Available online at www.sciencedirect.com

ScienceDirect

www.journals.elsevier.com/journal-of-environmental-sciences

JOURNAL OF ENVIRONMENTAL SCIENCES
www.jesc.ac.cn

Investigation on removal pathways of Di 2-ethyl hexyl phthalate from synthetic municipal wastewater using a submerged membrane bioreactor

Mehdi Zolfaghari[1], *Patrick Drogui*[1,*], *Brahima Seyhi*[1], *Satinder Kaur Brar*[1], *Gerardo Buelna*[2], *Rino Dubé*[2], *Nouha Klai*[1]

1. *National Institute of Scientific Research, Water, Earth and Environment (INRS-ETE), University of Quebec, Quebec City, Quebec G1K 9A9, Canada*
2. *Industrial Research Center of Quebec, Quebec City, Quebec G1P 4C7, Canada*

ARTICLE INFO

Article history:
Received 8 January 2015
Revised 19 February 2015
Accepted 5 March 2015
Available online 2 July 2015

Keywords:
Di 2-ethyl hexyl phthalate
Submerged membrane bioreactor
Removal efficiency
Soluble microbial products
Toxicity

ABSTRACT

Highly hydrophobic Di 2-ethyl hexyl phthalate (DEHP) is one of the most prevalent plasticizers in wastewaters. Since its half-life in biological treatment is around 25 days, it can be used as an efficiency indicator of wastewater treatment plant for the removal of hydrophobic emerging contaminants. In this study, the performance of submerged membrane bioreactor was monitored to understand the effect of DEHP on the growth of aerobic microorganisms. The data showed that the chemical oxygen demand (COD) and ammonia concentration were detected below 10 and 1.0 mg/L, respectively for operating conditions of hydraulic retention time (HRT) = 4 and 6 hr, sludge retention time (SRT) = 140 day and sludge concentration between 11.5 and 15.8 g volatile solid (VS)/L. The removal efficiency of DEHP under these conditions was higher and ranged between 91% and 98%. Results also showed that the removal efficiency of DEHP in biological treatment depended on the concentration of sludge, as adsorption is the main mechanism of its removal. For the submerged membrane bioreactor, the pore size is the pivotal factor for DEHP removal, since it determines the amount of soluble microbial products coming out of the process. Highly assimilated microorganisms increase the biodegradation rate, as 74% of inlet DEHP was biodegraded; however, the concentration of DEHP inside sludge was beyond the discharge limit. Understanding the fate of DEHP in membrane bioreactor, which is one of the most promising and futuristic treatment process could provide replacement for conventional processes to satisfy the future stricter regulations on emerging contaminants.

Introduction

The structural similarities between phthalate esters and endogenous estrogens may result in interruption of human growth and reproduction hormones, especially at early age. Therefore, they are known as potential endocrine distrusting compounds (Tan et al., 2007), already controlled and banned by European, North American, and east Asian countries (Sun

* *Corresponding author*. E-mail: patrick.drogui@ete.inrs.ca (Patrick Drogui).

http://dx.doi.org/10.1016/j.jes.2015.03.025
1001-0742/

et al., 2014). Around the world, especially in Europe, Di 2-ethyl hexyl phthalate (DEHP) has also been considered as the most detectable plasticizer and one of the most problematic emerging contaminants (Zolfaghari et al., 2014). In Canada, DEHP was accounted as the highest non-steroidal synthetic compounds in both municipal influent and effluent samples (Fernandez et al., 2007).

Frequent detection of these compounds in environment, typically near municipal areas represent its anthropogenic sources, which are closely connected with the continuous discharge of trace concentrations by treated wastewater. For instance, DEHP concentration increased from an average of 150 μg/L in upstream to 171 μg/L in river downstream, due to constant release of 162 μg/L by wastewater treatment plant (WWTP) effluent (Olujimi et al., 2012). Another example in the province of Quebec showed constant release of 54 μg/L of DEHP from Montreal WWTP effluent into Saint-Lawrence River raised its concentration to 180 μg/L in running water. Conventional physicochemical processes in Montreal WWTP are reported to remove only 23% of inlet DEHP (Barnabé et al., 2008).

