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Improving transformer oil decontamination: A synergistic approach integrating adsorption and radiative treatment for polychlorinated biphenyls

Chems Eddine Gherdaoui^{a,b,*}, Hanene Oumeddour^b, Hussam Aldoori^b, Chakib Alaoui^d, Jean-Philippe Delbarre^a, Zohra Bouberka^c, Philippe Supiot^b, Djahida Lerari^e, Ulrich Maschke^b

^a Maxei Group - R&D Department, Zone industrielle Zac Artoipole, 170 Allée de France - BP 22004, 62060 Arras, France

^b Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France

^c Laboratoire Physico-Chimie des Matériaux-Catalyse et Environnement, Faculté de Chimie, Université des Sciences et de la Technologie d'Oran, BP 1505, 31000 El-Mnaouer, Oran, Algeria

^d Laboratoire de Chimie des Matériaux Inorganiques et Applications, Faculté de Chimie, Université des Sciences et de la Technologie d'Oran, BP 1505, 31000 El-Mnaouer, Oran, Algeria

^e C.R.A.P.C., B.P. 384, Zone industrielle Bou-Ismaïl, Tipasa, Algeria

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ABSTRACT

Addressing the challenge of removing polychlorinated biphenyls (PCBs) from transformer fluids is crucial for environmental protection in the energy sector due to the widespread use of transformers in various industries. However, current methods lack efficiency in enabling fluid reuse, creating a significant research gap. In this study, we focus on the recycling of oils from power transformers contaminated with polychlorinated biphenyls while preserving the chemical and physical attributes of the original transformer oil. To this end, we employ a combination of UV-visible radiation exposure and an adsorption treatment using activated bauxite Fuller's earth (BFE) (containing 92% Al₂O₃). The effects on fluid remediation are systematically assessed using various analytical methods, including nuclear magnetic resonance spectroscopy (NMR), breakdown voltage testing, acidity titration, and gas chromatography coupled with mass spectroscopy (GC/MS).

The experiments in static mode showed that the concentration of PCBs was reduced to a value lower than 50 ppm after 8 h of irradiation while the formed chlorinated acid compounds can be removed using BFE sorbent.

The results of our treatment demonstrated the performance of the combination of UV-visible radiation and the adsorptive treatment of transformer oils while improving their physicochemical characteristics.

1. Introduction

Polychlorinated biphenyls (PCBs) are complex organic compounds characterized by their high molecular weight, comprising two benzene rings substituted by chlorine atoms whose number varies from 1 to 10 [1,2]. These molecules were extensively manufactured during the 20th century mainly as dielectric fluids for their electrical insulation

properties, outstanding chemical stability, resistance to high temperatures, and excellent thermal conductivity. They have thus been used in electrical devices, such as power transformers, capacitors and even in oil bath heaters [3]. PCBs are recognized by various trade names, with the most prevalent ones being Pyralenes, Aroclors or Askarels. Nevertheless, it has been proven that these molecules are toxic and promote carcinogenic processes, fertility and growth problems as well as a

Abbreviations: ¹H NMR, Proton nuclear magnetic resonance; ASTM D1500, A standard test method for color measurement of petroleum products; BFE, bauxite (Fuller's earth); CDC13, Chloroform-d (deuterated chloroform); EI, Electron impact; GC/MS, Gas chromatography/mass spectroscopy; H, Hydrogen; LOD, Limit of detection; LOQ, Limit of quantitation; MALDI-TOF/MS, Matrix Assisted laser Desorption Ionization - Time of Flight/mass spectroscopy; mg KOH/g, Milligrams of potassium hydroxide per gram; m²/g, Square meters per gram; m/z, Mass-to-charge ratio; PCB, Polychlorinated biphenyls; ARP, Average removal percentage; ARmi, average removal percentage of molecule i; ppm, Parts per million; POPs, Persistent organic pollutants; SD, Standard deviation; TAN, Total acid number; UV-A, Ultraviolet A; UV-B, Ultraviolet B; UV-visible, Ultraviolet-visible; °C, Degrees Celsius.

* Corresponding author at: Maxei Group, 170 VC All. de France, 62118 Monchy-le-Preux, France.

E-mail addresses: gherdaouchemseddine@gmail.com, chemseddine.gherdaoui@maxei.fr (C.E. Gherdaoui).

degradation of the immune system [4]. Another alarming facet of PCB exposure lies in its capacity to exert neurotoxic effects on the human nervous system. Furthermore, research has demonstrated that PCBs can disrupt the intricate balance of the nervous system, impacting both its central and peripheral components [5–7].

As a consequence of their adverse environmental and health effects, PCBs were officially categorized as persistent organic pollutants (POPs) under the Stockholm Convention in 2004 [8], and their use was banned in 1980 in all applications [9]. Nowadays, used transformer oils contaminated with polychlorinated biphenyls (PCBs) are classified as “hazardous waste” and Europe in particular has implemented specific regulations for their collection and disposal [10]. Furthermore, according to the report from the United Nations Environment Program, the total quantity of PCBs has been estimated to exceed 14,000 kilotonnes. It is also noteworthy to emphasize that due to the sensitivity of this issue, some countries do not disclose the actual quantities in circulation, thereby suggesting that the total estimate could be even more substantial [11]. Hence, it is imperative to recognize that any transformer fluids containing PCBs are unequivocally regarded as hazardous waste, necessitating stringent monitoring and handling protocols [12,13]. At present, it is forbidden to retain products or devices containing PCBs at more than 50 ppm while waiting for their total abatement in the European Union by 2028 [14–16]. In addition, PCBs have a low biodegradability, which poses many uncertainties in the long term concerning the problem of deterioration of the ecological environment [17,18].

In the current state, addressing this issue typically involves shutting down transformers and replacing the contaminated oil with fresh oil [19]. This procedure needs to be repeated a minimum of two times. The process essentially involves the straightforward application of a dilution method to reduce PCB derivative concentrations below the levels prescribed by legislation [20]. As for the treatment of these toxic molecules present in the transformers (mixed in a hydrocarbon oil), it is currently carried out by the implementation of various techniques. The main technique used in an industrial scale is high-temperature incineration under strictly controlled conditions because the thermal decomposition of PCBs causes the formation of highly toxic compounds such as furans (PCDF) and dioxins (PCDD) [21–23]. Due to the risk of release of these contaminants into the atmosphere, there have been attempts to develop other more environmentally friendly methods. In particular, some methods have focused on the dechlorination of PCBs, since the toxicity of PCBs depends on the number and position of the chlorine atoms substituting the benzene rings [24].

Chaychian et al. [25] have suggested the potential degradation of PCBs using ionizing radiation, such as electron beams. However, it's important to note that this method also results in the degradation of the oil, rendering it unusable and transforming it into a waste product. Feng et al. [26] reported that 4-chlorobiphenyl PCB can be dechlorinated in hexane using UV radiation with a maximum wavelength of 254 nm. The radiation forms free diphenyl radicals, which capture a hydrogen atom from the hexane, to form diphenyl. This method remains a laboratory method and requires the mixing of the organochlorine aromatic compound with hexane. Other investigations have reported that it is possible to dechlorinate a PCB-contaminated transformer oil containing more than 800,000 mg/g of various PCBs. This oil is diluted with 2-propanol and triethylamine (v/v/v, 1/79/20). This mixture is introduced into a sealed quartz reactor and put under a nitrogen atmosphere. Subsequently, it is irradiated with radiation generated by a xenon lamp, which notably emits wavelengths below 300 nm. After 120 h of irradiation, the PCBs are completely transformed into biphenyl. It seems that the reaction involves the transfer of an electron from the tri-ethanolamine to a chlorinated or non-chlorinated benzene ring which thus becomes an activated radical. This method requires the prior dilution of the contaminated oil, making it challenging to apply at an industrial scale, as a transformer can contain thousands of liters of contaminated oil. Furthermore, this method cannot be used to treat a transformer on site, let alone a transformer in operation [27,28].

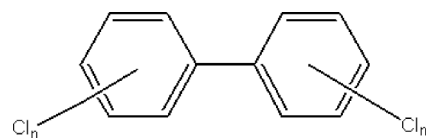


Fig. 1. Generalized chemical structure of polychlorinated biphenyls (PCBs). The case $n = m = 0$ corresponds to the chlorine-free PCB No. 0 (Biphenyl).

Document EP 0 257 170 A1 describes a dechlorination process for dechlorinating halogenated and polyhalogenated compounds which comprises an irradiation step in the presence of a reagent selected in particular from polyethylene glycols and polyalcohols [29,30]. US 2008/319246 A1 details a method for treating a PCB-contaminated matrix. The described method requires the addition of an oxidant during the irradiation with UV [31]. It's noteworthy that the matrix under consideration can exist in liquid form, encompassing substances such as mineral oil or technical fluids.

All these methods, which require the addition of solvent(s) and/or other compounds, are difficult to implement in an industrial way. Furthermore, the introduction of solvent or other compounds affects the chemical and physical properties of the oils. As a result, this process generates large amounts of waste and may only ensure a dilution of the initial PCB level in the transformer.

To the best of our knowledge, there are no other ways to treat PCB-contaminated oils. The aim of this work is therefore to propose a process for the dechlorination of PCBs contained in transformer oils, which remedies some of the drawbacks of prior methods. The process proposed in this article enables the achievement of a comprehensive PCB concentration lower than 50 mg per kilogram of transformer oil, while preserving the quality and in particular the dielectric properties of the oil.

To this end, we consider two methods of remediation: exposure of the contaminated oil to UV-visible radiation and adsorption of the by-products generated on alumina-based materials such as activated BFE which also allow the regeneration of transformer oils if needed.

