

Role of Iron-Carbon Micro-Electrolysis in Constructed Wetlands for Nitrate Removal: A Review

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Nitrate (NO_3^-), as one of the main causes of eutrophication in water body, has contaminated seriously groundwater and surface water due to the excessive discharge of nitrogenous wastewater from agriculture and industry. Compared to other nitrate removal techniques, constructed wetlands (CWs) are frequently used to reduce nitrate to nitrogen gas (N_2). Among the numerous methods of enhancing nitrate removal performance in CWs, iron-carbon Micro-Electrolysis (Fe/C-M/E) system, provides a unique occasion of waste material (iron scrap) for handling wastewater containing nitrate. Currently, the introduction of Fe/C-M/E structure could enhance nitrate removal rates by 20 % ~ 50 % in different types of CWs. Although the application of iron as the special substrate in nitrogenous wastewater treatment is intensively investigated with a large variety of CWs, research about Fe/C-M/E impact on the removal of nitrogen in CWs so far is very limited. Particularly, the information about the comprehensive interaction of biological and electrochemical effects with several distinct factors is inadequate, making it hard to obtain essential and universal conclusions. This paper offers a summary of research regarding Fe/C-M/E system in CWs used to remove nitrogen, discussing nitrogen removal pathways and mechanism via the effect of microorganism or Fe/C system. It also mainly focuses on the influence in the converting NO_3^- to N_2 process by different operation parameters such as the type of carbon, the iron-carbon doping ratio, dissolved oxygen (DO), hydraulic retention time (HRT) and pH. It is worth noting that Fe/C-M/E CWs have not only high nitrate remove rate, but also relatively very little emissions of nitrous oxide (N_2O), which as one of the main potential sources of greenhouse gases. Finally, this paper proposed some suggestions on future study and application.

1. Introduction

The frequent living and productive activities of human beings promote the development of society, but also lead to more and more serious nitrate pollution in water body. Excessive input of nitrate in the water not only cause eutrophication and damage the ecosystem, but also harm human health (Deng et al., 2011). Among the measures to deal with nitrate pollution in water bodies, constructed wetland (CWs) has been widely used due to its advantages of low cost and easy maintenance (Shuai and Jaffe, 2019). The primary way to remove nitrate in CWs is microbial heterotrophic denitrification, where the organic carbon source is served as an electron donor for the reduction of nitrate to N_2 . However, in practice, CWs often fail to effectively remove nitrate from the wastewater owing to the shortage of electron donors (Liu et al., 2020). Compared with the high cost of external carbon sources, the research to enhance the autotrophic denitrification process to improve the overall denitrification has attracted more attention and interest. In addition, low temperatures greatly weaken the effect of denitrification, which is an inevitable problem in the long-term operation of CWs. The main reason may be that the activity of denitrifying bacteria is inhibited when the temperature is below 10 °C to generally poor nitrate removal during the winter months (Yan and Xu, 2014).

Micro-electrolysis technology, as a vital application of electrochemical denitrification, plays an important role in strengthening the denitrification of CWs due to its high nitrate removal efficiency, stable operation and low temperature dependence (Gao et al., 2017). The iron-carbon micro-electrolysis structure (Fe/C-M/E) requires no extra power supply, and has been widely used in the treatment of printing and dyeing wastewater (Qin et al., 2012), landfill leachate (Wu et al., 2015), pharmaceutical wastewater (Xu et al., 2016), while relatively few

studies have been done on the combination of Fe/C-M/E and biological denitrification processes applied to nitrate removal in CWs (Wu et al., 2019). Under different redox conditions, the conversion between divalent and trivalent iron is easily achieved, and this cycle of different valence states as provides potential for enhancing the nitrogen removal from CWs. Since the sewage is equivalent to an electrolyte solution, then a mixture of iron and carbon can be placed in the sewage to form numerous typical micro-galvanic cell structure. Then, the existence of [H] from cathode and the oxidation of ferric ions from anode offer additional electrons for denitrification reaction, which provides opportunity to facilitate iron autotrophic denitrification and increase the nitrate removal efficiency (Liu et al., 2018). Currently, this enhancement technology was done mainly in laboratory studies. For instance, the nitrate removal rate of the CWs with Fe/C-M/E could reach 99 % under the influent nitrate concentration of 15 mg/L, compared with 57 % in the control group (Shen et al., 2019). Nevertheless, little systematic research is known about the effects of different operating parameters on the denitrification results of Fe/C-M/E CWs, such as the type of carbon, iron-carbon doping ratio, dissolved oxygen (DO), pH and hydraulic retention time (HRT), and the theoretical support and experience in the application design of corresponding CWs are extremely lacking.

