Extraction of contaminants from HDPE wastes: is a rinse sufficient?

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EXTRACTION OF CONTAMINANTS FROM HDPE WASTES: IS A RINSE SUFFICIENT ?

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Abstract

The issue of plastic waste valorisation or recycling has become urgent lately. With China's decision to recycle plastic wastes only if those are thoroughly cleaned and decontaminated, EU faces an impasse. Some European waste collectors use solvents or lye while grinding wastes to ensure decontamination. Nevertheless, that method has not be proven to be efficient enough. The goal of the following study is to evaluate the decontamination effects of a rinse and consequently assess if chemical migration into plastic takes place in the plastic jar lifetime.

Present work dealt with real plastic waste provided by a waste collector. Consequently, it a blend of chipped jerry cans that had contained several chemicals.

In order to evaluate the solvent rinsing decontamination capacity, an Accelerated Solvent Extraction (ASE) was performed (110 bars for 120°C) on plastic wastes ground to 1 mm particles (HDPE-1mm). As a results, 21 molecules were extracted, quantified an identified with GC-MS analysis. A comparison with clean HDPE showed that this method did not extract organic additives at required levels to be detected. The quantification of minerals was not performed. Same not grounded plastic wastes (HDPE-2cm) were also rinse for 24h with several solvents: either pure acetone, acetonitrile, dichloromethane or mixtures of acetone / acetonitrile, acetone / dichloromethane and acetonitrile / dichloromethane at different proportions (9:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:9). Using GC-MS analysis, the contaminants in the rinse solutions were identified and quantified to be compared with the analysis performed after ASE.

Firstly, as expected, 24h rinsing process performance was lower than ASE. Best observed extraction performance was 57% of ASE. Besides, not every molecules were extracted with a simple rinse, this method is not selective and thorough enough. Secondly, some mixtures were more efficient than pure solvents: acetone/acetonitrile 1:1.

As a result, those contaminated plastics cannot be cleaned thoroughly by rinsing. They must be excluded from recycling in favour of valorisation.

1- INTRODUCTION

Plastics are fossil materials widely used in several sectors such as packaging (39.9% in 2016 in EU), building and construction (19.7%) or automobile (10%) [1]. The demand in Europe for plastics increases each year and reached 49.9 Mt in 2016 [1], [2]. In the context of the environmental and energy global issue, those plastic wastes are reconsidered as a new source of power. Indeed, the European Union Directive 2008/98/CE [3] demands to limit the landfilling of wastes. Therefore, two solutions are considered: recycling or energy recovery. In 2016, for the first time recycling overcame landfill with respectively 31.1% and 27.3% of the 27.1 Mt of collected plastics post-consumption [1]. The rest was used for energy purposes. The tendency to recycle or valorise is mainly due to some policies, pushed for in Northern Europe, limiting landfilling [1], [2].

In October 2017, China announced that it refuses from now on to import the plastic wastes [4], [5], considered uncleaned. Indeed, they couldn't ensure a proper recycling and guarantee the safety of the workers. With this operation, called "Blue Sky", 9 million of tons of post-consumption plastics are concerned. As a result, EU must find a new way to valorise wastes on its own territory. Only China possesses the appropriate infrastructure to treat the amount of plastic wastes collected by Europe.

Furthermore, several standards limit the presence of contaminants (metals, halogens, etc.) in the polymer matrix [6]–[11]. That is why some studies quantify the amount of contaminants in the plastic matrix which have diffused from the contained product toward the container. Some focus on the additives' quantification [12]–[17] while others characterise the amount of organics and volatiles [18]–[23]. Both types may be qualified as contaminants as they are not the polymer itself. Several methods of extraction are commonly used such as Solid Phase Micro-Extraction (SPME) [19], [22], Microwave Assisted Extraction (MAE) [17], Supercritical CO_2 Extraction (SCCO$_2$) [14], [16], [18], [23] and Accelerated Solvent Extraction (ASE) [20], [21]. The cited methods use high pressure, high temperature or both to enhance the natural diffusion of contaminants within the polymer matrix. After the extraction, the solvent is analysed through Gas Chromatography (GC) or High Performance Liquid Chromatography (HPLC).

