Functionalization of polystyrene and its use as an adsorptive material

Master's Thesis

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Kia Koskinen

Abstract

The contamination of water resources, particularly by emerging organic contaminants, presents significant environmental and health concerns worldwide. Insufficient wastewater treatment processes contribute to the presence of these contaminants that are typically found in trace amounts in the environment, posing risks to aquatic ecosystems and human health. Polymer-based adsorptive materials offer a promising solution for this challenge. This thesis investigates the functionalization of polystyrene, a commonly used polymer, for its potential application as an adsorbent for emerging organic contaminants, with a main focus on pharmaceuticals naproxen and diclofenac.

The literature review provides a comprehensive investigation of emerging organic contaminants, with particular emphasis on pharmaceuticals. Pharmaceuticals is one of the largest and the most problematic class of emerging organic contaminants known for their adverse effects on the environment and challenges in wastewater treatment. Polymer chemistry has gained scientific interest for decades and is now increasingly recognized for its potential in water purification applications.

In the experimental part of this master's thesis, polystyrene underwent functionalization via Friedel-Crafts acylation where succinic anhydride was substituted onto the aromatic ring of polystyrene. The success of this process was evaluated using solid-state characterization techniques including NMR, FTIR, and TGA, while the degree of functionalization was quantified through acid-base back titration. The functionalized polystyrene material was assessed for its adsorption capacity towards naproxen and diclofenac, two commonly known and widely used pharmaceuticals, using UHPLC-MS.

Preface

This master's thesis was written during the autumn 2023 and spring 2024. The master's degree has been completed at the University of Turku at the Department of Chemistry, but the master's thesis was completed in its entirety at the University of Jyväskylä at the Department of Chemistry.

Supervisors of this thesis are professor Matti Haukka and doctorate student Janne Frimodig from the University of Jyväskylä and professor Pasi Virta from the University of Turku. Janne Frimodig has received funding from LIFE21-IPE-FI-PlastLIFE/101069513, which has been used to cover some material and equipment expenses. I would like to thank my supervisors for this exciting and futuristic topic. I would also like to thank for the amazing support I have received from my supervisors and the university community. It has been a privilege to be able to work in this environment, and I can happily say that I had fun!

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Abbreviations

$AlCl_3$	Aluminium chloride
ABS	Acrylonitrile butadiene styrene
APCI	Atmospheric pressure chemical ionization
ATRP	Atom transfer radical polymerization
BSE	Backscattered electron
CD	Circular dichroism
CTA	Chain transfer agent
DCM	Dichloromethane
DMA	Dynamical mechanical analysis
DMF	dimethyl formamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
E1	Estrone
E2	17β-estradiol
EE2	17α-ethynylestradiol
E3	estriol
ECHA	European Chemicals Agency
EDC	Endocrine disrupting compound
EDX	Energy-dispersive X-ray
EOC	Emerging organic contaminant
EQS	Environmental Quality Standard
EQSD	Environmental Quality Standards Directive
EM	Electron microscopy

ESI	Electrospray ionization
EU	European Union
GPC	Gel permeation chromatography
GWD	Groundwater directive
HCl	Hydrochloric acid
HRMS	High-resolution mass spectrometry
IR	Infrared
LC-MS	Liquid chromatography-mass spectrometry
NaOH	Sodium hydroxide
NMP	Nitroxide-mediated polymerization
NMR	Nuclear magnetic resonance
NSAID	Non-steroidal anti-inflammatory drug
MALDI	Matrix-assisted laser desorption/ionization
MeCN	Acetonitrile
MeOH	Methanol
MS	Mass spectrometry
MRM	Multiple Reaction Monitoring
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene
PET	Polyethylene terephthalate
Phph	Phenolphthalein
PP	Polypropylene
PS	Polystyrene

PVC	Polyvinyl chloride
POP	Persistent organic pollutant
PPCP	Pharmaceuticals and personal care products
T_g	Glass transition temperature
T_m	Melting temperature
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMA	Thermomechanical analysis
TOF	Time-of-flight
TP	Transformation product
TPU	Thermoplastic polyurethane
SA	Succinic anhydride
SAXS	Small-angle X-ray scattering
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
SVOC	Semi-volatile organic compound
UHPLC	Ultra-high-performance liquid chromatography
UV-Vis	Ultraviolet-Visible
UWWTD	Urban Wastewater Treatment Directive
VOC	Volatile organic compound
WAXS	Wide-angle X-ray scattering
WFD	Water Framework Directive

WWTP Wastewater treatment plant

XPS X-ray photoelectron spectroscopy

XRD X-ray diffraction

1 Introduction

Water is the foundation of life and one of the most crucial resources for the survival of all living organisms. However, its purity is under constant threat from various contaminants and pollutants originating especially from urbanization, inadequate wastewater treatment processes, agriculture runoffs, incorrect disposal of waste, and industrialization. This widespread contamination affects nearly every water body on Earth.[1]

Aquatic environmental contaminants can be broadly divided into two main classes, inorganic and organic contaminants. Recent scientific attention has increasingly focused on water pollution caused by organic contaminants, and in the last few decades even more precisely on the presence of emerging organic contaminants, found in trace amounts in the environment. The group of inorganic contaminants includes a wide range of toxic metals, such as heavy metals, and various types of nutrients and salts. Among these contaminants, heavy metals like lead, mercury, and cadmium have been extensively studied, focusing on their occurrence, environmental fate, and the adverse effects they impose on ecosystems.[2,3]

Ecosystems, in general, are impacted by the presence of various types of contaminants but especially aquatic environments are sensitive and also particularly exposed to the contaminants. The balance of aquatic environments is easily disrupted, aquatic organisms and ecosystems are harmed, and the effects of these can be far-reaching and long-lasting.[4] Human health is easily affected by everything present in the breathable air, and similarly aquatic environments are exposed to those contaminants that are dissolved or suspended in the water, through permeable skin or respiratory surfaces. From the group of emerging organic contaminants especially pharmaceuticals are often relatively stable compounds in the environment. Not only these contaminants are potentially harmful to plants and animals, but they have the potential to persist and bioaccumulate in humans as well. Little is still known about the adverse effects of contaminants on human health but exposure to these contaminants is inevitable through food and drinking water sources.[5]

Polystyrene is a widely used polymer that offers an attractive platform for modifications owing to its chemical structure (Figure 1). Functionalization of polystyrene enhances its adsorption capacity, modifying it well-suited for the efficient removal of organic contaminants from liquid samples, and even larger water bodies. Through processes like Friedel-Crafts acylation, the benzene ring structure of polystyrene can be modified without affecting the properties of the polymer backbone. Modifications aim to introduce functional groups to the polymer structure to facilitate attractive interactions with target molecules, such as naproxen and diclofenac. This enables efficient adsorption through interactions such as hydrogen bonds and electrostatic interactions (Figure 2).

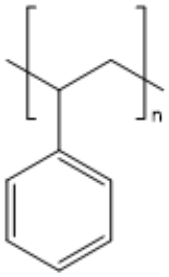


Figure 1. Chemical structure of polystyrene.

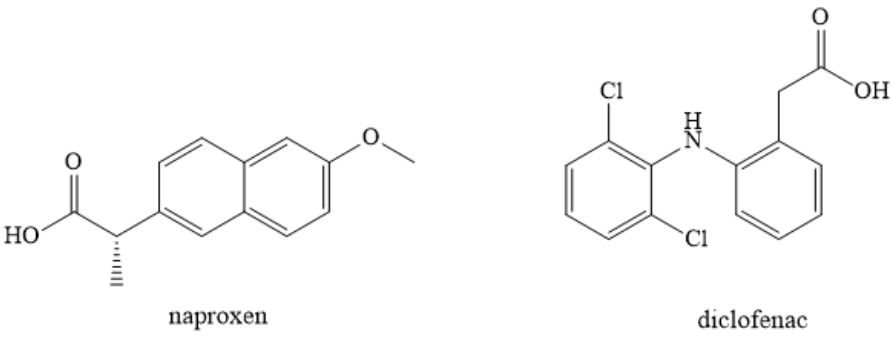


Figure 2. Chemical structures of naproxen and diclofenac.

