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Critical Review

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[Critical Review Proposal]

Critical Review: Biogeochemical Networking of Iron, Is It Important in Constructed Wetlands for Wastewater Treatment?

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Abstract：

Iron is present in all types of wastewater, however besides acid mine drainage, where it is a major constituent of concern, it is usually neglected in other types of wastewaters. However, in all constructed wetlands iron plays important role in removal of organics, phosphorus and does have an impact on transformation of nitrogen and sulphur. The biogeochemistry of iron is well understood in natural wetlands but knowledge about iron impact on microbiological and chemical transformations during wastewater treatment in constructed wetlands is very limited. So far the sparse research in this area provides limited information on observed interactions with several varying parameters across the studies, making it difficult to draw fundamental and mechanistic conclusions. A critical review of the complex biogeochemical networking of iron in CWs is therefore necessary to fill the gap in knowledge on the role of iron and its biogeochemical multi-interactions in wastewater treatment processes of CWs. This review is the first with specific focus on iron, discussing its mitigation and retention in CWs with different configurations and operational strategies, and presenting both seasonal dynamics and the potential remobilization of Fe. It also comprehensively discusses the interactions of redox-controlled iron turnover with the biogeochemical processes of other elements, e.g. carbon (C), nitrogen (N), phosphorus (P), sulphur (S), and heavy metals. The health response of wetland plants to both deficiency and toxicity of Fe in CWs designed with specific treatment targets has also been evaluated. Due to the complexity of various wastewater compositions and micro-redox gradients in the root rhizosphere in CWs, future research needs have also been identified.

Keywords： Constructed wetlands; Wastewater treatment, Iron cycling, Multi-interactions; Wetland design

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[Captions of Tables and Figures]

[Justification for the need of this review]

(1) The proposed topic is important. The speciation of iron in constructed wetlands for the purpose of wastewater treatment is redox-dependent and involves many significant transformations, affecting the removal of organics, phosphorus, nitrogen and sulphur. A critical review of the complex biogeochemical networking of iron in CWs is therefore important to fill the gap in knowledge on the role of iron and its biogeochemical multi-interactions in wastewater treatment processes of constructed wetlands.

(2) The proposed topic is new and needed. During 2008-2018, we found 93 review articles in total in Web of Science Core Collection. Based on the quality of the review and similarity of the same topic, we selected 40 key reviews as listing below. The yellow marked keywords of these published reviews indicated a high diversity of topics in field of constructed wetlands. However, the knowledge of biogeochemical networking of iron is beyond the state-of-the-art.

(3) The authors are capable to draft the proposed review. Dr. Shubiao Wu expertises in exploring the understand of the microbial transformations and interactions in constructed wetlands. As a young scientist, he have published more than 30 impacted peer-review journal articles in this field. Prof. Hans Brix is a pioneer of this technology research and development and he was the first to discover and document the ubiquitous occurrence of convective throughflow of air inside the plants as an important root ventilation mechanism in many wetland plants. Prof. Jan Vymazal is a world-famous ecologist and has been working in this field for more than 40 years. He is also the editor of journal Ecological Engineering and has a insight understanding of this technology. Moreover, the first 17 review articles in the above list were published by the authors of the current proposed review. It also indicates the expertise of the authors in this field and their capacity to draft this proposed review.

[Five authors' papers related to the review topic]

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[List of key previous reviews on the subject of constructed wetlands for wastewater treatment in the past 10 years]

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[Topical outline]

