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Supercritical extraction of polymers from printed circuit boards using CO2 and ethanol

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ABSTRACT

The printed circuit boards are the fundamental components of waste electrical and electronic equipment (WEEE). The PCBs stand out due to the amount of metals in their composition as well for their complex and heterogeneous constitution that make their recycling difficult. In this context, the aims of the study was to evaluate the application of supercritical CO_2 modified with ethanol in order to remove the polymers contained in PCBs from discarded mobile phones. The PCBs were characterized and an evaluation of the supercritical extraction was performed through experimental design. The characterization showed that PCBs contained 64.02 wt% of metals, 20.51 wt% of ceramics and 15.47 wt% of polymers. The fractional factorial experimental design showed that 69.53 wt% of the polymers present in the PCBs were extracted, at 170 °C and 7.5 MPa. As the remaining polymers are no longer covering the metals, they could be more easily leached and therefore more effectively recovered.

1. Introduction

Mobile phones are among the main items found in electrical and electronic equipment wastes (WEEEs) [1,2] and had a useful lifetime of approximately one year [3]. In addition, the production of printed circuit boards (PCBs) is the basis of the electronics industry because the PCBs are essential components of waste electrical and electronic equipment (EEEs) [4]. Although PCBs correspond to only about 6% of the total weight of the WEEEs, they represent a significant portion of the value contained in the WEEEs since PCBs contain large amounts of precious metals, such as Au and Ag [5]. PCBs are a very heterogeneous material composed of by large part of the elements found in the periodic table [6]. In accordance with Yamane et al. [3], PCBs from mobile phones comprises approximately 63% of metals, 24% of ceramics and 13% of polymers. Among all metals present in PCBs, copper is present in the highest percentage [7] about 34.5 wt% in PCBs from mobile phones [3]. Copper is a highly valued metallic element from the industrial point of view and is widely used in its pure state, it acts as an essential metal to making various circuit boards, electric wires, different types of contact points, etc. [8].

The main three basic parts that composes the PCBs are: the non-conductive or laminate substrate; the printed circuit conductor (printed on the surface or within a substrate) typically made of copper; and the mounted components (capacitors, connectors, chips, etc). Among the various types of substrates used in the PCBs, the Flame Retardant 4 (FR4) is the most used. This substrate is produced using an epoxy resin reinforced by fiberglass, with a brominated flame retardant dispersed in the epoxy matrix [6]. Typically, the laminated substrate presents in its composition about 15 wt% of the brominated flame retardant, tetrabromobisphenol A (TBBPA) [9].

The proper treatment of PCBs is needed because the great number of toxic substances in its composition, such as brominated flame retardants, plastics and heavy metals that can cause serious environmental problems and even harm to human health if not correctly disposed [7,10]. If the PCBs are incinerated, they will produce dangerous by-products such as dioxins and furans, generated by burning of brominated flame-retardants compounds, epoxy resins and plastics [7]. Dioxins, for example are known to be lipophilic carcinogens and endocrine disruptors, which accumulate in living organisms and in food chains [11].

However, recycling of PCBs is limited due to the heterogeneity of the materials and complexity of their production [12]. The polymers present in the PCBs are thermoplastic and thermosetting resins, containing the metals within their structure, making it difficult to separate

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the materials [13]. For this reason, the studies of recycling techniques for these materials include different routes such as mechanical, thermal, and chemical processing, or different combinations of these procedures [14].

Supercritical fluids have been considered as an alternative to conventional methods, due to their advantageous mass transfer properties, compared to others solvents [15]. The use of carbon dioxide (CO_2) has been investigated because it has a relatively low critical point (Tc = 31.1 °C, Pc = 7.38 MPa), is environmentally acceptable, can be recycled and reused, and can be used together with co-solvents [16].

The use of supercritical CO_2 and co-solvents have been studied for the recycling of PCBs. Supercritical fluid extraction presents an attractive alternative to organic solvent extraction for flame retardants [17]. Water was used as a co-solvent, in order to de-laminate the PCBs and separate its constituents by removing the polymers [18]. The supercritical CO_2 is also used with others co-solvents, such as sulfuric acid and hydrogen peroxide [19,20], and acid citric and hydrogen peroxide [21] to recover valuable metals from wastes. Copper was recovered from PCBs [19], cobalt was recovered from lithium-ion batteries [20] and indium was recovered from discarded LCD screens [21] using supercritical extraction. Altwaiq et al. [22] studied the bromine extraction of the brominated flame retardants from various polymers through supercritical CO_2 and obtained an improvement in the extraction efficiency with toluene, acetonitrile, and tetrahydrofuran (THF) as co-solvents. Furthermore, Liu et al. [23] employed supercritical extraction in two steps to recycling PCBs. They combined supercritical water oxidation, and supercritical carbon dioxide extraction techniques. In the first step non-metallic components were degraded and in the second step Pd and Ag were extracted using supercritical CO_2 modified with acetone and KI-I_2.

