ARTICLE IN PRESS

Process Biochemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Process Biochemistry

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

The performance of biocarrier containing zinc nanoparticles in biofilm reactor for treating textile wastewater

Feng Wang[a,b], Lu Zhou[a,*], Jianqiang Zhao[b]

[a] School of Environment, Tsinghua University, Beijing, 100084, China
[b] School of Environment Science and Engineering, Chang'an University, Xi'an, 710064, China

ARTICLE INFO

Keywords:
Textile wastewater
Zinc nanoparticles
Biocarrier
Biofilm reactor

ABSTRACT

Zinc (Zn) is a necessary microelement for microorganisms to perform various vital functions, which can influence the diversity of microorganisms and get them involved in pollutant degradation in biological wastewater treatment plant. In this study, a novel biocarrier containing different weight fraction (wt%) of zinc nanoparticles (Zn NPs) (0, 10, 15, 20 and 30 wt%) were developed by mixing and melt compounding technology to deal with textile wastewater (TW). The moving bed biofilm reactor (MBBR) filled with biocarriers containing 20 wt% Zn NPs, with zinc ion release profile of 0.4 mg/L had the best performance. It could shorten the start-up time to 11 d, and had higher attached biomass (2460 mg/L) and biofilm dehydrogenase activity (nearly 350 μg TPF/g). As a result, the removal efficiencies of COD and NH_3-N were higher than reactors filled with other biocarriers. It indicate that the biocarriers containing Zn NPs is expected to increase the metabolic activity of microorganisms and to improve pollutant removal efficiency in the bioflim reactor for TW treatment.

1. Introduction

Biological technologies are considered as aptly applicable technology for textile wastewater (TW) treatment, because its simplicity and cost-effectiveness [1,2]. However, poor biological treatment efficiencies were usually addressed caused by including lower biomass and bioactivity in the biological TW treatment process. Many reasons have been reported and among them micronutrients imbalance is one of the most important reason [3,4]. At low concentrations, micronutrients, such as Zn, Cu, Co, Fe, Mn, Ni, and so forth, are essential components for vital cofactors of metalloproteinases and certain enzymes. However, excessive micronutrients concentrations would be inhibitory or even toxic to biochemical reactions and microorganisms due to the chemical binding of cationic elements to enzymes, resulting in the disruption of enzymatic structure and activities. Zn is one of the most common micronutrient for microorganisms, for instance ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB), nitrifying bacteria and Anammox in biological wastewater treatment process [5]. Our previous studies proved that dosing micronutrients, particularly Zn, was beneficial for microbial shift towards *Planctomyces* and *Bacteroidetes.* It could possibly help to accumulate dyeing degradable bacteria in activated sludge process resulting in higher removing efficiency [6]. While, it is difficult to keep the dosing of micronutrient balanced at the appropriate concentration for microorganism growth.

Controlled release method (which can help targeted substance release in a controlled manner from a medium) is considered as a solution to the problem [7,8]. Poly (lactic acid) (PLA) as a biodegradable aliphatic polymer with hydrolysable ester bond, which can be biodegraded eventually to products as carbon dioxide and water [9]. It have been utilized for continuous drug release for different periods of time including prolonged administration of a wide variety of medical agents such as contraceptives, narcotic antagonists, local anesthetics, peptides, and proteins [10,11]. Polymeric drug release can find one of three possible ways: erosion, diffusion and swelling [12]. For PLA, the breakage of ester bonds occurs randomly through hydrolytic ester cleavage, which then lead to subsequent erosion [13]. PLA and their copolymers in the form of micro or nanoparticles were used in encapsulating drugs, such as restenosis, hormones, oridonin, dermatotherapy, and proteins (BSA) [14–16].

