IMPROVING THE ODOUR REMOVAL FROM FLEXIBLE PACKAGING WASTE BY OPTIMIZING THE WATER MANAGEMENT IN PLASTIC RECYCLING PLANTS

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Master's Dissertation submitted to Ghent University in partial fulfilment of the requirements for the degree of Master of Science in Bioscience Engineering: Chemistry and Bioprocess Technology

Academic year: 2022-2023

GHENT UNIVERSITY

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PREFACE

When I found this thesis topic in a list of about a hundred possibilities, I immediately thought this could be something for me. Plastic, the problems associated with it and its recycling are things that have interested me for some time. Following the course *Environmental Technology: water* in third bachelor, I was more convinced to broaden my knowledge in this subject. Since this thesis could combine both interests, it seemed an appropriate choice. Now, about a year later, I am writing the final words of my dissertation. I often heard that writing a thesis is demanding, challenging and asks countless hours of dedication and persistence. I can confirm that now, but I can look back with pride at the journey I have taken with this.

I would like to thank my promotor and tutors for the good cooperation and sharing their expertise and feedback. I would particularly like to thank Dave for his continuous guidance and support and for always having an answer ready to my many questions, even sometimes in weekends. He taught me the necessary lab techniques, to work in a structured way, to always think critically about everything and dare to question own work. Without his help, the thesis would not be where it is today.

Furthermore, I would like to thank my family for their support over the past five years. They were always on the side line supporting me and always believed - sometimes more than myself - in my abilities. I would also like to thank my friends for supporting me but also for the necessary relaxation during this period. Also a big "thank you" to my fellow students for being their of throughout this five-year journey and 'om samen te thesissen' this year. An additional thank you goes here to Lies and Ismail, for proofreading this work.

Finally, I would like to thank you, reader(s), for your interest in my master's thesis and wish you good luck in reading it. I hope that this dissertation can provide a valuable contribution to research already carried out and guide future studies.

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Noa Collier
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June 2023

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LIST OF ABBREVIATIONS

COD	Chemical oxygen demand
CTAB	Cetyltrimethylammonium bromide
EC	Electrical conductivity
EU	European Union
EU27+3	European Union Member States, Norway, Switzerland and the UK
GAC	Granular activated carbon
GC-MS	Gas Chromatography-Mass Spectrometry
GC-O	Gas Chromatography-Olfactometry
HDPE	High density polyethylene
HS-SPME	Headspace solid-phase micro-extraction
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
K$_{ow}$	Octanol-water partition coefficient
LDPE	Low density polyethylene
MAE	Microwave-assisted extraction
NTU	Nephelometric turbidity unit
PAC	Powdered activated carbon
PC	Post-consumer
PE	Polyethylene
PET	Polyethylene terephthalate
PI	Post-industrial
PP	Polypropylene
RFO	Reversible first order
S/L	Solid/liquid
SAFE	Solvent assisted flavour evaporation
SD-GC-MS	Solvent Desorption Gas Chromatography-Mass Spectrometry
SFE	Supercritical fluid extraction
SVOC	Semi-volatile organic compound
T$_b$	Boiling temperature
TD-GC-MS	Thermal Desorption Gas Chromatography-Mass Spectrometry
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
VOC	Volatile organic compound
VVOC	Very volatile organic compound
VSS	Volatile suspended solids
W1	Washing water after 1 wash step

ABSTRACT

Unwanted odours, presumed to be originating from volatile organic compounds (VOCs), often lead to downcyling of post-consumer flexible packaging from mechanical recycling. The upper limit for the price of recycled plastics is set by virgin plastic prices and recyclates quality. Optimizing the washing process is crucial to improve the removal of these components, while keeping the costs low. Water consumption is a cost factor, but treated wastewater can potentially be reused in subsequent washing cycles. First, the washing process was evaluated using water alone and then using washing media such as caustic soda and detergent. An attempt was made to describe the kinetics of the washing process and implement it in an Aspen Plus model. Coagulation, granular activated carbon (GAC) adsorption and membrane filtration (MF) were tested as treatment techniques. Simulations in Aspen Plus compared two and three washing steps, demonstrating that a three-step process with a final polishing wash achieved 78% VOC removal, compared to 60% for two steps. The influence of the S/L ratio was investigated and results revealed that lower S/L ratios yield higher removal efficiencies and 0.03 kg plastics/L water gives good results (78% VOC removal). Key parameters to measure the performance are COD, TN and VOCs, as COD cannot serve as a surrogate for VOC removal from the plastics. TP seems not to pose a problem. Using washing media should improve washing efficiencies but requires further investigation due to its impact on subsequent treatment (increased COD, TN and pH). Coagulation with ferric chloride, combined with GAC or MF, showed promising results for (partial) wastewater treatment before reuse, achieving 99% and 91% COD and 87% and 69% TN removal, respectively.

SAMENVATTING

Ongewenste geuren, vermoedelijk afkomstig van vluchtige organische stoffen (VOC's), leiden vaak tot devaluatie van *post-consumer* flexibele verpakkingen uit mechanische recycling. De bovengrens voor de prijs van gerecycleerde plastics wordt bepaald door de prijzen van *virgin* (primaire) plastics en hun kwaliteit. Het optimaliseren van het wasproces is cruciaal om de verwijdering van deze componenten te verbeteren en tegelijkertijd de kosten laag te houden. Waterverbruik is een kostenfactor, maar behandeld afvalwater kan mogelijk hergebruikt worden in volgende wascycli. Eerst werd het wasproces geëvalueerd met alleen water en daarna met wasmiddelen zoals natriumhydroxide en detergent. Er werd geprobeerd om de kinetiek van het wasproces te beschrijven en te implementeren in een Aspen Plus-model. Coagulatie, adsorptie van granulaire actieve kool (GAC) en membraanfiltratie (MF) werden getest als zuiveringstechnieken. Simulaties in Aspen Plus vergeleken twee en drie wasstappen en toonden aan dat een driestapsproces met een laatste polijstwasbeurt gemiddeld 78% VOC-verwijdering opleverde, vergeleken met 60% voor twee stappen. De invloed van de *S/L*-ratio werd onderzocht en de resultaten toonden aan dat lagere *S/L*-ratios hogere verwijderingsefficiënties opleveren en dat 0,03 kg plastics/L water goede resultaten geeft (78% VOC-verwijdering). De belangrijkste parameters om de prestaties te meten zijn COD, TN en VOC's, aangezien COD niet kan dienen als surrogaat voor VOC-verwijdering van de plastics. TP lijkt geen probleem te vormen. Het gebruik van wasmedia zou de wasefficiëntie moeten verbeteren, maar vereist verder onderzoek omwille van de impact op de waterzuivering (verhoogt COD, TN en pH). Coagulatie met ijzerchloride, gecombineerd met GAC of MF, toont veelbelovende resultaten voor de (gedeeltelijke) zuivering van afvalwater vóór hergebruik met respectievelijk 99% en 91% COD- en 87% en 69% TN-verwijdering.

CHAPTER 1

1. Introduction

Over the past years, the global plastic production has increased exponentially (Soto et al., 2020). A major part of this plastic is utilized to make short-lived goods that are discarded within a year of production (Hopewell et al., 2009). Due to increased attention for proper waste management of used plastics, the European Commission is imposing more ambitious targets for plastic packaging recycling. In addition, the demand for high quality secondary materials is increasing (Horodytska et al., 2020; Roosen et al., 2022). One of the main barriers to achieve that higher quality is the presence of volatile organic compounds (VOCs), which often have an unpleasant smell (Cecon et al., 2021). Moreover, plastic films are highly contaminated with inks, coatings, dust, organic waste etc. (Horodytska et al., 2020). This makes the secondary materials only appropriate for applications that require a low quality in terms of smell, such as garbage bags and garden furniture (Lase et al., 2022). PET already has a more established recycling process (Cecon et al., 2021) and according to Commission Regulation (EU) 2022/1616[1], mechanical recycled PET is allowed to be used in food contact materials. This makes plastic films to be the focus of this work.

VOCs can migrate into the packaging material during their use phase but can also be the result of cross-contamination during waste collection (Fuller et al., 2020; Roosen et al., 2023). In order to be removed, they have to migrate out of the polymer structure and this does not seem to be evident (Cabanes, Strangl, et al., 2020; Strangl et al., 2018). One way to remove contamination is by subjecting the plastics to a washing process, where plastics and water are mixed for a fixed period of time (Soto et al., 2020). Washing with water alone does not appear to have a very high efficiency (Demets et al., 2020), so also other washing media, such as caustic soda, detergents and even some organic solvents, such as ethyl acetate, are being considered. Other parameters influencing the performance of the process are temperature, plastic particle size, solid/liquid ratio, and turbulence. (De Somer et al., 2022; Roosen et al., 2021). Hence, it will be necessary to optimize all these parameters to obtain the highest possible VOC removal efficiencies.

The feasibility of polyolefins recycling is influenced by several factors. In addition to the market price differences between recycled polymer and virgin plastics, the cost of recycling compared to landfill or energy recovery plays a role in its economic viability. Since recycled plastic generally has lower quality compared to virgin, the price of virgin plastic sets the upper limit for the prices of recycled plastics (Hopewell et al., 2009). This means that the price of the washing process must remain within certain limits, so a trade-off between quality (and thus the selling price) of the recycled materials and the cost of the washing steps is inevitable. Nowadays, the water is often discarded after being used several times in the recycling plant with limited or even no water treatment in between, which is done to reduce the overall costs of the recycling process (Soto et al., 2020). According to Nikiema & Asiedu (2022), mechanical recycling of plastics requires 3.5 m³ water/ton. However, solid/liquid ratios

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[1] Commission Regulation (EU) 2022/1616 of 15 September 2022 on Recycled Plastic Materials and Articles Intended to Come into Contact with Foods, and Repealing Regulation (EC) No 282/2008. http://data.europa.eu/eli/reg/2022/1616/oj

employed by several recycling plants to wash plastic films (typically between 0.01 and 0.02 kg plastic/kg water), indicate that a larger amount of water is needed (Roosen et al., 2021). Instead of reusing the water in a closed loop without purification, an appropriate treatment of the water could be applied, which would positively impact the final quality of the secondary materials (Jabłońska, 2018). Supposing a wastewater treatment would be installed in this loop or existing treatments would be improved, following question arises: How should an optimal washing process and water treatment look like? This dissertation aims to address this question by breaking it down into several sub-questions:

1) How many washing steps are necessary, and what is the optimal water-to-plastic ratio to achieve clean plastics of good quality?
2) Which parameters should be monitored in order to optimize the washing process?
3) What are the wastewater treatment techniques that facilitate water reuse in the process by effectively removing contaminants?

This work will try to provide comprehensive answers to these questions, thereby offering valuable insights and recommendations for the development of an optimized process. Therefore, it starts with an exploration of the existing research on flexible plastic packaging recycling, focussing on the washing process and the removal of VOCs from the plastic waste to ensure that the recycled plastic reaches a better quality. Some important parameters related to odour and VOCs are discussed, including an exploration of the specific groups of VOCs that are commonly responsible for causing off-odours. Different methods to characterize odour are being looked at, highlighting the need to differentiate between odour and VOCs. This is followed by an analysis of the washing process, exploring the contaminants that pose some challenges in recycling and examining the impact of various parameters on their removal. Additionally, insight is provided on the utilization of washing media and into the kinetics of the washing process. Finally, some water treatment techniques are explored and linked to the economic and ecological aspects of the recycling process. Several options are being considered, mainly focussing on techniques that offer efficient removal of the main contaminants present in the water, while also considering the additional costs involved.

The acquired knowledge will support the research that will be conducted further on. This includes a series of laboratory experiments measuring different parameters to verify the performance of the washing process. By incorporating the experimental data and findings obtained from these experiments, an Aspen Plus model is developed as a tool for understanding the influence of the process parameters and to predict the removal efficiencies of certain contaminants in different scenarios. The developed Aspen Plus model can be used to optimize the washing processes and wastewater treatment in the plastic recycling industry, which will be key to further increase recycling rates for plastic packaging waste.

CHAPTER 2

2. Literature review

2.1   The fate of plastic waste

Nowadays, European plastics manufacturing industry is transitioning to meet net-zero emissions by 2050, which fits in the frame of the European Green Deal. Since 2006, the recycling rate of post-consumer plastics waste in EU27+3 has more than doubled, the amount of plastics sent to energy recovery increased more slowly by 77% and the amount sent to landfill decreased with 47%. In 2021, the recycling rate increased and plastics sent to energy recovery processes and to landfill decreased, which is a trend that will hopefully be sustained in the future (Figure 1) (Plastics Europe, 2022a).
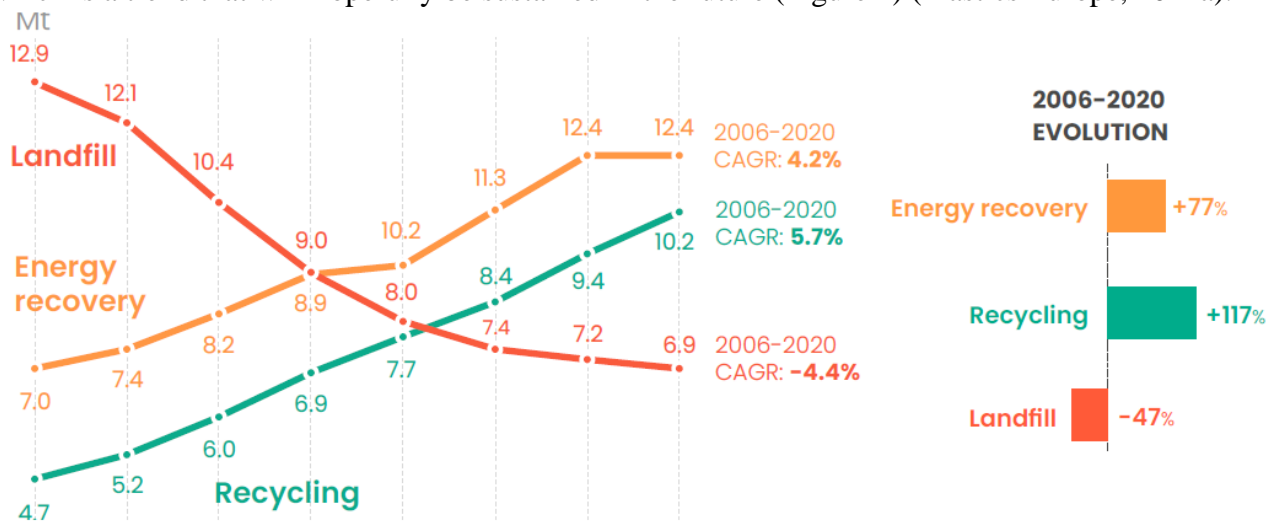

Figure 1: Evolution of post-consumer plastics waste treatment in EU27+3 (Plastics Europe, 2022a).
(CAGR: Compound Annual Growth Rate)

From the 29.5 million tonnes post-consumer waste collected in 2021, more than 10 million tonnes of plastic waste were sent to recycling in EU27+3. Due to process losses in the recycling plants and the surplus of plastic that cannot be processed that is exported, only 5.5 million tonnes were used in new products. This is less than 20% of the collected waste (Plastics Europe, 2022a). To achieve a fully circular plastic production – which in theory means recycling those 29.5 million tonnes of waste - innovations and investments are needed. Investments of governments and businesses in new production sites and new infrastructure to increase production of recycled plastic, but also in business models to design plastics for reuse and recycling in place (Ellen MacArthur Foundation, 2023). However, the recycling sector is (slowly) progressing, knowing that about 20% more plastic waste is recycled than in 2020. Although, when comparing the amount of collected waste to the 57.2 million tonnes produced in the EU27+3, there is still a lot of effort needed (Plastics Europe, 2022a). Only four countries in EU27+3 have recycling rates above 40%, while the European Commission has proposed that 55% of plastic packaging should be recycled by 2030 (Ragonnaud, 2023). The entire waste management value chain is important to further increase recycling rates of plastics, starting with proper waste collection systems and extended producer responsibility (EPR) schemes (Kol et al., 2021). In separated waste collection, end-users sort the different types of waste on a product level, while in mixed waste collection, different types of waste, such as household residual waste and municipal waste are not sorted. Recycling rates are 13 times higher when collected separately than

via mixed waste collection schemes. The EU should therefore focus more on this by applying separate collection in all Member States and spread awareness to the consumers (Plastics Europe, 2022a).

A large part of plastics used for packaging applications are categorized as polyolefins, i.e., polyethylene (PE) and polypropylene (PP) (Horodytska et al., 2021). About 24% of the in Europe produced plastics are made of polyethylene (Plastics Europe, 2022a), which is logically also one of the plastic materials that is found most frequently in municipal solid waste (Soto et al., 2020). Therefore, this dissertation will concentrate on recycling this type of plastics. PE is made up of a long chain of carbon atoms with two hydrogen atoms attached to each carbon atom. High-Density Polyethylene (HDPE), Linear Low-Density Polyethylene (LLDPE) and Low-Density Polyethylene (LDPE) are the three main types. LDPE and LLDPE are mostly used for reusable bags, trays and containers and packaging films. HDPE is used in milk bottles, shampoo bottles, pipes, etc. and is the most readily recycled type of PE (Plastics Europe, 2021). This is for several reasons: first, HDPE has a rigid, crystalline structure, whereas LDPE has a more branched structure and is thus softer and more flexible. Therefore, LDPE risks to get clogged in recycling machinery. Next, due to its lower melting point, LDPE cannot withstand great temperatures which makes it more likely to degrade under stress (OMICO Plastics Inc., 2020). PE's low cost, excellent chemical resistance, good processability, flexibility and transparency are its most attractive qualities (Ronca, 2017).

Unlike certain plastic waste streams, such as polyethylene terephthalate (PET) bottles, other post-consumer waste streams, especially plastic films, are still recycled at low rates (Roosen et al., 2021). The post-consumer waste streams cannot obtain a quality comparable to that of new virgin plastics (Cabanes, Valdés, et al., 2020). Currently, the most frequently used recycling technology for thermoplastic polymers such as PE is mechanical recycling, where the plastics are cleaned and remelted in secondary materials that can be used to manufacture new products. More details about this process can be found in section 2.3. However, there are still some challenges to face (Delva et al., 2019; Roosen et al., 2021): post-consumer packaging from households, such as PE film, is highly contaminated and heterogeneous. The dirtier and the more heterogeneous the plastic films, the more challenging the recycling process (Horodytska et al., 2021). Common contaminants are paper, inks, coatings, dust, additives, organic residues, etc. These contaminants can be transferred from one to another packaging during collection. This causes a complexity which makes it harder to recycle the plastics (Horodytska et al., 2020; Kol et al., 2021; Soto et al., 2020). The contaminants that pose the biggest obstacle in recycling are inks and unpleasant odours. Current recycling processes fail to remove these contaminants sufficiently, leaving the resulting pellets with limited mechanical properties, functionalities, unwanted odours and bad colour qualities (Strangl et al., 2021). Therefore, plastic waste, especially from polyolefins, is often downcycled into trash bags, irrigation pipes and outdoor applications (Horodytska et al., 2021). The heterogeneity of post-consumer packaging is due to the fact that plastics are often collected and sorted in different ways when comparing different households, but also when comparing different waste companies. Moreover, the differences in waste management between countries inside the EU alone leads to this heterogeneity. Harmonized collection and sorting methodologies will therefore be necessary to be able to process more homogeneous bales of plastic that lead to improved process efficiencies and more consistent qualities of recycled plastics (Plastics Europe, 2022b).

Landfill, incineration and energy recovery cannot support a circular economy. This technical challenge must be supported by the government and companies through investments and new regulations (Ellen MacArthur Foundation, 2023). The reduction trend of plastic waste sent to landfill in Figure 1 should continue in the same way, while the upward trend of energy recovery should be

redirected towards a descending trajectory (Figure 1). Sorting, washing and grinding are known pre-treatment technologies that are already helpful to achieve a more circular economy for plastics (Kol et al., 2021). However, according to Kol et al. (2021), more advanced treatments such as deodorization are necessary and according to Hopewell et al. (2009), energy and water should be used in a more eco-efficient way. These topics will be further elaborated in the sections below.

2.2 Volatile organic compounds

2.2.1 Volatile organic compounds present on plastic waste

The acceptability of recycled plastic as a low-cost and environmentally friendly alternative for virgin plastic is greatly reduced due to the existence of unpleasant odours that are presumed to be caused by volatile organic compounds (VOCs), including aldehydes, esters and alcohols. This is also a known problem in the recycling of plastic films (PE, PP). The volatile compounds evaporate easily from the resins at temperatures close to room temperature and produce odours that intensify at elevated temperatures (Fuller et al., 2020). The overall odour intensity depends on the way of collecting plastics, the origin of the feedstocks, the concentration and chemical properties of the constituents and the cleaning and processing process (Cabanes, Strangl, et al., 2020; Roosen et al., 2021). Namely, migration of compounds from one packaging to another during waste collection or from the content of the packaging to the plastics. This can be cosmetics and washing agents, that often contain a complex mixture of various fragrances and are frequently packaged in HDPE materials. Also, microbial activity can cause degradation of organic matter on packaging and cause the formation of odorants (Cabanes, Strangl, et al., 2020; Strangl et al., 2018). Moreover, some of these malodorous compounds can be formed due to environmental conditions including heat, light, oxygen and radiation that cause oxidation of lipids or polyolefins (Strangl et al., 2018). Lastly, during the recycling processes, residual by-products or degradation products from added compounds are formed. The combination of all these factors give rise to a complex mixture of odour-causing compounds (Demets et al., 2020). This mixture often presents a barrier when trying to use recycled plastics for high-value applications intended for consumer products. It is therefore crucial to minimize VOCs when recycling post-consumer PE waste (Strangl et al., 2018). Thus, waste that is not collected separately and only sorted at the waste management facility often contains higher levels of contamination and more intense overall smells, making it unsuitable for recycling. Waste fractions separated at the source in a plastic bin increase the recyclability because of the higher quality (Cabanes, Strangl, et al., 2020).

Different authors analysed the VOC-composition present on PE recycled plastic. In Table 1, the VOCs were divided into chemical groups to give a better overview. The chemical groups were chosen based on Roosen et al. (2023). The number of compounds per group are mentioned per author. Fuller et al. (2020) used headspace solid-phase microextraction coupled with Gas Chromatography-Mass Spectrometry (HS-SPME-GC-MS) to analyse VOCs. By means of Strangl et al. (2018) investigated the odorant composition by both comprehensive sensory analysis and instrumental analysis by means of high resolution Gas Chromatography-Olfactometry (GC-O) followed by Gas Chromatography-Mass Spectrometry. Cabanes, Valdés, et al. (2020) gathered from literature all VOCs identified in recycled polymers, including post-consumer HDPE. Roosen et al. (2023) performed VOCs analysis on a PE film bale using HS-SPME-GC-MS. A selection of most occurring VOCs on the analysed packaging was made. Finally, Demets et al. (2020) analysed waste streams mainly consisting of flexible post-consumer plastic packaging waste using GC-MS using one of following sampling techniques: HS-SPME, active sampling on activated charcoal followed by solvent desorption (SD-GC-MS) and active sampling on Tenax-TA tubes followed by thermal desorption (TD-GC-MS).

Diverse measurement techniques are employed by the different articles, which will be elaborated on in section 2.2.2.

Table 1: VOC composition on PE recycled plastic.