2 Emerging organic contaminants

The term organic contaminants is used to describe a wide range of thousands of chemical compounds that include for example dyes, surfactants, pharmaceuticals and personal care products (PPCPs), illicit drugs, pesticides, flame retardants, volatile and semivolatile organic compounds (VOCs, SVOCs), endocrine disrupting compounds (EDCs), industrial chemicals, and other toxic chemicals. These compounds are used in our everyday lives in large quantities, but they pose challenges when released or ended up in the environment.[1,6] Recent studies have shown that the impact of organic contaminants on our aquatic environments is a significant concern. In general, aquatic environments and aquatic organisms are very sensitive to even low concentrations of organic contaminants, and these contaminants pose an emerging threat to the aquatic biota. However, organic contaminants do not only cause adverse effects on aquatic life, but the effects also extend to animals and humans through contaminated drinking waters and indirectly via the food chain. [1,6–8]

For a long time, the focus of water pollution research has primarily been on traditional pollutants which include for example heavy metals, persistent organic pollutants (POPs), nutrients, such as nitrogen and phosphorus, and microbial contaminants, such as bacteria and viruses. This area of pollutants is already regulated, and the effects of these pollutants on the environment have been extensively studied. It can also be said that wastewater treatment plants (WWTPs) are quite effective in removing these pollutants with prevailing wastewater treatment processes. However, in recent years, the focus has shifted more towards so-called emerging organic contaminants (EOCs).[9]

Emerging organic contaminants are usually unregulated and not commonly monitored contaminants that still have potential adverse ecological and/or human health effects. When compared to persistent organic pollutants (POPs), emerging organic contaminants do not need to be persistent in the environment to cause negative effects because they are continuously introduced into the environment. This is due to the high daily consumption of products concerned as emerging contaminants originating for example from pharmaceuticals, personal care products, industry, and agriculture.[9] It is noteworthy that metabolites and different degradation products of the parent compounds are also classified as emerging organic contaminants.[8]

The release of emerging contaminants to the environment has likely occurred for a long time. However, the presence of emerging organic contaminants in the environment and the challenges they pose have been identified along with new sensitive analytical methods and lower detection limits over the last few decades. Therefore, it can also be said that emerging organic contaminants and their detection have become an environmental concern.[10,11]

One remarkable factor for the presence of emerging organic contaminants in the environment is insufficient wastewater treatment. EOCs enter the environment, especially the aquatic environment, mainly through insufficiently treated wastewater effluents. Emerging contaminants are often detected in trace amounts in effluents, and natural water samples generally, ranging from micrograms per liter (μg L^{-1}) to nanograms per liter (ng L^{-1}), and thus these are often referred to as microcontaminants. In addition to the presence of organic contaminants in effluents and natural waters, such as surface and ground waters, EOCs are also detected in drinking waters around the world.[12]

Several studies have proven that conventional wastewater treatments are not sufficient for the removal of microcontaminants. These treatments are not designed for this purpose, and emerging contaminants largely show either partial or even no removal during the applied wastewater treatment process. In addition to effluents, there are also other point sources through which EOCs are generally released into the aquatic environment, such as runoffs and improper disposal of expired and unused drugs through sinks and drains.[1]

However, it is noteworthy that the concentrations of emerging organic contaminants in effluents fluctuate greatly. This can be a consequence of different regional regulations for the required wastewater treatments and their efficiency, and also there are regional differences in the consumption of certain products, for example, pharmaceuticals.[1,13] It is well known, that the treated wastewater, as well as untreated sewage waters, may eventually make their way into the environment especially when treated effluents are commonly released into surface water bodies.[13,14] This leads to growing concern and awareness of the need to monitor the presence of the EOCs in waters. Additionally, there is an imperative to explore and implement more efficient methods for the removal of EOCs.

2.1 Pharmaceuticals

Pharmaceuticals can be considered one of the largest classes of emerging organic contaminants as well as one of the most dangerous and harmful. The most researched groups of EOCs are analgesics and non-steroidal anti-inflammatory drugs (NSAIDs), hormones, antibiotics, lipid regulators, beta-blockers, and psychiatric drugs, such as antidepressants. This is due to their frequent presence in environmental detection studies which again is either due to their persistence in the environment and/or large consumption.[14,15] Research of more than 20 years has indicated that pharmaceuticals and their residues are detected in all compartments of water bodies around the world.[12]

Pharmaceuticals are often highly stable and are not readily biodegradable.[16] One of the emerging challenges of pharmaceuticals in the environment is the fate of the parent compound. The possible threats of parent compounds have been the main focus of the research but for the last few years, the attention has also been shifted more towards the transformation products (TPs) of the pharmaceuticals. Transformation products of pharmaceuticals include both the degradation products from the biotic and abiotic transformations and the formed metabolites that humans excrete. The transformations that pharmaceuticals undergo may occur either in the environment or already in the wastewater treatment plants. These products may bioaccumulate in the environment for example in fish tissue, may cause toxicity by itself or degrade even further by photolysis, hydrolysis, or biodegradation.[17] Accumulation and transformation to metabolites can also make the compounds biologically active.[12,15]

The persistence of certain pharmaceuticals in the environment also poses an emerging issue. Some pharmaceuticals, such as non-steroidal anti-inflammatory drug naproxen and antibiotic erythromycin, can persist in the environment for more than a year but some can persist for multiple years depending on the environmental conditions.[15] However, it is slightly controversial whether pharmaceuticals can be considered guilelessly persistent but to be rather so-called “pseudo-persistent” compounds. The term pseudo-persistent suggests that the continual use instead of the physico-chemical characteristics of pharmaceuticals results in persistent occurrence in the environment. Araujo *et al.*[18] have proved that for example naproxen is rather photolabile and possesses a relatively short half-life, and will degrade at a moderate

rate. This pseudo-persistency characteristic is congruent with the main definition of the term "emerging organic contaminants". The root cause of why emerging organic contaminants are considered to be hazardous and persistent in our environment is the fact that pharmaceuticals end up in the environment in ever-increasing amounts. One remarkable factor enabling this is the increasing consumption.

The production, consumption, and the global pharmaceutical market are increasing continuously. The pharmaceutical sector has been, and still is, largely dominated by markets in Europe and North America. However, there is an increasing market of pharmaceuticals in Asia, Latin America, Russia, the Middle East, and Africa as well.[19] The increasing market is a result of increasing demand and need. There is an increase in the lifespan as well as the population age of humans. Economic growth has also been marked as one of the reasons for increasing pharmaceutical use as the ability and expectation to treat different diseases is increased. Other factors are intensified livestock and aquaculture practices, and climate change which worsens already existing diseases.[20] As a conclusion it can be said that the amount of pharmaceuticals in the environment will not decrease but rather increase already in the next few years.

2.1.1 Analgesics and non-steroidal anti-inflammatory drugs (NSAIDs)

NSAIDs and analgesics are used to reduce inflammation, pain, and fever both in human and veterinary health care. Especially NSAIDs are reported to be the most abundant contaminants found in the environment as well as most commonly detected therapeutic group.[21,22] This group includes common pain medications such as acetaminophen (paracetamol), acetylsalicylic acid (aspirin), diclofenac, ibuprofen, ketoprofen, and naproxen. Anti-inflammatories have been reported in the environment already in the late 1970s but in the last few decades, they have been detected in an increasing amount in aquatic environments as well as in sediments, soils, snow, and even in the Antarctic glaciers.[22] Most of the NSAIDs and analgesics are sold over-the-counter, leading to the consequence of high consumption of these products.[17] NSAIDs and analgesics also belong to a group called endocrine disruptor compounds (EDCs) (see below). Endocrine disruptors affect the reproductive processes for example by decreasing fertility and affecting sexual behaviour leading to effects on population stability.

