EXTRACTION AND DETERMINATION OF PHARMACEUTICAL COMPOUNDS ADSORBED INTO MICROPLASTICS

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Abstract Microplastics (MPs) are pollutants of emerging concern. These small particles are found throughout the world. Its best-known negative effects are that they can confuse marine organisms that would feed on them, or block their airways. In addition, they have been shown to act as vectors of contamination too.

In this work, a methodology for the extraction of ten widely used pharmaceutical compounds adsorbed into MPs has been developed. This methodology is based on Ultrasound Assisted Extraction (UAE) followed by Ultra-High Performance Liquid Chromatography Tandem Mass Spectrometry (UHPLC-MS/MS). In the optimal conditions, Limits of Detection (LODs) between 0.25 and 15.8 $ng \cdot g^{-1}$ were obtained. The optimized method was successfully applied to different MPs samples taken from three beaches of Canary Islands. The results indicated the detection of all target pharmaceuticals at least one time in the analysed samples.

Keywords: Microplastics, Pharmaceuticals, Ultrasound-assisted extraction, Beach pollution

1. Introduction

Microplastics (MPs) are dangerous substances because, due to their size, they can be ingested by marine organisms, which can cause them to starve, and can block their airways [1]. In addition, due to the properties of plastics, they could act as vectors of contamination of toxic organic compounds that are adsorbed into them [2]. In fact, in the last five years, numerous studies have been carried out in this regard, which have detected the presence of various compounds, such as polyhalogenated carbazoles, perfluoroalkyl substances, metals, etc. [3]. Moreover, Bakir et al., [4] published a paper in which they concluded that the pollutant adsorbed in the MPs desorbs faster in the fish's intestine than in seawater, which, without a doubt, could cause a serious contamination problem if it were magnified in the chain trophic.

The effluents from Wastewater Treatment Plants (WWTPs) are considered one of the main inputs of MPs to the marine environment [5], as well as of emerging pollutants, such as pharmaceutical compounds. For all the above, this work presents an optimization of a methodology for the extraction of widely used pharmaceutical compounds from MPs [6]. The procedure consists in an extraction through Ultrasonic Assisted Extraction followed by the determination of the analytes by Ultra-high Performance Liquid Chromatography Tandem Mass Spectrometry (UHPLC-MS/MS). Ten pharmaceutical compounds belonging to different families were selected for this study, detecting all of them in the samples analysed.

2. Sampling

Samples were taken in accordance with the protocol stablished for the IMPLAMAC project (Project MAC 2/1.1a/265). Briefly, samples were collected at high-tide line. The surface layer of sand and up to a depth of 5cm was sieved through a 1mm mesh. Then, the plastic pellets were carefully separated in the laboratory with tweezers and extracted directly, without any clean-up procedure.

3. Results and discussion

The optimisation of the extraction conditions was performed through an experimental design. A 3^3 experimental design with the variables solvent volume, solvent and extraction time was done. The levels selected for each variable were; solvent volume: 5, 7.5 and 10 mL, solvent: MeOH, ACN and MeOH-ACN (50:50) and extraction time: 10, 30 and 50 minutes. The results of the experimental design were studied by surface response plots. It was found that an intermediate value of volume (7.5 mL) and low extraction time (10 minutes) were the conditions that achieved the best extraction for most of the compounds. Regarding to the solvent type, no significant differences were found between them, so, the solvent that presented the best signal in the UHPLC-MS/MS was selected, in this case, MeOH. Finally, in order to achieve a better preconcentration factor, the sample was dried with nitrogen and reconstituted in 1mL of MeOH.

Analytical parameters were studied at four levels, obtaining an intraday and interday deviation lower than 15% for all of the compounds, except one (nicotine). In addition, a limit of quantification (LOQ) ranging from 0.82 to 52.7 $ng \cdot g^{-1}$ was obtained.

The methodology was then applied to MPs samples taken in the sand from three beaches of Canary Island (Spain). All the studied compounds were detected, at least, in one occasion. Among them, caffeine, carbamazepine and trimethoprim highlighted by their frequency of detection, nevertheless, the concentration of the studied compounds did not exceed the 100 $ng \cdot g^{-1}$ level on almost no occasion.

4. Conclusions

Contaminants adsorbed on MPs is a current problem. Several studies have focused on determining priority contaminants adsorbed to microplastics, but, to our knowledge, none had studied pharmaceutical compounds. In this work, a methodology for the extraction and determination of pharmaceutical compounds adsorbed into MPs have been developed and applied. The analytes were successfully extracted by using only 7.5mL of MeOH and in 10 minutes, obtaining low relative standard deviations and LOQs. The application of this methodology confirmed the capacity of MPs to adsorb also emerging pollutants, such as pharmaceutical compounds.

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