Author	Fuller et al. (2020)	Strangl et al. (2018)	Cabanes, Valdés, et al. (2020)	Roosen et al. (2023)	Demets et al. (2020)
Plastic type	90:10 PP:HDPE	HDPE	HDPE	PE	Mixture of PE, PP, PET, PS, PA and multilayers
Analytical equipment	HS-SPME-GC-MS	High resolution GC-MS-O	Combination of different techniques[1]	HS-SPME-GC-MS	HS-SPME-GC-MS, SD-GC-MS, TD-GC-MS
Chemical group	Number of compounds (% of total)				
Alkane	31 (67.4%)	/	18 (10.2%)	5 (23.8%)	17 (23.3%)
Alkene	3 (6.5%)	/	7 (4.0%)	1 (4.8%)	1 (1.4%)
Ether	/	/	5 (2.8%)	1 (4.8%)	/
Aldehyde	/	5 (15.6%)	11 (6.3%)	/	10 (13.7%)
Alcohol	1 (2.2%)	1 (3.1%)	10 (5.7%)	3 (14.3%)	8 (11.0%)
Ketone	/	3 (9.4%)	17 (9.7%)	2 (9.5%)	11 (15.1%)
Amide	/	/	/	2 (9.5%)	/
Aromatic	4 (8.7%)	/	26 (14.8%)	2 (9.5%)	12 (16.4%)
Ester	3 (6.5%)	2 (6.3%)	46 (26.1%)	/	4 (5.5%)
Carboxylic acid	/	6 (18.8%)	8 (4.5%)	3 (14.3%)	1 (1.4%)
Sulphur compound	/	/	/	/	1 (1.4%)
Terpene	4 (8.7%)	15 (46.9%)	27 (15.3%)	2 (9.5%)	8 (11.0%)
Other	/	/	1 (0.6%)	/	/
TOTAL	46	32	176	21	73

It can be seen from Table 1 that the VOC composition on PE plastic waste is very diverse, which is in line with section 2.1. Alkanes, aromatics, esters and terpenes are the most abundant groups. Most of these functional groups have a characteristic odour. The smell of aldehydes is described as fatty. Ketones have a butter-like, coconut-like, soapy or perfume-like smell while esters are fruitier. Amines are known to have a fishy, fecal-like smell. Sulfuric compounds typically have a pungent or food-like smell such as garlic-, onion-, cabbage-like and so on. Carboxylic acids are either sour, cheesy, fruity, soapy or honey-like. Terpenes have a typical soapy, flowery, fruity smell... The flowery, fruity, soapy smell mostly related to fragrance and flavour compounds is often used to distinguish post-consumer plastics from other sources (Cabanes, Valdés, et al., 2020; Pullen, 2007). It is, however, important to note the difference between VOCs and odorous compounds. Deodorisation is therefore not exactly equivalent to the VOC removal. First of all, not all VOCs have a smell. The odour of a specific component is influenced by its concentration and chemical structure (Demets et al., 2020). Secondly, VOCs that contain an odour have a so-called odour threshold value. To perceive the odour, the concentration of a component must exceed this value. It is expressed in parts per billion (ppb) or

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[1] This article gathered the all VOCs and odour-active substances identified in PE polymers from literature. The various articles employed different measurement techniques.

micrograms per cubic meter (µg/m³) and may be very low (a few ppb) or higher (several hundred ppb) (Pullen, 2007). This means that certain VOCs will have to be removed more than others to obtain odour removal. So, depending on this value, it may or may not be difficult to remove the odour (Strangl et al., 2019). In Table 2, an overview is given of odour threshold values in air from typical VOC groups. These are values in air as no threshold values on plastics could be found in literature. The range of values are taken from De Somer et al. (2022) and Roosen et al. (2023). Carboxylic acids typically have a very low odour threshold value meaning they will be odorous even at low concentrations (Table 2). This makes them, together with terpenes, aromatic and oxygenated components, the main VOCs that typically are of concern in deodorization. The threshold values for hydrocarbons vary a lot. The mean of the threshold for these compounds is 1192 ppb, from which there could be said that they are of less concern. Nevertheless, depending on the compound, these will or will not be a problem in deodorisation. To measure the deodorisation, several methods are available (Table 1). These methods are also discussed in the next section (2.2.2). It will be important to keep in mind that some methods measure odour and others measure VOCs present on the plastics.

Table 2: Selection of VOC groups and their corresponding odour threshold value (De Somer et al., 2022; Roosen et al., 2023).

Functional group	Odour threshold value (µg/L air)
Carboxylic acids	0.2 - 4.1
Aromatic compounds	0.1 - 23.1
Oxygenated compounds	0.07 - 9.6
Terpenes	0.4 - 33.1
Hydrocarbons	0.5 - 6452

Before going further into the measurement techniques, there are some parameters that need to be discussed to characterize odour and VOC. Odour molecules are typically of low molecular weight. Roosen et al. (2023) detected VOCs on plastics with molecular weights ranging from 71.1 to 296.5 g/mol. This parameter affects the removal efficiency: when the molecular weight increases, the removal efficiency decreases (De Somer et al., 2022; Strangl et al., 2019). It is an essential element in terms of diffusion limitations of washing (Demets et al., 2020). When the plastics are washed, the VOCs are removed as they diffuse out of the polymer matrix and desorb from the plastics. Larger molecules have a lower diffusion rate than smaller molecules as they face more steric hindrance. Furthermore, already desorbed molecules can re-adsorb and this can be done at sites that are more easily accessible so they suffer less from that steric hindrance (De Somer et al., 2022). Other parameters that influence the diffusion rate are the swelling of the polymer and its polarity. When the polymer swells, its permeability is increased which makes it easier for molecules to diffuse (Ügdüler et al., 2020). Polymers, such as PE and PP, so-called rubbery plastics, have higher diffusion coefficients because they have more volume between their molecules compared to glassy polymers (Roosen et al., 2022). The polarity of a polymer can also determine the diffusion rate of certain molecules. More apolar molecules diffuse relatively faster through apolar polymers such as PE and PP than through polar ones such as PET and vice versa (Ügdüler et al., 2021).

The boiling temperature (Tb) is another parameter to characterize VOCs. It defines the volatility of the VOC. Based on Tb, VOCs are divided into three groups: very volatile organic compounds (VVOCs, Tb < 100°C), volatile organic compounds (VOCs, 100°C < Tb < 240°C) and semi-volatile organic compounds (SVOCs, 240°C < Tb < 400°C) (Demets et al., 2020). The VOC-composition is different in different life stages of the plastics: virgin plastics, manufactured post-industrial (PI) or post-consumer (PC) recycled plastics. It appears that most of the VOCs are volatile and semi-volatile organic compounds (Figure 2), they probably devolatilize less than the VVOCs and remain in the

polymers because of their higher boiling point. PI waste is waste from industry that was not contaminated and has stayed unused, while PC waste has fulfilled its intended purpose and has been retrieved from municipal solid waste (Cabanes, Valdés, et al., 2020). Post-consumer recycled plastics contain the most VOCs, consisting of mainly volatile and semi-volatile organic compounds, meaning that the concentration of VOCs increases when used by consumers (Figure 2). This higher contamination is one of the reasons why these post-consumer plastics are not yet used for food contact applications. These contaminants could migrate from the packaging to the food causing public health problems. More research is still needed to know to what extent which components can pose a hazard. This is why strong regulations about the use of polyolefins for food packaging still exist and are now spread by governments around the world (Cecon et al., 2021).
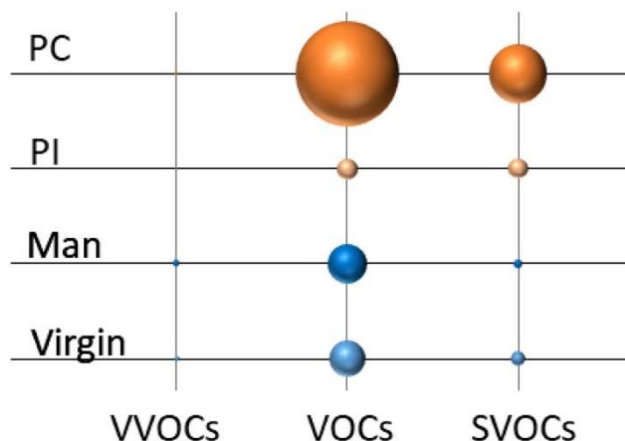

Figure 2: Composition of the VOCs found in post-consumer (PC), post-industrial (PI), manufactured (Man) and virgin plastics, based on their boiling point (Cabanes, Valdés, et al., 2020).

The next important parameter is the polarity of the VOCs. This property can help determining to which extent a VOC will be properly removed. For instance, when plastics are washed with water, more polar VOCs will dissolve better in the polar water and will therefore be better removed (Demets et al., 2020). Polarity can be measured by the octanol-water partition coefficient (log K_{OW}). It describes the logarithm of the ratio of the concentration in equilibrium of a solute in a two-phase system consisting of two immiscible solvents, namely water and 1-octanol, resulting in values varying between -3 (very hydrophilic, polar) and +10 (very hydrophobic, apolar) (Cumming & Rücker, 2017).

2.2.2   Analysing odours and VOCs present on plastics

There are several methods for characterizing odours or VOCs. In the next sections, a brief overview is given of the different methods, with their advantages and disadvantages, including:

1) Olfactometry
2) Electronic Nose (E-nose)
3) Gas Chromatography-Mass spectrometry (GC-MS): headspace techniques or solvent-extraction techniques

2.2.2.1 Olfactometry

Olfactometry is often used in plastic recycling to evaluate the intensity and type of odours present. This sensory evaluation is qualitative and performed by a trained panel that smell a sample and rate the intensity and hedonic tone (Fuller et al., 2020). Odour intensity can range from 0 (not perceived) to 10 (strongly perceived). The hedonic tone is a subjective parameter and refers to the pleasure or

unpleasantness of an odour. It can range from 0 (dislike) to 5 (neutral) to 10 (like) (Cabanes, Strangl, et al., 2020). To accurately assess the odour present in each sample, several evaluators are preferable because these tests are typically subjective (Fuller et al., 2020).

Gas chromatography-Olfactometry (GC-O) can be used to prepare the samples, known as dynamic olfactometry. The GC separates and identifies the chemical compounds, while the panellists determine afterwards whether there is an odour present, the odour intensity or the hedonic tone (Strangl et al., 2019). The samples are placed in headspace vials and evaluated via a wafting technique under room temperature (Fuller et al., 2020). Wafting is a technique to smell chemicals where the panellists cup their hand above the vial and wave the vapours towards their face, taking small, short sniffs. Sniffing the chemicals directly could risk damaging the membranes in the nose (Ashbrook, 2009). For the description of the odour, sniffing pens are used as references for certain attributes, such as earthy, mouldy, cheesy, fruity… (Cabanes, Strangl, et al., 2020).

Due to the need for continuous screening and training of panellists, olfactometry can be both time-consuming and expensive. Continuous measurements are not possible and furthermore the duration of the analysis is limited as odour samples are hard to store because of their instability (Brattoli et al., 2011). However, it is a good tool to have a screening of the odours present present that go beyond the results that are obtained with more conventional GC-MS methods, as discussed in section 2.2.2.3. To better understand the principles of odour characterization, analytical studies will be necessary to use and to couple with the sensory evaluation (Strangl et al., 2019). Olfactometry is still very valuable as instrumental analyses are not as sensitive and powerful as the human sense of smell. For example for the detection of trace compounds, which contribute mostly to the off-odour, it is still regarded as the most important instrument for odour evaluation (Brattoli et al., 2011; Cabanes, Valdés, et al., 2020).

2.2.2.2 Electronic nose

Electronic nose (E-nose) analysis is utilized as an instrumental tool to mimic the human nose. Unlike other analytical instruments, it allows the identification of mixtures of organic samples as a whole, instead of having to identify individual chemicals (Wilson & Baietto, 2009). This technique is composed of a chemical electronic sensor array to detect and measure traces of chemicals in a gas-mixture considered by humans as odour. Each sensor is sensitive to certain chemicals and creates a characteristic response, comparable with the human nose. A pattern of responses is then generated, known as a chemical fingerprint. Finally, data analysis is performed processing the chemo-electronic signals, in analogy with what happens in the human brain (Figure 3) (Brattoli et al., 2011; Karakaya et al., 2020).

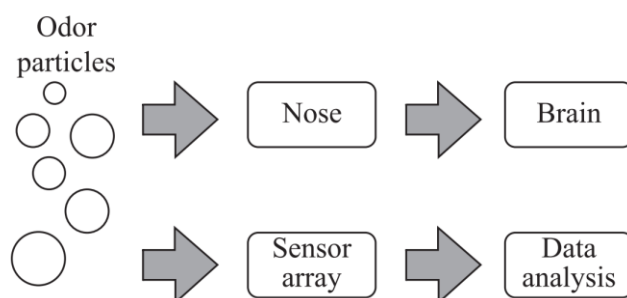*Figure 3: Analogy between perception of odour in the human nose (above) and the E-nose (below)* (Karakaya et al., 2020).

The human olfactory system is very complex so it is not easy to transfer it to an analytical instrument, however not impossible (Karakaya et al., 2020). Technical limitations of the E-nose are that it is not a chemical analyser so it must be trained for any specific application. The suitability of an electronic

nose system for a specific application depends on the composition of the gases being detected so a case by case evaluation is needed (Wilson & Baietto, 2009). However, in contrast to GC-O, continuous measurements are possible. Moreover, using E-noses is interesting as they are less time-consuming, cheaper are more objective than using human test panels. They can also be employed for real-time, in site and remote control (Brattoli et al., 2011).

2.2.2.3 Gas Chromatography-Mass spectrometry

GC-MS is used for chemical characterization of VOCs present on the plastic. Because this technique requires sample pre-treatment, direct measurement of VOCs on the sample surface is challenging for a heterogeneous waste stream. Two groups of sample pre-treatment techniques exist: headspace techniques and solvent-based techniques. In headspace techniques, VOCs are collected by diffusing them from a solid matrix to a gas phase. The solvent extraction methods are based on the extraction of VOCs from the polymeric matrix to a solvent phase by stirring a sample in the solvent. The former is used in most cases, mainly due to the fact that these can offer an environmentally friendly option and that these are less time-consuming. Additionally, headspace techniques are equal or more sensitive than solvent extraction techniques for the recovery of VOCs (Cabanes, Valdés, et al., 2020). Solvent extraction is preferred when identifying SVOCs as it is the most appropriate when sampling lower volatile and thus higher boiling compounds (Horodytska et al., 2020). The biggest drawback is the use of a solvent, which can be harmful. Furthermore, due to limitations in solvent solubility, higher molecular weight analytes are not detected. Moreover, the solvent delay built in the analytical procedure masks more volatile compounds. Additionally, it dilutes the compound, requiring longer sampling times and volumes (Demets et al., 2020).

There exist multiple headspace and solvent-based extraction techniques, summarized in Table 3, describing the advantages and disadvantages based on Cabanes, Valdés, et al. (2020), Cristancho et al. (2012), Demets et al. (2020), Engel et al. (1999), Horodytska et al. (2020) and Möller et al. (2008). Only the most-used headspace techniques are discussed: 50% of the publications uses HS-SPME as sampling method and 41% uses TD. Flask-shake, Microwave-assisted extraction (MAE), Solvent assisted flavor evaporation (SAFE) and Supercritical fluid extraction (SFE) will be discussed as solvent-based techniques as they are used for PE samples (Cabanes, Valdés, et al., 2020).

When not only characterizing the VOCs but also identifying odorous compounds, molecules leaving the GC are split into two other capillary columns, one of which is connected to the MS and the other to a sniffing port for sensory evaluation. GC-MS is then combined with olfactometry (GC-MS-O), as mentioned before in section 2.2.2.1 (Cabanes, Valdés, et al., 2020).

Table 3: Summary of headspace and solvent-based techniques.

Sampling method	Description	Advantages	Disadvantages
Headspace techniques			
Headspace solid-phase microextraction (HS-SPME)	SPME fibre (polydimethylsiloxane (PDMS), PDMS-divinylbenzene or carboxen–PDMS) adsorbs the VOCs to introduce them in the injection port of the GC	- Economic and ecological (no solvent) - Reliable - Rapid scan of a wide range of volatiles	- Selective adsorption of VOCs, depending on the affinity of the fibre with the molecules - Less sensitive for low volatility compounds, lower limit of detection than TD
Thermal desorption (TD)	Sending VOCs through a tube filled with a solid absorbent or a cold trap (carbon molecular sieves, graphitized carbon or Tenax-TA), and transferring onto the GC-column	- Ecological (no solvent), clean technique - Allows to measure VVOC - No dilution of the analytes	- Expensive - Selective adsorption of VOCs, depending on the affinity of the adsorbent bed material with the molecules - Less sensitive for high molecular weight components
Solvent-based techniques			
Flask-shake	Sample is shaken in contact with the solvent at a predetermined temperature and amount of time. The solvent phase is analysed	- Simplicity	- Low limit of detection - Solvent is harmful and masks more low volatile components
Microwave-assisted extraction (MAE)	Heating an extracting solvent in contact with a sample with microwaves to penetrate into the sample matrix	- Fast and effective - Low solvent use - Any solvent mixture if it contains at least one microwave-absorbing unit (permanent dipole)	- Expensive - Solvent is harmful and masks more low volatile components - Time-consuming sample treatment
Solvent assisted flavor evaporation (SAFE)	Collecting all volatiles in a liquid nitrogen trap at -196°C and concentrating them by distillation of the solvent	- Easy to handle and stable apparatus - Preservation of odour-active substances during extraction	- Solvent is harmful and masks more low volatile components
Supercritical fluid extraction (SFE)	Supercritical fluid (mostly supercritical CO_2) used to cause polymer swelling to increase the mobility of the VOC and extracted when they are soluble in the supercritical fluid	- Low solvent use - Nontoxic and non-hazardous solvent - Can be automated	- Expensive, complex equipment due to high pressure

2.3 The washing process

Washing is an important process for the mechanical recycling of plastics because it removes impurities such as contaminants, adhesives or labels, without changing the polymer structure (Soto et al., 2020). Currently implemented washing processes are mainly based on cold or hot water, with or without addition of chemicals, such as caustic soda, detergents or ethyl acetate (Roosen et al., 2021). In Figure 4, a typical conventional mechanical recycling process is depicted based on Larrain et al. (2021) and adapted for PE films. The process consists of a shredder, a first washing step, a second washing step, a float-sink installation, a mechanical and/or thermal dryer and an extruder (Figure 4). The shredder is used to obtain a homogeneous sample, lower the particle size and therefore increase the washing efficiency (De Somer et al., 2022). A first washing step can consist of a rotating drum washer that separates the biggest dirt gravitationally, such as rocks, metals and glass. The second washing step can consist of a friction washer that vigorously cleans the plastics through mechanical agitation. Organic residues, adhesives and labels are removed from the surface of the plastics. A water-based medium is used. After another shredding step the polymers are separated according to their density in a float-sink installation. PE and PP are usually the polymers with lower density, which means they will float. Extrusion includes a melt filtration to remove fractions such as higher-melting polymers, wood and paper and gives re-granulated plastic pellets (Kol et al., 2021; Lase et al., 2022; Soto et al., 2018).
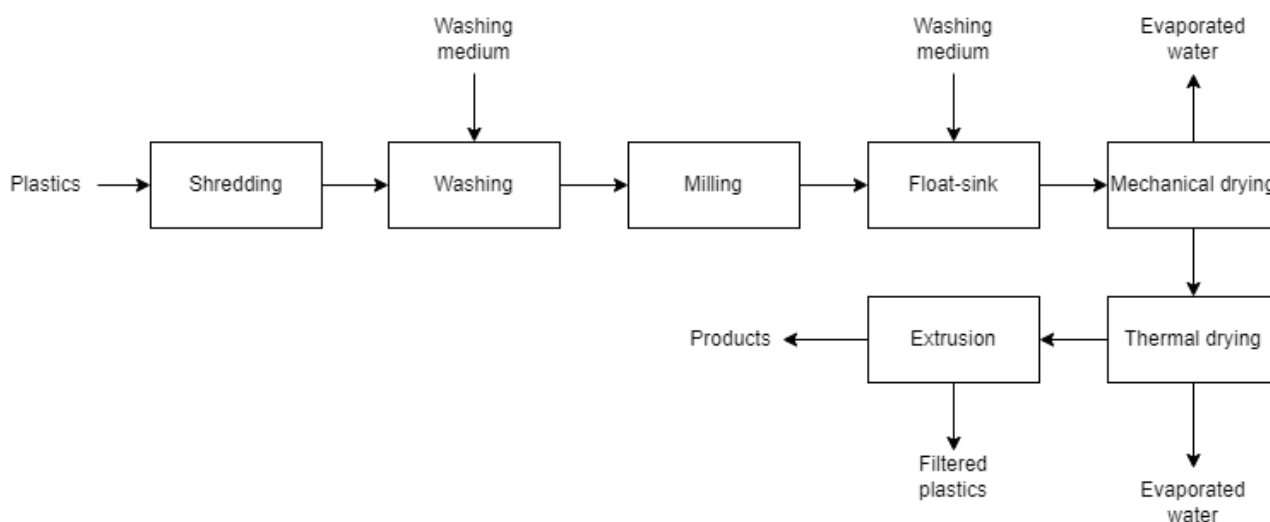
Figure 4: Mechanical recycling scheme, based on Larrain et al. (2021).

During washing of the plastics, contaminants are transferred to the water phase (Santos et al., 2005). For superficial contamination, such as dirt and organic residues, molecules desorb from the plastics into the water and can be removed only by washing (Prior et al., 2023). Polyolefins are difficult to decontaminate due to their higher permeability compared to PET, which results in a deeper penetration of contaminants into the polymer structure (De Somer et al., 2022). Examples of these persistent contaminants are VOCs and additives which are therefore harder to remove during washing (Cabanes, Strangl, et al., 2020; Ügdüler et al., 2020). As mentioned in section 2.2, when removing VOCs, they must diffuse out of the polymer structure before desorption from the matrix. The desorbed molecules can re-adsorb at more easily accessible sites of the polymer. It means an equilibrium between desorption and adsorption will be established after a certain amount of time. Thermodynamics indicate that adsorption of VOCs is favoured over desorption, which implies that the contaminated washing medium will have to be renewed regularly to avoid an increase in contamination of the plastics (De Somer et al., 2022). The kinetics of this adsorption-desorption mechanism will be discussed in section 2.3.3.

However, washing does not ensure complete removal of contaminants (Soto et al., 2020). Next to odorous compounds, inks, different polymer layers and non-polymer layers can still be present on the surface of the plastics (Roosen et al., 2022). Furthermore, if the washing medium is not changed regularly, re-adsorption of the contaminants will occur (De Somer et al., 2022). As mentioned in section 2.1, these compounds will result in limited mechanical properties, functionalities, unwanted odours and bad colour qualities of the pellets. A third, more advanced purification washing step will therefore be needed, such as chemical washing technologies, deodorization, deinking, delamination and solvent-based extraction methods. These methods are mostly still under development and can be implemented after the two already mentioned washing steps (Kol et al., 2021). New methods to remove VOCs from post-consumer plastic waste are steam stripping and polyethylene glycol extraction, where steam stripping exhibits the highest reduction in overall VOCs. Moreover, steam stripping reaches improved reductions in VOCs content compared to hot air stripping, which is the current applied technology (Cabanes & Fullana, 2021). As the focus in this work lies on the improvement of the washing procedure, this will not be discussed further.

In the next sections, an in-depth discussion on important parameters in the washing process is given, for instance, the typical contamination load on plastic packaging films and the influence of the particle size, the solid/liquid (S/L) ratio, the turbulence and the temperature. Also, the kinetics of the washing process are reviewed. Finally, the possible added value from the use of different washing media will be discussed.

2.3.1 Washing process parameters

2.3.1.1 Contamination load

To evaluate the process parameters of a washing line in the plastic recycling process (e.g., contaminant removal (in terms of COD for example) or change in pH), effluent characteristics can be used when no chemicals are added (Santos et al., 2005). Several authors characterized the load of contamination on plastics by analysing this liquid effluent. As the focus of this work is flexible packaging waste, selection was made on articles about PE loads. The values of the measured parameters are shown in Table 4. Mostly the values are given in mg/L, so a calculation was made to have all values in g contaminant/kg plastic to be able to make a comparison (Table 5). The four articles give comparable results except for the electrical conductivity (EC), which is considerably higher for Bordonalli & Mendes (2009), probably due to their higher concentration of solid material in relation to the liquid phase, compared to the other authors. pH-values are around 7, chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP)-load is between 10-60 g/kg, 0.4-1 g/kg and 0-0.3 g/kg, respectively. Total suspended solids (TSS) on the plastics are between 10-40 g/kg, except for the work of Calero et al. (2018), where it was 81.5 g/kg. Volatile suspended solids (VSS) are present between 3-12 g/kg, however with big uncertainty intervals. Only in Bordonalli & Mendes (2009), a value for turbidity was found, but with a large uncertainty interval (750 ± 533 NTU). For both Calero et al. (2018) and Soto et al. (2020), 10% of the weight of their incoming plastic stream is C+N+P+TSS, indicating the high contaminant loading of these samples.