As with pharmaceuticals in general, the characteristic of persistence/pseudo-persistence of analgesics and anti-inflammatories in the aquatic environment poses challenges.[23] Other challenges cause the formation of transformation products (TPs). These TPs may cause toxicity and bioaccumulation and/or they may degrade even further in the environment. It is noteworthy, that some of the pharmaceutical transformation products can be even more toxic than their parent compounds. Maculewicz *et al.*[17] have listed that for example more toxic transformation products of NSAIDs and analgesics are formed in the photodegradation of naproxen and diclofenac, while photodegradation products of ibuprofen are commonly less toxic compared to the parent compound.[17] The transformation of NSAIDs and analgesics in the environment, and their possible degradation is affected by multiple factors, including pH, temperature, light exposure, and time of incubation. Hydrolysis and biodegradation of TPs of pharmaceuticals are more studied than for example the effects of light exposure. However, Maculewicz *et al.*[17] have summarized greatly that not enough research has been done on the transformation products and their effects, and especially studies on single TPs should be conducted.[17]

Quantitative analyses performed for NSAIDs present in natural waters are limited.[24] As mentioned, the detected amounts of NSAIDs and analgesics are typically low, ranging between ng L^{-1} to µg L^{-1}, and commonly natural water bodies hold NSAIDs concentration below 1 µg L^{-1}.[25] Trace level analysis of NSAIDs has its challenges, especially when it comes to the required pretreatment methods. The presence of a large amount of interferences in the natural water samples and the complex matrix complicates the measurements, leading to a situation where most instruments are incapable of detecting the trace amounts of NSAIDs, or any other pharmaceuticals in the samples. Currently, solid-phase extraction is the most commonly used pretreatment technology for NSAIDs. However, in the past few years, multiple novel pretreatment technologies have been introduced, including for example utilization of polymer materials, magnetic materials, carbon-based materials, silica-based materials, MOFs (metal-organic frameworks), and COFs (covalent organic frameworks). The main method for the detection of NSAIDs and analgesics is liquid chromatography-mass spectrometry (LC-MS) due to its high sensitivity and accuracy, and its general suitability for NSAID analysis. In the future, improvements in detection technology, such as the utilization of high-resolution mass spectroscopy (HRMS), ultra-high-performance liquid chromatography (UHPLC), and two-dimensional gas chromatography, are expected to affect the detection and analysis of samples

including analytes in trace levels with possible complex matrices.[24] Only a few NSAIDs, including diclofenac, ibuprofen, indomethacin, mefenamic acid, codeine, phenazone, propyphenazone, piroxicam, and naproxen, have selective analytical methods generated which are focused mainly on the analysis on fish tissues.[26]

Out of the NSAIDs, diclofenac is the most detected and also the most problematic anti-inflammatory found in the environment. Another commonly discovered is naproxen. Little research has been done on plausible ecotoxicological risks that diclofenac, and other NSAIDs, possess, or what are the possible effects after prolonged exposure.[27] Even though acute toxicity studies have been much more common, the concern of chronic exposure to NSAIDs and analgesics has risen. To name a few, Schwaiger *et al*.[27] have shown through chemical analyses done in laboratory settings how diclofenac accumulates mostly in the liver, kidney, muscle tissue, and the gills of fish in environmentally relevant concentrations. Xu *et al*.[28] have also shown that prolonged exposure of 60 days of naproxen has a clear effect on growth inhibition and thyroid disruption in zebrafish, and can cause bioconcentration. Almeida *et al.*[29] have stated that the effects of pharmaceutical drugs on marine organisms have not been studied to a large extent compared to those in the freshwater compartment. Almeida *et al.*[29] have studied bioconcentration and effects of diclofenac, ibuprofen, and paracetamol in marine bivalves under laboratory conditions, which proved the bioconcentration of these three pharmaceuticals.[29] Bioaccumulation and bioconcentration are greatly affected by the physico-chemical characteristics of the pharmaceuticals, it varies between individuals, and also the chronicity of the exposure has an effect on the amount of bioaccumulation. For instance, the ionized forms of pharmaceuticals may have a lower uptake, and lipophilicity of the compound is one of the main criteria in the bioaccumulation prediction.[30] No direct generalization can be made about the connection between lipophilicity and bioaccumulation, but many persistent/pseudo-persistent pharmaceuticals have relatively high K_{ow} values which indicate lipophilicity.

Generally, the concentrations detected in the environment vary depending on the location, and also the water body from which the samples have been taken. Puckowski *et al.*[30] have summarized concentrations of diclofenac, ibuprofen, naproxen, and acetylsalicylic acid found in different water bodies. The study has indicated that wastewater influents have much higher concentrations of NSAIDs and analgesics than surface waters. Noteworthy is also that out of

the listed NSAIDs and analgesics, ibuprofen and diclofenac were also found in river waters in small concentrations, as well as in drinking waters in ng L^{-1} scale.[30]

2.1.2 Hormones

The most used, detected, and studied hormones are from the class of estrogens, including the natural steroid hormones estrone (E1), 17β-estradiol (E2), estriol (E3), and a synthetic contraceptive 17α-ethynylestradiol (EE2). Other classes of steroids include androgens (e.g. testosterone, androsterone, dihydrotestosterone, methyltestosterone), glucocorticoids (e.g. cortisol, cortisone, prednisone), mineralocorticoids (e.g. aldosterone, spironolactone), and progestogens (e.g. progesterone, norethisterone).[31] One important characteristic of hormones is endocrine disruption. The endocrine disrupting effects in the aquatic environment are mainly studied on fish that are the most exposed to steroid hormones.[32] Hormones may pose a threat even at nanograms per liter to fish and multiple organisms by affecting the liver, kidney, brain, and gonads.[14] In humans, even little changes in plasma concentration have large effects on the body and mind.[30] Hormones are widely used in livestock farming together with other veterinary medications. The aim is to improve reproduction, and hormones are generally used as a hormonal treatment. Steroid hormones are also often used in fattening beef cattle, and E2 can be used in livestock farming as a growth promoter.[14] In humans, estrogen hormones can be used for example to treat symptoms of menopause, in fertility treatments and hormonal imbalances, and probably most commonly as a contraceptive. Estrogen hormones also have cardiovascular functions and have effects on bone strength.[33]

Both humans and animals excrete hormones. Hormones can make their way into the environment by going through the wastewater treatment system, or without for example through animal feces and urine. Effluents from wastewater treatment plants are considered to be the main source from which steroid hormones make their way into the environment but livestock farming, agricultural runoffs, and industrial discharges also have a significant role in causing environmental pollution.[33] It has been studied that concentrations found near intensive agriculture facilities are greatly higher than those reported in multiple studies done in surface waters. The concentration of individual veterinary steroid hormones is often found to be above

1 µg L^{-1}, sometimes even above 10 µg L^{-1} while mostly reported amounts of steroid hormones are in the range of ng L^{-1}.[31]

Just like other pharmaceuticals, hormones are also broken down into many transformation products (TPs), but unlike analgesics and NSAIDs, the TPs of hormones are usually not as toxic as the parent compounds. Depending on the hormone, humans and animals either metabolize them in the liver forming metabolites or conjugates, or then the excretion occurs as an unchanged parent compound. In the environment, hormones undergo further transformation, such as degradation. Bradley *et al.*[34] have for instance studied that unlike previous studies have shown, especially EE2 is less biodegradable compared to natural estrogens, and has shown environmental persistence. They have also observed that aerobic conditions promote the degradation of natural estrogens in sediments. In addition to the presence of oxygen, other environmental conditions also affect the degradation of steroid hormones in the aquatic environment, such as light.[34] Estrogens have low solubility in water and are often sorpted into soil and sediment. Even though the stability of estrogen in water is highly dependent on the environmental conditions, it can be considered to be persistent.[30] Steroid hormones are lipophilic, which makes them capable of sorption to lipid portions of organisms, and further to bioaccumulate. Especially, EE2 has been reported to be highly bioaccumulative.[35]

2.2 Current monitoring and legislation of chemical contaminants

In Europe, the two leading organizations and regulatory bodies in the field of chemical contaminants are the European Commission, which sets regulations for the European Union (EU), and the European Chemicals Agency (ECHA) which is responsible for REACH Regulation (Registration, Evaluation, Authorization, and Restriction of Chemicals). The EU Water Framework Directive[36] (WFD) has been considered the main legal instrument associated with water protection since 2000. The WFD includes the legislation for inland, transitional, and coastal surface waters, as well as for groundwaters. The directive has set deadlines and provisions for the listed objectives, as well as provisions for exemptions. The WFD includes a list of priority substances that require the Member States to monitor in their surface waters. However, The Environmental Quality Standards Directive (EQSD) has set the standards for these substances. At the moment, EQSD has listed 45 priority substances in the WFD on top of the eight pollutants that were already regulated in the EU before the year 2001. The Member

