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Research on the effects of ferric salt added into aeration tank for phosphorus removal on biochemical system

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Abstract

In this paper, two iron salts, ferrous chloride (FeCl_2) and ferric chloride (FeCl_3), are directly added into an aeration tank for phosphorus removal, and their effects on the biochemical system are studied; the water quality parameters such as pH and alkalinity are also investigated. The extent of influence of the added iron salts on the pH and alkalinity of aerated solutions is demonstrated to be $\text{FeCl}_3 > \text{FeCl}_2$. When the dosage of iron ions is 20 mg/L, the decrease in pH and alkalinity caused by FeCl_3 is 0.5 and 65 mg/L, which is higher than FeCl_2 by 2% and 26%. The initial phosphorus removal effect of FeCl_2 is worse than that of FeCl_3 , but after continued aeration and oxidation, the phosphorus removal effect of FeCl_2 can be improved; however, the final phosphorus removal effect is basically the same as that of FeCl_3 added directly. The results show that FeCl_2 is preferred when iron salt is added directly into the aeration tank to remove phosphorus. The proposed scheme can reduce the effect of iron salts on the alkalinity of the biochemical system on the premise of ensuring the phosphorus removal effect of the system, and is conducive to ensuring the stable operation of the biochemical system.

Keywords: iron salt, aeration tank, pH, alkalinity, total phosphorus

1 Introduction

As the urbanisation process is expedited and people's living standards have improved in China, the quantity of wastewater discharge is also rising year by year [1], and the black odour water body and eutrophication are increasingly becoming a serious concern [2–4]. In order to reduce the total wastewater and pollutant discharge,

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the level-I A discharge standard of GB 18918–2002 has been fixed: The Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant is being implemented comprehensively and may become even more stringent than usual [5–7]. This has caused most wastewater treatment plants to upgrade their standard of water quality indexes, such as the total phosphorus and nitrogen, mainly by process adjustment or extension to enhance the nitrogen and phosphorus removal effect [8,9]. In terms of phosphorus removal, there are mainly two approaches: (1) directly adding coagulated phosphorus removing agent into aeration tanks, and (2) extending the coagulative precipitation tank [10,11]. Extending an aeration tank requires large investment, takes a long period of construction, and requires increasing the floor area. On the other hand, adding a phosphorus removing agent directly into aeration tanks requires only minimal investment, and does not increase the land area along with fast reconstruction, and so is widely applied, although its impact on the biochemical system cannot be ignored.

Coagulated phosphorus removing agents mainly include aluminium and ferric salts. Since aluminium ions may have certain effects on microorganisms [12], and the phosphorus removing effect of ferric salt coagulant is better than aluminium salt [13], ferric salt is more widely used in actual phosphorus removing projects. The common ferric salt coagulants are FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, FeCl_2 , FeSO_4 and so on [14], among which FeCl_3 is frequently used in phosphorus removing projects. In projects that involve removal of phosphorus from wastewater, the FeCl_3 used is primarily prepared on the basis of FeCl_2 . By adding oxidising agent, catalyst and hydrochloric acid, the FeCl_2 is oxidised to FeCl_3 . The added hydrochloric acid accounts for 20% [15,16], so the FeCl_3 added will influence the pH and alkalinity of the biochemical system to a certain extent, and will further produce adverse effects on the performance of the biochemical system, especially the sludge nitrification system. If FeCl_2 is directly added to aeration tanks, it will be transformed into FeCl_3 under the oxidation effect of aeration oxygenation. This not only reduces the hydrochloric acid added and the agent preparation cost but also prevents the effects of FeCl_3 on the biochemical system. Recently, there are no reports related to the research on the effects of FeCl_2 and FeCl_3 added to the biochemical system.

This paper mainly investigates the changes in pH, alkalinity and phosphorus removing effect after adding FeCl_2 and FeCl_3 into a solution, and studies the effects of FeCl_2 and FeCl_3 on the biochemical system of aeration tanks, so as to provide a reference for wastewater plants, which directly add coagulated phosphorus removing agents; this will enable us to select the appropriate phosphorus removing agent in upgrading standards and reconstruction projects.

2 Materials and methods

2.1 Experimental device and test water

Experimental drugs used were sodium bicarbonate (AR), sodium carbonate (AR), sodium phosphate (AR), ferric chloride (AR), ferrous chloride (AR), and hydrochloric acid (AR).

Coagulants used were solid ferrous chloride and ferric trichloride; these were placed in a beaker to prepare the solution with iron ionic concentration of 10%.

The experimental device is shown in Table 1.

