

ABSORPTION OF DIOXIN USING HIGH TEMPERATURE STABLE IONIC LIQUIDS

Kulkarni Prashant^[a,b], Neves Luisa^[b], Afonso Carlos^[a], Crespo Joao^[b]

^{a)} CQFM, Dept. de Engenharia Química, IST, 1049-001 Lisboa, ^{b)} REQUIMTE, Dept. de Química, CT/UNL, 2829-516 Caparica, PORTUGAL.

Introduction

Dioxin mainly originate from the incineration and combustion sources, are considered to be among the most dangerous pollutants on earth¹. Absorption of dioxin using high temperature stable ionic liquids (HTSILs) can offer a unique separation solution for the removal and concentration of these compounds from such sources. HTSILs may withstand the high temperature of these gaseous effluents and, simultaneously, exhibit an extremely low vapor pressure²⁻³. Therefore, the safety and environmental friendliness of absorptive separation techniques can be improved with the use of HTSILs. The present work demonstrates the absorption of dioxin compounds using HTSILs as a selective and versatile separation process, competent to quantitatively capture dioxin from the gaseous streams.

Materials and Methods

Thermally stable ILs having degradation temperature more than 250 °C were prepared based on the combination of the cations containing trioctyl-methyl ammonium [Aliquat]⁺, 1-benzyl-3-methyl-imidazolium [Bzmim]⁺, 1-*n*-octyl-3-methyl-imidazolium [C₈mim]⁺ and dimethyl-tetra-hexyl guanid-inium [DMG]⁺ units and the anions *p*-toluene sulfonate [TSA], bis-trifluoromethanesulfonimide [Tf₂N] and dicyanamide [DCA]. Absorption studies were performed by measuring the amount of dioxin compounds present in the HTSIL after constant exposure, above room temperature (100–200 °C), to a saturated air stream containing a synthetically simulated gaseous dioxin stream. HTSIL blank experiment was performed in order to find the concentration of dioxin in the vapor phase at a given temperature.

A specially devised glass assembly having a capacity of 100 mL was used for the absorption studies. The dioxin gases were generated inside the chamber using compounds, dibenzo-*p*-dioxin, 2-chlorodibenzo-*p*-dioxin, and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin. For the absorption purpose each dioxin compound (50-200 mg) was placed in the glass vials. The HTSIL (500 -1000 mg) to be tested was also placed in the separate glass vial and stirred. The whole assembly was kept at ambient pressure and at a constant temperature (100 – 200 °C) inside the microwave oven. The concentration of dioxin in the vapor phase was found to be 0.1 – 0.12 µg/mL⁴.

The toxic gas generated was absorbed into the ionic liquid. Absorption runs were performed from 10-100 h. Further, the IL containing the absorbed dioxin compound was weighed accurately and passed through a column of silica for desorption and analysis. A mixture of 40% of ethyl acetate in ether was used as an eluent. The concentration of absorbed compound in the ILs (mg/g) was determined by GLC analysis by prior addition of benzophenone as an internal standard.

Results and Discussion

The system was validated by measuring the amount of dibenzo-*p*-dioxin absorption in ionic liquid [Aliquat][DCA] at 100 °C. Equilibrium was achieved within 48 h. The measured dibenzo-*p*-dioxin capacity was found to be 15.6% by weight at equilibrium (Figure 1). The gain in mass of ionic liquid due to the absorption was measured by using weighing balance and by Gas Chromatography. At this equilibrium, the molar ratio of dibenzo-*p*-dioxin to [Aliquat][DCA] was 0.39:1. The ¹H NMR spectrums of the dibenzo-*p*-dioxin treated [Aliquat][DCA] and untreated are presented in Figure 2. Integrations of the NMR spectra also exhibited same molar ratios. Two new resonances were observed at δ = 6.85 ppm (multiplet, 4H) and 6.81 ppm (multiplet, 4H). These observations may suggest that there is no considerable specific bond formed between the ionic liquid [Aliquat][DCA] and dibenzo-*p*-dioxin during the absorption. Probably, the absorption of dioxin in the ionic liquids is merely governed by weak van der Waals forces of attraction and/or via the formation of inclusion type compounds⁵. This impressive absorption capacity of the ionic liquid in one equilibrium stage clearly demonstrates the enormous potential of this media for the efficient capture of dioxins present in the environment at several contaminated sources, with diverse concentrations¹.

Screening for an optimal solution involved also the design and synthesis of task-specific, HTSILs, from which six best candidates having absorption capacities equal to or higher than 1 wt% of dioxin were selected. It was observed that at equilibrium, the HTSIL took up 4.1 wt% [DMG][DCA], 4.8 wt% [Bzmim][DCA], 15.6 wt% [Aliquat][DCA], 18 wt% [C₈mim][DCA], 1 wt% [C₈mim][TSA], and 7.5 wt% [C₈mim][Tf₂N] of dibenzo-*p*-dioxin. Interestingly, the HTSIL

[C₈mim][TSA] is more prone to crystallize and provides the lowest absorption capacity. It was found that irrespective of the cation the anion [DCA] has exhibited best absorption capability than the others. Further, an imidazolium cation with a long alkyl chain has revealed more affinity for the dioxin compound. These studies demonstrate that the absorption ability of the HTSILs is extremely dependent on the selected combination of cation and anion structure in which the HTSIL anion-cation and HTSIL-dioxin balance interactions plays an important role.

