TAMPERE UNIVERSITY OF TECHNOLOGY
Department of Environmental Technology
Institute of Environmental Engineering and Biotechnology

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FENTON TREATMENT OF PCB-CONTAMINATED SURFACES

Master of Science Thesis

Inspector: Prof. Tuula Tuhkanen
The subject has been approved at
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ABSTRACT

PCBs are man-made organic compounds classified as persistent organic pollutants (POPs). They are characterised by their high applicability as cooling liquid, softener, surfactant, flame retardant, lubricator or dispergent. Such applicability leaded to a production of more than one million tones since the 1930s. They were mainly used in closed systems as dielectric fluids in transformers and capacitors, but also highly used in open applications as plasticizers in building materials. From this usage, release of PCB from the falling plaster of buildings, the flaking paint or the volatilisation of lower chlorinated congeners has been happening since the begins of 1980s, when the use of PCBs was banned.

This project has focused on the degradation of PCBs directly over the surfaces in means of the advanced oxidation process known as Fenton. This technique is based on the capability of H_2O_2 for creating hydroxyl radicals when catalyzed with iron. The final aim is to treat real surfaces in order to decrease the PCB concentration to acceptable level. Also might be suitable for treating contaminated surfaces affected by condensator fires or explosions.

Two different surfaces have been used in order to simulate the real conditions. These surfaces have been glass and brick. They both have been artificially contaminated with a commercial mixture of PCBs known as Aroclor 1260, which was typically used in paints and sealants. The concentrations used are found among the real ones detected in several causes in Finland. Subsequently, the surfaces were treated with the Fenton reagents. Then, an extraction of the PCBs has been made in order to analyse them with GC-MS.

The effects of the ratio of H_2O_2 and Aroclor 1260, the time of reaction, the way of adding the reagents and the degree of chlorination of the PCB congeners, are the main subjects involved in this study. Also two ways of extracting the PCBs from the surfaces, one with a solution of hexane/acetone and other with wiped cotton, have been compared.

Results show a reduction around 70% in both surfaces, but lower weight ratio Fe^{2+}/H_2O_2/Aroclor is needed in the glass (204:250:1) than in the brick surface (136:500:1). It seems that more than seven days are needed for maximal degradation. Degradation occurs in a higher grade on the low chlorinated congeners. Also it has been found that the extraction of PCBs with cotton wiped in alcohol does not seem to be very repeatable when compared with the extraction by hexane-acetone solution.

PREFACE

This research was carried out in the Institute of Environmental Engineering and Biotechnology of the Tampere University of Technology.

I thank my supervisor and director of the study, Professor Tuula Tuhkanen for introducing me into the field of this project and for her guidance and valuable advices during the writing of this thesis. I am highly grateful to Niina Kulik for making this project come true, for her help in practical work and her enormous patience with all my questions. I would also like to express my gratitude to Professor Jose Luis Cortina for his support in this project from the E. T. S d’Enginyeria Industrial of the Universitat Politècnica de Catalunya (Spain).

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My warmest thank belongs to my family for their patience and understanding even from the distance, for their unconditional love, encouragement and because without them, I could never had been able to come in Finland.

Once I had a dream… and this is it.

Tampere, June 6th, 2007

PAULA CAJAL MARIÑOSA

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LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Processes
CAS	Chemical Abstracts Service
COD	Chemical Oxygen Demand
ECP	Electrochemical Peroxidation Process
FAO	Food and Agriculture Organization
GC-MS	Gas Chromatograph with Mass Spectrometer
GC-MSD	Gas Chromatograph with Mass Selective Detector
IARC	International Agency for Research on Cancer
IPCS	International Program of Chemical Safety
m	Mass
NOM	Natural Organic Matter
OECD	Organization for Economic Co-operation and Development
PCB	Polychlorinated Biphenyl
PCDF	Polychlorinated Dibenzo Furans
PCE	Perchloro Ethylene
PCT	Polychlorinated Terphenyl
POP	Persistent Organic Pollutant
ppm	Parts Per Million
PTFE	Polytetrafluoro Ethylene (Teflon)
PVA	Polyvinyl Acetate
rpm	Revolutions Per Minute
RTECS	Registry of Toxic Effects of Chemical Substances
TCE	Trichloro Ethylene
UNEP	United Nations Environmental Program
US EPA	United Stated Environmental Protection Agency
UV	Ultraviolet
V	Volume
w	Weight
WHO	World Health Organization

1 INTRODUCTION

Polychlorinated biphenyls (PCBs) are a type of man-made organic compounds whose low water solubility and high stability classifies them into the persistent organic pollutants group (POPs). They were composed for the first time in 1881 but it was not until 1929 that started their mass production.

A high fire resistance, low electrical conductivity and slow degradation, makes them useful as cooling liquid, softener, surfactant, flame retardant, lubricator or dispergent. Such high applicability leaded to a production of more than one million tones since the 1930s with a peak of production in 1970 of 33000 tones.

Nevertheless, PCBs have been recognized as hazardous substance due to their proved harmful effects on humans, animals and plants and, as there is sufficient evidence for carcinogenicity to animals, they are classified as probably carcinogenic to humans (Group 2A). This toxicity caused the prohibition of their use during the 1980s and 1990s in the major part of the world.

The usage of PCBs has been classified in completely closed systems, nominally closed systems and open-ended applications. The main percent of the production (a 56%) was used as completely closed system in dielectric fluids (capacitors and transformers); therefore, the main loss of PCB comes from the volatilisation in rubbish dumps that contain transformers and capacitors with PCBs. On the other hand, an important part of the production (30%) was used in open-ended applications as plasticizers on several building materials as concrete, joint sealants or plaster. That’s why another important source comes from the falling plaster of buildings, the flaking paint or volatilisation of the smaller congeners of PCBs. Also surfaces that did not contain contaminated paint or plaster but that have been affected by a PCB-container condensator fire or explosion are harmful as they become source of PCB. Moreover, it has been found that aggressive techniques for extracting the paint and plaster such as sandblasting release also a high amount of PCB into the environment.

PCBs were discovered to be bioaccumulative and so the main exposure path had been traditionally considered to be the ingestion, but the latest researches showing the presence of PCB in surfaces and in dust coming from this surfaces, have opened a new exposure path for taking into consideration and is the inhalation.

Industrial buildings were the ones where this PCB-containing paintings and plasters were more widely used. Problematic now rises when these industries are proposed to be transformed into offices or residential houses, since acceptable levels of concentration for occupational and residential uses should not be raised in the surfaces.

This project focuses the research on the treatment directly over these contaminated surfaces containing PCBs by the advanced oxidation technique known as Fenton treatment. In this technique, the OH radicals forming capacity of the hydrogen peroxide is used, catalyzed by iron, in order to oxidize the PCB molecules of several surfaces. This treatment has been proved efficient when applied to the oxidation of other substances such as pesticides, PCE, TCE, PCDD/Fs, PAHs and also when applied to PCBs both in water and soil remediation, but never tested before applied over a surface.

This research will be carried out in order to optimize the removal of the mentioned pollutant from artificially contaminated surfaces with a final aim of *in situ* remediation of real contaminated surfaces. Aroclor 1260 will be used as pollutant, which is a mixture of PCB congeners commercialized by the company Monsanto US and which was typically used in the open application as plasticizer of building materials. To achieve the optimal removal, several ratios between Aroclor 1260 and H_2O_2 and different times of reaction will be tested for two different ways of application of H_2O_2: applying all the needed quantity at once the first day of reaction or applying a proportional amount every day during the reaction.

2 LITERATURE REVIEW

2.1 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls were composed for the first time in 1881 by SCHMITT - SCHULZ in Germany. By 1899 a disease called chloracne had been identified between workers from the chlorinated organic industry (Koppe and Keys 2001). Following the emergence of mass production in 1929 by the US Company Monsanto, cases of occupational diseases among workers were reported mainly as skin irritations, but sometimes also the liver was affected. Safety precautions were taken among the workers, but the production carried on due to the high applicability of PCBs. Their commercial utility was based mainly on their chemical stability and low flammability as well as on their quite good physical properties such as electrical insulation capability. As a result they were well received in the market as replacement for products that were more flammable, less stable and bulkier.

By 1966 the warning that PCBs were discharging into the environment appeared. Søren Jensen detected unknown peaks during a liquid-gas chromatographic separation in samples from the muscles of white-tailed eagles while working with DDT (Koppe and Keys 2001, WHO/IPCS 1993). After two years of study he was able to demonstrate that these molecules were PCBs. In 1969 Jensen published his findings (Koppe and Keys 2001) on where it was explained that there were high concentrations of PCBs in the Baltic Sea fauna that had infiltrated the environment in large quantities during more than 37 years and were bioaccumulating in the food chain.

With the Yusho accident in Japan in 1968, the first signal that PCBs were dangerous for humans came. About 1800 people were seriously harmed because of the ingestion of rice oil with high concentration of Kanechlor 400, a brand of PCB. The factory producer of the oil used Kanechlor for the heat transfer system. The chemical leaked from the pipe to the tank container of the oil, resulting in the poisoning of many litres (Yoshimura 2003, Koppe and Keys 2001). The disease was characterised among other symptoms by acne-like eruptions, pigmentation of the skin, increase or discharge from eyes, loss of appetite and increase of mortality due to cancer (Yoshimura 2003). After this, a similar accident happened in Taiwan called Yu-Cheng. By the end of 1980, the number of persons poisoned was 1843 and only 3 years later, the number had increased to 2061 (WHO/IPCS 1993).

After the Japan accident, awareness among the public opinion grew. By the beginning of the 1970s PCBs were found in soils of Arctic, Netherlands or Germany. Animals from these areas, especially fish and fish-eating birds, were found to be highly polluted, making it possible to determine that PCBs are bioaccumulative (Koppe and Keys 2001).

In1972 Sweden banned the PCBs for open uses such as sealants, paints and plastics. After this, several governmental actions have been carried out. At the first North Sea conference in 1984, it was agreed that the phasing out of the use and discharge of PCBs should be intensified. During the second North Sea conference in 1987 targets to reduce the discharges were agreed. Also in 1987, the OECD (Organisation for Economic Co-operation and Development) made a further decision on PCBs with the recommendation that the member countries should cease the production, import, export and distribution of PCB by January 1989. During the 1980s some national governments recommended the reduction of fish consumption and the introduction of time limits on breast-feeding because both were important sources of PCBs. In the third North Sea conference of 1990 a specific plan for the phasing out of PCBs was carried out. In 1995 the Barcelona Convention for the Protection of the Mediterranean Sea against Pollution agreed to reduce by the year 2005 the discharges and emissions which could reach the marine environment of substances which are toxic, persistent and liable to bioaccumulate, in particular organohalogens, to levels that are not harmful to man or nature, taking a step towards their gradual elimination. In the same year Sweden prohibited the use of seasoned equipment which contained PCBs. The UNEP (United Nations Environmental Programme) in the May 1995 meeting agreed a global programme of action to abolish POPs, including PCBs. In 1996 Directive EC96/59 of the European Union demanded for the elimination of PCBs and PCTs and their complete expulsion by 2010 (Koppe and Keys 2001).

Nowadays, although the production of PCBs has been banned, their release in the environment still occurs from many sources as they have still not been removed from all the devices that used them as a refrigerating agent or from plaster in buildings.

2.1.1 General characteristics

PCBs are a class of organic compounds with a general chemical formula of $C_{12}H_{10-x}Cl_x$ (where x is the number of chlorine atoms in the molecule), whose nature are from 1 to 10 chlorine atoms attached to a biphenyl. They are manufactured by progressive chlorination of biphenyl in presence of catalyst, achieving a degree of chlorination between 21 and 68% (w/w). Their chemical structure is shown in the figure 1:

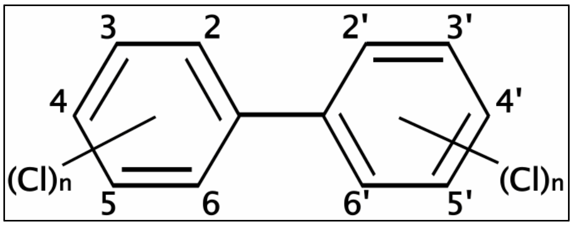

Figure 1: General structure of PCBs

Their CAS Registry number is 1336-36-3 and the RTECS Registry number is TQ 1350000.

Theoretically 209 chlorinated biphenyls are possible, but only 135 congeners have been found up to now. Their relative molecular mass depends on the degree of chlorination: while monochlorobiphenyl has a relative molecular mass of 188, completely chlorinated biphenyl ($C_{12}Cl_{10}$) has one of 494.

Each manufacturer has its own system of identification. In the Aroclor series, for example, a 4-digit code is used. Biphenyls are indicated by the 2 first digits as 12 and the 2 last numbers indicate the percentage in weight of chlorine. Other manufacturers use different identification for the quantity of chlorine, thus Clophen A60, Phenochlor DP6 and Kanechlor 600 are biphenyls with an average of 6 atoms of chlorine per molecule (WHO/IPCS 1993).

Although most of the PCBs known are colourless, odourless crystals; commercial mixtures are clear viscous liquids, often light yellow or dark colour. They do not crystallize at low temperatures but turn into solid resins. Their density is high due to the presence of chlorine atoms in the molecule.

At low temperatures, instead of crystallizing, they turn into solid resins. They are soluble in most organic solvents, oils and fats and practically insoluble in water. They are very stable regarding a wide range of oxidants.

Physical and chemical properties vary across the class, but all of them can be characterised with a high fire resistance. They form vapours heavier than air, but they do not form any explosive mixtures with it. They show very low electrical conductivity, an extremely high resistance to thermal breakdown and they don't degrade easily. These characteristics make them useful as cooling liquid, softener, surfactant, flame retardant, lubricator or dispergent in different materials and products. (WHO/IPCS 1993).

The physical properties have lead PCBs to be present in building materials such as joint sealing materials, glue used in the production of double glazing, concrete, paint and plaster. PCBs were used mainly in polyvinyl acetate (PVA) mixtures to improve the properties of the concrete and plaster. PCB gives a better flexibility of the material, a better dried, resistance against mechanical erosion and better adherence to a high variety of building materials (Andersson 2003). PCB has been also used as flame retardant coating for acoustic ceiling tiles (Heinzow 2006).

Studies among humans have shown that PCB exposure leads to skin abnormalities (chloracne), but there is strong evidence that this occurs in combination with polychlorinated dibenzofurans (PCDFs). Poisoning has been observed to cause retardation of the foetal growth and alteration of calcium metabolism related to hormonal dysfunction (UNEP/FAO 1992). Concerning others forms of life, such as soil microbes, it has been observed lower nutrient recycling rates and lower respiration rates when exposed to PCBs. In plants, the growth, the water uptake and the leaf development are inhibited. In birds and mammals, due to the high lipophility, PCBs cause lower egg production, changes in behaviour, thinner shells and are transferred to the offspring (Env. Canada 2005).

