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Effects of iron and calcium carbonate on contaminant removal efficiencies and microbial communities in integrated wastewater treatment systems

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HIGHLIGHTS

- Abundant *PLANCTOMYCETES* promoting nitrogen removal existed only in treatment ACW10.
- Treatment ACW10 realized 5 consecutive treatment cycles under optimal conditions.
- HCO_3^- increased the power and current density of bacteria in the treatment ACW10.
- The treatment ACW10 was applicable to purify different types of wastewater.

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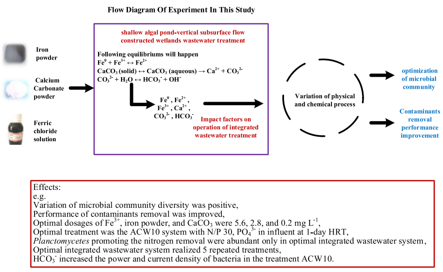
GRAPHICAL ABSTRACT



Effects:
e.g.
Variation of microbial community diversity was positive,
Performance of contaminants removal was improved,
Optimal dosages of Fe^{3+}, iron powder, and $CaCO_3$ were 5.6, 2.8, and 0.2 mg L^{-1},
Optimal treatment was the ACW10 system with N/P 30, PO_4^{3-} in influent at 1-day HRT,
Planctomycetes promoting the nitrogen removal were abundant only in optimal integrated wastewater system,
Optimal integrated wastewater system realized 5 repeated treatments,
HCO_3^- increased the power and current density of bacteria in the treatment ACW10.

ABSTRACT

In the paper, we explored the influences of different dosages of iron and calcium carbonate on contaminant removal efficiencies and microbial communities in algal ponds combined with constructed wetlands. After 1-year operation of treatment systems, based on the high-throughput pyrosequencing analysis of microbial communities, the optimal operating conditions were obtained as follows: the ACW10 system with Fe^{3+} (5.6 mg L^{-1}), iron powder (2.8 mg L^{-1}), and $CaCO_3$ powder (0.2 mg L^{-1}) in influent as the adjusting agents, initial phosphorus source (PO_4^{3-}) in influent, the ratio of nitrogen to phosphorus (N/P) of 30 in influent, and hydraulic retention time (HRT) of 1 day. Total nitrogen (TN) removal efficiency and total phosphorus (TP) removal efficiency were improved significantly. The hydrolysis of $CaCO_3$ promoted the physicochemical precipitation in contaminant removal. Meanwhile, Fe^{3+} and iron powder produced Fe^{2+}, which improved contaminant removal. Iron ion improved the diversity, distribution, and metabolic functions of microbial communities in integrated treatment systems. In the treatment ACW10, the dominant phylum in the microbial community was *PLANCTOMYCETES*, which positively promoted nitrogen removal. After 5 consecutive treatments in ACW10, contaminant removal efficiencies for TN and TP respectively reached 80.6% and 57.3% and total iron concentration in effluent was 0.042 mg L^{-1}.

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1. Introduction

Ecological wastewater treatments, such as algal ponds (AP) and constructed wetlands (CWs) (Barat et al., 2011), can efficiently remove contaminants from wastewater. In algal ponds, the main contaminants removal mechanism is algal assimilation (Ruiz-Marin et al., 2010). In CWs, contaminants removal involves physicochemical and biological mechanisms. Physical mechanisms include absorption and retention by CWs substrates (Mateus et al., 2012). Chemical mechanisms include precipitation and oxidation-reduction reactions (Thongtha et al., 2014). Biological mechanisms include immobilization of microorganisms and phytoremediation (Chang et al., 2012). However, these systems have some disadvantages, such as blocking, carbon source shortage and the lack of oxygen in CWs, toxin release and damage in AP, and the low operation efficiency in CWs and AP at low temperatures (Zhao et al., 2016a). Some composite wastewater treatment systems, such as Anaerobic-Anoxic-Oxic treatment (Wang et al., 2012), were designed to improve the contaminant removal efficiency. Therefore, algal ponds combined with constructed wetlands (ACW) were a good option to increase the contaminant removal in surface wastewater.

Iron has been widely applied in ecological wastewater treatments to improve the removal efficiency of nutrients because its changeable chemical valence can induce various physico-biochemical processes (Ma et al., 2014). Fe (II) can be easily oxidized into Fe (III) under aerobic conditions, whereas Fe (III) can be easily reduced into Fe (II) under reductive conditions (Shrestha et al., 2009). Especially in CWs, various oxidation-reduction zones are found. In addition, Fe (III) reducing bacteria are regarded as crucial mediators of C and N processes (Tan et al., 2006; Wang et al., 2009). Anaerobic NH_4^+ oxidation is coupled to Fe^{3+} reduction with N_2, nitrite, or nitrate as the end-product and acts as an important pathway for nitrogen loss (Ding et al., 2014).

