

2013-06-01

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Citación recomendada

Marulanda, Víctor F. and Valencia, Pady O. (2013) "Tecnologías catalíticas y supercríticas para la destrucción de desechos de bifenilos policlorados: una revisión," *Épsilon*: Iss. 20 , Article 5.

Disponibile en:

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Catalytic and Supercritical Technologies for the Destruction of Polychlorinated Biphenyls (PCBs) Wastes: A Review

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ABSTRACT

PCBs are one of the best known of the twelve compound classes defined as persistent organic pollutants (POP) by the Stockholm Convention and, therefore, actions are required to reduce the utilization of, and to eliminate, in an environmentally sound manner, all wastes contaminated with PCBs as soon as possible, but before 2028. An initial inventory of PCBs in Colombia, according to the guidelines of the Stockholm Convention, accounts for the existence of approximately 13,000 tons of PCBs wastes. However, there are no available state-of-the-art incineration facilities that can deal with PCBs in the region, and thus local PCBs wastes must be exported. Accordingly, this paper presents a critical, not necessarily exhaustive, review of catalytic and supercritical technologies for the destruction of PCB wastes. Data concerning the destruction of PCBs reported during the period 2000-2010 are evaluated in this review. The possibility of application of such technologies is assessed by taking into account the technical maturity of these processes as indicated by batch or continuous pilot scale runs and PCBs destruction efficiency. Although some other technologies, such as the radiolytic process and plasma arc, have also been used for PCB destruction, a lack of recent publications indicates a decreased interest in their industrial application and therefore these are not discussed in this review.

Keywords: PCBs, destruction, hydrodechlorination, SCWO, review.

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RECEPTION DATE: JUNE 23, 2012 • ACCEPTANCE DATE: APRIL 13, 2013

How to cite this article: Marulanda, V.F. & Valencia P.O. (2013). Catalytic and Supercritical Technologies for the Destruction of Polychlorinated Biphenyls (PCBs) Wastes: A Review. *Épsilon* (20), 83-99.

Tecnologías catalíticas y supercríticas para la destrucción de desechos de bifenilos policlorados: una revisión

RESUMEN

Los PCB son una de las clases de compuestos más conocidas, definidos como contaminantes orgánicos persistentes (COP) por la Convención de Estocolmo, lo que también requiere acciones para reducir el uso de, y para eliminar, de una manera ambientalmente racional, los desechos contaminados con PCB, tan pronto como sea posible, pero antes del 2028. Un inventario inicial de los PCB en Colombia, conforme a los lineamientos de la Convención de Estocolmo, explica la existencia de cerca de 13.000 toneladas de residuos de PCB. Sin embargo, no existen instalaciones de incineración de tecnología de punta capaces de tratar los PCB en la región, de tal modo que los residuos locales de estos contaminantes deben ser exportados. Este artículo presenta una revisión crítica, no necesariamente exhaustiva, de las tecnologías catalíticas y supercríticas para la destrucción de residuos de PCB. En esta revisión se evalúan los datos relativos a la destrucción de los PCB reportados durante el periodo 2000-2010. Se evalúa la posibilidad de aplicar dichas tecnologías teniendo en cuenta la madurez técnica de estos procesos, según lo indicado por la realización de pruebas por lotes o continuas a escala piloto y la eficiencia de destrucción de PCB. Aunque algunas otras tecnologías, tales como el proceso radiolítico y el arco de plasma, también han sido utilizados para la destrucción de PCB, la falta de publicaciones recientes indica una disminución del interés en su aplicación industrial, de tal modo que no son discutidos en esta reseña.

Palabras clave: PCB, destrucción, hidrodcloración, OASC, reseña.

