Journal of Cleaner Production 181 (2018) 618–630

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Nitrogen removal via core-shell bio-ceramic/Zn-layer double hydroxides synthesized with different composites for domestic wastewater treatment

Chenjia Fang, Xiangling Zhang*, Yu Lei, Ye Yuan, Yang Xiang

School of Civil Engineering and Architecture, Wuhan University of Technology, Wuhan 430070, China

ARTICLE INFO

Article history:
Received 14 August 2017
Received in revised form
29 January 2018
Accepted 30 January 2018
Available online 1 February 2018

Keywords:
Layered double hydroxides
Bio-ceramic/zn-layer double hydroxides
Nitrogen removal
Bio-ceramic substrates
Domestic wastewater treatment

ABSTRACT

Powdered layer double hydroxides are small with low density, which results in problems when they are applied to constructed wetlands. The removal efficiency of many original substrate materials tends to decrease with nitrogenous saturation. To overcome these defects, a co-precipitation method was used to prepare modified bio-ceramic coated with ZnFe-layer double hydroxides (Zn:Fe = 1:1, 2:1, 3:1) and ZnAl-layer double hydroxides (Zn:Al = 1:1, 2:1, 3:1) under alkaline conditions. Different molar ratios were firstly considered in bio-ceramic/Zn-layer double hydroxides to screen for the best modification methods. Fourteen simulated columns were produced to treat the nitrogen-containing domestic wastewater, and these columns were filled with different modified bio-ceramics and original bio-ceramics. The nitrogen removal rates of modified bio-ceramic improved. Group A was the experimental group, and group B was the control group. Group B had chloroform added to influent wastewater to retard the microbial growth. The NH_4^+-N removal rates in group A were higher than group B. Nitrates accumulated and fluctuated throughout the purification experiments due to the dominance of dissolved oxygen in the vertical-flow simulated columns. Isothermal adsorption tests were subsequently performed. The nitrogen adsorption capacity and microbial action were measured to verify the best-modified coating method for bio-ceramics and to explore the mechanisms of nitrogen removal. Bio-ceramic/ZnFe (2:1)-layer double hydroxides were the best coating for the bio-ceramics. The treated water met Class 1A level for Chinese discharge standards from municipal wastewater treatment plant (GB18918-2002) in the aspect of the NH_4^+-N concentration. The reagent cost of the bio-ceramic/ZnFe (2:1)-layer double hydroxides was RMB ¥0.07/kg. Within an assumed service cycle of one year, bio-ceramic/Zn-layer double hydroxides could increase the cost to ¥0.3500/m^3 wastewater, while the NH_4^+-N removal rates improved 15.11%. In summary, the layer double hydroxides-coating modification of the original bio-ceramic is an economical and promising strategy for new types of highly efficient, durable, and stable substrates. It enhances the adsorption capacity and improves the microbial effect.

1. Introduction

Nitrogen-containing compounds are heavily discharged into natural watercourses, which cause eutrophication of lakes and rivers and can damage aquatic eco-systems. Thus, economical, efficient, and clean sewage treatment technologies are urgently needed.

Constructed wetlands (CWs) are a promising technology for wastewater treatment and have been widely expanded in recent decades (Drizo et al., 1999). Versus conventional treatment technologies, CWs are low-cost, efficient, and easily maintained and offer ecological treatment of municipal or domestic wastewater (Lee et al., 2009; Lu et al., 2016). This is consistent with the requirements of sustainable development (Yang et al., 2017). Due to their convenience in construction and low operating costs (Lutterbeck et al., 2017; Wu et al., 2017), CW technology is increasingly popular for municipal sewage—especially in many developing countries like China (Kivaisi, 2001).

Wetland substrates remove pollutants through physical interception, chemical adsorption, and biofilm formation (Li et al., 2008). The treatment performance of CWs can be directly

* Corresponding author. School of Civil Engineering and Architecture, Wuhan University of Technology, 122, Luoshi Road, Hongshan District, Wuhan, 430070, China

E-mail address: ZXLCL@126.com (X. Zhang).

https://doi.org/10.1016/j.jclepro.2018.01.249
0959-6526/

affected by the type, gradation, combination, and modification of wetland substrates. There are a variety of natural substrate materials including slag, zeolite, anthracite, vermiculite, bio-ceramic, and other fillers (Zhang et al., 2007a). However, due to the limited adsorption capacity, many substrate materials can be saturated, which lowers the removal rates. Therefore, high-efficiency wetland substrates are urgently needed to enhance the removal rates of nitrogen.

Layered double hydroxides (LDHs) are novel functional materials that can control environmental pollution, especially for organic and inorganic anionic pollutants (Goh et al., 2008). LDHs are characterized by positively charged layered structures with isomorphous substitution of M^{2+} to M^{3+} (Cavani et al., 1991). In the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]_x+(A^{n-})_{x/h}\cdot mH_2O$, the type of M^{2+}, M^{3+}, A^{n-} and the value of x ($x = M^{3+}/(M^{2+} + M^{3+})$) can be changed as needed (Rives, 2002). LDHs are excellent at capturing organic and inorganic anions due to their relatively weak interlayer bonding. Moreover, because of the high anionic exchange capacity, LDHs can be applied to wastewater treatment for nitrogen purification (Hsueh and Chen, 2003; Zhou et al., 2014).