The moving bed biofilm reactor (MBBR) has been employed successfully in treating various types of industrial wastewater for its high biomass attachment [17]. Biocarrier is the core of MBBR for supporting microbial adhesion, and which is made of hard plastics such as polyethylene (PE), polypropylene (PP) and high-density polyethylene (HDPE) [18]. The properties of biocarrier can directly influence the ability to form biofilms, attached quantity of biomass and the treating efficiency. Though plastic biocarrier have the poor hydrophilicity, biocompatibility and electronegativity [19], many efforts have been

* Corresponding author.
E-mail address: zhoulu@tsinghua.edu.cn (L. Zhou).

https://doi.org/10.1016/j.procbio.2018.08.022
Received 3 March 2018; Received in revised form 5 August 2018; Accepted 20 August 2018
1359-5113/

Please cite this article as: Wang, F., Process Biochemistry (2018), https://doi.org/10.1016/j.procbio.2018.08.022

devoted in the development and application of novel modified biocarriers. Mao et al. [20] used positively charged polymers to modify the electronegativity of HDPE carriers, achieved shorter reactor start-up time and higher attached biomass. Deng et al. [21] developed a hybrid MBBR-membrane bioreactor (MBBR-MBR) system with sponge modified plastic carrier, which enhanced the hydrophilicity of biocarrier and performed a better effluent quality with lower levels of soluble microbial products (SMP) in mixed liquor. Chen et al. [22] applied the tube chip type of polymer modified with nano-size inorganic materials in the pretreatment of pesticide wastewater by integrating MBBR and Fenton coagulation, high removal efficiency and stable operation could be achieved in the biological process even at a high COD loading of 37.5 g COD/(m^2 carrier day). All of the modified biocarriers mentioned above can increase the amount of attached biomass, while have little stimulate effect on the bioactivity of the microorganisms.

This study focused on investigating a biocarrier containing Zn NPs, which can release zinc ion in a controlled manner to enhance the bioactivity optimally. It is made of HDPE, Zn NPs and PLA by mixing and melt compounding technology. Five kinds of biocarriers containing different weight fraction of Zn NPs were developed, and the TW treatment performance, bioactivity and the pollutant removal efficiencies in MBBRs were evaluated.

2. Materials and methods

2.1. Preparation of biocarriers containing Zn NPs

HDPE (SINOPEC® HDPE L501(5000S) with melt flow index (MFI) of 7.5 g/10 min (230 °C/2.16 kg), density of 0.955 g/cm^3 and average molecular weight of 200,000 g/mol was supplied by Tianjin Petrochemical Co., Ltd, China. PLA (ESUN™ A-1001), with MFI of 12.5 g/10 min (190 °C/2.18 kg), was purchased from Bright Industrial Company Ltd., Shenzhen, China. It has a density of 1.24 g/cm^3 and average molecular weight of 100,000 g/mol. Zn NPs with a mean diameter of 5 μm and purity more than 99.9% were purchased from Longxin Technology Development Co., Ltd., Shanghai, China.

The biocarriers were fabricated by the combination of mechanical mixing and melt compounding technology [23]. Zn NPs were proportionally (0, 10, 15, 20 and 30 wt%) dispersed in PLA granules by mechanical mixing using a cylindrical blender (100 rpm for 5 min) and dried in a vacuum oven at 70 °C for 24 h, and then homogeneously mixed in HDPE granules. The mixtures were carried out by using a single screw extruder of D = 25 mm, L/D = 30 (Yulong Co., Ltd., Jiangsu, China). The screw speed was set at 70 rpm, and the temperature profile along the barrel was 175 °C, 205 °C, 205 °C and 190 °C (from feed zone to die). The biocarrier is honeycomb-shaped (Fig. 1) with length, diameter and specific surface area as 25 mm, 10 mm, and 620 ± 20 m^2/m^3, respectively.

The surface characterization, mechanical properties and zinc ion release profile of the biocarriers containing Zn NPs were measured by the following methods: (i) ATR-FTIR transmission spectra were obtained in the range of 550–4000 cm^{-1} by using a FTIR spectrophotometer (VERTEX 70, Bruker, Germany); (ii) XRD analysis was recorded with a Rigaku D/max-IIIB diffractometer (Tokyo, Japan) with Cu Kα irradiation (λ = 1.54178 Å). The experiments were performed in a period of 2 h from 5 to 100°, with a scan rate of 5° min^{-1}; (iii) Biocarriers containing Zn NPs were immersed in four 1 L beakers containing pretreated TW, which was collected from the TW treatment system in a textile mill (Huafang textile Co., Ltd. China). The characteristics of pretreated textile wastewater are shown in Table 1. The filling ratio of biocarriers was 40% and magnetic stirrer (MS-H280-Pro, Dragon lab of China) running at 550 rpm to keep the biocarriers fluidizing. Zinc ion concentration in the TW was measured by ICP-MS (ELAN DRC-e) (PerkinElmer, American) once in 24 h. To avoid retarding the zinc ions release, TW was replaced by a freshly prepared batch every day, and zinc ion concentration in the TW was measured again after one day.

