Removals of Phenolic Compounds and Phthalic Acid Esters in Landfill Leachate by Microbial Sludge of Two-stage Membrane Bioreactor

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Abstract

Removals of bisphenol A (BPA), 2,6-di-tert-butylphenol (2,6-DTBP), 2,6-di-tert-butyl-4methylphenol (BHT), di-ethyl phthalate (DEP), di-butyl phthalate (DBP) and bis (2-ethylhexyl) phthalate (DEHP) were monitored in two-stage membrane bioreactor (MBR) by operating under no sludge wastage condition for 500 days. Those emerging contaminants were removed by 99.5%, 99.0%, 99.5%, 97.9%, 96.8% and 95.7% under long term operation in MBR without reaching maximum adsorption capacity of sludge. Biodegradation was the main mechanism for their removals in MBR systems and the microbial activities were enhanced by long sludge age operating condition. The removals of those compounds by microbial sludge in MBR by adsorption and combined (adsorption & biodegradation) mechanisms were well explained by pseudo-second order and first order kinetics respectively.

Keywords

Emerging contaminants, Membrane bioreactor, Municipal solid waste leachate, Phenolic compounds, Phthalic acid esters

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1. Introduction

Leachate from municipal solid waste can be contaminated with several emerging contaminants, such as phenolic compounds and phthalic acid ester (PAEs), and these are found in some household and industrial plastics. These emerging contaminants are known as plasticizers used in various plastic to improve mechanical properties during manufacturing to provide greater flexibility and be easily molded [1]. In many countries, these emerging organic compounds are not strictly controlled by hazardous waste regulations [2]. Those phenolic compounds which are commonly used in commercial products are bisphenol A, 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, 2-chlorophenol and the U.S. Environmental Protection Agency has classified these compounds as carcinogen and the World Health Organization has also classified catechol in 2B group - a compound of carcinogenicity [3]. Phthalic acid esters (PAEs), for example ethyl phthalate, butyl phthalate and bis (2-ethylhexyl) phthalate, are classified as a toxic compounds to endocrine system of human bodies and adverse reproductive system outcomes, neurodevelopmental, and the effects of the immune system in both humans and wildlife. These compounds were reported in many countries and detected at higher concentration in leachate from municipal solid waste landfill sites [4,5,6].

In order to eliminate the emerging contaminants from wastewater, an advanced wastewater treatment system has employed and required advanced chemical oxidation [7] or adsorption [8] processes. Biological treatment can also partially remove them but their removal efficiencies are generally found to be low to moderate due to the fact that several of the emerging contaminants are relatively resistant to biodegradation. The study varied from natural ecosystems [9] to mechanical based wastewater treatment system [10,11]. Among several newly developed wastewater treatment processes, membrane bioreactors (MBRs) is reported as an effective wastewater treatment system in removal of hardly biodegradable or toxic organic compounds and therefore has become a good option for the treatment of municipal solid waste leachate that contains hazardous organic compounds [12,13]. In MBR, biological treatment is conducted under unique environmental condition in which microorganisms are maintained at much higher concentrations when compared to other conventional biological treatment processes. Meanwhile, membrane filtration has provided additional barrier for pollutant removal after biological treatment. These combined biological

and physico-chemical processes has yielded much better removal efficiency of micro-pollutants both with hydrophobic or hydrophilic properties [12]. MBR can also enhance the biodegradation of toxic organic compounds when operating under long sludge age condition and long-term operation [12,13].

