Preliminary study of some plasticizers compounds in sewage before and after the treatment in a sewage treatment plant

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In this work it was described the extraction and analysis of plasticizers compounds, namely: dioctylphthalate (DOP) and diisobutylphthakate (DBP) in samples of liquid residues of the sewage treatment plant of the Caxias do Sul university (ETE-UCS). The samples were extracted by pH reduction, precipitation and filtration of the organic content and solvent extraction. The organic extracts were analyzed by gas chromatography with flame ionization detection (GC-FID). The target compounds were identified in the samples by comparison with the retention times of standard compounds. The analysis of the chromatographic peaks areas of the target compounds, at the entrance and launch points of the ETE-UCS shows that the percent removal grade were of 99.37 for DOP and 33.68 for DBP. These results suggest that for a satisfactory reduction of the DBP levels, other treatment methods have to be employed.
Keywords: Plasticizers, liquid residues, GC-FID, DOP, DBP.

1. Introduction

Plasticizers are organic esters added to polymers to facilitate processing and to increase flexibility and toughness of the final product by internal modification of the polymer molecule. Some of these plasticizers are generally high-boiling esters of dicarboxylic acids called phthalates which dominate the production and consumption of plasticizers. Dioctyl phthalate (DOP) in many instances is the sole general-purpose plasticizer produced.
A chronic bioassay, completed in 1980 by the US National Toxicology Program, which was performed at extremely high doses of DOP, labeled it as a possible carcinogen. The Toy Manufacturers Association entered into a voluntary agreement with the Consumer Products Safety Commission to limit the amount of DOP in children's pacifiers and teething rings (articles specifically intended to be mouthed) to no more than 3% of the total weight of the article. As phthalate esters (PE) are used specially in the soft polyvinyl chloride production (Bauer and Herrmann, 1997), they are widely spread in all environments, by your employment in packages, clothes, films, paints, adhesives, cosmetics, ink printers and many

other products. Although PE are not acute toxicants, the long term exposition to high levels can produce damages to the liver and testicles in mammals and death in aquatic species. Beyond this, PE are suspect to be environmental estrogens (Bauer and Herrmann, 1997; Crosby, 1998; Baird, 1999). PE can also influence the mobility and bioavailability of toxic substances like polychlorinated biphenyls and metal ions by changes in your water or lipid solubility (Möder et al., 1998). PE was identified in several kinds of environmental samples, like municipal solid waste compost (Gonzalez-Vila et al., 1982), sludge of sewage and wastewater treatment (Boyd et al., 1979), river sediments (Möder et al., 1998) and landfill leachate (Bauer and Herrmann, 1997).

Sewage commonly shows high amounts of biochemical and chemical oxygen demand and can contaminate the soil, superficial and groundwater (Keenan et al., 1984). As plasticizers are compounds of hard microbial decomposition, it is very probable that the common treatment applied to the sewage (independently of the source, domestic or industrial plants) it is not able to reduce their concentrations to safe levels, before the discard into superficial waters. In this way, plasticizers can persist in the environment and contaminate superficial and groundwater. This situation can be worse if the government policies regulations referring these compounds are fail or simply does not exist.

The main objective of this work is to investigate, for the first time in Brazil, the presence of DBP and DOP, in samples of liquid residues of the sewage treatment plant of the Caxias do Sul University (ETE-UCS). The samples were extracted by precipitation and filtration of the organic content and solvent extraction. The instrumental analysis was performed by GC-FID analysis.

2. Materials and Methods

2.1 Samples

The samples of sewage used in this work were collected at every 15 days, during 45 days, from the sewage treatment plant of the Caxias do Sul university located in Caxias do Sul, Rio Grande do Sul state, Brazil. This station receive exclusively the sewage generated in the university. The samples were collected in glass bottles with caps protected by an aluminum foil, to prevent contamination. The samples were filtered at low pressure, maintained at 4 °C and protected from light until the extraction procedures (at maximum 24 h after the collection). All the glass material was carefully washed with acetone, n-hexane and dichloromethane and was dried in an oven at 300 °C.