States must also set Environmental Quality Standards (EQS) for substances of national concern. For groundwaters, there is also its own directive, the Groundwater Directive (GWD). The lists of pollutants and priority substances of the GWD and the WFD are reviewed every 6 years, and necessary updates are made.[36] The aim of both the GWD and the WFD is to achieve 'good' statuses in all surface water and groundwater bodies. The status of a water body can be determined in two different ways. The good chemical status of surface water means that the concentrations of all priority substances remain below the environmental quality standards. Ecological status, however, refers to the responsibility of Member States to set and maintain the quality standards for the substances that pose risks only regionally but not EU-wide. If both of these standards are met, the water body is said to be 'overall good'. The requirement for good groundwater chemical status is to not exceed the standards that are set for the concentrations of specified substances. The concentrations of these substances cannot prevent surface waters from achieving good status.[37]

In October 2022, The European Commission tabled a proposal in which the lists of surface water and groundwater pollutants, as well as the standards, were suggested to be revised. The proposal also included in the concept of monitoring that Member States would be required to apply so-called effect-based methods to assess the cumulative effects of estrogen hormones in surface waters. The cumulative effects would have to be measured over a period of at least 2 years to set possible effect-based trigger values for estrogen hormones for the future. The trigger values would consider both the adverse effects on human health as well as the environment. As understood from the proposal, at the moment the watch list for pollutants in groundwater is not yet mandatory but the proposal would make it mandatory. Along with the list, the Member States would have to conduct monitoring of the substances on the list at least once per year over the period of 2 years. The updated surface water watch list along with the proposal would order the Member States to monitor the listed substances at least twice a year over 2 years as well. In the proposal, it was also mentioned that the ECHA would provide scientific support in compiling the pollutants lists and in devising appropriate quality standards.[37] In September 2023 this proposal was adopted in the plenary session for trilogue negotiations to update the legislation on water pollution.[38]

In addition to proposals for the monitoring of water pollution and the priority substance lists, there is also a consideration for a Commission proposal to update the Urban Wastewater Treatment Directive (UWWTD). The UWWTD is aimed at protecting the aquatic environments from the adverse effects that wastewater effluents cause. The new requirements along with the UWWTD would require advanced wastewater treatment processes to maximize the removal of micropollutants and to minimize their entry into the environment.[37] Even though a lot of progress has been made in recent years considering water pollution, emerging contaminants are still not under official monitoring and legislation. On a good note, pharmaceuticals, and other emerging (organic) contaminants, have been recognized being emerging problems in the European Commission, and for example in HELCOM, too. The concept of EOCs in the aqueous environment will probably be taken more specifically into consideration along with the possible updates on UWWTD.[39,40]

2.3 Occurrence and adverse effects of EOCs

As mentioned before, emerging organic contaminants, such as pharmaceuticals, cause contamination of the environment and water bodies. Even if these contaminants are detected at trace levels, the adverse effects are inevitable and have gained scientific interest in the last few decades. The main sources of emerging organic contaminants in the environment are wastewater treatment plants (WWTPs), hospital effluents, industry, agricultural runoffs, and livestock farming.[1] Emerging organic contaminants have reached all different water bodies around the world, such as groundwaters, surface waters, wastewater influents, and effluents, drinking water sources, coastal waters, and seawater.[41–44] Emerging organic contaminants have even been found from Antarctica which is a specially protected region and which has been previously reported to be unaffected by human impacts.[22] The focus of the adverse effects will be on NSAIDs, analgesics, and hormones which are the most concerning classes of EOCs detected in aqueous environments.

NSAIDS and analgesics have high biological activity, and can potentially cause both acute and chronic toxicity. However, most of the studies have shifted the focus more on the chronic toxicity to which the required amounts are rather low. Acute toxicity requires exposure to such high concentrations of NSAIDs or analgesics that are not even measured in water bodies

worldwide. In general, it can be said that NSAIDs in chronic exposure cause molecular, biochemical, and cellular adverse effects.[45]

As mentioned before, NSAIDs and analgesics, as well as hormones, belong to a group called endocrine disruptors. Endocrine disruptors affect the reproductive processes for example by decreasing fertility and affecting sexual behaviour leading to an effect on population stability.[21,46] Endocrine disruption of hormones can also affect by acting on liver, kidney, brain, and gonads of fish, as well as other organisms in small quantities.[14] In the case of NSAIDs, analgesics, and hormones, this endocrine disruption has been recognized especially in fish which are the most exposed organisms to these contaminants.[21,46] Recent studies have also shown how mixtures of steroid hormones can cause adverse effects on reproduction even when individual hormones in the mixture fall behind the concentration that would cause a measurable effect only on its own. This highlights the concern about the effects of hormones since ever-decreasing concentrations are enough to cause adverse effects.[31]

The adverse effects of emerging organic contaminants to humans, especially pharmaceuticals, are not yet completely, or even well understood. However, it is well known that emerging organic contaminants, especially pharmaceuticals, may affect non-target organisms and are pseudo-persistent due to the high consumption and discharge. [30] Mukhopadhyaya *et al.*[47] have listed the potential effects of EOCs on human health relating to possible chronic exposure, including risks for antibiotic resistance, respiratory and cardiovascular illnesses, effects on thyroid, eyesight, and nervous system, headaches, infertility, and chronic hepatitis.[47] Recent years have also shown clearly the direction of the future research of EOCs. This can be seen for example in the European Union, where a clear and strict strategy for pharmaceuticals is currently under updating.

It is known that emerging organic contaminants have entered drinking waters, mainly because the groundwaters are contaminated with EOCs, which again are the major sources of the community drinking water plants. The main source of EOCs for humans is however through food due to the food chain -transfer. Fish are the most exposed organisms to EOCs in the aquatic environment, and they transfer the EOCs to higher trophic levels. Some of the EOCs present in the aquatic environment will get absorbed into the skin of aquatic organisms, or via

different routes, such as direct ingestion and respiratory surfaces. Fish, for example, have a slow metabolism, which promotes the bioaccumulation of EOCs.[47]

As mentioned, EOCs have reached all water bodies worldwide. European Parliament[37] has published the latest data from WFD reporting in 2015, that 46 % of surface water bodies did not achieve good status (see above), and out of the groundwater bodies, 24 % did not achieve good status.[37] However, there were large differences between the Member States of the European Union.[37] Chaturvedi *et al.*[48] have summarized occurrences of commonly detected pharmaceuticals giving a little glimpse of how dispersed pharmaceuticals are in the aqueous environment. To list a few out already earlier mentioned NSAIDs and analgesics, ibuprofen and diclofenac have both been found in the groundwater and diclofenac also in seawater, naproxen in groundwater, and paracetamol in municipal and hospital wastewaters. The most common hormones, synthetic EE2, and natural steroid hormone E2 are respectively found in waters in wastewater treatment plants and sediments and sludges most likely due to their hydrophobicity.[48] Even though the detected amounts are still low and do not cause immediate concern, it is still concerning how so many different EOCs and their transformation products can be found already in most surface waters, groundwater, drinking water, and all other environmentally studied matrices.[49]

3 Polymers

Polymers get their name from their large size. Polymers, generally also called macromolecules, are very large molecules that are formed from smaller units known as monomers. Monomers are used to synthesize polymers in a reaction called polymerization. Due to the large size of polymers similarly their molecular weights are high, and polymer chains are long. Other characteristics polymers have are low density, and the capability to shape and mold them at relatively low temperatures. These characteristics of polymers, especially those of plastics have made them so commonly used materials that they have even displaced components traditionally made of wood, metal, ceramics, or glass.[50,51]

3.1 General properties of polymers

Polymers can be divided into multiple different classes. The most straightforward division is the one into natural and synthetic polymers. Natural polymers, such as DNA and RNA, proteins, cellulose, lignin, and natural rubber, are materials that can be found in nature and may be for example extracted from plants or animals.[51] Already in the 1800s natural polymers were used to be chemically modified to produce other materials, such as celluloid. Synthetic polymers, however, are considered to be rather modern materials. Synthetic polymers became the topic of interest in the first decades of the twentieth century, and especially World War II along with the post-war years increased the research and development of new polymer materials. Most of the synthetic polymers were developed between the 1920s and the 1950s. These polymers included cellulose acetate, polyvinyl chloride (PVC), polyamides (PA, Nylon), polyvinyl acetate, acrylic polymers, polystyrene (PS), polyurethanes, melamine, polyethylene (PE), polytetrafluoroethylene, epoxies, acrylonitrile-butadiene-styrene (ABS), linear polyethylene, polypropylene (PP), polyacetal, polyethylene terephthalate (PET), polycarbonate (PC) along with many more. The kickoff for polymer synthesis, and development of new polymer materials, were mainly due to the realization and model proposed by Hermann Staudinger that polymers were linear molecular chains.[50,51] From this point on, the term polymer is used to describe different characteristics of especially synthetic polymers.