Tecnologias catalíticas e supercríticas para a destruição de resíduos de bifenilas policloradas: uma revisão

RESUMO

Os PCB são um dos tipos de compostos mais conhecidos, definidos pela Convenção de Estocolmo como contaminantes orgânicos persistentes (COP) fato que também requer ações com o objetivo de reduzir o uso de, e para eliminar, de uma maneira ambientalmente racional, os resíduos contaminados com PCB, o mais brevemente possível, mas antes de 2028. Um inventário inicial dos PCB na Colômbia, de acordo com os alinhamentos da Convenção de Estocolmo, explica a existência de aproximadamente 13.000 toneladas de resíduos de PCB. Porém, não existem instalações de incineração de tecnologia de ponta capazes de tratar os PCB na região, de tal modo que os resíduos locais de PCB devem ser exportados. Por conseguinte, este artigo apresenta uma revisão crítica, não necessariamente exhaustiva, das tecnologias catalíticas e supercríticas para a destruição de resíduos de PCB. Nesta revisão avaliam-se os dados relativos à destruição de los PCB reportados durante o período de 2000-2010. Avalia-se a possibilidade de aplicar estas tecnologias, levando em consideração a maturidade técnica destes processos, de acordo com o indicado pela realização de provas por lotes ou continuas à escala piloto e a eficiência de destruição de PCB. Ainda que algumas outras tecnologias, tais como o processo radiolítico e o arco de plasma, também têm sido utilizadas para a destruição de PCB, a falta de publicações recentes indica uma diminuição do interesse em sua aplicação industrial, de tal modo que não são discutidos nesta resenha.

Palavras chave: PCB, destruição, hidrodcloração, OASC, resenha.

Introduction

There is a growing concern, as reflected from governmental and nongovernmental organizations and from the scientific community research efforts, that stockpiles of obsolete chemicals and POP-contaminated wastes must be rapidly identified, properly collected and properly destroyed, in order to minimize their environmental impact. Combustion technologies, which have historically been used to attempt the destruction of POP stockpiles and POP-contaminated materials, may fail to meet the stringent environmental conditions progressively being set in the last decade. Indeed, combustion technologies themselves are identified as major sources from which POPs and other hazardous substances are released into the environment (UNEP, 2002; Rahuman et al., 2000). Nonetheless, incineration continues to be the only commercial scale process to treat POPs such as PCBs in an efficient way. State-of-the-art incinerators, capable of treating PCB wastes in an efficient way, are not available in South American countries, and therefore PCB wastes must be delivered to incineration plants overseas at prohibitively high costs for the industrial sector. The lack of appropriate destruction technologies for handling PCBs wastes is, without a doubt, a serious difficulty and a national concern due to the existence of international treaties that have set datelines for safe destruction of PCBs (MMAVDT, 2007). During the last decade, intense research efforts have been conducted on the development of a process alternative to incineration to effectively destroy PCB wastes; this paper reviews recent experimental findings in the catalytic dechlorination and supercritical water oxidation of PCB wastes, which are the process alternatives that have received the most attention. Biodegradation studies with oxic and anoxic bacteria have also been conducted with relative success and recent findings are widely summarized in literature (Ang et al., 2005; Furukawa & Fujijara, 2008).

Polychlorinated Biphenyls

PCBs are aromatic compounds consisting of two benzene rings linked by a carbon-carbon bond. Chlorine atoms are substituted on any or all of the ten remaining available sites. The number and position of these chlorine atoms determine the properties of the different molecules. According to the number and position of the substitutions, there are 209 possible configurations or PCB congeners. PCBs are either oily viscous liquids or solids and are colorless to light yellow, with a mild

smell to hydrocarbons (Erickson, 1992). These compounds are among the most stable and resistant to thermal, chemical and biological degradation. Due to their excellent insulation properties, low dielectric constant and high boiling point, PCBs were widely used in electrical equipment, such as transformers and condensers, heat exchangers, hydraulic systems and in paints and plastic manufacture. The commercial use of PCBs was banned by the end of the seventies by the USEPA (1979). These chemicals were never manufactured in South America, and current PCB stockpiles correspond to electrical equipment and oily wastes imported from several countries. An initial inventory of PCBs in Colombia, according to the guidelines of the Stockholm Convention, accounts for the existence of approximately 13,000 tons of PCB wastes. Similar figures are reported for other South American countries with similar degree of economic development (MMAVDT, 2007).