2,2 Samples extraction

Three organic solvents were tested: dichloromethane, n-hexane and acetone. The n-hexane was choice because the better solubility of DOP and DBP in this solvent The samples (40 mL) were extracted in 3 mL glass syringes (Figure 1). The extraction procedures were as fallows:

a) A volume of 10 mL of sulfuric acid (conc.) was added to 40 mL of the sample (entrance and launch points of the treatment plant) to reduce the pH to ≈ 2,0.This procedure is necessary to avoid the ionization of the plasticizers molecules ;

b) After this, the sample was percolated in a glass syringe (3 mL), used as extraction column, and the velocity of the mobile phase (sample) was of 5 mL/min. The stationary phase was cotton previously treated by Soxhlet by four hours;
c) After the extraction, the column was dried at 50 °C by two hours;
d) After this, the column was washed with 1 mL of n-hexane and the organic extract was collected for instrumental analysis.

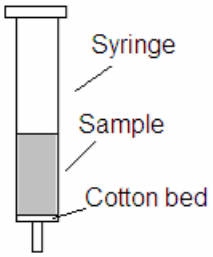

Figure 1. Extraction syringe

The precipitation method, used in this work was slightly modified from Nascimento et al. (2003) where plasticizers compounds in landfill leachate were successfully analyzed. The chemical structures of DOP and DBP are represented in the Figure 2.

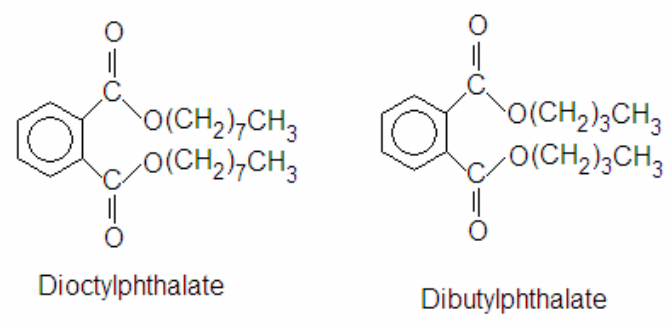

Figure 2. Chemical structures of DOP and DBP

2.3 Instrumental analysis

A Gas Chromatograph, Autosystem XL, PerkinElmer with Flame Ionization Detector was used for identification and quantification of the target compounds. A 60 m x 0.25 mm i.d. fused silica capillary column (crossbond 5% diphenyl – 95% dimethyl polysiloxane) Elite-5 (0.25 mm film thickness) was used for the GC separation using the following oven temperature program: 150 °C (5 min hold) heating to 220 °C at 3 °C/min and heating to 300

°C at 10 °C/min (5 min hold). The injector temperature was 250 °C. The volume of 1.0 μL was injected in split mode (1:50).

3. Results

Figure 3 shows the extraction blank where can be seen that no plasticizers contamination occurred during the extraction procedures. Figure 4 shows the chromatogram of the organic extract of the launch point, where plasticizers are highlighted.

