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ARE AVAILABLE SAFETY METHODS FOR DEGRADATION OF HAZARDOUS POLY-HALOGENATED WASTES (CONTAINING PBDEs, PCBs)?

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Summary

Polybrominated diphenyl ethers (PBDEs) are a new class of global and toxic contaminants. A group of brominated fire retardants called PBDEs have come to the attention of scientists because of evidence of their environmental persistence and bioaccumulation in living organisms, as well as their potential toxic effects. Brominated fire retardants are found in everyday consumer products: plastics, textiles, polyurethane foam, rubber, paints. It is known, that PBDEs are found in surface and waste waters and that some part of PBDEs will end up in the municipal water sludge. The general population is targeted by the PBDEs due to their application and via the food web. A review of the use, occurrence and physico-chemical characteristics and chemical behavior of PBDE indicates many parallels between some PBDEs, PCB (polychlorinated biphenyls) and another poly-halogenated persistent organic pollutants. However, in contrast to PBDEs, PCBs were used primarily in electrical transformers and capacitors that were external to the home environment. PBDEs, in contrast, are applied to products found in almost every home. The decontamination of PBDEs may be a significant environmental challenge in the future. However, possible degradation pathways of both PBDEs and PCBs are the formation of much more toxic intermediates like dioxins and furans. At present there are no widely accepted environmentally friendly and safety methods for remediation of wastes contaminated with PBDEs and the knowledge of their degradation kinetic is rather limited.

The paper deal with the development and application of the technologies for the decontamination of solid and aqueous wastes polluted by mentioned compounds. One method can be considered as fundamental and safety for solving the problem at real conditions, namely the reductive degradation of organic polyhalogented substances on catalyst with Pd deposited on different supports at the presence of zero-valent Fe.

To test the efficiency of the selected decontamination methods simulated and real water samples contaminated with both PBDEs (the congener No.209 containing 10 bromine atoms in the PBDE, concentrations in micrograms/L) and PCBs (Czech commercial product DELOR 103 which is a mixture with prevailing content of tri-(64.0%) and tetra-(24.1%) chlorinated congeners, concentrations in milligrams/L) were chosen and treated at laboratory conditions. The results presented made evidence of the feasibility of the method. The principal reaction intermediates were identified and the formation of dioxins and/or furans was not detected. The weak point of the method is a tendency to gradual blocking of catalyst with reaction products, mainly at the higher concentrations of PCBs in samples of water (adhesion of the dechlorinated biphenyl to the surface of the catalyst).

Keywords: polybrominated diphenyl ethers, polychlorinated biphenyls, methods of degradation, reductive dehalogenation, palladized zero-valent iron, safety

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1. Introduction

Chemical fire retardants have become ubiquitous in highly flammable synthetic materials in consumer products. There are many different kinds of fire retardants with varying degrees of toxicity. A group of brominated fire retardants (BFR) called polybrominated diphenyl ethers, or PBDEs, have come to the attention of scientists because of evidence of their environmental persistence and bioaccumulation in living organisms, as well as their toxic effects. PBDEs are in thousands of products, in which they typically comprise to 30 percent of product weight. During manufacturing, PBDEs are simply mixed into the plastic or foam product, without being chemically bound to the material, making them more likely to leach out into the human environment.

Brominated fire retardants are found in everyday consumer products all over the world: plastics (DecaBDE, OctaPDE, PentaBDE), textiles (DecaPDE,PentaBDE), polyurethane foam (PentaBDE), rubber (DecaBDE,PentaBDE), paints and lacquers (DecaBDE,PentaBDE). Contamination of flame retardants is one of the most important factors that affect the recyclability of polymers.