In previous study, the two-stage MBR is utilizing inclined-plate separator in first stage anoxic reactor and followed by an aerobic reactor with a submerged membrane module for solid-liquid separation which have been developed and successfully applied to low and high strength wastewater including municipal solid waste leachate [14,15]. At the first stage reactor, highly concentrated sludge is maintained through incline plate separation and second stage of aerobic reactor is operated at appropriate biomass concentrations for controlling membrane fouling whilst whole system is operated at high organic loading rate. The system can be applied in practice in the treatment of wastewater with their characteristics fluctuated greatly with time [12,15]. The advantages of MBR systems are including maintaining high performance, low operating cost and simplicity of operation without removal of excess sludge. In particular, its efficiency in removing contaminants of emerging which is presented with low concentration levels of $\mu\text{g/l}$ mainly depended on the properties of compounds and operating conditions of the treatment system, e.g. biomass concentration, hydraulic retention time and pH. In previous study, the adsorption and biodegradation had been reported as the main removal mechanisms of these emerging contaminants in this new MBR treatment system for municipal solid waste leachate [12]. However, the removal efficiencies of emerging contaminants by microbial sludge operated in long term and the analyses of emerging contaminant removal kinetics have not yet been performed. Therefore, the main objectives of this study are to investigate long-term fate of emerging contaminants in MBR system and determination of their maximum removal capacities by MBR sludge in batch experiments. The kinetic rate constants of the removals of emerging contaminants by MBR sludge cultivated under long term operation (500 days) without any sludge withdrawal are revealed.

2. Materials and methods

2.1 Experimental set-up and MBR operation

In this study, we installed pilot-scale two-stage MBR at a solid waste disposal site in Thailand. The system consisted of two reactors connected in series (Fig. 1). The first anoxic reactor had a total volume of 1.25 m³ - volume of 1 m³ was used for operation and the other volume of 0.25 m³ was used for sludge storage zone. The reactor was equipped with inclined tube module - size 0.15 m channel width, 0.45 m depth - for sludge separation and followed by another aerobic reactor with 1 m³ working volume which had two hollow fiber membrane modules (Sterapore SURTM, PE, 0.4 µm pore size, 9 m² surface area per module) immersed inside the tank for solid-liquid separation. Intermittent suction (10:10 min on and off) was performed to withdraw permeate from the membrane module and maintain permeate flow at 2 m³/d. Therefore total hydraulic retention time (HRT) in the two-stage MBR was maintained at 1 day which found appropriate for high strength leachate in our previous study [15]. Aeration was continuously supplied to the MBR reactor for maintain the dissolved oxygen (DO) level at 4-5 mg/l. The sludge was cultivated and maintained within the system for 500 days. They were re-circulated at a rate of 100% of feed flow rate from aerobic tank back to anoxic tank to maintain mixed liquor suspended solids (MLSS) concentration in the aerobic reactor at about 7-9 g/l. Due to this re-circulation, DO level in anoxic reactor was maintained at 0.5 mg/l. There was no sludge drainage from system except a minimal amount for analytical purpose (approx. 500 mL every 7 days).

Insert Figure 1

The operation of MBR consists of two phases. The 1st phase (day 0-95) was a start-up period to allow the biomass within the system to build up and be ready for a research in both anoxic and aerobic reactors until we achieved steady reactor performance in terms of organic and nitrogen removals. During this period, sludge re-circulation was not performed. The 2nd phase (from day 96-500) was continuously conducted after the 1st phase. In this phase, we controlled MLSS concentration in aerobic reactor with sludge re-circulation to study about the removals of emerging contaminants in the reactors (from day 212-500). Leachate used for the experiment was prepared by mixing fresh leachate collected from solid waste collection truck and stabilized leachate obtained from a leachate storage pond. The fresh and stabilized leachate was mixed at a mixing ratio of 1:4 (v/v) to represent average characteristics of leachate of both operating and closed landfill cells. In preparation, water in the system would remain constant of water in the system and not significantly fluctuated during the experiment period. Throughout the operation, we regularly monitored the system every week.

The characteristics of landfill leachate were analyzed according to Standard Methods for the Examination of Water and Wastewater [16]. pH was analyzed by using portable meters. Organic compounds were determined in term of Biochemical Oxygen Demand (BOD₅) using a 5-day BOD test, Chemical Oxygen Demand (COD) using closed dichromate reflux method. Suspended solids (SS) were determined by gravimetric method. Ammonia nitrogen (NH₃-N) and Total Kjeldahl Nitrogen (TKN) were analyzed by distillation and macro-kjeldahl methods.