1. Introduction

Constructed wetlands (CWs) are the decentralized eco-systems that are constructed and operated with the purpose of wastewater treatment, by manipulating the simultaneous physical, chemical, and biological processes occurring in natural wetlands [1]. Because of their cost-effective and eco-friendly way of treating wastewater, CWs have been developed as an alternative in the last few decades to conventional centralized wastewater treatment systems. From the technical application point of view, along with the growing attention to CW technology, the design and construction of CWs has been extended from traditional basic models to various new configurations, technical amendments and operations to improve the performance for pollution removal.[2, 3]. From the point of view of exploring scientific knowledge, the flourishing publication record of individual experimental research as well as review in the Web of Science might be seen as a simple and direct indicator for the increasing transparency of the knowledge "black box" in this field. For example, microbial transformations of carbon (C), nitrogen (N), phosphorus (P), and sulphur (S) have been extensively investigated and reviewed[3-8]. Moreover, reviews on dynamics of heavy metals [9-11] and emerging organic pollutants, e.g. antibiotics and pharmaceutical contaminants [12, 13] in remediating process of CWs, have also been performed. All these reviews undoubtedly have enabled the mechanisms of these transformations to be more evident in the last few decades. Because iron (Fe) is an essential element, the mitigation and mobilization of Fe in CWs not only participates in many physiological processes, e.g. plant photosynthesis, but Fe reduction-oxidation turnover also affects the geochemical cycle of other elements in CWs [14]. Even though the removal performance of iron in some CWs, particularly those treating acid mine drainage, has been observed[15-17], the comprehensive knowledge on the dynamic mitigation of iron and retention in various emerged wetland configurations and intensive operations has not been well understood. How iron cycling interacts with the microbial transformations of the above mentioned four basic elements and emerging pollutants in CWs also needs to be more clearly explained. So far the sparse research in this area provides limited information on observed interactions with several varying parameters across the studies, making it difficult to draw fundamental and mechanistic conclusions.

In this review, the biogeochemistry of Fe in natural wetland systems will be firstly described, in order to give an overall knowledge background before getting into the comprehensive discussion later. The presence of Fe in various wastewater treated in CWs and its basic redox-controlled turnover in CWs with different configurations and operational strategies will then be summarized. Subsequently the interactions of iron cycling with geochemical processes of other elements (C, N, P, S) will be comprehensively discussed. The health response of wetland plants to both deficiency and toxicity of Fe in CWs designed with specific treatment targets will be evaluated. The role of iron plaque in sequestration and translocation of various trace metals will also be discussed. Finally, future research perspectives associated with Fe in CWs will be pointed out.

2. Iron biogeochemistry

Iron, making up at least 5% of the earth's crust, is one of the earth's most plentiful resources. Iron is a transition element and exist in a wide range of oxidation states varying between -2 to +6, although +2 (Fe^{2+} in soluble form) and +3 (Fe^{3+} in insoluble form) are the most common oxidation states encountered. This section will mainly introduce the basic iron biogeochemistry in treatment wetlands related environments, such as (1) oxidation of ferrous iron to ferric iron and subsequent hydrolysis to ferric hydroxide, Fe(OH)3 or oxy-hydroxide; (2) characteristic reaction of the few chemoautotrophic bacteria that deposit hydroxides and oxides; (3) ferric sulfate, the product of the oxidation, reacts with water to form ferric hydroxide and sulfuric acid; (4) nitrate-dependent Fe(II) oxidation[18]; (5) Feammox[38, 40]; (6) reduction of ferric oxide proceed chemically by the involvement of sulfide[19, 20].

3. Presence of Fe in various wastewaters treated in CWs

The presence of Fe in CWs for wastewater treatment comes from two main sources: influent wastewater and wetland matrix. Because of the unavoidable contact of water with underlying geologic formations, iron becomes a common constituent in many wastewaters, e.g., domestic and municipal sewage, landfill, or acid mine drainage. The content of Fe in various wastewaters will be summarized and discussed in this section.

4. Mitigation and retention of Fe in CWs

The process of mitigation and retention of Fe in CWs mainly involves sedimentation of Fe^{3+} precipitates and plant uptake. The sedimentation process includes several abiotic and biotic sub-processes which depend on the flow path of water along the length of wetland as well as the depth. The Fe uptake performance of wetland plants and immobility in roots will be discussed in this section, but the role of plants in driving dynamic Fe transformations in CWs by mediating redox potential in the rhizosphere with the release of oxygen and various other exudates will be discussed in later sections. Seasonal and diurnal changes of Fe reduction and oxidation in the wetland bed, as well as how heavy rain influences remobilization are also included in this section to enrich our understanding the dynamic mitigation and retention of Fe in CWs.

