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Anaerobic Removals of Polybrominated Diphenylether (PBDE), Hexabromocyclododecane (HBCD) and Tetrabromobisphenol A (TBBPA) in Hospital Wastewaters

Sponza DT* **and Guney G**

Department of Environmental Engineering, Dokuz Eylul University, Buca-Izmir, Turkey

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2. Keywords

Brominated flame retardants (BFRs); Polybrominated diphenylether (PBDE); Hexabromocyclododecane (HBCD); Tetrabromobisphenol A (TBBPA); Anaerobic UASB

1. Abstract

The this study, the anaerobic degradation and sorption of 3 polybrominated micropollutants (polybrominated diphenylethers (PBDE), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) was studied in UASB reactor at increasing SRTs. The optimum SRT for maxi-mum total removals of TBBPA, HBCD and PBDE were 93%, 96% and 97% at a SRT of 35 days at 37$_o$C. It was found that TBBPA was mainly removed via sorption to sludge (67%) while removal with biodegradation is low(26%) at a SRT of 35 days. It was found that The removals of HBCD was mainly biodegradation (60%) while PBDE was partly removed via biodegradation (50%) and sorption at a SRT of 35 days.

3. Introduction

A numerous brominated flame retardants (BFRs) have been pro-duced and they are incorporated as additives such as, electronics, polyurethane foams, and textiles etc. [1]. Three main groups of BFRs, namely polybrominated diphenylethers (PBDE), hexabro-mocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) are considered conventional" flame retardants, Their presence in the surface waters and[2], their biodegradation [3,4], and their toxicological properties[5-8] was detected. The problem relevant with their biodegradation in the ecosystem is associated with their aromatic moiety[2]. The problem is very serious in the pres-ence of bromine atoms, and this limit their microbial transforma-tions. HBCD is not readily biodegradable under aerobic condi-tions; the expected time of aerobic primary degradation is in the order of months. Some researhcher found that the bromines are degraded with anaerobic de halogenation like hexachlorobenzene (Field and Sierra-Alvarez, 2008). However, reductive dehalogena-tion where halogens acted as terminal acceptors of electrons has not been documented. Limited information is available about the fate of these new flame retardants under anaerobic conditions[3].

In Turkey the hospital wastewater are were not pre-or not fully treated with conventional and advanced treted treated processes and their dıscharge are directly given to the channel system. In the characterization of the hospital wastewaters it was found that among these NBFR, PBDE, HBCD and TBBPA were detected. The source of these NBFR in hospital wastewaters originated from the fire retardants utilized and from the polystyrene foams, from the waste electrical equipment, in the reparation of the hos-pital building and from the cleaning of polyethylene packaging, containers, bottles and buckets, from the waste polypropylene resin used in the cleaning of surfaces as reported by [9].

Therefore, in this study it was aimed to remove the PBDE, HBCD and TBBPA under anaerobic conditions at different sludge ages and to detect the removal mechanisms of these NBFRs[4].

4. Material and Methods

1.1. Analytical Procedure

The targeted compounds were two PBDE congeners (BDE-28,47), TBBPA and HBCD were used as internal standards.The samples were measured on Soxhlet extraction, then the elimination of

***Corresponding Author (s):** *Delia Teresa Sponza,Department of Environmental Engineering, Dokuz Eylul University, Turkey, E-mail: delya.sponza@deu.edu.tr and gokce.pehli-vaner@deu.edu.tr*

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lipids were performed with the sulfuric acid. The recoveries of PBDE, HBCD and TBBPA were 69%, 68% and 85%, respectively. PBDEs were analyzed on a GC–MS. The TBBPA and HBCD iso-mers were determined by an HPLC-MS/MS. LOD values were (signal-to-noise ratio is 3,2), in the range of 0.01-2,3 µg/L and 0,01-2,3 µg/L [5].

4.2. Reactor Configuration and Operational Conditions

3 upflow anaerobic UASB reactos with a volume of 5 liter was used and they were filled with raw hospital wastewater at 37°C. UASB reactor was inoculated with 30g/L MLVSS of anaerobic sludge taken from the Pakmaya Yeast industry anaerobic reactor Two pumps were used to feed the UASB and to recirculate the liquid phase to the UASB. The sludge age (SRT) was adjusted to 5 days, 35 days, and 55 days by wasting of the certain amount of sludge. Biogas samples were collected to determine the methane percentages. Volatile fatty acids (VFA) and pH were monitored 4 days in a weak.The UASB reactor was operated during 95 days, in order to test the effects of SRT on studied 3 PHBr yields. The re-moval mechanism with adsorption and biodegradation in UASB were evaluated for PBDE, HBCD and TBBPA[6].