Before any recycling, the plastic wastes are rinsed with an organic solvent for decontamination. Although, this method may eliminate the surface contaminants, it has not be proven to be efficient in the core of the polymer. The following study is composed of two parts: firstly an extraction of the additives was attempted, secondly a characterisation of the rinse for several solvents was made, and compared with the results of the ASE.

2- MATERIALS AND METHODS

2.1 – Samples

For the following study, contaminated High Density PolyEthylene (HDPE) was compared with clean and unused HDPE. The former was a mix of different plastics which had been formerly chipped to 2 to 3 cm thick flat particles (about 10 cm^2) and rinsed with lye by a waste collector. Each type of plastic in the mix contained unknown products, which have migrated within the polymer jar lifetime. The second studied HDPE came from new jerry cans, which had never contained any product. Each one's contamination was characterised using ASE extraction, and/or simple solvent extraction, coupled with GC-MS. In order to quantify the amount of each contaminant extracted, 1.36 µmol of heptane was injected into each solution before GC-MS analysis.

2.2 – ASE method

The ASE method consists in enhancing a solvent extraction by increasing the pressure and the temperature to approximately 100 bars and 100°C. As a result, the time of extraction can be reduced to 15-30 min; decreasing by extension the amount of used solvent [24], [25]. ASE may extract low polarity molecules but has a tendency to solubilise oligomeric fractions of the polymer matrix [26]. A filtering is often required after the extraction. The figure 1 represents the ASE system.
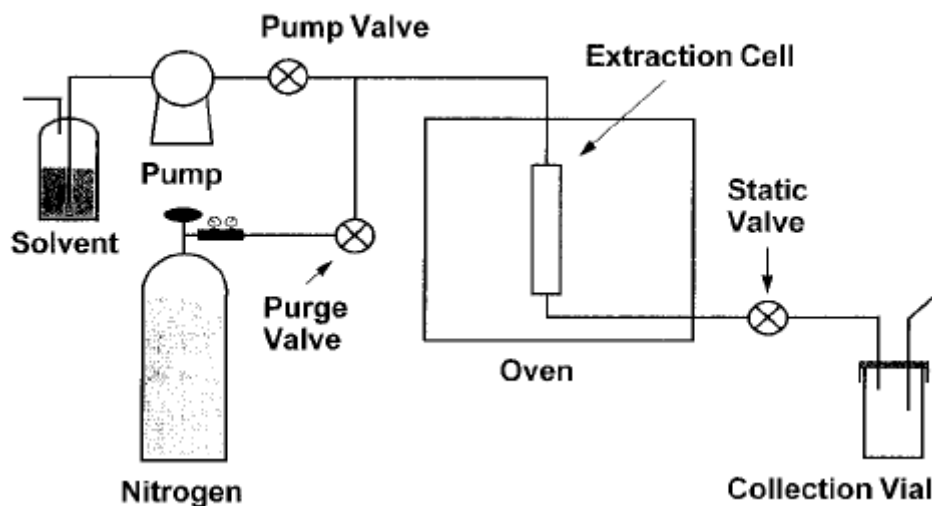

Figure 1 : ASE System from [24]

For the following study, the ASE tests were performed at 120°C for 110 bars. Two cycles of extraction were executed, lasting 5 min each. The solvent used was pure acetone. Each sample was ground to approximately 1 mm beforehand, to enhance the contaminants' diffusion.

2.3 – Rinse method

For the contaminated mix of plastics, a study of the influence of the rinse solvent was performed. Between 2 to 4g of HDPE-2cm were plunged into approximately 10mL of a solvent for 24h, at room temperature, and removed afterwards for the liquid to be analysed by GC-MS. The solvents were pure acetone, acetonitrile, dichloromethane, or mixes of acetone/acetonitrile, acetone/dichloromethane and acetonitrile/dichloromethane at different proportions (9:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:9). For each solvent, 3 samples were prepared and analysed.