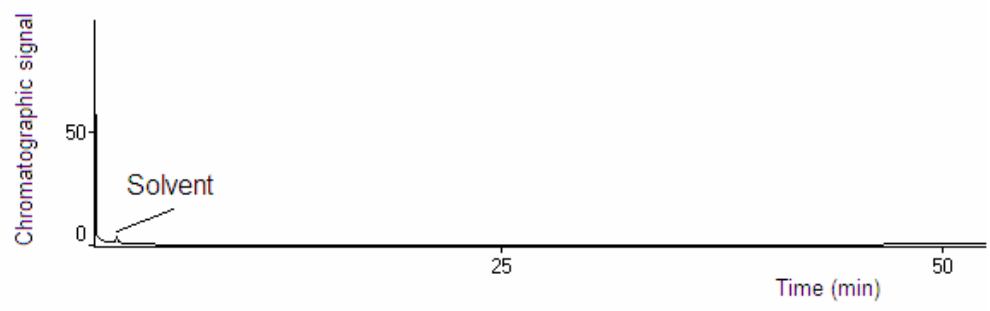

Figure 3. Extraction blank

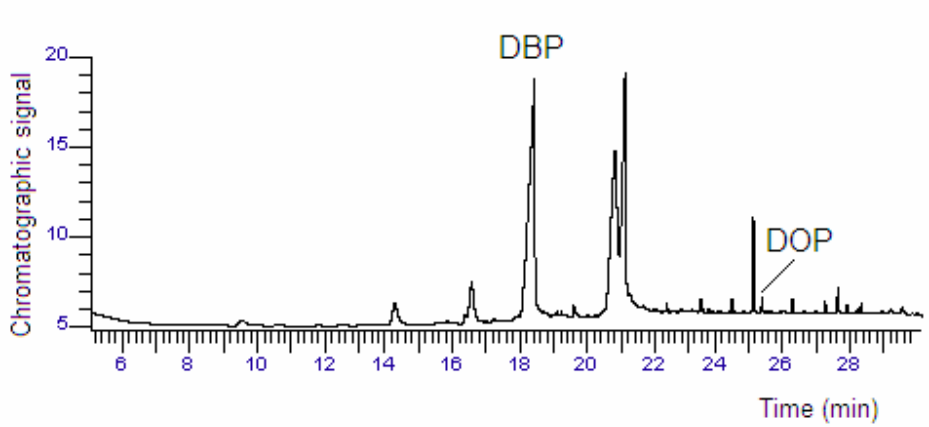

Figure 4. Chromatogram of the organic extract of the launch point

Figure 5 shows the percent reduction of DOP and DBP, considering the individuals peak areas at the entrance and exit points.

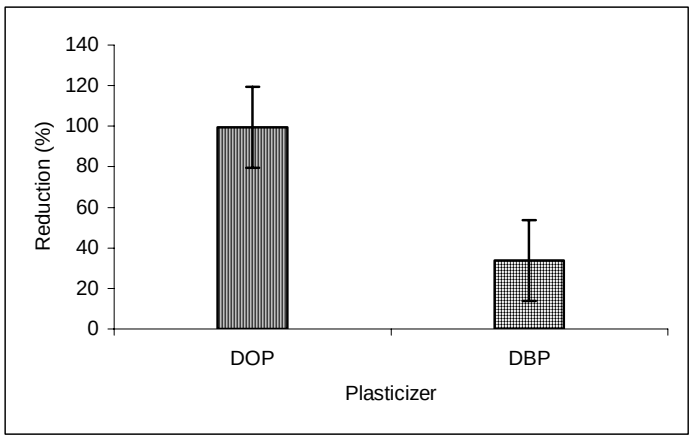

Figure 3. Removal grade comparing the peak areas of the target compounds at the entrance and launch points of the treatment plant.

As can be seen in figure 2, the DOP was almost completely degraded (99.37%, RSD = 1.51) while the elimination rate of DBP was quite low (33.58%, RSD = 1.99). Probably, these results are due to the longer carbon chain of DOP, in relation to DBP, that turns the DOP a better carbon source for the microbiological development. Otherwise, the low water solubility of DOP in relation to DBP (0.0025 and 9.9 mg L^{-1}, respectively – Staples, 2001) can also enhance their biological degradation. These results also indicate that the major part of the DBP that entries the ETE is discarded at the launch point and can contaminate the superficial and groundwater.

By other side, considering the percent peak area of DOP at the launch point, the concentration of this plasticizer is around 0.2 mg L^{-1} (SD = 0.007). This concentration is around 30 times higher that the maximum contaminant level, stated by the US-EPA (0.006 mg L^{-1}).

4. Conclusions

The precipitation extraction method is rapid, simple and allows the isolation of compounds of environmental concern.

These preliminary results suggest that the DOP is almost complete removed from the sewage by the traditional treatments. By other side, the DBP removal is quite low (less than 34%). Since that DBP is a compound of environmental concern other advanced treatments must be employed to reduce their concentration in the discarded water. Even for the DOP, that shows a high percent removal, the residual concentration of plasticizers launched in the superficial waters can be harmful for the aquatic and human life.

Obviously, these are preliminary results and the next steps of this work will be the quantitative analysis of these plasticizers in a extended sampling period and the application of advanced sewage treatments to reduce these plasticizers levels.

Acknowledgements

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