Upon the preparation of mixed leachate, major types of emerging contaminants were classified into phenolic and PAEs groups. There were three major phenolic compounds and three major PAEs which were detected in most samples and found at higher concentrations in range of hundred µg/l, i.e. bisphenol A (BPA), 2,6-di-tert-butylphenol (2,6-DTBP), 2,6-di-tert-butyl-4-methylphenol (BHT), di-ethyl phthalate (DEP), di-butyl phthalate (DBP) and bis (2-ethylhexyl) phthalate (DEHP). Upon the preparation of mixed leachate, major types of emerging contaminants were classified into phenolic and PAEs groups. There were three major phenolic compounds and three major PAEs which were detected in most samples and found at higher concentrations in range of hundred µg/l, i.e. bisphenol A (BPA), 2,6-di-tert-butylphenol (2,6-DTBP), 2,6-di-tert-butyl-4-methylphenol (BHT), di-ethyl phthalate (DEP), di-butyl phthalate (DBP) and bis (2-ethylhexyl) phthalate (DEHP). The analyses of emerging contaminants are described in details in section 2.3. Table 1 shows water quality parameters and concentrations of emerging contaminants detected in fresh and stabilized leachate during the study.

Insert Table 1

2.2 Emerging contaminants removal and kinetic expression

Batch experiments were performed to investigate the maximum removal capacity of emerging contaminants by MBR sludge at the end of the experiment (500 days). In order to differentiate the removals of target compounds via adsorption and biodegradation mechanisms, batch experiments were performed by using active (untreated) and inactivated MBR sludge following the procedures described in our previous study [12]. Sludge from

anoxic and aerobic reactors were tested for their capacity in removing six target compounds present in municipal solid waste leachate. Batch experiments were performed under non-aeration (only agitation provided) and aeration at DO of 4-5 mg/l for anoxic and aerobic sludge respectively. In the batch experiment, sludge samples having MLSS of 3.0 g/l were spiked with BPA, 2,6-DTBP, BHT, DEP, DBP and DEHP at an initial concentration of 3,000 µg/l and their concentrations were determined every 2 h during a 24 h experiment which was equal to the HRT of the MBR. The initial concentration of those compounds was selected based on preliminary experiments to ensure that the tested compounds remained after 24 h during batch experiment so that maximum removal capacity by sludge in batch experiment could be reached. These batch experiments were conducted in triplicate.

For sludge inactivation, the MBR sludge was repeatedly autoclaved at 121°C for 15 min three times in order to completely terminate microbial activities. The removals of emerging contaminants by active sludge were due to both adsorption and biodegradation mechanisms whereas the removal by inactivated sludge was only due to adsorption of compounds onto sludge particles. As an alternative to heat treatment, chemical inhibition was also considered using antiseptic disinfectant (chloroxylonol) in our preliminary experiments. It was found that adsorption capacity of thermal treated sludge and chemical treated sludge were not significantly different (<15%) Therefore, thermal treatment was used for inactivation of microbial activities in subsequent experiment to avoid having direct chemical oxidation reaction of the target compounds by the disinfectant.

The rates of emerging contaminant removal in batch experiment were found following first order kinetic expression. Therefore, the following equation was applied to determine the rate constant for the removals of emerging contaminants by combined adsorption and biodegradation mechanisms (for active sludge case).

$$\ln (q_t/q_0) = -k_t t \quad (1)$$

where q_0 (µg/l) and q_t (µg/l) are the concentrations of emerging contaminants in aqueous solution at initial time and time t (hours or h). k_t (h^{-1}) is first order rate constant for the removal of the contaminants.

For adsorption experiment using inactivated sludge, pseudo first order (PFO) and second order (PSO) kinetic models [17,18] were applied to explain adsorption of emerging contaminants onto MBR sludge using equation (2) and equation (3) respectively.

$$dq_t/dt = k_1(q_e - q_t) \quad (2)$$

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (3)$$

where q_e ($\mu\text{g/g}$) is the solid phase concentration of the emerging contaminants at equilibrium which represents maximum adsorption capacity of sludge in this batch experiment, q_t ($\mu\text{g/g}$) is the solid phase concentration at contact time t and k_1 (h^{-1}) and k_2 ($\text{g}/\mu\text{g.h}$) are the pseudo first order and pseudo second order rate constant, respectively. If the sorption followed the PFO equation, a plot of $\ln(q_e - q_t)$ against t should be a straight line. Similarly, t/q_t should change linearly with t if the sorption process obeyed the PSO equation.