Table 4: Plastic and water use + effluent composition after washing plastic with water (mg/L water).
[1]Soto et al. (2020), [2]Bordonalli & Mendes (2009), [3]Altieri et al. (2021), [4]Calero et al. (2018).

Plastic type	$M_{plastic}$ (kg)	V_{water} (L)	pH	EC (µS/cm)	Turbidity (NTU)	COD (mg/L)	TN (mg/L)	TP (mg/L)	TSS (mg/L)	VSS (mg/L)
PE film[1]	0.5	20	7.16	426	/	1509	24.3	6.3	1060	/
HDPE[2]	1	2-3	7.1 ± 0.6	10601 ± 5521	750 ± 533	4757 ± 1542	/	/	4734 ± 5726	1455 ± 1339
LDPE[3]	23000	200000	7.5 ± 0.4	1425 ± 194	/	1779 ± 1731	53.6 ± 30.2	11.6 ± 10.3	2378 ± 2873	1286 ± 1390
PE film[4]	1	10	/	/	/	1920	/	/	8150	/

Table 5: Contaminant load on the plastics after washing with water (g/kg plastic).
[1]Soto et al. (2020), [2]Bordonalli & Mendes (2009), [3]Altieri et al. (2021), [4]Calero et al. (2018).

Plastic type	S/L ratio	COD (g/kg)	TN (g/kg)	TP (g/kg)	TSS (g/kg)	VSS (g/kg)
PE film[1]	1/40	60.36	0.972	0.252	42.40	/
HDPE[2]	1/2.5	11.89 ± 3.86	/	/	11.84 ± 14.32	3.64 ± 3.35
LDPE[3]	1/8.7	15.47 ± 15.05	0.466 ± 0.263	0.101 ± 0.090	20.68 ± 24.98	11.18 ± 12.09
PE film[4]	1/10	19.20	/	/	81.5	/

2.3.1.2 Solid-liquid ratio and turbulence

As can be seen in Table 5, the plastic was washed with water at different S/L ratios. Soto et al. (2020) washed 500 g plastic with 20 L water, Bordonalli & Mendes (2009) used 2 to 3 L water per kg plastic, corresponding a S/L ratio 1/40 and 1/2.5, respectively. Altieri et al. (2021) washed 23 tonnes plastic packaging per day with 200 m³ water per day, which equals a ratio of approximately 1/9 which corresponds to Calero et al. (2018) who used a ratio of 1/10. In general, lower S/L ratios result in higher VOC removal efficiencies (Roosen et al., 2021). Roosen et al. (2022) washed 5 g of plastic material with 100 mL washing medium. Finally, Cabanes, Strangl, et al. (2020) washed 20 g plastic waste per litre water, corresponding to a ratio of 1/20 and 1/50, respectively. These ratios are based on lab experiments. All the S/L ratios in the lab studies vary a lot, but it can be concluded that a ratio between 1/2.5 and 1/50 should be used, ratios 1/10 and 1/25 are mentioned the most. When the plastics and washing medium are mixed, the speed of mixing is also an important parameter, as this creates a certain turbulence to remove the contaminants from the plastics. In an experimental lab set-up, Roosen et al. (2021) claimed that when using a rotary shaker at rotational mixing speeds greater than or equal to 200 rpm, no higher deodorisation efficiencies are observed, however, it is expected that in an industrial context this value might be different.

2.3.1.3 Particle size

As mentioned in section 2.2.1, during washing, VOCs must diffuse out of the polymer matrix and desorb from the plastics to be removed. The diffusion path shortens by decreasing the particle size, allowing molecules to desorb more easily from the plastics. Moreover, re-adsorption is promoted less by a decrease in particle size because it occurs at easily accessible sites. The specific surface area of an adsorbent (the plastics) has a strong impact on the sorption processes. It is estimated by multiplying the average thickness of the plastic particles with the average mesh size of the applied sieves. When it comes to plastic films, the impact of the particle size is minimal, as it highly depends on the thickness of the polymer. For PE bottles, on the other hand, having a larger thickness, the particles

size is more important because, as particle size is reduced, the specific surface area increases, increasing the removal efficiency. The VOC removal efficiency increases from 37-38% for particles of 1.1 cm to roughly 60% and 80% for particles of 0.1 mm for plastic films and PE bottles respectively. In addition, it is necessary to consider the industrial applicability of a reduced particle size (De Somer et al., 2022). In the industrial setting from Figure 4, prior to the first wash, the waste is shredded into 10 cm pieces and before the second wash milled into flakes of 3.5 cm (Larrain et al., 2021). More important than the size of the particles is the uniformity and homogeneity of the plastics to avoid having varying quality and properties throughout the process. This is why they are cut up into equal pieces (Demets et al., 2020).

2.3.1.4 Temperature

The washing process can be conducted at room temperature but also at higher temperatures. Soto et al. (2020) claim that differences between washing in water at room temperature and at 60°C are not significant in terms of COD, TN and chloride removal. De Somer et al. (2022) studied the effect of temperature on the removal of VOCs and the removal kinetics and stated that an increase in temperature increases the final degree of both. An increase in temperature results in an increase of the desorption coefficient of VOCs from plastics films ($k_{desorption}$ /$k_{adsorption}$). The VOC removal from plastic waste in water increased from 69% to 79% when increasing the temperature from 28°C to 85°C. In their experiments, Roosen et al. (2022) found that raising the temperature from 25°C to 65°C improved the average removal efficiencies by 5% to 15%. Although temperature impacts removal efficiencies, in deodorization it does not appear to be a major element in the batch experiments that are performed. If a suitable medium is chosen, reasonable efficiencies can be attained at room temperature, as long as the washing medium is not saturated with contaminants (Roosen et al., 2022). However, the impact of heating on energy consumption must be considered against the limited increase in VOC removal. As a result, washing plastics at room temperature is preferred to minimize costs (De Somer et al., 2022). Nevertheless, several reports do conclude that washing at elevated temperatures (60°C to 85°C) with caustic soda as washing medium, significantly increases removal efficiencies. The average removal of VOCs in this setting increased from 43% to 65% when raising the temperature from 28 up to 85°C (De Somer et al., 2022). In addition, the removal of COD, TN and TP also appears to be improved when washing with caustic soda at 60°C (Soto et al., 2020). Strangl et al. (2021) observed a 46% odour intensity reduction when applying an additional hot caustic wash of approximately 80°C compared to only a cold wash. However, in this article a cold wash is compared to a cold wash followed by a hot wash. A comparison should be made between this additional hot wash and an additional cold wash to determine whether this odour reduction is due to the higher temperature or due to fresh washing medium. It should be noted that this hot wash can be used to remove paper labels present on packaging (Roosen et al., 2020).

2.3.2 Washing media

From an economic perspective, water is mostly applied by industry as washing medium for plastic waste. However, physicochemically speaking, water is not the most efficient washing medium for removing contaminants with a broad polarity range that are adsorbed on apolar plastics (Demets et al., 2020; Roosen et al., 2021). Other, more tailored washing media could improve removal of contaminants. One option is to add detergents or/and caustic soda to the water (NaOH) (Lange, 2021; Santos et al., 2005). Nowadays, also interest in organic solvents, such as ethyl acetate, is growing as it has deep-cleaning capabilities with polymers (Roosen et al., 2022). Moreover, it can also be used as a solvent-based extraction medium for deinking (known as the patented Nordenia Extraction and

Cleaning process) and deodorization (Kol et al., 2021). Nevertheless, its application would result in higher CAPEX and OPEX costs (Roosen et al., 2022).

When deciding on the washing medium, not only the removal percentage will have to be considered. The associated cost and environmental impact of the medium and of any heating and subsequent wastewater treatment will also have to be considered. The possible wastewater treatment techniques and the influence of the washing media on the treatment will be discussed in section 2.4.

2.3.2.1 Caustic soda

Where water and caustic soda were efficient to wash PET bottles, these washing media have lower deodorization efficiencies when washing PE or PP bottles (Roosen et al., 2022). This can be explained by the higher permeability of polyolefins compared to PET, which makes them more difficult to decontaminate (De Somer et al., 2022). Moreover, caustic soda can hydrolyse PET, which can lead to surface activation of the polymer (Roosen et al., 2022). For PET, efficiencies up to 80% were found, whereas for PE and PP it was around 30-40%. Consequently, caustic soda is seen as a relatively poor washing medium for polyolefins that only partly removes the odorous components (Lange, 2021; Roosen et al., 2022). As stated before, the apolar and high-boiling components are difficult to remove with polar (water-based) washing media and caustic soda is even more polar than pure water, which makes the removal of apolar components even more difficult (Demets et al., 2020; Roosen et al., 2021). Furthermore, the addition of caustic soda results in a change in pH, which generates a basic effluent after the washing process which must again be considered during wastewater treatment (Santos et al., 2005).

2.3.2.2 Detergent (and caustic soda)

The addition of a detergent improves the removal efficiency of VOCs from plastic film waste with 20 to 30% compared to only caustic soda. An example is cetyltrimethylammonium bromide (CTAB) dissolved in a 1 m% caustic soda medium to a concentration of 0.92 mM, corresponding to 10 times the critical micelle concentration. This yields removal efficiencies of 65% and higher in a batch washing step at lab-scale (Roosen et al., 2021). De Somer et al. (2022) stated that washing with CTAB + caustic soda results in a rather similar VOC removal as water, whereas Roosen et al. (2022) reported 10-20% higher efficiency for CTAB + caustic soda. Table 6 shows their comparison in removal efficiencies of five different VOC categories (the same as in Table 2, section 2.2.1) between washing in water and washing in CTAB + NaOH. The latter article also stated that only applying detergent without NaOH is recommended. For PE films, CTAB + caustic soda results in a removal efficiency of 62.4%, whereas only CTAB results in 69.2% VOC removal. Moreover, it facilitates the wastewater treatment afterwards. A water-based solution of CTAB with a concentration of 0.92 mM is used. Deodorization will occur slower using only CTAB (5 minutes until equilibrium compared to 3 minutes for CTAB + NaOH), yet this can be countered by increasing the temperature to 65°C, reaching equilibrium after 3 minutes (Roosen et al., 2021). Because of the amphiphilic structure of the molecule, a detergent decreases the surface tension of the washing medium and decreases the contact angle between the washing medium and the surface of the plastic, which makes it easier to remove the apolar compounds. Furthermore, the detergent stabilizes the dissolved compounds, acting as a scavenger, so redeposition on the plastic surface is lowered (Horodytska et al., 2021). Roosen et al. (2022) tested different detergents in the washing process, such as CTAB, non-ionic surfactants and a mixture containing non-ionic surfactants and oxidizing agents. They reported that one category of detergents is not significantly better in deodorization than another. The addition of detergent is

essential for polyolefins, as it increases the deodorization efficiency by 20-30% compared with washing with caustic soda. Whereas for PET, adding caustic soda is required (Roosen et al., 2022).

Table 6: VOC removal efficiencies for five different chemical classes in water or CTAB + NaOH (Roosen et al., 2022).

Functional group	Removal in water	Removal in CTAB + NaOH
Carboxylic acids	60%	60%
Aromatic compounds	60%	70%
Oxygenated compounds	48%	65%
Terpenes	30%	55%
Hydrocarbons	30%	62%

It should be noted, as stated in section 2.3.1, that an increase in temperature to 60°C and more can significantly increase the removal efficiencies when using caustic soda (De Somer et al., 2022). Moreover, NaOH might be needed for label removal or dissolving glues for example. When washing PE films at 25°C with CTAB, a removal efficiency of 69.2% is observed, whereas a NaOH + CTAB mixture at 65°C results in an efficiency of 73.2% (Roosen et al., 2022).

2.3.2.3 Ethyl acetate

Ethyl acetate achieves a significantly higher average removal efficiency of VOCs (80-90%) compared to water-based solutions. The organic solvent has a lower surface tension than water and is more hydrophobic than water (logP = 0.7; National Center for Biotechnology Information, 2023). This results in better removal of apolar compounds (Roosen et al., 2021). As described in section 2.2, the octanol-water partition coefficient of the VOCs will pay a role in the extent of removal efficiency. As indicated, the washing step might induce higher costs but knowing the solvent cannot only remove VOCs, but also certain additives and inks, this downside might be less important compared to the benefits that come with it (Roosen et al., 2022). Unlike the other washing media, washing with ethyl acetate is seen as a chemical wash and not mechanical so this is not the scope of this work.

2.3.3   Kinetics

Santos et al. (2005) studied the effluent of their pre-washing step, where 3 kg of a homogenized mixture of polyolefins was washed with water at 16 L/min and concluded that the optimal residence time was around 5 minutes. Beyond that duration, there is not significantly more removal of COD or TSS (Figure 5) (Santos et al., 2005). Nevertheless, this arrangement, where plastics remain in the batch and water is continuously refreshed, is not practical for industrial application due to its excessive water consumption. However, this was the only paper that could be found in literature that described anything about kinetics to describe removal of COD, TN or TP from plastics.
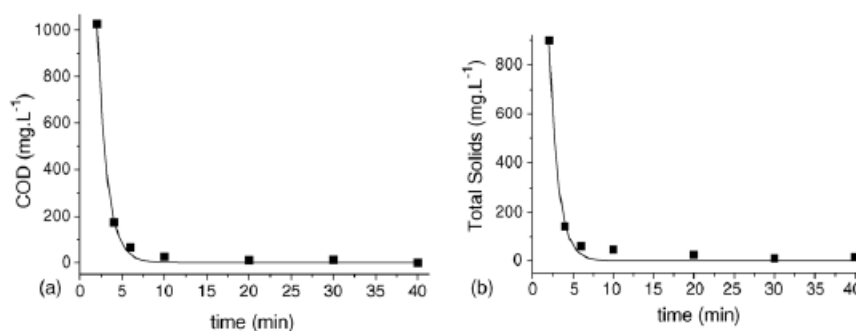

Figure 5:COD and total solids in the effluent from polyolefins pre-washing step (Santos et al., 2005).

When discussing the VOC removal more in detail, adsorption-desorption kinetics can be used to describe the washing process. The effectiveness of the washing process in reversible kinetic models is based on the adsorption and desorption via the reversibility of the sorption process (Roosen et al., 2021). These kinetics were described by De Somer et al. (2022) by a reversible first order (RFO) model. equation 1 describes the VOC removal kinetics in batch, where q is the relative concentration of adsorbate on the adsorbent (ppm/ppm), C the relative concentration of adsorbate in the liquid phase (ppm.kg.ppm^{-1}.L^{-1}), $k_{desorption}$ the desorption rate constant (s^{-1}), $k_{adsorption}$ the adsorption rate constant (L.kg^{-1}.s^{-1}), q_0 the relative concentration of adsorbate on the adsorbent at the beginning (ppm. ppm^{-1}), m the mass of adsorbent (kg) and V the volume of the liquid phase (L).

$$\frac{dq}{dt} = -k_{desorption} * q + k_{adsorption} * (q_0 - q) * \frac{m}{V} \qquad (1)$$

An experiment was carried out where water, NaOH and a mixture of NaOH and CTAB were tested as washing media at three different temperatures (28°C, 45°C and 85°C). It was shown that for all three media and temperatures, the equilibrium between desorption and adsorption of the VOCs is reached after approximately 2.5 minutes (De Somer et al., 2022). Roosen et al. (2021) even mentioned that a residence of 1 minute seems sufficient to achieve a steady state.

Cabanes, Strangl, et al. (2020) washed their plastics for 15 minutes, Roosen et al. (2022) for 10 minutes and Calero et al. (2018) for 30 minutes. These are the values most often found in literature and will therefore be applied in this study. However, it should be noted that residence time seems to be a less important factor compared to S/L ratio when removing VOCs (Roosen et al., 2021).

2.4 Wastewater purification techniques

Recycling facilities can repurpose the water used in the various stages of washing to lower the water consumption and wastewater production (Camperos et al., 2004), as the water is currently considered waste. Before the water can be reused, it will have to be treated (Jabłońska, 2018). Roosen et al. (2021) already studied the influence of the recirculation rate of the water on the removal efficiency of VOCs from the plastics. The recirculation rate is defined as the amount of water reused in proportion to the amount of fresh water that is added. The article showed that the higher these recirculation rates, the lower the VOC removal efficiencies, as the higher the accumulation of VOCs in the medium, the more re-adsorption of VOCs onto the films can take place. However, due to the need to reduce water consumption, many recycling industries currently use a relatively high recirculation rate of more than 0.9 kg/kg. This implies that internal water treatment will be needed to prevent re-adsorption and thus failing washing operations (Roosen et al., 2021). Primary and secondary wastewater treatment can already remove the majority of COD and SS. Although, this level of treatment has increasingly shown to be insufficient to provide reusable water for industrial and/or domestic recycling or to safeguard the receiving waters, so additional treatment steps will have to be applied (Sonune & Ghate, 2004). Such additional treatment can be among others, coagulation together or without flocculation, a sand filter, ultrafiltration and adsorption with activated carbon (Camperos et al., 2004; Jabłońska, 2018). These technological advances in plastic recycling can improve the economical and environmental feasibility (Bordonalli & Mendes, 2009). Optimizing the water management can be one of these advances, lowering the costs of the process. Moreover, as climate change and unsustainable management practices have led to drought in many regions, reusing wastewater can be a way to cope with water scarcity and provide security of water supply during dry periods (Gude, 2017). Different wastewater treatment options are discussed below.

2.4.1 Coagulation/Flocculation

Soto et al. (2020) suggest purifying the wastewater after washing with a physical-chemical treatment using a coagulation-flocculation process. In coagulation/flocculation, an attempt is made to agglomerate fine particles and colloids into larger particles that are afterwards precipitated and removed as sludge (Teh et al., 2016). The process of agglomeration is based on the DLVO theory (Derjaguin, Landau, Verwey and Overbeek) which states that the equilibrium of the attractive and repulsive forces between particles determines the stability of colloidal suspensions (Derjaguin & Landau, 1941; Verwey, 1947). Van der Waals attractive forces make particles clump together due to their fluctuating dipole. Whereas electrostatic repulsion is present between the ions of the electric double layers surrounding each particle. Van der Waals forces promote coagulation, while the double layer forces stabilization of the suspension. The DLVO curve in Figure 6 shows that if the distance between two particles increases, the potential energy or the interaction energy approaches zero. When the particles get closer together, they can end up in a secondary minimum, where they can stick together and form aggregates/flocs. This is a weak interaction and is reversible and is known as flocculation. Yet, when particles want to come even closer to one another, they encounter a potential energy barrier. If they manage to overcome this barrier, they enter a state of minimal energy and become stuck together (Figure 6). This is known as coagulation. In normal circumstances it is almost impossible for the particles to overcome the barrier and the suspension will remain stable. The height can be lowered by shear or by lowering the electrostatic repulsion and thus increasing the ionic strength, induced from the addition of a certain critical concentration of indifferent electrolyte. On the other hand, adsorption of counterions such as metal hydrolysis species or polyelectrolytes on the surface of the particles can help the lowering too. Depending on their mode of action, the additive used for the process may be termed as coagulants or flocculants (Derjaguin & Landau, 1941; Dukhin & Goetz, 2010; Langford et al., 2022; Teh et al., 2016; Verwey, 1947).
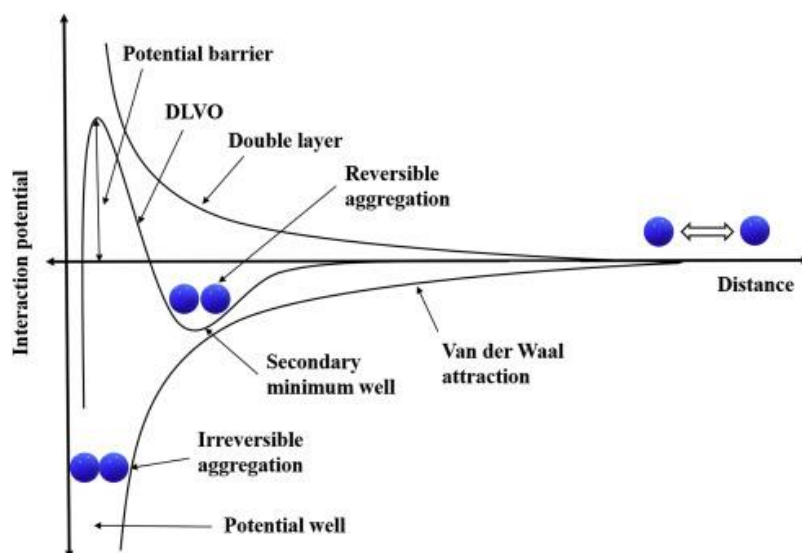
Figure 6: DLVO behaviour: interaction potential in terms of the distance between two colloidal particles (Langford et al., 2022).

The coagulation/flocculation procedure consists of rapid mixing of the distributed coagulant into the water, creating shear. After that, if needed, flocculation can follow which involves mild agitation to agglomerate small particles into well-defined larger flocs that can be more easily removed. The process ends with a settling phase where the flocs are removed as sludge (Figure 7). Both coagulation and flocculation can occur alone (Teh et al., 2016). There exist numerous process conditions for coagulation and the optimal conditions must be determined ad hoc. In general, it can be deducted, based on literature, that a rapid mixing step should be employed with mixing rates of 100 to 500 rpm

lasting 1 to 5 minutes (longer mixing at lower speeds). This is followed by a slow mixing step between 45 and 60 rpm for 10 to 30 minutes. Settling times range from 45 minutes to 1 hour (Amuda & Amoo, 2007; Aziz et al., 2007; Liang et al., 2010; Song et al., 2004; Zouboulis & Tzoupanos, 2010).

Figure 7: The coagulation/flocculation process (Teh et al., 2016).
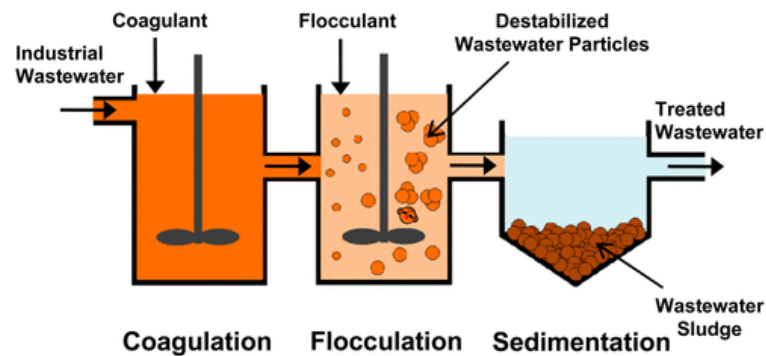
Coagulation and flocculation are primary processes in wastewater treatment given its relatively simple design, easy implementation, low energy consumption and high effectiveness for low costs. A wide range of chemicals are commercially available as coagulants (Crini & Lichtfouse, 2019). Natural organic matter and other soluble organic and inorganic pollutants can be removed from the wastewater and thus also turbidity is lowered (Teh et al., 2016). The effectiveness of this technique depends on the pH of the wastewater, temperature, contact time and on coagulant type and dose (Jabłońska, 2018). Drawbacks include the necessity of adding non-reusable chemicals (coagulants/flocculants) and the generation of an increased sludge volume. The sludge can still contain interesting nutrients that are more challenging to recover because of the addition of these chemicals (Crini & Lichtfouse, 2019).

Commonly used coagulants are aluminium- or iron-based, including aluminium sulphate, chloride or chlorohydrate, and sodium aluminate, and polyaluminium, sulphate or ferric chloride, and ferric sulphate (Bratby, 2016). Jabłońska (2018) washed PET bottles and tested five different flocculants and six coagulants for the coagulation/flocculation process. The best total organic carbon (TOC) removal was obtained with ferric sulphate (PIX123), however best turbidity removal was with aluminium sulphate (ALS). PIX-123 was chosen as the best option due to its comparable turbidity reduction. The best flocculant choice for TOC removal was a weakly cationic flocculant (Praestol 611BC), however a strongly cationic (Praestol 658 BC-5) and medium anionic (Praestol 2440) flocculants also gave good removal rates. The latter having the best turbidity removal. Camperos et al. (2004) also washed bottles from soft drink industry and tested different coagulants. More than 90% turbidity and TSS was removed with ferric chloride, PAX18 and an anionic BL5086-polymer, nevertheless polyaluminium chloride (PAX18) obtained the largest COD removal so that one was chosen as best option. In conclusion, there are many different coagulants and flocculants available, and each one will need to be tested for each specific application.