There is limited evidence for carcinogenicity to humans although the available studies assume an association between cancer and exposure to PCBs (WHO/IARC 1998). Nevertheless, there is sufficient evidence for carcinogenicity to animals, which leads to classify PCBs as probably carcinogenic to humans (Group 2A) (WHO/IARC 1998).

2.1.2 Sources of exposure

Polychlorinated biphenyls do not occur naturally in the environment as all of them are manmade. The usages of PCBs can be classified in: completely closed systems, nominally closed systems and open-ended applications (WHO/IPCS 1993).

In completely closed systems uses, PCBs have been widely used as dielectric fluids in capacitors and transformers, due to their chemical and physical properties. In transformers there were used highly chlorinated biphenyls such as Aroclor 1254 and Aroclor 1260. During 1970s and 1980s both transformers were superseded by others without PCBs, for instance in Sweden and Finland this happened in 1982 and in Norway in 1985.

PCBs have also been used in nominally closed systems as fire resistant liquids or as working fluid in vacuum pumps.

As open-ended applications, PCBs can be found in plasticizers, surface coatings, paints, ink, adhesives or pesticide extenders. Due to their semi-volatile character, PCB continuously diffuse from PCB-containing materials and evaporation from buildings still result in considerable house-dust contamination. Also, but in less quantity, PCBs can be found in immersion oil for microscopes, catalysts in the chemical industry and casting waxes in the iron/steel industry.

Since 1930s, there have been produced more than one million tons of PCBs. In the United States, the peak of production was reached in 1970 with 33000 tones, which were used as follows: 56% in dielectric (36% in capacitors and 20% in transformers), 30% as plasticizers, 12% as hydraulic fluid and lubricants and 1.5% as heat transfer liquids. After 1970 the production decreased (WHO/IPCS 1993).

During 1980-84, the production in the states members of the European Union comprised 16200 tones in France, 24200 tones in the Federal Republic of Germany, 4500 tones in Italy and 3400 tones in Spain. After 1984 the production only continued in France and Spain (WHO/IPCS 1993)

As said before, over one million tons have been produced since 1930s, most of them finally released into the environment. The spread can take place either by atmospheric transport or by a release into water as well as with mobilization in the soil and landfills.

The main loss of PCB comes from the volatilisation in rubbish dumps that contain transformers, capacitors and other wastes with PCBs and also the waste waters and mud. Another source is the falling plaster of buildings, as PCBs were used to improve its properties. Contamination can come also from the incineration of municipal and industrial wastes, because the major part of incineration is not effective in the destruction of PCBs. Finally, explosion and overheating of transformers and capacitors can liberate quantities of PCB to soil and nearby surfaces (WHO/IPCS 1993).

2.1.3 Transport and distribution

Once released, PCBs can volatise or disperse as aerosols. The existence of PCBs in remote areas such as Arctic suggests that they are transported in the air due to the strong south to north winds that occur over west Eurasia (Koppe & Keys 2001). As PCBs volatilizes from landfills to the atmosphere and resists degradation, the primary mode of distribution is considered to be transport by air. Several studies have estimated that there is a presence of approximately 18000 kg in the USA atmosphere at any time and that if PCBs have a residence time in the atmosphere of one week, then 900000 kg/year cycle throughout the USA atmosphere (WHO/IPCS 1993). From the atmosphere, PCBs can be transferred to water bodies by dry deposition or precipitation deposition and this last one also can be a source for soil contamination.

PCB content in soil comes from particulate deposition, wet deposition, the use of sewage sludge as a fertilizer and leaching from landfill sites. They are highly lipophilic and because of this reason they are strongly absorbed by the soil particles. PCB tends to concentrate in fine-grained sediments that are abundant in natural organic matter (NOM) (Cassidy *et al.* 2002).

PCBs enter water from discharges from industry and urban wastes into rivers, lakes and coastal waters. Due to the dry deposition from air, they are more concentrated in the surface micro-layer than in subsurface, but due to their low water solubility, they can be found mainly in the sediments at the bottom of the rivers. A study made on the sediments of a lake has revealed the migration of the contaminant downward as there was found the presence of PCBs in sediments of 8000 years old. Also in this study, it was found the decline of contaminant concentrations towards the surface indicating the purification of the sediment after the banning of PCB production (Isosaari *et al.* 2002).

Due to the high lipid solubility, PCBs accumulate in almost all the organisms, mainly in the fat-rich tissues. As they have a slow rate of metabolism and elimination, their bioaccumulation is very high as they can be transferred via food or via mother-offspring.

2.1.4 Human exposure

2.1.4.1 *General population*

As said before, one of the main releases of PCBs is to the air, where it is possible to find the highest levels in kitchens and offices with electric installations. Reports from US EPA and Japan verify a quantity of PCB in the air from 1 to 50 ng/m^3. Van der Kolk in 1985 calculated the intake for the Dutch population and the result was 1000 times lower than the intake via food (WHO/IPCS 1993). Due to the low solubility in water of the PCBs, the quantity of PCBs ingested via water can be considered negligible.

The intake via food is the main route of human contamination and inside the food option, fish seems to be the major cause of PCB intake, but this depends, of course, on the geography and eating habits. In countries where fish consumption is not very common, the exposure to PCBs through this route is less than in countries for which a great part of the daily nutrition program consists of fish.

Another important scenario that should be taken into account is the direct skin contact, dust ingestion, inhalation or hand to mouth transfer which can be found in situations of contaminated surfaces (Kuusisto *et al.* 2006-b). Contaminated surfaces do not only exist in houses built with contaminated plaster and paints, but also in old factories where PCB-containing paints were used and now they are converted into modern flats or in surfaces affected by an PCB-container capacitor explosion.

2.1.4.2 *Accidental exposure*

Exposure can happen due to an accidental discharge as it happened in Yusho and Yu-Cheng accidents. As said in the chapter 2.1, almost 4000 people between two accidents were contaminated with high doses of PCB due to rice oil polluted with refrigerant liquid PCB container.

It should also be taken into account when, due to a fire, PCB-containing surfaces are burnt since PCBs volatilize and degrade to dioxins and furans that may be dangerous to the ones that should face the fire.

2.1.4.3 *Occupational exposure*

Another way of exposure comes from the workers of the PCB manufacturing industries. Occupational exposure happens during the manufacture of the PCBs but also during their use. This means that contamination can happen to mechanics in contact with lubricating oils or hydraulic fluids, to workers in contact with varnishes and paints, to office workers in contact with duplicating paper, and the list follows as above (WHO/IPCS 1993).

Not only is dangerous to work in the PCB manufacturing industry, but also inside contaminated buildings. When an edifice is constructed with PCB-containing materials or a contaminated industry is transformed into offices, workers of the reconstruction process or posterior workers of these offices are on risk if surfaces exceed the acceptable limit of concentration.

2.2 Contamination of surfaces by PCBs

This project is focused on the usage of PCB in sealants, paints, plasters and concretes in buildings. This use started to be applied during the 1950s and was much extended during the 60s and 70s decades. The use was banned in the latest 1970s, but contamination due to flaking paint (figures 2 and 3) or volatilisation of the smaller congeners of PCBs is happening also at this moment. Also it has been found that aggressive techniques for extracting the paint and plaster such as sandblasting release also a high amount of PCB into the environment (Hellman and Puhakka 2001, Priha *et al.* 2004, Tuhkanen *et al.* 2005).

Figure 2: Flaking PCB-containing paint from a school building (Kuusisto et al. 2006-a)

2.2.1 Antecedents

Several researches around the world indicate the presence of PCB in surfaces and dust from surfaces. The occurrence of PCB in surface soil, plaster and paint and the differences between age and usage of buildings were studied in Norway (Andersson *et al.* 2003). Higher concentrations of PCBs were found in residential buildings and schools rather than in offices. Storages of industries and buildings dated from the 1950-1960 decade were found to have higher concentration than buildings from later age. Thirty percent of the buildings happened to raise the Norwegian action level (0.5 mg/kg). Moreover, the surrounding soil was found to have higher concentration than the corresponding plaster from the adjacent wall, which was explained through the retention of PCB caused by the high soil organic matter contents (Andersson *et al.* 2003).

Similar studies were carried out in USA, where several buildings were analyzed in order to get an approach of the content of PCBs (Coghlan *et al.* 2002, Herrick *et al.* 2004). Coghlan demonstrated that PCBs can be released from the walls and that the main exposure pathway due to this source is the inhalation. In the research it is pointed out that the age of a building can be critical in determining if the materials of a building are likely to contain PCB (Coghlan *et al.* 2002). In his research, Herrick shows that one third (8 of 24) of the investigated buildings contained PCB content exceeding the limit of the U.S. Environmental Protection Agency for considering a material as bulk product waste, which is situated in 50 ppm by weight (Herrick *et al.* 2004). Also PCB was found in air and dust taken from the ventilation system. Buildings such as schools presented high concentrations, so the research demonstrated that further action was needed in the USA as far as PCB treatment and disposal are concerned (Herrick *et al.* 2004).

Also in Switzerland PCBs were found in the building materials, especially in the joint sealants. In a big research around the country, about half of the samples (48%, n = 647 out of 1348) were found to have a concentration higher than 20 mg/kg (which was the detection limit) and 42% of the samples were found to have higher concentration that 50 mg/kg, which is the lower limit for the PCB content materials to be disposed as hazardous waste. Also it was found that 21% of the samples contained more than 10 g/kg, indicating that PCBs were widely used as plasticizers in joint sealants in Switzerland. While talking about year of construction, most of the high concentrated samples were found in buildings from 1970 – 71, while a tendency of diminishing the content is seen from these years on. These data is useful for, as in the research of Coghlan, determining if the materials of a building are likely to contain PCB due to the year of construction (Kohler *et al.* 2005, Zennegg *et al.* 2004).

In northern Germany (Land Schleswig-Holstein), samples from indoor-air buildings with PCB were taken. In this case it was found that air from both rooms with acoustic ceiling tiles treated with PCB-containing flame retardants and rooms with PCB-containing permanent elastic sealants had high levels of PCB (Heinzow *et al.* 2006).

In Finland the presence of PCBs in paints and sealants has been proved (Tuhkanen *et al.* 2005, Hellman and Puhakka 2001, Priha *et al.* 2004, Kontsas *et al.* 2004). The cleaning of this surfaces with dust creating techniques such as sandblasting, also results in contamination of building surfaces with PCB-containing dust (Kuusisto *et* *al.* 2006-a & b, Tuhkanen *et al.* 2005). Moreover, as in Norway, it was proved that the flaking paint and the volatilisation of these PCBs is causing contamination in the surrounding soils (Hellman and Puhakka 2001, Priha *et. al* 2004). Another exposure pathway was showed by Kontsas when analysing the content of PCBs on the blood serum of workers of renovation buildings. In her study, it is showed that workers' blood contains PCBs despite appropriated working equipment, methods and personal protection (Kontsas *et al.* 2004).

Figure 3: Flaking PCB-containing paint from a wooden floor of a military building (Kuusisto et al. 2006-a)

Further studies also in Finland have lead to risk analysis of those situations (Kuusisto *et al.* 2006-b, Hellman and Puhakka 2001, Priha *et al.* 2004). In these studies it is revealed a insignificant toxicity risk to the children in both cases of occurrence of PCBs in surrounding soils (Hellman and Puhakka 2001, Priha *et al.* 2004). Nevertheless, in the case of risk assessment of contaminated dust on indoor surfaces the results were opposite, as calculated health risks were quite high both as residential and occupational use (Kuusisto *et al.* 2006-b).

All these commented researches point out the need of concern about this not well known source of PCB contamination. Now that contamination via food in gradually declining, indoor air might become a more visible source for human exposure. A new way of treatment for PCBs in surfaces is presented in this project in order to avoid the spills due to flaking paint or volatilisation.

2.2.2 Limit and guidance values

In order to protect workers from the impurities in air, Finland has given HTP values to the PCBs (Concentrations Known to be Hazardous). The recommended limit value for contaminated surfaces is 100 μg/m^2 and for the air are 0.5 mg/8 h and 1.5 mg/15 min per cubic meter (PCB-Committee 1984).

For non-cancer harmful health effects, the United States National Institute for Occupational Safety and Health (NIOSH) gives as limit value 0.001 mg PCB/m^3 for a 10-hour workday or 40-hour workweek. The US Occupational Safety and Health Administration (OSHA) proposes the non-cancer exposure limits in 0.5 mg PCB (54% chlorine)/m^3 or 1 mg (42% chlorine)/m^3 for a 8-hour workday (PCB-Committee 1984).

On the other hand, in an exposure assessment study, acceptable surface concentrations in residential and occupational settings were given. In the research it was found out that for a protection of 95% of the exposed population, the acceptable concentrations on surfaces should be 7 μg/m^2 for residential use, 65 μg/m^2 for residential use if only adults will be exposed and 140 μg/m^2 for occupational use (Kuusito *et al.* 2006-b).

2.3 Degradation techniques for PCBs

The traditional treatments for PCB contamination include incinerations, solvent extraction or stabilization (Tuhkanen 2001, Magar 2003). Incineration is conventional but includes also many disadvantages: it is expensive, as the cost may reach 1000$ per ton, the temperatures of destruction raise 540 °C and long residence times are required (Magar 2003). A control of the air discharges is also required when using this method as the incineration of PCB produces dioxins. Solvent extraction is a non-destructive technique that extracts the PCB and concentrates it in one single phase. After the extraction, incineration or safely disposal is needed. Stabilization is a non-destructive technique that relies on amendments to stabilize PCBs and prevent their release in the environment after disposal (Magar 2003). Anyhow, these methods cannot destroy contaminants or can lead to secondary pollution such as polychlorinated dibenzofurans or p-dioxins. In order to avoid a problem of final disposal, degradation techniques have been developing lately.

2.3.1 Biodegradation

Many investigations have been carried out as far as the biodegradation of PCBs is concerned. Generally, degradation of PCB by bacteria and fungi depends highly on the degree of chlorination and the position of the chlorine substitution and it is possible for the lower chlorinated biphenyls in soil with low organic matter content (from 0.1 to 3.3 %) and in diverse kinds such as loamy and clay, although time of reaction is long (WHO/IPCS 1993).

Pseudomonas seems to be good biodegrading bacteria for PCBs (Tandlich *et al.* 2000, Gibson *et al.* 1993), although *alcaligenes xylosoxidans* have also been reported as good oxidants (Haluška *et al.* 1994). In his article, Tandlich makes a research about the effect of the terpenes carvone and limonelle as inducers of PCB degradation when using glucose, biphenyl, glycerol or xylose as sole carbon energy source and *Pseudomonas stutzeri* as degrading bacteria. The aim of the research was to find the best biodegradant of Delor 103 without the use of biphenyls, which are the best degradants known although they are harmful. Reduction from 30 to 70% depending on the congener was achieved by using xylose and carvone. Xylose is a non-toxic compound which, combined with the reduction rate, makes it an attractive and prospective candidate for this application (Tandlich *et al.* 2000).