2.3 Emerging contaminants analyses

The concentrations of emerging contaminants were analyzed separately in solid and soluble forms. The analyses of emerging contaminants in water sample were determined by solid phase extractions (SPE) and gas chromatograph-mass spectrometry (GC-MS) method. To determine their concentrations in soluble form, the water samples obtained after separation of suspended solids by GF/C filtration were used. The VertipakTM-C18 tubes or SPE tubes were used for emerging contaminant extraction. First, SPE tubes were clean with 10 ml dichloromethane: methanol (1:9 v/v) and followed by 10 ml pure water then followed by 50 ml filtrated water sample. The SPE tubes were left for drying with clean air and eluted with 5 ml of dichloromethane: methanol (1:9 v/v). The fraction of elution step were concentrated by evaporation with nitrogen gas and then analyzed by GC-MS.

For determination of emerging contaminants in solid bound form, sludge samples were added to 20 ml dichloromethane: methanol (1:9 v/v) and mixed for 1 h followed by sonication for 15 min. The solvent were transferred then to C18-SPE tubes and eluted with 5 ml of dichloromethane: methanol (1:9 v/v). Then the fraction elution step were concentrated before analyzed by GC-MS.

Gas chromatography with mass spectrometry (Shimadzu, GCMS-QP2010 plus) was used for determination of emerging contaminant concentrations. The device was equipped with a 30 m RTX-35MS capillary, 0.25 mm I.D. with thickness of 0.5 μ m. Helium was used as carrier gas. Sample 1 μ l was injected automatically. Three different GC-MS programs were set for the analyses of six emerging contaminants targeted in this study. The first program for BPA analysis having the operating condition as follows oven temperature was set at 60°C and then increased to 150°C at a rate of 7°C/min with holding time of 5 min. The instrument condition was set at electron impact of 70 eV, ion source temperature of 200°C and interface temperature of 250°C. The second program for BHT and 2,6-DTBP analyses was set at oven temperature of 60°C, increased to 100°C with holding time of 2 min and then further increased to 150°C at a rate of 3.5°C/min with holding time of 5 min. The instrument condition was set at electron impact at 70 eV, ion source temperature at 150°C and interface temperature at 250°C. The third program for DEP, DBP and DEHP analyses was set at oven temperature of 60°C, increased to 100°C with holding time of 5 min, then increased from 100°C to 150°C at a rate of 10°C/min and holding time of 5 min, followed by an increase from 150°C to 195°C at a rate of 3°C/min with holding time of 5 min, increased from 195°C to 205°C at a rate of 1°C/min with holding time of 10 min and finally increased from 205°C to 250°C at a rate of 10°C/min with holding time of 15 min. The instrument condition was set at electron impact of 70 eV, ion source temperature of 200°C and interface temperature of 270°C. The peak chromatogram were referenced with Wiley library MS-spectra. Each sample were analyzed for three times to ensure the accuracy for the determination of their concentrations. The lower detection limit for the analyses was 1.0 μ g/l and the analyzed results were compared with blank samples using MilliQ water (molecular grade pure water). The same analytical procedures were applied to internal standards of known concentrations (3,000 μ g/l) of all six compounds targeted in this study. The recovery percentages for BPA, 2,6 DTBP, BHT, DEP, DBP and DEHP were found to be 91.37, 86.53, 89.13, 91.43, 97.23 and 90.26% respectively.

In both fresh and stabilized leachates, BPA, 2,6-DTBP, BHT, DEP and DBP were all found in soluble phase only whereas DEHP was detected both in soluble and solid bounded forms. Table 2 presents the chemical properties of emerging contaminants found in leachate of this study. The form of compounds detected in leachate (soluble or solid bound) could be influenced by molecular weight (MW) and mainly on the hydrophobicity ($\log K_{ow}$) properties

of those compounds as DEHP with highest MW and log K_{ow} were only found in solid bounded form.

