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Graphene-oxide modified polyvinyl-alcohol as microbial carrier to improve high salt wastewater treatment

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ABSTRACT

This work discussed the preparation and characterization of graphene oxide (GO) modified polyvinyl alcohol (PVA) for bacteria immobilization to enhance the biodegrdation efficiency of saline organic wastewater. GO–PVA material has lamellar structure with higher surface area to support bacterial growth and high salinity tolerance. It significantly stimulated the bacterial population by 1.4 times from 2.07×10^3 CFU/mL to 5.04×10^3 CFU/mL, and the microbial structure was also improved for salinity tolerance. *Acinetobacter*, *Pseudomonas* and *Thermophilic hydrogen bacilli* were enriched inside GO–PVA materials for glucose biodegradation. Compared to the COD_{Cr} removal efficiency with only PVA as the carrier (52.8%), GO–PVA material had better degradation performance (62.8%). It is proved as a good candidate for bioaugmentation to improve biodegradation efficiency in hypersaline organic wastewater.

1. Introduction

As a novel functional nano-material, graphene has drawn many attentions recently [1–3], with a wide range of applications in modified electrodes [4], chemical power sources [5], solar batteries [6], catalysts [7], pharmaceutical carriers [8] and gas sensors [9]. Containing sufficient carboxyl, carbonyl, hydroxyl and epoxy groups, graphene oxide has excellent chemical and physical properties [10]. Therefore, together with the features of high hydrophily and reaction activity, graphene oxide is suitable as the carrier material for bacteria immobilization.

Hypersaline organic wastewater is one of the major problems in wastewater treatment industry. The high salinity inhibited the survival, growth and reproduction of microorganisms, consequently causing the difficulties in biodegradation for the saline wastewater [11,12]. Bacteria immobilization is an appropriate technique for wastewater treatment [13]. It could also improve microbial tolerance of toxic or hazardous substances [14] during water treatment process [15], significantly increasing the amounts and activities of microbes.

This study, for the first time, developed the bacteria immobilization on graphene oxide and tested the performance in biodegradation for hypersaline organic wastewater. The microbes from the activated sludge could tolerate high salinity and achieve high organic pollutants removal. From further phospholipid fatty acids (PLFAs) analysis, the dynamics of microbial community structure revealed the dominancy of halotolerant bacteria and their functions in the graphene oxide carriers.

2. Experimental section

2.1. Graphene oxide synthesis

Compared to previous research on surface modification of polyvinyl alcohol (PVA) by graphene oxide (GO) to improve the mechanic properties, this research addressed its bacterial friendly and immobilization, and the GO synthesis method was therefore modified accordance with Hummers' protocol [16]. Briefly, 5.0 g potassium peroxymonosulfate and 5.0 g phosphorus pentoxide were added into 25 mL sulfuric acid at 90 °C with constant mixing. The 6.2 g graphite was slowly added and the reaction was kept at 80 °C for 4.5 h. By adding water to the volume of 1.0 L, the mixture was kept standing overnight and treated with suction filtration. The particles on the film were collected and dried at room temperature for 24 h. The preliminary graphene oxide was then added into 240 mL iced sulfuric acid with 30.0 g $KMnO_4$. After stirring for 20 min, the mixture was further stirred at 35 °C for 2 h, followed by adding 460 mL deionized water with further reaction for another 2 h. Twenty-five milliliters of 30% H_2O_2 solution was subsequently added into the mixture and kept standing overnight.

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Discarding the supernatant, the pellet was resuspended in 500 mL 5% hydrochloride and centrifuged at 10,000 rpm for 30 min to remove the supernatant with residual reagents. The washing step was repeated three times, followed by another three times washing by deionized water to remove the salts.

2.2. Microbial carrier synthesis and immobilization

Halotolerant bacteria were embedded with two different types of microbial carriers for wastewater treatment, as PVA and GO/PVA. The PVA carrier solution was prepared by dissolving 22.5 g PVA in 122.5 g deionized water. Seventy-five milliliter graphene oxide stock solution (20 g/L) was added into the 150 mL PVA carrier solution to make the GO–PVA carrier solution. After 1 h water bath agitation at 90 °C and cooled down to 30 °C, the 75 mL enriched halotolerant bacteria were mixed with material solution and kept stirring for 1 h. The carrier gel was further frozen at −18° C for 24 h, followed by natural thawing at room temperature and crushed into granules.

2.3. Bacteria cultivation and wastewater treatment

The halotolerant bacteria were enriched from the wastewater biosludge of Village Li Waste Water Treatment Plant (120°21.11′E, 36°9.32′N). The high salinity wastewater was prepared by adding 0.72 g glucose and 0.62 g NH_4Cl in 1.0 L deionized water. Ten grams of PVA or GO–PVA with halotolerant bacteria were added into each 1.0 L wastewater respectively, and another treatment was carried out with only halotolerant bacteria. The water and PVA/GO–PVA materials were sampled at 0, 4, 6, 8, 10, 12 and 24 h for analysis.