In general, inadequate or excess dosages of coagulants/flocculants can cause poor performance of the treatment process (Teh et al., 2016). Table 7 compares different dosages of coagulants and flocculants from different authors and the removal percentages obtained with them. The various articles describe the purification of different types of wastewater. The initial concentration of the contaminants in the wastewater is mentioned, giving the chance to compare this with the wastewater obtained in this research. Based on the type of wastewater, different dosages of coagulant are needed and therefore for each application a series of preliminary jar tests should be employed (Naceradska et al., 2019).

The optimal dosage of ferric chloride expressed in terms of the ratio of metal to organic carbon removed was found to be 0.73-0.81 g Fe^{3+}/g COD, however, the type of wastewater used must be considered as a higher density of organic fraction may require more coagulant (Liang et al., 2010). This ratio can thus be used as an indication to start preliminary testing.

Table 7: Coagulant and flocculant dosages and their respective removal rates.

Author	Wastewater type	Coagulant + dose/L wastewater	Flocculant + dose/L wastewater	Removal %
Jabłońska (2018)	PET bottle washing wastewater, 29 650 mg/L COD, 3700 mg/L TOC	$Fe_2(SO_4)_3$, 5 g/L	Weakly cationic flocculant, 2 mg/L	85% COD, 70% TOC
Liang et al. (2010)	molasses effluent, 950-1000 mg/L COD	$FeCl_3 \cdot 6H_2O$, 3.5 g/L	/	85% COD
		$Al_2(SO_4)_3 \cdot 18H_2O$, 5 g/L	/	64% COD
Amuda & Amoo (2007)	beverage industrial wastewater, 1750 mg/L COD, 1620 mg/L TSS	$FeCl_3 \cdot 6H_2O$, 0.300 g/L	Non-ionic polyelectrolyte, 10 mg/L	73% COD, 97 % TSS
Song et al. (2004)	tannery wastewater	$FeCl_3 \cdot 6H_2O$, 0.8 g/L	/	37% COD, 45.6% SS
		$Al_2(SO_4)_3 \cdot 18H_2O$, 0.8 g/L	/	32% COD, 37.6 SS
Gotvajn et al. (2009)	tannery wastewater, 3300 mg/L COD	$FeCl_3$, 1.75 g/L	Anionic polyelectrolyte, 2.5 mg/L	26% COD or with flocculant 51% COD
		$Al_2(SO_4)_3$, 1.0 g/L	Anionic polyelectrolyte, 2.5 mg/L	25 % COD or with flocculant 50% COD
Aziz et al. (2007)	landfill leachate, 2098 mg/L COD, 297 mg/L SS	$FeCl_3$, 2.5 g/L	/	44.7% COD, 99% SS
		$Al_2(SO_4)_3$, 2.5 g/L	/	26.9% COD, 70.4% SS
		$FeSO_4$, 2.5 g/L	/	21% COD, 42.4% SS

The optimal pH is dependent on the coagulant type and the type of wastewater. For example, pH of 3 or 9 for $FeCl_3$ or $Al_2(SO_4)_3$ respectively are needed to treat dye wastewater with a pH of 7, domestic wastewater (pH 6.6-6.7) needs a pH 5.7-5.9 for treatment with $Al_2(SO_4)_3$ (Teh et al., 2016). According to Jabłońska (2018), the effect of coagulant dose is smaller than pH. Maximal reduction of turbidity and TOC is reached when the pH is 9. This is confirmed by Amuda & Amoo (2007). When NaOH is added as a washing medium, this results in an increase of the pH of the solution and will therefore affect the treatment. The pH has an effect on the isoelectric point of the coagulants. For instance, for iron or aluminium-based salts, an increase in pH results in hydrolysis resulting in an ever greater reduction in charge. Furthermore, amorphous precipitates of $Fe(OH)_3$ and $Al(OH)_3$ are formed, resulting in a reduction of their ability for neutralization. The pH value needs to be tested for every coagulant dosage chosen. It is sometimes required to adjust the pH of the wastewater before treatment to reach the optimum range for the coagulant by adding a base or acid. The pH should therefore be optimized for each specific application (Naceradska et al., 2019; Sun et al., 2019).

CTAB may also be used as a washing medium. In that case, coagulation must also be able to remove this surfactant. Conventional coagulants (aluminium sulphate or iron chlorides) are only able to remove detergent from an aqueous solution to a low degree. Adding polyelectrolyte alone was proved to be more effective. Complete removal was obtained when the surfactant was sorbed on activated carbon, that was added before the coagulant (Kaleta & Elektorowicz, 2013). However, this will result in an increased cost of the purification process.

After the treatment, conductivity and total dissolved solids increase due to introduction of reagents (coagulant and flocculant). However, COD and SS decrease, which shows the validity of the process (Soto et al., 2020). Camperos et al. (2004) reached 80% to 95% turbidity removal, 75% to 90% TSS and up to 80% COD removal. Jabłońska (2018) achieved 90% turbidity removal, 100% TSS and 85% COD removal. The process decreases the number of contaminants to levels allowing the water to be reused, which could have positive effects on the environment and the economy of the whole washing procedure. However, coagulation and flocculation processes are not very effective in removing VOCs (Shouli et al., 1992). Integrating this process with different treatment methods, such as membrane filtration is therefore recommended to enhance contaminant removal, including these VOCs (Teh et al., 2016). This integration will be shortly discussed in section 2.4.4.

2.4.2 Active carbon adsorption

Due to the large surface area, porous structure, and high surface reactivity, activated carbon is the most widely used adsorbent for the purification of organic compounds (Li et al., 2011). It can be used to adsorb organic, for the most part refractory, toxic, coloured and/or odorous compounds, and remove them from the wastewater (Brinkmann et al., 2016). It is generally known for its affinity towards apolar compounds (Roegiers & Denys, 2021). It can be produced from any organic material with high carbon content (such as coconut shells, wood, charcoal, nutshell, fruit pits etc.) and exists in different forms: powdered activated carbon (PAC) or granular activated carbon (GAC). The cost of manufacture is the main difference between PAC and GAC, where PAC is less expensive. GAC is mostly used in continuous processes as it can be regenerated in contrast to PAC that is general used in batch processes (Tancredi et al., 2004). It should be noted that the performance of GAC after repetitive regeneration cycles diminishes gradually (Liu et al., 2012). GAC can effectively reduce volatile and non-volatile compounds to undetectable levels and preventing their re-emission to the atmosphere (Bansode et al., 2003). When coupled to coagulation, the process is highly efficient to reduce SS, COD and colour (Crini & Lichtfouse, 2019).

The GAC particles need to be pre-treated before use to removal colloidal fractions. It is mostly done by rinsing the particles exhaustively with (double-)distilled water. Afterwards, they are dried at least overnight at 105°C, after which they are stored in a desiccator until use (Gur-Reznik et al., 2008; Liu et al., 2012; Syafalni et al., 2012). For water treatment, GAC is used in the form of carbon beds, usually packed columns, in which organic molecules are adsorbed onto the surface of the carbon. After some time, the carbon becomes saturated and needs to be regenerated (Bansode et al., 2004). The adsorption process can also be performed by adding GAC to a solution in a shaking flask. The GAC dose in a shaking flask ranges from 0.075 g/L to 10 g/L, agitating at 105 to 250 rpm for 2 to 4 hours (Aljeboree et al., 2017; Bansode et al., 2003; Gur-Reznik et al., 2008; Liu et al., 2012). By increasing the adsorbent dose, the amount of adsorbed organic compounds increases as more active sites are available for adsorption. However, the removal rate increases slowly due to the low adsorbate concentration in the aqueous solution. Moreover, the adsorption uptake decreases due to the fact that adsorption sites remain unsaturated. If the adsorption capacity of GAC is not fully utilized, the process

is not economical. Therefore, both the removal rate and GAC utilization efficiency should be considered for optimizing the GAC dose (Aljeboree et al., 2017; Liu et al., 2012).

Bansode et al. (2004) studied COD removal and used carbon dosages ranging from 0.1 to 15 g/L. The initial COD concentration ranged from 40 to 66.5 mg/L and when adsorbing for 2h, the COD removal was between 70 to 90%. Liu et al. (2012) found a removal rate of COD from industrial chemical wastewater of about 90% at a GAC dosage of 2.0 g/L. According to Brinkmann et al. (2016), GAC can reach 80-95% removal efficiency of VOCs and odour in water, however usually not suitable for very high VOC concentrations (> 50 mg/Nm³). When Bansode et al. (2003) used commercial GAC, 72.0 to 88.9% of the tested VOCs in air were removed. This confirms what was previously stated that GAC provides good COD and VOC removal. Although, adsorption onto activated carbon requires a relatively high investment cost and the regeneration is also costly, it is a very simple treatment technique and a lot of commercial products are already available. It is often the preferred procedure for the removal of many types of pollutants because it offers the best results in terms of efficiency and technical feasibility on an industrial scale (Crini & Lichtfouse, 2019).

2.4.3 Membrane filtration

Physical, membrane-based techniques have increased popularity over the last decades (Sonune & Ghate, 2004). Based on type of filtration, degree of purification needed, size of the contaminant particles, cost and other parameters, different types of filters are used. Sand filters are used to remove suspended solids, floating matter and settleable particles from the wastewater by absorption and physical encapsulation. They are often applied in combination with coagulation (Dubey et al., 2022; Mohamed et al., 2022). Membrane filters act as barriers and remove from suspended solids, bacteria, viruses, to minerals based on the pore size of the filter in the presence of a driving force (Santhmayor et al., 2020). Different types of membranes exist: micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO) membranes, according to the particle size of retained species, as shown in Figure 8 (Yang et al., 2019). The smaller the pores, the higher the required operating pressure and, therefore, the higher the operating costs. UF and MF membranes are cheaper than RO and NF membranes (Brinkmann et al., 2016). A wide range of commercial membranes are already available from several manufacturers. It is a simple, rapid and efficient process, no chemicals are required and it produces a high-quality effluent. However, the membranes can clog relatively fast, the flow rates are limited, the waste stream is not treated but only more concentrated and the process requires high energy input (Crini & Lichtfouse, 2019).
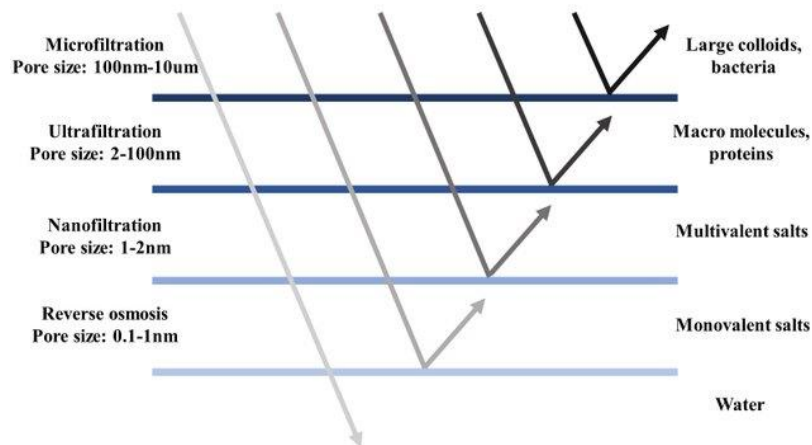

Figure 8: Existing membranes for water treatment, their corresponding pore size and retained species (Yang et al., 2019).

For VOC removal, NF/RO membrane filtration can achieve enhanced removal of sixteen VOCs with molecular weights between 78.11 g/mol (benzene) and 260.76 g/mol (hexachlorobutadiene) as tested by Altalyan et al. (2016). Furthermore, hydrophilic VOCs could be more retained than hydrophobic VOCs. However, it was seen that the performance of the membranes diminished when using them for a longer period of time. Santhmayor et al. (2020) used a sand filter along with a MF membrane of 5 µm to treat wastewater generated from waste plastics recycling machines. Camperos et al. (2004) performed filtration experiments using different filtrating materials to treat bottle washing water in the soft drinks industry. 68% removal of TSS was obtained, while parameters such as COD and turbidity were only removed for 20% and 15%, respectively. Thus, filtration alone is not enough to obtain high removal rates. The sand-anthracite bed media showed greater removal in all parameters than the sand bed alone. The difference in removal with fine or coarse sand grains was negligible. The combination of coagulation-filtration achieved greater removal of turbidity and COD (63% and 30% respectively), however TSS removal was lower. Filtration can also be followed by adsorption using activated carbon which resulted in 85% removal of turbidity, 92% for TSS and 40% for COD and a conductivity of around 550 µS/cm. The combination of filtration-adsorption with reverse osmosis completely removed TSS and turbidity and obtained 80% COD removal, which meets the quality of clean water. Galambos et al. (2004) treated high organic content industrial wastewater with a COD concentration of 1160 mg/L. NF achieved 91-94% COD removal, while treatment with an RO membrane achieved 98% COD removal. However, it should be noted that RO membrane processes require large amount of energy, due to their need for high operating pressures of about 20-100 atm. MF and UF membranes, in contrast, operate at low to moderate pressure (0.5-5 atm and 1-10 atm respectively) meaning their operating costs are lower, whilst NF membranes are somewhere in between, operating at pressures of 7-30 atm (Shon et al., 2013).

In summary, membrane filtration has shown to be an effective method for removal of pollutants from the wastewater. However, the extent to which they are removed affects directly the cost of the process. MF and UF membranes are effective in removing suspended solids, including COD and TSS, while NF and RO are better for removing dissolved solids such as VOCs. Additionally, in order to avoid membrane fouling and therefore the additional operational costs, it is recommended to pre-treat the wastewater with other purification techniques before using the membranes.

2.4.4 Integration of wastewater treatment techniques

One can conclude that one water treatment technique is unlikely to be sufficient and that a combination of different techniques could give a well-purified effluent in the most economical way. The main processes for the decontamination of industrial wastewater are depicted in Figure 9 (Crini & Lichtfouse, 2019). From this figure, a treatment process starting with coagulation/flocculation, followed by an adsorption process and finally membrane filtration could be proposed (Figure 9). This is just one example of such a process. In this section, the focus will lay on combining coagulation/flocculation with other treatments to enhance the removal rates, as this process is still said to be essential in wastewater treatment (Teh et al., 2016). Not only removal rate, but also the cost of the purification techniques will play a role. According to Tarpani & Azapagic (2018), the CAPEX (Capital Expenditures) for coagulation followed by granular activated carbon and for nanofiltration are 0.47 million and 3.89 million euros, respectively. Although, when viewed as a whole, the life cycle costs of nanofiltration are lower than the GAC process (€155 compared to €236/1000 m³ wastewater). This is mainly due to the coagulant and regeneration costs for GAC (operating costs). Moreover, in a follow-up study, Tarpani & Azapagic (2023) found nanofiltration to be the best option

when looking for the most sustainable technique. When it is necessary to combine different techniques for higher water quality, it is also sustainable to do nanofiltration followed by GAC.
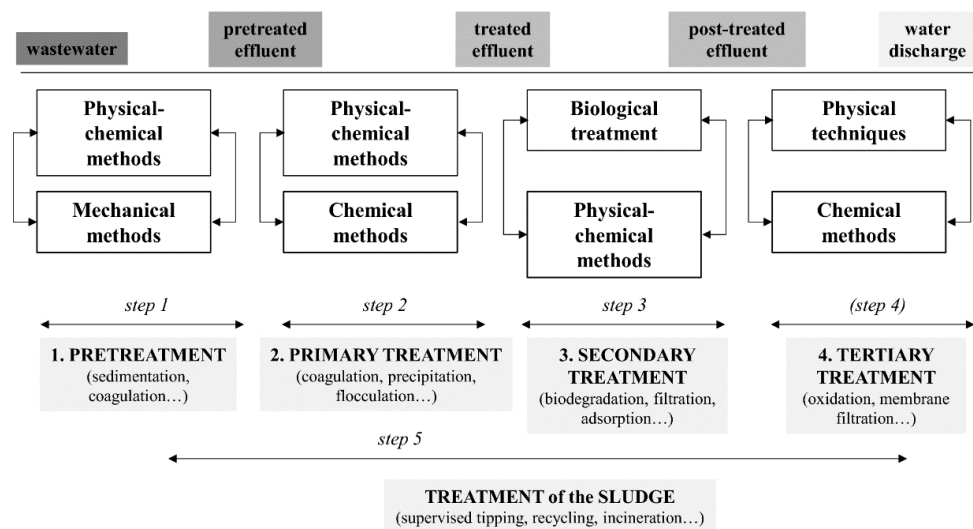

Figure 9: Main processes for the decontamination of industrial wastewaters (Crini & Lichtfouse, 2019).

Some of these integration processes are summarized in Table 8, including their removal efficiencies for common pollutants. From this table, it could be concluded that the integration of coagulation leads to better pollutant removal rates (Teh et al., 2016). The types of wastewater have approximately the same load as the plastic washing water (Table 4), so the same removal efficiencies can be expected for the application in this study. No removal percentages could be found in literature on integrated systems including coagulation/flocculation for VOC removal. However, when dairy wastewater is treated with coagulation and PAC, in addition to the removal efficiencies listed in Table 8, complete odour removal can be observed. Moreover, when adding an RO membrane to this process, 98% COD and 96% TDS removal can be achieved (Sarkar et al., 2006). According to Harrelkas et al. (2009), it will be interesting to combine membrane filtration as well as activated carbon adsorption with coagulation/flocculation for textile wastewater treatment to obtain water of good quality to be reused.

Table 8: Removal efficiencies from the integration of coagulation-flocculation (CF) with other wastewater treatment techniques, MF = microfiltration, UF = ultrafiltration, NF = nanofiltration, PAC = powdered activated carbon, GAC = granular activated carbon (Teh et al., 2016).

Integrated treatment	Type of wastewater	Removal% only coagulation	Removal% integration
CF + MF	Textile dye effluent, COD 1000-1200 mg/L, turbidity 45-117 NTU	10% COD, 20% turbidity	48% COD, 100% turbidity
CF + UF	Textile dye effluent, COD 1000-1200 mg/L, turbidity 45-117 NTU	10% COD, 20% turbidity	50% COD, 100% turbidity
CF + NF	Textile wastewater, COD 227-627 mg/L, turbidity 31-85 NTU	85% colour, 93-98% turbidity	60% COD, 100% colour
CF + PAC	Textile dye effluent, COD 1000-1200 mg/L, turbidity 45-117 NTU	65% COD, 20% turbidity	80% COD, 50% colour
	Dairy industry effluent, COD 1500-3000 mg/L, TDS 800-1200 mg/L	40% COD, 44% TDS	62% COD, 57% TDS
CF + GAC	Tannery wastewater, COD 2290-6100 mg/L, TSS 890-4200 mg/L	45% COD, 97% TSS	72% COD, 98% TSS

2.5   Conclusion of the literature review

The European plastic manufacturing industry is transitioning to meet net-zero emissions by increasing the recycling rate of plastics and decreasing the number of plastics sent to energy recovery processes and to landfill. Whilst PET is already recycled at relatively high rates, this is not yet the case for PE and PP. One of the main hurdles in flexible packaging recycling is the presence of contaminants from which odour and inks are of most concern. Conventional washing processes fail to sufficiently remove them, limiting the quality of the secondary materials. The focus in this work is on the removal of VOCs.

Contamination load, solid-liquid ratio, turbulence, particle size and temperature are important parameters to consider when optimizing the process. The washing medium has a great effect on the removal efficiencies too. Water, caustic soda and detergent were considered. Water alone is not sufficient to remove contaminants. Detergents give better removal of VOCs than caustic soda (about 20-30% more). A mixture of caustic soda and detergent gives a slightly weaker removal of VOCs than detergent alone but it also removes labels or glues. It should be kept in mind, however, that using these washing media can have an impact on the subsequent water treatment. As the washing process consumes a lot of energy and water, it is essential to explore ways to reuse the water used in the different washing steps to improve the overall sustainability of plastic recycling. The recirculation of water can affect the removal efficiency of odour compounds from plastics due to re-adsorption. Different purification techniques exist, but a combination of techniques can give good removal rates.

The aim is to improve the washing line of flexible plastic and, more specifically, remove VOCs before reuse. To do so, optimal washing parameters and a water treatment system that allows the water to be reused must be employed. Much research is still needed on how to characterize and remove VOCs, and possible purification techniques to make the process economical and to increase plastic recycling rates.

CHAPTER 3

3. Material & methods

3.1 Chemicals and reagents

In Table 9, a summary was made of the used chemicals. Acenaphthene-d_{10} was used as internal standard for Gas Chromatography-Mass Spectrometry (GC-MS) analysis due to its similar polarity to the components of interest and comparable volatility, allowing for the use of relative peak areas. CS_2 was used as solvent and spiked with 50 ppm of this internal standard for the analyses. HNO_3 was used for the inductively coupled plasma optical emission spectrometry (ICP-OES) analyses. For the adsorption experiments, granular activated carbon (ORGANOSORB 10-AA; 0.60-2.36 mm) provided by Desotec was employed. Prior to use all glasswork was cleaned with water and soap to avoid the presence of contaminations.

Table 9: Chemicals and reagents, their purity and provider.

Compound	Purity	Provider
Sodium hydroxide, pellets (NaOH)	> 99% a.r.	Chem-Lab
Cetyltrimethylammonium bromide (CTAB)	≥ 98%	Sigma-Aldrich (Merck)
Carbon disulfide (CS_2)	> 99%	Sigma Aldrich (Merck)
Acenaphthene-d_{10}	99%	Sigma Aldrich
Nitric acid (HNO_3)	65% a.r.	Chem-Lab
Iron (III) chloride, anhydrous ($FeCl_3$)	> 98%	Chem-Lab
Calcium chloride, technical ($CaCl_2$)	94-98%	VWR chemicals

3.2 Sample description

A post-consumer polyethylene film bale was provided by a sorting site of SUEZ SA (Belgium). The polyethylene (PE) bales were manually sorted into 17 different fractions by Roosen et al. (2023) according to the intended content of the packaging. The authors used the BS EN 14899:2005 standard as a reference to define the types and quantities of samples and manage the sampling plan (Roosen et al. (2023) for more details). In total, 137.9 kg of flexible PE film bales was sorted in the respective categories (24.5 kg packaging used for food products and 113.4 kg packaging used for non-food products). An overview of the 17 categories and their respective mass percentage in the PE bale is given in Figure 10.

After sorting, each fraction of the PE bale was shredded with a Universal Cutting Mill PULVERISETTE 19 from FRITSCH using a sieve with square perforations with a diameter of 4 mm to obtain homogeneous samples. Prior to analysis, these plastic fractions were stored in sealed plastic bags in a freezer at -18°C. Some of the analyses were performed on the whole PE bale, so these fractions were combined and manually mixed after shredding using the mass fractions in Figure 10. In that way, uniform and more homogeneous samples were obtained.
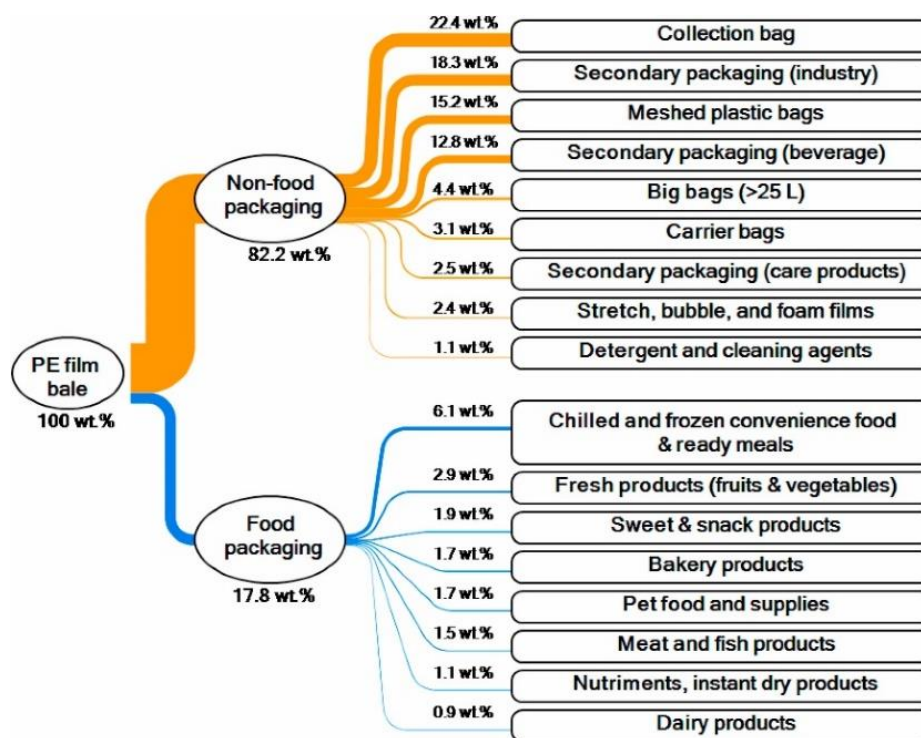
Figure 10: Composition of the PE bale divided in 17 categories with their respective weight percentages (Roosen et al., 2023).

