



# Removal of halogenated emerging contaminants from water by nitrogen-doped graphene decorated with palladium nanoparticles: Experimental investigation and theoretical analysis



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## ABSTRACT

The removal performance and mechanisms of halogenated emerging contaminants from water by palladium decorated nitrogen-doped graphene (Pd/NG) were investigated in this study. For comparison, three catalysts of Pd/NG, palladium decorated graphene (Pd/G) and commercial Pd/C were initially explored to degrade tetrabromobisphenol A (TBBPA). After that, the influence of various environmental parameters on TBBPA removal by the Pd/NG catalyst was evaluated. Moreover, both Langmuir–Hinshelwood model and density functional theory (DFT) were adopted to theoretically elucidate the adsorption and the activation of TBBPA on the catalyst. The results show that the apparent rate constant of TBBPA dehalogenation was increased by 26.7% and 39.0% in the presence of the Pd/NG catalyst compared to the Pd/G and Pd/C ones. Higher temperature, catalyst dosage and alkaline conditions resulted in the enhancement of TBBPA dehalogenation by the Pd/NG catalyst, while humic acid in the solution had a negatively effect on the transformation of TBBPA. The corresponding rate constant value exhibited a 2.1- and 1.8-fold increase with the rise of temperature from 298 to 328 K and initial pH from 6.5 to 9.0, respectively. On the contrary, the rate constant was decreased by 78.9% in the presence of 15 mg L<sup>-1</sup> humic acid. Theoretical analysis revealed that both adsorption and activation processes of TBBPA on the Pd/NG catalyst were enhanced through the N doping into graphene framework.

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## 1. Introduction

The increasing worldwide emerging contaminants have brought in the significant environmental problems (Petrie et al., 2015; Schwarzenbach et al., 2006). Among them, halogenated emerging contaminants, such as brominated flame retardants and halogenated pharmaceuticals and personal care products, are widely manufactured, used, emitted and detected in environment, which pose a potential threat to human health (Gautam et al., 2014; Richardson and Ternes, 2014). For instance, besides sediment/sewage sludge and human tissues, brominated flame retardant tetrabromobisphenol A (TBBPA) has also been widely detected in water and wastewater such as lake and municipal wastewater treatment plant effluents (Liu et al., 2016; Morris et al., 2004).

Halogen substituents generally decrease the biodegradability of an organic compound and thus conventional activated sludge process has been demonstrated to exhibit the poor performance in the oxidative removal of such halogenated emerging pollutants (Brenner et al., 2006). Therefore, it is valuable to reduce their toxicity and promote biodegradability through initial reductive dehalogenation by various methods (Liang et al., 2013; Mohn and Tiedje, 1992). For instance, TBBPA and personal care product ingredient triclosan (TCS) could be reductively dehalogenated by using nanoscale zero valent iron and Pd/Fe bimetallic catalysts, respectively (Bokare et al., 2010; Huang et al., 2013; Lin et al., 2012).

Palladium-catalyzed reactions have attracted worldwide attentions and are facing both opportunities and challenges (Seechurn et al., 2012; Zhang et al., 2013). Carbon materials are excellent support for Pd nanoparticles, mainly due to large specific surface area, high stability and convenient flexibility in tailing chemical properties such as heteroatoms doping and surface modification (Gupta et al., 2013; Zhai et al., 2015; Zhou et al., 2015b). Furthermore, the raw materials for carbon support are extensive, which

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can be made out from waste materials (Gupta et al., 2015; Saleh and Gupta, 2014). In addition, carbonaceous materials showed excellent ability of adsorption on numerous pollutants (Gupta et al., 2011; Mittal et al., 2009a). Recently, graphene has been reported as a promising candidate for supporting Pd nanoparticles (Mao et al., 2015; Scheuermann et al., 2009). However, Pd-decorated graphene (Pd/G), as same as other solid catalysts, always encounters the leaching of active species as a result of weak interaction between metal nanoparticles and graphene surface (Gupta et al., 2014; Mallat and Baiker, 2004). Modification of graphene is one of strategies to enhance such interaction. For instance, incorporation of nitrogen into graphene network could contribute additional electron density, induce more defects and activate neighboring carbon, resulting in the improved binding and catalytic performance of Pd nanoparticles (Panchokarla et al., 2009; Vinayan et al., 2013). Palladium decorated nitrogen-doped graphene (Pd/NG) has already shown the superior capabilities in both hydrogen storage and catalytic activities for C–C coupling reactions (Jiang et al., 2014; Parambath et al., 2012). Recently, Zhou et al. (2015a) reported that hydrodechlorination of 2, 4-dichlorophenol could be enhanced by the Pd/NG catalyst, but it was majorly focused on the influence of catalyst properties on pollutant removal. So far, very few studies have been conducted to evaluate the catalytic capability of the Pd/NG on the reductive removal of contaminants from water, especially in terms of influence of environmental factors and adsorption and activation mechanisms of pollutant on the catalyst.

Therefore, the main objective of this study is to investigate the removal performance and mechanisms of halogenated emerging contaminants from water by using Pd/NG as catalyst. For comparison, both the Pd/G and Pd/C catalysts were also explored to better understand the catalytic capability of the Pd/NG as well as the function of nitrogen atoms. Additionally, the influence of various environmental parameters on the reductive performance of TBBPA by the Pd/NG catalyst was evaluated, since these factors could affect the adsorption capacity as well as catalytic activity of materials (Gupta et al., 2012; Mittal et al., 2009b, 2010). Furthermore, the adsorption and the activation of TBBPA on the catalyst were theoretically analyzed by using both Langmuir–Hinshelwood model and density functional theory (DFT). After that, dehalogenation of another halogenated emerging contaminant TCS by the Pd/NG catalyst was further investigated. Lastly, the feasibility of the Pd/NG catalyst for the reductive removal of TBBPA and TCS at a much lower contaminant concentration was also evaluated in this study.