Polymer resins are always either thermoplastic or thermoset. Thermoplastics become soft and moldable upon heating and will solidify when cooled down. This process is reversible since the cooling down only prevents the long polymer chains from passing each other. The neighboring chains interact with physical bonds, such as van der Waals forces or hydrogen bonds, depending on the structure of the polymers. Thermoset polymers, however, undergo an irreversible curing (hardening) process. Thermoset polymers can be defined as so-called prepolymers that upon heating, radiation, or processing with chemicals, will harden. The hardening is due to the formation of chemical links, crosslinks, between neighboring molecular chains which are usually very permanent structures. These characteristics of thermoplastics and thermosets highly define the possible applications for which these polymers can be used.

Thermoplastics can be even further divided into amorphous and semi-crystalline polymers. Amorphous polymers will remain in disorder as the material cools down, while semi-crystalline polymers will form a certain molecular structure. Even though the ordered structure of a polymer indicates that the structure is crystalline, crystalline polymers very often include disordered regions changing the naming to semi-crystalline.[51] The temperature at which amorphous polymer, and amorphous regions of a polymer, will solidify and be in a glassy state is called glass transition temperature (T_g). Above T_g, the polymer will be a viscous liquid. The term melting temperature (T_m) is used for semi-crystalline polymers due to their crystalline regions, and it indicates the temperature below which the polymer will harden. Above T_m the crystalline regions will melt and become disordered. It is noteworthy that semi-crystalline polymers will exhibit both T_g and T_m.[51,52] Examples of thermoplastics are very common polymers polystyrene (PS), polypropylene (PP), thermoplastic polyurethane (TPU), and polyvinyl chloride (PVC). To the group of thermosets belongs polyesters, epoxy resins, and polyurethanes.[50] Other four groups to which polymers can be identified are elastomers, fibers, paints, and coatings. Elastomers are not as crosslinked as thermosets. The crosslinking is quite low but the polymer molecules cannot still slide past each other.[52]

Polymers as materials are not composed of only polymer chains of certain lengths but they are rather a mixture of various lengths. The characteristics a polymer material holds are strongly connected to the molecular weight of the polymer. It has been described that in the case of polystyrene, the material is stiff and brittle at room temperature when the degree of polymerization is 1000 but sticky and soft when the same degree is 10. Another factor affecting the final structure and properties, such as the crystallinity of the polymer, is the polymer chain branching. The less there are branches, and the shorter they are, the higher degree of crystallinity and density the polymer has.[52]

One last term concerning basic concepts of polymers is copolymer. Copolymers are polymer chains that include two or more different monomer types. Copolymers may be rando, alternating, block, or graft copolymers depending on how the different monomers are arranged in the chain. Copolymerization may be utilized for example to enhance the physical properties of the chosen polymers by making polymer blends.[52]

3.2 Polymer synthesis and modification techniques

3.2.1 Polymerization techniques

One broad classification of polymerization techniques is the division into a step-growth and chain-growth polymerization based on the mechanism. Another used classification is to divide the polymerization techniques into three classes depending on the reaction and how the polymer chain is formed. These three classes and polymerization techniques are chain polymerization, polycondensation, and polyaddition.[50]

In step-growth polymerization, the polymerization reaction proceeds gradually, advancing through a series of steps to form polymer chains, resulting in slow reaction progression and chain formation. Figure 3 shows the simplified mechanism of step-growth polymerization and the formation of a polymer chain. However, it is noteworthy that it is also possible that a monomer reacts with a longer polymer chain, or two polymer chains of any length react with each other. For the reactions to occur, the monomer requires some form of functionality typically at the ends of a monomer.[50] The monomers may be bifunctional or multifunctional.[53] When the step-growth polymerization reaction has occurred, dimers, trimers, and longer polymers have been formed. Monomers typically disappear already at low conversion percentages (see Figure 3). The name step-growth comes from the fact, that the formed polymer retains functionality typically at both ends of the chain and will proceed with further polymerization reactions. In general, any species may react with each other in polymerization as long as they have different functionalities at their chain ends. The reaction proceeds nearly at the same rate all the time because the reactivity of the functional groups does not change but the increase in molecular weight increases exponentially as seen in Figures 3 and 4. Step-growth polymerization reactions are reversible, and the terminal functional groups may undergo reactions with other molecules present in the reaction mixture rather than the building blocks of the polymer chain.[50]

In chain-growth polymerization, the polymer chain is built one monomer at a time. Compared to step-growth polymerization, the length of a polymer does not double after every step and therefore does not follow an exponential trend (Figure 4). In a chain-growth polymerization,

the molecular mass of the polymer and the conversion of functional groups occur linearly. Unlike in a step-growth technique, monomers in a chain-growth polymerization are always present in the reaction mixture, and those monomers are added to the growing polymer chain.[50]

In chain-growth polymerization, there are three phases; initiation, propagation, and termination. One crucial factor in chain-growth polymerization is the presence of active centers. The monomer can only be added to the active center in the propagation step, but the active center needs first to be activated with a so-called generator and/or initiator in the initiation step. Generators are used to activate initiators and their active centers which are further used to kickstart the polymerization reaction. Typically these initiators are either radicals or ionic species, such as anions or cations. Depending on the initiator, the chain-growth polymerization can be said to be either radical or anionic/cationic polymerization. There are also other techniques of chain-growth polymerization in which the basic principle of chain elongation is congruent but there might be small differences in the initiation and control of the reaction, as well as in the mechanism and reaction conditions. As mentioned earlier, step-growth polymerization typically prohibits the simultaneous presence of both monomers and long polymer chains within the reaction mixture. Consequently, monomers are cleared already at low conversion rates. In chain-growth polymerization, however, monomers are the dominant building blocks, and polymer chains of intermediate sizes are not usually present.[50]

The other classification style is to divide the polymerization reaction into chain polymerization, polycondensation, and polyaddition. Chain polymerization does not differ in any way from the chain-growth classification. In a polycondensation process, the reaction between monomers or polymers of any length is a condensation reaction which follows the basic principle of the definition of step-growth polymerization. Polyaddition is the equivalent again for the principles of chain-growth polymerization. In polyaddition, monomers and polymers of any length react by addition reactions where the breakage of the monomer’s double bond enables its attachment to the growing polymer chain. The formed polymers are commonly classified as addition polymers and condensation polymers according to the chemical polymerization reaction. Examples of addition polymers are PVC and polyethylene, and condensation polymers are polyamides and polyesters.[50]