Gibson found relation between substrate and quantity of degradation by the bacteria. In his report it was compared the degradation by *Pseudomonas* sp. Strain LB400 with *Pseudomonas pseudoalcaligenes* KF707 using biphenyls 2,3-dioxygenase as carbon source. LB400 bacteria oxidize a much higher number of congeners than KF707 do and the report attributes these differences on the substrate: the biphenyl 2,3-dioxygenase catalyzes in a higher grade LB400 than KF707 (Gibson *et al.* 1993).

Haluška, studies the behaviour of the *Alcaligenes xylosoxidans* in front different soils. Although it was found that degradation occurs easily in sterilized soils, differences between types of soil were higher. The results show that degradation is related not only to the capabilities of the strain of soil employed but also to the soil sorption of the PCB congeners (Haluška *et al.* 1994).

2.3.2 Photo degradation

It has been reported that both simple and commercial PCB mixtures undergo photoreduction in organic solvent and aqueous systems in the laboratory (WHO/IPCS 1993, US EPA 1998). Two bench scale studies reported effectiveness when removing contamination due to Aroclor in wastewaters. Lin and others, in 1995, studied the photodegradation with diethylamine of five PCB congeners present in the Aroclor 1254 and the reduction was between 78 and 99 % depending on the congener. Zhang and others, in 1993, treated the Aroclor 1248 present in a sample of wastewater with solar radiation and TiO_2. The removal achieved after four hours of treatment was of 84% (US EPA 1998).

It was also found that PCBs degraded faster in hexane solution than in aqueous solution and benzene solution. Significant amounts of highly chlorinated biphenyls degrade in water by the action of the sunlight (WHO/IPCS 1993).

2.3.3 Oxidation techniques

Oxidation techniques are an alternative to those treatments mentioned above and their aim is to mineralize pollutants to carbon dioxide, water and inorganic compounds (Parsons 2004). Despite this fact, the molecules are often not mineralised but partially degraded to intermediate products that are more easily biodegraded (Huston and Pignatello 1998), although sometimes can be found that the products have higher toxicity than the parent compounds (Fernández-Alba *et al.* 2002).

Chemical oxidation has been proved useful in the destruction of a wide range of organic pollutants such as chlorophenols, octachlorodibenzo-p-dioxin, nitrophenols, petroleum hydrocarbons, chlorinated ethylenes, chlorinated biphenyls and polycyclic aromatic hydrocarbons (Aunola 2004).

Among these oxidation techniques, the newer form of oxidation can be found in the advanced oxidation processes (AOPs). All AOPs are characterised by the same chemical feature, which is the production of OH radicals ($^{\bullet}OH$), although each of them offers a different possibility of OH radical production. The most commonly used AOPs use ozone (O_3), Fenton's reagent (Fe^{2+} and H_2O_2 or catalyzed hydrogen peroxide (CHP)), permanganate (MnO_4^-) and persulfate ($S_2O_8^{2-}$) (US EPA 2004, Huston and Pignatello 1998).

Ozone (O_3) reacts with organic substances in aqueous solution by two mechanisms depending on the pH. At neutral to acidic pH, an electrophilic addition of molecular ozone takes place at the electro rich parts of the organic molecules like C-C double bonds. At alkaline conditions, ozone decays mostly to OH radicals ($^{\bullet}OH$) and by chain reactions, to other radicals (Kornmüller and Wiesmann 2002).

$KMnO_4$ is a crystalline solid from which aqueous solutions can be prepared on site. Although the mechanism of reaction has been widely discussed, it seems clear that at pH > 9, permanganate ions (MnO_4^-) react with hydroxyl ions and form OH radicals which are the principle oxidizing entities in high pH systems. In the reaction manganese is reduced into a manganese oxide. $KMnO_4$ has been proved efficient in the degradation of TCE, PCE, naphthalene, pyrene and phenanthrene (Gates-Anderson *et al.* 2001).

Recent applications have developed in situ processes for the treatment of soil and groundwater contamination (Aunola 2004). In situ oxidation treatments offer several advantages such as the cost of reagents, which is relatively low. Also these kinds of treatments do not generate large volumes of waste and are quicker than other techniques like the biological, which shows, for instance, a slow response under cold climate conditions or limited application for biorefractory pollutants. However, this technology can interrupt other remedies that occur naturally in a specific ground during the time that the technique is acting (Goi 2005).

2.4 Fenton treatment

2.4.1 Theory

The Fenton process is based on the use of one or more oxidising agents (usually hydrogen peroxide (H_2O_2) and/or oxygen) and a catalyst (a metal salt or oxide, commonly iron). The reaction between the iron and the hydrogen peroxide in acidic solution produces the oxidation of Fe(II) into Fe(III) and the highly reactive hydroxyl radical ($^{\bullet}OH$) is formed. This reaction is spontaneous also without the influence of light (Parsons 2004).

The process was first described by Fenton in 1894, when he discovered that tartaric acid is oxidized by the addition of ferrous iron, but actually it is used the Haber-Weiss reaction for their investigation came up with a more suitable specific example of the Fenton reaction. Reactions that take place in the process are demonstrated in equations 1-6 (Parsons 2004):

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III} + {}^{\bullet}OH + OH^- \qquad (1)$$

$$Fe^{III} + H_2O_2 \rightarrow Fe^{II} + HO_2^{\bullet} + H^+ \qquad (2)$$

$$Fe^{II} + {}^{\bullet}OH \rightarrow OH^- + Fe^{II} \qquad (3)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (4)$$

$$Fe^{II} + HO_2^{\bullet} + H^+ \rightarrow Fe^{III} + H_2O_2 \qquad (5)$$

$$Fe^{III} + HO_2^{\bullet} \rightarrow Fe^{II} + O_2 + H^+ \qquad (6)$$

Although Fenton treatment requires relatively inexpensive and easily transported chemicals, the process requires a strict control of the pH and a fixed ratio between contaminant, oxidant and catalyst. Moreover, the time of reaction has a high dependence on the final result. These processes have been mainly studied at laboratory scale, with only some pilot-scale studies and few full-scale applications.

In soil and groundwater remediation, the Fenton treatment makes use of the iron oxides naturally present in the ground, but also may require an addition of iron salts or solid iron. The amount of H_2O_2 added largely determines the operating cost of the process, so here lays the importance of establishing the correct dosage of it. The concentration of the added H_2O_2 depends on the amount of water, the amount of organic contaminant and the degree of treatment required (Parsons 2004).

The process is highly affected by the type of soil (Manzano *et al.* 2001, Parsons 2004). If a large amount of mineral forms exist in the soil, the soil is mainly crystalline and the reaction is favoured, on the other hand, a soil rich in clays is less effective for it is mainly amorphous. If the carbonate alkalinity of waters is high, a large amount of mineral acid will be required to decrease the pH. On the contrary, if natural pH is low, the organic acid produced by the reaction will be sufficient. Finally, the higher the natural organic matter concentration, the more hydroxyl radicals will be used in degrading this material, a fact which leads to fewer radicals available to degrade the contaminant.

There are several variations of the Fenton treatment. One of the most used ones has been the photo-Fenton process, which is given when the reaction is irradiated with light of suitable wavelength (180 – 400 nm). Thus, Fe (III) can catalyse the formation of hydroxyl radicals (Gernjak *et al.* 2002, Parsons 2004). Another important variation is the electrochemical Fenton process, where it is combined the dechlorination made by zero-valent iron with the Fenton's reagent, since they are used electric current and sacrificial electrodes to supply soluble Fe^{2+} (Arienzo *et al.* 2000, Parsons 2004). Another interesting variant of the traditional Fenton is the ethanol-Fenton treatment, where the hydrogen peroxide and the iron are added to a liquid phase of ethanol. This method has been found to enhance the reaction for hydrophobic contaminants since reaction occurs in ethanol phase instead of water (Lundstedt *et al* 2006).

Studies have revealed the effectiveness of Fenton reaction when applied to organic pollutants. Two different kinds of soil organically polluted with volatile organic compounds such as PCE and TCE, benzene, naphthalene, phenanthrene and pyrene were treated with Fenton by Gates-Anderson. Although sensitive to contaminant and soil type, degradation over 90% was achieved at pH = 3 (Gates-Anderson *et al.* 2001). Also in treatment of soils, PCP and TCE were oxidized effectively on the sand surface using hydrogen peroxide and the natural content of iron of sand (Ravikumar and Gurol 1994). Fenton has showed more than 80% of reduction when treating dioxins and furans (PCDD/Fs) with a ratio of 8:1 Fe(II) / H_2O_2 (Isosaari, 1997). When applied to different kinds of waste waters Fenton treatment has also been effective (Sedlak and Andren 1991, Gernjak *et al.* 2002). Fenton combined with solar radiation was found to degrade easily phenolic compounds both in the laboratory and in the pilot plant (Gernjak *et al.* 2002). On the other hand, complete mineralisation of different pesticide active ingredients was achieved when using the catalytic photo-Fenton, Fe(III)/H_2O_2/UV in a dilute aqueous solution (Huston and Pignatello 1998). Finally, Fenton presented acceptable results when treating the desizing waste waters of the textile industry, which contain a mixture of polyvinyl alcohol (PVA), corn starch, carboxymethyl cellulose (CMC), These waters present a high COD concentration and the treatment ranks them below the acceptable limits (Lin and Lo 1997).

The major advantages of using Fenton reagent over other oxidation processes are: 1) both iron and hydrogen peroxide are inexpensive and non-toxic; 2) there are no mass transfer limitations because the reaction is homogeneous; 3) no light is required as catalyst and, therefore, the design is much simpler that ultraviolet light systems; 4) and, H_2O_2 can be electrochemically generated in situ (Yin & Allen 1999).

2.4.2 Fenton treatment of PCBs

Several studies reveal the efficiency of the Fenton treatment when applied to the removal of PCBs, showing the high dependence of the treatment to the ratios and the nature of the PCB mixture (Dercová *et al.* 1999, Aunola 2005, Fronduti 2005, Tuhkanen 2001, Arienzo *et al.* 2000, Manzano *et al.* 2001).

A laboratory scale study related to the oxidative degradation of a commercial mixture of DELOR 103 (Dercová *et al.* 1999) show different results as far as rate and extent of reaction is concerned. In the study it is proved that the oxidation effect of the Fenton treatment is amplified with increasing the molar ratio Fe^{2+} / H_2O_2 and also by increasing the concentration of the hydrogen peroxide until 1M. Higher concentration does not enhance the oxidation effect significantly. Results also show higher elimination rate constants when decreasing the number of chlorine atoms in the biphenyl molecule and when also using abiotic chemical degradation (Dercová *et al.* 1999).

When applied to real matrixes, Fenton has been also proved efficient in the PCB removal (Aunola 2005, Fronduti 2005, Manzano *et al.* 2001). It showed up to an 87% of removal used in treatment of contaminated lake sediments, being the extent of reaction improved when adjusted the pH with SO_4^{2-} instead of Cl^- . The studies also proved that the stabilization of hydrogen peroxide had no effect on the outcome of the treatment (Aunola 2005, Fronduti 2005). When a applied to a matrix of sandy soil, 98% of elimination of the original structure and 82% of dechlorination was achieved when applying a concentration of 5% H_2O_2; 100 ppm of Fe^{3+}; a ratio of sandy soil mass/volume of oxidizing solution (m/V) of 1/3 g/ml and a time of reaction of 72 hours (Manzano *et al.* 2001). These tests also showed the need for agitating the reaction and that the reaction occurred in the solid phase.

Nevertheless, the influence of the matrix has resulted very high in the Fenton treatment. As has been proved in several researches, the optimal pH for the reaction is 3. When ash matrix with high pH and buffer capability was used (Tuhkanen 2001), removal of PCBs was only of 6.1%. This proved that the treated material should be neutralized before the treatment with the consequent waste of chemicals (Tuhkanen 2001).

Also variations of the Fenton treatment have proved to be effective applied to PCBs. ECPs (electrochemical peroxidation processes) (Arienzo *et al.* 2000) and application of UV radiation (Kaštánek *et al.* 2004) have been utilized to treat groundwater and wastewater PCB contamination respectively.

Electrochemical peroxidation combines the dechlorination made by zero-valent iron with the Fenton's reagent as it uses electric current and sacrificial electrodes to supply soluble Fe^{2+}. The process is showed in equation 7. Results are satisfactory: on one hand, 90% of the PCBs of the solution had been removed in 4 hours and it was observed that increasing the iron mass and surface area decreased the absorption rate. On the other hand, when acidifying or basifying the solution, no significant change was observed. Finally, by this method there were achieved concentrations of Fe^{2+} over 100 ppm in 5 minutes, which suggest that electrolysis is an efficient alternative to the addition of ferrous salts as catalysers for Fenton (Arienzo *et al.* 2000).

$$Fe^0 + RX + H^+ \rightarrow Fe^{2+} + RH + X^- \qquad (7)$$

Considerable reduction of concentrations of PCBs was achieved by application of Fenton reaction enhanced by UV radiation (Kaštánek *et al.* 2004). It was observed that for low contaminated water the role of Fe^{2+} as catalyst is subsidiary. Moreover, the research of Kaštánek leaded to a pilot plant experiment where it was achieved a relatively high reduction, which came with the conclusion that UV/OX is a viable method for the reduction of PCB concentration on wastewater. When treating high chlorinated waters, the method was satisfactory but results were better in presence of Fe^{2+} as catalyst. (Kaštánek *et al.* 2004).