The test water is the simulation solution and the effluent is taken from the aeration tank of a wastewater treatment plant in Qingdao. In studying the effects of two ferric salts, FeCl_2 and FeCl_3 , added to the pH, alkalinity and phosphorus removing effect of aeration tanks, in view of the complex quality of wastewater in wastewater plant, to prevent the disturbance of other elements in the solution to test results, the simulation solution is used for study, and the test results are verified in real wastewater.

Table 1 Main instrument table for testing.

Experimental device	Type
Digital electronic analytical balance	AUY220
Precise PH meter	PHS-3C
Vacuum extractor	MC-600D
Stirrer used in coagulation test	ZR4-6
Magnetic stirrer	MS7-H550-Pro
Silent air pump	AP9903A
UV spectrophotometer	UVmini-1240

2.2 Test scheme

2.2.1 Effects of ferric salt added on simulation solution

(1) Prepare a simulation solution with alkalinity of 120 mg/L (calculated with CaCO_3 , same as below), and measure its initial pH value. Add FeCl_2 and FeCl_3 (with iron ion content of 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L, 30 mg/L and 35 mg/L, respectively) into two groups of solutions, stir them with magnetic stirrer (at a speed of 200 r/min) and aerate (for 30 min), then let it stand still. Next, measure the pH value of the solution, take the supernatant and measure the alkalinity of the solution. Add ferric salt into two groups of solution, respectively, stir them with stirrer (at speeds of 200 r/min 1 min; 100 r/min 5 min), let them stand still and then measure the pH value and alkalinity of the solution.

(2) Prepare a simulation solution with alkalinity of 120 mg/L and total phosphorus content of 4 mg/L. Mix the solution with HCl to make its pH the same as the initial pH of solution in step (1). Operate according to the addition quantity of ferric salt in step (1) and the test steps, filter it and measure the remaining phosphorus content of the filtrate.

2.2.2 Effects of ferric salt added on aeration tank

The effluent from the aeration tank of a wastewater plant in Qingdao is taken and we measured its total phosphorus content as 4 mg/L. Based on the test results of simulation solution, the optimal dosage of ferric ion is determined. The test steps are the same as in Section 1.2.2, and the changes in pH value and alkalinity of the solution and its phosphorus removing effect are observed.

2.3 Analytical method

Potentiometric titration in the Water and Wastewater Analysis and Test Method (fourth version) is used to measure the alkalinity content.

The standards specified in the Water quality-Determination of total phosphorus-Ammonium molybdate spectrophotometric method (GB 118993-89) are used to measure the total phosphorus content.

3 Results and discussion

Activated sludge is the key to the effect of wastewater disposal in aeration tanks, while the pH value and alkalinity of aeration tanks are closely related to the survival, propagation and metabolic function of microorganisms [17–19]. Therefore, in order to enhance the phosphorus removing effect without influencing the biological removal of nitrogen, this paper studies the effects of adding FeCl_2 and FeCl_3 on the biochemical system of aeration tanks through three indexes: the pH value, alkalinity and phosphorus removing effect.

3.1 Effects of ferric salt added on pH value

It can be seen from Figure 1 that adding FeCl_2 and FeCl_3 to the solution and conducting aeration treatment will reduce the pH value of the solution; as the dosage increases, the decreasing trend of pH value becomes more obvious. When the initial pH value of the solution is 8.5, and the ferric ion dosage is 10 mg/L and 35 mg/L, FeCl_2 makes the pH value to reduce by 0.2 and 0.9, and FeCl_3 makes the pH value to reduce by 0.2 and 1.8, which results in a greater impact on pH. The reason why addition of ferric salt can lead to a decrease in pH is that ferric ions need to consume OH^- during hydrolysis. The reaction equation of ferric ion and OH^- is as follows:

Under neutral or alkalescence condition, ferrous ions can easily be oxidised to ferric ions. Its chain reaction with OH^- is as follows:

That is, adding 1 mol FeCl_2 to oxidise to FeCl_3 can consume 1 mol OH^- less than directly adding 1 mol FeCl_3 . So, directly addition of FeCl_2 into aeration tanks has lesser impact on pH than FeCl_3 .

The pH value is an important factor that affects biological nitrogen and phosphorus removal. Li Nan [20] et al. found that in acidic conditions, the glycogen-accumulating organisms fight with phosphorus-accumulating bacteria on the substrate, leading to a decrease in biological phosphorus removal performance. In neutral or alkalescence conditions, however, the phosphorus-accumulating bacteria account for 60% in activated sludge, which is a dominant bacteria with stable and efficient biological phosphorus removal performance. Nitrifying bacteria react very sensitively to pH, and Li Li et al. [21] discover from research that in neutral and alkalescence conditions, it is more conducive for microorganism floccules to assimilate the ammonia nitrogen in the water body. Hence, the neutral and alkalescence conditions are the optimal pH range of biological nitrogen and phosphorus removal. When the FeCl_2 dosage is 35 mg/L, the pH of solution is 7.6, which is still within the optimal pH range of biological phosphorus removal and ammonia nitrogen assimilation; but when the FeCl_3 dosage is 35 mg/L, the pH of solution is 6.7, showing faintly acidic nature, which has a certain effect on biological nitrogen and phosphorus removal.