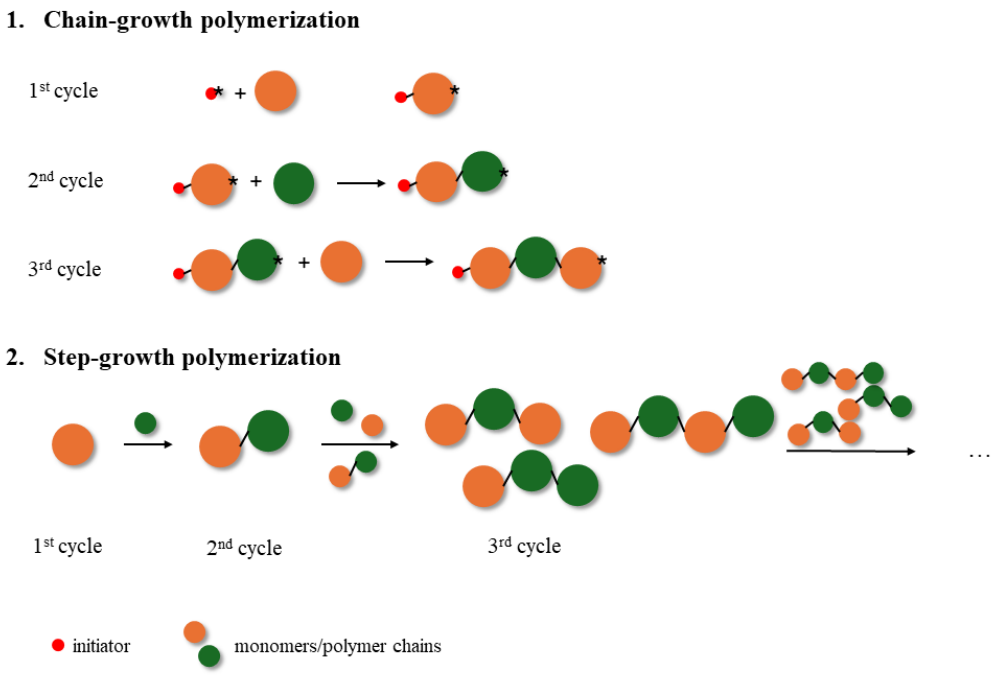


Figure 3. Illustration of chain-growth polymerization and step-growth polymerization.

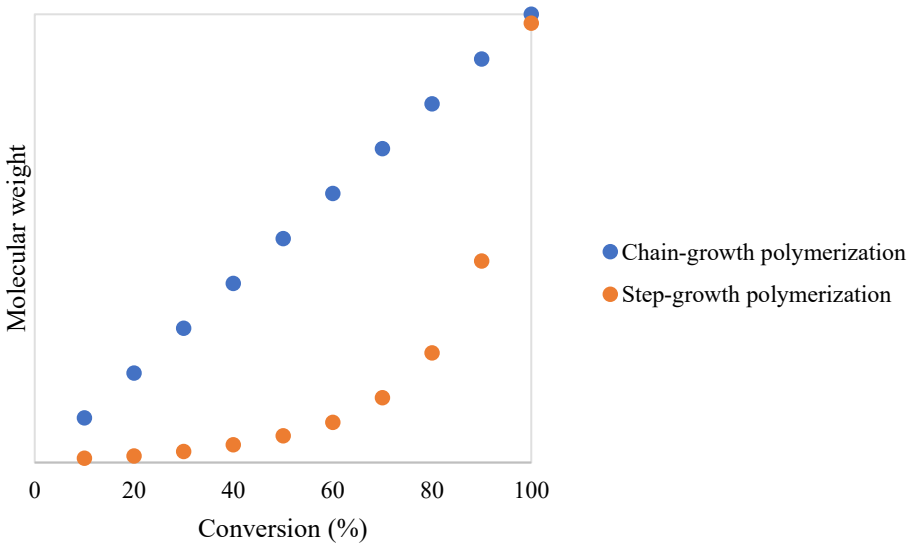


Figure 4. The comparison between chain-growth polymerization and step-growth polymerization.

3.2.2 Polymer functionalization

Polymer functionalization and modification have been a topic in polymer chemistry probably as long as polymer chemistry has been an interest of research, and polymeric materials have been modified from as early as 1840. Polymeric materials are used in an ever-increasing amount in different applications in academia and industry, as well as in the fields of optics, catalysis, electronics, and for example analytical devices. Polymer functionalization offers a great opportunity to produce new polymeric materials with enhanced properties for specific applications typically via rather simple and effective chemistry. In general, the term functionalization means that new functional groups are being introduced to the existing polymer chain.[54] However, this term is quite broad and does not distinguish when the functionalization process occurs in relation to the polymer synthesis. Therefore, the classification of functionalization techniques into so-called pre-polymerization functionalization and post-polymerization functionalization techniques informs whether the functionalization occurs before or after the polymerization.

Pre-polymerization may be characterized as a reaction where monomers holding a specific functionality are added to the polymerization reaction, yielding a polymer with functionality. Copolymerization is one example of these pre-functionalization techniques, which follow the basic idea of the pre-polymerization technique. Another one is chain transfer. Direct copolymerization has been an attractive technique for forming functional polymers. However, copolymerization has its challenges when it comes to functionalization. When the monomers are functionalized beforehand, the required polymerization conditions may not be compatible with the added functional groups and the risk of side reactions may increase. The added functional groups can also decrease the polymerizability as well as the diversity of the monomer structure.[50,54] Even though the polymerization conditions are often brought up as a challenge in direct copolymerization and functional groups, it has been noted that radical-based methods in polymerization, such as nitroxide-mediated polymerization (NMP), reversible addition-fragmentation chain-transfer (RAFT), and atom-transfer radical polymerization (ATRP) do not usually affect the added functional groups even the groups may be reactive otherwise.[54]

Chain transfer can also be classified as one of the pre-polymerization techniques. In a chain transfer reaction, new functional groups are either introduced to the side groups of a polymer chain or the polymer's end groups. In chain transfer, there is an active chain transfer agent (CTA) that typically holds the functional group that is being added to the growing polymer chain, and which can be used for further modification of the polymer. CTA can either react with the polymer's pendants or the end groups and thus these agents can also be used to control the molecular weight of the forming polymer.[55]

The downsides of pre-polymerization functionalization have increased the interest in post-polymerization functionalization techniques. These techniques include for example chemical modification, grafting, end-functionalization, and surface modification, to name a few.[56] Commonly when talking about post-polymerization functionalization techniques, the addition of functionality in the polymer is based on active monomers that after polymerization yield a reactive precursor polymer for further modification and functionalization. The reactivity of these precursors is often based on monomers that feature active ester groups, carbonyl groups, thiols, anhydride functionalities, isocyanates, oxazolines, and epoxides, among many others.[54,57] Grafting as a technique produces graft polymers, where the polymer backbone can be pictured as a tree, and the added chains/grafts along with functionality are the branches. Different structures with desired functionalities can be added to the backbone, or even longer polymer chains. There are multiple ways how the grafting can be performed depending on how the polymer is desired to be modified, including techniques "grafting-onto", "grafting-from", and "grafting-through" with slight differences in mechanisms. The utilization of active precursor polymers is the most used post-polymerization technique to form functionalized polymers, and it also offers endless possibilities to form new polymeric materials. However, this technique requires the reactive monomers as starting materials which is one of the downsides of this technique.[50]

Direct chemical modification of polymer materials is a rather less-used technique in functionalization and has fewer opportunities compared to those techniques where monomers as starting materials bear reactive groups. By direct chemical modification it is meant that polymer material is modified chemically without the need to break the polymer into monomers at any given point, and monomers are not needed as a starting material but polymers are

modified as polymers. The commonly used polymer materials, such as polystyrene, polyethylene, thermoplastic polyurethane, and polypropylene do not have high functionality and hold simple structures. This characteristic may cause challenges in reactivity but on the other hand, these polymers offer a simple template that can be modified with specific and desired functionalities. This approach offers many possibilities especially when considering polymer upcycling, and improves the possibilities to reuse polymeric materials. Polymer materials are often recycled either by reusing the material or by mechanical or chemical recycling. Chemical recycling means that the polymer is turned back into smaller units, often monomers, and mechanical recycling means the physical grounding of the polymer. Monomerization as a process is however very energy-demanding, and the reuse of the monomer material would require a second polymerization reaction in any situation. Therefore, if the polymer can be modified without affecting the polymer backbone structure, the modification process becomes more energy-friendly and the reuse requires fewer steps.[58]

The classification of different strategies of polymer waste treatment is generally landfilling, mechanical recycling, functional recycling, chemical re-/upcycling, and incineration. All of these techniques require either bond breakages in the polymer structure, or the costs or the energy required is high. Recently, the term ‘functional upcycling’ has been introduced as one potential alternative to reuse polymer waste inexpensively without the need for chain destruction. The term functional upcycling contains different post-polymerization modifications as well as surface modifications of polymer materials. The potential applications of upcycled polymers are for example used in adsorption, electrode materials, and as catalysts.[59] Functional upcycling and post-polymerization techniques of polymers have a lot of potential for future research.