3 MATERIALS AND METHODS

3.1 Materials and reagents

3.1.1 Characterisation of the reagents

3.1.1.1 Aroclor 1260

Aroclor is a trade mark of the company Monsanto U.S which corresponds to a mixture of PCBs with a 60% of degree of chlorination. It has been the most typical commercial mixture used as plasticizer in paints and sealants. The Aroclor 1260 possess a total quantity of dibenzofurans of 0.8 mg PCB/kg, from which 25% are tetrachlorinated, 38% are pentachlorinated and approximately 38% are hexachlorinated (WHO/IPCS 1993). Table 1 gives the proportions of the different PCBs presents in the commercial mixture:

Table 1: PCB composition of Aroclor 1260 (WHO/IPCS 1993)

IUPAC No.	**22**	**37**	**40**	**42**	**47**	**?(*)**	**52**	**55**	**66**
mol %	trace	0.09	0.04	0.66	0.88	0.44	1.91	0.12	0.22
IUPAC No.	**70**	**72**	**74**	**76**	**77**	**79**	**80**	**83**	**84**
mol %	0.85	0.28	0.09	0.01	0.04	0.04	trace	0.09	0.69
IUPAC No.	**85**	**?**	**87**	**91**	**92**	**97**	**99**	**101**	**102**
mol %	0.31	0.14	1.10	3.22	0.21	0.68	0.82	5.04	trace
IUPAC No.	**106**	**110**	**113**	**114**	**118**	**120**	**121**	**?**	**126**
mol %	0.06	3.57	0.01	0.03	2.00	3.01	0.57	1.88	1.59
IUPAC No.	**128**	**131**	**132**	**133**	**134**	**135**	**136**	**138**	**148**
mol %	0.47	0.01	2.77	0.06	1.01	0.29	1.12	5.01	0.06
IUPAC No.	**149**	**151**	**153**	**156**	**157**	**158**	**159**	**163**	**167**
mol %	9.52	0.06	8.22	0.41	0.03	0.18	1.48	trace	0.17
IUPAC No.	**168**	**170**	**171**	**174**	**176**	**177**	**179**	**180**	**181**
mol %	0.59	0.62	4.31	0.09	0.57	trace	0.83	7.20	2.72
IUPAC No.	**182**	**183**	**185**	**186**	**187**	**189**	**190**	**192**	
mol %	0.47	2.58	5.65	0.37	1.12	0.13	0.02	0.97	

(*) it can vary according to the producer

The physical and chemical properties of the Aroclor 1260 are shown in table 2:

Table 2: Physical and chemical properties of Aroclor 1260 (WHO/IPCS 1993)						
Water solubility (mg/l) 25°C	**Vapour pressure (torr) 25°C**	**Density (g/cm^3) 25°C**	**Appearance**	**Henry's law constant (atm-m^3/mol) 25°C**	**Refractive index**	**Boiling point (750 torr, °C)**
0.0027	4.0 x 10^{-5}	1.58	Light yellow, sticky resin	4.6 x 10^{-3}	unknown	385-420

In the figure 4 it is possible to appreciate the GC-MS spectra for the Aroclor 1260:

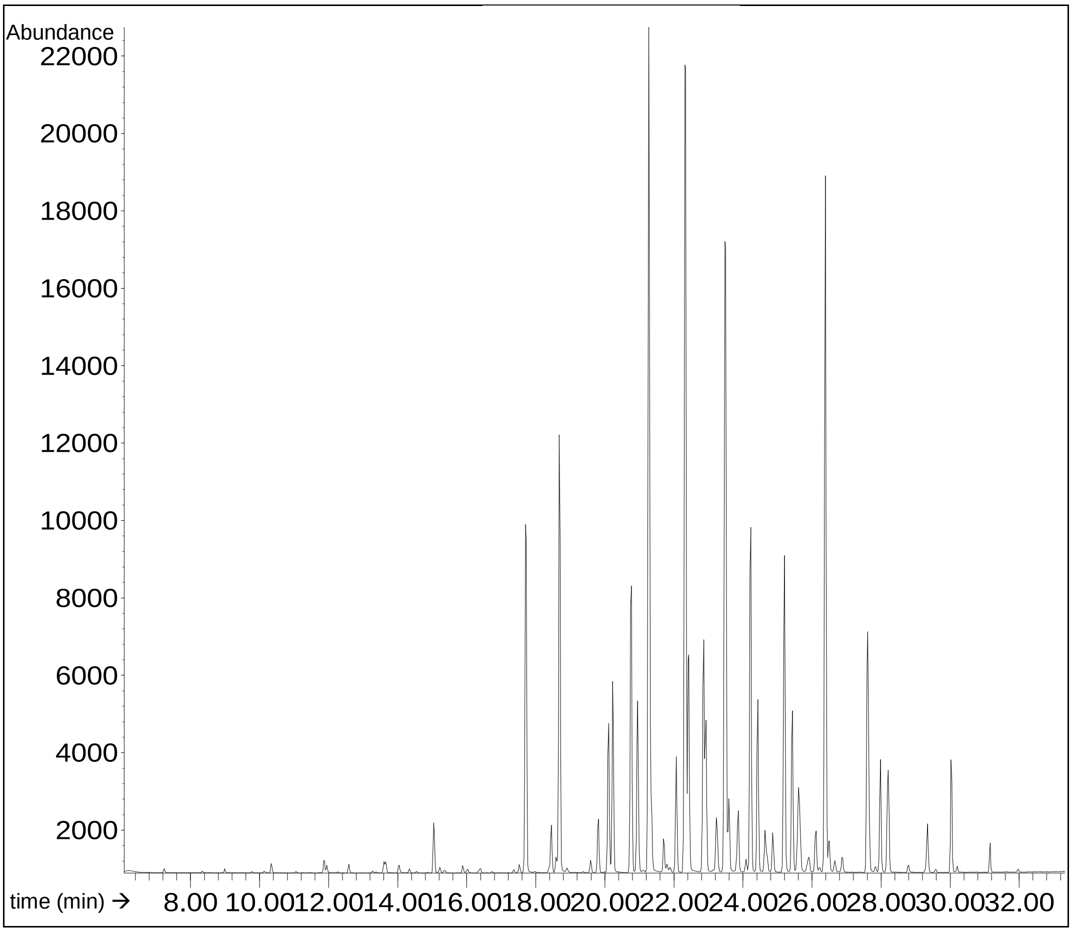

Figure 4: GC-MS spectra for the Aroclor 1260

Aroclor 1260 is the commercial mixture from Montanto US that contains the highest degree of chlorination. A high degree of chlorination means that all the congeners that the mixture contains are highly chlorinated. In the case of Aroclor 1260, the congeners are mainly penta, hexa, hepta and octo-chlorinated. In the spectra is possible to appreciate this thus, from retention time 18 to approximately 20.5 minutes, they appear the peaks from the PCBs with five chlorines. From 20.5 to 23 minutes, the ones with 6 chlorines, from 23 to 28 minutes, the ones with seven and from 28 to 30 minutes, the ones with eight (Schulz 1989).

3.1.1.2 Fenton reagents

For the Fenton treatment it has been used hydrogen peroxide (H_2O_2) with a concentration of 30% and a density of 1.11 g/ml and $FeSO_4.7H_2O$ which has a molecular weight 278 g/mol.

3.1.1.3 Adjust of the pH

The Fenton reaction has been proved to achieve the highest reduction at pH=3 (Parsons 2004). In order to have this pH, the pH of the solutions of all the reagents has been adjusted. For adjusting the pH it has been used 1M NaOH, 0.1M NaOH and dissolved NaOH for basifying and 0.5M H_2SO_4, 0.05M H_2SO_4 and dissolved H_2SO_4 for acidifying.

3.1.2 Preliminary test

As a preliminary approximation to surface treatment, the inner surfaces of three test tubes were contaminated with 10 mg/m^2 of Aroclor 1260 and then treated by Fenton treatment. The following figure shows a sketch of the glasses and their contaminated surface.

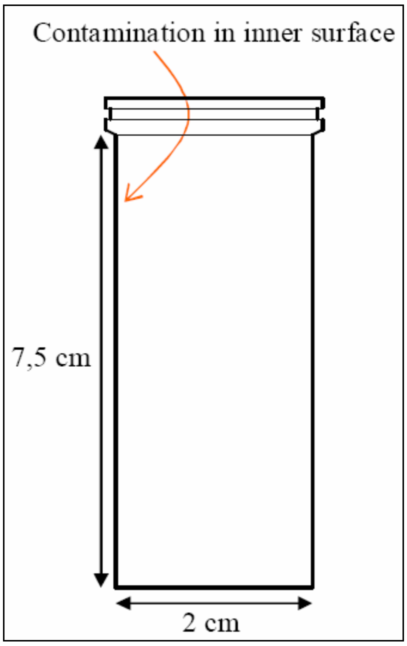

Figure 5: Sketch of the contaminated surface of the glass test tubes

3.1.2.1 *Characterisation of the tubes*

The tubes were made from glass and had a cap made from PTFE. Their diameter was 2 cm and their height 7.5 cm. With these dimensions it was possible to calculate the test tube's surface:

Length of the circumference = Lc = 2 x π x r = 2 x π x 1 cm = 6.28 cm

Side area = Lc x High = 47. 12 cm^2

Circumference area = π x r^2 = π x 1^2 = 3.14 cm^2

Total area = A = Side area + Circumference area = **50.26 cm^2 ≈ 50 cm^2**

3.1.2.2 *Contamination of the surfaces*

The surfaces were contaminated with a concentration of 10 mg/m^2 of Aroclor 1260. This concentration, though big, has been found to be inside possible ranges (Kuusisto *et al.* 2006-a & b). It was chosen because, provided the fact that the area of the tube was very small, the quantity of reagents to add would had been impossible to take. The concentration of the sample of Aroclor was of 100 mg/l.

In order to know the needed quantity of Aroclor, the following calculus was made:

$$\boxed{50\ \mathrm{cm}^2 \cdot \frac{\mathrm{m}^2}{10^4\,\mathrm{cm}^2} \cdot \frac{10\ \mathrm{mg}}{\mathrm{m}^2} \cdot \frac{1\mathrm{l}}{100\ \mathrm{mg}} \cdot \frac{1000\ \mathrm{ml}}{\mathrm{l}} = 0{,}5\ \mathrm{ml}}$$

The procedure of contamination consisted firstly of the addition of the 0.5 ml of Aroclor in the tubes and then a 5 ml quantity of acetone. The Aroclor dissolved in acetone was spread though all the calculated surface trying to avoid the cap and the acetone was then evaporated under a gently stream of nitrogen.

3.1.2.3 *Quantity of H_2O_2*

The ratio used for this treatment was 100 H_2O_2 : 1 Aroclor (w/w). This ratio was chosen randomly as a first approach. The solution of H_2O_2 used was in 30% in weight and had a density of 1.11 g/ml. With this information the quantity of hydrogen peroxide (pH = 3) was possible to calculate:

$$0{,}5\ \text{ml Aroclor}\cdot\frac{\text{l}}{1000\ \text{ml}}\cdot\frac{100\ \text{mg Aroclor}}{\text{l}}\cdot\frac{100\ \text{mg } H_2O_2}{1\ \text{mg Aroclor}}=5\ \text{mg } H_2O_2$$

$$5\ \text{mg } H_2O_2\cdot\frac{\text{g}}{10^3\text{mg}}\cdot\frac{100\ \text{g solution}}{30\ \text{g } H_2O_2}\cdot\frac{1\text{ml}}{1{,}11\ \text{g}}=0{,}015\ \text{ml solution}$$

A quantity of 15 µl of hydrogen peroxide (pH = 3) was added.

3.1.2.4 Quantity of Fe^{2+}

The ratio used was of 10 H_2O_2 : 1 Fe^{2+} (m/m). It was decided that the volume of the reaction would be 10 ml, so the addition of the Fe^{2+} was in 10 ml of a solution $FeSO_4$. 100 ml of $FeSO_4$ solution were prepared in such a way that, in 10 ml of this solution, all the Fe^{2+} needed for the reaction was provided. The quantity of $FeSO_4.7H_2O$ (M = 278 g/mol) needed, can be found with this calculus:

$$5\ \text{mg } H_2O_2\cdot\frac{\text{mmol}}{34\ \text{mg}}\cdot\frac{1\ \text{mmol } Fe^{2+}}{10\ \text{mmol } H_2O_2}=0{,}0147\ \text{mmol } Fe^{2+}$$

$$100\ \text{ml}\cdot\frac{0{,}0147\ \text{mmol}}{10\ \text{ml}}\cdot\frac{278\ \text{mg}}{\text{mmol}}=40{,}87\ \text{mg } Fe^{2+}\ (\text{in } 100\ \text{ml})$$

The solution of $FeSO_4$ was 14.7 µM and was prepared by adding 40.87 mg of $FeSO_4.7H_2O$ to 100 ml of miliQ water. The pH was adjusted to 3.

3.1.3 Enhancement of reduction

In order to get better results than in the preliminary tests, different ratios between the contaminant and the H_2O_2 and different ways of application were tested in glass tubes contaminated with 7.38 mg/m^2 of Aroclor 1260.

3.1.3.1 Characterisation of the tubes

The tubes, as the preliminary ones, were made from glass and had a cap made from PTFE. Their dimensions were a bit bigger than the previous, having a diameter of 2.5 cm and a height of 8 cm. With these dimensions it was possible to calculate the test surface, which is also the inner one:

Length of the circumference = Lc = 2 x π x r = 2 x π x 1.25 cm = 7.85 cm

Side area = Lc x High = 62.83 cm^2

Circumference area = π x r^2 = π x 1.25^2 = 4.90 cm^2

Total area = A = Side area + Circumference area = **67.74 cm^2 ≈ 68 cm^2**

3.1.3.2 *Contamination of the surfaces*

The surfaces were contaminated with a concentration of 7.38 mg/m^2 of Aroclor 1260. This concentration supposes the same amount of Aroclor to add as in the preliminary test (0.5 ml) and also slightly decreases the previous concentration bearing more resemblance to real PCB surface concentration.

The procedure of contamination, like in the preliminary tests, consisted firstly of the addition of the 0.5 ml of Aroclor in the tubes and then a 5 ml quantity of acetone. The Aroclor dissolved in acetone was spread through all the calculated surface trying to avoid the cap and the acetone was then evaporated under a gently stream of nitrogen.

3.1.4 Treatment of bricks

3.1.4.1 *Characterisation of the bricks*

For the experiment two new bricks made from clay have been used. The red colour is due to the presence of ferrous oxide, FeO_2 that becomes Fe_2O_3 with the burning. The dimensions of the bricks used are 26.5 x 12.5 x 8 cm.

The surface used for the treatment is the one with dimensions 26.5 x 12.5 cm. Thus, the total area of this surface is 331.25 cm^2.

Bricks have been divided in eight smaller surfaces of 5.9 x 5.75 cm and a separation between them of 1 cm and in each of this divisions a different ratio and time of reaction has been carried out. The area of the surfaces is 33.8 cm^2. The divisions of the bricks can be appreciated in the figure 6:

Figure 6: Treated bricks

3.1.4.2 Contamination of the surfaces

The surfaces were contaminated with a concentration of 1 mg/m^2 of Aroclor 1260. The concentration is smaller than in the glasses because the surface of the bricks is bigger and the quantity of reagent to add was inside the limits and nearer to the real concentration found in the surfaces (210 µg/m^2) (Kuusisto *et al.* 2006-a). The concentration of the sample of Aroclor was also of 100 mg/l.

In order to know the needed quantity of Aroclor, the following calculus was made:

$$\boxed{331\ \text{cm}^2 \cdot \frac{\text{m}^2}{10^4\,\text{cm}^2} \cdot \frac{1\,\text{mg}}{\text{m}^2} \cdot \frac{1\text{l}}{100\ \text{mg}} \cdot \frac{1000\ \text{ml}}{\text{l}} = 0{,}331\ \text{ml}}$$

The 331 µl of Aroclor were dissolved in 10 ml of acetone and this mixture was applied to the surface of the bricks with a non-reactive pastry brush.

