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Influences of iron and calcium carbonate on wastewater treatment performances of algae based reactors

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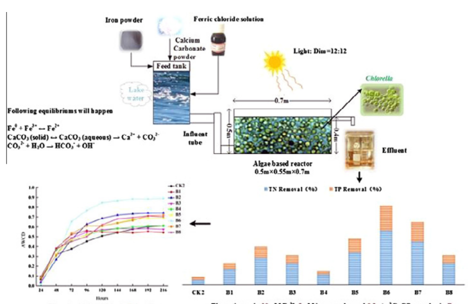
HIGHLIGHTS

- Accumulated HCO_3^- driven by carbonate–bicarbonate increased algae biomass.
- 10 μM Fe^{3+} allowed 20-day continuous operation with high removal efficiency.
- A synergistic effect exists among Fe^{3+}, iron, and $CaCO_3$.

GRAPHICAL ABSTRACT



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ABSTRACT

The influences of iron and calcium carbonate ($CaCO_3$) addition in wastewater treatments reactors performance were investigated. Adding different concentrations of Fe^{3+} (5, 10, 30 and 50 mmol/m^3), iron and $CaCO_3$ powder led to changes in algal characteristics and physico-chemical and microbiological properties. According to the investigation results, nutrient removal efficiency in algae based reactors was obviously increased by the addition of 10 mmol/m^3 Fe^{3+}, iron (5 mmol/m^3) and $CaCO_3$ powder (0.2 g m^{-3}) and the removal efficiencies of BOD_5, TN, and TP in Stage 2 were respectively increased by 28%, 8.9%, and 22%. The improvements in physico-chemical performances were verified by microbial community tests (bacteria quantity, activity and community measured in most probable number, extracellular enzymes activity, and Biolog Eco Plates). Microbial variations indicated the coexistence of Fe ions and carbonate–bicarbonate, which triggered the synergistic effect of physico-chemical action and microbial factors in algae based reactors.

1. Introduction

Nowadays, algae based techniques have been applied in wastewater treatment and nutrient removal (Ramaraj et al., 2015). Algal assimilation of nitrogen (N) and phosphorus (P) plays an important role in contaminant elimination from wastewater. N can be eliminated not only by algal assimilation but also algae-induced chemical processes, such as nitrification and denitrification (Kesaano and Sims, 2014). P can be removed by algae through a combination of adsorption and algae-induced chemical precipitation and microbial reactions (Sanudo-Wilhelmy et al., 2004). Algae grow rapidly and can assimilate nitrogen and phosphorus from wastewater at low operational costs in the less land area (Aslan and Kapdan, 2006). Moreover, algae assimilate nutrients such as nitrogen and phosphorus from sewage water for their growth (Renuka et al., 2015), require less organic carbon (Abdel-Raouf

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et al., 2012), and produce lower CO_2 emission (Boelee et al., 2011). However, traditional algae based water treatment systems also face many challenges: slow algal growth, low algal biomass concentration, and difficult algae harvesting (Xu et al., 2014).

Fe element is required in the growth of plants and animals. The growth and reproduction of algae also requires iron. Iron deficiency and iron overload are both harmful to aquatic organisms. Iron deficiency will restrain or even stop the vital actives of species in environment (Kerry et al., 2008). Iron overload will force some living beings, such as algae, to release the poisonous stuff to ambient which can contribute to the death of the other animals and plants (González et al., 2014). In algae based reactors, optimal iron dosage can maintain algae biomass growth stable. Iron has been widely used in ecologic wastewater treatments to increase the removal performance of nutrients because of the physico-biochemical processes that can be induced by its changeable chemical valence. (Ma et al., 2014). Fe (II) can be easily oxidized into Fe (III) under aerobic conditions, while Fe (III) can be easily reduced to Fe (II) under reductive conditions. Theoretically, the reaction between Fe (0) and Fe (III) may yield Fe (II). This reaction between Fe (0) and Fe (III) is governed by the equilibrium:

$$Fe^0 + Fe^{3+} \leftrightarrow Fe^{2+} \tag{1}$$

Calcium carbonate ($CaCO_3$) is a chemical compound composed of three main elements: carbon, oxygen, and calcium. It is a common substance in rocks, such as limestone. $CaCO_3$ exists in different forms with different specific stability. $CaCO_3$ is important in several industrial processes. The main reaction of $CaCO_3$ as strong electrolyte is governed by the following equilibrium:

$$CaCO_3(\text{solid}) \leftrightarrow CaCO_3(\text{aqueous}) \rightarrow Ca^{2+} + CO_3^{2-} \tag{2}$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \tag{3}$$

$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^- \tag{4}$$

In algae based water systems, atmospheric air provides carbon dioxide (CO_2), which can be transferred into water (Putt et al., 2011). The main reaction between CO_2 and water is regulated by the carbonate–bicarbonate equilibrium (CO_2–H_2CO_3–HCO_3^-–CO_3^{2-}):