This article includes other research aspects such as the maximum number of uses of BFE, and a new method for qualitative analysis of PCBs by ^1H NMR. In addition to ^1H NMR the PCBs, abatement was followed by gas chromatography (GC) coupled with mass spectroscopy (GC/MS). This technique is a powerful tool for the identification and understanding of the chemical kinetics of the reactions involved. The alterations in physicochemical properties, both pre- and post-irradiation, as well as after the combined adsorption treatments, were assessed using an acid-base titration method, dielectric measurement, and impedance spectrometry according to IEC 60296 [32].

2. Materials and methods

2.1. Chemical products

2.1.1. Polychlorinated biphenyls

The following PCB molecules were selected for this work (Fig. 1): Biphenyl (PCB No. 0), 2-Chlorobiphenyl (PCB No. 1), 3-Chlorobiphenyl (PCB No. 2), 2,2'-Dichlorobiphenyl (PCB No. 4), 2,3-Dichlorobiphenyl (PCB No. 5), 2,4-Dichlorobiphenyl (PCB No. 7), 3,4-Dichlorobiphenyl (PCB No. 12), 3,5-Dichlorobiphenyl (PCB No. 14), 4,4'-Dichlorobiphenyl (PCB No. 15), 2,4,4'-Trichlorobiphenyl (PCB No. 28), 2,4',5'-Trichlorobiphenyl (PCB No. 31), 2,2',5,5'-Tetrachlorobiphenyl (PCB No. 52), 3,3',4,4'-Tetrachlorobiphenyl (PCB No. 77), 2,2',4,5,5'-Pentachlorobiphenyl (PCB No. 101), 2,2',3,4,4',5'-Hexachlorobiphenyl (PCB No. 138), 2,3',4,4',5'-Pentachlorobiphenyl (PCB No. 118), 2,2',4,4',5,5'-Hexachlorobiphenyl (PCB No. 153), 2,3,3',4,4',5'-Hexachlorobiphenyl (PCB No. 156), 2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB No. 180), and Decachlorobiphenyl (PCB No. 209), which were provided by Sigma-Aldrich (St. Quentin Fallavier, France). The choice of PCBs was mainly

Table 1
Characteristics of virgin mineral oil and contaminated mineral oil.

Oil Name	Density (g/cm ³)	Breakdown Voltage (kV)	Acidity (mgKOH/g)	Water Content (ppm)	Dissipation factor	[PCB] (ppm)
Unused Mineral oil	0.89	80	0.01	3	0.005	0
Real system	0.91	24	0.3	38.9	0.12	350

Table 2
Characteristics of BFE.

Composition	SiO ₂	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	Na ₂ O	K ₂ O
Weight %	2.75	0.33	3.99	92.5	0.05	0.11	0.27

Loss on Ignition at 1000 °C = 6.32%.

focused on the so-called indicator PCBs accounting for nearly 80% of all PCBs: most often PCBs No. 118, 138, 153 and 180, but also PCBs No. 28, 52 and 101. In 2017, these 7 indicator PCBs among the 209 congeners were selected by the Community Reference Office of the European Commission in Brussels as being the compounds to be searched for in priority in the analysis of organic matrices (sediment, blood, flesh, fat) due to their persistence and abundance in the environment as well as their toxicological properties [33]. Other congeners of the same family with the same chlorine numbers have been added to this study in order to obtain more information on the chromatographic separation parameters.

2.1.2. Transformer mineral oil

Virgin mineral oil (Nytro Taurus) were purchased from Nynas AB (Sweden) and the sample of used transformer oil contaminated with PCBs (referred to as “real system”) were provided by Arras Maxei, a

French company. Both oils under investigation (Table 1) were primarily comprised three hydrocarbon families: paraffins, naphthenes, and non-chlorinated aromatics. The molar mass of the mineral oil was determined in our earlier research utilizing MALDI-TOF/MS (Matrix Assisted Laser Desorption Ionization - Time of Flight/mass spectroscopy). The obtained result indicates that the molar mass of this oil exceeds 100 g/mol. The spectrum reveals mass fragments at 600, 800, and 1200 *m/z* [34].

2.1.3. Fuller's earth

The Fuller's earth used in this work is bauxite (BFE) supplied from Mineração Curimbaba Ltda. (Brazil) through Arras Maxei group (France). Bauxite is a hydrated aluminum silicate of the montmorillonite group. This alumina-based adsorbent is suitable for the regeneration of PCB-contaminated waste oil after the radiative treatment. The composition of the BFE was validated through X-ray fluorescence spectrometry (Fig. S1), and is shown in Table 2.

2.1.4. Description of the irradiation source

The irradiation of samples was performed out using a Xenon lamp LC8 (Hamamatsu Photonics France S.A.R.L, France), which emits a broad spectrum in the UV-visible range. This lamp is equipped with an optical fiber with an outer beam diameter of 5 mm. The emitted light is

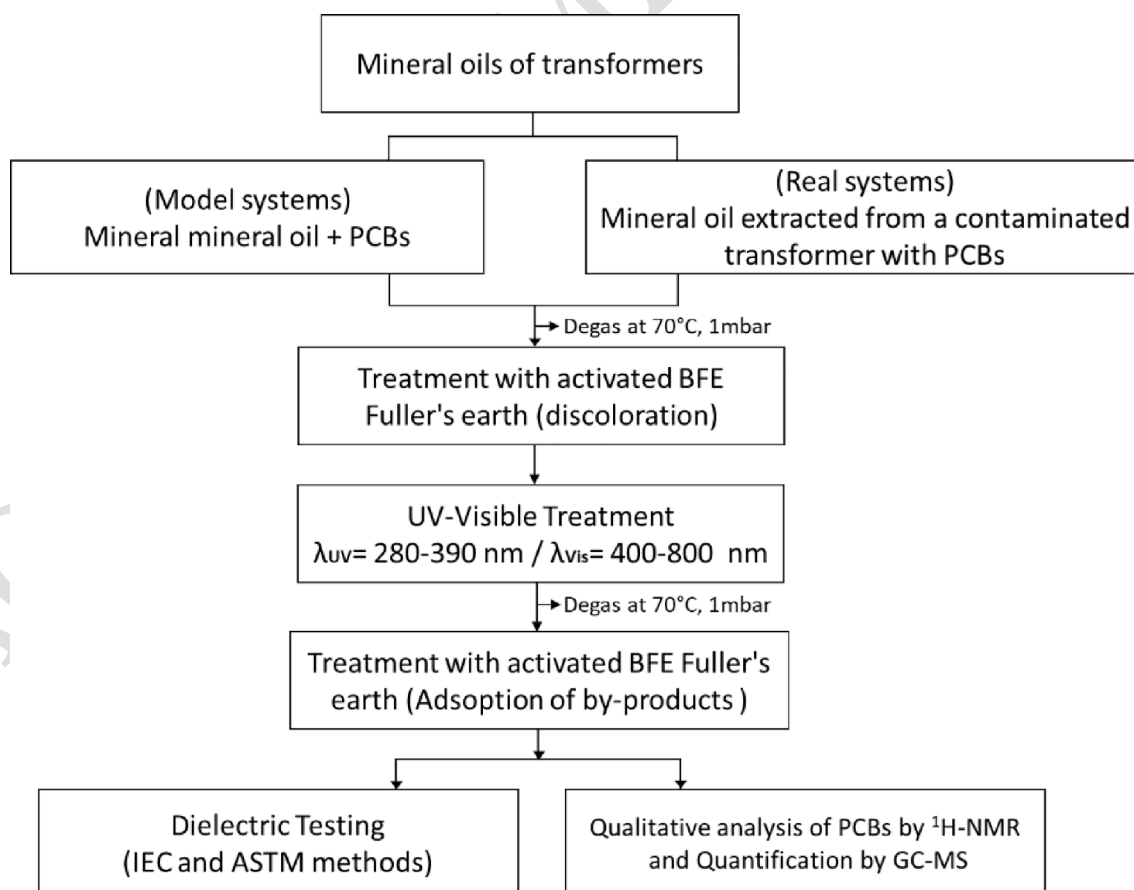


Fig. 2. Scheme of the protocol for transformer mineral oil treatment.

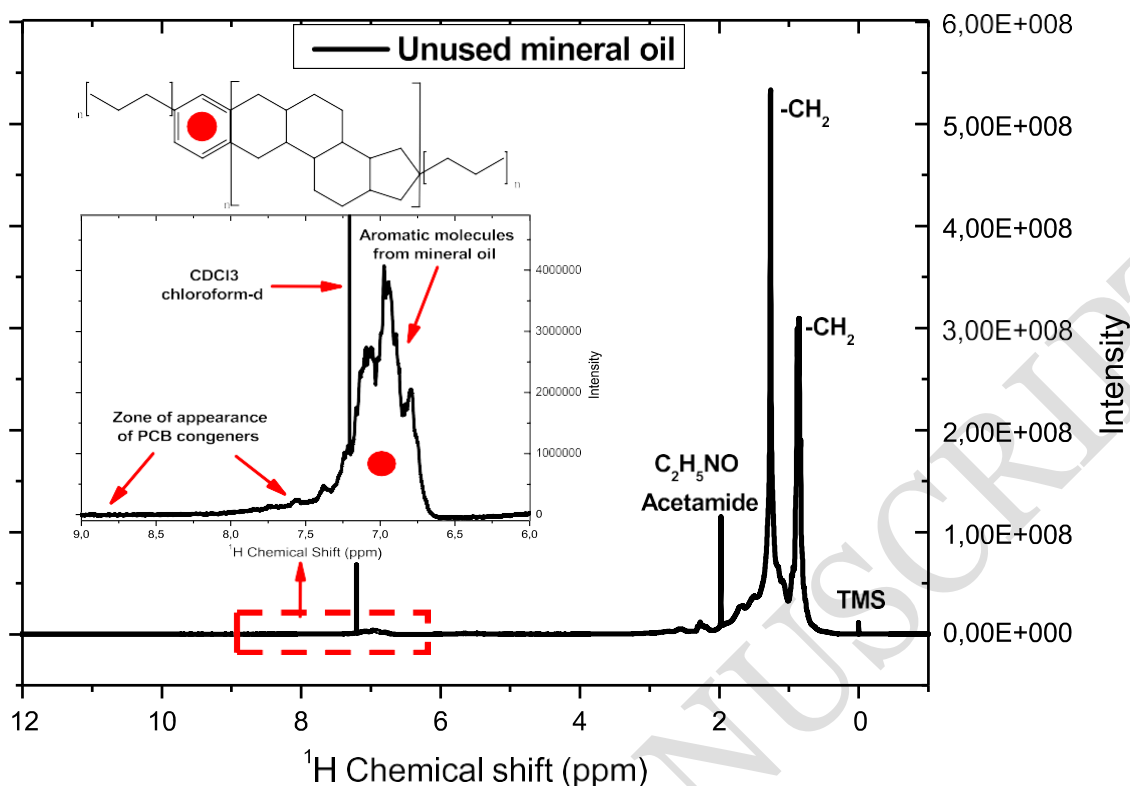


Fig. 3. ^1H NMR spectrum of unused transformer mineral oil.