4.3. Sorption Analysis

Harvested biomass samples were washed and re-suspended in distilled water for sorption experiments.The anaerobic and aero-bic sludges were inactivated in an autoclave at 121°C for 15 min-utes under a pressure of 1.5 atm. The autoclaved sludge were inoc-ulated on the glass plates containing suitable media and incubated to determine whether they were alive. It was found that all the sludge samples were death. Control and 2L reactors containing 1 L of raw wastewater were seeded with autoclaved anaerobic and aerobic biomasses. The anaerobic biomass had 14.40, 19.12, 20.52 and 27.60 gr VSS L-1 at 5, 30, 45 and 55 days of SRTs, respectively. They were incubated for two days at an ambient temperature. The anaerobic reactors were sealed with teflon lined caps and shaken at 21°C for 3 days. The control bottles contained no wastewater. The micropollutant concentrations in the samples taken from the test reactors were measured periodically and compared with a control[7,8]. After three days, the glass bottles containing sample and bacteria were centrifuged sufficiently to remove the bacte-ria, the supernatant was harvested and the micropollutants in the supernatant were analyzed. The glass bottles containing control without biomass were compared to glass bottles with biomass to determine the amount of micropollutants sorbed (Sponza and Gok,2010)[1]. The samples prepared from the supernatants of the anaerobic reactors were extracted according to the appropriate solid-phase extraction (SPE) method and then, they were mea-sured in LC-MS/MS.

4.4. Biodegradation Analysis

Micropollutant measurements were carried out in100ml samples removed from the supernatants of the anaerobic reactors to de-tect the micropollutant removal efficiencies.The biodegradation removal efficiency was determined according to the following equation: Biodegradation remova lefficiency(%)=

Cinf-CeffCeff×100

Where; Cinf represents the influent micropollutant concentra-tion in the supernatant of the biological reactor inµgL-1and Ceff represents the effluent micropollutant concentration in the su-pernatant of the biological reactor in µg/L.The samples prepared from the supernatants of the anaerobic reactors were extracted according to the appropriate solid-phaseextraction(SPE)method and then,they weremeasured LC-MS/MS[9,10].

4.5. Source of Hospital Wastewater

The raw hospital wastewater was taken from a full hospital lo-cated near İzmir in Aegean region of Turkey.

5. Results and Discussion

The results of this study showed that in the fist 10 days accli-mation period low HBCD and TBBPA and PBDE removals was obtained at a 5 days SRT (Tables 1,2,3). As the sludge age was in-creased from 5 days to 35 days the yields of all studied parameters increased. At this sludge age all the anaerobic microorganisms are in good contact with the micropollutants and the anaerobic bacteria have enough time to uptake and to metabolise these pollutants. At high SRTs long contact time can be cause toxicity the anaerobic microorganisms. Furhermore, with endogen res-piration process some of anaerobic bacteria can be cause to their death[11]. The most biodegradable brominated pollutant was found to be HCBD (60%) while the less biodegradable pollutant was found to be TBBPA (26%) at a SRT of 35 days(Table 1). The maximum HBCD, PBDE and TBBPA removal efficiencies in the effluent of the UASB were 96%, 97% and 93%, respectively. It was found that TBBPA was mainly removed via adsorption (67%) to the sludge performed by anaerobic bacteria at 35 days SRT. A part of PBDE also was removed via adsorption to the sludge (47%) at the same SRT. The biological biodegradation removals in TBBPA is low (26%) compared to HBCD (60%) and PBDE (50%) since TBBPA have high octanol–water coefficient, ther-fore adsorption was significant compared to biodegradation. In the UASB reactor, HBCD and TBBPA concentrations inside the anaerobic sludge were high (Tables 1,2). This can be explained by the sorption of HBCD and TBBPA inside biomass granules, since adsorption onto the granule surface is followed by an intra-molecular diffusion inside the granule [12]. Additionally, the enhancement in sorption might be explained by the increasing of the aforementioned brominated pollutants to the granular size during the continuos operation of UASB and, under these condi-tions, the specific surface of sludge increased and more bromi-nated pollutant were sorbed. Therefore, the solid–liquid equilib-rium was achieved and a constant sorption coefficient Kd was be considered due to the high variability of the values determined under anaerobic conditions.The high adsorption efficiencies in TBBPAcouldbe attributed tohigh log K_{oc} (5.07, PCKoc WIN) with low aqueous water solubility (2.1-49 μg/L) and has a high adsorp-tive properties (Log K_{ow} 7.74 unitless. HBCD has slightly higher solubility and high octanol–water partition coefficients (4.13) than TBBPA. Therefore sligtly lower adsorption yields was ob-tained. The maximum Although HBCD has high bioaccumula-tion potential compared to PBDE the maximum biodegradation yield was obtained in the UASB containing this polybrominated compounds(Table 3). Although PBDE has high bioaccumulation potential due to their relative high log octanol/water partition coefficient ($K_{ow=}$6.44) and low water solubility (2.089 × 10^{-5}g/l) and high Log K_{ow} (7.74 unitless) it was found that this pollutant was effectively biodegraded (50%) in the wastewater of the UASB. These can be attributed to the pH, to the temperature to the ionic strength and to the operational conditions of the UASB reactor.