$CaCO_3$ exists in various forms with different stability. It is important in several wastewater treatment processes. $CaCO_3$ as strong electrolyte can produced HCO_3^-, which are easily absorbed by algal cells. In the carbonate-bicarbonate system, HCO_3^- is the preferred carbon source for algal growth (Zhao et al., 2016b; Guo et al., 2015). In ecological treatments, HCO_3^- affects the diversity of microbial community and can improve microbial activities (Zhao et al., 2016b; Tian et al., 2015). HCO_3^- was used to control pH (neutral in CWs) and provide sufficient conductivity for the flow of ions (Fan et al., 2007). In addition, Ca^{2+} produced by $CaCO_3$ can precipitate with phosphorus for removal improvement.

Nowadays, two major problems in ACW treatments should be solved. Firstly, in wastewater treatment systems, the removal efficiency is affected by many factors, such as the ratio of nitrogen (N) to phosphorus (N/P) and initial chemical compounds (CCs) of phosphorus in influent (Zhao et al., 2016c). Previous researches focused on one type wastewater with fixed N/P ratio and CCs of phosphorus in influent (Ruiz-Marin et al., 2010; Prochaska et al., 2007; Stefanakis and Tsihrintzis, 2009). However, the applicability of the treatment systems under different types of wastewater was seldom identified. Secondly, iron combined with $CaCO_3$ play an important role in wastewater treatment removal process. However, previous studies on iron utilization were mainly focused on the physical process in ecological wastewater treatment systems for the purpose of improving the system efficiency (Gutierrez et al., 2010). The chemical and biological processes in integrated ecological treatments were unknown, especially in ACW. Oxidation reduction zones and microbial communities in ACW was the prerequisite to study the changeable chemical valence of iron and hydrolyzed $CaCO_3$, which could induce the variations of microbial community in integrated ecological treatment systems. DNA sequences or genetic diversity of microbial communities in soil and solid waste, such as activated sludge, were widely explored, but related results of microbial communities in ecological wastewater treatment systems were seldom reported (Huang et al., 2015; Yu et al., 2015).

The study aims to investigate the effects of iron and $CaCO_3$ on the contaminant removal efficiency in integrated treatment systems with/without algae under the conditions of different N/P ratios and different CCs of phosphorus in influent in four seasons, determine the optimal conditions in influent in ecological treatment systems, obtain the optimal dosages of iron and $CaCO_3$ in ecological treatment systems, and explore the variations in microbial communities in optimal ecological treatment systems.

2. Materials and methods

2.1. Laboratory-scale units

The composite wastewater treatment systems were designed according to the shallow algal pond combined with constructed wetlands shown in Fig. S1 (Zhao et al., 2016a) and established in Donghua University in Shanghai, China.

The established 9 laboratory-scale composite wastewater treatment systems were shallow algal ponds combined with vertical subsurface flow constructed wetlands. In these systems, various N/P ratios (N/P = 60, 30, and 15) (Zhao et al., 2016c) and different chemical compounds (CCs) of phosphorus (PO_4^{3-}, PO_3^-, and $P_2O_7^{4-}$ were main phosphorous contaminants in groundwater in China) in influent were respectively designed. The 9 systems were respectively named NP60-P1, NP60-P2, NP60-P3, NP30-P1, NP30-P2, NP30-P3, NP15-P1, NP15-P2, and NP15-P3 (P1, P2, and P3 were PO_4^{3-}, PO_3^-, and $P_2O_7^{4-}$, respectively).

Additional 6 ACWs treatment systems were constructed with different dosages of Fe^{3+} in influent. The 6 systems were respectively named ACW0, ACW1, ACW10, ACW20, ACW50, and ACW100. All the abbreviations in this study are shown in Table 1.

2.2. Algal cultivation and system stabilization

The algae (*chlorella sp.* from Freshwater Algae Culture Collection at the Institute of Hydrobiology, FACHB-collection, Wuhan, China) were cultured and enriched with SE (selenite enrichment) medium (Zhao et al., 2016b) and tap water in the laboratory. The initial concentration of chlorophyll *a* (Chl-a) was 10 mg L^{-1} (water quality multi-probe Manta 2, EURERA, USA).

The environmental parameters were provided as follows. Air temperature ranged from 0 °C to 38 °C (Air Quality Measure Meter, Pranus, China); relative humidity ranged from 40% to 85% (Air Quality Measure Meter, Pranus, China); daylight illumination intensity was 3000–10000 Lux (water quality multi-probe Manta 2,

Table 1
Abbreviations used in this study.

Names	Abbreviations
Algal pond	AP
Constructed wetlands	CWs
Algal pond combined with constructed wetlands	ACW
Chemical Compounds	CCs
The ratio of nitrogen and phosphorus	N/P
Dissolved total phosphorus	DTP
Dissolved orthophosphate	DIP
Dissolved organic phosphate	DOP
Oxidation reduction potential	ORP
Total iron	TI