## 2. Materials and methods

### 2.1. Materials

TBBPA ( $\geq 97.0\%$ ), TCS ( $\geq 97.0\%$ ), palladium on activated charcoal (5% Pd basis) and solid humic acid were purchased from Sigma Aldrich (USA).  $\text{Na}_2\text{PdCl}_4$  ( $\geq 98.0\%$ , Macklin Biochemical Co., Ltd., P.R. China) and  $\text{NaBH}_4$  ( $\geq 98.0\%$ , Sinopharm Chemical Reagent Ltd., P.R. China) were used as received. Both graphene and nitrogen-doped graphene (NG) were obtained from Chengdu Organic Chemicals (Sicuan, P.R. China). Graphene was chemically reduced from graphene oxide, while NG was manufactured from the reaction of chemically reduced graphene oxide with nitrogen-containing polymers at temperature above 900 °C. The preparation of palladium decorated NG and graphene as well as their characterizations are described in the Supporting Information (SI).

### 2.2. Batch dehalogenation tests

For investigating the kinetics of TBBPA dehalogenation, the reaction was conducted in 250 mL three-necked flask. A specified

high concentration of TBBPA was dissolved in a 160-mL mixture of ethanol and water (50/50, v/v). The addition of ethanol was due to the poor solubility of TBBPA in water. Before reaction, the air in the flask was evacuated and replaced by nitrogen for several cycles. After the temperature reached to the desired value in a water bath with a magnetic stirring at 500 rpm, hydrogen was immediately bubbled into the reactor at a flow rate of 10 mL min<sup>-1</sup>. The influence of different environmental factors was investigated and each experiment setup is summarized in Table 1. The different initial pHs were adjusted by sodium hydroxide. Dissolved humic acid was introduced by a stock solution which was prepared according to the protocol mentioned in the literature (Wang et al., 2014).

For comparison, both the Pd/G and Pd/C were also adopted as catalysts for TBBPA removal. Initial TBBPA concentration was around 3.4 mM and the dosage of catalyst was set at 30 mg L<sup>-1</sup>. The debromination was carried out at 308 K with pH value of 6.5. The replacement of air in the flask and the flow rate of hydrogen were as same as those in the experiments with Pd/NG as catalyst. The aqueous solubility of TBBPA is only  $4.15 \pm 0.36$  mg L<sup>-1</sup> at 298 K and pH 7.56 (Kuramochi et al., 2008). However, at the concentration lower than 4 mg L<sup>-1</sup>, we found that it was a bit difficult to investigate the kinetics of TBBPA degradation on the three catalysts due to rapid transformation of TBBPA, but also cannot accurately identify and quantify the reductive intermediates and products of TBBPA transformation. In order to clearly understand TBBPA degradation mechanisms in terms of kinetics and transformation pathway, ethanol was used to enhance the solubility of TBBPA to a higher concentration in this study.

For the dechlorination of TCS, the initial TCS concentration was 63  $\mu\text{M}$  and the catalyst dosage was 10 mg L<sup>-1</sup>. The pH of aqueous solution was controlled at 8.5 with 20 mM Tris-HCl solution. The flow rate of hydrogen was maintained at 10 mL min<sup>-1</sup> after the reaction temperature heated up to 308 K.

Lastly, the catalytic ability of the Pd/NG was further evaluated for removal of halogenated pollutants at a much lower concentration, where 10  $\mu\text{g}$  L<sup>-1</sup> TBBPA or TCS was dissolved in 20 mM Tris-HCl (pH 8.5) with 5 mg L<sup>-1</sup> catalyst dosage. The reaction was also conducted at 308 K with 10 mL min<sup>-1</sup> hydrogen.

### 2.3. Chemical analysis

The liquid was sampled at appropriate time intervals and mixed immediately with ethanol to extract analytes which might be adsorbed on the catalysts. After filtered through 0.22  $\mu\text{m}$  membrane, the concentrations of both TBBPA and TCS in the samples were analyzed for by high-performance liquid chromatography (HPLC) equipped with a 4.6  $\times$  250 mm Eclipse Plus C18 column and diode array detector (Agilent Technologies, USA). The mobile phase was methanol-water (80:20) with a flow rate of 1.0 mL min<sup>-1</sup> and the detection wavelength was 230 nm. All calibration curves contained at least six concentration levels over the test concentration range ( $R^2 \geq 0.999$ ). Identification of TBBPA reductive intermediates was further performed by Agilent 6460 LC/QQQ Liquid chromatography/mass spectrometry (Agilent Technologies, USA). The concentration of Br<sup>-</sup> was quantified by ICS-1100 ion chromatograph (Dionex, Sunnyvale, CA, USA) with an IonPac AS19 analytical column (4.0  $\times$  250 mm, Dionex) at 30 °C. KOH gradient elution ranged from 10 to 40 mM and the flow rate was 1.0 mL min<sup>-1</sup>. Nonpurgeable organic carbon (NPOC) was measured by a TOC analyzer (Multi N/C 2100, Analytik Jena, Germany).

### 2.4. Kinetic analysis

Langmuir–Hinshelwood (L–H) kinetics is the commonly used kinetic model for heterogeneous catalytic processes including Pd–

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