Recent evidence suggest PBDEs and PCBs may work together to cause adverse health effects (1,2,3,6). The use of these BFRs increased in the last three decades. DecaBDE is the most widely used of the PBDEs with 83 percent of the global market by weight, followed by PentaBDE with 11 percent and OctaBDE with 6 percent (4,5,6). Today, half of the PBDEs used worldwide are used in the Americas (36 000 tonnes in 2001- Deca, Penta, Octa). The European market is a little more than 9 000 tonnes (2001). Another sources (7) estimated the annual worldwide market demand for Penta-,Octa-,and DecaBDE technical products in 2001 was 7500,3790,56 100 metric tons (brominated PBDE technical products such as Bromkal, 70-5DE, DE-71 and FR-1205 contain primarily Tetra-,Penta-and some Hexa-BDE (8)). In Europe, the use of higher brominated PBDE technical products, particularly DecaBDE (BDE-209) has increased due to the discontinuation of PentaBDE and the impeding ban in the EU. DecaBDE products such as Saytex 102E, DE-83 and FR-1210 contain primarily BDE 209. Since the PBDE are used as additives, they can migrate from products and spread into the environment. The major PBDEs looked for and found in environment samples have been BDE 47, BDE 99 and BDE 100.

PBDEs have been found in sediments and sewage sludge, lower brominated BDEs have been found in a variety of different organisms and since the 1970s, environmental concentrations of Tetra-to HexaBDE have been increased including in human mother milk. The lower brominated BDEs have been found to bioaccumulate in both aquatic and terrestrial ecosystems. DecaBDE is usually incorporated into high-impact polystyrene that is commonly found in the casing of TV sets and computers.

Higher BDE have been shown to affect liver enzyme activity, negatively influence the regulation of the thyroid system. Induce immunotoxicity and affect neurological development at a sensitive period of brain growth. The predominance of BDE 47 may be due to its higher potential for bioaccumulation (the source has been PentaBDE).

In the last few years, it has become clear that PBDEs have joint PCBs (polychlorinated biphenyls) and dioxins on the list of persistent bioaccumulative chemicals contaminating people. These fire retardants are now found in house dust, sewage sludge, and the water and sediments of rivers and seas. They have been found in human breast milk, fat and blood. Brominated retardants have been even detected in animals far from areas in which they are used. Around the world the researchers have documented dramatic increase of PBDE in wildlife and humans. In spite of the fact that the concentration of PCBs in the human tissues have decreased in the last years, the concentration of PBDEs in the environment and in the breast milk exponentially increases. Research shows that the PBDEs containing 3,4, and 5 bromines are the most likely of the PBDEs to be absorbed and build up in the living organisms. PentaBDE is almost exclusively used in flexible polyurethane foam for home and office furniture, carpet padding and mattresses, as well as to automobile sets to meet the stringent standards for fire suppression. Foot is thought to be the major PBDE exposure route for Europeans (fish, chicken, other meat and fats), as well as inhalation and ingestion of PBDEs in the ambient environment.

The general population is targeted by the PBDEs due to their applications and via the food web. Occupational exposure occurs not only during direct handling of BFRs, but also during handling, repair and dismantling of flame retardants. The results clearly show that workers were exposed to PBDEs when handling PBDE containing products or goods. The serum PBDE levels in computer technicians were found to correlate to the estimated cumulative work hours with computers. Exceptionally high concentrations of BDE-209, almost up to 300 pmol/l lipid weight were observed in serum from rubber workers handling rubber compound that was flame retarded by BDE-209 (35). Few studies have measured the flame retardants PBDEs in the indoor environment. Concentrations of total PBDEs ranged from 780 ng/g dry mass to 30 100 ng/g (36). The present scientific knowledge of the potential health risks of these BFR still needs to be further developed.

During the 1990s, concern about the risks of brominated flame retardants, especially polybrominated diphenylethers, has increased. This concern has led the European to conduct risk assessment of the three major PBDE technical products. Based on the risk assessments of the pentabromo- and octabromodiphenyl ether products, the EU decided in February 2003 to ban these, with the ban going into effect in August 2004. The DecaBDE mixture was exempted from this ban; however, because it is photolytically and biologically (32) debrominated to lower molecular weight congeners.