Insert Table 2

3. Results and discussion

3.1 Performance and removal efficiency of emerging contaminants in MBR treatment

The two-stage MBR treatment was operated in total of 500 days which the influent and effluent samples as well as emerging contaminant concentrations were regularly monitored. During start-up period, MLSS concentration in the aerobic reactor was gradually increased from 2,000 mg/l to more than 10,000 mg/l before sludge re-circulation started **between aerobic and anoxic reactors. This was to help** control biomass in system and the MLSS concentrations in the aerobic reactor were remained at 7-9 g/L whereas those in anoxic reactor increased from about 3 to 7 g/L from day 150 to day 500 without losing the excess sludge from the system.

Average influent measured by BOD and COD parameters throughout the study were 7,402 (SD= 1,203) and 13,531 (SD = 1,861) mg/l and food to micro-organisms (F/M) ratio in the system was between 0.4-0.7 d⁻¹. **After the treatment, we found the effluent with BOD and COD average of 36 (SD=20) and 648 (SD=310) mg/l.** As a result, the removal efficiency in BOD and COD **parameters were** 99.5% and 95.2% on average. Majority of organic removals (about 65%) occurred in anoxic reactor. For NH₃ and TKN, the removal efficiencies were 94.5% and 75.2% respectively. The effective treatment showed relatively stable during the entire operation, despite gradual change in sludge biomass in anoxic reactor.

Figure 2 shows **varied concentrations of six emerging contaminants detected in the influent water, anoxic effluent, system effluent.** During day 212-500, it was found that concentrations of all compounds were rated from hundred µg/l to more than 1 mg/l. **After the treatment, most of emerging contaminants were mostly removed - the effluent concentrations found to be lower than 10 µg/l except DEP which was less than 50 µg/l.** In most cases, the removal efficiency of emerging contaminants was improved **by the time that we run the system.** Table

3 presents the concentrations of each emerging contaminant in leachate, effluent from anoxic and aerobic reactors together with their removal efficiency. During the operation, average removal efficiency of BPA, 2,6-DTBP, BHT, DEP, DBP and DEHP were 99.58%, 99.05%, 99.51%, 97.97%, 96.82% and 95.77% respectively.

From the result, it shows that **emerging contaminants** were removed in both anoxic and aerobic reactors but majority of the removals **were from** the aerobic reactor. The BPA, 2,6-DTBP, BHT, DEP, DBP and DEHP were removed in anoxic reactor with the removal efficiency of **37.7%, 33.8%, 31.9%, 27.4%, 24.9% and 13.0%**. Higher removals were observed in aerobic condition for all compounds. During the treatment, BHT, DBP and DEHP were also found adsorbed onto sludge particles resulting in detectable level of their concentrations in solid bounded form. During 500 days of operation, maximum concentrations of BHT, DBP and DEHP adsorbed onto sludge particles were found to be **3, 23 and 155** µg/g sludge (dry wt.). Among them, accumulation of DEHP was only noticed at the end of 500 days of operation at **77** µg/g dried sludge. These observations suggested that most of the emerging contaminants in this study could be well biodegraded by microbial sludge of MBR system - resulting low accumulation of those compounds in sludge even during long term operation. Their chemical properties were one of the key factors that affects the removal efficiency. The compounds with higher octanol-water partition coefficient (K_{ow}) or hydrophobic in nature tended to adsorb onto the particles and later on biodegraded in the system whereas those with lower K_{ow} were removed in aqueous form without accumulation to sludge particles [12,13].

Insert Figure 2

Insert Table 3

3.2 Maximum removal capacity of emerging contaminants by MBR sludge

The maximum removals of emerging contaminants by MBR sludge were investigated in batch experiments. This sludge samples were obtained from both anoxic and aerobic reactors with approximate sludge age condition of 500 days. The experiment was conducted by using active and inactivated sludge samples. The results of batch experiments are shown in Figure

3. By using active sludge samples from the aerobic reactor, the total removals of BPA, 2,6 DTBP, BHT, DEP, DBP and DEHP were 98.0%, 96.8%, 96.1%, 96.4%, 96.4% and 98.4% after 24 hours. Meanwhile, their removals by inactivated sludge were found to be 18.3%, 27.8%, 31.7%, 14.7%, 24.9% and 53.1% respectively. Considering the differences in removal efficiency between active and inactivated sludge samples, the removals through biodegradability of those compounds were found to be 79.7%, 69.0%, 64.4%, 81.7%, 71.5% and 45.3%. The results suggested that most of emerging contaminants in this study were mostly removed by biodegradation except DEHP which was mainly removed by adsorption during 24 h of batch experiment. In case of anoxic reactor, the removal of emerging contaminants by biodegradation were 44.1% for BPA, 31.8% for 2,6 DTBP, 28.8% for BHT, 50.4% for DEP, 44.5% for DBP and 15.1% for DEHP (Table 4).