3.3   Washing experiments

For the washing process, a sample of 3 g of the shredded PE-bale was weighed, transferred in an Erlenmeyer flask (glass, 250 mL) and 100 mL of washing medium was added. This solid/liquid (S/L) ratio was chosen based on Roosen et al. (2021) (section 2.3.1.2). The Erlenmeyer flask was covered with parafilm and the plastics and washing medium were mixed for 10 minutes using a rotary shaker (IKA magnetic stirrer Mini MR standard) at a rotation speed of 200 rpm, as experiments showed that higher rotation speed does not result in an increase in washing efficiencies (Roosen et al., 2021). Tap water of drinking quality, distilled water, NaOH in a water solution (2% w/w) and CTAB in a water solution (9.2 mM, corresponding to ten times the critical micelle concentration) were tested as washing media. After these 10 minutes, the plastics and washing medium were separated with a filtration step (Figure 11). Cabanes, Strangl, et al. (2020) and Roosen et al. (2021) used a similar methodology for their washing experiments. If multiple washing steps were performed, the filtered plastics were again added to an Erlenmeyer flask with fresh 100 mL washing medium and the washing cycle was repeated (1 in Figure 11). The water samples were analysed as described in section 3.4. In what follows, the washing water from wash 1 is called W1, in wash 2, W2 and so on. For further experiments, the wash water W1 and W2 were mixed to W1+2 after each experiment and stored in a cool, dark place. The same was done for W3. If the goal was to analyse the contamination on the plastics, the plastics were placed on a vacuum filtration unit and rinsed with distilled water to remove the remaining chemicals (Roosen et al., 2022). Afterwards, they were dried in a desiccator filled with $CaCl_2$ for 72 hours (2 in Figure 11). The analyses were performed as described in section 3.5.
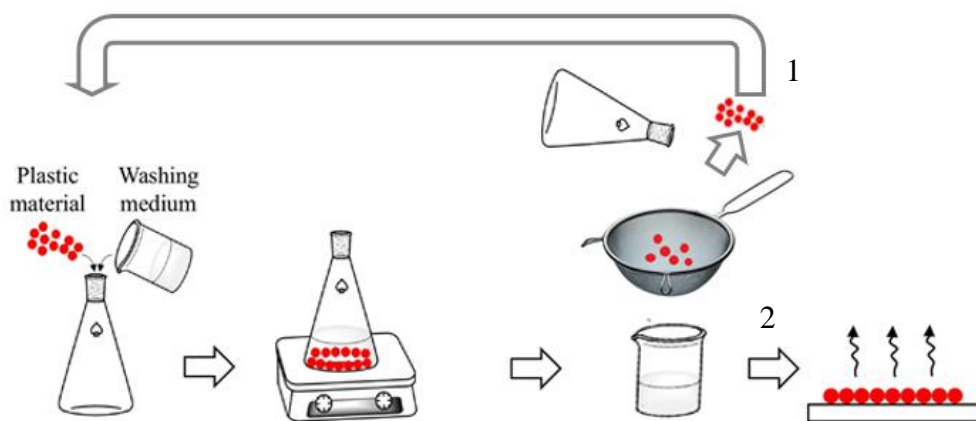
Figure 11: Schematical methodology of the washing procedure, based on Roosen et al. (2021).

3.4   Characterization of the contamination load on the plastic

To characterize the total amount of contamination present on the plastics, these plastics were washed five consecutive times as described in section 3.3, followed by the analysis of the five water samples. For each water sample, the following parameters were measured using Hach Lange cuvette test kits and Hach's UV-VIS spectrophotometer (DR6000): COD (LCK114, LCK314 and LCK1414), TN (LCK238 LATON and LCK138 LATON), and TP (LCK348). TSS and VSS were gravimetrically determined according to the Standard Methods for the Examination of Waste Water (Baird et al., 2017). VWR 698 glass fibre filters with pore size 0.7 µm were used. After these measurements, a mass concentration was obtained for every parameter. The waste load on the plastics in g/kg plastic was calculated from these values using equation 2.

$$q \ = \ \sum_{i=1}^{n} \frac{C * V}{m_{pl}} \tag{2}$$

With:

q =   relative concentration of contamination on the plastics (g contaminant.kg plastic^{-1})
C =   the relative concentration of contamination in the liquid phase (g adsorbate.L^{-1})
V =   the volume of the liquid phase (L)
m_{pl} =   the mass of plastics (kg)
n =   number of washing steps

Turbidity was quantified according to Standard Methods for the Examination of Wastewater with the Hanna instruments HI 98703 turbidimeter and expressed in nephelometric turbidity units (NTU) (Baird et al., 2017). Before every use, the turbidimeter was calibrated with standards at <0.10, 15, 100 and 750 NTU. Electrical conductivity (EC) and pH of the water samples were measured with the Hach HQ series multimeter (Baird et al., 2017). These measurements were calibrated using a one-point calibration (1000 µS/cm) and a three-point calibration (pH 4, 7 and 10), respectively.

Heavy metals (Na, Ni, Fe, Ca, Mg, Zn, Cu, Al, Cd, Cr, Mn, Pb, Sr) present in the water samples were analysed by ICP-OES. A calibration standard series (ranging from 0 – 10 ppm) was prepared from a 65% HNO_3 solution diluted with double-distilled water until a concentration of 5% HNO_3 was achieved. The water samples were also acidified to 5% HNO_3 to ensure matrix match. Afterwards, the samples were filtered with a 0.45 µm syringe PP filter (CHROMAFIL). Three wavelengths per element were observed and three repetitions were performed. The analyses were performed on a Thermo Scientific iCAP 7000 series model, equipped with a CETAC ASX 560 autosampler, a Thermo Scientific ThermoFlex 900 recirculating chiller and Qtegra Software. The operational parameters are shown in Table S1.

The PE bale used consisted of several fractions (section 3.2). In order to determine which fraction contributed most to the contamination of the whole PE bale, the fractions were also separately characterized. This was also done by washing them five consecutive times using the method described in section 3.3. Table 10 gives an overview of the characterization parameters tested per sample.

Table 10: Overview of characterization parameters tested per sample.

	COD	TN	TP	TSS/ VSS	ICP-OES	EC	pH	Turb-idity	GC-MS
PE bale	x	x	x	x	x	x	x	x	x[1]
Non-food	x	x	x	x		x	x	x	x[1]
Food	x	x	x	x		x	x	x	x[1]
Collection bags	x	x	x	x		x	x	x	x[1]
Secondary packaging (industry)	x	x	x	x		x	x	x	x[1]
Detergent and cleaning agents	x	x	x	x		x	x	x	x[1]
Chilled and frozen convenience food and ready meals	x	x	x	x		x	x	x	x[1]
Fresh products	x	x	x	x		x	x	x	x[1]

[1]Performed by Roosen et al. (2023)

3.5 VOC characterization

After the washing procedure and the filtration, a water sample and a plastic sample are obtained (section 3.3). Volatile organic compound (VOC) measurements can be performed on both samples. VOCs present on the plastics were analysed by GC-MS using different sampling techniques such as headspace solid-phase micro-extraction (HS-SPME) or solvent desorption (SD). These VOCs were either measured by ourselves or taken from Roosen et al. (2023), as their analysis were performed on the same PE bale. This will always be clearly stated in the Results & Discussion section. The VOCs present in the water were analysed by using a gas washing bottle with fritted disc as sampling technique.

3.5.1 VOC-analysis on the plastics

3.5.1.1 Headspace-solid phase microextraction GC-MS

The VOC analysis on the plastics was based on a method developed by Demets et al. (2020). First, a screening was performed on the PE bale input material using HS-SPME-GC-MS, as depicted in Figure 12 (left). Prior to sampling the fibre was conditioned at 300°C to desorb any remaining VOCs. Blank tests were performed to exclude carry-over. The plastic material was transferred to a 40 mL vial until it was filled for a fourth. The vial was previously washed with acetone and dried at 105°C to avoid contamination. The vial was sealed with a Mininert valve and was placed in a thermal bath at 65°C to release the VOCs from the plastics. A 75 µm carboxen/polydimethylsiloxane (CAR/PDMS) fiber (Supelco, Sigma-Aldrich) was then introduced in the headspace of the vial for 60 min to adsorb the VOCs. Next, the loaded fiber was placed in the inlet of the GC apparatus. Detailed description of the analysis procedure is described in section 3.5.3, based on Demets et al. (2020).

3.5.1.2 Purge and trap followed by solvent desorption GC-MS

The VOC present on the washed plastics were analysed using purge and trap followed by SD-GC-MS, also following the method from Demets et al. (2020) (Figure 12 right). For this semi-quantitative analysis, 2 g of plastic material was transferred to a 40 mL sealed vial that was again previously washed with acetone and dried at 105°C. The vial was placed in a thermal bath at 65°C and flushed with pressurized air at a constant flow rate of 0.4 L/min for 35 minutes. An Activated Charcoal Tube Type NIOSH (Dräger) was used to adsorb the VOCs that were flushed from the plastics. The AC tubes have a 100 mg adsorption layer of coconut shell charcoal and a 50 mg backup layer (Demets et al., 2020). When no further analysis was done immediately, the vials were wrapped in aluminium paper and placed in a dark environment at 4°C. Afterwards, the activated charcoal was transferred from the tube into a 1.5 mL microvial and 1.5 mL of CS_2 spiked with 50 ppm internal standard (acenaphthene-d_{10}) was added to desorb the VOCs. The vials were shaken to allow good desorption, sealed with screw caps and stored overnight in a dark environment at 4°C. Thereafter, 1 mL of the solution was transferred to a new vial and sealed with another cap. Finally, 1 µL of CS_2 was injected in the inlet of the GC device. The analysis procedure from these samples is described in detail in section 3.5.4.
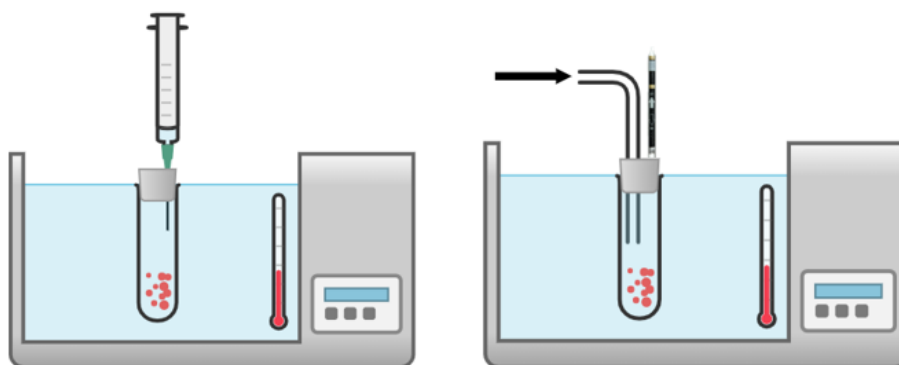

Figure 12: Sampling techniques: SPME sampling (left); Activated charcoal sampling and solvent desorption (right).

3.5.2 VOC-analysis in water

A gas washing bottle with fritted disc (porosity grade 0) was used to see whether VOCs can also be measured in water. The water sample was added to the bottle and flushed with pressurized air at a constant flow rate. This created gas bubbles in the water sample which released the VOCs from the sample. These VOCs were then adsorbed on an Activated Charcoal Tube Type NIOSH (Dräger), as illustrated in Figure 13. The activated charcoal was then transferred to a vial as described in section 3.5.1. Some preliminary tests were performed on the flow rate and duration: 40 mL/min for 60 mins, 150 mL/min for 15 mins, 150 mL/min for 30 mins and 100 mL for 30 mins.

Figure 13: Sampling technique: VOC measurement in water using a washing bottle.

3.5.3   Analytical procedure HS-SPME-GC-MS

The SPME sampling method was used to identify the VOCs present on the PE bale. An Agilent 6890 GC coupled to a Hewlett Packard 5973 mass-selective detector was used to perform the VOC measurements. Separation of the compounds took place in a cross-linked (5% phenyl)-methylpolysiloxane column (30 m x 0.25 mm, 0.25 µm). For the SPME fiber, an unpacked liner with straight design (direct type; Supelco (Merck)) was used. The temperature of the injection port was set at 300°C. The column oven temperature was initially set at 50°C and kept for 1 minute, next it was increased to 175°C at 5°C/min, which was kept for 1 minute, followed by an increase to 325°C at 25°C/min. The compounds were separated using helium as a carrier gas at an average velocity of 17 cm/sec. After separation, the compounds were identified on the MS, using the National Institute of Standards and Technology (NIST) mass spectral library.

3.5.4   Analytical procedure SD-GC-MS

When measuring the solvent desorbed samples from the plastic and water samples, 1 µL of CS_2 was injected using the automatic injector 7683 (splitless, 3mL/min), through a wool packed liner with straight design was applied (Split/Splitless type; Supelco (Merck)). As CS_2 was used as a solvent, a solvent delay was set at 4 minutes. The column and program were applied as in section 3.5.3. The measurements were done in Scan and Selective Ion Mode (SIM) for a semi-quantitative analysis. The components and their respective ions were selected based on the outcomes of the SPME analysis. The output signals were processed using Agilent MSD Chemstation software.

3.6   Kinetics of the contamination removal

To analyse the washing process kinetics, again 3 g plastic was washed in 100 mL water, following the procedure outlined in section 3.3, but with varying duration. This enables the determination of the optimal washing time and the speed at which the removal efficiency is reached. The plastics were washed for 1 min, 3 min, 5 mins, 7 mins, 10 mins and 15 mins, respectively. The obtained water samples were then analysed as described in section 3.4 on COD, TN, TP, TSS/VSS and turbidity. This procedure was performed once with tap water and once with W1+2.

To correctly establish the kinetics, the equilibrium concentration of COD, TN and TP in water was also determined, meaning the concentration in the water at which no further contaminant removal was observed. Therefore, 3 g plastic was washed in 100 mL water, in the same way as described in section 3.3. However, after the 10-minute washing cycle and the separation of the plastics and the water, the water was analysed. The washing cycle was repeated with the same water sample and a new 3 g plastic sample. To make up for water losses and the uptake of some water by the plastics, some water was added after every cycle to always have 100mL medium. This was repeated for 15 times.

3.7   Wastewater treatment

3.7.1   Coagulation

Ferric chloride was chosen as coagulant as this is often used in scientific literature and industry. To optimize the coagulant dose in the treatment process for this application, a series of standard jar tests were performed at room temperature. Based on literature (section 2.4.1), it was chosen to prepare a 1.2 g/L $FeCl_3$-solution (corresponding to 2.5 g/L $FeCl_3·6H_2O$) using tap water. A known volume of this solution was added to a jar containing 100 mL wastewater (a mixture of water samples after one and two washes), beginning at 500 µL with increments of 500 µL, while mixing at a speed of 120 rpm in the VELP Scientifica FC 6S flocculation stirrer. The volume after which the first flocs were noticed was written down. In the next step, coagulant doses between 0 and 2 times the determined volume were added to the water. Based on these tests, jar tests were first conducted at coagulant doses between 3 mL and 7 mL of a 2.5 g/ L $FeCl_3$-solution, with increments of 1 mL at mixing speeds described in the next paragraph. Based on these results, there was chosen to perform new jar tests at coagulant doses between 5 mL and 13 mL of this $FeCl_3$-solution. In order to find the optimum dose, the COD, TN, TP and VOC removal were determined, as well as the pH, EC and turbidity.

Based on scientific literature (Amuda & Amoo, 2007; Aziz et al., 2007; Liang et al., 2010; Song et al., 2004; Zouboulis & Tzoupanos, 2010), it was chosen to perform rapid mixing for 2 mins at 300 rpm (which is the maximum mixing rate of the apparatus) during coagulation, slow mixing at 60 rpm for 15 mins during flocculation, followed by 1 hour of settling. After settling, the supernatant and settled particles were separated using a Buchner filter with VWR qualitative filter paper 413 with pore size 20 to 45 µm. The water sample was then analysed on COD, TN, TP and VOC content to verify the coagulation performance. pH, EC and turbidity were also measured.

3.7.2   Activated carbon adsorption

Granular activated carbon (GAC) was used for adsorption. Prior to use, it underwent a pre-treatment procedure where it was washed with a generous amount of demineralised water until the wash water became relatively clear. Afterwards, it was dried overnight in an oven at 105°C and placed in a desiccator until use. 40 g GAC was put into a 100 mL column and was activated with 100 mL demineralized water. Two tests were performed: one where 100 mL of the wastewater (this time the water sample after washing step 3) was sent over the column once, and another where it was sent over the column twice. The performance of this purification test was verified by determining the COD, TN, TP and VOC removal. pH, EC and turbidity were also measured.

3.7.3   Membrane filtration

After coagulation, the supernatant can be purified using GAC but also using a membrane filtration step. Therefore, 50 mL of the supernatant is sent over a cellulose acetate membrane (Porafil, Macherey-Nagel) with a pore size of 0.45 mm, under vacuum (Vacuubrand MZ 2C). Again, after the filtration step, COD, TN, TP and VOC removal and pH, EC and turbidity were measured.

3.8 Modelling in Aspen Plus

3.8.1 Kinetics

The washing process was modelled and simulations were performed using Aspen Plus version 14. Removal kinetics of COD, TN, TP and VOC were calculated via equation 3, which consists of two terms: contaminant desorption from the plastics to the water and re-adsorption from the water to the plastics. This is based on De Somer et al. (2022), as mentioned in the literature review (section 2.3.3).

$$\frac{dq}{dt} = -k_{desorption} * q + k_{adsorption} * \left((q0 - q) * \frac{m}{V} + C_{ini,H_2O} \right) \qquad (3)$$

With:

$q =$ Relative concentration of adsorbate on the adsorbent (mg adsorbate.kg adsorbent^{-1})

$C =$ Relative concentration of adsorbate in the liquid phase (mg adsorbate.L^{-1})

$k_{desorption} =$ Desorption rate constant (s^{-1})

$k_{adsorption} =$ Adsorption rate constant (L.kg^{-1}.s^{-1})

$q_0 =$ Relative concentration of adsorbate on the adsorbent at the beginning (mg adsorbate. kg adsorbent^{-1})

$m =$ Mass of the adsorbent (kg)

$V =$ Volume of the liquid phase (L)

$C_{ini,H2O} =$ Relative concentration of the adsorbate in the liquid phase at the beginning (mg adsorbate. L^{-1})

The two parameters, $k_{desorption}$ and $k_{adsorption}$, were calibrated by minimizing the sum of squared errors (SSE) between the modelled (q_{model}) and experimental values (q) (equation 4). To this end, the Solver function in Microsoft Excel was used, using the Solver function GRG Nonlinear (Generalized reduced gradient). The SSE was calculated for three data sets: (1) the kinetic test in tap water, (2) the kinetic test in wastewater (W1+2) and (3) the equilibrium test (section 3.6). In that way, the model parameters consider the removal in clean water, dirty water and the equilibrium concentration obtained for the PE bale.

$$SSE = \sum_{i=1}^{n} ((q - q_{model})^2)_i \qquad (4)$$

With:

$n =$ Number of experimental values

$q =$ Experimental relative concentration of adsorbate on the adsorbent (mg adsorbate.kg adsorbent^{-1})

$q_{model} =$ Modelled relative concentration of adsorbate on the adsorbent (mg adsorbate.kg adsorbent^{-1})

3.8.2 Stoichiometry

Model stoichiometry exists of a one on one shift between water and plastic (equation 5). The same stoichiometry was applied for COD, TN and TP. The VOCs were subdivided into the five categories mentioned in Table 2. For further model development, reference is made to section 4.4.

$$C_{plastic} \leftrightarrow C_{water} \qquad (5)$$

With:

$C_{plastic} =$ Concentration of the contaminant on the plastic (g contaminant.kg plastic^{-1})

$C_{water} =$ Concentration of the contaminant in the water (mg contaminant.L^{-1})

CHAPTER 4

4. Results & Discussion

4.1 Characterization of the polyethylene (PE) bale

The following sections provide a comprehensive overview of the contaminants (COD, TN, TP, TSS, VSS, VOC, metals) found on the PE bale along with their respective concentration levels.

4.1.1 Chemical contaminants (COD, TN, TP, TSS, VSS)

COD, TN, TP, TSS and VSS were measured in duplicate as described in section 3.4. Figure 14 indicates the contaminant load on the PE bale in g contaminant per kg plastics. The total load is calculated by the summation of the contaminant concentrations in the washing water of five consecutive wash steps. To convert the concentration in the water to concentration on the plastics, equation 2 is used (section 3.4). The total COD, TN and TP load is 51.10 ± 1.98 g/kg, 1.32 ± 0.11 g/kg and 0.17 ± 0.02 g/kg plastic, respectively. TSS is present on the plastics in a concentration of 38.19 ± 2.10 g/kg. On average, 81% of these TSS are VSS. For each water sample, pH and EC were also measured. The pH range was 8.46 ± 0.15, the electrical conductivity (EC) 843 ± 112 µS/cm. The pH and EC of tap water were 7.81 and 864 µS/cm, respectively. The EC is higher after washing due to the presence of inorganic dissolved solids such as metals and minerals. The pH increase might be explained by the leaching out of additives from the plastic waste when washing them, such as, for instance, $CaCO_3$ that is often used as filler material (Hesabi et al., 2021; Novotna et al., 2023).
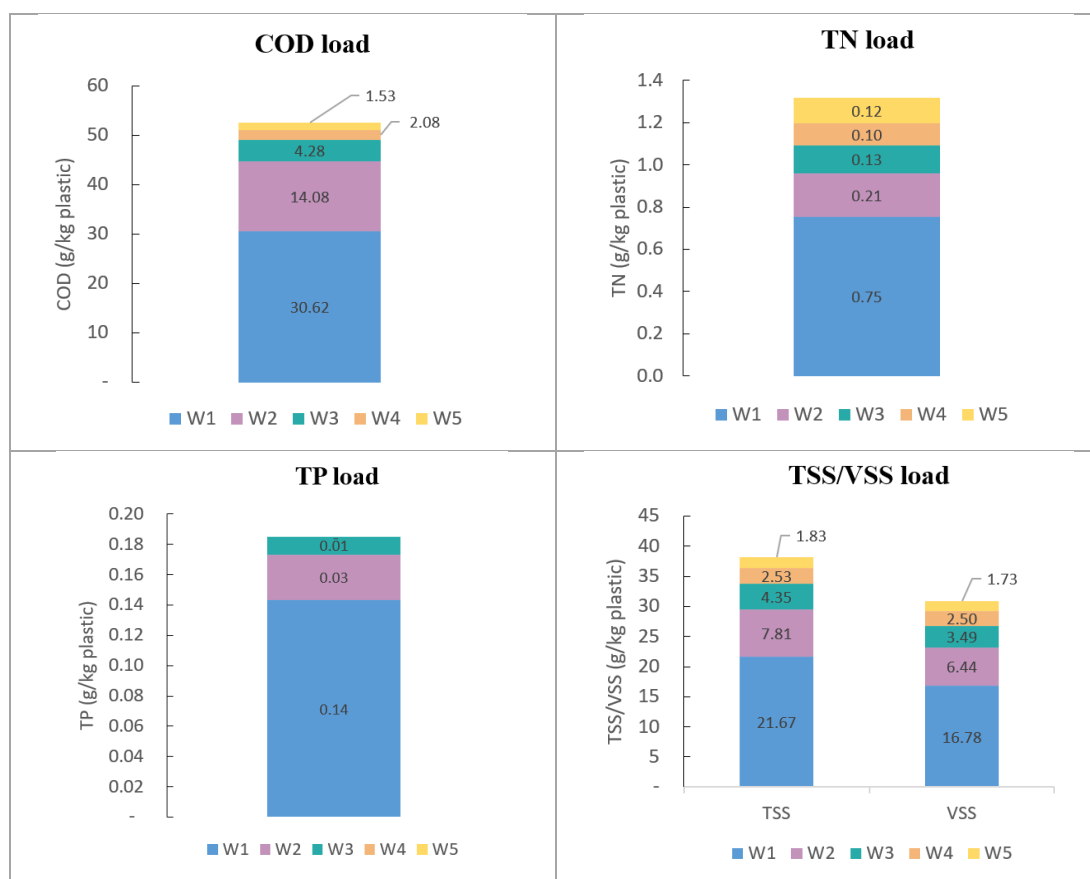

Figure 14: Characterization of PE bale contaminant load (g/kg plastic) (n = 2), W1 = after one washing step.