BFR in the environment: Concentrations of PBDEs in water are expected to be low due to their low solubility in water. However, almost no studies of PBDEs concentrations were found.

The PBDE concentrations measured in effluent wastewater from one sewage plant in Denmark (9) are shown in a Table 1:

Table 1

The example of concentrations of PBDE in effluent wastewater from sewage plant

PBDE congener	17	28	47	49	66	85	99	100	153	154	183	209
Waste water, ng/l	0.02	0.02	0.42	0.02	0.02	0.05	0.25	0.06	0.05	0.02	1.0	1.4

Similar values (3 – 513 pg/l) are reported from the US (31).

The PBDEs are more strongly absorbed to sediments than are PCB and are therefore more likely to persistent in the environment compartment. Concentration of PBDE congeners in soil and sewage sludge reportedly closely agree with concentrations in commercial mixtures. There are not relevant data concerning the volume of PBDEs in the Czech environment at hand, however, probably the data reported in other European countries comparable as for industrial level and area could be taken as rough estimates for the Czech Republic as well. High concentrations of BDE-209 were detected in river sediment in Ireland (up to 1800 ng/g wet weight, a study of sediment cores in the Netherlands from two fresh water lakes revealed a time- dependent increase in the concentrations of PBDEs that correspond to the first appearance of technical PentaBDE (Bromkal 70-5DE-the agent also used in the Czech Republic) in the last 30 years and the appearance of technical DecaDBE about 20 years ago. In a study of river sediments in England, it was shown that levels of PBDEs were significantly higher downstream from plants where flame retardants are used. A recent study of sewage sludge in the United States revealed that the composition of PBDEs in the biosolids closely matched the commercial formulation (on dry weight basis, the samples contained 499-1049 g BDE-

47/kg,377-851 g BDE-99/kg and 70-134 g BDE -100/kg !). All of the sewage sludge biosolids were intended for land application as fertilizer. Another study reported that sewage sludge in Sweden contained 15 and 19 g/kg of TetraBDE and PentaBDe, respectively. Determination of BFR in sewage sludge in South-West Germany showed (10) a strong dependence of the concentration of PBDE on the properties of the sediments and the occurrence of substances like detergents and oils. In all samples of surface water (0.2-0.7ng/l), sediments (0.2-29.6 ug/kg), influents of liquid phase (0.5-0.7 ng/l), sludge (77.7 -338.4 ug/kg) and effluents (0.6 ng/l) which were analyzed PBDE were mainly represented by BDE-47,-99,-and -100.

The information concerning the dispersion of PBDE in the environment of Central and South Americas are lacking but, because of import of varied articles containing PBDE from US and European countries it is expected the presence of that contaminant in those countries of Americas as well. The contaminations of soils and waste and/or ground waters with PCBs in the US and Americas are principally caused by the penetration of commercial mixtures of the US products Aroclor into the environment.

More studies on the leaching of PBDE due to accumulation in soil and sediments are recommended and lack of information on leaching to the water table.

According to the estimate of the EU risk assessment the predominant source of PBDE release to waste water in EU is textile washing. However, there is no data on brominated flame retardants in waste water effluents from Czech industries. The discharge of BFR from plastic process industries to water was roughly assessed, the dates were not sufficient to make any calculation of the discharge of BFR. We estimate that in total about 200 tons /year of BFR were disposed of to solid waste incinerators. Analysis of the fate of other organic compounds during incineration show that trace amounts of these compounds will pass the combustion chamber and end up in residuals from the incinerators. These BFR passing the combustion chamber may act as precursors for formation of brominated dioxins and furans. The BFR disposed of landfills may in the long term be released to the landfills leachates. However, measurements of BFR in landfill leach have not been identified. Potential emission/disposal in Denmark in 1997 (which could be roughly comparable with the situation in the CR) indicates the release in tons:

Air (0.2-1.6), Water (0.005-0.07), Soil (0.03-0.3), Landfills (90-200), Incinerators (170-360).

