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Co-metabolic enhancement of organic removal from waste water in the presence of high levels of alkyl paraben constituents of cosmetic and personal care products

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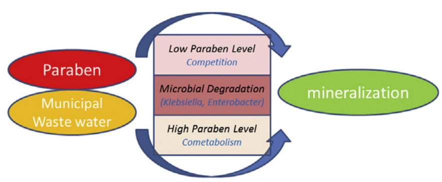
HIGHLIGHTS

- A biofilm system was used to treat municipal waste water containing alkyl parabens.
- Paraben, BOD, COD and TOC removals increased as HRT increased.
- Competition occurred when waste water contained low concentration level of parabens.
- Co-metabolism occurred in the presence of high concentration level of parabens.
- The mineralization was enhanced with increasing HRT due to oxygenase production.

GRAPHICAL ABSTRACT



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ABSTRACT

The enhanced removal of organic material from municipal waste water containing 50 mg/L of chemical oxygen demand and a given amount of alkyl paraben using a biofilm system was investigated. The parabens used were methyl, ethyl, and propyl paraben. The experiments were conducted at influent paraben concentrations of 10 and 50 mg/L. The influent pH was measured around 4.6 because of paraben hydrolysis. The effluent pH increased due to hydrogen consumption and small molecular acid generation. The higher removal rates were observed for the paraben with longer alkyl chains, which were more hydrophobic and capable of penetrating into microbial cells. The co-existing organic constituents in municipal waste water were found to be competitive with paraben molecules for microbial degradation at low paraben loading (i.e., 10 mg/L). Instead, the co-metabolic effect was observed at a higher paraben loading (i.e., 50 mg/L) due to more active enzymatic catalysis, implying the possible enhancement or organic removal in the presence of high levels of parabens. The difference in BOD and TOC removing ratios for parabens decreased with increasing HRT, implying their better mineralization than that of municipal organic constituents. This was because the microbial organism became more adapted to the reacting system with longer HRT, and more oxygenase was produced to facilitate the catechol formation and ring-opening reactions, causing apparent enhancement in mineralization.

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1. Introduction

Over the past few decades, advancement in societal modernization has led to elevated living standards for human beings and growing self-consciousness in personal care and hygiene. These social evolutions also result in the progress of medical cosmetics and the extensive use of cosmetic and personal care products (CPCPs). The occurrence of CPCP residues in domestic sewage, municipal waste water and waste water treatment systems is inevitable. Waste and residuals of CPCPs enter the aquatic environment through a variety of pathways including domestic sewer systems and storm water drainage channels. The monitoring results showed their ambient accumulation exhibiting a slightly increasing trend during the past few years. More importantly, they have received a lot of attention due to their ubiquity and adverse effects on public health, as well as on the environment (Capela et al., 2016; Hopkins and Blaney, 2016; Roberts et al., 2016; Dai et al., 2015).

Among the observed constituents of CPCP residuals, alkyl p-hydroxybenzoate (paraben) is a group of compounds of concern because of their popularity as additives, either singly or in combination, because of their desired germicidal effect, especially against mold and yeast formation, in the production of CPCPs. Due to their potential toxicity and estrogen-mimicking property, the presence of parabens poses a potential threat to the stability of microbial communities in a biological treatment system as well as in the ecological environment (Kang et al., 2016; Tran et al., 2016; Li et al., 2015; Błędzka et al., 2014).

The study by Jiménez-Díaz et al. (2016) indicated that methyl paraben (MP), ethyl paraben (EP) and propyl paraben (PP) were found in more than 60% of the collected human urinary samples at a concentration range from 1.4 to 30.0 ng/L in Tunisia. Molins-Delgado et al. (2016) conducted monitoring in 19 major waste water treatment plants, finding maximum influent and effluent alkyl paraben concentrations around 5700 and 137 ng/L, respectively. In the study by Gonzalez-Marino et al. (2011), the sewage occurrence and biodegradability of seven parabens and their derivatives were investigated, and the results showed that n-butylparaben degraded rapidly in real sewage with half-lives less than 10 h, while di-halogenated species were found more stable with half-lives longer than a week. For the treatment practice of industrial waste water, the concentration of alkyl paraben in the raw influent may range from 20 to 40 mg/L (Haman et al., 2015; Błędzka et al., 2014), and such a high paraben loading often impoverishes the waste water treatment capacity for removing organic contaminants.