When the results are compared with the concentrations in Table 5 of the literature review, our concentrations most closely resemble those of the PE film from Soto et al. (2020). An explanation may be that both samples are PE films originating from post-consumer waste. Generally, variation in experimental conditions, such as the washing techniques can lead to differences in the results. Even though Bordonalli & Mendes (2009) and Calero et al. (2018) also analysed post-consumer PE waste, their plastics were much less polluted. This could mean that our PE bale is a rather contaminated bale and clearly shows the typical heterogeneity of plastic waste, as already mentioned in section 2.1. The LDPE from Altieri et al. (2021) came from the agro-industrial sector, so that can explain its lower concentrations compared to our plastics.

4.1.2   Heavy metals

Besides these chemical contaminants, there are also metals present on the PE bale. Elemental analysis was performed in the washing water to know which metals come off during washing. Once tap water was used and once distilled water, in duplicates. Na, Ni, Fe, Ca, Mg, Zn, Cu, Al, Cd, Cr, Mn, Pb and Sr concentrations were measured. Since some of these metals are also present in tap water, the difference between both media is looked at to obtain the concentration of metals that were present on the PE bale. Only heavy metals Fe, Al and Zn and the minerals Na, Mg and Ca will be discussed, because the other metals could not be detected on the ICP-OES (<LOD, Table S2). These are, among others (NH_4^+, NO_3^-, PO_4^{3-}), elements that could be responsible for the higher EC value in the water after washing. For the heavy metals, there was no difference in concentration between tap water and distilled water. In total, concentrations of 0.122 ± 0.012 g Fe/kg, 0.041 ± 0.011 g Al/kg and 0.057 ± 0.012 g Zn/kg plastic were observed (Figure 15).
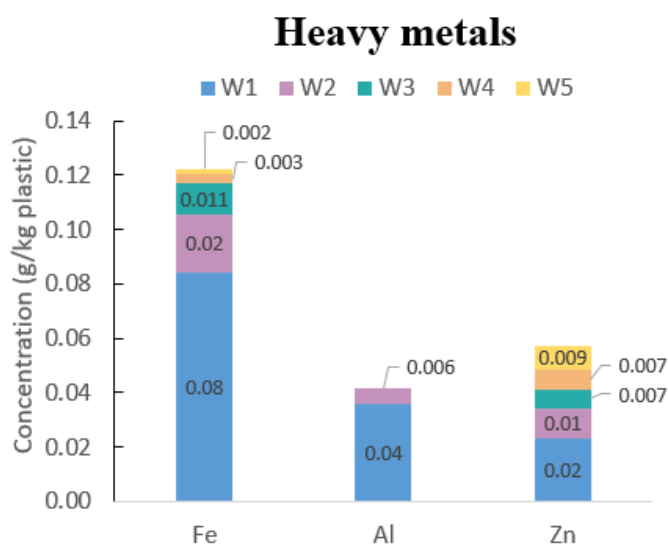

Figure 15: Heavy metals (Fe, Al, Zn) concentration on the PE bale (g/kg plastic) (n = 2), W1 = after one washing step.

The concentration of the elements Na, Mg and Ca varied clearly between tap and distilled water. To confirm that this difference was due to the presence of these minerals in tap water, the concentration in distilled water was subtracted from that in tap water. For the five washing water samples, this resulted in a value that was fairly constant. Therefore, the metal concentrations in distilled water were used to calculate the concentration on the plastics. Concentrations of 1.080 ± 0.003 g Na/kg, 0.071 ± 0.001 g Mg/kg and 2.875 ± 0.010 g Ca/kg plastic were observed (Figure 16). They are more abundant than the heavy metals. The relatively higher presence of Ca might again be explained by the leaching of $CaCO_3$, as mentioned in section 4.1.1, however this hypothesis should be proven. Given the low concentrations of the detected elements, they are not considered as a problem in the washing process, since this is also not the scope of this work.
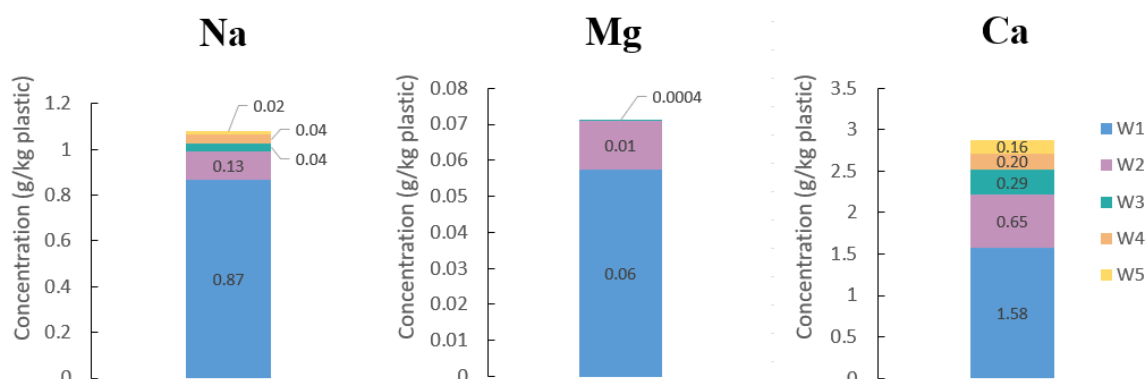
Figure 16: Minerals (Na, Mg, Ca) concentration on the PE bale (g/kg plastic) (n = 2), W1 = after one washing step.

4.1.3 Volatile organic compounds (VOCs)

Roosen et al. (2023) measured the VOC concentrations on the same PE bale and its subfractions by means of headspace solid-phase micro-extraction GC-MS and using their results, the graph in Figure 17 was constructed. They selected 21 compounds coming substance classes with various polarities, molecular weights and volatilities from different chemical groups, obtaining a physicochemical relevant and diverse group of compounds. The VOCs were classified into the same five categories as Table 2 (section 2.2.1): carboxylic acids, aromatic components, oxygenated components, terpenes and hydrocarbons. Since some VOCs had multiple functional groups, it was decided that if the VOC was a terpene, it was categorized in this group. If the VOC was not a terpene but had a carboxylic acid group, it categorized as carboxylic acids. When a VOC had no carboxylic acid group and was not a terpene, but was aromatic, it belonged to the aromatic compounds. When the VOC had none of the above functions, but did have an oxygen atom in its structure, it was placed with oxygenated compounds. Most of the VOCs present on the bale are aromatic compounds, oxygenated compounds and terpenes. The hydrocarbons and carboxylic acids are present in lower concentrations. Nevertheless, this does not mean that the latter will necessarily contribute less to the smell, as their odour threshold value (in air) is very low (Table 2). For example, the concentration of carboxylic acids on the PE bale is 435 µg/kg and their threshold value is in the range of 0.2-4.1 µg/L air. In the context of obtaining odour-free secondary materials, it is important to elucidate if the process is sufficiently effective to reduce the respective odorant concentrations to below their odour threshold levels. Literature data on the odour thresholds of the selected substances in a PE polymer matrix are currently unavailable. Strangl et al. (2019) indicated that the odour threshold is not only strongly dependent on the vapor pressure of the substance (depending on temperature and matrix), but also on its partition coefficient as well as on the interactions with the matrix molecules. Hence, it becomes imperative to determine the odour thresholds in the PE matrix to ensure a clear and unambiguous interpretation of the odour quality of the produced secondary materials. Thus, it is not necessarily needed that all VOCs must be removed from the plastics to obtain virgin-like quality in terms of odour. Moreover, also virgin plastic already contains some VOCs (Figure 2; section 2.2.1). These are mainly hydrocarbons, aromatics and some oxygen-containing components (Cabanes, Valdés, et al., 2020).
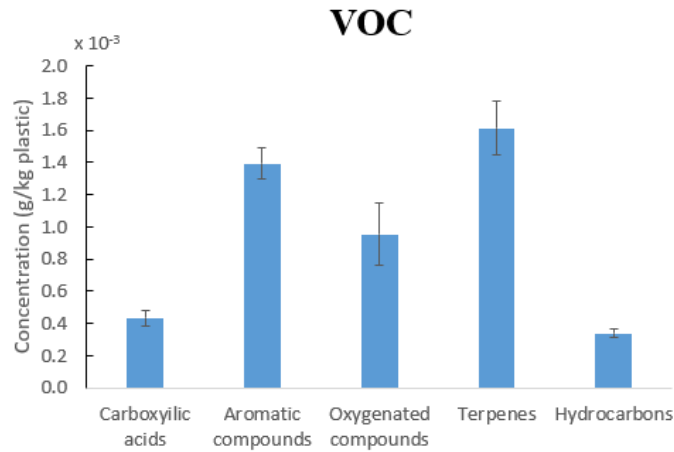
Figure 17: VOCs present on the PE bale (g/kg plastic), from Roosen et al. (2023) (n = 3).

4.1.4 Fractions

As already mentioned in section 3.2, the PE bale can be divided into different fractions. A first subdivision is food versus non-food. In general, the non-food fraction is slightly more responsible for the contamination of the PE bale (Figure 18). This is somewhat counterintuitive, as one would think that plastic that has been in contact with food would be more contaminated. However, it must be taken into account that on a mass basis the collection bags form a large part of the non-food fraction (Figure 10) and that food packaging is also collected in these bags, which could lead to cross-contamination. It should also be noted that the difference between the two fractions is small, so it is not exactly one of the two fractions that is responsible for the contamination load of the whole bale. The EC and pH of the washing water for the food and non-food fraction were 884.2 ± 62.6 and 886.4 ± 42.3 µS/cm, and 8.48 ± 0.02 and 8.43 ± 0.04, respectively.
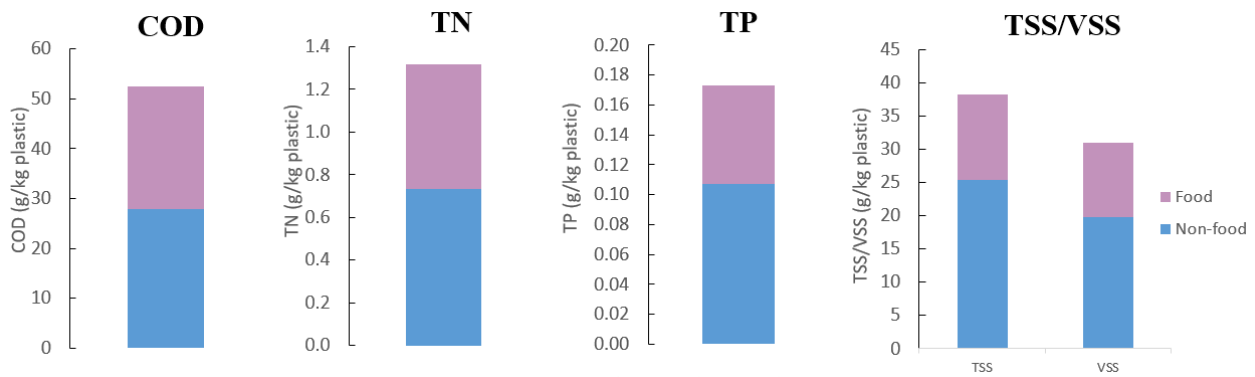

Figure 18: Characterization of PE bale fractions food and non-food contaminant load (g/kg plastic) (n=1).

Roosen et al. (2023) also measured the VOC concentrations of the different fractions. They selected compounds that were quantified across the 17 subfractions. Figure 19 was obtained based on their work, according to the same VOC classes as those mentioned in section 4.1.3. It is important to mention that VOC concentrations are a factor thousand smaller than the other contaminations. It can be deduced from the graph that, in general, the VOC concentration on the food fraction is higher than on the non-food fraction. Not only the concentration but also the number of VOCs is higher (Roosen et al., 2023). Especially the aromatic compounds and terpenes are present in significantly higher concentration. As both groups have low odour threshold values (Table 2), this is, in contrast to the COD concentration, in line with expectations. The food residues on the packaging can spoil and cause a strong smell. Brinkmann et al. (2016) measure VOC as total carbon and Alvarez et al. (2020) used the COD concentration in water as a surrogate measurement for VOC concentration in water.

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Comparing Figure 18 and Figure 19 shows that this is not the case for the concentration of COD and VOC on the plastics. It is likely that there is a link between COD and VOC, but a clear difference should be made between the plastic and the water phase. The COD that is removed may corresponds to VOCs that are removed, but the recalcitrant VOCs remain on the plastics and are not removed with the COD, which can be an explanation why the trends in removal do not match. These recalcitrant VOCs can be the ones that are deeply adsorbed in the matrix, or the ones that experience diffusion limitations due to high molecular weights, polarity differences with the polymer matrix and/or due to lower volatility. The VVOCs may also have already volatilized from the plastic before they were washed. Moreover, a one-on-one relation between a number of VOCs and COD is probably not correct since not all organic components are volatile.
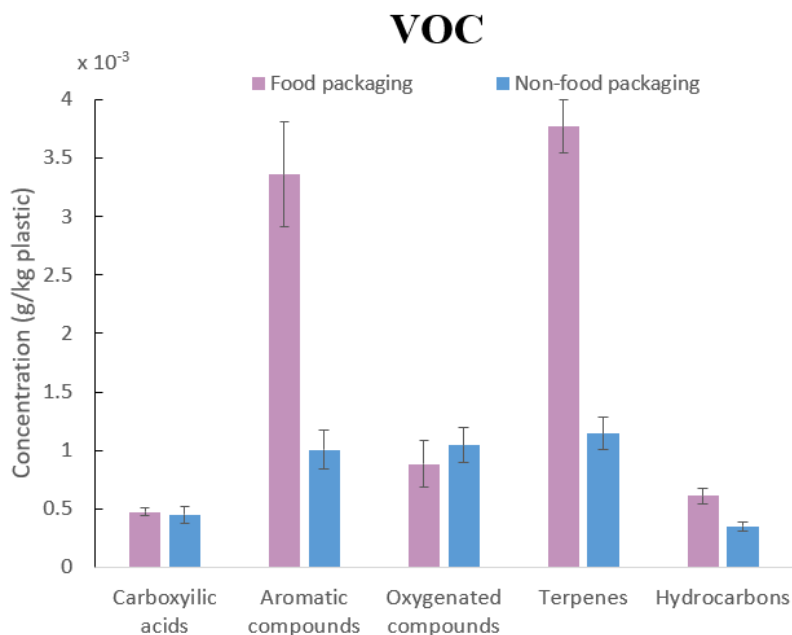

Figure 19: VOCs present on the PE bale fractions food and non-food (g/kg plastic), from Roosen et al. (2023) (n=3).

Five of the 17 fractions were analysed separately. The fractions with the highest mass fractions in the PE bale (Figure 10) and the highest VOC load (Roosen et al., 2023) were selected. From the non-food fraction, collection bags, secondary packaging (industry), and detergent and cleaning agents were chosen. From the food fraction, chilled and frozen convenience food and ready meals, and fresh products. The contamination on these fractions and the EC and pH range in the water samples after washing are summarized in Table 11. The collection bags clearly have the highest chemical contamination. This confirms what was assumed previously: this fraction will make a major contribution to the contamination of the non-food fraction. Secondary packaging from industry is the least contaminated, together with the detergent fraction. The washing water has a comparable EC and pH range for all fractions. Figure 20 presents the VOC concentration on the different fractions, again of a factor thousand lower than COD, TN or TP, measured by Roosen et al. (2023). It is clear from the graph that the highest VOC concentrations are present on the fresh products fraction, which is in line with expectations. As mentioned, the food residues left on the packaging can give off strong odours. The secondary packaging from industry shows both a low COD and VOC concentration, which can be expected since packaging from industry is often less contaminated (Figure 2; section 2.2.1). Detergents have high VOC values, which was expected. It can be noted again that the VOC concentration on the plastics is not in line with the COD concentration. Sometimes they show the same trend and sometimes not. Where the COD concentration of the collection bags is almost double than that of the fresh products, this is not the case for the VOC concentration. It can be concluded that based on the type of plastic and even on the application of the plastic, the input will have a

different composition and this will also have an influence on the washing process. Depending on the input stream, there will be more or less saturation of the washing water. Thus, it will be an important factor in the purification and recirculating rate of the washing water.

Table 11: Contamination on the different fractions of the PE bale (g/kg plastic).

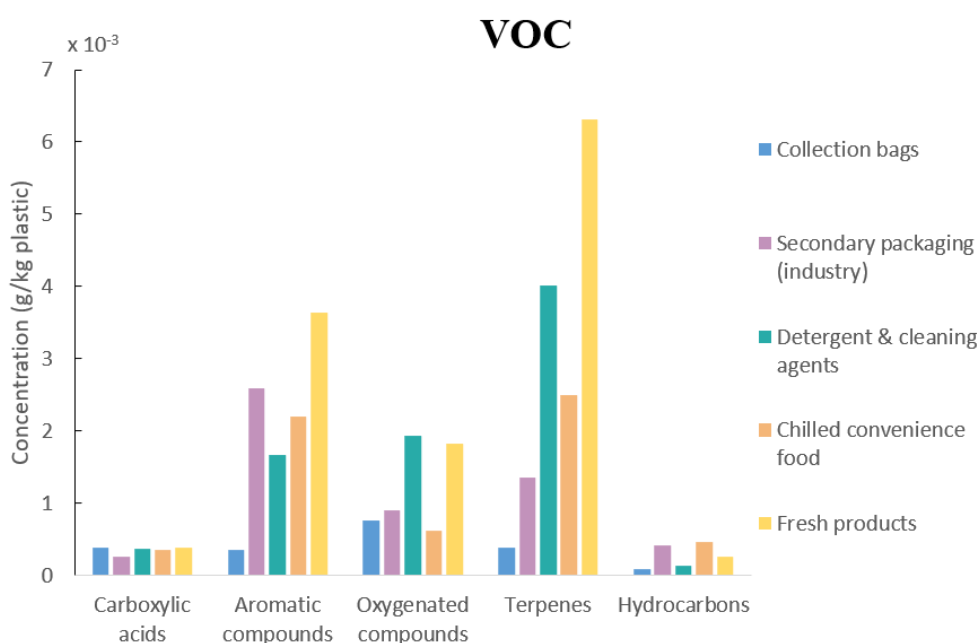| Fraction	COD (g/kg)	TN (g/kg)	TP (g/kg)	TSS (g/kg)	VSS (g/kg)	EC (µS/cm)	pH
Collection bags	85.9	2.33	0.53	53.6	43.7	982 ± 158	8.39 ± 0.04
Secondary packaging (industry)	32.0	1.11	0.07	12.0	10.6	923 ± 32	8.33 ± 0.09
Detergent & cleaning agents	40.0	0.97	0.05	17.1	15.4	897 ± 39	8.25 ± 0.04
Fresh products	51.2	1.46	0.16	30.8	25.9	889 ± 102	8.34 ± 0.04
Chilled and frozen convenience food & ready meals	45.1	1.31	0.13	25.0	23.1	880 ± 22	8.41 ± 0.10

Figure 20: VOCs present on the PE bale fractions (g/kg plastic), from Roosen et al. (2023) (n=3).

4.2   Washing process

4.2.1   Washing with water

After shredding, 3 g of plastics was washed with five times 100 ml tap water. The water samples were collected and analysed. In the Supplementary Materials (Figure S1), a picture of what these five samples look like is shown. Figure 21 shows the concentrations of the contaminants in the water. The washing water from step 1 is represented in this figure as W1. With each washing cycle, fewer contaminants are removed from the plastics. The same trend was observed for TSS and VSS. However, TN shows a slightly different behaviour, where about the same amount is removed in W3, W4 and W5. In W4 and W5 no TP could be measured anymore (< LOD: 0.5 mg PO_4-P/L). It is clear that two washing steps are not sufficient to remove these components. A third washing step will certainly be necessary. A fourth or fifth wash step does not remove much more so therefore three wash steps are recommended. This is also visually confirmed. Where in W1 and W2 the turbidity is 617 and 150 NTU, respectively, in W3 this is only 87 NTU. W4 and W5 show lower turbidity values (48 and 32 NTU, respectively) but this decrease is not as pronounced as before.
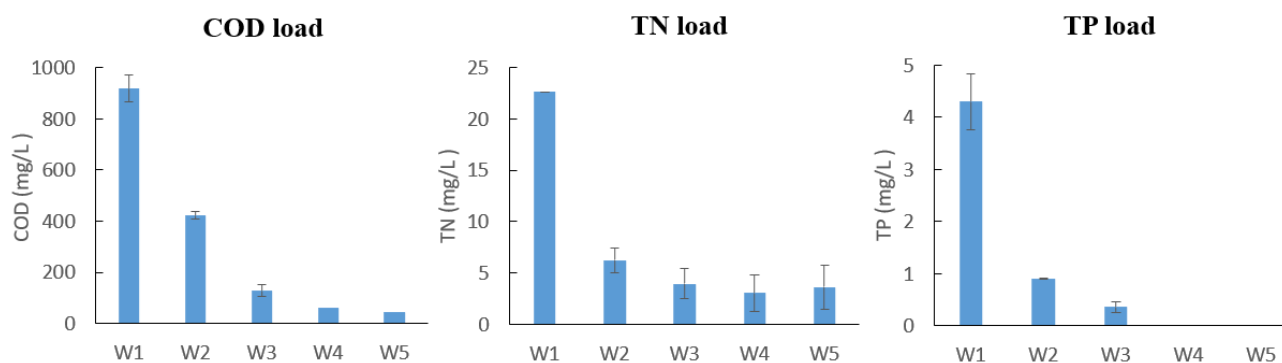
Figure 21: COD, TN and TP released in the washing water (mg/L) (n=2). W1 = wastewater from wash step one.

At each washing step, a sample of the washed plastic film was kept after filtration to measure the concentration of VOC. This was done semi-quantitatively using SD-GC-MS. Figure 22 shows the intensity of the main VOC groups. After one wash with water, a large part of the VOCs was already removed from the plastics, mainly the aromatics. It can be noted that oxygenated compounds, carboxylic acids and hydrocarbons decrease in intensity less than the other groups. When looking at the odour, this is especially a problem for the first two as they can cause unpleasant fatty or cheesy odours (section 2.2.1). The third wash step is necessary as it provides more removal of the VOCs in case of the carboxylic acids, aromatics and terpenes. This figure also shows once again that more than three washing steps is unnecessary.
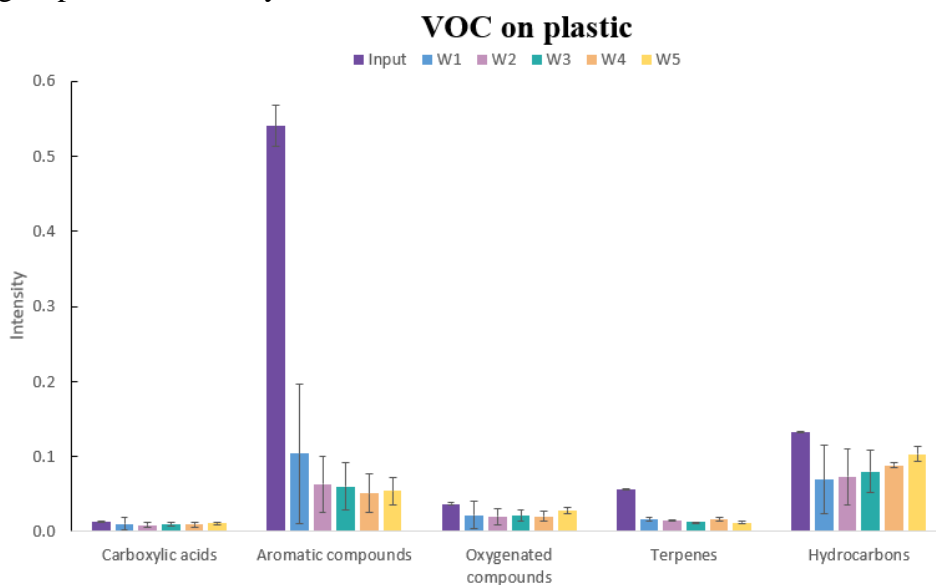
Figure 22: Intensity of VOC groups on the plastics after washing, measured by SD-GC-MS (n=2), W1 = after one washing step.