Although the use of brominated flame retardants with protective clothing in the CR compared to other countries is limited, laundry of clothing with BFR is estimated to be one of the major sources of BFR to the waste water. Roofing foils containing BFR initially evaporated to the air are estimated to be other major source of BFR to waste water.

A wide range of man-made chemical designed for use in industry, consumer goods and emissions from the combustion of wastes are the main sources for pollution of soil. Within the water cycle, soils act as the key zone for storage, filtration and transport of water and associated pollutants. If the accumulation of pollutants exceeds the buffer capacity, than soils and sediments treated by direct pollution due to the disposal/use of sewage sludge, incineration sludge, compost and/or atmospheric deposition, can become a source of diffuse pollution releasing pollutants to adjacent compartments such as groundwater and surface water. There is a lack of adequate quantitative system understanding and pertinent models. For this reason indirect effects of large- scale pollution are difficult or even impossible to predict.

Emerging contaminants are suspected of causing adverse effects in humans and wildlife. For instance, PBDEs have been listed as priority hazardous pollutants in the field of water policy by EC Water Directive 2000/60/EC and the final EU decision No.2455/2001/EC.

State-of-the- art of the decontamination technologies:

Emerging techniques for a gentle remediation of already polluted agricultural soils, clean-up and site-stabilization schemes, are still not operational at the field scale. This is a great need for theoretical knowledge how water quality can be influenced to achieve the goals of pollution reduction and sustainable land-use and how respective policies can be implemented in practice.

Therefore, the philosophy of decontamination of water contaminated by emerging persistent organic pollutants including the hazardous PBDEs, at the points of their origin (waste water from plants using the flame retardants, waste waters from incineration plants, extracts from dumps, etc.,), as well as a treatment of an influent waste water to the sewage plant, seems useful for a reduction of contact of people with such a hazardous substances.

Methods of decontamination: The methods of decontamination of PBDE in liquid (aqueous) phase are almost lacking compared with decontamination of solid wastes.

Practically all flame retarded plastic from discarded products will ultimately be disposed off by incineration or land filed. The content of brominated flame retardants or elemental bromine in flue gas or residues from solid waste incinerators has not been currently measured in the Czech Republic.

High-temperature incineration and/or melting system have become a major focus as a destruction technology for bromine containing materials (11-13, 29).

Melting treatment was performed at more than approx.1500°C with coke-based gasification furnace (capacity 20 tons/day). In this system, the addition of small amounts of coke and limestone flux to the melting furnace makes it possible to directly melt waste, including incombustibles, at high temperatures. The waste gas is then discharged after rapid cooling and waste gas decomposition in a catalytic reactor followed. The study aims at obtaining fundamental knowledge concerning behavior of dioxin related compounds in the process of gasification of wastes including brominated flame retardants. Target material was waste TV casing which were supplied into melting with normal municipal solid waste.

The major concern is the formation of brominated dioxins and furans but also HBR, Br_2 and non aliphatic compounds emissions.

During ***pyrolysis*** of scrapped electronic circuit boards, it was reported by others that 72% of the bromine was released to the gas phase, mainly bromobenzene and HBr.

Previous research has indicated that the presence of bromine during the combustion of hazardous wastes increases the production of PBDD/Fs. It has also been established that brominated flame retardants are known processors of PBDD/Fs (30).

The capability of ***anaerobic microorganisms*** (14) associated with the marine sponge to transform haloaromatic compounds under different electron-accepting conditions (i.e. denitrifying, sulfidogenic and methanogenic) was tested. The abundance of halogenated compounds in sponge tissue and the bacterial biomass imply that sponge-associated microorganisms might have the ability to dehalogenate and degradate brominated compounds. However, more studies are needed to elucidate the role of degrading microorganisms involving also the tests of eco-toxicology (it is well known, that in the biodegradation pathways the origin of compounds even more toxic than original polyhalogenated compounds can be formed).