3.2 Laboratory methods

3.2.1 Preliminary Fenton treatment

3.2.1.1 Addition of reagents

The three test tubes which were previously contaminated, were treated in the following way: one was left as blank and only 10 ml of miliQ water were added, another one was led only with hydrogen peroxide in order to know its behaviour without the catalyst and the last one was prepared with the Fenton treatment (the hydrogen peroxide and the iron. All the solutions have been added at pH=3 since this is the optimal pH (Parsons 2004). Table 3 presents a summary of the three test tubes:

Table 3: Preparation of the test tubes

Tube number	H_2O_2 (µl)	$FeSO_4$ 14.7 µM (ml)	miliQ water (ml)
1 (Fenton)	15	10	-
2 (H_2O_2 blank)	15	-	10
3 (blank)	-	-	10

3.2.1.2 Reaction

The time of reaction was 72 hours (3 days). The reaction was carried out by continuous stirring at 150 rpm.

The stop of the reaction was done by addition of Na_2SO_3. The stopping reaction is shown in equation 8:

$$Na_2SO_3 + H_2O_2 \rightarrow Na_2SO_4 + H_2O \qquad (8)$$

5mg of H_2O_2 were added to the tubes. The quantity of Na_2SO_3 needed, which is contained in a solution of 20% in weight, is:

$$\boxed{5\ \text{mg}\ H_2O_2 \cdot \frac{1\ \text{mmol}}{34\ \text{mg}} \cdot \frac{1\ \text{mmol}\ \ Na_2SO_3}{1\ \text{mmol}\ \ H_2O_2} \cdot \frac{126\ \text{mg}}{1\ \text{mmol}} \cdot \frac{100\ \text{mg solution}}{20\text{g}\ \ Na_2SO_3} \cdot \frac{1\ \text{ml}}{10^3\ \text{mg}} = 0{,}092\ \ \text{ml solution}}$$

Theoretically, 0.092 ml of solution are needed, but it was necessary to multiply this number with 2 to apply an excess of 100%. The excess is needed to ensure that all the hydrogen peroxide will be reduced, as other products can be also reduced in this addition. 0.092 ml times 2 is 0.184 ml, so rounding up, 0.2 ml will be added.

3.2.1.3 Extraction of PCBs

For the extraction, 10 ml of acetone/hexane (1:9 v/v) were added to the tubes. The tubes were put 15 minutes to the ultrasonic bath and shaken vigorously during one minute. With a Pasteur pipet the organic phase was extracted and the extraction was carried out again in the aqueous phase.

3.2.2 Fenton treatment of glass tubes

3.2.2.1 Distribution of the treatment

The treatment has been carried out at different ratios, ways of application and ways of extraction. The time of reaction has been fixed in 72 hours. Ratios of 41:50:1, 82:100:1, 204:250:1, 408:500:1 and 816:1000:1 Fe^{2+}/H_2O_2/Aroclor (w/w/w) were applied, which suppose a ratio of Fe^{2+}/H_2O_2 constant and equals to 1:10 (mol/mol). Two ways of application and two ways of extraction have been tested for each ratio. One way of application was to add all the hydrogen peroxide in time and the other way was to apply it on one third per each one of the three days. On the other hand, one way of extraction was, as in the preliminary tests; add 5 ml of 4:1 hexane/acetone mixture and the other way was to clean the surface with ethanol moisturized cotton. As in the preliminary tests, the solutions of the reagents have been added at pH=3 (Parsons 2004).

3.2.2.2 Quantity of H_2O_2

The quantity of H_2O_2 depends on the ratio used. For instance, for the tubes with a treatment ratio of 100 H_2O_2 : 1 Aroclor (w/w), the quantity of H_2O_2 3% in weight and density of 1.11 g/ml is:

$$\boxed{\begin{array}{c} 0{,}5\ \text{ml Aroclor} \cdot \dfrac{\text{l}}{1000\ \text{ml}} \cdot \dfrac{100\ \text{mg Aroclor}}{\text{l}} \cdot \dfrac{100\ \text{mg}\ H_2O_2}{1\ \text{mg Aroclor}} = 5\ \text{mg}\ H_2O_2 \\ 5\ \text{mg}\ H_2O_2 \cdot \dfrac{\text{g}}{10^3\ \text{mg}} \cdot \dfrac{100\ \text{g solution}}{3\ \text{g}\ H_2O_2} \cdot \dfrac{1\text{ml}}{1{,}11\ \text{g}} = 0{,}150\ \text{ml solution} \end{array}}$$

3.2.2.3 Quantity of Fe^{2+}

As in the preliminary tests, the ratio used was of 10 H_2O_2 : 1 Fe^{2+} (m/m). There have been used three different ratios, so three different Fe^{2+} solutions have been added. It has been decided also in this case that the volume of the reaction would be 10 ml, so the addition of the Fe^{2+} was in 10 ml of a solution $FeSO_4$. As the calculus is the same as in the preliminary tests, is going to be omitted. As a summary, table 4 shows for the three ratios, the quantity added of each reagent for the tubes with reagents added at once and table 5 shows the quantity for the reagents added once per day.

Table 4: Fenton reagents on the case of addition at once

Ratio	H_2O_2 (µl)	10 ml $FeSO_4$ (mM)
50 H_2O_2 : 1 Aroclor	75	0.74
100 H_2O_2 : 1 Aroclor	150	1.47
250 H_2O_2 : 1 Aroclor	375	3.68
500 H_2O_2 : 1 Aroclor	750	7.35
1000 H_2O_2 : 1 Aroclor	1500	14.7

Table 5: Fenton reagents on the case of addition once per day

Ratio (w/w)	H_2O_2 (µl)	10 ml $FeSO_4$ (mM)
50 H_2O_2 : 1 Aroclor	25	0.74
100 H_2O_2 : 1 Aroclor	50	1.47
250 H_2O_2 : 1 Aroclor	125	3.68
500 H_2O_2 : 1 Aroclor	250	7.35
1000 H_2O_2 : 1 Aroclor	500	14.7

3.2.2.4 Reaction

The time of reaction was 72 hours (3 days). As in the previous tests, the reaction was carried out by continuous stirring at 150 rpm.

The stop of the reaction was done again by addition of Na_2SO_3. For the first ratio of 50:1, 0.2 ml of Na_2SO_3 were added, for the ratio of 100:1, 0.4 ml, for the ratio of 250:1, 1 ml, for the ratio of 500:1, 2 ml and for the ratio of 1000:1, 4 ml were added.

3.2.2.5 Extraction of PCBs

As commented before, two ways of extraction were carried out in this part of the research. The first way coincides with the previous treatment, although the ratio of hexane / acetone slightly changes. They are used 5 ml of acetone/hexane (1:4 v/v). In order to know the loss of contaminant during the extraction procedure, 500 µl of PCB#209 2 mg/l are used as surrogate. Then, the tubes have been put 15 minutes to the ultrasonic bath and shaken vigorously during one minute. With a Pasteur pipet the organic phase has been extracted and the extraction has been carried out again in the aqueous phase.

The second way of extraction has been with a cotton moisturized with 2.5 ml of ethanol. For extracting the PCBs from the cotton, 5 ml of 4:1 hexane/acetone (v/v) mixture have been added to the glass containing the cotton and 500 µl of surrogating agent are added. The glasses are vortexed during 10 seconds and then they are treated in the ultrasonic bath during one hour. Then the liquid phase is separated from the cotton with a Pasteur pipet and the extraction is repeated in the cotton. In the tube with the two extractions, firstly 1 ml of miliQ water is added, and after shaking vigorously the upper layer (hexane) is removed. Secondly an addition of 3 ml of miliQ water is needed and the procedure is repeated.

3.2.3 Fenton treatment of bricks

3.2.3.1 Distribution of the treatment

In the same bricks, different time of reaction (one, three or seven days) and applications (all the H_2O_2 at once or one part per day) have been tested maintaining the same ratio between reagents (for brick #1 the ratio H_2O_2/Aroclor was 100:1 (w/w) and for the brick #2 500:1 (w/w)). At the same time, different ratios have been tested maintaining the same time of reaction of 3 days and one application per day in brick #1 the ratio tested has been H_2O_2/Aroclor 50:1 (w/w) and in brick #2 H_2O_2/Aroclor 1000:1 (w/w) and 250:1 (w/w). The ratio of H_2O_2/Fe^{2+} has been maintained constant and equal to 30:1 (mol/mol). All the solutions have been added at pH=3 (Parsons 2004). A summary of the distribution can be observed in the next two figures:

Brick #1:

Sample 11 time reaction = 3 days application = at once H_2O_2 / Aroclor 100:1 Without Fe^{2+}	Sample 12 time reaction = 1 day application = at once H_2O_2 / Aroclor 100:1 1 Fe^{2+}:30 H_2O_2	Sample 13 time reaction = 3 days application = at once H_2O_2 / Aroclor 100:1 1 Fe^{2+}:30 H_2O_2	Sample 14 time reaction = 7 days application = at once H_2O_2 / Aroclor 100:1 1 Fe^{2+}:30 H_2O_2
Blank	Sample 15 time reaction = 3 days application = 3 times H_2O_2 / Aroclor 50:1 1 Fe^{2+}:30 H_2O_2	Sample 16 time reaction = 3 day application = 3 times H_2O_2 / Aroclor 100:1 1 Fe^{2+}:30 H_2O_2	Sample 17 time reaction = 7 days application = 7 times H_2O_2 / Aroclor 100:1 1 Fe^{2+}:30 $H_2O_2^+$

Figure 7: Distribution of treatment for brick #1

Brick # 2:

Sample 21 time reaction = 3 days application = 3 times H_2O_2 / Aroclor 1000:1 1 Fe^{2+}:30 H_2O_2	Sample 22 time reaction = 1 day application = at once H_2O_2 / Aroclor 500:1 1 Fe^{2+}:30 H_2O_2	Sample 23 time reaction = 3 days application = at once H_2O_2 / Aroclor 500:1 1 Fe^{2+}:30 H_2O_2	Sample 24 time reaction = 7 days application = at once H_2O_2 / Aroclor 500:1 1 Fe^{2+}:30 H_2O_2
Blank	Sample 25 time reaction = 3 days application = 3 times H_2O_2 / Aroclor 250:1 1 Fe^{2+}:30 H_2O_2	Sample 26 time reaction = 3 day application = 3 times H_2O_2 / Aroclor 500:1 1 Fe^{2+}:30 H_2O_2	Sample 27 time reaction = 7 days application = 7 times H_2O_2 / Aroclor 500:1 1 Fe^{2+}:30 $H_2O_2^+$

Figure 8: Distribution of treatment for brick #2

3.2.3.2 Addition of H_2O_2

The quantity of hydrogen peroxide added depends on the ratio used in each square and in the number of times that this reagent will be applied. The solution of H_2O_2 used has been diluted 100 times from the solution 30% in weight because the quantities needed from the original were too small. The calculus for the first division (sample 11) is:

$$33{,}78\ \text{cm}^2 \cdot \frac{1\ \text{mg}}{\text{m}^2} \cdot \frac{1\ \text{m}^2}{10^4\ \text{cm}^2} \cdot \frac{100\ \text{mg}\ H_2O_2}{1\ \text{mg Aroclor}} = 0{,}3378\ \text{mg}\ H_2O_2$$

$$0{,}3378\ \text{mg}\ H_2O_2 \cdot \frac{\text{g}}{10^3\ \text{mg}} \cdot \frac{100\ \text{g solution}}{0{,}3\ \text{g}\ H_2O_2} \cdot \frac{1\text{ml}}{1{,}11\ \text{g}} = 0{,}1014\ \text{ml solution}$$

For the sample 11, 100µl of H_2O_2 were applied with a non-reactive pastry brush. In case of the samples with many times of application, the quantity of H_2O_2 was divided by the number of times that had to be applied. An image of the application with a pastry brush can be observed in figure 9:

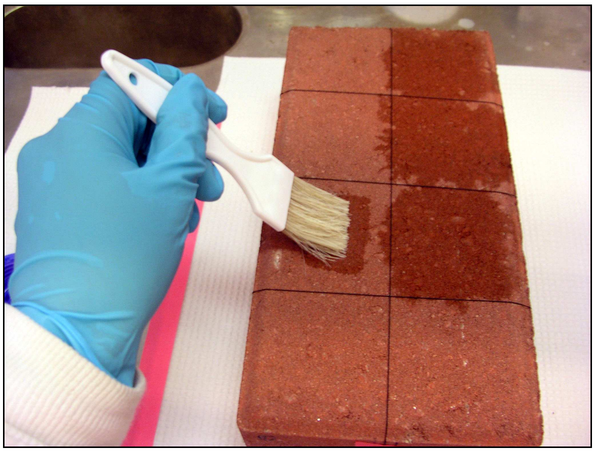

Figure 9: Image of the application of the treatment

3.2.3.3 Addition of Fe^{2+}

The ratio used was of 30 H_2O_2 : 1 Fe^{2+} (m/m). The application of the Fe^{2+} has been carried out with non-reactive pastry brush in a solution of 2.5 ml. The quantity of $FeSO_4.7H_2O$ (M = 278 g/mol) needed in sample 12, can be found with this calculus:

$$\boxed{\begin{array}{c} 337{,}8\ \mu g\ H_2O_2 \cdot \frac{\mu mol}{34\ \mu g} \cdot \frac{1\ \mu mol\ Fe^{2+}}{30\ \mu mol\ H_2O_2} = 0{,}331\ \mu mol\ Fe^{2+} \\ \frac{0{,}331\ \mu mol}{2{,}5\ ml} \cdot \frac{mmol}{10^3\ \mu mol} \cdot \frac{10^3\ ml}{l} = 0{,}132\ mM \end{array}}$$

For the sample 12, 2.5 ml of Fe^{2+} 0.132 mM have been added. In all the division the quantity of Fe^{2+} has been added at once.