VOCs can also be measured using a gas washing bottle with fritted disc. A plastic sample (3g) was washed once in tap water (100 mL) and then the water was placed in the gas washing bottle and flushed with pressurized air. Experiments were carried out to know at what flow rate and for what time the best results would be obtained with the gas scrubber in terms of VOC measurements. This was done for the four options (Table 12). The VOCs were measured on GC-MS. These correspond to the VOCs that have been washed off the plastic after one washing step. This therefore corresponds to the difference of the VOC load on the input (PE bale) and the plastic after one washing step. Table 12 gives the VOC measurements at the input and after one wash per group and their difference, together with the measurements with the gas washing bottle. From this it could be concluded that flushing air for 150 mL/min for 30 minutes gave the best agreement in general. Previously, VOCs were mainly measure on plastic via SD-GC-MS. This can be a way to measure VOC in the water,

which can be interesting when measuring for example VOC removal from water in the water purification steps. However, more tests will need to be performed to confirm this hypothesis.

Table 12: Intensities VOC measurements gas washing bottle by GC-MS, W1 = after one washing step.
VOC 40-60 = 40 mL/min for 60 mins.

Functional group	Input	W1	Input –W1	VOC1 40-60	VOC2 150-15	VOC3 150-30	VOC4 100-30
Carboxylic acids	0.0131	0.0103	0.0028	0.0011	0.0020	0.0016	0.0019
Aromatic compounds	0.5402	0.1038	0.4364	0.0710	0.1403	0.1897	0.1371
Oxygenated compounds	0.0373	0.0223	0.0150	-	-	-	0.0013
Terpenes	0.0571	0.0162	0.0409	0.0127	0.0287	0.0217	0.0155
Hydrocarbons	0.1328	0.0692	0.0636	-	-	0.0018	0.0070

After each washing step, plastics and water were separated by filtration. It was noticed that there was always some water left on the plastics. The plastics were weighed before and after washing and this was done ten times. It could be deduced that 2.7 ± 0.2 kg of water per kg of film remains behind, which corresponds to 73% of the total mass. This will become important when water is reused, as it implies that some water will have to be added to maintain the same volume in every wash. The high water uptake is confirmed by Horodytska et al. (2018), who stated that this is because of the high surface area and tortuosity of the films. It should be noted that effective drying is needed before extrusion and this dewatering process will therefore be highly energy-consuming (Horodytska et al., 2018).

4.2.2 Kinetics

By washing the plastic films for varying durations (t = 1-3-5-7-10-15 minutes), the kinetics of the washing process could be clarified. To assess the influence of dirty water on the removal kinetics, this experiment was performed both with tap water and with wash water collected after wash steps 1 and 2 (W1+2), in duplicate, however from a statistical point of view a third repetition is recommended. The concentration of the contaminants in the water was measured for both. For W1+2, the initial concentration of these compounds in the washing water (C_0) was subtracted from the measured concentrations after the experiment (C_t).
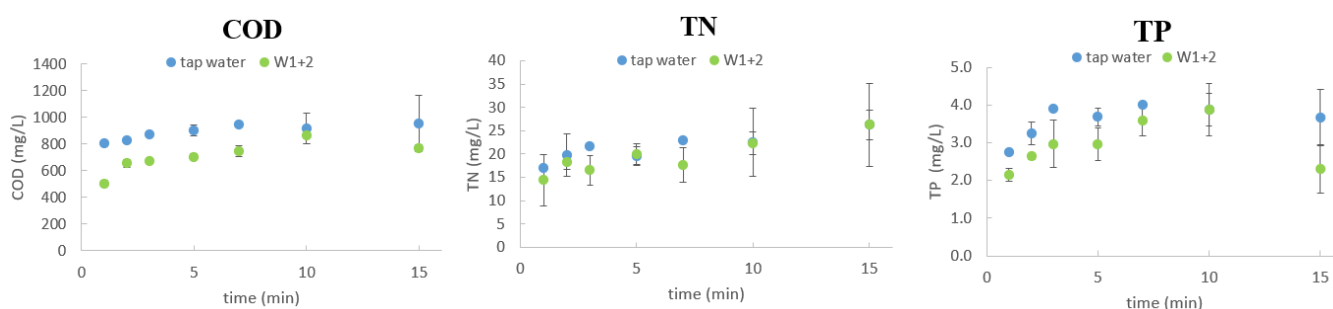
Figure 23: COD, TN and TP removal kinetics, W1+2 = wastewater after one and two wash steps (n=2).

Between one and seven minutes of washing, a higher concentration of COD, TN or TP was found in the water when the duration of the washing process increased. This means that more contaminants were removed from the plastics (Figure 23). After ten minutes, no further removal was observed and an equilibrium was reached. This is longer than the duration mentioned in section 2.3.3, however their method employed a maximum driving force to remove these components by continuously changing their water. In the setup used in this work, therefore, more time will be needed to achieve

the same removal (Santos et al., 2005). The behaviour is similar as observed for VOCs by Roosen et al. (2021). The article explained this by a reversed first order model where two processes take place: desorption of the VOCs from the plastic waste to the water and re-adsorption from the water to the plastics. In the first few minutes, more desorption of the impurities to the water takes place and from a certain moment in time, re-adsorption on the particles takes the upper hand until an equilibrium between the two processes is reached (Figure 23). This is clearly observable for COD and TP, where even for TP re-adsorption becomes so important after 15 minutes that less TP is removed than with a 10-minute wash. The same was observed for TSS and VSS. For TN, this trend is less prominently present. Since this was also the case in Figure 21, it might be that TN exhibits a different behaviour in removal, compared to COD and TP. Again, the leaching of the filler in PE ($CaCO_3$) could be an explanation for the decrease in TP. After longer washing times, $CaCO_3$ might leach out of the plastics and precipitate phosphorus (section 4.1.1). This remains to be proven. Tap water and W1+2 as a washing medium show approximately the same trend. However, when dirtier washing water (W1+2) is used, the removal rate of contaminants from the plastic films is slower. Although the removed concentration after ten minutes is approximately the same for both media. An explanation may be that the concentration gradient between plastic and water is lower and that re-adsorption to the plastics will take place more quickly due to the contaminants already present in the water. This means that washing water must be replaced regularly or a purification step will be necessary before the water is reused.

After washing repeatedly new samples of plastic films (3 g) in the same water (100 mL), an equilibrium curve could be drawn (Figure 24). This is referred to as equilibrium and not saturation, since, for instance COD concentrations in water can be found in literature that are much higher than the equilibrium concentrations depicted here (Jabłońska, 2018; Sanni et al., 2022; Wenqiang & Shan, 2023). The water is therefore not saturated with COD, but an equilibrium occurs, which is explained in this paragraph. 0.9 mL of water had to be added after each wash to maintain a constant volume of 100 mL. This corresponds to the 2.7 L water/kg of plastics that was mentioned in section 4.2.1. From these curves, it can be deduced in what amount the water is still able to remove the contaminants from the plastic after several washing steps. In the first repetitions, a stronger increase in the contaminant concentration can be observed than towards the end of the experiments. For COD, this is slightly more pronounced than for TN and even more than for TP, where an outlier can also be noticed after seven repetitions. This could be a measurement error. The reason the why COD reaches equilibrium faster than TN and TP might be because the concentrations of TN and certainly TP on the plastic are much lower and equilibrium may not have been reached yet. More experiments have to be performed to support this hypothesis.
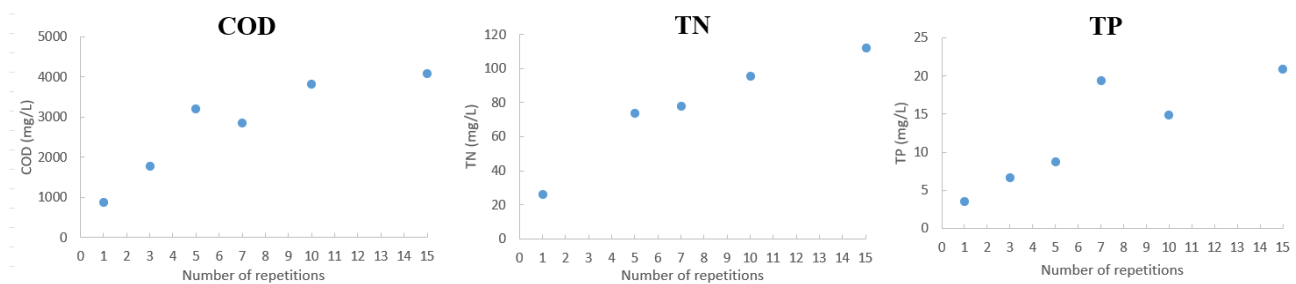

Figure 24: COD, TN and TP equilibrium tests (n=1).

The measured parameters are summarized in Table 13. The turbidity of the water increases after each wash, as does the EC. The pH remains almost constant. It can therefore be concluded that the more polluted the water is, the lower the contaminant removal will be. This is again in line with the results

obtained for VOCs by Roosen et al. (2021) and the proposed reversible first order (RFO) model. This again means that water will have to be removed after a few washing steps to ensure that the plastic is effectively washed. This decreasing washing capacity can be attributed to an equilibrium being reached in the water between desorption of the contaminants from the plastics and re-adsorption back onto them. The dirtier the water, the higher the initial concentration of the contaminants and thus the faster re-adsorption will occur. This is confirmed by equation 3: if $C_{ini,H2O}$ increases, the term containing $k_{adsorption}$ increases, which means the rate of adsorption is increased. These experiments were not conducted for VOCs, but they are expected to show the same trend, as indicated by De Somer et al. (2022) and Roosen et al. (2021). Since they showed that the rate of VOC-desorption was lower than the rate of re-adsorption, the VOCs are more likely to adhere to the plastics than to be removed to the water phase. It remains to be proven whether the same behaviour applies to COD, TN and TP. Using dirtier water for washing is likely to results in less effective VOC removal and, consequently, in many cases a higher odour perception.

Table 13: Summary of the parameters after repeatedly washing fresh plastic in the same wash water (n=1).

Number of washes	COD (mg/L)	TN (mg/L)	TP (mg/L)	Turbidity (NTU)	EC (µS/cm)	pH
1	875	26.0	3.54	683	1079	8.33
3	1764	48.8	6.70	1698	1308	8.34
5	3196	73.6	8.72	1840	1407	8.31
7	2864	77.8	19.4	2912	1609	8.38
10	3828	95.5	14.9	3695	1805	8.33
15	4084	112.0	20.9	4848	1960	8.30

4.2.3 Other washing media

In addition to water, caustic soda (NaOH) and cetyltrimethylammonium bromide (CTAB) were also used as washing medium. These were added to water in the second and third washing step, respectively at concentrations of 2% w/w and 9.2 mM. Before washing, these solutions were analysed as a kind of blank (Table 14). After the three washing steps, the water samples were also analysed (Table 14). After washing with NaOH, a considerably high value is obtained for EC (89400 µS/cm) and the pH has increased. Furthermore, the high COD and TN concentrations after washing with CTAB (> 5000 mg/L and 67.5 mg/L, respectively) are notable. However, this can be explained with the concentrations already present in the media. The high COD concentration in the washing medium with CTAB itself is responsible for the high measured concentration after washing with this detergent (Table 14). The influence of the washing medium with NaOH on these values is relatively small, when compared to the concentrations of tap water. The media have no influence on the measured TP concentrations. The high EC and pH values after washing with NaOH or CTAB can be explained in the same way. The pH-increase after washing with CTAB is not entirely due to the medium itself, as its pH is not much higher than tap water. This could also be because some residue of the water from the previous washing step with NaOH has remained attached to the plastics.

Table 15 shows the concentrations still present on the plastics after washing and is built up by subtracting the concentration in the washing medium before from that after the washing process. After the second washing step with NaOH, the contaminant removal from the plastic is comparable to the second washing step with water as conducted in section 4.2.1. However, no conclusions can be drawn

for the third washing step with CTAB. The COD concentration on the plastics after this wash could not be determined due to the already very high concentration of this detergent. It is unexpected that the concentration of TN in the CTAB in water before washing is higher than after the plastics were added (Table 14). There are several hypothetical explanations that could be explored in future research. It might be that because of the high TN concentration already present, the equilibrium is shifted towards re-adsorption onto the plastics. Furthermore, it could be that CTAB forms micelles around dirt particles, causing the ammonium groups to become less accessible for reaction with the reagents in the Hach test kits. Additionally, it can be noted that when the concentration of COD exceeds 1000 mg/L, it can interfere with the measurement by the Hach test kits for TN. Moreover, the pH of the water sample must be between pH 3-12 for the measurement, so this can also influence the measured concentration after the washing process. A final explanation could be that this was simply due to a measurement error. To confirm this, repetitions of this test will be necessary. Therefore, in this case, the TN concentration cannot be considered reliable and no concentration on the plastics can be given.

Table 14: Characteristics of the washing media + contaminants released in the washing media after the washing process (n=1).

Medium	COD (mg/L)	TN (mg/L)	TP (mg/L)	EC (µS/cm)	pH	Turbidity (NTU)
Before the washing process						
Tap water	13.6	3.42	< LOD	864	7.81	0.20
NaOH in water (2% w/w)	28.4	2.03	< LOD	104100	12.7	78.9
CTAB in water (9.2 mM)	6710	87.2	< LOD	1005	8.36	271
After the washing process						
Tap water	886	19.9	3.83	936	8.07	577
water + NaOH	522	7.16	1.45	89400	13.1	206
water + CTAB	>5000	67.5	0.527	9450	12.5	569

Table 15: Contamination on the plastics after washing with NaOH and CTAB (g/kg) (n=1).

Load after washing with	COD (g/kg)	TN (g/kg)	TP (g/kg)
Tap water	29.5	0.66	0.13
NaOH in water (2% w/w)	17.4	0.24	0.05
CTAB in water (9.2 mM)	?	?	0.02

It might be contested whether these washing media are really necessary, since they do not provide much better removal in terms of COD, TN or TP. However, NaOH shows its utility in the removal of labels or glue (section 2.3.2.2). Moreover, in terms of VOC removal, these washing media do show their utility. The VOC were measured semi-quantitatively using SD-GC-MS. Figure 25 (right) shows the intensity of the main VOC groups before and after the washing process with NaOH and CTAB. The intensities of all groups decreased considerably and almost no carboxylic acid VOCs could be found. On the left side of the figure, the same is shown for a washing process with three steps where only water was used. In general, both figures resemble each other, although it seems that the washing process with NaOH and CTAB gave the best removal. Both figures can be compared to Table 6. In this table, the removal efficiency of carboxylic acids was the same in water or CTAB+NaOH, whereas in the figures, there is clearly better removal when using the latter (82% compared to 29% in tap water). According to the table, CTAB+NaOH would result in better removal for the other VOC categories. This can also be observed in Figure 25, except for aromatic compounds, where the

removal was the same in both cases. From this it can be concluded that different VOC classes have varying levels of removal in NaOH and CTAB, and even within a single category, there can be variations. This may explain why the results are sometimes different from those presented in Table 6. The presence of components with different polarities within the same group could potentially account for the differences in removal efficiency.

It should be noted that when these washing media are used, there is an expected impact on the subsequent water treatment process (Table 14). The high COD and TN concentrations and the high turbidity in the water after the washing process with CTAB will have to be reduced to be allowed to be used again. More so, the increased pH of the washing water will affect pH-dependent processes such as coagulation. More research will be needed on the removal of COD and TN from the plastics with CTAB, and the effect of both wash media on the purification of the wash water and its possible reuse. In addition, a test at elevated temperatures could be conducted to see if this would give better removal efficiencies. Other detergents that would have a smaller influence on COD and TN concentrations could also be considered.
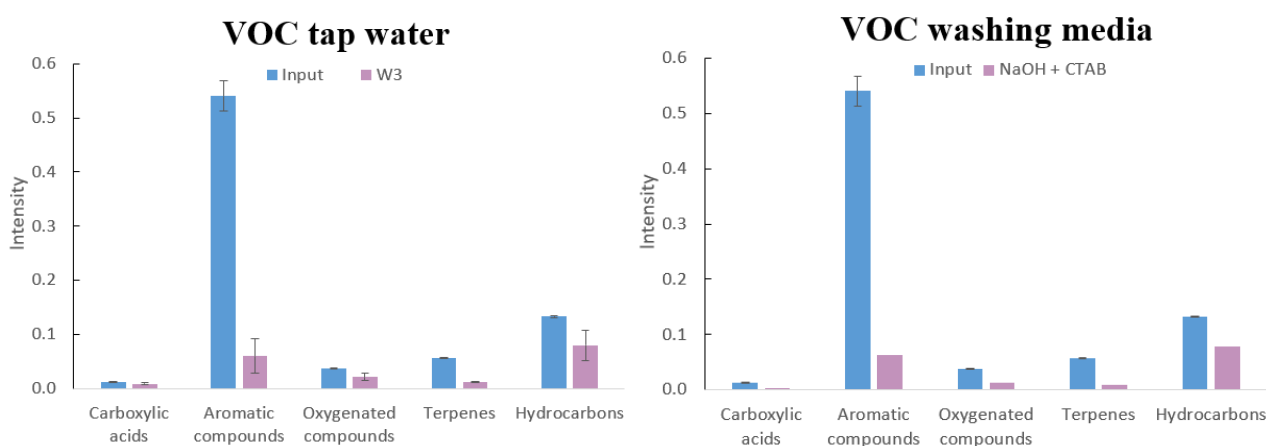

Figure 25: Intensity of the VOCs present on plastics after three washing steps with tap water (left, n =2) and after a washing process with NaOH and CTAB (right, n=1), measured by SD-GC-MS.

4.3 Wastewater treatment and reuse

4.3.1 Coagulation with ferric chloride

Jar tests were conducted to determine the optimal coagulant dose to purify W1+2 (a mixture of washing water coming from the first and second wash step). Coagulant doses between 5 and 13 mL of a 2.5 g/L $FeCl_3$-solution were added to 100 mL W1+2. The results can be found in Table 16. At every dose, all TP was removed. The best COD removal (95.3%) was obtained with the addition of 11 mL of this solution, the best TN removal (64.3%) with 9 mL, although there is only a small difference with 11 mL (63.7%). From 11 mL and above, the influence of the coagulant on the pH plays a greater role. The solution also started to turn yellow at 11 and 13 mL. As a result, 9 mL of a 2.5 g/L $FeCl_3$ was decided to be the best coagulant dose to purify 100 mL of a W1+2 sample. This dosage resulted in removal percentages for COD and TN of 93.6% and 64.3%, respectively, and corresponds to a 100 mL solution containing 0.225 g/L $FeCl_3$ or to 0.116 g Fe^{3+}/g COD removed. This is inconsistent with what was reported in Liang et al. (2010) (section 2.4.1) and demonstrates the importance of these jar tests. Thus, coagulation with $FeCl_3$ is a good way to purify the wastewater after our washing process. The parameters in Table 16 show that the water quality after purification approaches tap water quality for the parameters considered in this work (Table 14). It is important to mention that the coagulant dose depends on the sample to be purified, so jar tests will have to be

performed again for another type of sample. Furthermore, after filtration of the supernatant, sludge will remain that will have to be discarded. This is a concentrated mass so it is important to take this into account when designing such a process. In addition, experiments that study the removal of VOCs in the water by coagulation should also be performed.

Table 16: Jar tests for determining the optimal volume of a 2.5 g/L FeCl₃-solution (coagulant dose) (n=1).

	COD (mg/L)	Removal %	TN (mg/L)	Removal %	TP (mg/L)	EC (μS/cm)	pH	Turbidity (NTU)
W1+2	678		9.62		2.05	933	7.49	201
5 mL	60.8	91.0%	4.47	53.5%	< LOD	938	7.05	4.74
7 mL	46.0	93.2%	4.56	52.6%	< LOD	949	7.38	2.50
9 mL	43.6	93.6%	3.43	64.3%	< LOD	925	7.02	2.99
11 mL	32.0	95.3%	3.49	63.7%	< LOD	980	6.72	3.32
13 mL	34.6	94.9%	3.61	62.5%	< LOD	1005	4.72	9.87

4.3.2 Granular activated carbon adsorption

Activated carbon purification is performed after the third washing step because the third step is seen as a polishing step to remove recalcitrant compounds such as odours. These will then end up in the washing water and in order to reuse that water, they must be removed again. 40 g granular activated carbon (GAC) was added to a column. 100 mL of the wastewater from the third wash step was sent through the column. In addition, it was tested whether there would be more removal when the wastewater was passed through the column twice. Table 17 represents the results of the experiments. Passing the water through the column twice resulted in better removal rates for COD and TN, 86.9% and 85.4%, respectively, compared to 80.0% and 82.4% when passing once. TP was again not of any concern since it was already sufficiently removed after three washing steps. In both cases the pH rises slightly and the EC decreases. Despite the better removal percentages, it is still recommended to pass the washing water through the column only once. The difference in removal is small between the two and already with one pass, the water reaches a quality similar to tap water in terms of COD, TN and TP. In addition, the GAC column will be saturated more quickly if the water is passed through twice each time.

Table 17: Contamination in the water after sending through a GAC column (n=1).

	COD (mg/L)	TN (mg/L)	TP (mg/L)	EC (μS/cm)	pH	Turbidity (NTU)
W3	124	2.19	< LOD	838	8.32	81.1
1x through column	24.8	0.39	< LOD	633	9.20	10.6
2x through column	16.2	0.32	< LOD	579	9.50	7.49

It can be concluded that a GAC column provides very good removal rates in terms of COD and TN and as such, would be a good water treatment step after the third wash step. A shortcoming here is that VOC removal from the water was not considered, despite the fact that it is the main application of activated carbon adsorption. For now, we assume that COD measurements in water can be used as a surrogate for measuring VOC removal (Brinkmann et al., 2016) and that they will therefore show

good removal rates as well. However, further research will need to focus on an in-depth analysis to see whether there is a difference in the removal of VOCs belonging to different chemical groups.

4.3.3   Integration of wastewater treatment techniques

Finally, the integration of different treatment techniques and their effect on the purity of the wastewater was examined. In a first test, the washing water after the first and second washing step was treated with coagulation (9 mL of a 2.5 g/L FeCl$_3$-solution), followed by activated carbon adsorption in a column. In the second test, membrane filtration followed coagulation. Both tests were performed twice. From Table 18, it can be seen that the first test gives better removal of COD and TN, and the EC decreases, but the pH has risen slightly. Membrane filtration ensures less removal of these contaminants, but here, the pH remains almost constant. Additional experiments could reveal whether a different membrane might provide better removal efficiencies. Again, the cost of this purification should be taken into consideration as well. Since the total life cycle costs for nanofiltration are lower than coagulation in combination with GAC, this membrane will certainly be cheaper, as it has larger pores. The choice of treatment technique will depend on the desired output quality and the acceptable costs. Further research will have to provide insights into the best cost-quality ratio.

Table 18: Contamination in the water after integration of WWT techniques:
coagulation + GAC column or coagulation + membrane filtration (n=1).

	COD (mg/L)	Removal	TN (mg/L)	Removal	TP (mg/L)	EC (µS/cm)	pH	Turbidity (NTU)
W1+2	576		10.9		2.06	947	7.85	202
Coagulation	50.2	91.3%	4.85	55.5%	< LOD	1047	6.85	1.18
GAC column	6.63	98.8%	1.41	87.1%	< LOD	678	9.13	0.83
Membrane filtration	51.2	91.1%	3.35	69.3%	< LOD	941	7.63	0.36

4.4   Modelling in Aspen Plus

4.4.1   Model calibration in MS-Excel

The rate constants were calibrated according to section 3.8.1, and are summarized in Table 19. It should be noted that no kinetic tests or equilibrium tests were performed for VOCs. Only the removal efficiencies from the five VOC groups were taken from Roosen et al. (2022) after washing for 15 minutes, both for tap water and NaOH+CTAB (section 2.3.2.2). The first estimate for $k_{desorption}$ and $k_{adsorption}$ was taken from COD to push the Solver in the right direction. This will involve slightly more uncertainty than the k-values of COD/TN/TP due to lack of equilibrium testing, but both the reversed-first-order model and the removal efficiencies have been validated (De Somer et al., 2022).