PCBs are bioaccumulated in the food chain and are easily absorbed in the gastrointestinal tract and fatty tissue. In pregnant women, PCBs can get through the placenta and are also excreted in breast milk, with the corresponding accumulation in the fetus (WHO, 2003). Recent assessments in Europe on PCBs concentrations in foods, particularly salmon, butter and cabbage, found that the daily intake of PCBs in several European countries is higher than the admissible according to international standards (Zuccato et al., 2008). Research conducted on humans exposed to PCBs found sperm motility and fetus development to be affected. Studies also suggested that PCBs exposure is directly related to liver cancer and malignant melanoma (PNUMA, 2005).

Technologies for the Destruction of Polychlorinated Biphenyls

The technology that has been used historically to carry out the destruction of POP stockpiles is combustion in either incinerators or modified cement kilns in the temperature range of 870 to 1200 °C (Brunner, 1993). Although some incinerators and cement kilns carry out the PCBs destruction efficiently (Karstensen, 2008; Karstensen et al., 2010), recent evidence suggests that incineration is responsible for the dispersion of unwanted, incomplete combustion byproducts, such as dioxins (PCDDs) and furans (PCDFs). This evidence has created a strong public resentment of this technology (Greenpeace, 1998). Nevertheless, incinerators and high temperature cement kilns have been used to treat organic hazardous wastes in

developed countries for decades and have shown to constitute an environmental sound option (Karstensen, 2008; Karstensen et al., 2010). Unfortunately, no cement factory in Colombia currently processes PCB containing wastes, because the existing facilities are located in very populated areas and such activity would face a strong public opposition, besides requiring a comprehensive infrastructure for waste management and PCDD/PCDF monitoring, which is not available at this moment.

Catalytic Dechlorination

Catalytic dechlorination is a process used to remove chlorine from PCBs by hydrogen or a reducing radical containing a hydrogen donor. Some of the first studies on catalytic dechlorination of PCBs were carried out by Liu et al. (1995), who accomplished the complete reductive dechlorination of pure Aroclor 1248 in 24 h by a titanium catalyst (Cp_2TiCl_2) and sodium borohydrate (NaBH_4), and Grittini et al. (1995), who studied the rapid dechlorination of a methanol water solution containing Aroclor 1260 and 1254 with a paladized iron catalyst and hydrogen generated in the oxidation of the catalyst. De Filippis et al. (1999) applied the KPEG process, which uses potassium hydroxide as a reducing agent in a mixture of polyethylene glycol (PEG) and dimethylsulfoxide, to treat dielectric oils contaminated with PCBs. 1015 mg/L PCBs were degraded in a reaction time between 2.5 to 5 h, at temperatures in the range of 80 to 125 °C. Although this process is safe, effective and tolerant of water and other contaminants, it requires a large excess of KOH, generates toxic byproducts and according to the results it is not very effective to degrade the less chlorinated PCBs.

Murena et al. (2000) conducted the catalytic hydrodechlorination of a commercial oil contaminated with PCBs with a sulfided Ni-Mo catalyst in a batch reactor pressurized with hydrogen at 50 bar. At 350 °C and 200 min reaction time a complete hydrodechlorination with biphenyl and hydrochloric acid was achieved as reaction products. Wu et al. (2005) treated transformer oil containing PCBs with nanometric sodium hydride (nano-NaH) and transition metal catalyst under mild conditions. Whereas a 89.8% removal efficiency in 8 hours was obtained with the use of nano-NaH, the addition of transition metal catalysts increased the removal efficiency to 99.9%. This method is suitable for contaminated transformer oils because the oil can be reused and because it avoids using plenty of organic solvents.

However, it requires long reaction times and the recovery of the nanometric size catalyst could be difficult to accomplish.

Mitoma et al. (2006) studied the Calcium promoted degradation of coplanar PCBs in 24 h through a simple stirring operation using metallic calcium, which acts as a scavenger and a reducing agent, and Rh/C catalyst in an alcohol solution in a sealed tube at 25 °C. This method achieved highly efficient and safe dechlorination of co-PCBs with a simpler operation that obviates dangerous treatments under bubbling hydrogen. Agarwal et al. (2007) conducted the dechlorination of PCBs by using bimetallic systems wherein enhanced corrosion of a reactive metal is combined with catalytic hydrogenation properties of a noble metal. These authors studied the bimetallic system Pd/Mg for dechlorinating 2 chlorobiphenyl solutions in water. Reaction times longer than 100 min were required for a complete dechlorination reaction. Noma et al. (2007) applied the sodium dispersion (SD) method to degrade nine PCB congeners and obtain detailed information about the decomposition mechanism and investigated the structures and the final degradation products of PCBs at high temperature. The SD method's main drawback is that it requires dispersing micrometric metallic sodium ($< 10 \mu\text{m}$) under N_2 atmosphere in a high excess, 11 Na/Cl and a completely water free PCB waste in order to prevent violent reactions of metallic sodium with water.

