

Study the drinking water treatment residue (DWTR) based on constructed wetlands with different plants: removal performance and adsorption mechanism.

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Abstract

To investigate the influence of plant types on the pollution removal efficiency of drinking water treatment residue (DWTR) based constructed wetlands, a pilot-scale experiment was constructed, and the adsorption mechanisms for phosphate ($\text{PO}_4^{3-}\text{-P}$) were investigated. The results demonstrated that regardless of plant types, the DWTRs-based constructed wetlands exhibited a high removal efficiency for $\text{PO}_4^{3-}\text{-P}$, but the contribution of plants in improving the adsorption rate was relatively negligible. Additionally, the Langmuir isotherm model can describe the adsorption behaviors well, which exhibited high adsorption capabilities of 162.11 mg/g. Furthermore, the pseudo-second-order model can describe the adsorption kinetics well, demonstrating chemical processes were the main force. This experimental study can provide theoretical guidance to enhance our understanding of the pollutant removal mechanisms in DWTRs-based constructed wetlands.

Keywords: constructed wetlands (CWs), sewage purification, adsorption, drinking water treatment residue (DWTR)

1. Introduction

In rural areas in China, domestic sewage contributes a lot to the source of pollution. Water bodies are often nutrient-rich because of the increasing desire to develop aquaculture. The ever-increasing ammonia nitrogen ($\text{NH}_4^+\text{-N}$) and phosphorus ($\text{PO}_4^{3-}\text{-P}$) cause the algae and plankton in the water to increase rapidly, even exceeding the number that the ecosystem can carry. The drastic increase of algal organisms leads to a decrease in the oxygen content of the water, which subsequently causes many organism deaths. In turn, the ecological balance in the water will be broken, damaging the quality and economic benefits of the water body. Therefore, treating $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ in water has become increasingly important[1].

Removal methods that already exist include chemical precipitation[2], membrane filtration process[3], biological treatments[4], and constructed wetlands (CWs). However, the disadvantages of the former conventional processes are conspicuous. Chemical precipitation requires a huge amount of chemical consumption, membrane filtration is a costly process limited by available materials, and biological methods are vulnerable to operational cost[5]. Considering the economic and development level of rural areas, CW is the effective method to address the water environment problem.

Wetlands are rich in biodiversity and often filter and

degrade pollutants. In short, CWs, engineered systems that use plants, soils, and microorganisms to simulate the biological and chemical processes found in natural wetlands, have been widely used [6-7]. Previous studies have reported the CWs in removing pollutants from water. Liu et al. (2023) have utilized sludge-based ceramsite as a filter to denitrify. However, the best adsorption performance of nitrogen and phosphate were 31.2 % and 64.5 % [8]. Moreover, carbon-based nanomaterials are always being incorporated into filters, coping with removing pollutants from water [9]. Nevertheless, these studies were influential in addressing potential methods for treating pollutants in wastewater, but they did not compare the effect of plant types.

Drinking water treatment residues (DWTRs) are industrial solid wastes with a wide range of applications from biological and chemical research perspectives [10]. They have a high iron and aluminum salt content, so iron and aluminum can be chemically complex with phosphorus in wetlands. More importantly, DWTRs have a high efficiency in removing phosphorus from water [11]. However, knowledge gaps concerning DWTRs-based CWs remain.

Therefore, pilot-scale CWs filled with DWTRs were constructed in this study to compare the removal efficiency for pollutants. Calamus and Phyllostachys heteroclita were considered plants due to their dominance

in shallow waters. Besides, the adsorption behaviors of DWTRs were also explored via adsorption isotherms and kinetic. Results obtained herein help us to understand the decontamination mechanism of DWTRs-based CWs and the adsorption efficiency of DWTRs.

2. Materials and Methods



2.1 CW set-up and operation

Fig.1 The device schematic of DWTRs based-CW

The size of the experimental equipment is 24cm(length)×16.5cm(width)×16cm(height) equipped with ten plants in each experimental device(as shown in Fig. 1). Specifically, group 1 served as the control (no planting + DWTRs) and groups 2 and 3 were experimental groups (filler was DWTRs, but planted with Phyllostachys heteroclita and calamus, respectively). Before startup, the DWTRs-based CWs were acclimated with tap water for 30 d via a pump (Longerpump@, BT100-2J). The experimental influent was synthetic wastewater with 10% domestic sewage as a mineral nutritional supplement. The main composition of the synthetic wastewater included C₆H₆OH, NH₄Cl, and KNO₃, and the concentration of chemical oxygen demand (COD), TN, NH₄⁺-N, and total phosphorus (TP) were 297 ± 24.47, 42.30 ± 3.47, 39.30 ± 4.47, and 5.03 ± 0.55mg/L, respectively. Synthetic wastewater with a flow rate of 0.10 mL/min was introduced from the bottom of BF-MFC to retain hydraulic retention time (HRT) of 24 h, and the

experimental temperature was conducted at approximately 25 °C in a thermostatic Laboratory.