As a highly hydrophobic compound ($\log K_{ow}$ = 7.5) and its non-volatility properties (henry constant low = 1.74–4.43 (Pa·m^3)/mol), it mainly adsorbed to suspended solid and macromolecules and rarely volatilized into the air. By gradual degradation of its carrier, the major part of DEHP remains in water or adsorbed onto soil and sediment. The rate of natural biodegradation and physicochemical (*e.g.*, photolysis and hydrolysis) degradation of DEHP in aqueous system was so slow, as its half-life is estimated in the range of 1–4.5 years (Magdouli et al., 2013). Free DEHP molecules, stripping into the air are vulnerable to photodegradation (Peterson and Staples, 2003). In solid phase, the degradation pace in sediment is faster than soil probably due to the presence of waterborne microorganisms and abundant oxygen. O'Grady et al. (1985) estimated the rate of removal of DEHP in activated sludge. For initial concentration of 3.3 mg DEHP/L, removal efficiency reached 71% and 91% in 24 and 48 hr, respectively. By considering the path of DEHP biodegradation, ether cleavage and production of alcohol and phenol derivatives, such as MEHP, di benzoic acid, and benzoic acid are the basic products of degradation (Magdouli et al., 2013). The hydrolysis of each chemical bond is more prone to electrophilic attack by oxygen of aerobic bacteria (Alturki, 2013; Tadkaew et al., 2011). As a consequence, the removal efficiencies of DEHP (electron donating group) are higher than anaerobic and anoxic processes. Similar results were obtained by Huang et al. (2008) who showed the removal efficiency proportion percentages of anaerobic, anoxic and aerobic reactors to be in the range of 14%–23%, 15%–19%, and 61%–68%, respectively.

Diverse kinds of plastic goods used by citizens, level of municipality, discharge of landfill leachate and industrial wastewaters into municipal wastewater and the method used by researchers substantially determine the concentration of DEHP. Levels of DEHP in municipal wastewater are widely fluctuated between the range of 0.716 (Tan et al., 2007) to 379 μg/L (Camacho-Muñoz et al., 2014), and even at 1.085 mg/L (Olujimi et al., 2012).

Recent studies mainly focus on the introduction of efficient system for emerging contaminant removal or optimization and modify the current systems, since slight change in operating condition affected the efficiency of treatment plants for hydrophilic compounds (Zolfaghari et al., 2014). Modification of conventional activated sludge could be the ideal option for enhancing the removal efficiency of hydrophobic compound, since membrane rejection of suspended solids and sludge diminished the emergence of lipophilic molecules owing to size exclusion (Clara et al., 2005). In all former studies, adsorption on suspended solids and/or mixed liquor suspended solid (MLSS) has been reported as the main removal mechanism of DEHP. Therefore, the concentration of DEHP sludge in WWTP reached 153 mg/kg, while the influent and effluent concentrations were 1.6 and 0.03 μg DEHP/L, respectively (Peterson and Staples, 2003). Adsorbed DEHP onto activated sludge later biodegraded, especially under high sludge age condition (Boonyaroj et al., 2012b). Therefore, increasing the age of sludge in membrane bioreactor (MBR) provided sufficient biodegradation time.

In this study the performance of submerged membrane bioreactor (SMBR) was closely studied to understand the effect of DEHP on the performance parameters, such as chemical oxygen demand (COD), NH_4-nitrogen, and PO_4-phosphorous removal. Synthetic wastewater used not only stimulated the municipal wastewater concentration, but also removed all mediating factors that may affect tracing of DEHP fate in the outlet. Furthermore, the ability of SMBR for removal enhancement was investigated by mass balance DEHP.

1. Material and methods

1.1. Experimental unit

A laboratory scale SMBR consisting of a aeration basin with an active volume of 4 L, a continuous mixer, air diffuser, a pressure gage, and influent and effluent pumps was employed. The stirred tank with 19.1 cm of water height was equipped with Zeed-Weed (ZW-1) hollow-fiber membrane manufactured by Zenon Environmental Inc. (Oakville, ON, Canada). It has 80 vertical fibers of 20 cm with the 0.04 μm pore diameter which provided 0.047 m^2 of total surface area for filtration. A pulsed peristaltic pump produced vacuum inside the membrane. In order to minimize the accumulation of sludge on the membrane surface (prevent fouling), the pump operated intermittently in cycle of 60/20 sec of filtration/rest. Furthermore, the extra air supply went right through membrane for cake removal. Besides, the negative pressure was controlled by manometer located on the membrane aspiration line. The fouling of membrane was constantly checked by trans-membrane pressure (TMP). For TMP less than −45 kPa, backwashing was carried out by the membrane permeate, while reaching TMP more than −69 kPa (the highest operation pressure) membrane chemical wash was performed. Firstly, membrane was washed by tap water to remove the cake layer and then, it immersed in a solution of NaOCl (1000 mg/L) for 2 hr. Strong oxidizing property of ClO^- removed the organic matters stuck in the membrane pores. Acidic cleaning by 3.0 g/L of citric acid solution for 30 min was sometimes performed for the removal of mineral clogged in the membrane pores.

Air flow was controlled for keeping the dissolved oxygen always more than 2 mg O_2/L. Even though mixing was provided by aeration, a variable speed mixer operated at