In comparison with chlorinated aromatic contaminants, research on the metabolism and environmental fate of PBDEs is limited. The metabolic pathways of PBDE include reductive debromination, hydroxylation and ether bond cleavage (3).

The ***aerobic and anaerobic biodegradation*** of PCBs with various types of microorganisms have been successfully accomplished in laboratory studies (22, 23), but the reaction require month and depend on the ability of the microorganisms to survive in systems containing the halogenated compounds. Analogous studies with PBDE are, however lacking for the present.

Some studies have demonstrated ***manganese oxide-mediated degradation*** (15, 33, 34) of halogenated organic pollutants occurs. In the Department of Earth and Atmosperic Sciences, School of Civil Engineering, Purdue University, IN, the potential reaction of PBDEs with manganese oxides in the environment was investigated. Decabromodiphenyl ether (BDE-209), the major PBDEs manufactured product, was added to tetrahydrofuran (THF) and water with birnessite (delta-MnO_2). The THF was used mainly to enhance salvation of BDE-209, such that if reaction did not occur under these "optimal" conditions, even very slow reaction in pure aqueous solution would be unlikely. In 60-90% THF in water, over 75% BDE-209 was degraded within 9 hrs (20 mg/ml birnessite). Release of Br^- into solution confirmed reductive debromination was occurring. Products with GC-ECD retention times similar to those of tetra-to octa-BDE were observed. Deuterated-water experiments indicated that THF was the hydrogen donor.

PBDEs belong to the group of organo-bromine compounds that absorb light in the UV- spectra. The energy supplied by UV-light often results in loss of bromine and thereby also a possibility for rearrangements. ***Photolytic degradation of organobromines*** is a well-known type of reaction (5). Studies on photolytic debromination of DecaBDE have been published previously by Norris et al (16) and Watanabe et al (17). Norris found that both DecaBDE and OctaBDE were degraded and identified PBDEs as degradation products down to hexaBDE. Watanabe also found that DecaBDE was debrominated to lower brominated BDE and also **that very toxic brominated dibenzofurans were formed.** Recently Eriksson et al (18) performed photodecomposition of DecaBDE. Soderstrom et al studied the course of photolysis of DecaBDE in toluene on silica gel, sand, sediment and soil using artificial and natural sunlight. DecaBDE formed debromination products in all matrices studied. After the maximum occurrence of hexaBDE, only minor amounts of lower brominated compounds are formed with a discontinued mass balance as a result. This indicates that that some unknown compounds lost in the sample cleanup are also formed. Possible degradation pathways is the formation of PBDFs (furans) as shown by Watanabe and Eriksson- the formation of PBDF was seen in some samples. With this knowledge, it is important to note that the toxicity of PBDD/Fs has been shown to be similar to the analogous PCDD/Fs (30).

At present there are no widely accepted methods for the remediation of water and aqueous sewage sludge contaminated with PBDE. It is important to develop potential remediation technologies for PBDEs. The same conclusion can be accepted in the case of PCBs as well.

Proposed "safe"method: Because halogenated hydrocarbons are in an oxidized state relative to their non-halogenated counterparts, a potential reaction pathway exists for degradation through reductive dehalogenation (21). Several kinds of elementary metals have been studied for remediation of highly oxidized organic pollutants such as polyhalogenated aromatic compounds end explosives. Zero-valent iron is one such metal and can reduce, PCBs, PCDDs and halogenated phenols (24-27). Among the halogenated contaminants, the current research with zero-valent iron is mainly focused on chlorinated alkanes/alkenes. Studies on contaminations with halogens are limited. In the recent study (28), degradation of PBDEs with zero-valent iron was investigated with six BDEs, substituted with one to 10 bromines. Within 40 days 92% of BDE-209 was transformed in lower congeners. No oxidation products were detected in all experiments. The results showed that a stepwise debromination from n-bromo to (n-1)-bromodiphenyl ethers was the dominant reaction in all congeners. The preferential accumulation of specific congeners was observed in the experiment, where the most abundant products were BDE-15, BDE-28, BDE-37 and BDE-47.