mainly in the UV-A and UV-B range, with wavelengths between 290 and 390 nm. This specific range of wavelengths facilitates optimal penetration of UV, allowing the cleavage of chloroaromatic bonds [20]. The efficiency of UV-visible irradiation can be enhanced by agitating the sample to vary the surface of the oil exposed to UV-visible irradiation. Under optimized conditions, the light intensity was determined to be 13 mW cm^{-2} at a wavelength of 365 nm using a C6080-13 dosimeter from Hamamatsu Photonics France S.A.R.L., France. The light source was placed 3 cm away from the irradiation zone ($5 \text{ mm} \times 5 \text{ mm}$) to maintain a temperature less than or equal to 70°C . The latter was determined by thermogravimetric analysis (TGA) of the oil to avoid any degradation (see Fig. S2).

2.2. Oil treatment process

Once collected, mineral oils contaminated with PCBs underwent a pre-treatment process involving degassing. The vacuum degassing of the oil contaminated with 350 ppm of PCBs entailed reducing the pressure to 1 mbar while maintaining a temperature of 70°C . This step aimed to extract water present in parts per million (ppm) at the oil interface. To ensure that PCBs were not released into the atmosphere under these conditions, we monitored the concentrations of PCBs in the oil both before and after degassing. The results indicated that the concentration of PCBs, remained unchanged during degassing under our specified conditions. Subsequently, the oils were treated by adsorption on BFE powder through a filtration. These first two steps were designed to remove moisture, regulate acidity, and eliminate ionic impurities [35]. BFE also allowed the discoloration of colored oils. This decrease in the opacity of the oils enhances the penetration of the UV-visible treatment that follows. Indeed, the UV-visible radiation can deactivate the PCB molecules, by providing a higher radiation energy than dissociation energy which results in the breakage of aromatic carbon-chlorine bonds. Once treated under UV-visible radiation, the oil underwent filtration to

adsorb the products of photodegradation. After treatment, the oil was subjected to characterization to verify and ensure its maintenance of desired physicochemical properties (Fig. 2).

2.3. Qualitative and quantitative analyses of PCBs

2.3.1. Qualitative analysis of PCB by ^1H NMR

The ^1H NMR analysis was performed using a Bruker AVANCE III HD instrument with a magnetic field strength of 300 MHz, following a defined preparation protocol: a few milligrams of the external standard (acetamide obtained from Merck France) were grinded into crystalline powder. Then, an amount of 1–5 mg was solubilized by 0.6 ml of chloroform-d (CDCl_3 , 99.8%) in a 5 mm diameter tube. Finally, a 10 min treatment of the NMR tubes in an ultrasonic bath was applied after the addition of the desired amount of the oils to be analyzed. In order to verify the qualitative and quantitative reproducibility of the standard signal, integrals of the single peak of acetamide with a chemical shift of 2 ppm were calculated. The response of the curve was proportional and linear and therefore allows the qualitative study in the case of pure and contaminated mineral oils [36,37].

2.3.2. Quantification and quantitative analysis of PCB by GC/MS (EI)

The oils systems containing PCB compounds were analyzed by GC/MS after drying in a vacuum oven at 70°C . The GC chromatograms and their associated MS spectra were obtained using a GC/MS apparatus (Clarus 680/Clarus 600 T from Perkin Elmer Waltham, MA, United States), equipped with a fused silica capillary column, with a maintained at 70°C (Elite-5 (5% Diphenyl) Dimethylpolysiloxane, $30 \text{ m} \times 0.53 \text{ mm}$ (internal diameter), film thickness $d_f=0.5 \mu\text{m}$). The MS appliance was equipped with an EI source and a quadrupole filter (ion separator) at DC (U) and AC (V) voltages set by the equipment.

The method and operating conditions of the GC/MS apparatus of analysis of PCBs by GC/MS have already been described in detail in our

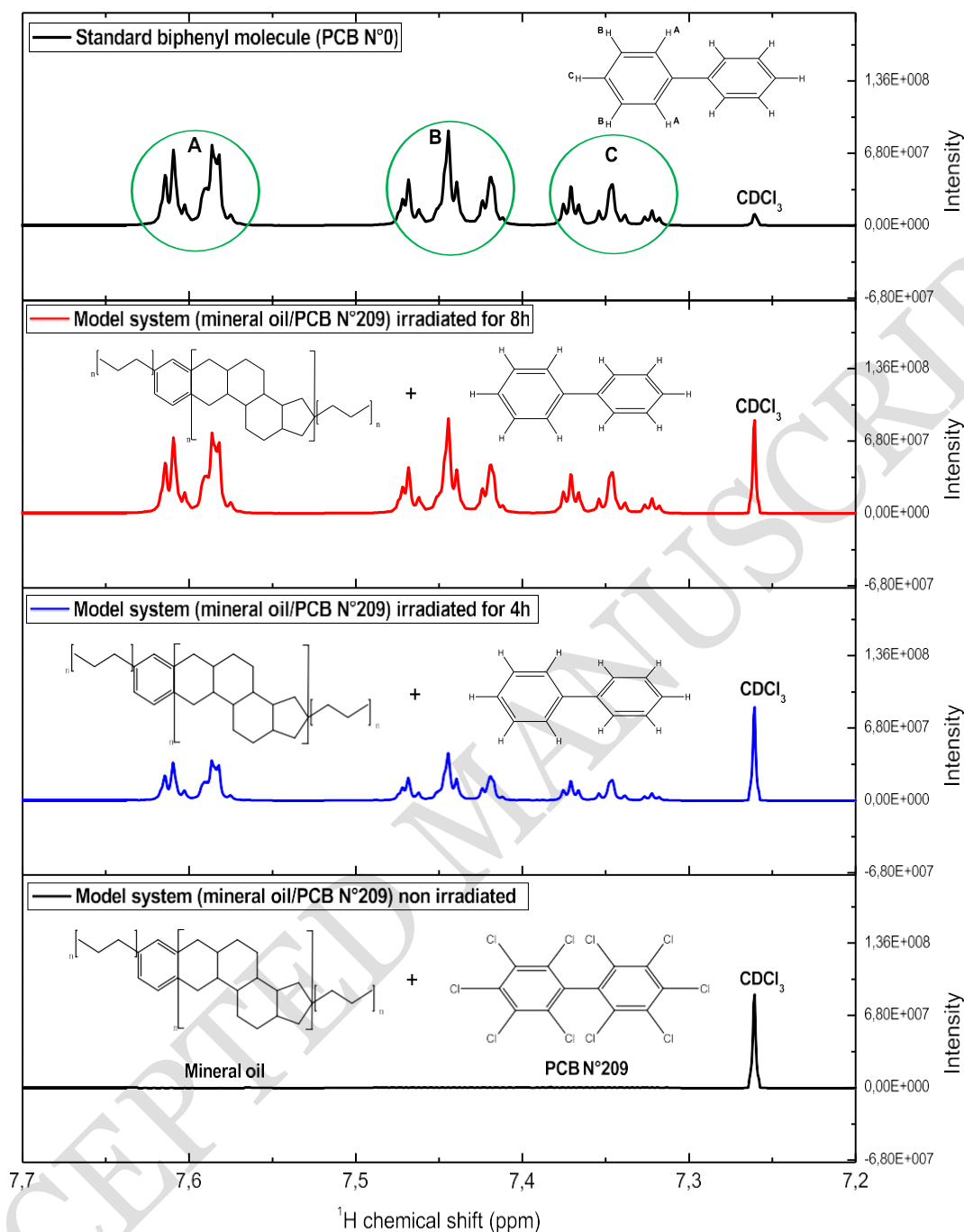


Fig. 4. Zoom on the aromatic zone of the ^1H NMR of the mineral oil/PCB No. 209 model system (concentration 200 ppm), non-irradiated and irradiated under UV-Visible radiation during 4hr and 8hr.

previous work [34] and are as follow: Initially, the column was held at a temperature of 70 °C for 4 min, followed by a ramp of 20 °C per minute until it reached 120 °C. Afterward, the temperature was gradually increased to 250 °C at a rate of 30 °C per minute. The oven remained at this temperature for 20 min, followed by a temperature increase at a rate of 20 °C per minute until reaching 300 °C. This final temperature was sustained for an additional 20 min. The injector and transfer line temperatures were maintained at 300 °C. For the detection and identification of PCB molecules, a reference standard, specifically FC-43 (Heptacos), was utilized. Masses obtained through mass spectrometry (MS) were confined to the range of 30 to 620 m/z due to the limitations of the electron ionization source, which cannot fragment molecules

exceeding 620 m/z . The ionization source temperature was set at 280 °C, and the filament voltage applied was 430 V.