3.2.3 Polymer additives

Polymer additives are used to enhance the processability of polymer materials as well as to improve their performance in different applications. One typical classification of polymer additives is to divide them into those that maintain the polymer’s properties and those that are used to extend the properties. The maintaining additives can also be named polymer stabilizers, and additives that extend the properties are often called functionalizing agents. As the name

suggests, maintaining additives are used to preserve the inherent characteristics and properties of polymer materials. These additives protect the polymer material generally from mechanical and chemical attacks. Polymer materials typically undergo challenging conditions during material processing and are exposed to challenging conditions during use as well, including exposure to high temperatures, challenging weather conditions, and ultraviolet light. Utilizing additives aligned with the degradation mechanism of the specific polymer can prevent polymer degradation caused by various conditions and processes. Different polymers may also have different stabilities against degradation. For example, polystyrene is not as sensitive to oxidation as polypropylene. Typically, only preventing one factor leading to degradation is not sufficient in stabilizing the polymer and therefore different additives are blended to reduce the chances of degradation. The group of polymer stabilizers includes for example antioxidants, processing and heat stabilizers, lubricants, and acid scavengers.[50]

On the other hand, sometimes the polymer properties must be extended with additives called functionalizing agents. Functionalizing agents are used to expand the possibilities of using polymers in different applications, even in demanding applications. With these additives, the life of the polymer or plastic application can be prolonged, and the commercial value of these materials can be enhanced. Some of the additives are used to affect the bulk or the surface properties of the material, or the additives may be used to modify the polymer structure. Thus, the range of additives in this group is large, and the additives are highly dependent on the use and the chosen application. Examples of these additives are flame retardants, antimicrobials, pigments, antistatic agents, and coupling agents.[50] Most commonly used polymer stabilizers and functionalizing agents and their use are summarized in Table 1.

Table 1. The most common polymer additives.[50]

Additive	**Purpose**
Antioxidants	Reduce oxidative degradation during processing and in applications by reacting with radicals by forming thermally stable products.
Light stabilizers	Reduce light degradation and photooxidation with the use of UV absorbers, quenchers, and free-radical scavengers by reacting with radicals.
Heat stabilizers	Prevent thermal degradation and color change under heat mainly by scavenging HCl and preventing further reactions.
Lubricants	The aim is to reduce friction between different polymer parts, minimize wear, and prevent overheating of the material.
Scavenging agents	Include acid scavengers, aldehyde scavengers, odor-reducing scavengers, and moisture scavengers.
Antimicrobials and biocides	Inhibit the growth of antimicrobials such as bacteria, fungi, and molds by interacting with microbial cells.
Flame retardants	Used to reduce the risk of fire for example in applications used in electronics.
Plasticizers	Used as a processing aid to decrease the melting and processing temperatures of polymer materials, and to make the polymer softer and more flexible.
Foaming agents	Used to introduce gas bubbles to polymer materials, forming an airy, foam structure. Foaming agents may be physical gases or chemical substances that later release gas into the material.
Cross-linking agents	Used to increase cross-linking between polymer chains to enhance the mechanical properties of a polymer.

Coupling agents	Increase the adhesion (coupling) between two different polymer materials and/or fillers and a polymer matrix by helping to form interfacial bonds.
Antistatic agents	Decrease the electric charges that may build up in polymeric materials making handling easier, and reducing risks for contamination and electrical discharges.
Antifogging agents	Inhibit water condensation on the polymer surface by increasing the surface energy of the polymer and decreasing the surface energy of the water droplet.
Nucleating agents	Used to increase the crystallization and crystallinity of polymer materials. Also speeds up the conversion from melted material to solid material.
Animal repellents	Used to eliminate the potential damage animals may cause to applications that are somehow exposed, such as cables. Animal repellents include for example substances with unpleasant odor/taste.
Antiblocking agents	Used to prevent sticking of polymer films or sheets together that may occur due to temperature, pressure, or humidity.

3.3 Polymer characterization techniques

Nowadays the number of polymeric materials is huge. This wide range of polymers includes materials that may be very different in physical properties, and the applications these polymeric materials are used may vary a lot. Polymer blends are commonly used these days to enhance the performance of a polymer in certain conditions. However, the use of polymer blends may introduce additional complexities to characterization studies due to distinct properties of different components, having an effect for example in melting and other thermal or thermodynamic properties, and crystallinity. Characterization studies of polymers are necessary in research in general, as well as in practical applications.[50]

The characterization studies of polymers include a wide range of techniques that can be used depending on the physical properties of the polymer. These techniques include for example different spectroscopic techniques, compositional analysis, molecular mass determination studies and elemental analysis, X-ray diffraction, microscopy, and thermal analysis.[50,60] These will be discussed briefly in the next chapters.

3.3.1 Polymer spectroscopy

Spectroscopic techniques play a crucial role in polymer characterization studies providing information about the molecular structure of the polymer, its composition, chemical groups, configuration, conformation, and behavior in general. Spectroscopic techniques that are utilized in polymer characterization are Infrared (IR) Spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, Mass Spectrometry (MS), Raman spectroscopy, Ultraviolet-Visible (UV-Vis) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Circular Dichroism (CD) spectroscopy, the first three of which will be discussed here.

Infrared (IR) spectroscopy is based on IR radiation which is passed through the sample. The infrared ray in the sample can either be absorbed or transmitted in the sample depending on the chemical groups the molecule possesses. The radiation causes changes in molecular dipoles, which is again caused by movements between atoms and chemical bonds. The molecular bonds will rotate and vibrate. Vibrational movement includes bending and stretching, which may either be symmetrical or asymmetrical. Different functional groups will absorb their characteristic frequencies, and the detected peaks in an IR spectrum correspond to the frequencies that specific chemical groups have absorbed. Consequently, the IR spectrum is a molecular vibrational spectrum. IR regions can be divided into near (15,000-4,000 cm^{-1}), mid (4,000-400 cm^{-1}), and far (400-10 cm^{-1}) IR regions. Polymers typically show important absorption bands in the mid-region. IR regions are used for the qualitative analysis of polymers, but quantitative analysis may also be employed with IR. For instance, the number of functional groups in a molecule of polymer can be measured since the absorptivity of the bands is proportional to the functional groups.[50,61]

There are two main types of IR spectrometers, IR-dispersive and Fourier transform (FTIR) spectrometers. FTIR has replaced the IR-dispersive spectrometers in most applications due to multiple advantages in the technique and use.[61] So-called attenuated total reflectance (ATR) FTIR is the most used method to measure a wide range of different types of samples quickly and easily, including solids, liquids, powders, semisolids, and pastes.[62] ATR-FTIR spectroscopy is utilized in the experimental part of this thesis as well to measure the characteristics of polystyrene powder.