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \tag{5}$$

$$H_2CO_3 + H_2O \rightarrow HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-} \tag{6}$$

Algae utilize hydrated carbonate (permeated from atmospheric CO_2 to water) as carbon source to synthesize organic compounds under phototrophic growth conditions. However, the relatively low transfer rate of CO_2 from air to water remains a problem to be solved for improving the growth rate of algae in traditional open algae pond (Stepan et al., 2002). In water, inorganic carbon mainly exists in several interconvertible chemical forms. CO_2 (aqueous), carbonic acid hydrate, H_2CO_3, HCO_3^- and CO_3^{2-} are the major forms influencing the pH in aqueous environments (Hammes and Verstraete, 2002). Carbonic acid hydrate and HCO_3^- are easily absorbed by algal cells and HCO_3^- is the preferred carbon source for algal growth in the carbonate–bicarbonate system (Goldman et al., 1981).

Theoretically, except HCO_3^-, iron ions can promote the growth of algae as well (Han et al., 2015). Chemical processes possibly occurred during algae based water treatment with Fe (0 and III) and $CaCO_3$, such as the reactions (1)–(6). Those processes would promote the growth of algae, which could partly solve the problem of low algal biomass in algae based wastewater treatment systems (Grobbelaar, 2004). Herein, dead algae and algae debris could be utilized as secondary carbon source in the algae based wastewater system. In the previous studies, iron utilization mainly focused on the dosage in ecological wastewater treatment for improving the system performance (Gutierrez et al., 2010). However, the iron-limit on algae biomass stability in algae based reactor was not reported and the dosing volume and utilization efficiency of iron were unknown. CO_2 injection has been widely used in ecological wastewater treatments to change the carbonate–bicarbonate system and improve the nutrient removal performance (Putt et al., 2011). CO_2 fixation by microalgae has been extensively studied to purify wastewater (Ramaraj et al., 2015). Previous microalgae studies focused on the growth environment catalyzed by algae and cyanobacteria, which appeared to be the primary factor for $CaCO_3$ precipitation (Lee et al., 2006) and bio-mineralization (Liang et al., 2013) to harvest the algae. However, $CaCO_3$ was not studied as a growth regulator to trigger the growth of algae biomass. Both $CaCO_3$ and iron benefit the algae growth. The effect of the mixed addition of $CaCO_3$, Fe^{3+}, and iron powder on algae growth in algae based reactor was not studied yet. The synergistic effect among $CaCO_3$, Fe^{3+}, and iron in algae based reactors were unknown.

In the study, algae based wastewater treatment systems were designed with/without adding Fe (0 and III) and $CaCO_3$ to improve the performance of the algae based wastewater systems by changing physico-biochemical characteristics and contaminant removal efficiency. Then, different concentration of Fe^{3+} and iron with/without $CaCO_3$ were added into algae based wastewater treatment systems. We obtained the optimal operation condition and utilization efficiency of iron. Finally, observation of microbiological characteristics showed that the improved performance of algae based water treatment systems was ascribed to the added iron and $CaCO_3$.

2. Materials and methods

2.1. Laboratory-scale units

One kind of laboratory-scale algae based wastewater treatment reactor was set up. In the 15-L transparent Polypropylene material reactor (0.7 m × 0.55 m × 0.5 m), influent tube and effluent tube were respectively arranged on two sides. The influent of contaminated surface water was fed via one input tube in the bottom of reactors from a tank. The volume of influent tank was 100 L. The effluent was taken from Polyvinyl chloride tube, which was set at 0.4 m above the reactor bottom.

15 reactors were used in the experiments. Six (one named CK_1 as the control and the other five reactors named A_1, A_2, A_3, A_4, and A_5) of them was used to study the changes of physico-biochemical characteristics caused by iron and $CaCO_3$ in algae based wastewater treatment systems. The other 9 reactors (one reactor was the control reactor named CK_2 and the other eight reactors were respectively named B_1, B_2, B_3, B_4, B_5, B_6, B_7, and B_8) were used to study contaminant reduction efficiencies and the utilization of iron.

2.2. Experimental design

2.2.1. Algae cultivation

The algae (*chlorella* sp. got from Freshwater Algae Culture Collection at the Institute of Hydrobiology, FACHB-collection, Wuhan, China) were cultured and enriched in laboratory with BG culture medium (Kesaano and Sims, 2014) and tap water. The initial concentration of chlorophyll a (Chl-a) was 10 mg L^{-1}. The cultivation parameters are provided as follows: Air temperature was 28–38 °C (Air Quality Measure Meter, Pranus, China), Relative humidity was 70–85% (Air Quality Measure Meter, Pranus, China), daylight illumination intensity was 7000–10,000 lux (water quality