Journal of Hazardous Materials 310 (2016) 152–160

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Removal of triclosan via peroxidases-mediated reactions in water: Reaction kinetics, products and detoxification

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HIGHLIGHTS

- Enzymatic treatment of triclosan in water by soybean and horseradish peroxidases.
- pH, H_2O_2 concentration and enzyme dosage affected the removal efficiency of TCS.
- The removal of TCS by SBP was more efficient than that of HRP.
- K_{CAT} and K_{CAT}/K_M values for SBP toward TCS were much higher than those for HRP.
- Polymers formed via radical coupling mechanism were nontoxic to the growth of alga.

ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form 1 February 2016
Accepted 17 February 2016
Available online 20 February 2016

Keywords:
Triclosan
Soybean peroxidase
Horseradish peroxidase
Wastewater treatment

ABSTRACT

This study investigated and compared reaction kinetics, product characterization, and toxicity variation of triclosan (TCS) removal mediated by soybean peroxidase (SBP), a recognized potential peroxidase for removing phenolic pollutants, and the commonly used horseradish peroxidase (HRP) with the goal of assessing the technical feasibility of SBP-catalyzed removal of TCS. Reaction conditions such as pH, H_2O_2 concentration and enzyme dosage were found to have a strong influence on the removal efficiency of TCS. SBP can retain its catalytic ability to remove TCS over broad ranges of pH and H_2O_2 concentration, while the optimal pH and H_2O_2 concentration were 7.0 and 8 μM, respectively. 98% TCS was removed with only 0.1 U mL^{-1} SBP in 30 min reaction time, while an HRP dose of 0.3 U mL^{-1} was required to achieve the similar conversion. The catalytic performance of SBP towards TCS was more efficient than that of HRP, which can be explained by catalytic rate constant (K_{CAT}) and catalytic efficiency (K_{CAT}/K_M) for the two enzymes. MS analysis in combination with quantum chemistry computation showed that the polymerization products were generated via C—C and C—O coupling pathways. The polymers were proved to be nontoxic through growth inhibition of green alga (*Scenedesmus obliquus*). Taking into consideration of the enzymatic treatment cost, SBP may be a better alternative to HRP upon the removal and detoxification of TCS in water/wastewater treatment.

1. Introduction

Triclosan (2,4,4′-trichloro-2′-hydroxydiphenyl ether, TCS), an polychlorinated aromatic antimicrobial, has been widely used in health care and consumer products (e.g., toothpastes, hand disinfecting soaps, medical skin creams) for over half a century [1]. The extensive and widespread use of TCS has made this compound being frequently detected in human samples such as urine, plasma, and breast milk [2,3]. Monitoring studies suggested that TCS was also ubiquitously detected in various aquatic environments such as natural streams/rivers, estuarine waters and even drinking waters, resulting from discharge of wastewater treatment plant (WWTP) effluents [4–6]. Concerns with TCS stem from the fact that it possesses endocrine-disrupting activity and potentially contributes to bacterial resistance to antibiotics at environmentally relevant concentrations [1,6]. Moreover, TCS serves as a precursor of several highly toxic environmental by-products such as methyltriclosan and chlorinated dioxins [6].

The continuous detection of TCS concentrations ranging from 0.027 up to 2.7 μg/L in WWTP effluents, corresponding to 4–10% of

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http://dx.doi.org/10.1016/j.jhazmat.2016.02.037
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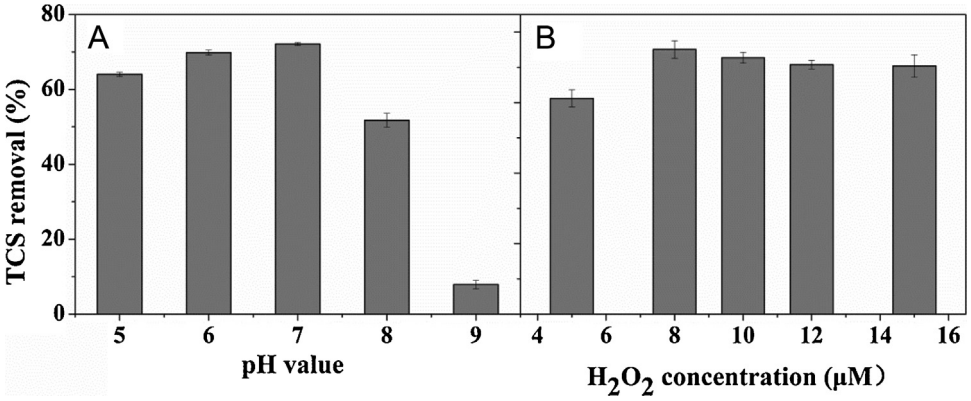

Fig. 1. SBP-catalyzed removal of TCS at different pH values (A), and H_2O_2 concentrations (B). Experimental conditions: (A) $[TCS]_0$ = 10 μM, [SBP] = 0.05 U mL^{-1}, $[H_2O_2]$ = 8 μM, pH controlled by 0.01 M PBS; (B) $[TCS]_0$ = 10 μM, [SBP] = 0.05 U mL^{-1}, pH 7.0 (0.01 M PBS). Error bars represent standard deviations (n = 3).