Catalytic reduction methods require organic solvents and high temperatures, which generate organic wastes, and the major product is the toxic biphenyl. To overcome these drawbacks, Liao et al. (2007) used the green solvent supercritical carbon dioxide (SF-CO_2) to replace organic solvents required for hydrodechlorination of PCBs, with hydrogen gas as a reducing agent and catalyzed by Pd nanoparticles stabilized in the polymer HDPE. SF-CO_2 has a high miscibility with hydrogen gas, which is a major advantage over traditional organic solvents that have low solubility and diffusivity for hydrogen gas. At 373 K and 100 atm, with a hydrogen partial pressure of 5 atm, around 90% PCBs were effectively converted to bicyclohexyl. The authors indicated that the catalyst did not suffer poisoning and that it could be reused several dozen times without losing activity.

Sajiki et al. (2002) found that PCBs could be thoroughly dechlorinated under ambient temperature and pressure with no other product than biphenyl by using a Pd/C catalyst activated by triethylamine. Complete degradation of a 10% PCB solution in methanol using 10% Pd/C was verified in 1 hour. In addition, all

reagents and solvents used are reusable and the reaction mixture only contains biphenyl and triethylammonium chloride. In a later study, Kume et al. (2008) found that this method was ineffective for PCBs congeners with chlorine atoms in the ortho-positions; however, they suggested that this limitation did not affect the performance of the process since these congeners are only slightly present in the commercial PCB mixtures. The delay of the reaction progress was attributed to a time dependently poisoning of the catalyst due to the exposure to HCl and Et₃N. HCl, which are formed during the dechlorination. When the catalyst weight was increased to 10% of the weight of Aroclor, PCBs were completely dechlorinated after 1 hour.

Rodríguez and Lafuente (2008) used the heterogeneous hydrazine hydrochloride/palladium (HZ/Pd) catalyst system at room temperature and ultrasonic radiation at 40 or 60 °C without ultrasonic assistance. The mixture of hydrazine hydrochloride and sodium carbonate gives the free hydrazine, which acts as hydrogen donor. Dechlorination of an industrial PCB mixture sample (2768 ppm), in mineral dielectric oil (100 g), was satisfactorily carried out with the sodium carbonate and the HZ/Pd system in a water bath at 60 °C. After 15 min by gas-chromatography analysis, the mineral oil showed < 25 ppm PCBs, and complete dechlorination happened after 30 min. The same experiment was carried out in a reactor with ultrasonic radiation at 487 kHz and room temperature. Complete destruction was observed after 15 min.

A recent variation of a typical catalytic reduction process is the mechanochemical dechlorination. In this process, grinding causes mechanochemical effects on solid catalytic particles, as well as being a simple operation to reduce particle size. One of the unique phenomena of this effect is the ability to dissociate the material by rupturing the bonds. Nah et al. (2008) examined the potential of mechanochemical method with fine metal powder aluminum, magnesium, iron and zinc, glycol and alkali for PCB removal from waste insulating oil. The assessed process parameters were chemicals and rate and time of milling. They found that polyethylene glycol was more effective as hydrogen donor and zinc was more effective than other metals for PCB removal. At these conditions, a maximum of 99.9% PCB removal (below 2 ppm) was achieved with the mechanochemical process for two hours, and it was concluded that the energy transferred by milling caused the nucleophilic substitution of Cl with H to occur.

In conclusion, the catalytic reduction methods are still at an early stage of development. In fact, most of the studies have been carried out in batch reactors with only a few efforts conducted on studies of a continuous process. As was previously mentioned, these methods always produce a byproduct, mostly biphenyl, which is also a concern from the environmental point of view. Due to the formation of hydrochloric acid, catalysts activity decays rapidly, which could not be very attractive for scaling-up purposes.