A summary of the different quantities added can be observed in the following figures:

Brick #1:

Sample 11 time reaction = 3 days application = at once 101. 4 µl H_2O_2 2.5 ml miliQ pH=3	Sample 12 time reaction = 1 day 2.5 ml Fe^{2+} 0.132 mM 101.4 µl H_2O_2 application = at once	Sample 13 time reaction = 3 days 2.5 ml Fe^{2+} 0.132 mM 101.4 µl H_2O_2 application = at once	Sample 14 time reaction = 7 days 2.5 ml Fe^{2+} 0.132 mM 101.4 µl H_2O_2 application = at once
Blank	Sample 15 time reaction = 3 days 2.5 ml Fe^{2+} 0.066 mM 16.9 µl H_2O_2 application = 3 times	Sample 16 time reaction = 3 day 2.5 ml Fe^{2+} 0.132 mM 33.81 µl H_2O_2 application = 3 times	Sample 17 time reaction = 7 days 2.5 ml Fe^{2+} 0.132 mM 14.49 µl H_2O_2 application = 7 times

Figure 10: Addition of quantities for brick #1

Brick # 2:

Sample 21 time reaction = 3 days 2.5 ml Fe^{2+} 1.32 mM 338.14 µl H_2O_2 application = 3 times	Sample 22 time reaction = 1 day 2.5 ml Fe^{2+} 0.66 mM 507.2 µl H_2O_2 application = at once	Sample 23 time reaction = 3 days 2.5 ml Fe^{2+} 0.66 mM 507.2 µl H_2O_2 application = at once	Sample 24 time reaction = 7 days 2.5 ml Fe^{2+} 0.66 mM 507.2 µl H_2O_2 application = at once
Blank	Sample 25 time reaction = 3 days 2.5 ml Fe^{2+} 0.33 mM 84.5 µl H_2O_2 application = 3 times	Sample 26 time reaction = 3 day 2.5 ml Fe^{2+} 0.66 mM 169.07 µl H_2O_2 application = 3 times	Sample 27 time reaction = 7 days 2.5 ml Fe^{2+} 0.66 mM 72.45 µl H_2O_2 application = 7 times

Figure 11: Addition of quantities for brick #2

3.2.3.4 Extraction of PCBs

The extraction from the surface of the bricks has been done with a wipe moisturized with 2.5 ml of ethanol. The reaction has been stopped with 100 µl of Na_2SO_4. An image of the method used for the extraction can be observed in figure 12:

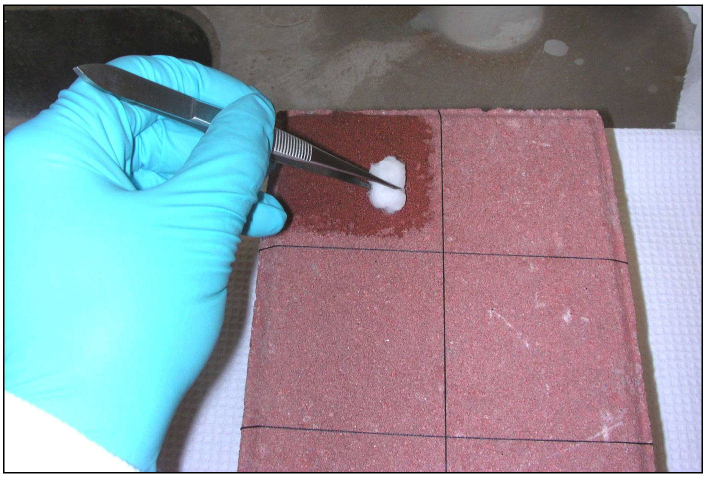

Figure 12: Image of the method of extraction

For extracting the PCBs from the cotton, the procedure that has been carried out is the same as the one used for the glass tubes. Firstly, 100 µl of PCB#209 2 µg/ml have been added as surrogating agent. Then 5 ml of a mixture 4:1 hexane/acetone has been added and vortexed during 10 seconds. The liquid phase has been separated and the extraction is repeated. In the tube with the two extractions, firstly 1 ml of miliQ water is added, and after shaking vigorously the upper layer (hexane) is removed. Secondly an addition of 3 ml of miliQ water is needed and the procedure is repeated.

3.3 Analysis (Gas Chromatography with Mass Spectrometry)

Measuring of Aroclor 1260 concentration was carried out using gas chromatograph with a mass-selective detector (GC-MSD) HP-6890 model G1530A in SIM mode. 1 μl was injected in a cross-linked (5%-phenyl)-methylpolysiloxane capillary column, HP-5MS (30.0 m x 251 μm x 0.25 μm film thickness).

The GC-MSD temperature program was as follows: the temperature was held at 80ºC for 1 min, then increased at the rate of 30ºC/min up to the temperature of 150ºC, 4ºC/min up to the temperature of 250º and 10ºC/min up to the temperature of 300ºC.

The velocity of carrier gas (helium) was 1 ml/min and the coefficient of variation for GC-MSD method was 3.8 %. Aroclor 1260 concentrations were measured as area of total ion chromatogram (TIC) from retention time of PCB#95 to retention time of PCB#205 (Schulz *et al.* 1989). The detection limit was 0.25 mg/l. Aroclor 1260; PCB#30 and PCB#209 were used as external, internal and surrogate standards, respectively. For GC-MSD method Aroclor 1260 contaminated surface recovery averaged was of 77.9%.

3.3.1 Calibration lines

In order to prepare the calibration line of the external standard, five solutions from Aroclor 1260 were prepared. The concentration of the five solutions was: 1 mg/l, 10 mg/l, 20 mg/l, 40 mg/l and 60 mg/l. As they were diluted from Aroclor 1260 with a concentration of 100 mg/l:

$$\boxed{10\ \text{ml} \cdot \frac{1\ \text{mg}}{\text{l}} \cdot \frac{\text{l}}{10^3\ \text{ml}} \cdot \frac{\text{l}}{100\ \text{mg}} \cdot \frac{10^3\ \text{ml}}{\text{l}} = 0{,}1\ \text{ml}\ \ \text{(for the 1 mg/l solution)}}$$

In the table 6 is shown the quantities added to each 10 volumetric flasks of the calibration line.

Table 6: Calibration line's characteristics for the Aroclor 1260					
Calibration point	1 mg/l	10 mg/l	20 mg/l	40 mg/l	60 mg/l
Quantity of Aroclor 1260	0.1 ml	1 ml	2 ml	4 ml	6 ml

The microvials for the analysis were prepared adding 1 ml of the calibration sample and 10 μl of internal standard PCB # 30.

The figure 13 for the calibration line for the Aroclor 1260 can be seen hereby:

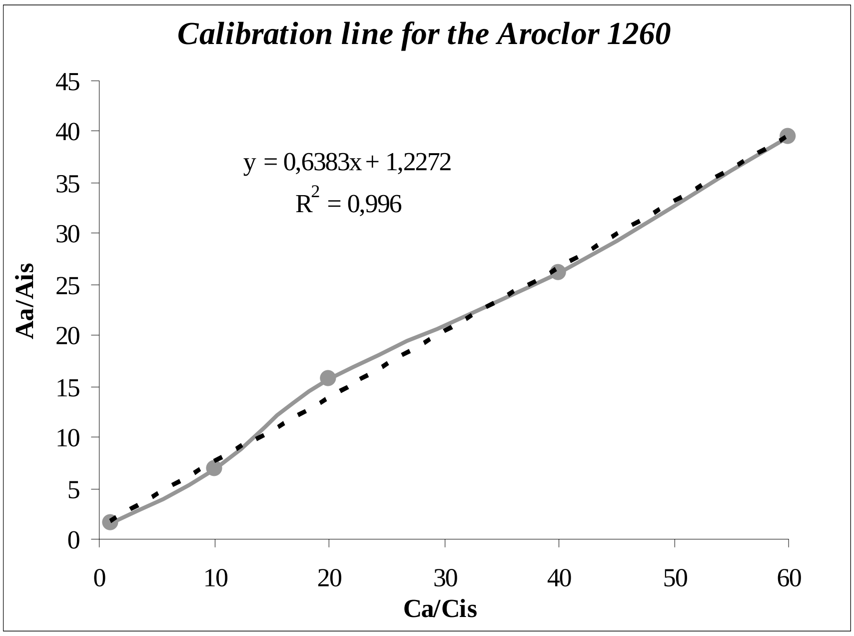

Figure 13: Calibration line for the Aroclor 1260

A calibration line has also been made for the surrogate. The line has been made with the concentrations of surrogate (C_{surr}) of 0.1 mg/l, 0.5 mg/l, 1 mg/l, 1.5 mg/l and 2 mg/l. The figure 14, which shows C_{surr}/C_{is} in front of the area of the peaks S_{surr}/S_{is}, has been:

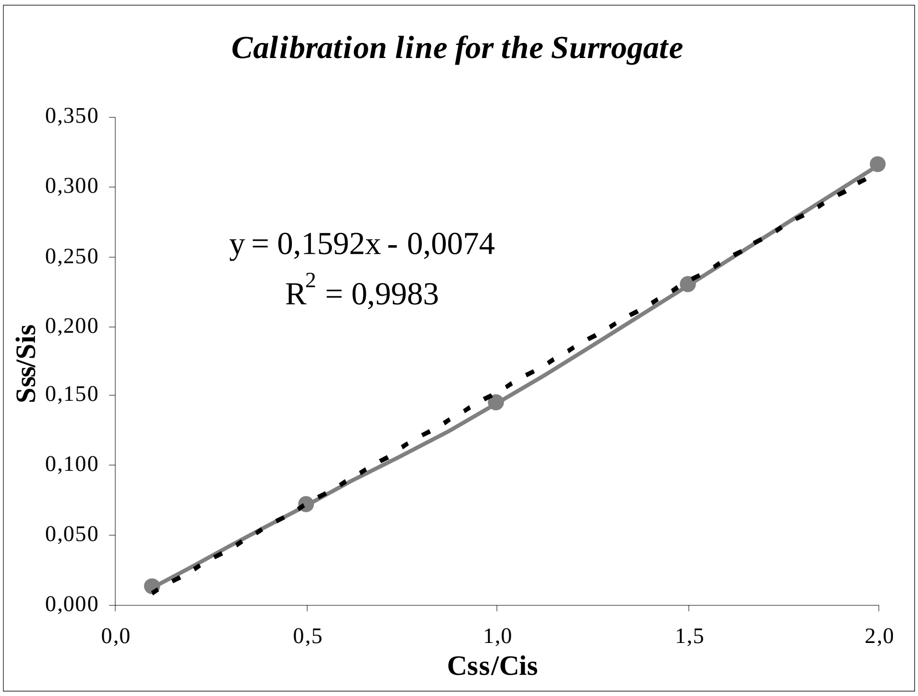

Figure 14: Calibration line for the surrogate

3.3.2 Preparation of the samples for the analysis

- <u>Samples from the preliminary glass test tubes</u>

15 ml of the organic phase from each tube were taken and put into new tubes. In order to concentrate the sample, hexane has been evaporated under gentle steam of N_2. 1 ml of hexane has been added and spread in all the walls.

- <u>Samples from the enhancement of reaction and from the bricks</u>

For both ways of extraction of the glass test tubes and for the cotton from the bricks, the first step is to concentrate the samples to 1 or 2 ml of hexane under a gentle nitrogen flux. Then, approximately the same amount of H_2SO_4 (98%) is added in order to clean the samples from non desirable substances. After 20 minutes of rest, the hexane is separated with a Pasteur pipet.

The hexane in the evaporated until complete dryness and 1 ml of internal standard (PCB#30 1 mg/l) is added. After a rest of one hour, the samples are transferred to a GC-MS microvial.

4 RESULTS AND DISCUSSIONS

4.1 Preliminary test

As an approach of the efficiency of the Fenton treatment on surfaces, a simulation over the inner surface of test tubes was made. Three tubes were contaminated and treated as explained in the previous section. P1, P2 and P3 were the names of the tubes with the Fenton treatment, the treatment without catalyst and the blank respectively. As it is a preliminary test, no calibration line has been used and only the relation between the blank and the sample has been studied. In the table 7 the results from the GC-MS analysis are shown. % of reduction shows the relation between the relation of areas from the samples (A_A/A_{IS}) and the relation of areas from the blank.

Table 7: Results from the preliminary tests

	Area IS	**Area Aroclor**	**A_A/A_{IS}**	**% reduction**	**Description**
P1	474256	4029541	8.5	45.4	*Fenton*
P2	530671	7521122	14.3	8.9	*Only H_2O_2*
P3	517255	8045864	15.5	0	*Blank*

As it can be appreciated from the table, an approximate 45% of reduction from the blank has been achieved in this preliminary method using the Fenton treatment, which corresponds to a weight ratio of 81.8:100:1 Fe^{2+}/H_2O_2/Aroclor 1260. On the other hand, if no iron as catalyst was used, the reduction after three days of reaction was only of 8%, which demonstrated that the use of catalyst is needed for the reaction to take place as has been demonstrated before (Kaštánek *et al.* 2004, Dercová *et al.* 1999, Manzano *et al.* 2001, Parsons 2004).

4.2 Enhancement of reduction

As explained before, there have been taken five different ratios between the hydrogen peroxide and the Aroclor: 50:1, 100:1, 250:1, 500:1 and 1000:1 H_2O_2 / Aroclor (w/w). The ratio between the iron and the H_2O_2 has been maintained constant and equals to 1:10 Fe^{2+}/H_2O_2 (mol/mol). Two ways of addition of hydrogen peroxide were tested in order to improve the results of the preliminary test. The first way was to add the complete amount of hydrogen peroxide at the beginning of the reaction and the other was to apply one third every day of the three that the reaction lasted. Two ways of extraction the PCBs were carried out, one with a solution of hexane and acetone and other with a wiped cotton.

In order to control the presence of PCBs in the water were the reagents were dissolved, it was kept and analyzed, once per each ratio and way of addition and both for the samples and for the blanks.

4.2.1 Influence of the ratio of hydrogen peroxide

The next figure shows the results of reduction of PCB vs. ratio on the surfaces for both ways of addition of hydrogen peroxide and for the extraction with a solution with hexane and acetone.

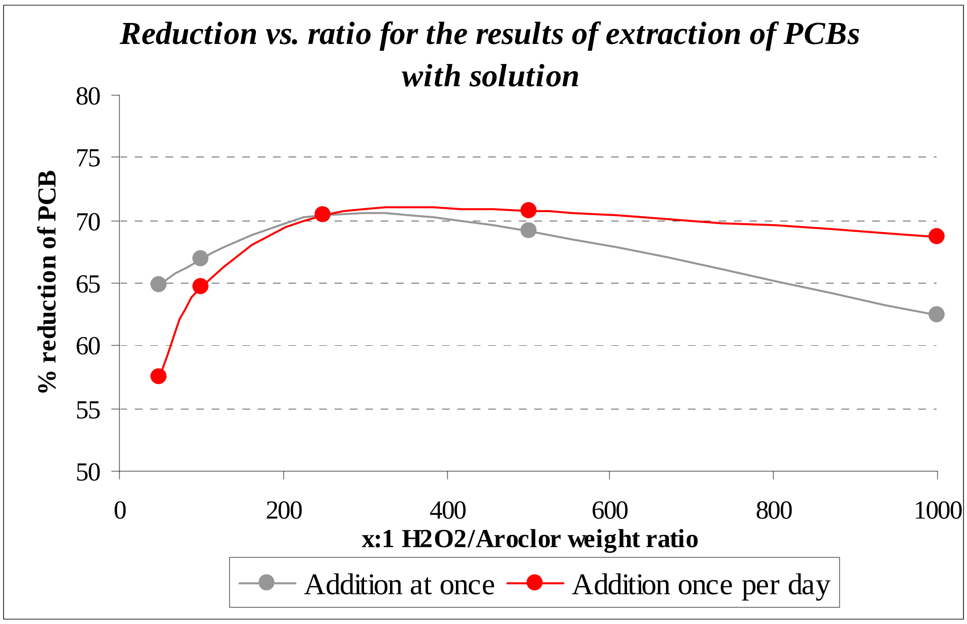

Figure 15: Results of % reduction vs. ratio for the extraction of PCBs with solution of hexane and acetone on the surfaces (ratio Fe/H_2O_2 constant and equals to 1:10 (mol/mol)

As it is possible to appreciate, no big difference can be seen between the two ways of adding the hydrogen peroxide. For the high ratios, addition once per day seems more favourable whereas for the small ratios, addition at once is clearly better. This might be caused because at low ratios, addition at once contributes with more hydrogen peroxide in the first day, fact that accelerates the reaction at the beginning. On the other hand, at high ratios, with the addition once per day, the first day a lower concentration of hydrogen peroxide exists and so it resembles the optimal concentration and the reaction is accelerated.