Fig. 1 Effects of adding ferric salt on pH value.

It can be seen from Figure 1 that adding FeCl_2 and FeCl_3 to the solution will reduce its pH value, and the pH value of aerated solution is one unit higher than that of non-aerated solution. This indicates that aeration is helpful to increase the pH value of a biochemical system, and to bring down the effects of ferric salt added to the pH value of the biochemical system. It is inferred that the causes of raised pH value of solution after aeration treatment may be that (1) the pH value is significantly positively correlated with the dissolved oxygen concentration in the water, with the correlation coefficient >0.9 [22]. Aeration can elevate the concentration of

dissolved oxygen in the water, resulting in a rising pH value of solution; and (2) aeration can release CO₂ in the water, leading to a decrease in carbonate and an increase in pH value by one unit [23].

In order to verify the specific reason for rising pH value of aerated solution, the following experiment was carried out. Test I: conduct aeration treatment on pure water, observe the change in pH value of pure water before and after aeration; Test II: fill CO₂ in pure water, conduct aeration treatment and observe the change in pH value of pure water before and after aeration. See test results in Table 2.

Table 2 Pure water test.

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Test I		Initial pH	The pH after aeration	
	Pure water	6.4	6.3	
	Tap water	7.7	8.3	
Test II		Initial pH	The pH after filling in CO2	The pH after aeration
	Pure water	6.2	5.3	6.4

From the data of Test I, it is observed that the pH value of pure water is basically the same before and after aeration, demonstrating that the dissolved oxygen is not the reason for the rising pH value of solution after aeration treatment. The pH value of tap water rises by 0.6 after aeration treatment. Compared to the change in pH value of pure water, it is inferred that aeration brings some substances out of tap water and leads to the rising pH value of solution. From the results of Test II, it is observed that the initial pH value of pure water is 6.2, the pH value of solution decreases by 0.9 after filling CO₂ in the solution and the pH value of solution after aeration treatment has little difference with the initial pH value. These observations indicate that the reason for the raised pH value of solution after aeration treatment is that aeration brings down the CO₂ content in the solution.

3.2 Effects of ferric salt added on alkalinity

Alkalinity is a vital factor that affects biological nitrogen removal. In the nitrification reaction, oxidising ammonia nitrogen into nitrate needs to consume 7.1 g alkalinity, so as to balance the acidity generated in nitrification. At the same time, nitrifying bacteria and nitrococcus also consume alkalinity to propagate. The denitrifying bacteria can produce 3.5 g alkalinity every time it reduces ammonia nitrogen [24]. If we want the biological nitrification reaction to proceed normally, it is essential to satisfy the remaining alkalinity to be >100 mg/L, and if the alkalinity is insufficient, it is necessary to add alkaline matter to supplement the alkalinity. So, when adding ferric salt to improve the phosphorus removal effect, it is required to consider the consumption of alkalinity by ferric salt. To guarantee the biological nitrogen removal effect, it is necessary to ensure the alkalinity. If the alkalinity is insufficient, it is required to add alkaline matter to supplement the alkalinity.

From Figure 2, it is observed that the initial alkalinity of the solution is 123 mg/L. After adding FeCl₂ and FeCl₃ to the solution and conducting aeration treatment, the dosage of ferric ion is 10~35 mg/L, and the FeCl₂ added makes the solution's alkalinity to reduce by 20 mg/L, 26 mg/L, 33 mg/L, 44 mg/L, 51 mg/L and 59 mg/L. Under the same dosage, FeCl₃ consumes twice as much alkalinity as compared to FeCl₂. When the dosage of ferric iron is 20 mg/L, FeCl₃ consumes >50% alkalinity. From the above data, it is shown that ferric salt added will consume the solution's alkalinity, and the more the dosage is, the more the alkalinity will be consumed; under the same dosage, FeCl₃ has a greater impact on the alkalinity. The reasons why addition of ferric salt can bring down a solution's alkalinity are that: (1) ferric ion consumes OH⁻ during hydrolysis (see reaction equation in Section 2.1) and (2) ferric iron consumes HCO₃⁻, and the reaction equation of ferric ion is as below:

In the process by which FeCl₂ reacts with O₂ to generate FeCl₃, partial ferrous ions reform to Fe(OH)₃ sediment; therefore, the free ferric ions are fewer in comparison with those obtained pursuant to direct addition of FeCl₃,

and HCO_3^- is consumed less. Thus, directly adding FeCl_2 into aeration tanks consumes less alkalinity of biochemical system than that of FeCl_3 .