2.4 – Comparison method

A first comparison between the ASE performed on the clean and the contaminated HDPE was used to determine if organic additives could be extracted by this method (no quantification of minerals was performed). Afterwards, the contaminants of the mix of plastic wastes were identified and quantified, ruling out the organic additives, if extracted.

The ASE was used as a reference for extraction. The number of extracted molecules, noted s_{ASE} was measured. It represents a reference for the selectivity of the rinse. If the rinse i extract $s_i > s_{ASE}$ molecules, then it has a lower selectivity than the reference: the ASE performed with acetone. The selectivity factor defined as such does not take into account any molecule which was not extracted by the ASE, but, having a better affinity with a solvent i, appeared on its GC-MS analysis.

Another parameter to take into account is the quantity extracted. For that, as the tracer is injected with a known quantity, the GC-MS analysis allowed to determine the quantity extracted for each contaminant j. We chose to represent the quantity extracted by doing a mean of the molar quantities, for each j contaminants, for a fixed solvent i. As ASE is the reference, the mean, called extraction factor, is calculated on a basis of s_{ASE} possible contaminants:

$$\mu_i = \frac{1}{s_{ASE}} \sum_{j=1}^{s_i} n_j^i \tag{1}$$

with n_j^i the molar quantity of the extracted contaminant i for the solvent j.

Finally, to compare each factor with the chosen reference, a relative extraction factor E_{i-ASE} and a relative selectivity factor S_{i-ASE} were defined as such for each solvent i:

$$E_{i-ASE} = \frac{\mu_i}{\mu_{ASE}} \tag{2}$$

$$S_{i-ASE} = \frac{s_i}{s_{ASE}} \tag{3}$$

3- RESULTS AND DISCUSSION

3.1 – Extraction of additives and contaminants with ASE for unused and contaminated HDPE

After the ASE performed on clean and contaminated HDPE, the solvents were analysed by GC-MS. The extract from the unused plastic showed no contaminants, whereas 21 species were identified for the mix of plastic wastes, presented in table 1.

Contaminant	Retention time (min)	Quantity extracted (µmol)
Toluene	3.825	0.173 *(s.d. 0.033)*
3-penten-2-one, 4-methyl-	4.436	2.31 *(s.d. 0.42)*
Eucalyptol	9.142	0.202 *(s.d. 0.021)*
Benzoic acid, ethyl ester	11.426	0.145 *(s.d. 0.057)*
Octanoic acid, ethyl ester	11.791	0.301 *(s.d. 0.083)*
Decanoic acid, ethyl ester	14.613	0.472 *(s.d. 0.13)*
Tetradecane	14.721	0.274 *(s.d. 0.05)*
2-propenoic acid, 3-phenyl-, ethyl ester	15.616	0.283 *(s.d. 0.10)*
Unidentified alkane or alkene	17.14	0.361 *(s.d. 0.076)*
Unidentified alkane or alkene	17.226	0.206 *(s.d. 0.072)*
Unidentified alkane or alkene	19.403	0.391 *(s.d. 0.086)*
Unidentified alkane or alkene	19.479	0.267 *(s.d. 0.071)*
2-ethylhexyl salicylate	19.56	0.258 *(s.d. 0.077)*
Unidentified alkane or alkene	21.455	0.499 *(s.d. 0.098)*
Unidentified alkane or alkene	21.515	0.246 *(s.d. 0.032)*
Unidentified alkane or alkene	23.328	0.553 *(s.d. 0.073)*
Unidentified alkane or alkene	23.378	0.24 *(s.d. 0.036)*
Unidentified alkane or alkene	25.198	0.561 *(s.d. 0.099)*
Unidentified alkane or alkene	25.248	0.246 *(s.d. 0.033)*
Unidentified alkane or alkene	27.850	0.536 *(s.d. 0.024)*
Unidentified alkane or alkene	27.928	0.231 *(s.d. 0.022)*