Supercritical Water Oxidation

Supercritical water oxidation (SCWO) appears as one of the most promising methods for the treatment of PCB wastes. This is a process carried out at temperatures and pressures above the critical point of water (647 K and 22.1 MPa). Under these conditions, organic compounds and oxygen are soluble and form a single fluid phase, so that fast oxidation reactions can be carried out without mass transfer limitations. This has been used to effectively destroy highly stable organic compounds in short residence times. Early work on SCWO of PCBs was carried out by Hatakeda et al. (1999), who studied the efficiencies of H_2O_2 and oxygen for the destruction of 3-chlorobiphenyl at temperatures in the range 473-723 K in a batch reactor. In a continuous system treating 3 PCB and a commercial PCB mixture at 673 K in the range of residence times 10.7 to 101.7 s, over 99% of PCBs was decomposed when an oxygen excess was used. Anitescu and Tavlari-des (2000) performed a global kinetic study of the destruction of Aroclor 1248, a mixture of around 76 PCB congeners at temperatures of 723, 748, 773 and 823 K. Experiments were conducted at a PCBs concentration of 5.75 E-5 mol/L , using a methanol solution and H_2O_2 as oxidant, providing 20 mol % excess of O_2 . Molar global conversions varied from 36.06% for residence time to 6.29 s at 723 K to 99.95% for 54.4 s at 823 K.

Methanol has been extensively used for delivering the water insoluble PCBs to the reaction system at supercritical conditions and a great deal of research has been conducted with this component (Vogel et al., 2005). For example, Anitescu and Tavlari-des (2002) assessed the role of methanol in the SCWO of PCB congener 3,3',4,4' tetrachlorobiphenyl, and obtained a 99.5% PCB conversion at 773 K and 20.7 s. An economic analysis of the supercritical fluid extraction-oxidation technology to remediate PCB-contaminated soils/sediments was carried out and the treatment costs were compared to alternative technologies. The obtained results

suggested that the SCFE/SCWO process is economically feasible and attractive for the remediation of real-world PCB highly contaminated soils/sediments (Zhou et al., 2004).

In a later study, Animescu et al. (2004) carried out studies of monochlorobiphenyl (MCB) decomposition in the presence of methanol and other co-solvents, both with and without oxygen, to understand the reaction kinetics and pathways of individual PCB isomers, and to determine the structure-reactivity relationships at 25 MPa and temperatures of 673, 723, and 773 K. Animescu et al. (2005) assessed the different effects that occur with respect to reaction products formed and reaction pathways developed when conducting PCB reactions in SCW in the presence of co-oxidants methanol and benzene (aliphatic and aromatic) at 25 MPa and 773 K.

O'Brien et al. (2005) carried out a kinetic analysis of the SCWO of the PCB congener 2-chlorobiphenyl, using hydrogen peroxide and methanol as a co-solvent at 2% volume at temperatures from 686 to 789 K and 250 bar, with residence times ranging from 1.1 to 5.8 s, obtaining conversions higher than 99.98% for a simulated PCB waste. Fang et al. (2005) studied the destruction of the solid PCB congener deca-chlorobiphenyl under oxidizing conditions with and without Na_2CO_3 as a neutralizing agent for the hydrochloric acid formed from PCB oxidation, in a hydrothermal diamond anvil cell to observe phase behavior and in batch reactors. The experimental results showed that when Na_2CO_3 was added to the reactor, higher conversions (99.7%) with lower oxygen excess (93%) were obtained, and little corrosion was observed. A later research with 10-CB explored the use of methanol and oxygen for promoting the destruction by supercritical water (Fang et al., 2008). It was concluded that the addition of methanol at 25% volume resulted in a lower dissolution temperature in comparison to hydrolysis experiments and when partial oxygen was added as a result of 10-CB decomposition by methanolysis reactions. One hundred percent 10-CB destruction was verified in batch oxidation reactions carried out with 25% volume methanol and without oxygen excess at 450 °C. Kawasaki et al. (2006) developed a practical reactor that consisted in a vessel followed by a plug flow reactor configuration for handling high concentration PCB streams (trichlorobiphenyl 8.4 wt%) that can include dioxins. In their studies, air was used as oxidant at 1.5 times the stoichiometric quantity required for total PCB oxidation, and experiments were carried out at 24 MPa. The most appropriate reaction temperature for stable decomposition of PCB and dioxin was determined to be 630 °C. The discrepancy of recommended temperature on pure PCBs and dioxin

waste streams, in comparison to results previously reported, could be attributed to the use of air as oxidant agent instead of hydrogen peroxide solutions.