Insert Figure 3

Insert Table 4

Table 4 shows the removals of emerging contaminants by adsorption and biodegradation under anoxic and aerobic conditions. Overall, the removal efficiency for all studied compounds was high (96.1-98.4%) but the contribution of adsorption and biodegradation were different depending on the chemical properties of those compounds. Under aerobic condition, BPA, 2,6 DTBP, BHT, DEP and DBP removals via biodegradation was predominant at 64.4-81.7% whereas adsorption was predominant for the removal of DEHP at 53.1%. The removals under aerobic condition were found higher than anoxic condition for all compounds. While the removals via adsorption between both conditions were not much different, the percentages of biodegradation under aerobic condition were improved from those under anoxic condition by 27-37% in the total removals. These observations confirmed the results obtained from long term MBR operation showing that majority of emerging contaminants were removed in the aerobic reactor.

In relation to the K_{ow} value of emerging contaminants, the compounds with highest K_{ow} value were mainly removed by adsorption whereas those with lower K_{ow} were removed well by biodegradation. DEHP was a largest molecular structure that had lowest biodegradation rate when compared with other targeted compounds. In addition to the K_{ow} value, other factors affecting the biodegradation of emerging contaminants were also including water solubility,

molecular weight and complexity of chemical structure of the compounds. The studies on phthalate biodegradation also suggested that it was influenced by alkyl chain length, i.e. phthalates with shorter alkyl chains are rapidly degraded whereas phthalates with longer alkyl chains are poorly degraded [19,20,21,22,23].

3.3 Kinetics of emerging contaminant removals

The changes in concentrations of emerging contaminants with time in batch experiment were used to derive first-order kinetic rate constant for the active sludge having both adsorption and biodegradation mechanisms. In case of inactivated sludge, pseudo first order (PFO) and pseudo second order (PSO) kinetic rate constant for adsorption under aerobic condition.

Figure 4 shows the experimental plots between $\ln (q_e - q_t)$ versus time, t/q_t versus time to explain adsorption kinetics by PFO and PSO for all six compounds. It was found that the experimental data fit better to the PSO plot ($r^2 = 0.98-0.99$) as compared to that of the PFO plot ($r^2 = 0.77-0.90$) as summarized in Table 5. The maximum adsorption capacities of BPA, 2,6 DTBP, BHT, DEP, DBP and DEHP onto MBR sludge derived from PSO plot were 32, 90, 177, 36, 160 and 341 $\mu\text{g/g}$ sludge (dry wt.). Comparing the maximum adsorption capacity of DEHP with those observed during long term operation of MBR, it was found that only 45% of adsorption capacity of sludge has been reached at maximum during 500 days of operation and finally the accumulation was reduced to only 23% at day 500 due to subsequent biodegradation of DEHP.

Overall removal of emerging contaminants could be well explained by first-order kinetics. As shown in Figure 4(c), the experimental plot between $\ln (C/C_o)$ versus time (t) presents a fairly good linear relationship between them ($r^2 = 0.87-0.92$). The rate constants for the removals of those six emerging contaminants were found to be 0.163-0.194 h^{-1} as shown in Table 5.

Insert Figure 4

Insert Table 5

4. Conclusion

This research provided a perspective on the removals of emerging contaminants from the landfill leachate by membrane bioreactor treatment system. Two-stage membrane bioreactor was applied as a treatment municipal solid waste landfill leachate that contains BPA, 2,6-DTBP, BHT, DEP, DBP and DEHP compounds in long term operation of 500 days. The emerging contaminants were effectively removed in both anoxic and aerobic conditions of MBR treatment but the removals were predominant under aerobic conditions. During long term operation, the removals of those emerging contaminants were 99.5%, 99.0%, 99.5%, 97.9%, 96.8% and 95.7% and the main mechanism responsible for those removals was biodegradation. The chemical properties of the samples was the key factor that affected the removal efficiency of emerging contaminants. Among the six compounds, BPA, 2,6 DTBP, DEP are relatively hydrophilic and highly soluble in water so their biodegradation rate were found higher. Meanwhile, DEHP molecular structure is more complex and it could be well removed by adsorption first and subsequently biodegraded in long term.