2.2 Analysis methods

2.2.1 Synthetic Artificial Wastewater Analysis

The influent and effluent were sampled from the 1-3 units at regular intervals (6 h) during the experiment. The collected water was firstly filtered by a membrane (0.22 μm), and the concentration of NH₄⁺-N and PO₄³⁻-P in the supernatant was monitored by Nessler reagent spectrophotometry[12] and molybdenum-antimony resistance spectrophotometry[14].

2.2.2 Adsorption experiments

The adsorption experiments were conducted at 25°C under dark conditions. For adsorption isotherms, 50 ml of phosphorus solution (1-1000 mg/L) was added to a glass vial containing 0.25g DWTRs. The mixture was firstly oscillated at 180 r/min for 24 h and then centrifuged and filtered (0.45μm) to determine the remaining PO₄³⁻-P concentration in the supernatant, and Langmuir (1) and Freundlich (2) were used to describe adsorption models were as followed [15]:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

$$q = K_F C_e^{1/n} \quad (2)$$

where q_e and q_m represents the equilibrium adsorption capacity (mg/g) and maximum adsorption capacity (mg/g), k_a and K_F represents the Langmuir adsorption constant and adsorption capacity (mg/g) in the Freundlich isotherm. Besides, pseudo-first-order and pseudo-second-order were used to explain the dynamic adsorption process, and the equations are demonstrated as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_v} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e} \quad (4)$$

3. Results and discussion

3.1 Wastewater Treatment Performance

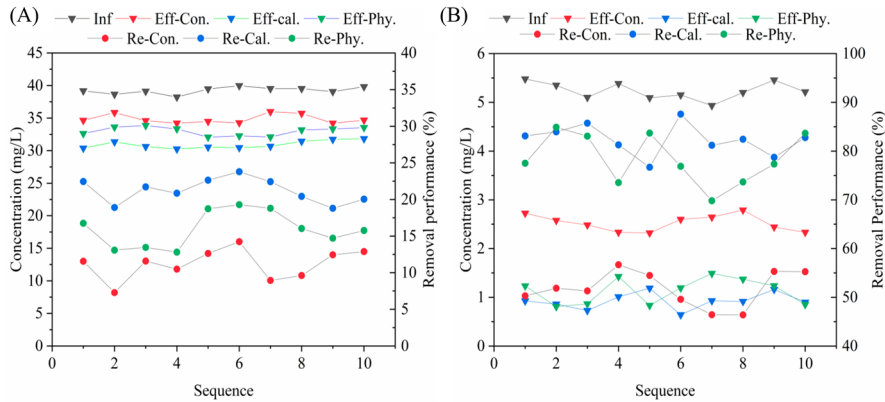


Fig. 3. The removal efficiencies of $\text{NH}_4^+\text{-N}$ (A) and $\text{PO}_4^{3-}\text{-P}$ (B)

The removal efficiencies were shown in Fig. 3, and the removal efficiency of individual units showed minimal variation with time prolonged. However, DWTRs based CWs with plants had better removal performance for $\text{PO}_4^{3-}\text{-P}$ (ranging from about 70% to 88%) than that of $\text{NH}_4^+\text{-N}$ (ranging from about 12% to 27%). The above phenomenon can be attributed to the combined effects of plant absorption and filler adsorption. Besides, owing to the different root growth conditions, the effluent $\text{PO}_4^{3-}\text{-P}$ of

DWTRs based CWs with *Phyllostachys heteroclada* has a slightly than those of *calamus*. In contrast, the opposite trends were observed in Fig.3 (A). The above phenomenon illustrated that the plant type had little influence on the removal performances. Thus, the adsorption caused by the filter was the main factor in pollutant-removal.