The concentration of PCBs was calculated from multiple calibration curves already performed. The average percent removal of organochlorine aromatics was calculated by the following formula:

$$\text{ARP} = \sum (X_{oi} \cdot \text{AR}_{mi})$$

where ARP: average removal percentage. AR_{mi} : average removal percentage of molecule i . X_{oi} : initial molar fraction of molecule i .

The limit of detection (LOD) and the limit of quantitation (LOQ) were calculated from each calibration curve, according to the international

Table 3
¹H NMR results of mineral oil/PCB-209 modal system.

Parameters	Model System (Mineral Oil/PCB No. 209)		
	Non-irradiated sample	100	100
The light intensity of the source (%)	Non-irradiated sample	70	70
Sample temperature (C°)	Non-irradiated sample	4	8
Radiation exposure time (hr)	No signal / no peak	0.26	0.36
Integration of the signal on the aromatic zone of the ¹ H NMR spectrum (PCBs)	Undefined ratio	1/0.2 = 5	1/0.36 = 2.77
¹ H NMR integration ratio (Acetamide) / (PCBs)	0	65	85
Percentage removal (%)			

regulatory agencies (Table S1). LOD was obtained by 3.3 times the ratio of the standard deviation of their response(s) and the slope of the calibration curve(s), $LOD = 3.3 \times (SD \text{ of intercept} \times \text{slope}^{-1})$. LOQ was obtained from $LOQ = 10 \times (SD \text{ of intercept} \times \text{slope}^{-1})$. The precision was obtained considering the relative standard deviation for both samples and standard solutions. The execution of the measurement protocols was carried out in strict accordance with established standards (Table S2) and the accuracy of the results was confirmed by the Laboratory Oskman Séraphin (France) using reference PCB samples certified by LGC Labor GmbH (Germany) in accordance with the standard ISO 17034. The variance between the two measured values falls within the uncertainty range of the analysis ($\pm 7\%$) for all PCB samples.

3. Results and discussions

3.1. ¹H NMR qualitative analysis of treated and untreated mineral oil/PCB model systems

¹H NMR spectrum of the pure unused mineral oil (Fig. 3) reveals, at first sight, the presence of the two intense signals corresponding to C-CH₃ and C-CH₂ groups. The latter reflects the composition of the mineral oil, thus inducing a considerable loss of sensitivity towards the detection of PCBs. It was therefore necessary to zoom in on the aromatic part (Fig. 3) in order to see the characteristic signals of the PCB congeners between 7.3 and 8.5 ppm which do not overlap with the aromatic part of the virgin mineral oil situated between 6.6 and 7.2 ppm. It should be noted that the external standard forms a single peak at the chemical shift of 2 ppm, and therefore does not overlap with neither the mineral oil nor the aromatic signals of the PCB compounds.

3.2. Effects of UV-Visible irradiation on model systems (mineral oil/PCB)

In order to test and confirm the feasibility of the radiative treatment described above, the model systems of the mineral oil/PCB No. 0 mixture and the mineral oil/PCB No. 209 mixtures were treated for a period of 8 h. The ¹H NMR spectra are observed mainly in the area of the characteristic PCB peaks between 7.35 ppm and 8.5 ppm. After irradiation, it was found that the UV-visible radiation has no effect on the pure mineral oil as there was no change observed in the spectrum of the pure mineral oil irradiated for 8 hr. It is also noted that the radiative effect on the model system, pure mineral oil/PCB No. 0, is insignificant. Indeed, the intensities of aromatic peaks and the integration ratios (Acetamide) / (PCB) remain constant, thus confirming the stability of the PCB No. 0 molecule [38]. Indeed the electronic cloud created by the delocalization of electrons in the aromatic rings reinforces the dissociation energies of the bonds that form the aromatic rings of biphenyl [39].

Before irradiation, the aromatic part of the ¹H NMR spectrum of the mineral oil/PCB No. 209 system does not show any peak since this

molecule is saturated in chlorine and does not have any proton grouping. After the irradiation, the photodegradation of PCB No. 209 contained in mineral oil is marked by the increase of the aromatic peaks between 7.3 ppm and 8.5 ppm thus forming the biphenyl (PCB No. 0) at a yield of 65% and 85% (Fig. 4), respectively after irradiation of 4 hr and 8 hr which confirms the substitution of the atoms of chlorine atoms of PCB No. 209 by protons coming from the mineral oil hydrocarbons. After 8 hr of treatment, it is observed that the aromatic part of the ¹H NMR spectrum of the model system overlaps with the aromatic part of the ¹H NMR spectrum of the standard biphenyl molecule (PCB No. 0).

Table 3 below summarizes the conditions and experimental results of a series of tests.

3.2.1. Mechanism for PCB No. 209 dechlorination

Drawing upon the outcomes of ¹H NMR spectroscopy assessments, we were able to suggest a subsequent mechanism for PCB No. 209 dechlorination (see Fig. 5). Initially, PCB molecules dispersed in mineral oil absorb UV photons in the 290–390 nm range, which trigger electronic transitions, leading to electron excitation. As a consequence, absorbed photons raise PCB electrons to higher energy levels, generating PCB* species in an excited state. In this excited state, PCB* undergoes homolytic cleavage of one or more C-Cl bonds, leading to the production of PCB radicals (PCB*) and chlorine radicals (Cl*) [40,41].

The specific chlorine atom that can be removed during the early phase of PCB No. 209 photodechlorination depends on the reaction conditions and the structural characteristics of PCB No. 209. Nevertheless, in a simplified representation, it is common for one of the terminal chlorine atoms in the para- or meta-position of PCB No. 209 to be removed first. This is because these species are more reactive and can be more easily split off in free-radical reactions, as the chlorine atoms are less sterically hindered than chlorine atoms closer to the center of the molecule.

Chlorine atoms located closer to the molecule's center (ortho position) may encounter steric hindrance owing to neighboring substituents (atoms or groups) and the presence of central benzene rings. This congestion or hindrance surrounding these central chlorine atoms can pose challenges for their involvement in chemical reactions. In addition, the electrons in ortho position of chlorine atoms are more engaged in the electronic system of the molecule PCB No. 209 [42].

The resultant PCB* radicals, featuring unpaired electrons, are exceptionally reactive entities. They can engage with hydrocarbons present within the mineral oil by abstracting hydrogen atoms from these hydrocarbons. When a PCB* radical interacts with the hydrocarbons in the mineral oil, it can extract a hydrogen atom (H*) from the hydrocarbon molecules, leading to the formation of PCB species with reduced chlorine content. The precise site of hydrogen atom abstraction on the PCB molecule may vary, resulting in different products exhibiting varying chlorine content. Collectively, these sequences of reactions culminate in the gradual elimination of chlorine atoms from PCB No. 209 molecules, ultimately transforming them into non-chlorinated or less chlorinated products.

3.3. Effects of UV-Visible irradiation on real system

The real mineral oil sample recovered from a PCB-contaminated transformer was processed and analyzed under the same conditions as the model system. After 4 h of irradiation, a significant increase in aromatic signals is observed, similar to what has been found with model systems. This radiative effect is more notable after 8 hr (Fig. 6). This phenomenon is due to the aromatic substitution between chlorine atoms of the PCB mixture contained in the mineral oil and H protons taken from the hydrocarbon chains of oil molecules, thus forming biphenyl at a yield of 49% and 86.1% and some weakly chlorinated PCBs (such as PCB No. 1, PCB No. 2 and PCB No.15), after irradiation of 4 hr and 8 hr respectively. One observes in particular a very weak decrease of the groups C-CH₂ and C-CH₃ belonging to the pure mineral oil, which