Acknowledgements

We appreciate the financial support for this study from the Japan Science and Technology Agency (JST) and Japan International Cooperation Agency (JICA) for providing research funds through the research and development for Water Reuse Technology in Tropical Regions (Water-Intro) project.

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Table 1 Water quality parameters and emerging contaminant concentrations in leachate

Parameters	Unit	Fresh leachate	Stabilized leachate
<u>Water quality parameters</u> *			
pH	-	6.3 (1.7)	7.6 (1.3)
BOD	mg/l	90,956 (30,137)	126 (95)
COD	mg/l	34,425 (12,661)	2,738 (549)
TOC	mg/l	12,253 (3,741)	348 (99)
TN	mg/l	1,380 (303)	85 (24)
TKN	mg/l	867 (206)	63 (18)
NH ₃ -N	mg/l	360 (164)	8 (4)
TP	mg/l	76.09 (41.68)	57 (24)
<u>Emerging contaminants</u> †			
<i>Phenols</i>			
Bisphenol A (BPA)	µg/l	276 (243)	216 (194)
2,6-Di-tert-butylphenol (2,6 DTBP)	µg/l	185 (109)	247 (108)
2,6-Di-tert-4methyl-butylphenol (BHT)	µg/l	173 (158)	196 (206)
<i>Phthalates</i>			
Ethyl phthalate (DEP)	µg/l	130 (121)	295 (276)
Butyl phthalate (DBP)	µg/l	275 (230)	384 (172)
Bis (2-ethylhexyl) phthalate (DEHP)	µg/l	25 (30) ^a , 276 (293) ^b	47 (12) ^a , 146 (139) ^b

Remark: average (SD) value
* No. of sample = 64, † No. of sample = 56
^a solid phase, ^b soluble phase. Other compounds were only found in soluble phase

Table 2 Chemical properties of emerging contaminants found in leachate

Compounds	CAS No. [†]	Molecular weight [†]	Alkyl chain length	log K _{ow} [†]
<i>Phenols</i>				
Bisphenol A (BPA)	80-05-7	228.29	*	3.32
2,6-di-tert-butylphenol (2,6-DTBP)	128-39-2	206.33	*	4.92
2,6-di-tert-butyl-4-methylphenol (BHT)	128-37-0	220.35	*	5.10
<i>Phthalates</i>				
Ethyl phthalate (DEP)	84-66-2	222.24	2 ^a	2.39
Butyl phthalate (DBP)	84-74-2	278.34	4	4.61
Bis (2-ethylhexyl) phthalate (DEHP)	117-81-7	390.56	8	7.54

[†] From Schwarzenbach et al., 2003 [12]

* No report

^a From Staples et al., 1997 [15]

Table 3 Concentration of emerging contaminants and their removal efficiencies in two-stage MBR

Compounds	log K _{ow}	Influent (µg/l)		Eff. _{Anoxic} (µg/l)		Eff. _{MBR} (µg/l)	Total removal efficiency (%)	
		Solid [†]	Soluble	Solid*	Soluble	Soluble	Anoxic (1 st stage)	MBR (2 nd stage)
<i>Phenols</i>								
BPA	3.32	-	479 (227)	-	298 (109)	2 (5)	37.7 %	99.5 %
2,6-DTBP	4.92	-	319 (146)	-	211 (87)	3 (10)	33.8 %	99.0 %
BHT	5.10	-	410 (115)	9 (12)	279 (113)	2 (9)	31.9 %	99.5 %
<i>Phthalates</i>								
DEP	2.39	-	394 (238)	-	286 (178)	8 (23)	27.4 %	97.9 %
DBP	4.61	-	597 (316)	23 (16)	448 (215)	19 (15)	24.9 %	96.8 %
DEHP	7.54	19 (22)	284 (153)	76 (74)	247 (96)	12 (8)	13.0 %	95.7 %