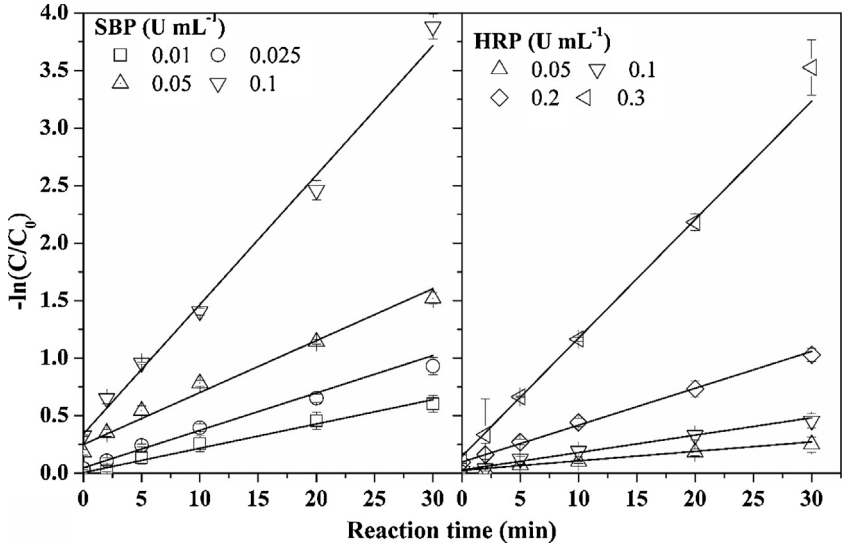

Fig. 2. Pseudo first-order rate plots for TCS removal at different enzyme dosages, Experimental conditions: $[TCS]_0$ = 10 μM, $[H_2O_2]$ = 8 μM, pH 7.0, 25 °C. Error bars present standard deviations (n = 3).

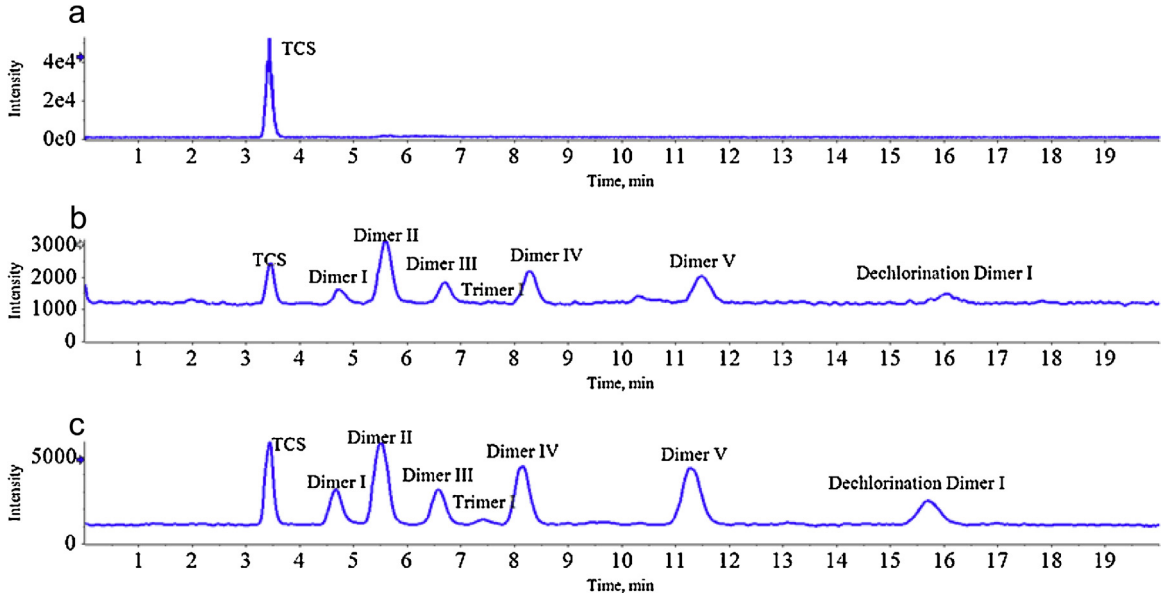

Fig. 3. LC–MS chromatograms of products from TCS transformation by SBP/HRP having various components: H_2O_2 + TCS (a), HRP + H_2O_2 + TCS (b), SBP + H_2O_2 + TCS (c). Experimental conditions: $[TCS]_0$ = 10 μM, $[H_2O_2]$ = 8 μM, [SBP] = 0.05 U mL^{-1}, [HRP] = 0.1 U mL^{-1}, pH 7.0.