From Table 19, it can be seen that $k_{desorption}$ is the greatest for TP, followed by COD and the smallest for TN. The VOC classes of carboxylic acids, aromatics and oxygenates have a higher $k_{desorption}$ than TN, the other groups a smaller one. A bigger $k_{desorption}$ means that the rate at which the contaminant is being desorbed from the plastics into the liquid phase is higher and thus it will be detached easier. $k_{adsorption}$, on the other hand, is the greatest for the VOCs (which do not differ much from each other) followed by COD, followed by TP and again the smallest for TN. This means that the re-adsorption

process is most favourable for VOCs and that the VOCs have a greater tendency to interact and adhere back to the plastic films compared to the other components. The higher adsorption k-value of COD could also explain why COD reaches equilibrium faster than TN or TP in Figure 24. The COD has a greater tendency to adhere back to the plastic, which is detrimental to its removal. $k_{adsorption}$ has to be converted to s^{-1} for the model so was multiplied by the solid/liquid (S/L) ratio. From there, K_{eq} could be calculated, which indicates the ratio between desorption and adsorption. The higher it is, the higher the removal efficiency. This shows why TP is removed very well, which was already observed in previous experiments. Furthermore, it shows that VOCs are more likely to re-adsorb than COD, TN or TP, that are more likely to dissolve in the water. Moreover, K_{eq} shows that the oxygenated VOC, terpenes and hydrocarbons are much likely to adsorb than desorb from the plastics, explaining why some odours are so difficult to remove. The higher k-value for desorption of VOCs with surfactant as a washing medium compared to tap water shows that the removal of VOCs will occur slightly faster. The re-adsorption of VOCs in the presence of a surfactant will occur somewhat more slowly, but to a much smaller extent. The better removal efficiency of these VOCs is also confirmed by the higher K_{eq}, except for carboxylic acids, where it remained the same. However, as already mentioned, the k-values of the VOCs should be interpreted with some caution.

Table 19: Desorption and adsorption rate constants for COD, TN, TP and five VOC classes. _SURF = when washed with NaOH + CTAB, CAR = carboxylic acids, ARO = aromatic compounds, OXY = oxygenated compounds, TER = terpenes, HC = hydrocarbons.

Compound	$k_{desorption}$ (s^{-1})	$k_{adsorption}$ $(L.kg^{-1}.s^{-1})$	$k_{adsorption}$ (s^{-1})	K_{eq} (-)
COD	0.007036	0.09809	0.002942	2.39
TN	0.003452	0.04233	0.001270	2.72
TP	0.01014	0.08445	0.002534	4.00
CAR	0.005295	0.1176	0.003528	1.50
ARO	0.005295	0.1176	0.003528	1.50
OXY	0.003759	0.1356	0.004068	0.92
TER	0.002317	0.1800	0.005401	0.43
HC	0.002317	0.1800	0.005401	0.43
CAR_SURF	0.005295	0.1176	0.003528	1.50
ARO_SURF	0.006900	0.09854	0.002956	2.33
OXY_SURF	0.006075	0.1090	0.003270	1.86
TER_SURF	0.006324	0.1725	0.005174	1.22
HC_SURF	0.007416	0.1515	0.004545	1.63

4.4.2 Model implementation in Aspen Plus

Figure 26 gives an overview of the flowsheet of the washing process in Aspen Plus. Three washing steps, two water treatment steps and three recirculation cycles were simulated. The model can be simulated for different S/L ratios. In addition, in the reuse of the water, the recirculation rate of water can be adjusted. This makes it possible to determine which fraction of the water will be treated before reuse. The wash water from the first step can be purified by coagulation and used as input for the second wash step. The wash water from this step is then reused in the first wash step without purification (counter current). In the third washing step, the detergent CTAB is used to obtain extra clean plastics in terms of VOCs. This washing water can be purified by means of coagulation and activated carbon adsorption, since it is assumed that more VOCs will be removed here, which will be

present in the water and must therefore be removed by means of activated carbon adsorption. Afterwards it is added back as input to the third step. In the properties tab, the model NRTL was chosen as method and the components were defined. Components included water, COD, TN, TP and VOC with a division made between contamination in water and contamination on plastic (for COD: CODW and CODPL, respectively). VOCs were split into the five groups mentioned in section 4.1.3, as they demonstrate different removal kinetics (Roosen et al., 2022). The washing steps themselves were presented using CSTR reactors. The residence time in these reactors was set at 10 minutes and temperature and pressure were set at 25°C and 1 bar, respectively. To describe the kinetics, the calibrated rate constants $k_{desorption}$ and $k_{adsorption}$ depicted in Table 19 were used. These k-values were added to the Aspen Plus Reactions, where a distinction was made between desorption (from the plastics to water) and adsorption (from water to the plastics). A user2 block was placed after the CSTR, representing the separation of plastics and water after washing. The user2 block refers to an Excel file that separates water and plastics. Given the high level of complexity to model coagulation-flocculation and activated carbon adsorption, no models have been drawn up for the wastewater treatment techniques. These were simulated as a black-box system using the experimental removal percentages. Implementation was done via user2 blocks. In the Excel file to which the user2 block refers, the removal percentages for COD/TN/TP of the purification techniques obtained in this study were entered. Based on scientific literature, it was assumed that VOC and COD in the water phase had the same removal percentage (section 4.1.4). The make-up water added just before the second wash makes up for the water uptake of the plastic films (2.7 L/kg plastic, section 4.2.1). This was modelled using a transfer block. The simulation is performed at a S/L ratio of 0.03, assuming that all the water undergoes treatment before reuse. The results can be found in the Supplementary Materials (Table S3).
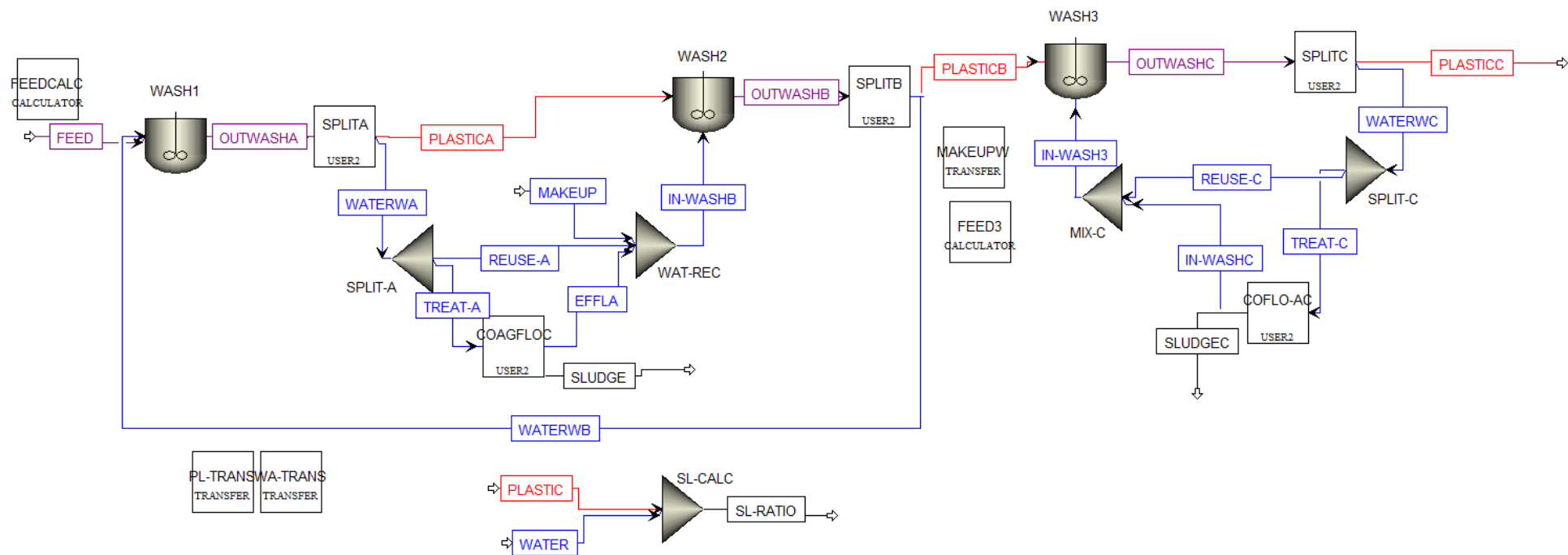
Figure 26: Flowsheet washing process in Aspen Plus version 14. Blue = water/washing medium stream, red = plastic stream, purple = both water and plastic, black = sludge stream. OUTWASH = mixture of water and plastics after a wash, SPLIT = filtration to separate plastics and water, TREAT = water treated before reuse, REUSE = water not treated before reuse, MAKEUP = water added to make up for water uptake by the plastics, IN-WASH = reused water that goes back to the washing tank.

4.4.3   Scenario analysis

The model was used to explore a number of scenarios and their impact on washing efficiencies. In the first scenario, the difference in removal efficiencies between the conventional two step washing process, where washing water from the second step is added to the first washing step (counter current), and the three step washing process, described in section 4.4.2 and Figure 26, was investigated. Results are depicted in Table 20. The table clearly demonstrates that the inclusion of a third washing step substantially enhances removal efficiencies. Particularly for VOCs, where the efficiencies improve by 18% on average. This highlights the importance of this polishing step to ensure clean plastics.

Table 20: Removal efficiencies of COD/TN/TP/VOCs for a two step and three step washing process, obtained via Aspen simulation. CAR = carboxylic acids, ARO = aromatic compounds, OXY = oxygenated compounds, TER = terpenes, HC = hydrocarbons.

# steps	COD	TN	TP	CAR	OXY	TER	ARO	HC
2	79.7%	71.8%	79.4%	66.4%	62.7%	50.8%	70.7%	47.5%
3	90.5%	74.8%	88.8%	78.2%	80.1%	73.7%	86.7%	71.2%

The second scenario focused on the influence of different S/L ratios on the washing process, namely 0.1, 0.05 and 0.03 kg plastic/L water, based on Roosen et al. (2021). The results of this simulation are shown in Figure 27. The best removal of COD, TN and TP after three washing steps is obtained at an S/L ratio of 0.03 kg plastic/L water (90%, 75% and 89%, respectively). All VOC groups show the same trend (Figure 28). At the lowest S/L ratio (0.03 kg plastic/L water), the highest removal efficiencies are obtained: 78% for carboxyilic acids, 80% for oxygenated compounds, 74% for terpenes, 87% for aromatics and 71% for hydrocarbons. This is what is expected when comparing with Roosen et al. (2021). The latter found that when the S/L ratio increases, removal efficiencies decrease exponentially. If the S/L ratio decreases, the m/V in equation 3 lowers, which causes the adsorption term in the equation to become smaller. Thus, since more water relative to plastics would suggest a slower establishment of the equilibrium between desorption and re-adsorption, a lower S/L ratio provides better removal.
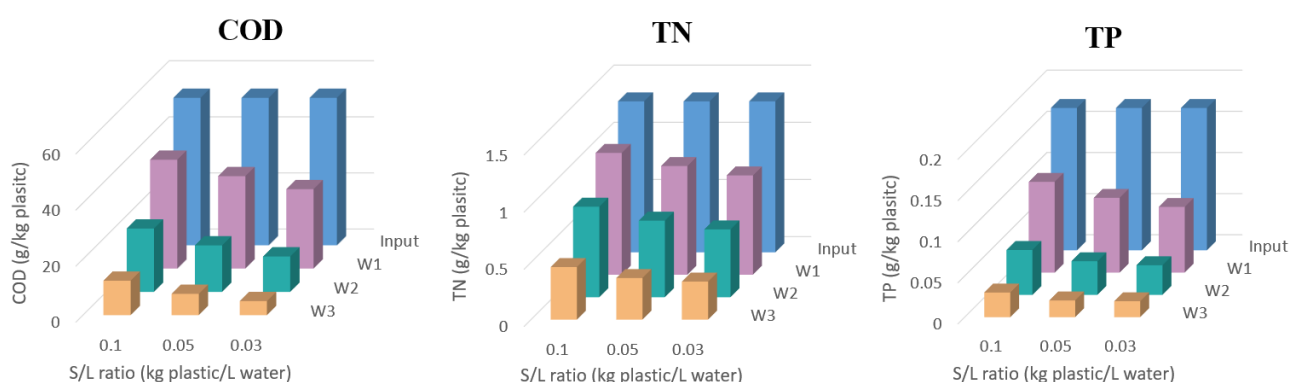

Figure 27: Concentration COD/TN/TP present on the plastics after every washing step (g/kg plastic), for three different S/L-ratios, obtained via Aspen simulation. W1 = after one washing step.
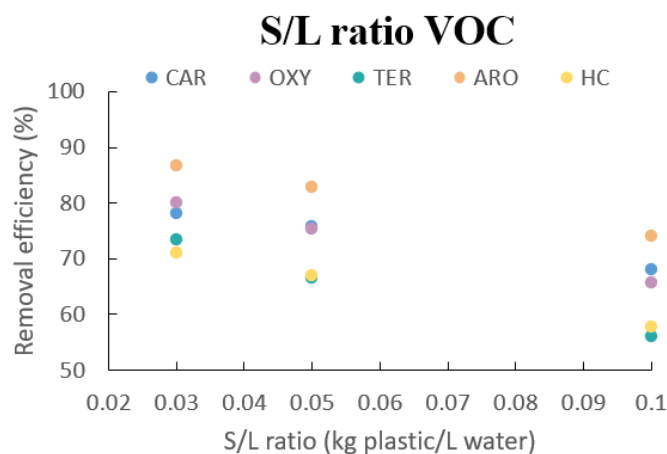
Figure 28: Removal efficiencies of VOCs for three different S/L ratios, obtained via Aspen simulation. CAR = carboxylic acids, ARO = aromatic compounds, OXY = oxygenated compounds, TER = terpenes, HC = hydrocarbons.

The final scenario that was tested was the difference in washing efficiency when water treatment after the third washing step was done with activated carbon or by membrane filtration. In Table 21, the concentration on the plastics after the third wash are given. Differences between the two treatment techniques are very small, however the removal efficiencies are always bigger when using GAC. For VOC, both treatments assumed the same removal efficiencies as COD. Again, model validation will be needed to obtain the exact efficiencies. Based on the results in Table 21, one could consider using membrane filtration instead of GAC since it is a more cost-effective option (Tarpani & Azapagic, 2018) and removal efficiencies are comparable.

Table 21: Removal efficiencies of COD/TN/TP/VOCs after three washing steps, when wastewater was treated with membrane filtration or GAC, obtained via Aspen simulation. CAR = carboxylic acids, ARO = aromatic compounds, OXY = oxygenated compounds, TER = terpenes, HC = hydrocarbons.

Treatment	COD	TN	TP	CAR	OXY	TER	ARO	HC
Membrane filtration	90.0%	73.8%	88.8%	77.9%	79.5%	72.7%	86.3%	70.5%
GAC	90.5%	74.8%	88.8%	78.2%	80.1%	73.6%	86.7%	71.2%

From the results obtained from running different scenarios, it can be decided that an S/L ratio of 0.03 kg plastic/L water gives good results in removing the unwanted contaminants. Lower S/L ratios will require more water, so more water will have to be treated and costs could potentially be higher. The model could be used to determine the optimal fraction of wash water that will be treated before reuse and which fraction will be returned without treatment. By playing with the two recirculation cycles in Figure 26, the optimal reuse ratio for both can be obtained. The model can be further optimized by conducting a number of experiments and several scenarios can still be tested.

CHAPTER 5

5. Conclusion

This thesis has explored the crucial issue of VOC removal from flexible packaging waste in plastic recycling plants. An innovative approach was proposed through optimizing the washing process by collecting experimental data on a broad range of parameters and linking them to an operational Aspen model. The investigation began with an in-depth review of the existing literature, highlighting the challenges associated with VOC removal from polyethylene, important parameters to consider in the washing process and some water treatment techniques to improve the water management. The importance of addressing this issue was emphasized, given the increasing demand in flexible packaging but also, on the other hand, the impact of plastics on the climate and the related targets that are stipulated by the European Commission.

The optimal washing process of PE films has not yet been fully unravelled, but suggestions can already be given to improve the washing process of these plastics, in terms of COD, TN, TP and VOC removal. Applying a washing process that is subdivided into several steps, each with their own water quality requirements and management, would facilitate the production of secondary materials with a higher quality in terms of their VOC content. Finding a balance between the number of washing steps, and related to this the overall cost of the recycling process, and the VOC removal that can be achieved, we suggest here to apply three washing steps. The first two washing steps take care of removing the biggest dirt, while the third washing step is mainly for removing more recalcitrant components, mainly VOCs. In this step, using only water as a washing medium will not create the highest quality and other washing media might be considered. Caustic soda and CTAB are media that have been tested. Yet, it should be noted that CTAB itself contributes to the COD and TN concentration in the water and caustic soda increases the pH, which will only complicate the subsequent water purification. Additional tests will have to be carried out to see if the advantages of these media outweigh the disadvantages and extra cost. Treating the wastewater can increase the economic feasibility of the washing process and avoid drought or discharge problems by reusing the washing water. Water treatment techniques, such as coagulation with $FeCl_3$, GAC adsorption and membrane filtration, showed their ability to remove certain contaminants from the water and can be employed in the process to reuse the wastewater. Coagulation combined with GAC adsorption achieved removal efficiencies of 99% for COD, 87% for TN and 100% for TP in water. Coagulation with membrane filtration 91% for COD, 69% for TN and 100% for TP. However, this remains to be confirmed for VOC removal from water.

The contamination load of the input stream will play an important role in the performance of the washing process. More loaded inputs will result in the water becoming contaminated at a faster rate, necessitating more frequent replacement or more advanced purification. Important parameters to be measured are COD, TN and VOCs. TP is not needed as it seems not to pose a problem due to its low loadings and good removal efficiencies. It appears that COD and TN show different behaviour in removal so both components need to be measured to monitor the performance of the process. COD concentrations measured on the plastics cannot serve as a surrogate for the VOC concentrations present on the plastic. Hence the importance of monitoring the latter as well since it is used as a measure of odour removal, keeping in mind that VOC and odour are not exactly the same.

The kinetics of the washing process can be described using a reversible first order model, which takes into account that contaminants desorb during the washing from the plastics in the water, but can also re-adsorb back onto the plastics. Depending on the rate constants ($k_{desorption}$ and $k_{adsorption}$), the equilibrium between the two will occur faster or slower. By monitoring this, the ideal washing time can be determined. An Aspen Plus model can be created by integrating the experimental data. This can help to understand the impact of different parameters on the process, predict the outcome of different scenarios and enhance washing efficiencies. Three washing steps, two water treatment steps and three recirculation cycles were simulated. The model showed that lower S/L ratios result in greater removal of contaminants, primarily because re-adsorption of contaminants to the plastics becomes less important. Compared to a S/L ratio of 0.1, 0.03 kg plastics/L water seems to give good results, improving the removal efficiencies of COD, TN, TP and VOCs by 14%, 10%, 6% and 14%, respectively. The comparison between the conventional two-step process with this introduced three-step process showed improved removal efficiencies for COD, TN, TP (91%, 75%, 89%, respectively) and VOC. The efficiency of the latter increased by 18%, on average, resulting in a VOC removal efficiency of 78%.

5.1 Limitations and further research

It is important to acknowledge that further research and development are required to optimize and validate the proposed washing process in industrial recycling plant scenarios. In general, replications of the experimental work can be performed to make more statistically correct statements. Furthermore, the equilibrium tests could be repeated with more contaminated inputs to see if there will be a shift in the equilibrium between desorption and adsorption. Equilibrium tests for the different VOC groups will also help to better estimate the rate constants (k-values) to get better insights on the VOC removal in the model washing process. Since when washing with CTAB, a portion of COD and TN comes from this washing medium, no conclusions could be drawn on the removal of these contaminants. Therefore, it is recommended to repeat these tests taking into account the contribution of this washing medium to measured concentrations. Moreover, it will then also be possible to test how the washing medium will affect the subsequent treatment.

Some limitations in the model are that the model does not take into account the impact of the detergent used in the third washing step on the following wastewater treatment. Furthermore, as already mentioned, the k-values of the VOC groups are estimated, based on those of COD. A lot more scenarios could be tested to get more insight into the washing process and treatment cycles, preferably in collaboration with industry. The removal efficiencies when other input materials are used can be studied. More or less contaminated fractions can influence the optimal process parameters. Moreover, the impact on removal efficiencies of treating only a portion of the washing water before recycling it back can be investigated. In addition, the optimal balance between S/L ratio and these recirculation rates can be studied. Finding an this balance between costs and quality will be key. In addition, a techno-economic analysis and life cycle assessment can provide more insight into the optimal ratio between process costs, environmental impact and quality of the secondary materials.

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SUPPLEMENTARY MATERIALS

Table S1: Operational parameters used for ICP-OES analysis.

Characteristics	Instrument conditions
RF generator	40 MHz
Power	1150 W
Spray chamber	Cyclonic
Nebulizer	SeaSpray
Cool gas flow	12.0 L min^{-1}
Auxiliary gas flow	0.5 L min^{-1}
Nebulizer gas flow	0.5 L min^{-1}
Injector	Alumina (2 mm diameter)
Nebulzation chamber	Scott (Ryton)
Peristaltic pump tubing	0.76 mm

Table S2: LOD and LOQ per analysed element for ICP-OES analysis.

Element	LOD (ppm)	LOQ (ppm)
Al	0.319	1.063
Ca	0.030	0.099
Cd	0.001	0.002
Cr	0.005	0.018
Cu	0.007	0.023
Fe	0.042	0.139
Mg	0.008	0.027
Mn	0.001	0.002
Na	0.252	0.841
Ni	0.004	0.014
Pb	0.006	0.021
Sr	0.001	0.002
Zn	0.002	0.006

Table S3: Summary results simulation in Aspen Plus, S/L = 0.03, return rate = 0.

	FEED	OUTWASH A	OUTWASH B	OUTWASH C	IN-WASH B	IN-WASH 3	SLUDGE	SLUDGE C
From		WASH1	WASH2	WASH3	WAT-REC	MIX-C	COAGFLOC	COFLO-AC
To	WASH1	SPLITA	SPLITB	SPLITC	WASH2	WASH3		
Mass flows (kg/hr)	54.80	33,414	36,071	36,049	33,338	33,333	43.50	8.95
WATER	-	33,333	36,033	36,033	33,333	33,333	-	-
CODPL	52.58	28.31	12.63	5.01	-	-	-	-
TNPL	1.32	0.87	0.59	0.33	-	-	-	-
TPPL	0.17	0.08	0.04	0.02	-	-	-	-
CARPL	4.35E-04	2.75E-04	1.58E-04	9.49E-05	-	-	-	-
OXYPL	9.55E-04	6.68E-04	3.90E-04	1.90E-04	-	-	-	-
TERPL	1.61E-03	1.30E-03	8.48E-04	4.24E-04	-	-	-	-
AROPL	1.39E-03	8.65E-04	4.56E-04	1.85E-04	-	-	-	-
ALKPL	3.38E-04	2.71E-04	1.87E-04	9.73E-05	-	-	-	-
CODW	-	43.76	19.49	7.71	3.81	0.09	39.95	7.62
TNW	-	1.31	0.86	0.31	0.58	0.05	0.73	0.27
TPW	-	0.14	0.05	0.02	1.38E-03	-	0.14	0.02
CARW	-	3.03E-04	1.43E-04	6.45E-05	2.64E-05	9.74E-07	2.77E-04	6.37E-05
OXYW	-	6.19E-04	3.32E-04	2.02E-04	5.39E-05	2.56E-06	5.65E-04	1.99E-04
TERW	-	8.35E-04	5.21E-04	4.29E-04	7.26E-05	5.09E-06	7.62E-04	4.24E-04
AROW	-	1.02E-03	4.98E-04	2.75E-04	8.90E-05	3.39E-06	9.34E-04	2.72E-04
ALKW	-	1.65E-04	9.76E-05	9.12E-05	1.44E-05	1.19E-06	1.51E-04	9.02E-05

Figure S1: Water samples after five washing steps, from left to right: W1, W2, W3, W4, W5.