Table 1: The 21 contaminants identified in the mix of HDPE wastes, identified and quantified by GC-MS after ASE

As a result, the two factors characterising ASE could be calculated: $s_{ASE} = 21$ and $\mu_{ASE} = 0.417$ µmol. To synthesise, the ASE method, used as such with acetone, could not extract additives from the polymer matrix. The procedure could, however, extract various organic compounds and they have been quantified and identified using GC-MS. The large variability of the resource may explain the wide standard deviation. Besides, species might have been adsorbed by the oligomeric fractions of polymer and washed out of the solution during the filtering. Some other methods of extraction might be less selective like SCCO$_2$ or MAE. To complete the identification of contaminants, an Inductively Coupled Plasma (ICP) analysis would be required.

3.2 – ASE/rinse comparison for contaminated HDPE

The second part of the study aims to characterise the efficiency of a rinse for different solvents. For each solution, the factors s_i and μ_i were calculated and compared with their equivalent for ASE. The results are presented in the table 2 and figure 2. As heptane is not miscible with acetonitrile, for high concentrations of that particular solvent, the results were not relevant. Indeed, the tracer was shared between the two solvents and the quantity injected varied, depending of the homogeneity. For pure acetonitrile, however, an agitation before injection was enough to obtain coherent results.

Solvent		F_{i-ASE}	S_{i-ASE}
Acetone		7.32%	38.10%
Acetonitrile		2.67%	33.33%
Dichloromethane		57.17%	57.14%
Acetone / Acetonitrile	9:1	27.75 %	33.33 %
	3:1	17.70 %	28.57 %
	2:1	18.88 %	42.86 %
	1:1	5.12 %	33.33 %
Acetone / Dichloromethane	3:1	14.15 %	47.62 %
	2:1	7.68 %	38.10 %
	1:1	17.86 %	52.38 %
	1:2	1.45 %	47.62 %
Acetonitrile / Dichloromethane	1:1	2.41 %	38.10 %
	1:2	21.46 %	47.62 %
	1:3	32.18 %	52.38 %
	1:9	37.54 %	57.14 %

Table 2: Extraction and selectivity factors for the rinse solvent, for contaminated HDPE-2cm, for 24h
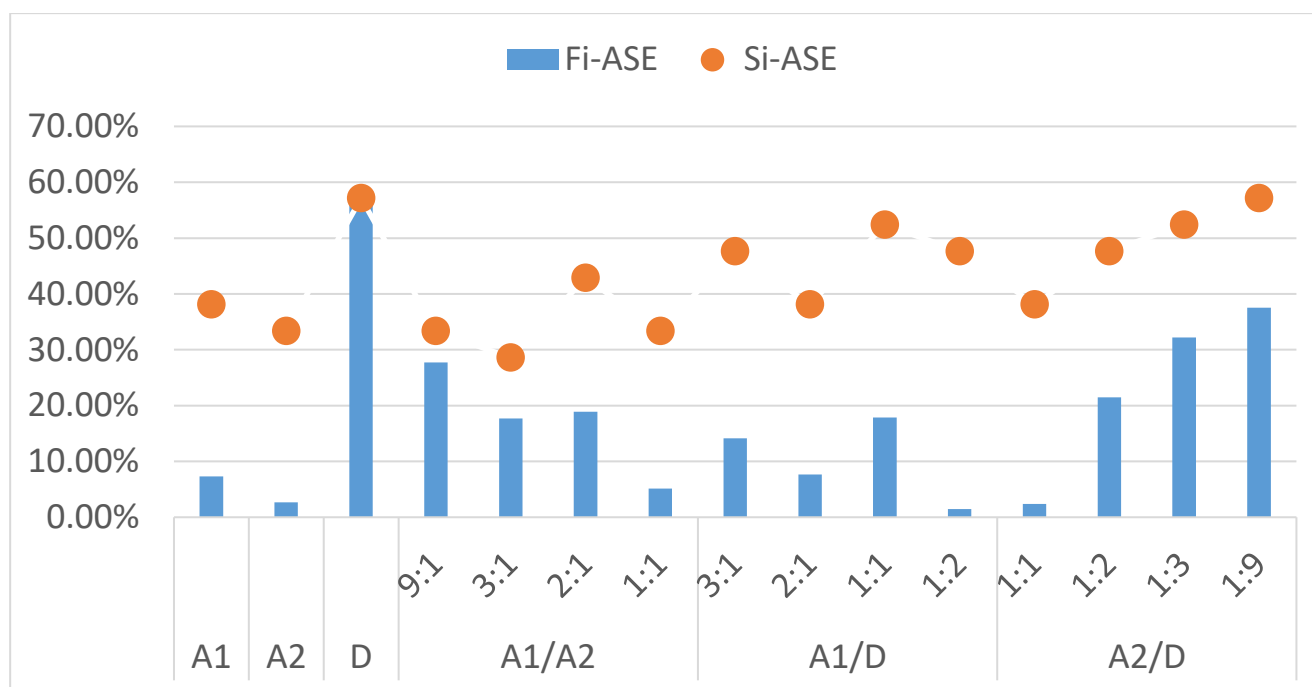
Figure 2: Extraction and selectivity factors for each mix of solvent for 24h rinse (A1=Acetone, A2=Acetonitrile, D=Dichloromethane)