Recently we have shown that the rate of reductive dechlorination of technical mixture of PCBs (Czech commercial product DELOR 103, containing mostly the congeners with 3- and 4- chlorine atoms in a molecule of PCB) with zero-valent iron is low, but complete dechlorination of PCBs in a aqueous solution (containing traces of methanol) can be achieved in a few minutes by contacting the solution with a simple ***bimetallic system (Pd/Fe)*** at an ambient temperature. The dechlorination occurs rapidly on the surface of the bimetallic system: all the chlorine atoms are replaced by hydrogen atoms to yield biphenyl. We have confirmed the results of another authors (19) obtained with the aqueous solution of PCB (however, in the excess of co-solvent here). We do believe that this chemical method has also the potential to remediate soils and water contaminated with PBDE. Our preliminary results have confirmed this assumption (the initial concentration of BDE-209 decreased from the initial value 670 ug/l to the 5.9 ug/l in 3 hours). The present scientific knowledge of the potential remediation technologies still needs to be further developed. Debromination of PBDEs by zerovalent iron and/or zerovalent iron + Pd has high potential values for remediation of PBDEs in the environment. A review of the use, occurrence, and physico-chemical characteristics and chemical behavior of PBDE indicates many parallels between some PBDEs, PCBs and poly-halogenated organic pollutants, and suggests that the PBDEs may be a significant environmental challenge in the future. Our previous knowledge in the area of decontamination of polychlorinated organics (20) could be effectively exploited also in this direction. However, in contrast to PBDEs, PCBs were used primarily in electrical transformers and capacitors that were external to the home environment. PBDEs, in contrast, are applied to products found in almost every home in percentages as great as 30% by mass of the product to which they are applied (4). European Union risk assessment (37) on PBDE concluded recently that there is need for further information on the degradation of PBDEs. We addressed this information gap by studying the fate of PBDEs under chemical decontamination conditions.

2. Materials and Methods

Pd-carriers: a) Powdered carbonyl iron was supplied by SIGMA, min. 99.7%.Fe, particle sizes between 4.5 to 5.2 microns. b) Steel wool-extra fine 00, was obtained from LUX-Werkzeuge, Wermelskirchen, Germany. BET Surface area (krypton)I s 0.04 m^2/g, the principal components are 98.9% Fe and 1.1% Mn. Bulk density has been determined as 0.192 g/ cm^3

Chemical used: Chemicals were supplied by Aldrich: Palladium(II) chloride, 99.9+% $PdCl_2$; Hydrazine, anhydrous, 98%; Pentabromophenyl ether, 98%, $(C_6Br_5)_2O$, K_2PdCl_6 ,99%. PCB: Czech commercial product DELOR 103.

Pd/Fe: *Laboratory batch experiments:* The solution was added to Erlenmeyer flasks containing Pd/Fe, the flasks were capped and placed in a wrist-action shaker. The course of the reaction was followed by periodical withdrawing a 1-microL sample of the solution.

Preparation of catalysts: *Catalyst carriers a),b),* have been palladized in the following way:

13.5 volume parts of deionized water was mixed with 2.5 volume parts of the solution of $PdCl_2$ (concentration was 2.48 mol Pd/l) and subsequently with 0.92 wt.parts of KCl (molecular ratio Pd:K = 1:2), at a laboratory temperature. Subsequently, 0.057 of volume parts of the resulting suspension of K_2PdCl_4 was added to the 5 wt.parts in 10 volume parts of deionized water and was mixed for another 30 minutes. The resulting catalyst Pd/Fe was then washed with deionized water. Only fresh Pd/Fe catalyst was used for the dehalogenation reaction. Pd/Fe after separation from washing water was mixed with aqueous solution of PCBs or PBDE.