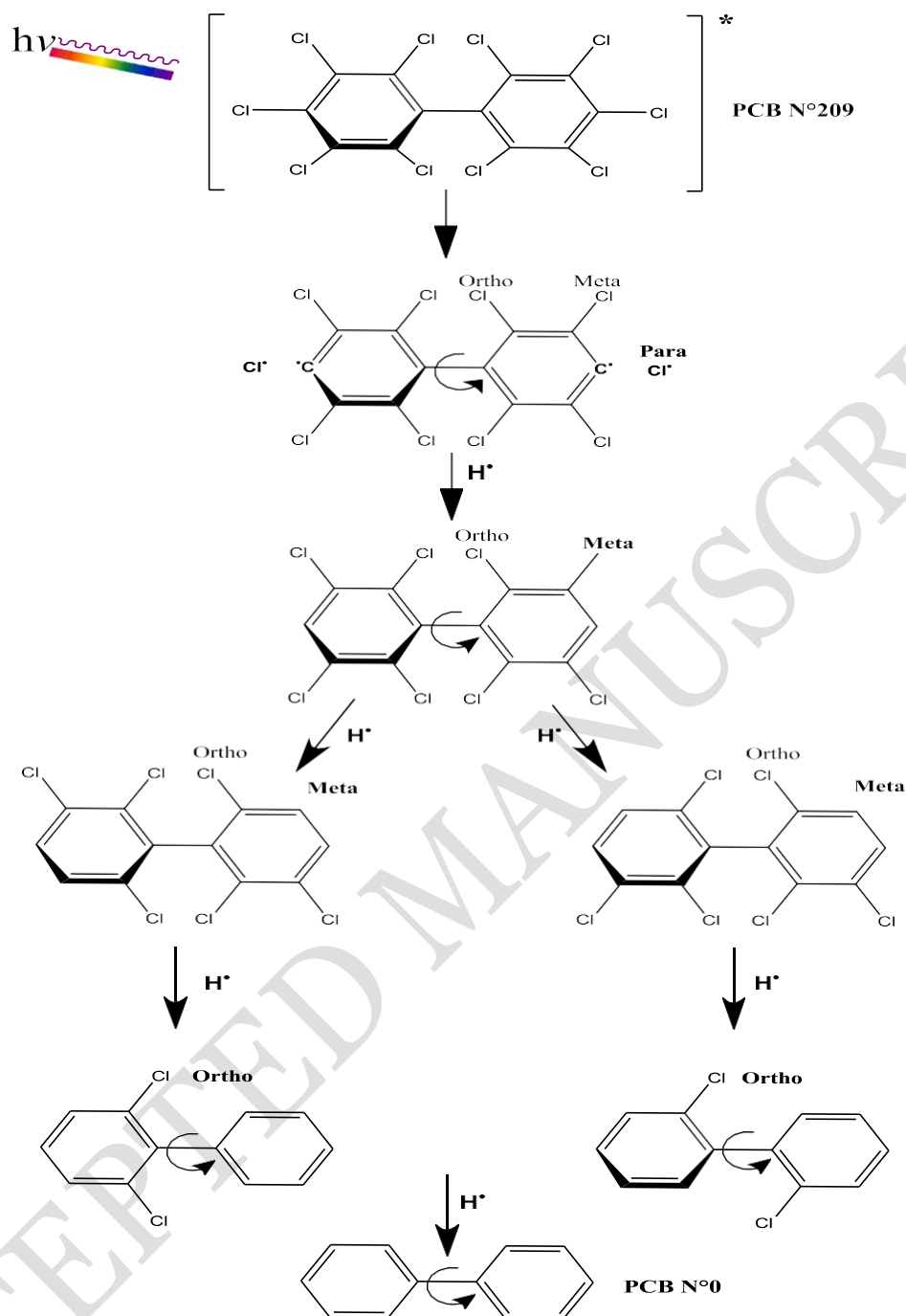


Fig. 5. Suggested dechlorination mechanism for PCB No. 209 from mineral oil under UV-visible irradiation.

confirms that the radiative effect on the pure oil (not represented by the figure) remains very weak.

Table 4 below summarizes the conditions and experimental results of a series of tests.

3.4. Photodegradation of PCBs in a real system monitored by GC

After UV-visible irradiation, a progressive decrease in the PCBs concentration is observed as the exposure time of the real mineral oil system increases [43–45]. At the end of 8 h of irradiation, the objective fixed by the current European legislation, which imposes concentrations in PCBs lower than 50 ppm is reached, with a concentration of 48 ppm, down from an initial 350 ppm. The calculated removal rate of PCBs from

the real system is approximately ~88% (see Fig. 7). The by-products of the radiation treatment are present in small quantities and are therefore not likely to deteriorate the electrical and dielectric properties of the treated oil.

This treatment limits the production of harmful species, of which biphenyl (PCB No. 0) is the ultimate waste product. Once dechlorinated, the chlorides combine with the protons of the oil chain branches ($-\text{C}-\text{H}$) to form chlorinated acid compounds such as Dichloroacetic acid, 2-pentadecyl ester [15]. After the PCB removal step, the real oil system undergoes a regeneration treatment. During this treatment, the chlorinated acidic compounds formed after UV-visible irradiation are adsorbed onto the reactivated BFE. The GC/MS results of the photodecomposition obtained from the transformation of chlorinated PCBs into PCB No. 0 in

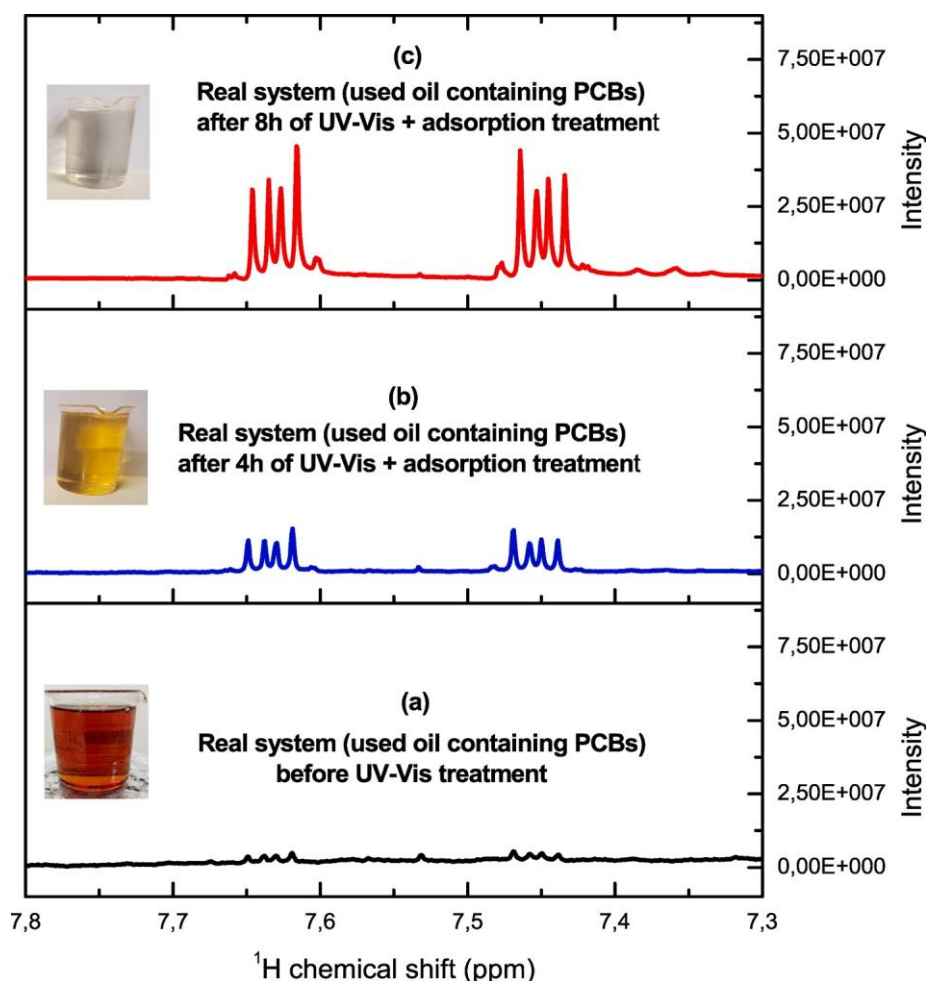


Fig. 6. Zoom on the aromatic zone of a ^1H NMR spectrum of the real system: (a) non-irradiated (b) irradiated during 4 hr (c) irradiated during 8 hr.

Table 4
Conditions and ^1H NMR results of real system.

Parameters	Real system (Used mineral oil contaminated by PCBs)		
The light intensity of the source (%)	Non-irradiated sample	100	100
Sample temperature ($^{\circ}\text{C}$)	Non-irradiated sample	70	70
Radiation exposure time (hr)	Non-irradiated sample	4	8
Integration of the signal on the aromatic zone of the ^1H NMR spectrum (PCBs)	Non-irradiated sample	0.07	0.23
^1H NMR integration ratio (Acetamide)/ (PCBs)	Non-irradiated sample	1/0.23 = 4.35	1/0.5 = 2
Percentage removal (%)	0	49	86.1

the real oil system are presented in Table 5. The other PCBs not listed in (Table 5) are omitted as they were not detected in transformer oil.

LOD and LOQ values were determined from the data of the calibration curves of PCBs (Table 5). These values confirm the reliability of the separation method described above, showing that the pre-treatment used is consistent for complex matrices such as transformer oils.

3.5. Regeneration of the physicochemical properties of mineral oils using BFE

The regeneration of the real oil system (S1) by the BFE presents excellent performances. Indeed, after 4 runs through the adsorbent, the

total acid number (TAN) of the real oil system was reduced from 0.3 mg KOH/g to 0.03 mg KOH/g. The TAN obtained after recovery of the regenerated and decolorized real oil system (S2) is comparable to the TAN of the unused oil. After irradiation of the system (S2), the oil becomes slightly more yellow under the effect of UV-visible radiation (S3). This yellowing effect corresponds to the breakage of the C-Cl bonds and some C-H bonds of the oil chain branches. The irradiated oil system undergoes a second regeneration/decolorization resulting in an oil (S4) similar to the unused oil with a TAN close to 0.03 mg KOH/g (see Table 6).

The color of the oil system is an important property that can be used as a diagnosis and contains critical information about the condition of the transformer. Generally, the dark color of the oil represents the inferior quality of the used/regenerated oil [46,47]. Nevertheless, in the oil recovery process, only the removal of colored contaminants from the used oil can be evaluated according to the color criterion.

The color change of the oil after the regeneration process is quantitatively compared on the basis of ASTM D1500 [47,48]. The corresponding qualitative change in color is presented in Fig. 8, as shown in the latter, the color of the real oil system S1 (dark brown) changes to a clear yellowish color after its recovery from a first color treatment (S1) corresponding to a reduction from 6 to 0.5 according to the standard. After irradiation the color of the oil changes from 0.5 to 1 (S3), before being effectively reduced to 0.5 (S4) thus having the same characteristics of an unused oil (Table 6).

3.5.1. Adsorbent reactivation

The reactivation of BFE is done by thermal treatment in a closed system [51]. The system temperatures range from 250 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$.