Remark: average (SD) value, No. of sample = 56

* MLSS of Eff. Anoxic = 857 mg/l (average value)

† SS of Influent = 217 mg/l (average value)

Table 4 Removal efficiencies of emerging contaminants in batch experiments

Compounds	anoxic condition*			aerobic condition*		
	Total	Adsorption	Biodegradation	Total	Adsorption	Biodegradation
<i>Phenols</i>						
BPA	1,929 (107) [†] 64.3 %	2,394 (78) [†] 20.2 %	44.1%	60 (45) [†] 98.0 %	2,451 (98) [†] 18.3 %	79.7%
2,6 DTBP	1,746 (87) 58.2 %	2,208 (89) 26.4 %	31.8%	97 (36) 96.8 %	2,166 (91) 27.8 %	69.0%
BHT	1,731 (71) 57.7 %	2,133 (102) 28.9 %	28.8%	117 (21) 96.1 %	2,049 (102) 31.7 %	64.4%
<i>Phthalates</i>						
DEP	1,929 (94) 64.3 %	2,583 (69) 13.9 %	50.4%	108 (39) 96.4 %	2,559 (56) 14.7 %	81.7%
DBP	2,139 (115) 71.3 %	2,196 (98) 26.8 %	44.5%	108 (52) 96.4 %	2,253 (78) 24.9 %	71.5%
DEHP	1,947 (68) 64.9 %	1,494 (114) 49.8 %	15.1%	48 (43) 98.4 %	1,407 (76) 53.1 %	45.3 %

* Average from triplicate experiments and initial concentration at 3,000 µg/l.

[†] Final concentration (SD) value at 24 h.

Table 5 Reaction kinetic constants for adsorption and total (adsorption & biodegradation) removals of emerging contaminants

Compounds	Adsorption						Total removal	
	Pseudo first order			Pseudo second order			First order	
	q_e	k_1	R^2	q_e	k_2	R^2	k_t	R^2
<i>Phenols</i>								
BPA	32	0.026	0.766	32	0.032	0.999	0.194	0.902
2,6 DTBP	90	0.069	0.864	90	0.079	0.999	0.165	0.899
BHT	177	0.093	0.808	177	0.101	0.998	0.169	0.905
<i>Phthalates</i>								
DEP	36	0.037	0.801	36	0.030	0.999	0.163	0.869
DBP	160	0.076	0.902	160	0.081	0.999	0.173	0.928
DEHP	341	0.093	0.890	341	0.145	0.987	0.163	0.909

Remark : Average from triplicate experiments

Figure 1 Schematic of two-stage MBR

Figure 2 Variation of influent and effluent concentrations of emerging contaminants (a) BPA, (b) 2,6 DTBP, (c) BHT, (d) DEP, (e) DBP and (f) DEHP

(a)

(b)

(c)

(d)

(e)

(f)

Figure 3 Removals of emerging contaminants (a) BPA, (b) 2,6 DTBP, (c) BHT, (d) DEP, (e) DBP and (f) DEHP by aerobic sludge from MBR

Figure 4 Kinetic plots of (a) pseudo-first-order and (b) pseudo-second-order for adsorption and (c) first order for total (adsorption & biodegradation) removals of emerging contaminants

Abstract

Removals of bisphenol A (BPA), 2,6-di-tert-butylphenol (2,6-DTBP), 2,6-di-tert-butyl-4-methylphenol (BHT), di-ethyl phthalate (DEP), di-butyl phthalate (DBP) and bis (2-ethylhexyl) phthalate (DEHP) were monitored in two-stage membrane bioreactor (MBR) by operating under no sludge wastage condition for 500 days. Those emerging contaminants were removed by 99.5%, 99.0%, 99.5%, 97.9%, 96.8% and 95.7% under long term operation in MBR without reaching maximum adsorption capacity of sludge. Biodegradation was the main mechanism for their removals in MBR systems and the microbial activities were enhanced by long sludge age operating condition. The removals of those compounds by microbial sludge in MBR by adsorption and combined (adsorption & biodegradation) mechanisms were well explained by pseudo-second order and first order kinetics respectively.