As known, the main drawback of supercritical CO_2 with low polarity is difficult to extract polar components [24]. However, when small quantities of polar co-solvents are added to nonpolar supercritical fluids, such as CO_2, they can significantly increase the solubility of organic compounds. This also can be applied for removal of the organic fraction of PCBs [25]. Thus, the use of ethanol as co-solvent emerges as an interesting alternative, since the ethanol is a polar protic solvent, completely miscible in water and soluble in most of common organic solvents [26]. Furthermore, ethanol can be obtained from biomass that is a renewable source. The production of ethanol using biomass is abundant mainly in the United States through the utilization of corn, and in Brazil through sugarcane [27,28]. Ethanol produced from biomass is considered non-toxic, inexpensive, affordable and renewable [28].

The aim of this study was to evaluate the removal of the polymeric fraction from PCBs, using supercritical CO_2 modified with ethanol. This study was conducted using a factorial design and the response surface methodology. Supercritical CO_2 and ethanol were used since they represent a renewable and environmentally acceptable technology, with great potential for extraction of organic material from the PCBs.

2. Materials and methods

2.1. Comminution process

Waste PCBs used in this work were obtained by manual disassembly of discarded mobile phones. Twenty-nine PCBs of the same model were selected by sampling. The selected PCBs presented an average weight of 14.32 g. The comminution process of the PCBs initially was done in a hammer mill (Tigre, A4 model) with a 5 mm sieve. Then the particulate obtained in the hammer mill was sent to a new comminution step using a knife mill (Rone, N-150 model) with a sieve of 2 mm. In this way, the PCBs were reduced from their initial size of 80 × 40 mm to particles with diameter smaller than 2 mm [19].

2.2. PCBs characterization

Samples of the material obtained in the comminution process (380.5 g) were separated by quartering, resulting in 3 samples with approximately 3 g each. These samples were used to determine the weight fraction of metals, polymers, and ceramics that constitutes the PCBs.

The loss-on-ignition (LOI) method was employed for determination of the polymeric fraction. Initially, three ceramic crucibles containing the 3 samples previously weighed were placed in a muffle furnace under a heating ramp of 10 °C min^{-1}, until reach 550 °C, with a dwell time of 60 min [29,30]. After volatilization of the organic fraction, the weight fraction of the polymers was calculated by the difference between initial and final weight (after LOI). The resulting inorganic fraction obtained corresponds to the fractions of metals and ceramics [3].

The samples resulting from the LOI were leached with aqua regia (HNO_3 and HCl in a 1:3 ratio) with a solid: liquid ratio of 1:50, 90 °C, 600 rpm and leaching time of 60 min [19]. After leaching, the remaining material were weighed and this resulting mass represents the ceramic fraction, while the leached mass corresponds to the metal fraction. Flame Atomic Absorption Spectrometry (240FS AA, Agilent Technologies) was used to determine the copper concentration contained in the leached solutions. Copper was analyzed because it is the metal present in higher concentrations in PCBs [7], then it is used to evaluate if the metals were concentrated in the sample after the supercritical extraction of the polymers.

The quantification of the polymeric fraction and evaluation of the PCBs thermal behavior was done by thermogravimetric analysis (DTG-60H, Shimadzu) using a sample of 33.14 mg. This analysis was made in the nitrogen atmosphere at a flow rate of 50 mL/min with a heating rate 10 °C/min to a temperature of 500 °C.

2.3. Supercritical extraction

The system used in supercritical extraction is composed of a 304 stainless steel reactor with an internal volume of 98 mL. The reactor is jacketed, allowing temperature control through an oil heating bath (model Q213-22, Quimis). After the extraction valve, there is the collecting flask, where the CO_2 is separated from the extracted solution. CO_2 (99.5%) was provided to the pressurized system, and the required pressure was achieved using a high-pressure syringe pump (model 500D, Teledyne ISCO). More information about the extraction system can be found in previous works [19,21].

Samples of approximately 2 g each, were obtained by quartering the previously comminuted PCBs (< 2 mm). Each sample was inserted into the reactor along with the co-solvent (ethanol 99.5%). The solid: liquid ratio of each experiment was determined in relation to the volume of ethanol that was used as a co-solvent. After reaching the set temperature, the reactor was kept at this temperature during the time corresponding to each test. The resulting oily-liquid samples were separated from the solid material by the extraction valve. The remaining solid material was removed from the reactor and weighed. The solid samples were weighed before (w_i) and after extractions (w_f). The weight percentage of extracted polymers was determined from the difference between the initial weight (w_i) and the final weight (w_f), considering the percentage of polymers contained in the PCBs, according to Eq. 1.

$$extractedpolymers\% = \frac{100 \times (w_i - w_f)}{w_i \times polymerspercentageinPCBs} \tag{1}$$

The oily-liquid samples resulting from the supercritical extractions performed with the fractional factorial design were diluted with ethyl acetate and analyzed by gas chromatography coupled mass spectrometry (GCMS-QP2010 Plus, Shimadzu) with a capillary column (HP-5MS) under the following conditions: 30 min at a heating ramp up to