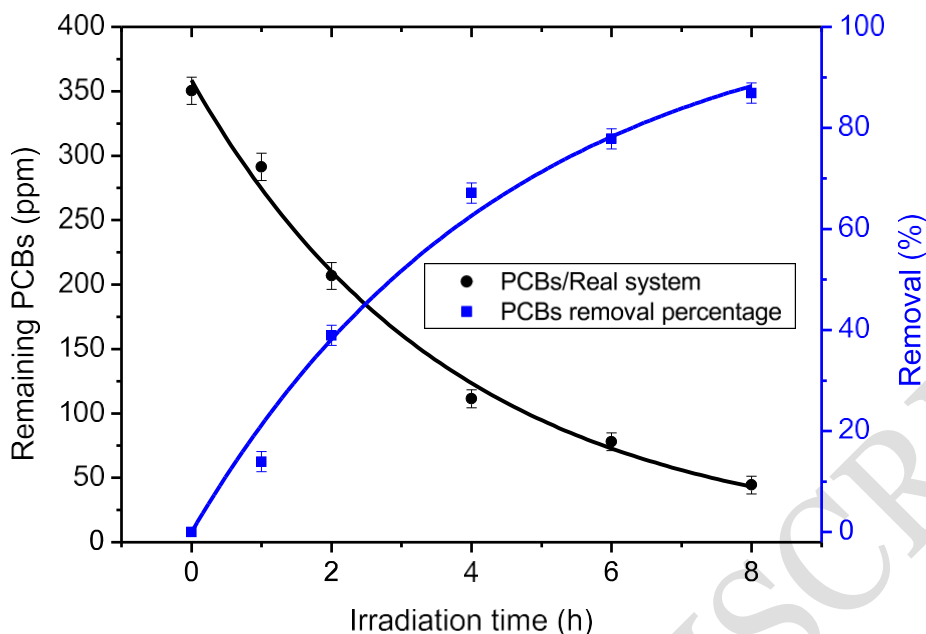


Fig. 7. Kinetics and photodecomposition efficiency of PCBs in a real mineral oil system from a used oil transformer after 8 hr treatment under UV–visible irradiation, the error bars represent the average standard deviation of the results obtained from repeating the experiment three times.

Table 5

Removal rate, LOD and LOQ obtained for each PCB detected in the real system.

Type of PCB	Concentration of PCBs before irradiation (ppm)	Concentration of PCBs after irradiation (ppm)	LOQ (ppm)	LOD (ppm)	percentage of removal (%)
PCB No. 180	27.9	0	1	1	100
PCB No. 153	14.0	0	1	1	100
PCB No. 52	24.6	0	1	1	100
PCB No. 31	52.4	0	1	1	81.3
PCB No. 18	1.3	0	1	1	100
PCB No. 15	14.2	12.2	1	1	14
PCB No. 7	61.4	0	1	1	100
PCB No. 2	70.5	10.3	1	1	85.4
PCB No. 1	85.4	22.8	1	1	73.2
PCB No. 0	91.8	200			increasing the concentration
Average removal of PCBs (%)		87.45			

LOD: limit of detection; LOQ: limit of quantification; PCBs: polychlorinated biphenyl, real system: Oil contaminated with PCBs from a power transformer collected by Arras Maxei Group.

Table 6

Characteristics of the unused oil, the used oil, and those after the regeneration of used oil.

Test	Standard	Unused Mineral oil ^a	Real system S1	Real system S2	Real system S3	Real system S4
TAN (mg KOH/g)	IEC 62,021	0.01	0.3	0.03	0.09	0.03
Color	ASTM D1500	< 0.5	6	0.5	1	< 0.5
Interfacial Tension (mN/m)	ASTM D971	Min. 22	18	43	33	44
PCB (ppm)		0	350	301	48	40
DDF at 90 °C	IEC 60,247	Max 0.005	0.12	0.006	0.006	0.009
Breakdown Voltage (kV)	IEC 156:1995	Min 30	24	50	60	75

^a Unused oil specifications [49,50].

During this treatment, the active sites release the acidic compounds and undesirable adsorbed by-products. After 350 cycles of reactivations, it was observed that the adsorption efficiency of the activated BFE was drastically reduced under the effect of thermal combustion reactions, from ~100% to 2% (Fig. 9).

This effect of thermal aging is the loss of adsorptive activity of the earth due mainly to the sintering of aluminum oxides which represents between 85% and 92% of the composition of BFE [52]. It should be noted that sintering is generally stronger from 350 cycles onwards due to the higher temperatures that are observed as a result of the heat

transfer from the combustion reactions (exothermic).

The phenomenon is translated by a thermally activated phase change. In the case of aluminum oxide, there is an allotropic transformation of its crystallographic forms, shifting from gamma to delta. (850–1050 °C), then theta (1050–1150 °C), and even alpha (greater than 1150 °C), leading to a growth and coalescence of the particles and an elimination of the pores. The water vapor favors the phenomenon. This results in a decrease of the specific surface, closing of the pores (the alpha form presents a typical specific surface of 1–5 m²/g) [52–55].

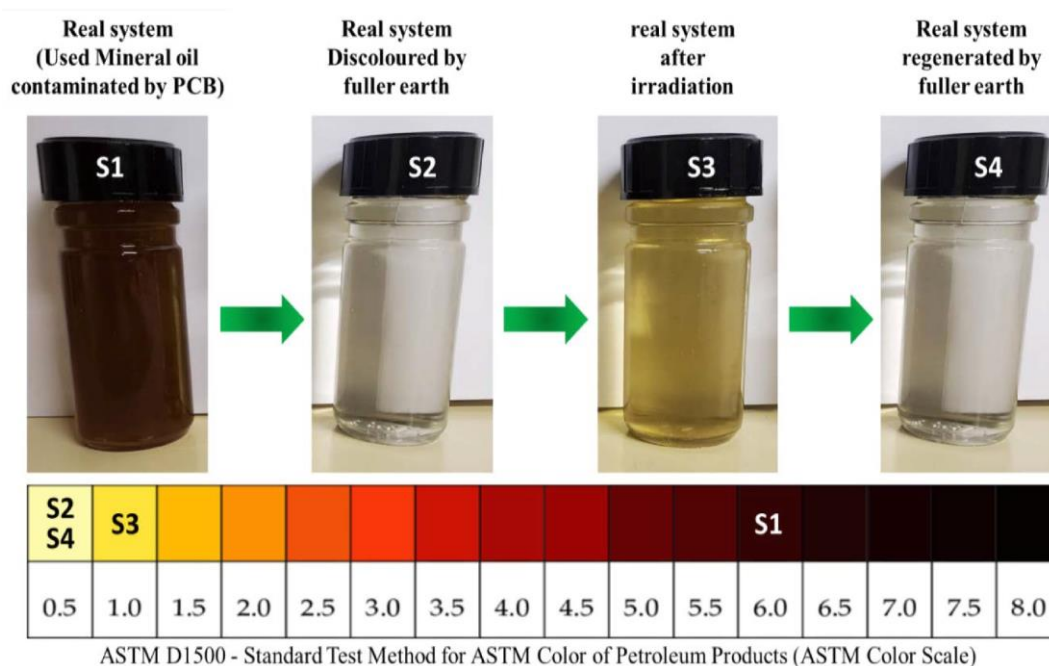


Fig. 8. Real system color before and after BFE treatment.

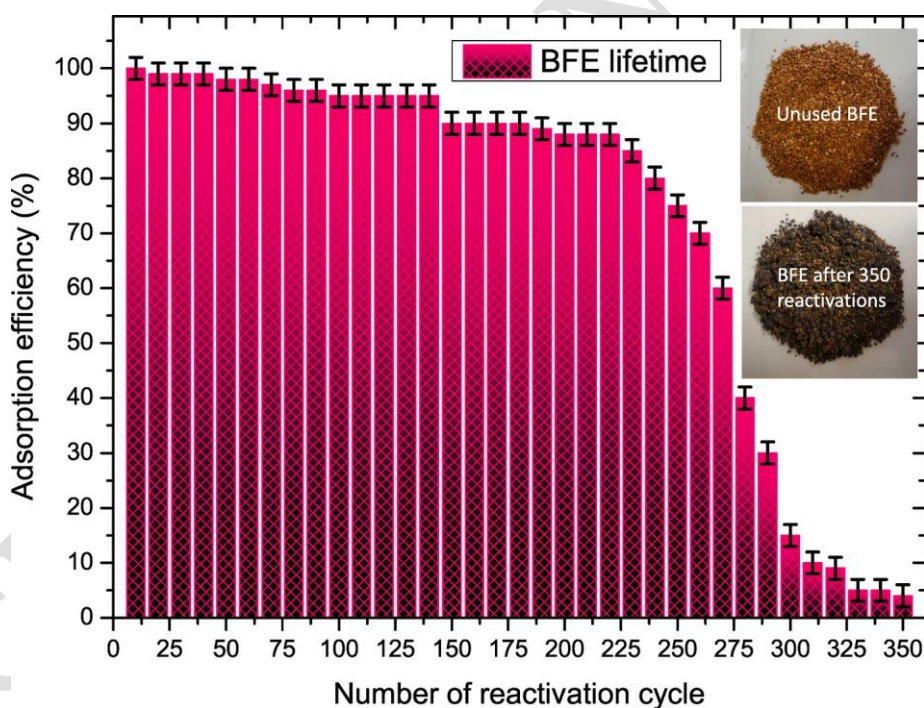


Fig. 9. BFE adsorption efficiency after 350 reactivations.