Generally, the biological process has been considered to be environmentally-friendly waste water treatment technology and is frequently applied to organic contaminant removal in real waste water treatment practice. Obviously, treating aqueous alkyl parabens through a biological process in the presence of co-existing organic constituents of waste water seems inevitable in order to preserve the aquatic environment in the near future. Fan and Wang (2012) investigated the aqueous methyl paraben degradation in synthetic municipal waste water, observing increasing paraben removal with increasing hydraulic retention time. However, the impact of co-existing organic chemicals on paraben degradation deserves further clarification in order to understand the removal mechanism in a biofilm system.

In this context, this research investigates the treatment efficiency of paraben-containing waste water by an aerated pebble-based biofilm system. The methyl, ethyl, and propyl-parabens were selected as the contaminants to be investigated because of their popular use in CPCP production. Their treatment efficiencies in waste water were studied, and the co-metabolism and competition between parabens and co-existing organic constituents was evaluated. In the present study, synthetic municipal waste water was chosen over the real waste water in order to maintain the equivalent background organic loading other than parabens across the experiments. In the practice of industrial waste water treatment, domestic sewage from the working staffs is usually combined with process waste water from production lines for subsequent treatment. Therefore, the mixed waste water contains regular organic constituents in a comparable background and range to municipal waste water, but with high loadings for specific industrial pollution, depending on the raw materials and by-products of the production lines (i.e., paraben loadings in the present study). Paraben degradation was also conducted using purified water as the reference to evaluate the capability of the investigated biological system in removing paraben without the influence of background organics. The paraben concentrations chosen in this study were of 10 mg/L and 50 mg/L as the high and low paraben loadings, respectively, since previous studies showed the occurrence of paraben at ~6 mg/L in influent municipal waste water and at ~40 mg/L in cosmetic-related industrial waste water (Molins-Delgado et al., 2016; Haman et al., 2015; Błędzka et al., 2014). The attached-growth biological system has been applied extensively in waste water treatment, but its performance and the implications for paraben removal in an industrial application (e.g., a factory using paraben as the raw material and producing waste water containing a high loading of paraben) has never been studied in detail. The study using a high paraben concentration may shed light on the future waste water treatment design for cosmetics and pharmaceutical industries, especially when domestic sewage resulting from employees' daily water consumption is combined with industrial waste water. This study is the first report that has explored the competition and co-metabolism between paraben and organic constituents with systematic variations in hydraulic retention time and alkyl functional structure in a waste water treatment process. Further evaluation of the system microbial community was conducted and compared to assess the toxic influence of the investigated anti-bacterial chemicals on the formation of the microbial community.

2. Methods

2.1. Reagents and chemicals

The methyl, ethyl and propyl parabens used were reagent grade chemicals. The synthetic municipal waste water was prepared following the composition recipe proposed by Fan and Chang (2009), in which the ratio of carbon (C): nitrogen (N): phosphorus (P) was 100: 5: 1, resulting in the influent COD of 50 mg/L. Additionally, the trace elements of Ca, Mg, Fe, Cl, and S were prepared at the concentrations of 9.93 ppb, 4.54 ppb, 0.086 ppb, 5.99 ppb, and 8.84 ppb in the synthetic municipal waste water, respectively. All the chemicals used including $C_6H_{12}O_6$, NH_4Cl, K_2HPO_4, KH_2PO_4, $CaCl_2$, $MgSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$ were all of reagent grade purchased from SIGMA (Taiwan). The background COD concentration of 50 mg/L was determined based on the past 5-year monitoring results in Taiwan. The biological seed purchased from High Quality Co. was used for the biofilm growth. All the water used was purified by a Millipore purification process (Merck, Taiwan).

2.2. Experimental and sampling procedures

The reactor used in the study is a rectangular channel with the dimension of 150 cm (L) × 9 cm (W) × 6.5 cm (H). Pebbles ranging in size from 3 cm to 7 cm were chosen as the contact media with an overall porosity of 37.6%. The biofilm formation was conducted following the procedure proposed by Fan and Wang (2012). After