From Figure 2, we can see that there is little change between the alkalinity of aerated and non-aerated solutions, which indicates that aeration has less effect on the alkalinity change of solution after adding FeCl_2 and FeCl_3 .

Fig. 2 Effect of adding ferric salt on alkalinity.

3.3 Impact of ferric salt added on phosphorus removal effect

In Figure 3, the initial total phosphorus content of the solution is 4 mg/L, and FeCl_2 and FeCl_3 added can reduce the total phosphorus content of the solution; as the dosage increases, the total phosphorus content of the solution tends to be stable after a decline. Without aeration treatment, the phosphorus removing effect of adding FeCl_2 is worse than that of FeCl_3 ; after aeration treatment, the phosphorus removing effect of FeCl_2 and FeCl_3 does not differ much. When ferric ion dosage reaches to 20 mg/L, the total phosphorus contents of their supernatant are 0.48 mg/L and 0.49 mg/L (<0.5 mg/L), respectively, which meets the level-I. A discharge standard of the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB18918-2002) ($\text{TP} \leq 0.5$ mg/L). Therefore, adding ferric salt into aeration tanks directly, whether FeCl_2 or FeCl_3 , can achieve the anticipatory phosphorus removing effect. But FeCl_2 added has less impact on the pH value and alkalinity of the solution, with more advantage of cost performance.

Fig. 3 Effect of adding ferric salt on phosphorus removal.

3.4 Effects of adding ferric salt on aeration tank

To avoid the effects of organophosphorus content in wastewater, the effluent from the aeration tank of a wastewater treatment plant in Qingdao was taken to verify the effects of adding FeCl_2 and FeCl_3 on the aeration tank. The initial pH and alkalinity of the solution are 7.1 mg/L and 126 mg/L, and the prepared total phosphorus content is 4 mg/L (the total phosphorus content of raw water is 0.27 mg/L). The dosage of ferric ion is 20 mg/L (see test results in Figure 4).

Fig. 4 Treatment results of effluent from aeration tank with different valence ferric salts.

It is observed from Figure 4 that, after adding FeCl_2 and FeCl_3 into the solution, the pH value of the solution reduces by 0.2 and 0.5, and the alkalinity reduces by 19.8% and 42.0%. After conducting aeration treatment on the solution, the aerated pH values rise by one unit more than the non-aerated solution, and the alkalinity remains unchanged, which conforms to the impact of simulation solution on pH value and alkalinity. After adding FeCl_2 in the solution, the solution is also treated by aeration, and the phosphorus removing effect can reach to 99.7%. At this time, the total phosphorus content of the supernatant is 0.01 mg/L < 0.50 mg/L, which meets the level-I A discharge standard of the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB18918-2002), and the phosphorus removing effect is better than that of non-aerated solution (with removing rate of 60.7%), which approximates to that of directly adding FeCl_3 in the solution (with removing rate of 97.2%). So, with regard to the premise of guaranteeing the phosphorus removing effect, directly adding FeCl_2 has less impact on the biochemical system of an aeration tank than FeCl_3 .

4 Conclusions

(1) Adding FeCl_2 and FeCl_3 may reduce the pH value of an aeration tank. Under the same dosage, FeCl_3 has greater effects on pH value than FeCl_2 . But aeration can improve the pH value of the biochemical system, and lessen the effects of adding ferric salt on the pH value of a biochemical system to a certain extent, so as to lessen the effects of pH value on the biological nitrogen and phosphorus removal performance.

(2) Adding ferric salt will consume the alkalinity of aeration tank and affect the biological nitrogen removal effect. Under the same dosage, FeCl_3 consumes more alkalinity than FeCl_2 , which tendency conforms to the required impact on pH value; though aeration can affect the pH value, it basically does not affect the consumption of alkalinity by FeCl_2 and FeCl_3 .

(3) FeCl_3 has a better phosphorus removal effect than FeCl_2 , so it is a priority selection in coagulated phosphorus removal process. When adding ferric salt in aeration tanks, FeCl_2 has a better phosphorus removal effect than FeCl_3 , so it is a priority selection in directly adding ferric salt in aeration tanks for phosphorus removal, with the ferric ion dosage of 20 mg/L.

(4) Directly adding ferric ions into aeration tanks for phosphorus removal has a certain effect on the pH

value and alkalinity of the biochemical system, while its specific impact on the nitrogen removal by nitrification and denitrification needs to be further investigated.

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