4. Conclusion

The focus of this study was to explore novel and straightforward techniques for decontaminating transformer oils loaded with PCBs. These organochlorine compounds have been widely used for a long time because of their excellent dielectric and flame-retardant properties, then progressively classified and banned because of their harmfulness. In order to elaborate a systematic study, model systems, such as pure oils, oil/PCB mixtures have been considered. Real systems coming from old transformers have also been treated and analyzed. The combination of

adsorption and UV-visible radiation treatment of PCB-contaminated mineral oil systems has proven to be an effective and innovative remediation method. A first qualitative proton nuclear magnetic resonance spectroscopy (^1H NMR) evaluation via model systems allowed us to qualitatively identify the occurrence of PCBs in the contaminated mineral oil. The application of ^1H NMR, as a new method to address this issue, allowed us to track the process of photodegradation and provided qualitative information about PCBs in oil by the integration of the aromatic part of the ^1H NMR spectra. The GC/MS allows at the same time to separate, identify and quantify the PCB congeners with precision, which

constitutes a big advantage. The multiple analyses carried out (dielectric spectroscopy, breakdown voltage, interfacial voltage, TAN, etc.) on the mineral oil systems, contaminated or not, confirm the preservation of their physical and chemical properties after treatment by the combination of UV-visible irradiation and adsorption processes on the BFE. The studies in static mode showed that the concentration of PCBs could be reduced to a value lower than 50 ppm after 8 hr of irradiation. The main by-products generated by the radiative treatment, which include chlorinated acids, mono-, bi-, tri-chlorinated and non-chlorinated biphenyl molecules, are neither toxic nor prohibited by the legislation. The BFE used as an adsorbent for the formed chlorinated acid compounds can be thermally reactivated from 250 to 350 times.

CRedit authorship contribution statement

Chems Eddine Gherdaoui: Conceptualization, Investigation, Methodology, Resources, Writing – review & editing. **Hanene Oumeddour:** Resources, Investigation. **Hussam Aldoori:** Investigation. **Chakib Alaoui:** Investigation. **Jean-Philippe Delbarre:** Methodology. **Zohra Bouberka:** Supervision. **Philippe Supiot:** Supervision. **Djahida Lerari:** Supervision, Formal analysis. **Ulrich Maschke:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2023.126028>.

References

- [1] M.A. Sadañoski, S.F. Benitez, J.E. Velázquez, M.I. Fonseca, P.D. Zapata, L.N. Levin, L.L. Villalba, Bioprocess conditions for treating mineral transformer oils contaminated with polychlorinated biphenyls (PCBs), *J. Environ. Chem. Eng.* 8 (2020), 104068, <https://doi.org/10.1016/j.jece.2020.104068>.
- [2] C.E. Gherdaoui, H. Aldoori, C. Alaoui, H. Oumeddour, Z. Taibi, N. Zeggai, D. Lerari, U. Maschke, Exploring organo-bentonite adsorption properties for biphenyl removal from organic-aqueous media: kinetic study and industrial perspective, *Braz. J. Develop.* 9 (2023) 29886–29910. <https://doi.org/10.34117/bjdv9n11-039>.
- [3] K. Li, M. Landriault, M. Fingas, A. Potvin, On site PCB analysis in support of a transformer rebuilding project, *J. Hazard. Mater.* 83 (2001) 123–134, [https://doi.org/10.1016/S0304-3894\(00\)00331-9](https://doi.org/10.1016/S0304-3894(00)00331-9).
- [4] S. Knerr, D. Schrenk, Carcinogenicity of “Non-Dioxinlike” polychlorinated biphenyls, *Crit. Rev. Toxicol.* (2008), <https://doi.org/10.1080/10408440600845304>.
- [5] C. Klocke, S. Sethi, P.J. Lein, The developmental neurotoxicity of legacy vs. contemporary polychlorinated biphenyls (PCBs): similarities and differences, *Environ Sci Pollut Res.* 27 (2020) 8885–8896, <https://doi.org/10.1007/s11356-019-06723-5>.
- [6] I.N. Pessah, P.J. Lein, R.F. Seegal, S.K. Sagiv, Neurotoxicity of polychlorinated biphenyls and related organohalogenes, *Acta Neuropathol.* 138 (2019) 363–387, <https://doi.org/10.1007/s00401-019-01978-1>.
- [7] C. Klocke, P.J. Lein, Evidence implicating non-dioxin-like congeners as the key mediators of polychlorinated biphenyl (PCB) developmental neurotoxicity, *Int. J. Mol. Sci.* 21 (2020) 1013, <https://doi.org/10.3390/ijms21031013>.
- [8] S.P.J. van Leeuwen, J. de Boer, Advances in the gas chromatographic determination of persistent organic pollutants in the aquatic environment, *J. Chromatogr. A* 1186 (2008) 161–182, <https://doi.org/10.1016/j.chroma.2008.01.044>.
- [9] L. Passatore, S. Rossetti, A.A. Juwarkar, A. Massacci, Phytoremediation and bioremediation of polychlorinated biphenyls (PCBs): state of knowledge and research perspectives, *J. Hazard. Mater.* 278 (2014) 189–202, <https://doi.org/10.1016/j.jhazmat.2014.05.051>.
- [10] M.D. Erickson, R.G. Kaley, Applications of polychlorinated biphenyls, *Environmental Science and Pollution, Research* 18 (2011) 135–151, <https://doi.org/10.1007/s11356-010-0392-1>.
- [11] U.N.E. Programme, Consolidated Assessment of Efforts Made Toward the Elimination of Polychlorinated Biphenyls, (2016). <https://wedocs.unep.org/xmlui/handle/20.500.11822/31249> (accessed November 20, 2023).
- [12] V. Vaccher, P. Marchand, M. Picherot, G. Dervilly-Pinel, E. Lesquin, A. Brosseau, A. Venisseau, B. Le Bizec, Field investigation to determine the environmental source of PCBs in a pig farm, *Food Chem.* 245 (2018) 394–401, <https://doi.org/10.1016/j.foodchem.2017.10.105>.
- [13] M. Cerasa, P. Benedetti, A. De Stefanis, E. Guerriero, S. Mosca, A. Bacaloni, M. Rotatori, Validation studies on activated carbon fiber passive sampler for PCDD/Fs and PCBs in water, *Chemosphere* 239 (2020), 124666, <https://doi.org/10.1016/j.chemosphere.2019.124666>.
- [14] D.-D. Nguyen, C.-L. Tsai, Y.-C. Hsu, Y.-W. Chen, Y.-M. Weng, M.B. Chang, PCDD/Fs and dl-PCBs concentrations in water samples of Taiwan, *Chemosphere* 173 (2017) 603–611, <https://doi.org/10.1016/j.chemosphere.2017.01.087>.
- [15] Official Journal of the European Union, Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on Waste Electrical and Electronic Equipment (WEEE) (recast), n.d. <http://data.europa.eu/eli/dir/2012/19/2018-07-04>.
- [16] Official Journal of the European Union L 243, Council Directive 96/59/EC of 16 September 1996 on the disposal of polychlorinated biphenyls and polychlorinated terphenyls (PCB/PCT), 2009. <http://data.europa.eu/eli/dir/1996/59/2009-08-07>.
- [17] V. Pelitli, Ö. Doğan, H. Köroğlu, Transformer oils potential for PCBs contamination, *Int. J. Metall. Mater. Eng.* 1 (2015) 1–8. <https://doi.org/10.15344/2455-2372/2015/114>.
- [18] U.N. Environment, PCB Elimination Network, UNEP - UN Environment Programme. (2017). <http://www.unep.org/explore-topics/chemicals-waste/what-we-do/persistent-organic-pollutants/pcb-elimination-network> (accessed March 27, 2023).
- [19] Manuel de formation visant la préparation d'un Plan National pour la Gestion Ecologiquement Rationnelle des PCBs et des équipements contaminés aux PCBs dans le cadre de la mise en oeuvre de la Convention de Bâle, 1999.
- [20] C.E. Gherdaoui, Z. Bouberka, P. Supiot, U. Maschke, J.-P. Delbarre, O. Hutin, R. Sansano, Method for dechlorination of one or more aromatic organochlorine compound(s) contained in an oil or forming said oil - associated electrical/electronic device and installation, 2021.
- [21] M. Yan, X. Li, T. Chen, S. Lu, J. Yan, K. Cen, Effect of temperature and oxygen on the formation of chlorobenzene as the indicator of PCDD/Fs, *J. Environ. Sci.* 22 (2010) 1637–1642, [https://doi.org/10.1016/S1001-0742\(09\)60300-4](https://doi.org/10.1016/S1001-0742(09)60300-4).
- [22] Paul.A. Helm, Terry.F. Bidleman, Current combustion-related sources contribute to polychlorinated naphthalene and dioxinlike polychlorinated biphenyl levels and profiles in air in Toronto, Canada, *Environmental Science & Technology.* 37 (2003) 1075–1082. <https://doi.org/10.1021/es020860a>.
- [23] M. Cobo, J.A. Conesa, C. Montes de Correa, The Effect of NaOH on the Liquid-Phase Hydrodechlorination of Dioxins over Pd/γ-Al₂O₃ 112 (2008) 8715–8722, <https://doi.org/10.1021/jp802570t>.
- [24] P. Thongkaow, T. Prueksasit, W. Siritwong, Activity-based exposure levels and lifetime cancer risk for workers exposed to polychlorinated biphenyls during electronic waste dismantling in Buriram province, Thailand, *Atmosph. Environ.* 287 (2022), 119289, <https://doi.org/10.1016/j.atmosenv.2022.119289>.
- [25] M. Chaychian, J. Silverman, M. Al-Sheikhly, D.L. Poster, P. Neta, Ionizing Radiation Induced Degradation of Tetrachlorobiphenyl in Transformer Oil, *Environ. Sci. Tech.* 33 (1999) 2461–2464, <https://doi.org/10.1021/es9900914>.
- [26] H.-F. Qin, H.-Y. Bao, A.-D. Liu, X.-G. Hou, Photodegradation of 4-chlorobiphenyl in hexane by UV irradiation, *Chin. J. Chem.* 24 (2006) 355–359, <https://doi.org/10.1002/cjoc.200690068>.
- [27] C.G. Jones, J. Silverman, M. Al-Sheikhly, P. Neta, D.L. Poster, Dechlorination of polychlorinated biphenyls in industrial transformer oil by radiolytic and photolytic methods, *Environ. Sci. Tech.* 37 (2003) 5773–5777, <https://doi.org/10.1021/es030412i>.
- [28] J. Kong, G. Achari, C.H. Langford, Dechlorination of polychlorinated biphenyls in transformer oil using UV and visible light, *J. Environ. Sci. Health A* 48 (2013) 92–98, <https://doi.org/10.1080/10934529.2012.707856>.
- [29] W. Tumiatti, G. Nobile, P. Tundo, Process for the fast chemical decomposition of halogenated and polyhalogenated organic compounds, such as polychlorobiphenyls, polychlorodibenzofurans and polychlorodibenzodioxins, and for the decontamination of surfaces or fluids, 1986. <https://patents.google.com/patent/EP0257170A1/fr?oq=EP0257170A1>.
- [30] C. Antonetti, D. Licursi, A.M. Raspolli Galletti, M. Martinelli, F. Tellini, G. Valentini, F. Gambineri, Application of microwave irradiation for the removal of polychlorinated biphenyls from siloxane transformer and hydrocarbon engine oils, *Chemosphere* 159 (2016) 72–79, <https://doi.org/10.1016/j.chemosphere.2016.05.066>.
- [31] C. Giancarlo, W. Tumiatti, C.M. Roggero, Process for the degradation and/or detoxification of Chemical and Biological Pollutants (2008). <https://patents.google.com/patent/US20080319246A1/en?oq=US2008319246A1>.