Lee et al. (2006) assessed the PCBs SCWO based on the redox reactions promoted by the reduction of nitrate and nitrite salts used as oxidant agents. The results suggested the reactions proceeded via nitrogen monoxide (NO) and dioxide (NO₂) intermediates in parallel with the neutralization of reactor-corrosive hydrogen chloride (HCl). One hundred percent destruction of a PCB mixture similar to Kanechlor-500 was achieved in batch and continuous systems using around twice the chemical equivalent of nitrate and nitrite salts at 450 °C, 39 MPa and 30 min. However, in the continuous process, at long processing times, plugging of the reactor occurred due to NaCl precipitation. To avoid plugging, the authors suggested introducing removal steps of the precipitated salts into the flow process.

Weber et al. (2002) studied the batch sub- and supercritical water oxidation treatment of PCB mixtures Clophen A 30 and Clophen A 60 with gaseous oxygen, and found that even at 450 °C and 5 min reaction time, the formed PCDFs resulted in an increase in total toxic equivalence (TEQ) compared to the starting PCB mixture. However, at 450 °C, 15 min reaction time, and a PCB destruction efficiency of 99.995%, no PCDFs could be detected with a detection limit of 0.003 ng.

Marulanda and Bolaños (2010) assessed the SCWO of a real world PCB heavily contaminated mineral transformer oil at a continuous lab scale unit in the temperature range from 520 to 560 °C and oxidant excess in the range 300 to 400% at 24.1 MPa. At 539 °C, 24.1 MPa and 350% oxygen excess a 99.6% conversion of the organic matter and a destruction of PCBs under the detection limit of the chromatographic technique was achieved. In this work, a process flowsheet of a mobile continuous pilot plant for PCB contaminated oil destruction by supercritical water oxidation was proposed, and an economic assessment of such process was carried out by means of a study estimate (Turton, 1998). Different economic indicators suggest that this process might be a feasible alternative when compared to incineration for treatment of PCB wastes in South American countries.

The detailed and critical analysis of the existing literature on PCB wastes destruction by SCWO allows inferring this process has reached a degree of maturity in comparison to other emerging technologies, such as the catalytic dechlorination, biodegradation or phytoremediation. In this aspect, the availability of detailed

kinetic studies on the reaction pathways of PCB dechlorination and destruction at supercritical conditions are valuable information for reactor design and optimization. At the same time, and different from most catalytic dechlorination studies, SCWO studies have been carried out in a continuous set up. Although there still remain technical issues to overcome, mainly the corrosion caused by the hydrochloric acid that is formed during the PCB oxidation, recent advances in reactor construction materials (Foy et al., 1996; Kritzer and Dinjus, 2001) and flow configurations (Baur et al., 2005, Bermejo & Cocero, 2006) give insights for the eventual scale-up of the process to an industrial level.

Other Emerging Technologies

More recently, several authors have proposed innovative alternatives for PCBs treatment that rely on thermochemical, ultrasound, ultraviolet irradiation assisted and bioremediation processes. The ultrasound technology applies a high power ultrasound to water to produce a diverse range of chemical transformations. Bubble implosions and fragmentation produce microregions of extreme conditions with temperatures within the range of 2000 to 4000 K in aqueous solution. In addition to direct high temperature decomposition of organic compounds, water undergoes thermolysis to release radical species (H^* , OH^* , HOO^*) and hydrogen peroxide (H_2O_2). These free radicals attack organic compounds present in solution. Zhang and Hua (2000) studied the sonolytic destruction of 2-PCB, 4-PCB and 2,4,5 PCB to explore the kinetics and transformation pathways at multiple frequencies.