The results obtained of the dibenzo-*p*-dioxin were compared with the 2-chlorodibenzo-*p*-dioxin, and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin. Experiments were performed under the same conditions of temperature and time by using HTSIL [C₈mim][DCA]. The concentration of each dioxin compound in the [C₈mim][DCA] was found to be of 18 wt% of dibenzo-*p*-dioxin, 19.2 wt% of 2-chlorodibenzo-*p*-dioxin and 14.8 wt% of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin. The results indicate that the absorption of dioxin 2-chlorodibenzo-*p*-dioxin is the highest in comparison with the dioxin dibenzo-*p*-dioxin and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin. We presume that the lowest absorption of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin in [C₈mim][DCA] is due to the high molecular weight (321.97 g mol⁻¹) of the compound which may have lower vapor equilibrium. These observations also suggest that the HTSIL may have better affinity for the high chlorinated congeners which is also the best. These studies highlights that the process is equally applicable to any chlorinated dioxin congeners.

The effect of temperature on the dioxin absorption was also studied by using dibenzo-*p*-dioxin and HTSIL [C₈mim][Tf₂N]. Figure 3 shows that with the increase in temperature from 100 to 200 °C the absorption capacity of [C₈mim][Tf₂N] slowly decreases. But, interestingly the absorption kinetics of dioxin was found to be increased with the increase in temperature. It may be due to the faster generation of gaseous dioxin molecules at higher temperature which in turn causes a decrease in the total absorption time. Further, there was no loss or degradation of the HTSIL [C₈mim][Tf₂N] was observed at higher temperature in 4 h. It indicates that the process is beneficial at high temperature as well. These observations are quite important and one can relate it with the absorption of SO₂⁶.

A possibility to desorb the dioxin back from the HTSIL is also a significant step for the accomplishment of an overall process of dioxin remediation. A desorption of dioxin from the HTSIL was found to be prompt compared to the absorption process (< 24 h). The method was validated by using the HTSIL [C₈mim][DCA] absorbed dibenzo-*p*-dioxin and vacuum at a constant temperature of 100 °C. Later, ¹H NMR analysis of the [C₈mim][DCA] was performed and as expected, it has not shown any traces of dibenzo-*p*-dioxin which proved a complete desorption of dibenzo-*p*-dioxin. Therefore, it is possible to re-use the same HTSIL repeatedly for the absorption of dioxin.

In conclusion, the unique properties of the HTSILs designed and selected (task-specific), which exhibit a high capability to absorb the dangerous dioxin compounds from a vapour phase above room temperature, together with their minimal volatility and thermal stability opens new perspectives to the academia, environmental scientist and industry⁷. This process may be used to develop efficient and specifically design equipment (e.g. ILs immobilized or incorporated in inorganic supports, such as particles and membranes) for absorption of dioxins directly from gaseous dioxin sources at high temperatures. Captured dioxins can then be safely recovered by desorption from the HTSIL media, concentrated, and destroyed using the most appropriate available technology. This process may use significantly less energy than current remediation technologies of dioxin.

Acknowledgements

This work was supported by the Fundação para a Ciência e a Tecnologia and FEDER (ref. SFRH/BPD/14848/2003). We gratefully acknowledge *Solchemar* company (<http://www.solchemar.com>) for providing some of the ionic liquids.

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Figure 1: Absorption of dibenzo-*p*-dioxin by HTSIL [Aliquat][DCA] as a function of time.

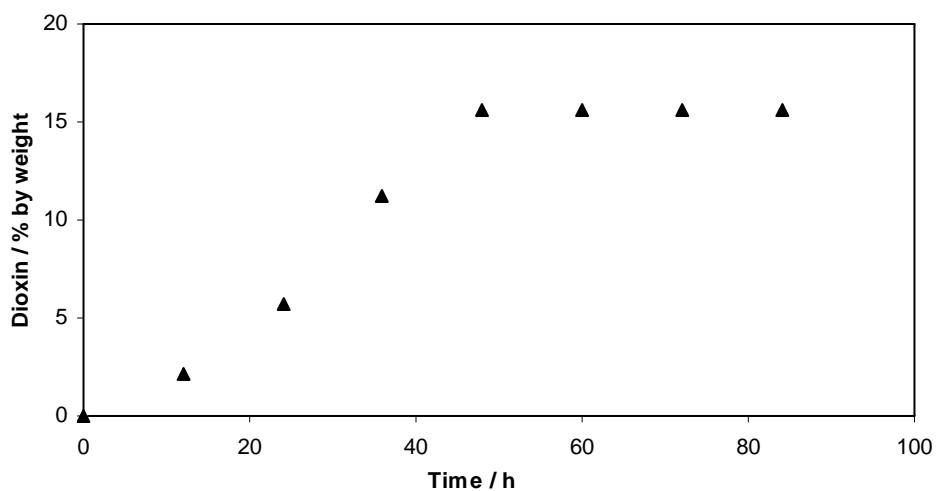


Figure 2. ¹H NMR spectra (400 MHz) of the a) [Aliquat][DCA] and b) dibenzo-*p*-dioxin –absorbed [Aliquat][DCA] in CDCl₃.

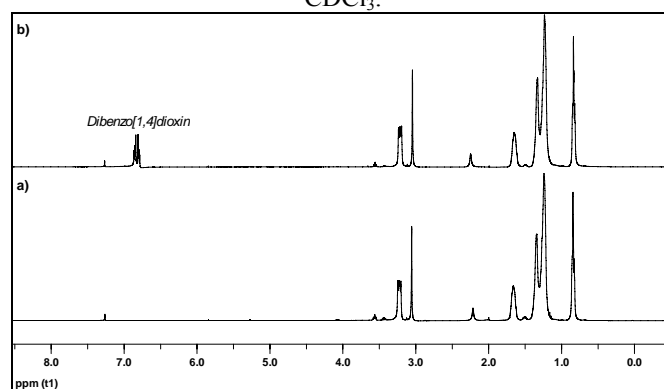


Figure 3. Effect of temperature on the absorption of dibenzo-*p*-dioxin in [C₈mim][Tf₂N].