Preliminary experiments showed that the modified substance can be synthesized by preparing LDHs through a co-precipitation method under alkaline conditions and coating it on the surface of the original substance (Zhang et al., 2014, 2016). The nitrogen removal rates can be efficiently enhanced by coating the Zn-LDHs on the surface of original substance. Here, the nitrogen removal performance of the bio-ceramic is excellent among all substances. Therefore, a co-precipitation method was used in this study to synthesize different bio-ceramic/Zn-LDHs composites. Subsequently, the removal performance of nitrogen was studied in column tests along with nitrogen adsorption and desorption experiments.

Microorganisms play an important role in material transformation and are an indispensable part of the constructed wetland. Most microorganisms are present as microbial aggregates such as biofilms. Various electron microscopy techniques have been used to confirm and observe the presence of extracellular polymeric substances (EPS) in pure cultures, activated sludge, granular sludge, and biofilms. EPS plays an effective role in the physicochemical properties of microbial aggregates including the structure, flocculation, surface charge, dewatering properties, settling properties, and adsorption ability (Flemming and Wingender, 2010; Mohanty et al., 2016). Thus, the degree to which microbes participate can be studied via the extraction and characterization of EPS. Most probable number (MPN) methods are used to detect the number of bacteria (Xu and Zheng, 1986).

This study aims to screen out the best modification method and molar ratios for the preparation of bio-ceramic/Zn-LDHs and to investigate the mechanism of nitrogen removal. Ultimately, this study can help enhance the nitrogen removal in constructed wetlands and popularize the application of constructed wetlands ultimately accelerate the development of low-cost and eco-friendly technologies.

2. Material and methods

2.1. Methods of coating modification

Bio-ceramics were purchased from Lvyuan Water Treatment Materials Co. Ltd in Wuhan, China. Six LDHs with varying M^{II}-M^{III} cations including Zn-Fe and Zn-Al were prepared in 1:1, 2:1, and 3:1 molar ratios from their respective chloride salts (AR grade). All reagents and chemicals were of analytical or guaranteed grade and were received from Sinopharm Chemical Reagent Co. Ltd. A co-precipitation method was used to synthesize bio-ceramic/Zn-LDHs.

In bio-ceramic/ZnFe-LDHs (Zn:Fe = 1:1) composites, two solutions of $ZnCl_2$ (0.75 mol/L) and $FeCl_3$ (0.75 mol/L) were simultaneously added to a 2 L beaker containing the original bio-ceramic washed with distilled water and heated to 80 °C in a water bath. The pH was maintained at 11 by adding the appropriate volume of 10 wt% NaOH. After continuous stirring for 2 h, the mixed compounds were washed thoroughly and then dried in an electrothermal blowing dry box (SHG-9140A, Shanghai) for 16 h. This ultimately produced bio-ceramic/ZnFe-LDHs (Zn:Fe = 1:1) composites. Other modified bio-ceramic composites were synthesized similarly. Each modified bio-ceramic was placed into the corresponding experimental columns. The experimental column numbers and the modifications are given in Table 1.

2.2. Characterization methods

SEM (Scanning electron microscopy, Zeiss Ultra Plus, Germany) was used to examine the morphological characteristics. XRFS (X-Ray fluorescence spectrometry, Axios, PANalytical. B. V. Holland) was used to analyze the chemical compositions. The physicochemical properties of the modified and original bio-ceramic were examined in Material Research and Testing Center, Wuhan University of Technology.

2.3. Characterization of system

The simulated lab-scale constructed wetland was assembled indoors with 14 test columns (0.4 m in length and 0.08 m in diameter). These were made of polyvinyl chloride (PVC). Seven columns were set in parallel by adding chloroform to the influent water. Each column was filled with different modified bio-ceramics and the original bio-ceramic, respectively. The filling height of the substrate was approximately 35 cm. The raw water was collected from the sewage well in Wuhan University of Technology. This was then mixed with tap water. The water quality indices are given in Table 2.

Wastewater flowed into the system from the top and out from the bottom. With intermittent operation, the hydraulic retention time (HRT) of the experiment was 24 h indicating that the hydraulic loading rate (HLR) was 90 L· $(m^2 \cdot d)^{-1}$. The entire purification experiments started in September and ended in December 2016. Parallel treatments were performed for different compositions that

Table 1
Experimental column and corresponding modification.

Column numbers*	A1	A2	A3	A4	A5	A6	A7
Modification ways	Zn:Fe (1:1)	Zn:Al (1:1)	Zn:Fe (2:1)	Zn:Al (2:1)	Zn:Fe (3:1)	Zn:Al (3:1)	No modified
Column numbers*	B1	B2	B3	B4	B5	B6	B7
Modification ways	Zn:Fe (1:1)	Zn:Al (1:1)	Zn:Fe (2:1)	Zn:Al (2:1)	Zn:Fe (3:1)	Zn:Al (3:1)	No modified

*Group A was set as experiment group, while group B was set as control group via adding chloroform into influent wastewater to restrain the microbial growth.