The best ratio for the reaction that involves this test is 204:250:1 Fe^{2+}/H_2O_2/Aroclor (w/w/w), with which is possible to achieve a 70.5% of reduction in both ways of addition. Further addition of oxidant does not seem to be as efficient. The higher degree of degradation when increasing the ratio is expected, due to the higher presence of hydroxyl radicals in the media. On the other hand, the decreasing after one point might be the result of the deactivation process of the hydroxyl radicals deriving from their high concentrations in the medium (equation 9) (Manzano *et al.* 2001). Additionally, at high ratios of hydrogen peroxide and Fe^{2+} it has been found that there is a consumption of hydroxyl radicals due to reaction with them (equation 4 and 10) (Walling 1975). Behaviour like this had already been observed in previous researches (Fronduti 2005, Manzano *et al.* 2001).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (4)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \qquad (9)$$

$$Fe^{II} + HO_2^{\bullet} \rightarrow Fe^{III} + HO_2^{-} \qquad (10)$$

Entering into the extraction with wiped cotton aspect, in order to compare both ways of extraction, there were taken blanks (replicated) and they were extracted from both ways. Whereas the blanks from the extraction with solution were found to have a mean concentration of 45 mg/l, data that supposes a recovery of 90%, the blanks from the extraction with cotton were found to be 38 mg/l, recovery of 76%, from where it can be seen that the extraction with cotton is not as effective.

Apart from the fact that a certain amount of PCBs were being lost in the extraction with cotton, results from these analysis presented high difference from results with extraction with hexane solution. Results from the reduction of PCB in front of the ratio for the samples extracted with wiped cotton are shown in figure 16.

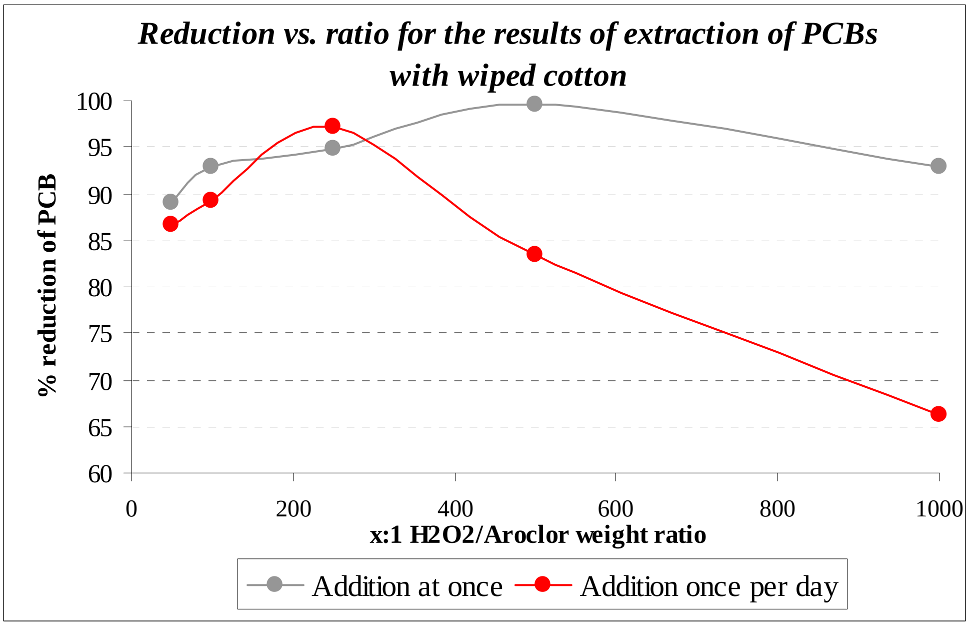

Figure 16: Results of % reduction vs. ratio for the extraction of PCBs with wiped cotton on the surfaces (ratio Fe/H_2O_2 constant and equals to 1:10 (mol/mol)

As it can be appreciated, despite the fact that the reactions were the same, results from extraction with cotton are pretty different than in figure 15, although tendency seems to be the same. Extraction with cotton is a method that entails more mistakes and uncertainties of procedure than the extraction with the solution, so the repeatability is poor. Although the same system for each of the cottons has been used, it exists a high variation between gained results. The problem may reside on the way that the cotton is scrubbed over the surface, as if one sample is scrubbed slightly more that other, the first one presents a higher concentration even if the surface the concentration was smaller.

4.2.2 Influence of the number of chlorine atoms of the PCB congener

The number of chlorine atoms in the PCB molecule is also a factor with influence in the degradation process. Figure 17 shows how as the number of chlorine increases, reduction decreases. The data of this graphic has been taken dividing the GC-MS spectra in four parts depending on the number of chlorine atoms of each peak according to the data extracted from the study made to the PCB's GC spectra made by Schulz (1989) and commented also in section 3.1.1. Then, the data were plotted as the average reduction of all the results classified in two groups: extraction with hexane and extraction with cotton.

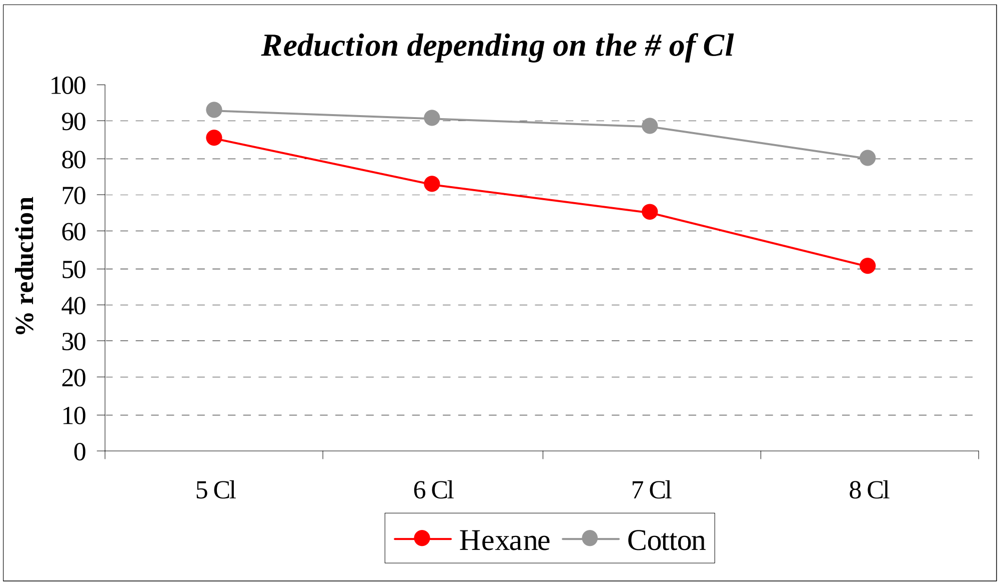

Figure 17: Results of reduction in front of the number of chlorine atoms in the molecule

This result is expected as it has been reported before (Dercová *et al.* 1999, Manzano *et al.* 2001, Aunola 2005) that degradation shows better results in low chlorinated congeners of Aroclor. Moreover, it can be noticed that depending on the number of chlorines, the difference is higher, as the cotton show better results. This might mean that extraction with cotton is worse when high chlorinated congeners are concerned, as they are less soluble in ethanol due to their bigger size. This explanation complements the one given with figure 14 where it was said that extraction with cotton in a less-reliable technique for analyzing the PCB content of a surface compared with the extraction with a solution of hexane and acetone. Nevertheless, in the section 4.2 where results from the treatment of the bricks are shown, it is explained that the only possible option for analyzing the PCB content was extracting them by wiping with an ethanol moisturized cotton, so results are expected to be worse and less accurate than in this section.

4.2.3 Presence of PCBs in the aqueous phase

In the case that involves this project, Fenton reagents were added dissolved in water. As said before, water of the reaction was separated from the surface, then kept and analyzed in order to know if there was being any presence of PCBs in the aqueous phase. Two samples of each ratio were taken, one per each of the addition methods. Additionally, the blank without Fenton reagents were given the same treatment as the samples as they were kept in stirring during three days with miliQ water in. PCBs were found in water, since as figure 18 shows, some loss was occurring during the reaction and it was highly dependent on the quantity of hydrogen peroxide used.

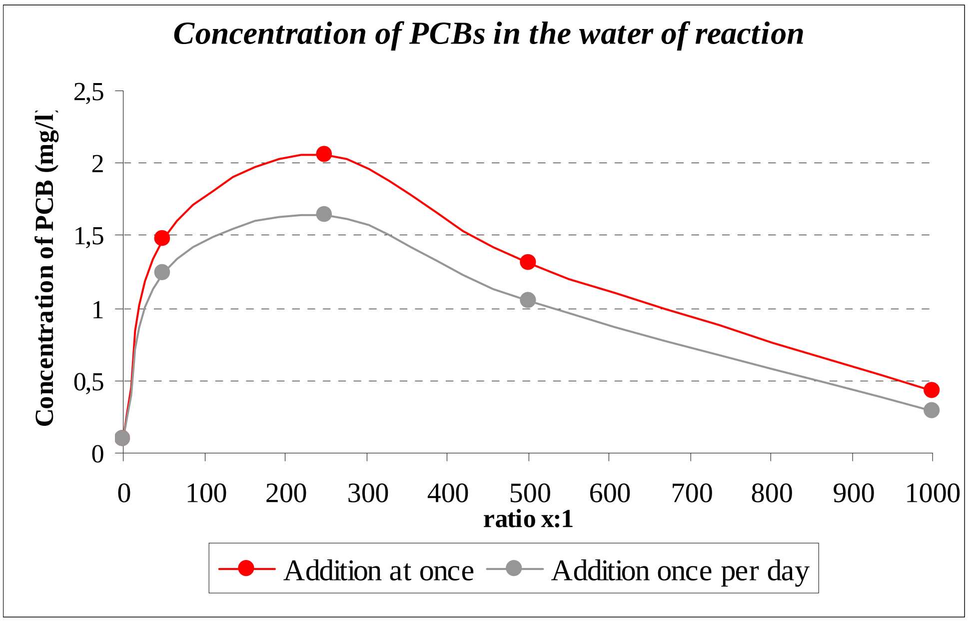

Figure 18: Results of concentration of PCBs vs. ratio for the water of the reaction in both ways of addition (the ratio 0:1 corresponds to the blank)

It can be noticed that the best result in reduction from surface coincide with the highest concentration in the water of the reaction, as at a ratio of 204:250:1 Fe^{2+}/H_2O_2/Aroclor (weight ratio) a loss of 4% existed (concentration of PCBs of 2.1 mg/l). Also it can be seen that in the blanks, that didn't contain any hydrogen peroxide, result of concentration of PCB is near zero. It means that, due to the presence of hydrogen peroxide, PCBs are not only oxidized but also passing to the water, result that is also favourable as the aim of this treatment is to clean the PCBs from the surface. Moreover, talking about possible real application, if PCBs pass to the water, they come to the outer side of the surface and they can be easier degraded by the UV of the sun, which has been also found to be a good method for degrading PCBs, as it was found that significant amounts of highly chlorinated biphenyls degrade in water by the action of the sunlight (WHO/IPCS 1993). Also in general, oxidation of PCBs with hydroxyl radicals is much faster and easy in aqueous phase than on surface.

Also shall be commented that this results might have been even better if ethanol would have been used instead of water. PCBs are highly hydrophobic compounds, so if no water but an organic compound PCB-solvent is used, an enlargement of the reduction can be appreciated (Lundstedt 2006). Tendency of PCB to solve into the ethanol would have increase its quantity in the liquid phase and so reduction would have been increased since reaction in liquid phase is faster that in solid phase.

It has been calculated the total degradation of PCBs, adding to the results of content on the surfaces, the results of content on water and reduction has been recalculated (figure 19). It can be noticed that global reduction slightly decreases, but it should be taken into account that at a ratio of 204:250:1 Fe^{2+}/H_2O_2/Aroclor (weight ration), posterior degradation by direct sunlight is possible, and this system would diminish the cost and facilitate the treatment. Shall be reminded that better results would have been achieved solving the reagents in ethanol.

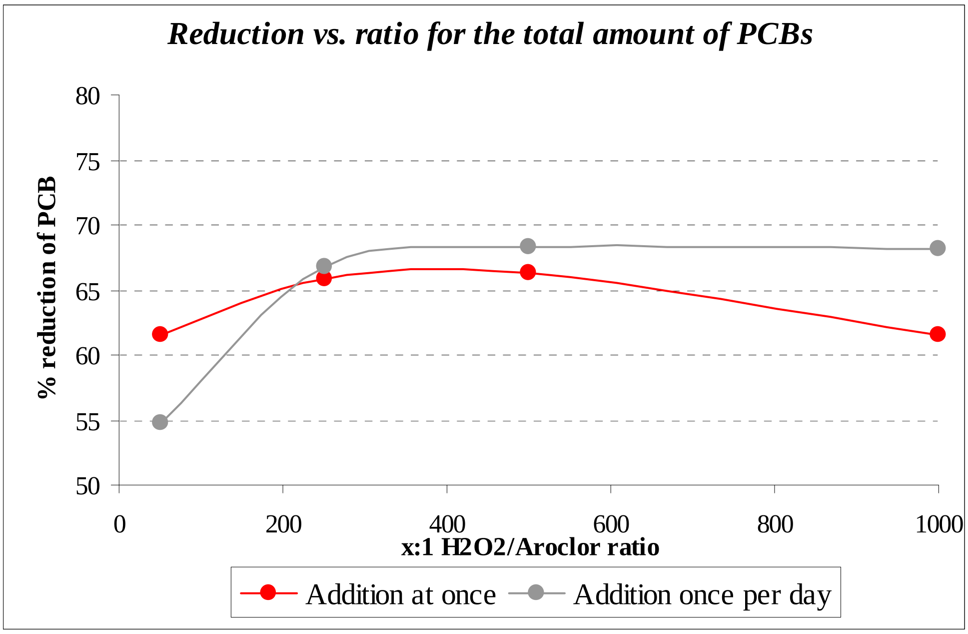

Figure 19: Results of global reduction of PCBs vs. ratio for both ways of addition (ratio Fe/H_2O_2 constant and equals to 1:10 (mol/mol)

4.3 Treatment of bricks

As final test in order to prove the treatment in real surfaces, two bricks have been contaminated and the Fenton treatment has been applied in different ratios and times of reaction, as explained in the previous section. For the analysis of the results, it has been calculated, apart from the area of the sample, the area of the internal standard in order to take into account the variation of the chromatograph and the area of the surrogate for taking into account the loss of PCB in the manipulation of the samples.