Accordingly, the purposes of this review were (1) to clarify the mechanism of nitrate removal in CWs coupled with Fe/C-M/E, (2) to analyse and summarize the influence of different operating parameters on the results of nitrate removal in Fe/C-M/E constructed wetland system, and (3) to provide the theoretical references and pertinent practical directions for the application of Fe/C-M/E in the CWs to remove nitrate from wastewater.

2. Mechanism of enhancing the nitrate reduction efficiency by Fe/C-M/E

Based on the enhanced nitrogen (N) removal efficiency of CWs with iron, macromolecular refractory organic compounds were transformed into biodegradable small molecular due to the Fe/C-M/E, which provided more available carbon sources for denitrification. The Figure 1 shows the schematic diagram of enhancing nitrate removal by Fe/C-M/E, where the reaction of galvanic cells formed via iron-carbon structure coupling with the nitrate removal pathways. Obviously, iron was oxidized to ferrous at the anode while hydrogen ion was reduced to H₂ at the cathode (Eqs(1) and (2) (Wu et al., 2013)). A large number of studies have demonstrated that Fe²⁺ was a critical factor to improve NO₃⁻ and TN removal rates, because the reaction of reducing NO₃⁻ to N₂ with Fe²⁺ is fundamental to autotrophic denitrification. The stoichiometry of the nitrate-dependent Fe (II) oxidation can be described as Eqs(3) and (4) (Ding et al., 2014). The presence of Fe/C-M/E can generate additional electrons for microorganisms to complete with the denitrification reaction. Besides, some NO₃⁻ was converted to NH₄⁺ through the process of dissimilatory nitrate reduction to ammonium (DNRA). The Fe/C-M/E structure not only coordinated the biological or biochemical reactions during the denitrification, but also affected the direction of N conversion. Iron can easily react with NO₃⁻ to produce NH₄⁺, which was the major way to remove NO₃⁻ via chemical reaction (Eq(5) (Liu and Wang, 2019). Although this process could remove vast NO₃⁻, it also brings overmuch NH₄⁺ as by-product. On the other hand, iron could also consume DO to achieve natural oxidation, which was also result in the NH₄⁺ accumulation. In addition, the anaerobic ammonium oxidation coupled with iron reduction (Feammox) may exist in the Fe/C-M/E under certain condition, which oxidizes NH₄⁺ to NO₂⁻ or N₂ (Deng et al., 2016).Iron is also an essential element for the synthesis of microorganisms and plant cells, which can facilitate the enzymes and coenzymes generation in related reactions and accelerate the chemical synthesis process.

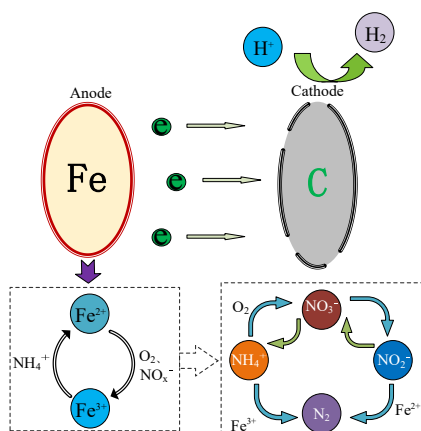
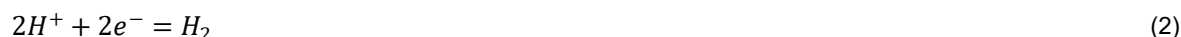


Figure 1: Schematic representation of enhancing nitrate removal by Fe/C-M/



3. Operating parameters

3.1 The type of carbon

The types of carbon in Fe/C-M/E structures included biochar (BC), activated carbon (AC), and solid carbon sources such as treated plant residues. Activated carbon is the earliest and most common carbon adsorption material used in internal-electrolysis structure, which has been widely applied in strengthening N removal. A mixture of iron chips and 4-6 mm diameter AC particles were used as substrate in the wetland and the NO₃⁻ removal efficiency reached more than 86 % (Guo et al., 2016). Generally, the smaller the particle size of AC is, the larger its specific surface area will be, and it is easy for AC to capture more free nitrate ions. AC after high heat treatment could enhance removal efficiency due to the expansion of pores (Khalil et al., 2017). The micro-electrolytic structure composed of BC (particle size 0-1 cm) and iron scraps could also significantly improve the removal efficiency of NO₃⁻ and TN, which were increased to 87 % and 78 % (Jia et al., 2020). However, the adsorption of nitrate ions by BC had little effect on nitrate removal. In addition, this study suggested that BC could improve microbial activity and increase cation and anion exchange capacity, boosting nitrate reduction. Compared with AC and BC, the influence of solid organic carbon as the structure component of micro-electrolytic on denitrification in CWs was less studied, but the effect was considerable. Canna leaves, straw and peanut shells were modified with organic reagent, and then loaded on iron to obtain different composite iron-carbon materials. The NO₃⁻ removal rates in the three types of CWs were from 75.3 % to 91.1 %, however, the effluent concentration of NH₄⁺ increased compared with that of no solid carbon source and iron (Zhao et al., 2019). The modified solid carbon source can not only play a role in adsorbing some NO₃⁻ in the wastewater, but also release organic carbon to act as the electron donor for the denitrification reaction (Wang and Chu, 2016).