2.4. Analysis

Images of scanning electron microscopy (SEM) were obtained by JSM-6700F at 8.0 kV (JEOL, UK). The infrared (IR) spectroscopy analysis followed the KBr pellet method (Supplementary material), and the Raman spectrum was obtained by inVia Raman Microscope (Renishaw, UK) with 633 nm laser. The determination of chemical oxygen demand (COD_{Cr}) followed the fast digestion-spectrophotometric method (Supplementary material). Phospholipid fatty acids (PLFAs) were extracted KOH–CH_3OH (0.2 M) solution and analyzed by Sherlock Microbial Identification System (MIDI Inc., USA, version 6.2) (Supplementary material).

3. Results and discussion

SEM images of GO, PVA and GO–PVA were illustrated in Fig. 1(a)–(c). The pristine GO has no significant reticulate structure, whereas it is only observed in PVA and improved in GO–PVA material. Similar to previous research [17,18], the pure PVA polymer composite has uniform grain distribution with small holes (2–20 μm) randomly distributed on the top surface. This structure is not suitable for bacteria attachment and proliferation. On the contrast, GO–PVA material has significant lamellar structure, which is formed by graphene oxide and can support the immobilization and growth of bacteria. The reinforcing PVA effectively suppresses the salt transportation and maintains biocompatible environment for bacteria [19]. It is therefore suggested that O–PVA materials have appropriate microstructure with higher surface area for bacteria to immobilize and provide suitable condition to help bacteria keep high biodegradation efficiency by tolerating high salinity wastewater.

Fig. 1(d) shows the infrared spectra of graphene oxide, showing the strong absorption peak at 3240 cm^{-1} referring to the

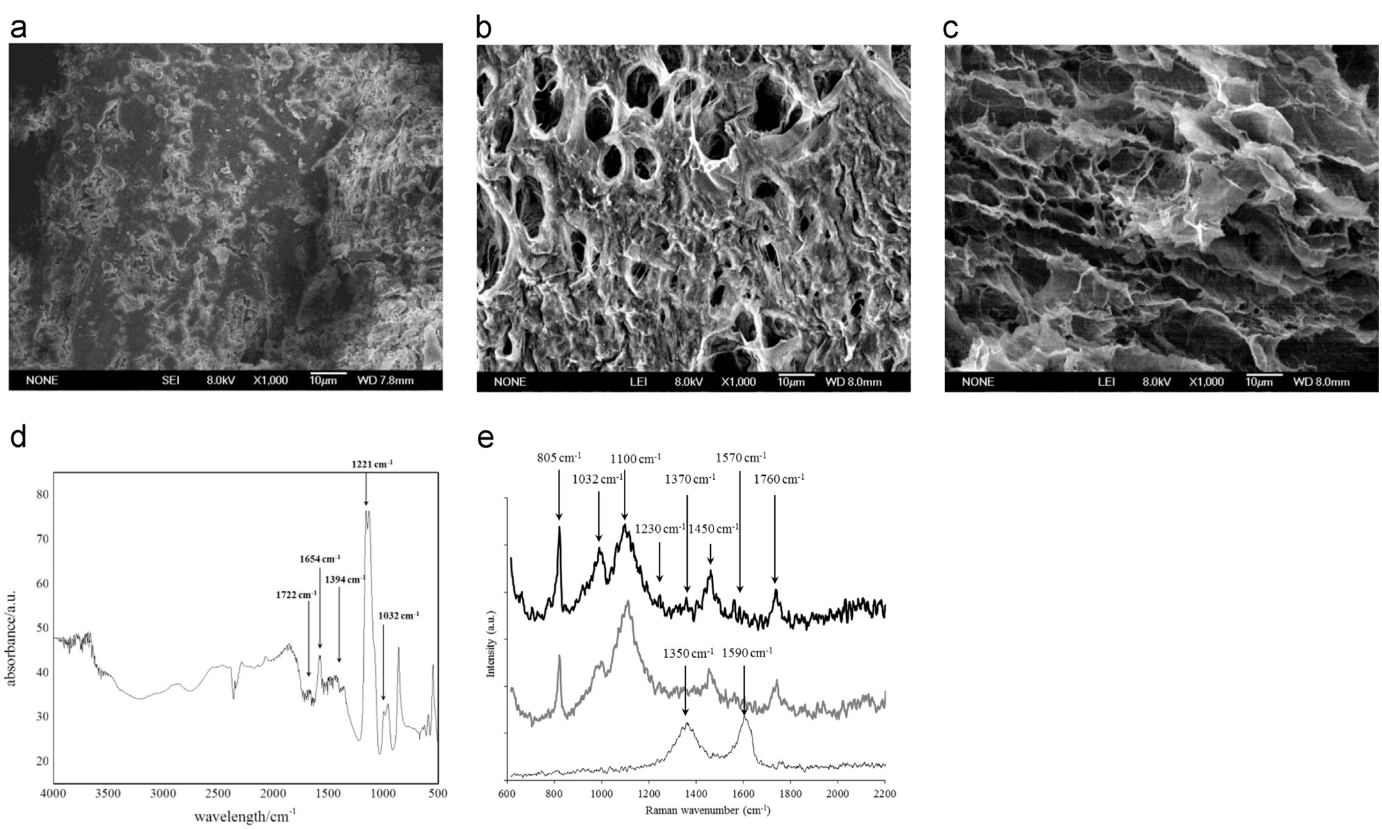

Fig. 1. SEM images of GO (a), PVA (b) and GO–PVA (c) carrier. The infrared spectrogram (d) and Raman spectrum (e) of GO–PVA materials.