Palladized steel wool as a catalyst: in some experiments steel wool was acided in advance with HNO_3. After the reaction of steel wool with $PdCl_2$, the catalyst was reduced by hydrazine and rinsed with ethanol.

Analytical procedure: The principle of the method of determination of PCBs was published in (20). The analysis of the sum of seven indicative congeners applies to an European Standard ESN EN 61619, based on extraction with *n*-hexane and HRGC with ECD. Samples of PBDE were analyzed by GC/MS in the certified Laboratory of State Hygienic Sanitary Installation in Frydek/Mistek, CR (38), and in the Institute of Technical Chemistry, Prague (39).

3. Results

3.1. Decontamination of PCBs

The obtained conversions were high. For the inlet concentrations of PCBs 20,40, or 100 mg/l the final concentration after 30 minutes of the contact of aqueous solution with catalyst, the average concentrations of PCBs were (the average from 3 repeated measurements) from 4.5 to 10 mg/l respectively. PCBs were determined as a sum of 7 indicative congeners (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-180, where the numbers assigned to the individual congeners correspond to the well known IUPAC nomenclature) in a Czech commercial product DELOR 103 which is a mixture with prevailing content of tri-(64.0%) and tetra- (24.1%) chlorinated congeners.) Unlike in the previously published results [19], complete conversion has unfortunately not been achieved in our experiments. The biggest problem was the fouling of the catalyst with reaction product (biphenyl).We was not able to reproduce the data with the catalyst used. The frequent regeneration of the catalyst is inevitable. This chemical method has perhaps the potential to remediate water contaminated with PCBs at much more lower concentrations of PCBs.

3.2. Degradation of Decabromodiphenyl Ether (BDE 209) by Pd/Fe

Preliminary results clearly showed that catalytic degradation of DecaBDE occurs under the experimental conditions tested. The samples kept in the dark and the blanks were analyzed to establish that only Pd/Fe exposure affected the samples. Reproducibility was investigated by running the samples in triplicates. The average values of deca-BDE in the course of its contact with the catalyst are shown in Table 2. Perceivable increments of BDEs 28,100,99,154,153 and recognizable diminution of BDE 183 and 47 were acknowledged. These preliminary experiments show that catalytic debromination of BDE seems a possible pathway for the formation of more bioavailable, lower brominated BDEs, particularly in the combined system including a reaction layer of Pd-Fe with a subsequent bioreactor.

The examined samples of aqueous solution of decaBDE contained elevated concentrations of PBDE (a fact which is unlikely in waste water). The reason was to suppress the possible influence of concomitant phenomena typical in the case of very low concentrations of PBDEs, which could cause false interpretation of the rate of debromination reaction.

Table 2

Typical course of the rate of degradation of decaBDE (209) in water with palladized steel wool (the average from 3 independent measurements)

0.001g of decaBDE was dissolved in 20 ml of ethanol, 0.001g of decaBDE was dissolved in 20 ml of n-heptane, both solutions were mixed with 200 ml of de-ionized water. The initial amount of Pd in the steel wool was 0.05%, total mass of the catalyst was 1.3427 g.

The temperature was 20°C, samples in Erlenmeyer flasks were shaken with the intensity 2 s^{-1}. Concentrations of decaBDE are in micrograms/l.

Time,h	0	1	2	3	4	5
decaBDE,ug/l	670	82	15	5.9	6	6

4. Conclusions

The presented results document the feasibility of the application of the catalytic Pd/Fe method for destruction of poly-halogenated organic compounds, even though its efficiencies digger from those reported in the literature, particularly as to the conversion and reproducibility is concerned, as demonstrated with reused catalysts. First exploratory experiments showed a surprisingly high ability of the degradation of PBDE 209 congener on the Pd/Fe system. During the degradation of both PCBs and PBDEs the formation of oxygenated hazardous intermediates was not detected. However, further studies of this method of decontamination of halogenated organic compounds in aqueous solutions are needed.

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