



## Efficient debromination of Tetrabromobisphenol A (TBBPA) by Au/Fe@biocarbon derived from bioreduction precious metals



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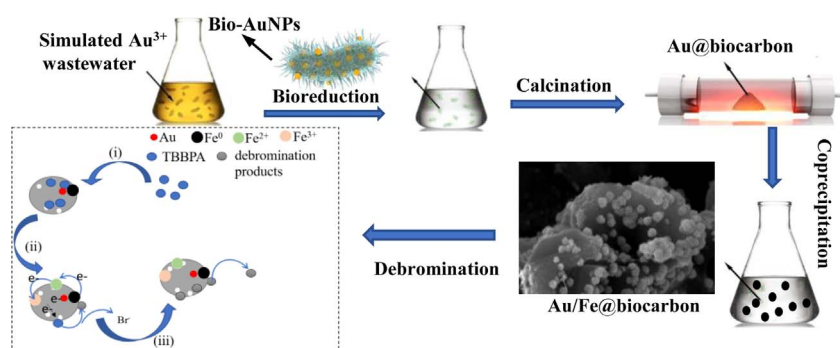
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### GRAPHICAL ABSTRACT



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### ABSTRACT

The utilization of nano zero valent iron is recognized as a potential approach for debromination of Tetrabromobisphenol A (TBBPA). In this study, *Pycnoporus sanguineus* cells were employed for biosupported Au nano particles (bio-AuNPs) preparation, then calcinated for obtaining porous carbon doped with Au nano particles (Au@biocarbon) and generated Au@biocarbon supported zero-valent iron nanoparticles (Au/Fe@biocarbon). The role of Au/Fe@biocarbon during debromination was evaluated by comparing with Au@biocarbon, biocarbon and Fe@biocarbon. Results showed that Fe<sup>0</sup> and Au<sup>0</sup> are successfully loaded on the surface of porous biocarbon with well-dispersion and higher specific surface area. The removal and debromination efficiency of TBBPA driven by Au/Fe@biocarbon was up to about 99.85% and 97.18% within 100 min, respectively. Higher dosage and acidic condition were more beneficial to removal of TBBPA with the most appropriated Au/Fe molar ratio of 2%, where the complete removal of TBBPA only took 20 min. The mechanism of TBBPA debromination by Au/Fe@biocarbon was the joint function of adsorption of biocarbon and galvanic cell of biosupported Au/Fe bimetals. Therefore, Au/Fe@biocarbon could be an alternative to effectively boost rapid and complete debromination of TBBPA.

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## 1. Introduction

Tetrabromobisphenol A (TBBPA) emerges as one of typical brominated flame retardants (BFRs) widely used in plastics, textiles and electrical circuit boards [1]. Due to its lipophilicity, bioaccumulation, persistence and atmospheric remote migration [2,3], TBBPA can be detected in the atmosphere, surface water, groundwater, soil, aquatic biology, human blood and even breast milk. TBBPA is regarded as a potential endocrine disruptor for its thyroxine-like structure exhibiting immune toxicity, thyroid-disrupting effects and interference effects of estrogen, and shows negative impact on people's living environment and health [4]. Therefore, it is urgent to develop rapid and effective techniques for the removal of TBBPA.

Till now, various approaches including biodegradation [5], pyrolysis [6], adsorption [7] and chemical routes [8,9] have been reported to efficiently remove TBBPA. While nano zero valent iron (nZVI) has been popularly applied to deal with environmental pollutants due to its capability of achieving debromination and a wide variety of sources, lower prices, lower secondary pollution on the environment [10,11]. For example, Lin et al. found that using nZVI could achieve a good performance for the debromination of TBBPA with a 80% efficiency in 16 h [12]. However, there are still limitations such as the rapid oxidation and the easy agglomeration of nZVI, which resulted in the sharp decrease of iron reactivity [13].

To address these drawbacks, combination nZVI with other metals as a strategy to compensate its activity has been paid much attention. A second metal (Pd, Ni, Ag, Co, etc.) is often doped on nZVI surface to form nZVI-based bimetallic materials, which accelerated electron transform [8,14,15]. Li et al. found that 72% of 10 mg/L TBBPA could be degraded by Ni/Fe bimetallic nanoparticles (1 g/L) within 120 min [16]. Fang et al. summarized that the removal efficiency of decabromodiphenyl ether by Ni/nZVI was significantly faster than that by nZVI [17]. Although the reductive activity of nZVI could be promoted with addition of other metals, dispersion still stands there and affects the process of pollutants removal.

Recently, in the field of biorecovery, microorganism shows feasibility of recovery precious metals and formation of biosupported precious metals, which had a potential to deal with environmental contaminants [18]. Zhu et al. gave an implement that biogenic gold nanoparticles are capable of degradation of 4-nitroaniline [19]. Zhou et al. found that Au@NC generated from recovery of Au<sup>(III)</sup> by *Pycnosporus sanguineus* could efficiently catalyze of hydrogen evolution and oxygen reduction reaction by increasing the number of electron transfer [20]. Consequently, if using the biorecovery of precious metals and nZVI, the biomass would not only provide the potential well-dispersed carrier for AuNPs and nZVI, but also increase the specific surface area of the whole materials.