4.3.1 Influence of the ratio of hydrogen peroxide

Five different ratios have been studied with a constant time of reaction and way of addition of hydrogen peroxide (3 days reaction and one third of the treatment applied every day). The ratios have been 14:50:1, 27:100:1, 68:250:1, 136:500:1, 273:1000:1 Fe^{2+}/H_2O_2/Aroclor (weight ratio) it can be noticed that the ratio between the iron and the Aroclor was constant and equal to 1:30 Fe^{2+}/H_2O_2 (mol/mol). Less quantity of iron was used in comparison with the precious test due to the inner quantity of iron present in the clay of the brick. The results of ratio in front of reduction with respect to the blank sample are shown in figure 20.

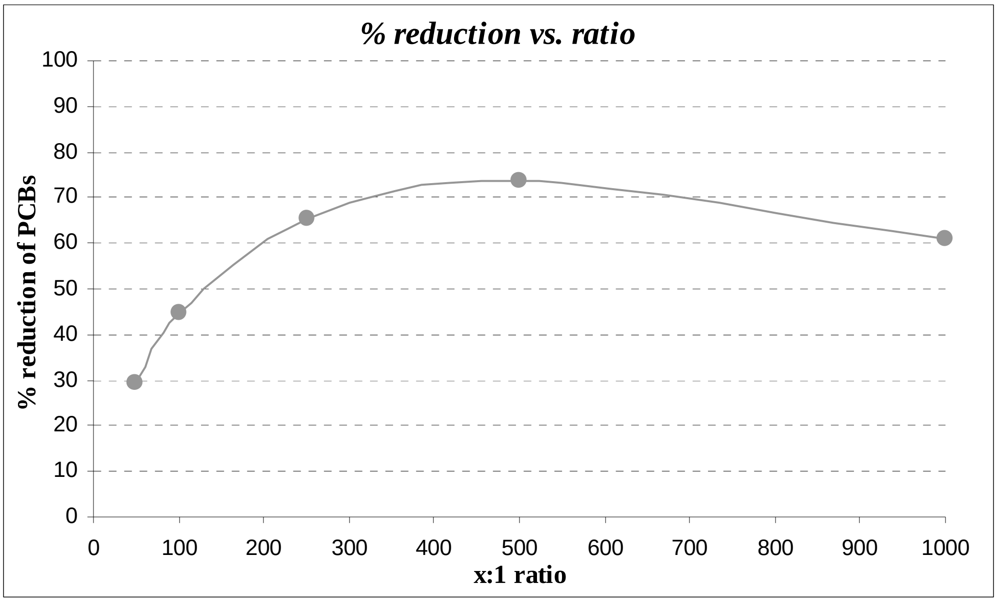

Figure 20: Results of % reduction vs. ratio for the bricks

As it can be seen in the graphic, per cent of reduction of PCBs on the surface of the brick increases when increasing the ratio of hydrogen peroxide for the four small ratios. In this case, hydrogen peroxide has a higher influence in the reduction since changes between different ratios are higher than in the treatment of glasses. As it happened in the glass tubes, the higher degree of degradation when increasing the ratio is expected due to the higher presence of hydroxyl radicals in the media. Also as in the tubes, in the high ratios reduction starts to diminish. This, as before, might be the result of the deactivation process of the hydroxyl radicals (equation 9) or reaction of reagent with them (equations 4 and 10) (Manzano *et al.* 2001, Walling 1975).

It shall be noticed that the best reduction is achieved with a weight ratio of 136:500:1 Fe^{2+}/H_2O_2/Aroclor, which means a higher amount of reagents than in the glass. This result is expected since surface of the brick is rougher and porous than glass.

4.3.2 Influence of the time of reaction and the way of addition of H_2O_2

For ratios 27:100:1 and 136:500:1 Fe^{2+}/H_2O_2/Aroclor (weight ratio), two different ways of application and three different durations of reaction have been studied. The treatment could have been applied at once or one proportional part every day. The reaction was studied for one day, three days and seven days of time. The results of concentration versus time of reaction in the application at once are shown in the figure 21 for both ratios. On the other hand, the results of concentration versus time of reaction when the application has been made once per day are shown in figure 22.

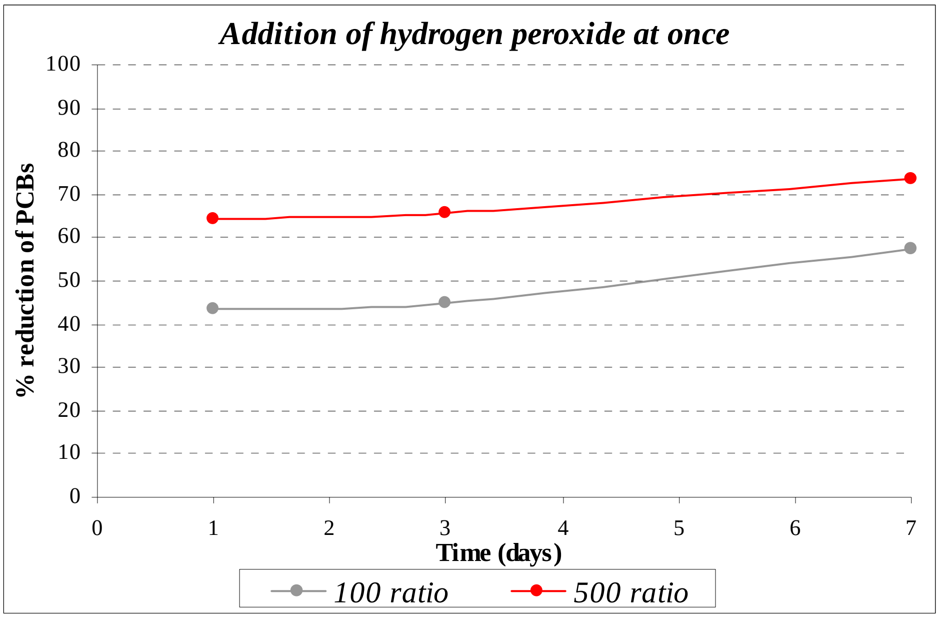

Figure 21: Results of concentration vs. time of reaction for the samples treated at once on the bricks

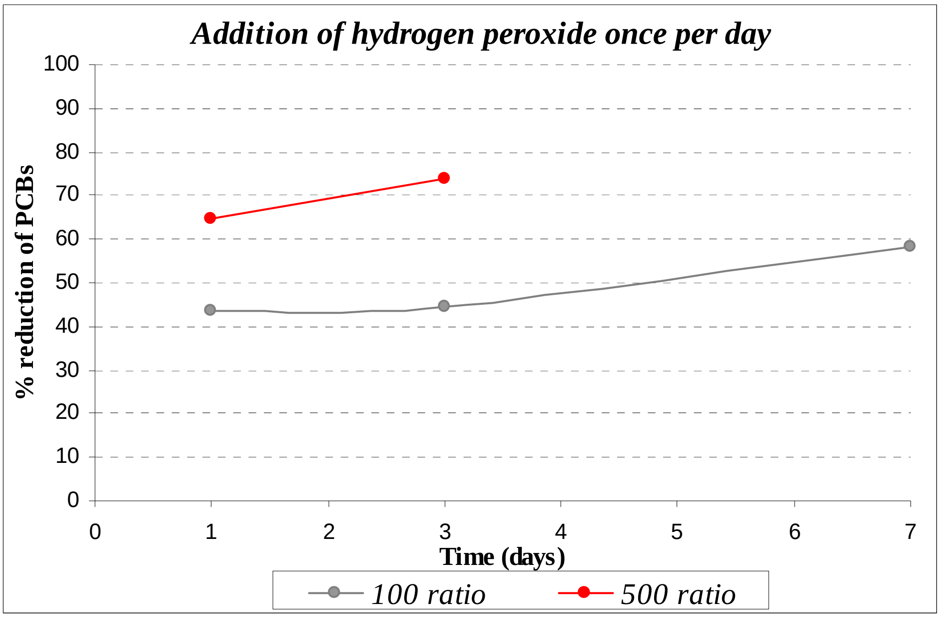

Figure 22: Results of concentration vs. time of reaction for the samples treated once per day on the bricks

As it can be seen in the results, in both ways of application 136:500:1 ratio shows lower final concentration, it can be concluded, as it is also shown in figure 20, that the higher concentration of hydrogen peroxide, the higher degree of degradation due to the higher presence of hydroxyl radicals in the media. This result has been reported by different authors in the literature (Dercová *et al.* 1999, Manzano *et al.* 2001).

It does not seem to be many differences between the ways of addition and almost the same concentrations are observed when H_2O_2 appears in a ratio of 27:100:1. On the other hand, when the ratio used is 136:500:1, a clearly enhancement is observed when hydrogen peroxide is added in small quantities.

When talking about times of reaction, it is possible to appreciate the enhancement of the reduction when reaction takes longer. The last part of the curve, which is an increasing line, might show that if reaction would have taken longer, reduction would have been better. The Fenton treatment over a surface seems to take longer than the one applied in the polluted water or soil. Time of reaction for treatment of water is the order of hours for water (Arienzo *et al.* 2000) and of 1 or 2 days for soil (Gates-Anderson *et al.* 2001) with an achievement of reductions over 90%. Over the bricks, more than seven days seems to be needed. This might be caused by the fact that treatment of surfaces can not be done by slurry, which is the fastest method for water and soil. Moreover, decontamination of water requires treatment to one phase (the liquid phase), whereas soil requires the treatment of three phases (the liquid, the gas and the solid phases). That’s why treatment in water is faster. When treating surfaces, like the case that concerns this project, the solid phase, which is the one that presents more difficulties when treated, is more stable and compact, which makes slower the treatment.

The best result is obtained when the reaction takes place during three days, with a ratio of 136:500:1 and the addition of hydrogen peroxide is done in three times, where the reduction achieved is of 73.8 %, although the tendency of the rest of the curves lead to think that possibly the missing point of the curve would be the best result (time of reaction of 7 days, addition of H_2O_2 in seven times. The result of seven days reaction but addition of hydrogen peroxide at once shows a very similar result (73.5 %). Whereas using a three times addition method may be uncomfortable because treatment requires being more in charge of, a seven days reaction is pretty long time to wait for the contaminant to be oxidized in comparison to the soil or water treated with Fenton.

Should be reminded that the acceptable level of PCB on a surface is 100 $\mu g/m^2$ (PCB-Committee 1984), and that the mean concentration on the surfaces after extracting the paints or plaster in buildings is 210 $\mu g/m^2$ (Kuusisto 2006-a). If this guidelines are followed, a reduction of 52% is needed for a mean contaminated surface to be reduced under acceptable levels. With the results taken from this project, reductions of over 50% are obtained with a weight ratio of 68:250:1 Fe^{2+}/H_2O_2/Aroclor in three days and a weight ratio of 27:100:1 Fe^{2+}/H_2O_2/Aroclor in seven days. Also if needed, a higher degradation of 70% can be achieved with a higher amount of H_2O_2. With this data it can be reinforced the suitability of the treatment as far as degradation of PCBs is concerned.

It could be commented that as the results of the glass tubes show, extraction with cotton is a low-reliable method as it entails errors. This may lead to a less reliable data. Moreover, brick surface is much more complex than glass surface and between the two bricks different behaviour in front of the treatment was observed: when the reagents (that were applied in water solution) were spread over the surface, the absorption trough the surface pores was faster in brick 1 than in brick 2. This different behaviour may affect the velocity of the reaction and the extent of the reaction and thus the results, showing differences that might not exist.

5 CONCLUSIONS

Polychlorinated biphenyls are man-made organic compounds commercialized from 1930s to middle 1970s. They were mainly used in closed systems as dielectric fluids and in open applications as plasticizers in building materials. Many surfaces have been found to be contaminated and thus the need of decreasing this concentration under acceptable residential or occupational levels has appeared.

This project has focused on the treatment of PCBs directly over the surfaces by the advanced oxidation technique known as Fenton, which by hydrogen peroxide catalyzed by iron molecules hydroxyl radicals are created and thus, PCB molecules oxidized.

A laboratory scale research has been made. Two different surfaces have been used in order to simulate the real ones; the first approach was made with glass and the second one with brick surfaces. They both have been artificially contaminated by a certain concentration of a mixture of PCBs known as Aroclor 1260 and subsequently treated with the Fenton reagents. Then, an extraction of the PCBs was made in order to analyse them with GC-MS. A study of the effects of the ratio of hydrogen peroxide and Aroclor 1260, the time of reaction, the way of adding the reagents and the number of chlorine atoms of the congeners of Aroclor 1260 has been carried out.

When talking about ratio, it seems to be the weight ratio 204:250:1 Fe^{2+}/H_2O_2/Aroclor the most suitable for the reduction of PCBs in the glass surfaces, although it has been found that at this ratio, a high quantity of PCB passes to the water of the reaction and that the reduction is not as effective as it seems. Nevertheless, the fact of PCBs passing to the water of reaction may lead to a subsequent degradation due to sunlight and so a cheaper degradation than a higher ratio of hydrogen peroxide. This fact would have been enlarged if ethanol would have been use as solvent agent for the reagents as PCB reacts easily in liquid phase.

In bricks the best ratio is observed at 136:500:1 Fe^{2+}/H_2O_2/Aroclor (weight ratio). This differs from the glass surfaces as more hydrogen peroxide is needed over the brick surfaces. Surface of the brick is rougher and more porous and thus more difficult to treat. Moreover, in the bricks, the possible PCBs that pass to the water were left over the outer surface and thus extracted with the cotton and taken into account in the results.

As far as the time of reaction is concerned, seven days seems not to be enough for having the best results of reduction. Treatment of surfaces is clearly slower than the treatment of water or soils. This can be caused by the fact that slurry, which is known to accelerate the oxidation, can not be applied in a surface. Moreover, the reaction takes place mainly in solid phase, which in a surface is more rigid, particles are more compacted and subsequently, reaction is slower. In posterior researches, more time of reaction is recommended in order to achieve better results.

It seems not to affect in a high percentage the way of adding the reagents for both surfaces although slightly better results occur with the addition of hydrogen peroxide at low quantities every day. If talking about real case, an addition of the reagent at once would be more suitable and convenient as it would reduce the cost of the treatment as far as workers salary is concerned for one day all the work could be done whereas the other way of addition concerns an everyday maintenance.

As in the other researches, in this study it has been also appreciated that reduction of PCBs depends highly on the number of chlorine atoms of the congener. This study was carried out with Aroclor 1260, which contain PCB congeners highly chlorinated, so better results might be expected if studying the degradation of another commercial mixture. The results of degradation in front of the number of chlorines also show that extraction with wiped cotton entails errors as the high chlorinated congeners are not as good extracted as the low chlorinated.

Continuing with the extraction with cotton, it shall be commented that this method of extraction is not as reliable as the extraction directly with a solution. Nevertheless, in the bricks surfaces, there in no possibility of using another method so results might be altered. This should be taken into account in further researches.

Chemical oxidation by Fenton reaction seems to be a suitable treatment of PCB-contaminated surfaces. A deeper study in this area is highly recommended observing the results achieved in this project.

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