Ultraviolet irradiation is known to dechlorinate PCBs partially. Reductive dechlorination of highly chlorinated congeners to lesser chlorinated has been shown to occur, but the process is slow and difficult to control. Shimura et al. (1996) developed a method combining ultraviolet irradiation followed by microbial treatment in order to achieve the complete degradation of polychlorinated biphenyls. This method was applied to a 500 ppm Kanechlor mixture. Irradiation was applied during 26 hours and achieve a 95% elimination of PCBs. Miao et al. (1999) studied UV photodegradations of eight individual PCB congeners in hexane. These authors determined that all degradation reactions were pseudo first order and that the principal products of PCB decomposition were the less chlorinated biphenyls, and no PCB-solvent adducts were formed. The experimental results suggested that photodechlorinations occurred mainly on the more substituted rings, when the numbers of chlorine atoms on the two phenyl rings were unequal. It was al-

so observed during photodegradation that some coplanar PCB congeners were formed, which makes the toxic equivalence (TEQ) of solutions even to increase.

Seok et al. (2005) studied the PCBs batch and continuous thermochemical destruction process, in which chlorinated hydrocarbons are degraded to salt and inorganic compounds with addition of alkali (CaO), at moderately high temperatures, in a nitrogen atmosphere at 600°C , and obtained CaCl_2 and carbon as major end products. The observed continuous test results indicated that over 99.99% of PCB destruction efficiencies were achieved when excess quicklime ($>3\text{Ca}:1\text{Cl}_2$ as a molar basis) was used. Although the PCB destruction efficiencies were satisfactory, the major end product CaCl_2 can be fused at high temperature resulting in problematic solid removal so that the reactor temperature, which can increase due to the heat released by the exothermic reaction, should be carefully controlled below the melting point of CaCl_2 (782°C). The biodegradation of PCBs has been studied from two perspectives, oxidative degradation by aerobic microbes and dechlorination by anaerobic ones. The aerobic biphenyl utilizing bacteria hardly attack highly chlorinated PCBs, but degrade less chlorinated ones. On the other hand, some dehalorespiring anaerobic bacteria reductively dechlorinate highly chlorinated PCBs to lesser chlorinated ones. Recent research on biodegradation has aimed to the isolation of biphenyl utilizing bacteria to degrade PCBs. Ang et al. (2005) provide a review on the recent advances in the bioremediation of persistent organic pollutants including PCBs via biomolecular engineering. Although microorganisms with enhanced capabilities have been created, the technology still faces constraints regarding public acceptability.

Conclusions

This review constitutes a reference document in the field of PCB wastes destruction technologies, and it is intended to allow the researcher to compare the available PCB treatment processes based on reaction conditions, destruction efficiency and formed byproducts.

Catalytic dechlorination and supercritical water oxidation are the most extensively studied processes for PCBs destruction. However, almost every catalytic dechlorination research mentioned in this review is carried out in batch mode, with different catalysts and process conditions employed. Not many efforts have been

oriented towards the study of the kinetic aspects of the catalytic dechlorination, so that every report can be thought of as a whole new study, without a proper correlation with previous findings. On the contrary, there exist several continuous PCBs SCWO experimental studies, and kinetic aspects of the reactions involved have been properly elucidated. Several authors have concluded that the SCWO process is a feasible technological alternative to incineration, due to the extremely high conversions obtained and the absence of toxic byproducts. In addition, economic assessments, which are not readily available for catalytic dechlorination, microbial degradation, phytoremediation and other emerging technologies, show that this process is economically competitive with incineration, which is a technology that is not available in South American countries.

Overall, it can be said that aside from state-of-the art incineration, which is not available in several countries with large PCB inventories, or cement kiln co-processing, which has been thought of as responsible for the formation of dioxins and furans as byproducts of PCB incineration (although recent evidence suggest differently), supercritical water oxidation shows a technological degree of maturity in comparison with other emerging technologies. This technical maturity is evidenced in several investigations that report PCB destruction efficiencies higher than 99.9999%, the detailed kinetic aspects that have been elucidated and that constitute valuable tools for process modeling and scale-up, and the economic assessments that deem the technology as feasible. Efforts are still needed to overcome the difficulties caused by the acid formed during the destruction process, so that the application on large-scale is efficient and economically competitive.

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