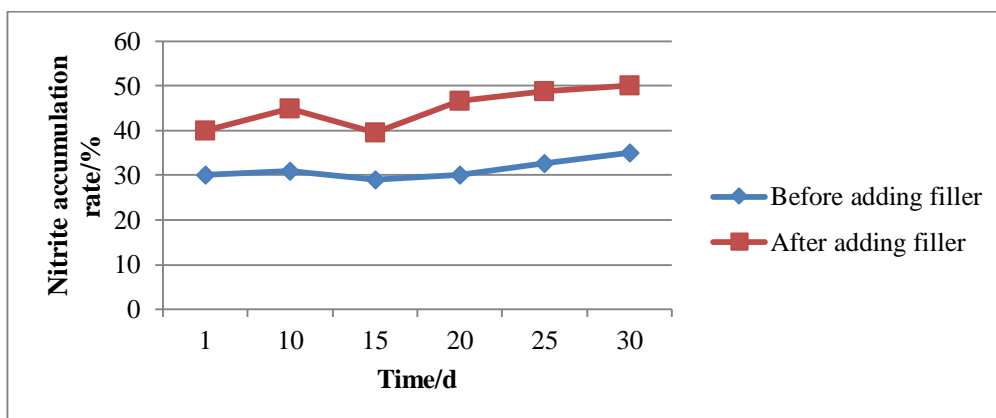


Figure 4: Effect of iron-carbon filler on nitrite accumulation.

3.3 Phosphorus removal

Phosphorus, like N, is assimilated by bacteria and removed from the water with the excess sludge. The degree of removal is related to the rate of sludge production. It has been found, however, that certain bacteria can remove more than the usual quantity of phosphorus as a result of the unusually high P content in the sludge mass. Figure 5 shows the change of phosphorus removal. From the statistics, we can know that the iron-carbon filler can have a great impact on the TP removal efficiency. The lines shows different trends before and after adding filler. Before adding filler, at the first day, the TP removal efficiency reaches only 68% and gets to 84% and then remains stable, reaching 85% after 6 days. However, after adding the filler, the TP removal efficiency reaches 85% at the first day, and then increases dramatically, getting to 97% at the sixth day. The average TP removal efficiency before adding filler and after adding filler are 80.1% and 90.5% respectively. Meanwhile, it shows that the phosphorus removal efficiency under different time is steady after adding iron-carbon filler, which implies that this technology can realize the high and steady phosphorus removal efficiency.

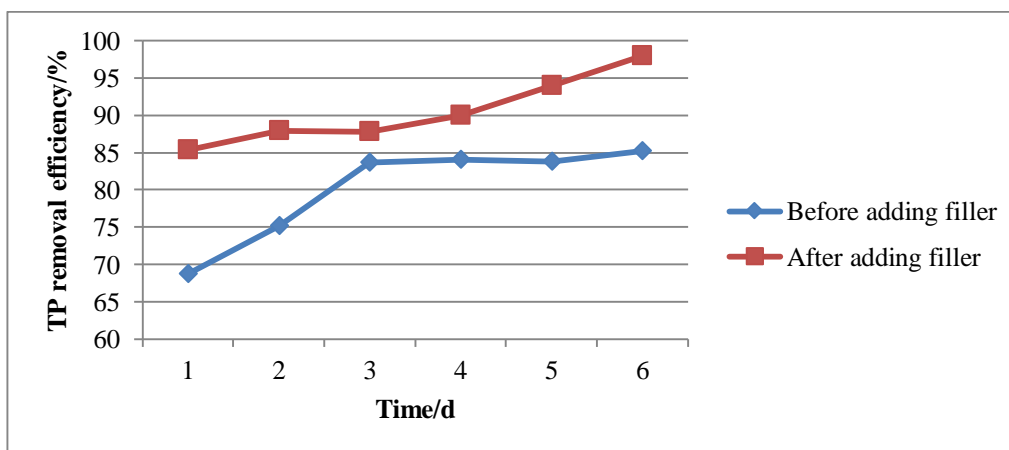


Figure 5: Effect of iron-carbon filler on phosphorus removal.

4. Conclusions

After the quick start-up of A/O/A process, under the steady working condition, the accumulation rate of nitrite in oxic unit can steadily reach 10mg/L, while the removal efficiency of $\text{NH}_4^+\text{-N}$, COD and TP can reach above 92%, 88% and 90.5%, respectively. In the anoxic unit, denitrifying phosphorus removal can be achieved which takes nitrite as electron acceptor.

Metal iron carrier has obviously effect on promoting nitrite accumulation. When pH and DO was controlled under 7.8-8.7 and 3-5 mg/L, the accumulation rate of nitrite can reach above 45%. There are biological denitrifying phosphorus removal and chemical phosphorus removal simultaneously in this system, so the phosphorus removal efficiency is satisfactory.

This system combines the short-cut nitrifying nitrogen removal with denitrifying phosphorus removal, which indicates new directions for urban wastewater nitrogen and phosphorus removal process. However, this process requires stricter control parameters and skilled operation staff. Therefore, this technology still needs to be improved and complete.

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