3.2 Adsorption performance

3.2.1 Adsorption isotherm analysis

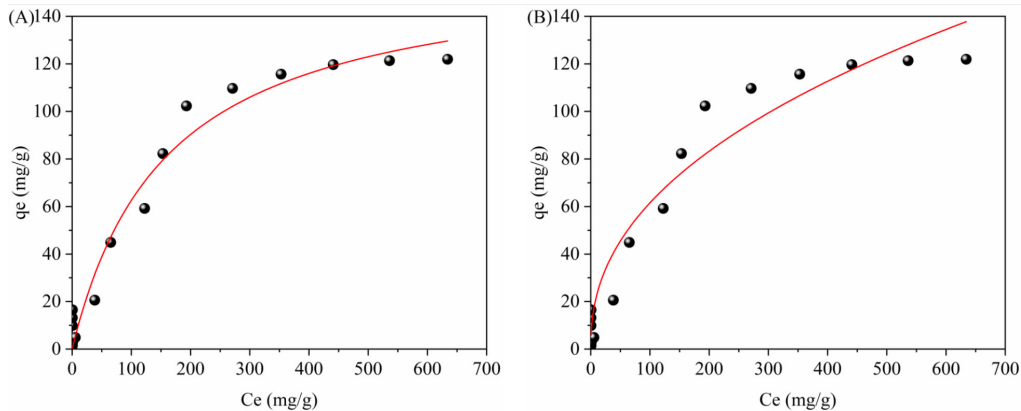


Fig. 2. Langmuir(A) and Freundlich(B) adsorption model

Table 1. Adsorption modeling data

| Langmuir adsorption | | | Freundlich adsorption | | |
|---------------------|---------------------|--------|-----------------------|---------|---------|
| $q_m(\text{mg/g})$ | $k_1(1/\text{min})$ | R^2 | $K_F(\text{L/mg})$ | $1/n$ | R^2 |
| 162.11 | 0.00629 | 0.9898 | 8.24935 | 0.43643 | 0.94371 |

Both methods indicated that the adsorption of $\text{PO}_4^{3-}\text{-P}$ by both DWTRs increased with increasing equilibrium

concentration(as shown in Fig. 2). According to Fig. 3 and Table 1, the Langmuir model ($R^2=0.9898$) was more

relevant to adsorption data for adsorbed phosphorus compared to the Freundlich model ($R^2=0.94371$). This leads to the conclusion that the adsorption of phosphorus by DWTRs is monolayer adsorption[15], and the adsorption process occurs at a localized site[16]. Besides,

according to the Freundlich model, the adsorption intensity $1/n$ is less than 1, which suggests that the process favors adsorption [17].

3.2.2 adsorption kinetic analysis

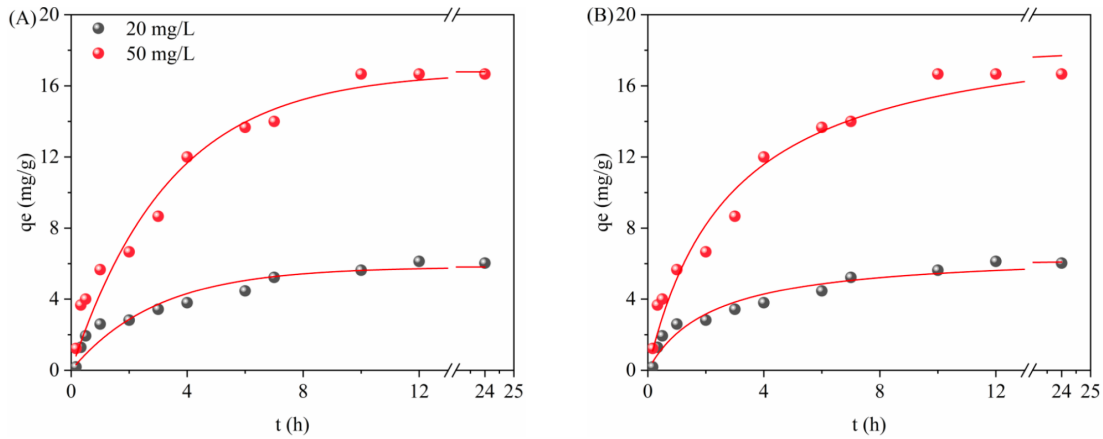


Fig. 3. The kinetics of pseudo-first-order (A) and pseudo-second-order (B) reactions were studied at initial concentrations of 20 mg/L and 50 mg/L.”

Table 2. The parameters of pseudo-first-order and pseudo-second-order

| Concentration (mg/L) | pseudo-first-order | | | pseudo-second-order | | |
|----------------------|--------------------|---------------|--------|---------------------|------------------|-------|
| | q_m (mg/g) | k_1 (1/min) | R^2 | q_m (mg/g) | k_2 (g/mg*min) | R^2 |
| 20 | 5.8179 | 0.33856 | 0.9121 | 6.622 | 0.068 | 0.977 |
| 50 | 17.008 | 0.2783 | 0.9426 | 19.78 | 0.178 | 0.966 |

Regardless of initial concentration, the adsorption process of PO_4^{3-} -P can be fitted via first-order and second-order kinetic models(as shown in Table 2). And the latter exhibiting a higher R^2 suggests that chemical adsorption mechanisms, such as H-bonds and π - π interactions, play a dominant role throughout the process [18]. Moreover, the adsorption pattern of PO_4^{3-} -P can be characterized by an initial rapid adsorption phase (occurring within the first 2 hours), followed by a slower adsorption phase. This behavior is attributed to the substantial specific surface area available for adsorption.

Conclusion

A pilot-scale experiment was conducted to explore how different plant types affect the efficiency of removing pollutants in DWTRs based CW, and the filter adsorption mechanisms were also explored. The results revealed that, regardless of the type pf plants, plants promoted pollutant-removal efficiencies and owned little effect. Furthermore, the adsorption processes were accurately characterized by the Langmuir isotherm and pseudo-second order,

which exhibited a notably higher adsorption capacity of 162.11 mg/g. This conclusion provided a new insight into removal-pollutants and underlying mechanisms for DWTRs based CW.

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