- [32] I. Atanasova-Höhlein, IEC 60296 (Ed. 5) – a standard for classification of mineral insulating oil on performance and not on the origin, *Transformers Magazine*, 8 (2021).
- [33] L. Turrio-Baldassarri, A. di Domenico, A.R. Fulgenzi, N. Iacovella, C. La Rocca, Differences in polychlorobiphenyl (PCB) contamination patterns in various environmental matrices, *Sci. Total Environ.* 134 (1993) 1439–1451, [https://doi.org/10.1016/S0048-9697\(05\)80149-4](https://doi.org/10.1016/S0048-9697(05)80149-4).
- [34] C.E. Gherdaoui, Z. Bouberka, J.-P. Delbarre, O. Hutin, R. Sansano, L. Leclercq, P. Supiot, U. Maschke, A simple and reliable method for separation of mineral oil/polychlorobiphenyl mixtures, *Waste Manag. Res.* 41 (2023) 182–194, <https://doi.org/10.1177/0734242X221105436>.
- [35] A. Raymon, R. Karthik, Reclaiming aged transformer oil with activated bentonite and enhancing reclaimed and fresh transformer oils with antioxidants, *IEEE Trans. Dielect. Electr. Insul.* 22 (2015) 548–555, <https://doi.org/10.1109/TDEI.2014.004094>.
- [36] N.M. Faber, R. Rajkó, How to avoid over-fitting in multivariate calibration—the conventional validation approach and an alternative, *Anal. Chim. Acta* 595 (2007) 98–106, <https://doi.org/10.1016/j.aca.2007.05.030>.
- [37] Z. Tretjak, A. Sebenik, J. Jan, ¹H NMR identification of some polychlorinated biphenyls (PCBs) and partially oxidized PCB congeners in human adipose tissue, *Chemosphere* 23 (1991) 383–390, [https://doi.org/10.1016/0045-6535\(91\)90192-G](https://doi.org/10.1016/0045-6535(91)90192-G).
- [38] U. Dr, R. Holzgrabe, C. Deubner, B.W. Schollmayer, Quantitative NMR spectroscopy - applications in drug analysis, *J. Pharmaceut. Biomed. Anal.* 38 (2005) 806–812, <https://doi.org/10.1016/j.jpba.2005.01.050>.
- [39] B. Vidal, Influence des interactions lointaines sur la transition secondaire du chromophore benz-nique dans des molécules du type ~b(CH~).X~Xz, *Spectrochimica Acta*. 38 A (1982) 367–381. [https://doi.org/10.1016/0584-8539\(82\)80010-X](https://doi.org/10.1016/0584-8539(82)80010-X).
- [40] C. Tu, N. Ma, Q. Xu, W. Guo, L. Zhou, G. Zhang, Computational study on the mechanism of metal-free photochemical borylation of aryl halides, *Int. J. Quant. Chem.* 122 (2022) e26920.
- [41] N. Kvasovs, V. Gevorgyan, Contemporary methods for generation of aryl radicals, *Chem. Soc. Rev.* 50 (2021) 2244–2259, <https://doi.org/10.1039/DoCS00589D>.
- [42] G. Su, L. Huang, R. Shi, Y. Liu, H. Lu, Y. Zhao, F. Yang, L. Gao, M. Zheng, Thermal dechlorination of PCB-209 over Ca species-doped Fe₂O₃, *Chemosphere* 144 (2016) 81–90, <https://doi.org/10.1016/j.chemosphere.2015.08.022>.
- [43] M. Lores, M. Llompert, R. Gonzalez-Garcia, C. Gonzalez-Barreiro, R. Cela, Photolysis of polychlorinated biphenyls by solid-phase microextraction “On-fibre” versus aqueous photodegradation, *J. Chromatogr. A*. 963 (2002) 37–47, [https://doi.org/10.1016/S0021-9673\(02\)00555-1](https://doi.org/10.1016/S0021-9673(02)00555-1).
- [44] Y. Yao, K. Kakimoto, H.I. Ogawa, Y. Kato, Y. Hanada, R. Shinohara, E. Yoshino, Reductive dechlorination of non-ortho substituted polychlorinated biphenyls by ultraviolet irradiation in alkaline 2-propanol, *Chemosphere* 35 (1997) 2891–2897, [https://doi.org/10.1016/S0045-6535\(97\)00282-8](https://doi.org/10.1016/S0045-6535(97)00282-8).
- [45] X. Ortiz Almira, N. Solà Yagüe, R. Gonzalez-Olmos, J. Díaz-Ferrero, Photochemical degradation of persistent organic pollutants (PCDD/FS, PCBS, PBDES, DDTS and HCB) in hexane and fish oil, *Chemosphere* 301 (2022), 134587, <https://doi.org/10.1016/j.chemosphere.2022.134587>.
- [46] L. Safiddine, A. Hadj-Ziane Zafour, I. Fofana, A. Skender, F. Guerbas, A. Boucherit, Transformer oil reclamation by combining several strategies enhanced by the use of four adsorbents, *IET Gener. Transm. Distrib.* 11 (2017) 2912–2920, <https://doi.org/10.1049/iet-gtd.2016.1995>.
- [47] L.S. Oumert, D. Rahal, A.H.-Z. Zafour, I. Fofana, Characterization and Rheological Behaviour of a Used Insulating Oil and a Transformer Sludge, in: 2019 Algerian Large Electrical Network Conference (CAGRE), IEEE, Algiers, Algeria, 2019: pp. 1–5. <https://doi.org/10.1109/CAGRE.2019.8713308>.
- [48] Do2 Committee, Test Method for ASTM Color of Petroleum Products (ASTM Color Scale), ASTM International, n.d. <https://doi.org/10.1520/D1500-12R17>.
- [49] R. Behmadi, M. Mokhtarian, K. Ghadrian, A. Davoodi, S. Hosseinpour, Development of a low-cost activated mesoporous bauxite for the reclamation of used transformer oil, *Separ. Purif. Technol.* 280 (2022), 119826, <https://doi.org/10.1016/j.seppur.2021.119826>.
- [50] V. Tumiatti, C. Roggero, M. Tumiatti, S. Di Carlo, R. Maina, S. Kapila, IEC 62697–2012: State of the art methods for quantification of DBDS and other corrosive sulfur compounds in unused and used insulating liquids, *IEEE Trans. Dielect. Electr. Insul.* 19 (2012) 1633–1641, <https://doi.org/10.1109/TDEI.2012.6311510>.
- [51] S. Bhargava, M. Allen, M. Hollit, S. Grocott, H. Hartshorn, D. Akolekar, Thermal activation of bauxite, *Chem. Australia*. 71 (2004) 6–8, <https://doi.org/10.3316/IELAPA.888276098758549>.
- [52] S. Román, B. Ledesma, A. Álvarez-Murillo, J.F. González, Comparative study on the thermal reactivation of spent adsorbents, *Fuel Process. Technol.* 116 (2013) 358–365, <https://doi.org/10.1016/j.fuproc.2013.07.019>.
- [53] A.K. Neyestanaki, F. Klingstedt, T. Salmi, D.Y. Murzin, Deactivation of postcombustion catalysts, a review, *Fuel* 83 (2004) 395–408, <https://doi.org/10.1016/j.fuel.2003.09.002>.
- [54] X. Ding, G. Xu, D. Wang, Z. Luo, T. Wang, Effect of Synergistic Aging on Bauxite Residue Dust Reduction Performance via the Application of Colloids, an Orthogonal Design-Based Study, *Polymers* 13 (2021) 1986, <https://doi.org/10.3390/polym13121986>.
- [55] A. Sassi, E. Rohart, G. Belot, Post-traitement des émissions polluantes des moteurs thermiques à combustion interne - Moteurs à allumage commandé, Véhicule et mobilité du futur. (2011). <https://doi.org/10.51257/a-v1-bm2508>.