Each solvent has extraction and selectivity factors lower to 1. In other words, whichever the solvent used for rinse, the plastic wastes contained residual contaminants after the experiment. Those have not been extracted from the core of the matrix. To enhance the rinse's effects, one could grind the HDPE to 1mm or use alternative methods such as ASE, MAE, $SCCO_2$ and so forth.

Furthermore, some solvents are more relevant to an extraction, being less selective and extracting a larger amount of contaminants. For example, pure dichloromethane is the more efficient solvent in regard to the quantity extracted ($F_{Dichlo-ASE} = 57.17\%$) and to the number of species identified ($S_{Dichlo-ASE} = 57.14\%$). Besides, the GC-MS analysis on pure dichloromethane rinse allowed to identify other alkanes that had not been extracted by the ASE.

Another observation, confirmed by the literature [21], is the effect of a mix of solvent compared with a pure solution. The mixture acetone / acetonitrile has extracted more contaminants than the pure solvents. As a result, a mixture of different solvents could improve the extraction compared with the effect of each one of them taken separately.

4- CONCLUSIONS

Plastics recycling or valorisation is becoming a priority for the European waste treatment sector. Given the Chinese decision concerning the import of plastic wastes, a solution must be proposed in Europe. This study was performed on HDPE wastes which have been contaminated by the contained products. As a result, those plastics cannot be recycled as they might contain toxic or polluting molecules.

Indeed, the result shows that even a complete rinse of 24h at room temperature could not penetrate entirely within the polymer. A possible improvement could be to optimize the solvent used, or grind the wastes. Solvents, however, are pollutants and limiting their use would be beneficial. Besides a too intensive grinding may deteriorate the quality of the plastics for reuse.

Furthermore, an intense extraction method such as ASE was inefficient to extract some additives. Yet, in some applications, plastics are reinforced with flame retardants, containing halogens like brome. Such an endocrine disruptor should not be recycled if the new application could endanger humans.

For all the cited reasons, recycling should not be promoted for plastic wastes which could contain dangerous contaminants. That particular category of waste may be valorise for energy purposes. One solution is the incineration, producing heat, electricity or both while eliminating the contaminants. Another developing solution is the gasification of the wastes. Indeed, gasification would convert any organic contaminant into syngas. This high-value-added product might be converted into hydrogen, methane, and so forth for chemical or energetic purposes.

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