5. Response of wetland plants to iron deficiency/toxicity in CWs

The health status of wetland plants in CWs is one of the important issues that needs to be considered for long-term operation [1, 21]. Iron is a well- known essential element for plant growth [22]. Either high concentrations of Fe in the reduced form (Fe^{2+}) or deficient bioavailability of Fe can cause serious health symptom of wetland plants and subsequently influence the function of CWs on wastewater treatment. This section will focus on discussing the effect of Fe deficiency or toxicity to wetland plants in different cases, regarding types of CWs, operational strategies and configurations.

6. Interactions of root iron plaque and heavy metals/nutrients sequestration

Formation of iron plaque on the root surface of plants which occurs commonly in CWs for treatment of various wastewaters can account for up to 10% of the total root weight and extend up to 15–17 μm into the rhizosphere [23]. The protons and exuded matter excreted from plant roots acidify the root surrounding micro-environment and dissolve the Fe from the wetland filling materials. When the dissolved Fe is diffused from anaerobic zones to oxygen-rich zones in the rhizosphere iron plaque formation occurs. So the formation of iron plaque is a result of the oxidation of Fe (II) to Fe (III) from the oxygen released from the root and the subsequent precipitation of iron oxide on the root surface. Root iron plaque present in natural systems is generally of highly specific surface area, due to its particular Fe phase and degree of crystallinity, and possession of hydroxyl (-OH) functional groups [24]. These characteristics enable iron plaque to be capable of reacting with various trace metals and nutrients, e.g. phosphorus, thereby affecting their cycles. Up to date, there have been extensive efforts made towards understanding the role of iron plaque in trace metals sequestration and nutrient (e.g. P) uptake [25-27]. Research from paddy soils and natural wetlands was also comprehensively reviewed by Tripathi et al. (2014) and Khan et al. (2016). Therefore from the point of view of using CWs for treating wastewater, the potential role of iron plaque on trace metal sequestration and interaction with phosphorus uptake is presented and discussed in this section.

6. Multi-interactions of Fe-phosphorus-sulfur in CWs

Phosphorus control is always one of the most important monitoring strategies in the wastewater treatment process to decrease the eutrophication risk. The adsorption of P to substrate in CWs plays a primary role. Strong affinity of phosphorus ions to iron oxides drives a preferred selection of iron-rich materials as substrate in CWs. Particularly, the selection of specific industrial wastes containing Fe as substrates to enhance P retention in the wetland bed is becoming an important design and construction strategy (Table S2). Besides, in the well-rooted zones of a wetland bed there exist numerous spatial and temporal micro-scale redox gradients due to the release of oxygen from plant roots [28, 29]. These redox gradients in the root zones can simultaneously enable complex interactions to occur between different processes, e.g. Fe-P sequestration and -P release, Fe reduction and/or sulphate reduction [30, 31]. The presence of sulphate may not be very problematic in CWs. However, the synergistic biogeochemical cycling of iron and sulphur due to redox dynamics has been shown to affect both the availability and mobility of P in CWs [7]. This section will mainly discuss the multi-interactions of Fe-phosphorus-sulfur in CWs.

7. Interactions of Fe with nitrogen transformations in CWs

The cycling of iron only involves turnover of two main chemical valences, but has great significance in the biogeochemical cycle of nitrogen[32, 33]. The oxidation and reduction of Fe were often coupled with different nitrogen transformations. Particularly under conditions of sparse organic carbon sources, the role of Fe cycling might be more significant. In this section, the process of denitrification based on nitrate-dependent Fe(II) oxidation and the process of ammonium oxidation coupled to dissimilatory reduction of iron oxides under anaerobic conditions (Feammox) will be mainly discussed.

8 Future research perspectives

Due to the complexity of various wastewater compositions and micro-redox gradients in the root rhizosphere in CWs, future research and development on the cycling of iron and its multi-interactions will be presented here.

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