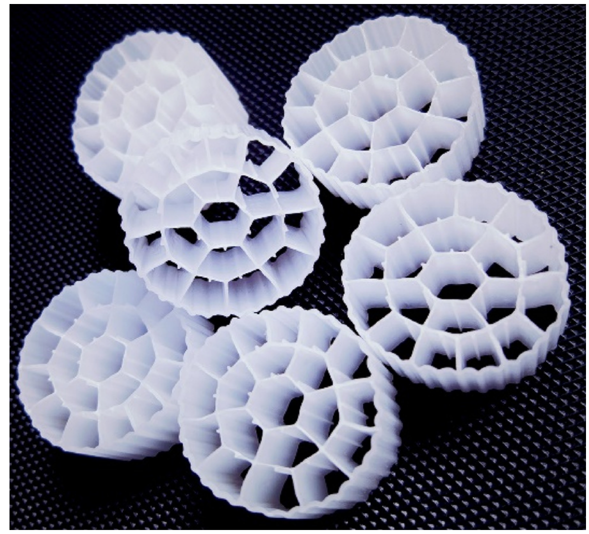

Fig. 1. The biocarriers containing Zn NPs.

Table 1
The real pretreated textile wastewater.

Analytical parameters	Concentration	Analytical parameters	Concentration
COD (mg/L)	1000–1200	Colour	142–189
BOD_5/COD	0.26–0.3	Alkalinity(mg/L)	500–800
NH_3-N(mg/L)	80–100	Turbidity(NTU)	150–200
pH	8	Sulphide(mg/L)	50–80
Temperature(°C)	30–35	Chloride(mg/L)	800–1000
TSS(mg/L)	50–80	Hardness(mg/L)	120–150
TDS(mg/L)	2000–3000		

2.2. Lab-scale MBBRs setup and operation

With a filling ratio of 40%, five sets of lab-scale reactors (inner diameter: 170 mm, height: 275 mm, working volume: 5 L) were established in parallel (Fig. 2). The biocarriers containing different Zn NPs (0, 10, 15, 20 and 30 wt%) in the five reactors were numbered Z-0, Z-10, Z-15, Z-20 and Z-30 respectively. All the reactors were inoculated with activated sludge mixed liquor suspended solids (MLSS) concentration of 3 g/L. After inoculation, TW was introduced into the reactors, air was diffused in order to supply oxygen to the biomass and mixed the biocarriers. After 12 h aeration, one-half of the mixed liquid was drained off and then replenished raw TW for next 12 h operation. This procedure was repeated for 7 d in the start-up phase, and then the

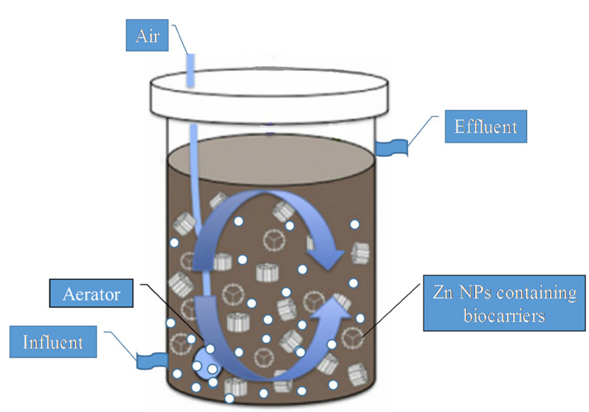

Fig. 2. Schematic diagram of the lab-scale MBBR.