In general, BC is further activated by physical and chemical means to AC at higher than 700 °C. There are differences in the structure and adsorption property of AC and BC. BC has a large amount of negative charge on the surface (Nguyen et al., 2020), which would have a negative effect on attracting nitrate ions in the iron-carbon galvanic cells structure and be not conducive to strengthening the denitrification process. In addition, with the pyrolysis temperature rises, volatile substances in biomass were removed, the micropore volume of BC became larger, and the specific surface area would increase (Ahmad et al., 2012). But the specific surface area is still about twice as small as AC (Inyang et al., 2010). From another point of view, numerous researches have shown that BC could release organic carbon for microbial to use (Lehmann et al., 2011), providing additional organic carbon source and enhancing denitrification, while AC does not have similar function due to the excessive degree of carbonization. In addition, compared with the complex production process of AC, BC was more accessible and cheaper (Ozcimen and Ersoy-Mericboyu, 2010), and suitable for large-scale and long-term application.

3.2 The iron-carbon doping ratio

During the laying of CWs substrate, the iron-carbon doping ratio can induce the NO₃⁻ conversion direction in the CWs operation process, affecting the denitrification efficiency (Wei et al., 2019). When the mass ratio of iron-carbon was 5:1, the influence of Fe/C-M/C on the denitrification performance of underground flow constructed wetland was studied. It was found that the TN removal rate reached 88.23 %, with the inflow concentration of NH₄⁺ and NO₃⁻ was 8 mg/L and 12 mg/L (Zheng et al., 2019). In addition, the average NO₃⁻ removal rate in the CWs with iron and no carbon was higher than 90 %, despite feeding 20.3 mg NO₃⁻-N/L in the influent, but the TN removal rate is less than 50 % duo to the 10.8 mg NH₄⁺-N/L was accumulated (Liu et al., 2020). On the contrary, the presence of carbon matrix alone also affects the removal rate. The average removal efficiency of NO₃⁻ and TN in the group with solid carbon but no iron increased by 16.3 ~ 18.5 % and

17.1 ~ 19.0 %, compared with the control group without iron-carbon structure (Zhao et al., 2019). In order to further reveal the mechanism of the impact of iron-carbon doping ratio on the denitrification, Shen et al. set up subsurface flow Fe/C-M/E CWs controlled trials with different mixture ratio. And the results showed that although the TN removal efficiency was observably improved, the removal rate of TN at 4:1 was 4.14 % lower than that at 1.5:1, which was also attributed to the NH_4^+ accumulation (Shen et al., 2019).

The influence of different mixture ratio of iron and carbon on the denitrification effect of CWs cannot be ignored. Particularly the special proportion, that is, the presence of only iron will make NO_3^- obviously inclined to the transformation of NH_4^+ . Also, the presence of only carbon will facilitate the transformation of NO_3^- into N_2 and NH_4^+ in a balanced way. Generally, the infinite tiny galvanic cell structures formed by iron-carbon can generate an electric potential difference in the wastewater. Through electrode interaction, it can accelerate the iron corrosion and attract nitrate ions to move towards the positive pole, which is conducive to the reduction of NO_3^- . Nevertheless, at the same time, the electrochemical reaction also played an important role in facilitating dissimilatory nitrate reduction to ammonium. In the process, iron serves as a reducing agent to reduce NO_3^- to NH_4^+ and the increase in iron content would also cause the accumulation of NH_4^+ (Choe et al., 2003). On the other hand, iron also used the DO to form ferrous ions through oxidation, which was competitive with nitrification (Hefa et al., 2007). This distinct induction direction has different influences on the final denitrification result in CWs. Considering that NH_4^+ is also a pollutant that needs to be removed, it is necessary to utilize the induction direction to serve the purpose of complete denitrification via exploring the optimal iron-carbon doping ratio in practical applications (Teng et al., 2018).