The mechanism of anaerobic biodegradation is the metylation of polybrominated compounds studies in this study. Thefully de-brominated diphenyl ether or to bromophenols contributed of structural analogues, particularly of MeO and MeO-BDEs. Bac-terial metabolic methylation was probabily detected in UASB as reported by (Bendig and Vetter 2013)[12]. The elongated C–Br bond, which occurs at the α position of the anionic congeners, is directly involved in the debromination of n-bromodiphenyl to (n−1)-bromodiphenyl ethers in the reductive debromination ex-periments (Bendig and Vetter, 2013)[12].

As shown in (Tables 1,2 and 3) the methane percenges increased as the SRT was increased from 5 days to 35 days. The VFA accu-mulation is high a 5 days SRT while decreased sharply at 35 days HRTs due to increasing activity of metanogenic Archae bacteria.

Tabke 1: TBBPA removal in anaerobic sludge and in wastewater in UASB

Pe-riod (days)	SRT (day)	TBBPA İnfluent(μ-g/L)	TBBPA effluent(μ-g/L)	TBBPA in sludge (μg/g)	% Bio-degra-dation	% Ad-sorp-tion	Total Re-mo-val (%)	VFA (mg/l)	CH4 (%)
0-10	5	0,98	0,34	0,09	26	32	58	900	20
10-35	5	0,98	0,27	0,36	23	40	53	880	20
36-56	35	0,98	0,05	0,58	26	67	93	210	56
57-87	55	0,98	0,27	0,34	18	60	78	500	45

Tabke 2: HBCD removal in anaerobic sludge and in wastewater in UASB

Period (days)	SRT (day)	HBCD İnflu-ent(μ-g/L)	HBCD efflu-ent(μ-g/L)	HBCD in sludge (μg/g)	% Bio-degra-dation	% Ad-sorpti-on	Total Removal (%)	VFA (mg/l)	CH4 (%)
0-10	5	1,45	0,67	0,04	35	20	55	900	18
10-35	5	1,45	0,27	0,24	40	30	70	890	19
36-56	35	1,45	0,02	0,42	60	36	96	340	49
57-87	55	1,45	0,35	0,32	23	40	63	440	40

Tabke 3: PBDE removal in anaerobic sludge and in wastewater in UASB

Period (days)	SRT (day)	PBDE İnflu-ent(μ-g/L)	PBDE efflu-ent(μ-g/L)	PBDE in sludge (μg/g)	% Biodeg-radation	% Ad-sorption	Total Re-mo-val (%)	VFA (mg/l)	CH4 (%)
0-10	5	1,89	0,87	0,04	30	20	50	789	20
10-35	5	1,89	0,37	0,24	36	30	66	700	20
36-56	35	1,89	0,05	0,42	50	47	97	260	60
57-87	55	1,89	0,55	0,32	25	40	75	400	45

6. Conclusions

In this study, 3 polybrominated micropollutant with low solubil-ity and high octanol–water coefficientS present in hospital waste-waters were effectively removed with high yields in an anaerobic UASB treactor via biodegradation and sorption. The optimum SRT for maximum removals of polybrominated compounds was found to be 35 days. TBBPA was mainly removed with sorption to the anaerobic sludge(67%) while HBCD was mainly removed vith biodegradation (60%) at a SRT of 35 days. HBCD partly re-moved with biodegradation (50%) and partly via sorption at a SRT of 35 days in UASB.

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