Therefore, this study focused on the synthesis of the Au/Fe@biocarbon by coupling biorecovery and coprecipitation, and investigation of the reductive activity of the Au/Fe@biocarbon for the debromination of TBBPA. The specific aims were: (i) to evaluate Au/Fe@biocarbon the reductivity and confirm the role of Au/Fe@biocarbon in removal process of TBBPA, (ii) to investigate the effect in terms of material dosage, Au/Fe molar ratio and pH for the removal of TBBPA by Au/Fe@biocarbon, (iii) to identify the transformation products and analyze the debromination pathway, and (iv) to analyze the debromination mechanism of TBBPA derived by Au/Fe@biocarbon.

## 2. Materials and methods

### 2.1. Fungal strain and growth conditions

The fungal strain *P. sanguineus* (CGMCC 5.00815) was purchased from China General Microbiological Collection Center and cultured in comprehensive potato dextrose agar (PDA) medium (potato 200 g/L, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> 20 g/L, KH<sub>2</sub>PO<sub>4</sub> 3 g/L, MgSO<sub>4</sub> 1.5 g/L, multi-vitamins as 5 mL,

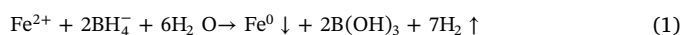
pH 6.0). The general incubation condition was at 25 °C for 3.5 days. The cells were harvested by filtering and washing three times with distilled water, and stored after freeze-drying.

### 2.2. Nanoparticle suspension preparation and characterization

The biorecovery of Au nano particles (bio-AuNPs) was based on our previous work [21]. Briefly, 4 g/L *P. sanguineus* freeze-dried powder was added into HAuCl<sub>4</sub> solution with different concentration (0, 0.1, 0.2, 0.4, 0.6 and 1.0 mmol/L) in a 200 mL serum bottle and incubated at 30 °C for 48 h, then freeze-dried for 24 h.

The biorecovered bio-AuNPs and KOH were mixed evenly with a mass ratio of 1:1.5, then carbonized in a tube furnace at 5 °C/min to 420 °C for 3 h under nitrogen flow. The solids remained were washed with 3% HCl followed by distilled water with a harvest of different Au content porous carbon doped with Au<sup>0</sup>-NPs (Au@biocarbon).

NaBH<sub>4</sub> solution (80 mmol/L) was added dropwise into mixing solution with FeSO<sub>4</sub>·7H<sub>2</sub>O (20 mmol/L) and above-mentioned Au@biocarbon particles under N<sub>2</sub> protection. Then, the solid products were separated and rinsed three times with deoxygenated water to obtain the final production of Au/Fe@biocarbon with different Au-Fe molar ratio. The overall process occurred according to Eq. (1).



The samples were characterized by scanning electron microscope (SEM) (Hitachi-7650 instrument (Hitachi Ltd., Tokyo, Japan) and X-ray energy dispersive spectroscopy (EDS) was used to identify the element composition and distribution. Brunner-Emmett-Teller (BET) surface area analysis of the Au/Fe@biocarbon was performed by nitro-gen adsorption desorption using an ASAP2020 M surface analyzer (Micromeritics Instrument Corp., USA). X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (DMAX 2200VPC, Rigaku, Japan). XPS method through PHI X-Tool instrument (ULVAC-PHI, Japan) equipped with Al<sub>Kα</sub> X-ray source was applied to analyze the chemical elements composition on the cell surface in the range of 1000–0 eV of the binding energy at 15 kV.

### 2.3. Batch experiments of TBBPA debromination

Experiments with different materials including Au@biocarbon, Au/Fe@biocarbon, biocarbon, Fe@biocarbon were conducted. Effects of different dosage of Au/Fe@biocarbon, Au and Fe ratios of Au/Fe@biocarbon, and initial pH were quantified by batch debromination experiments. All of the experiments were carried out in 200 mL serum bottle without oxygen conditions and shaking at 165 rpm and 30 °C. The initial aqueous TBBPA solutions contained methanol and water at a volume ratio of 2:3 [13]. Unless otherwise stated, the conditions are 10 mg/L initial concentration of TBBPA, 1.0 g/L Au/Fe@biocarbon and initial pH 7.0. The solution samples were collected at regular time intervals and analyzed immediately after being filtered through a 0.22 μm nylon filter membrane. All experiments were conducted at least three times.

The amount of degradation and adsorption by nZVI was identified. Firstly, 2 mL 0.2 mol/L HCl was added to the samples after centrifuging to terminate the reaction between nZVI and TBBPA and then centrifuged at 12,000 rpm for obtaining the solid. Secondly, 2 mL n-hexane was used to extract TBBPA adsorbed on the surface of materials with ultrasonication for 10 min and repeated the process three times. Finally, the supernatant of the above sample after centrifugation at 12,000 rpm was rotating evaporated and diluted with methanol to final volume of 2 mL. The absorbed amount of TBBPA was the sum of the first step and the extracted solution. To test the effect of the initial pH on removal behavior, the initial pH of the TBBPA solutions was adjusted with 0.1 M HCl or 0.1 M NaOH.

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