3.3 Dissolved oxygen

Dissolved oxygen (DO) is an important factor affecting the denitrification process, because microorganisms involved in the denitrification process can carry out normal life activities under specific oxygen content conditions in the system. In general, denitrification reaction can be maintained normally with DO below 0.5 mg/L, while denitrification and nitrification occur simultaneously with the DO varied in the range 0.5-1.0 mg/L. The enhancement performance of Fe/C-M/E on denitrification in CWs is subject to the DO condition. Without controlling the DO, the TN removal rate of the Fe/C-M/E group was still higher than that of the control group, but the NH_4^+ accumulation became obvious with the decrease in DO (Shen et al., 2019). The reason was that iron and NH_4^+ competed for oxygen, which inhibited nitrification reaction, and the oxygen secreted by plant roots was not enough to promote the transformation of NH_4^+ . The research that DO was controlled in the range of 4-6 mg/L has been carried out, and the results indicated that NH_4^+ and TN removal rates in the iron-carbon group are as high as 98.63 % and 81.21 %, which were the comprehensive function of microbial action and electrochemical effect (Zheng et al., 2019). It is worth noting that the introduction of aeration can destroy the original anoxic or anaerobic environment. A better measure could be intermittent aeration, such as twice a day and each time for 1 h. In this way, the DO was controlled from 0 to 2 mg/L, and the removal rates of NO_3^- and TN were increased to 87 % and 78 % (Jia et al., 2020).

Normally, the CWs seldom be equipped with aeration device in order to protect the denitrification microorganisms. However, iron inevitably leads to the surplus of NH_4^+ , which is not conducive to denitrification. Aeration operation, as the most direct and convenient measure, can improve the DO and remove a lot of accumulated NH_4^+ through nitrification. Nevertheless, the addition of oxygen would cause incomplete denitrification, resulting in the more accumulation of N_2O needed to be avoided (Lee et al., 2018). In previous research, aeration did not cause a sharp increase in N_2O emissions, perhaps due to the presence of Fe/C-M/E (Jia et al., 2020). Under the premise of not obviously impairing the denitrification effect, less aeration amount and shorter aeration time are of great significance to reduce the cost in practical application.

3.4 Hydraulic retention time and pH

In general, when the HRT becomes longer, the N removal amount will be increased in CWs due to the extended reaction time. When treating the influent with 20.3 mg NO_3^- -N/L, Liu et al. (2020) set three different HRT of 6 h, 12 h and 24 h, and the results showed that the nitrate removal efficiency increased from 48.7 % to 98.4 % with the extension of HRT. In addition, this study demonstrated by calculation that NH_4^+ was produced by the abiotic reaction of iron. It is a remarkable fact that shorter HRT is beneficial to the abiotic reaction, while autotrophic denitrification tends to be longer HRT. In addition, the decrease in NH_4^+ concentration may as result of redox reaction between ammonium ion and ferric iron (Zhao et al., 2018).

Similar to the reduction of nitrate through biological processes, the chemical reaction between iron and nitrate is also one of the nitrate removal pathways, which is affected by pH in the environment. In the research of using iron to remove nitrate in the low carbon-to-nitrogen ratio wastewater, the findings suggested that pH in the water gradually risen to 10.5, inhibiting the normal growth of denitrifying bacteria and iron were also prone to precipitation (Liu et al., 2018). Although reducing nitrate with iron work well only under a controlled pH of less than 4, the introduction of Fe/C-M/E is able to mitigate this limitation. In the wastewater treatment with

influent nitrate concentration of 50 mg/L, the NO₃ removal efficiency in the Fe/C-M/E group decreased from 97 % to 73 % as the increase of initial pH from 2 to 6, while the removal rate in the iron group only reached about 10 % (Luo et al., 2014). The higher reduction rate was maintained because the iron-carbon structure established the galvanic cell and accelerated the iron corrosion. Accordingly, electron transfer may be a crucial step in limiting nitrate reduction at a higher pH value. The advantage of the iron-carbon structure was that electrons could be supplied more quickly and NO₃ was reduced with less time (Deng et al., 2016). However, it is worth considering that measures should be taken to further accelerate the corrosion rate of iron in the Fe/C-M/E, which is also conducive to the dissolution of surface iron oxides, such as improving the conductivity of wastewater.

4. Conclusions

In general, the nitrate removal efficiencies in F/C-M/E CWs is 70 % ~ 90 %, while that of in traditional CWs is 30 % ~ 50 %. In this review, the effects of Fe/C-M/E on nitrate removal have been widely discussed with many kinds of operation parameters such as the type of carbon, the iron-carbon doping ratio, DO, pH and HRT. Biochar can not only establish tiny galvanic cell structure with iron to accelerate the iron corrosion but also release organic matter, which both could contribute to enhance denitrification of microorganisms. However, high iron-carbon mixing ratios results in ammonia accumulation, which would be mitigated by moderate aeration and properly prolonging HRT. It is undeniable that in the long-term application of Fe/C-M/E, iron oxides or other sediments may be attached to the surface of iron and block its reaction with carbon, leading to the weakening of the strengthening effect. These findings would conducive to a better comprehension of the interactions between nitrate removal and Fe/C-M/E, particularly in CWs treatment system. A suggestion should be attempted by applying F/C-M/E to salt marsh, as it may promote both corrosion of iron and electron transfer due to the high electrical conductivity. It is feasible and efficient to improve the denitrification limitation in CWs at low temperature.

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