Nuclear magnetic resonance (NMR) spectroscopy can be used either for qualitative or quantitative analyses of polymers, and also in compositional analysis. NMR spectroscopy is based on the magnetic characteristics of NMR active atomic nuclei. The atomic nuclei, and their nuclear magnetic moments, will interact with the external applied magnetic field, and in the magnetic field these nuclei will align either parallel or antiparallel along the magnetic field. When a radiofrequency pulse (RF) is applied, the nuclei will absorb the electromagnetic radiation and are temporarily perturbed from their original positions. After the applied RF pulse, the nuclei will relax and release their excited energy as radiofrequency signals. These signals can be processed through Fourier transform to generate the NMR spectrum. The molecule structure can be elucidated from the chemical shifts of the NMR spectrum. The local magnetic environment of the nuclei will affect the position of the generated peaks.[50]

NMR can be performed both for solids and solutions. Liquid-state NMR for solutions is the most commonly used NMR experiment. The resolution and sensitivity are often very good for liquids, sample preparation is easy, and it gives good molecular structure information in general.[50] The main difference between liquid-state and solid-state NMR is that solids lack the molecule-level movement of which liquid samples are capable. The resolution and the quality of the spectrum are also highly dependent on the sample packing, and homogeneity of the sample, and the resulting signals may easily overlap. However, solid-state NMR is invaluable in certain situations and can be utilized for example for crystalline solids, inorganic solids, polymers, and plastics.[63] The qualitative analysis of polymers is beneficial for example in monitoring the progress of polymer synthesis by comparing the spectra of the original polymer to the spectra of the synthesized polymer. Quantitative analysis may however be utilized for example in compositional analysis where the composition of a mixture of polymers, polymer

blends, or components of copolymers can be analyzed by measuring the intensities of peaks to each component in the mixture.[50]

Mass spectrometry may also be used either for qualitative or quantitative analysis. Mass spectrometry can be used to identify unknown compounds, in an analysis of the degradation products of polymers, in structural characterization, and also in polymer additive analysis. Copolymer/Comonomer composition identification is possible with mass spectrometry, as well as the analysis of end group composition and molecular weight with which the degree of polymerization can be elucidated. Soft ionization sources are used in the mass spectrometry of polymers, including matrix-assisted laser desorption/ionization (MALDI), electrospray ionization (ESI), and atmospheric pressure chemical ionization (APCI).[64] MALDI has gained relatively much attention a few years back especially in polymer analysis since it is suitable for thermolabile, unstable, and nonvolatile samples. The most commonly used mass spectrometer along with the MALDI ionization source is the time-of-flight (TOF) mass spectrometer mainly due to its large mass range. MALDI-TOF-MS is considered to be a fast and accurate method in polymer characterization. For instance, functionalized polystyrene and non-functionalized polystyrene are commonly analyzed by MALDI-TOF. MALDI is a good choice as an ionization method especially when polymers have functional groups in their chains.[50,64]

3.3.2 Elemental analysis and molecular mass determination

Elemental analysis is used mainly in copolymer characterization, as well as in the characterization of polymer blends. It can also be used in the determination of the molecular weight of homopolymers. Elemental analysis is used to ascertain the composition of the sample mostly as a supporting technique while other methods, such as spectroscopic methods, are used in more precise structural elucidation. However, it can be an important factor in indicating the polymer. The most common way to do elemental analysis is by combustion techniques, for instance by burning the sample in an oxygen-containing atmosphere. In this manner, the composition of the sample, and the amounts of carbon, hydrogen, nitrogen, sulfur, halogens, and oxygen may be determined.[50]

For molecular mass determination, there are several different methods, including viscosimetry, osmometry, light scattering techniques, mass spectrometry, NMR, gel permeation chromatography (GPC), and size exclusion chromatography (SEC). GPC and SEC are based on determining the weight distribution of polymers as they separate while going through a porous gel matrix. Osmometry, more precisely vapor-pressure osmometry, is based on the osmotic pressure of a polymer solution where the polymer particles reduce the solution's vapor pressure. The viscosity of polymer solutions is also related to the molecular weight of the polymers.[50]

3.3.3 X-ray diffraction

The X-ray diffraction (XRD) technique utilized for polymer characterization nowadays is more precisely small-angle X-ray scattering (SAXS). This is used to determine the structure of the polymer: what are the distributions of the crystalline and amorphous regions, and how thick these regions are. SAXS is capable of dealing with large-scale structures while so-called wide-angle X-ray scattering (WAXS) only with the atomic and molecular structure of crystals. In addition, there are differences between the crystalline and amorphous phases and their electron densities in polymer materials, and thus SAXS is more suitable for the analysis of semicrystalline polymers and their morphology.[65]

The polymer structure and the composition of different forms detected in the polymer are commonly dependent on how the polymer has been formulated and processed. As mentioned before, polymer materials do not usually consist of only one form or phase but are rather formed from a few different forms of polymer which include highly-crystalline, semi-crystalline, microcrystalline, or amorphous forms. Even though XRD methods are used for the characterization of polymer structures, there are also challenges in their use since many polymers are not capable of forming crystals. And even those polymer materials that can crystallize, they often have large fractions of amorphous material which cannot be detected by using XRD.[65]

3.3.4 Microscopy

Microscopy is used to provide information about polymer structure, morphology, topology, elemental composition, and chemical bonding. The most commonly used microscopic techniques that are used in the characterization of polymers are electron microscopy (EM) techniques which can be broadly divided into two classes; scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Both SEM and TEM include a variety of different subtypes, which can provide high-resolution images compared to other techniques. Electron microscopy is an applicable technique for polymer characterization since the surface and surface morphology of a polymer are closely related to the composition, the processing conditions, and the sample preparation. However, with more advanced microscopy techniques the internal structures of polymers can also be investigated.[66]

SEM has been reported to be used in the examination of particle size and shape. It is the most popular microscopic technique used mainly due to easy sample preparation, and its simple use.[65] The four main classical modes of SEM are SE (secondary electron) imaging, BSE (backscattered electron) imaging, EDX (energy dispersive X-ray) spectroscopy, and STEM (scanning transmission electron microscopy), which also belongs to the group of TEM techniques. SE provides information about the topology of a polymer, BSE is related to the chemical composition, EDX yields the elemental composition on a microscopic scale, and STEM may be used in the visualization of the polymer material. STEM is applicable to the visualization of the interior morphology, surface and sub-surface morphology, and even direct visualization of surface/internal morphology of thin nanomaterials. It is noteworthy, that numerous SEM techniques are available for the characterization of polymers which may provide valuable information on the structure of the polymer. In addition to 2D information which is provided from the most common microscopic techniques, there are also multidimensional techniques with which 3D visualization may be achieved.[50]

TEM is used to give information about the structure and morphology of polymers. Compared to STEM, which is one variation of SEM, TEM can provide better contrast but the detected resolution is lower. TEM in characterization studies is used for detailed internal morphology studies, surface and subsurface morphology studies, as well as in the determination of

morphology of polymer nanomaterials. These are analogous to the studied properties in STEM. Even though TEM can provide valuable information in polymer characterization studies, it is considered to be a secondary technique while SEM methods have the dominant role.[66]

3.3.5 Thermal analysis

The main basis of thermal analysis is to investigate what happens to certain materials and their properties while being heated, held at a specific temperature, or cooled down. The main thermal analysis techniques are differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA), of which DSC and TGA are the most popular ones. The property that is being measured changes depending on the technique that is used. For instance, DSC measures the heat flow into or out of a sample as a function of temperature, TGA measures the mass of the sample as a function of time and temperature, TMA tracks changes in length or volume in response to temperature or force, and DMA is used to analyze viscoelastic properties. There are various combinations of thermal analysis to improve the specificity of the analysis or characterization. TGA and Mass spectrometry, or FTIR can be combined.[67]

The thermal properties of polymers include heat capacity, glass transition (T_g), crystallization, and melting. Heat capacity presents the amount of heat that is needed to increase the system's temperature certain amount. Glass transition temperature is the interface in which the material's properties change due to changes in chain mobility. Glass transition temperature is reached when a melted polymer is cooled down, and the material changes from elastic material to more solid. When the temperature is above the polymer's glass transition state, the polymer chains have high mobility. Crystallization is reached when the polymer chains can form ordered structures. Crystallization is an exothermic process and therefore can be often detected in a plot of heat flow versus temperature. When melting temperature is reached, polymer chains can move around freely. While the polymer melts, no temperature changes are detected but after the whole polymer has melted, the temperature starts increasing again. However, the heat capacity changes after melting, just as it changes on both sides of the glass transition temperature. After melting, the heat capacity of the material is higher meaning more heat is required to increase the system's temperature, and thus the increase in temperature is slower.[68]

Differential scanning calorimetry (DSC) is the most popular technique in thermal analysis. The instrument is rather inexpensive, and the technique is simple and easily applied to samples. In DSC, temperature is the crucial quantity that is measured while all the other quantities are measured, or calculated, as a function of temperature. DSC measures the heat absorbed or released by a sample as its temperature is increased or decreased. This provides insights into the material's thermal behavior and how it responds to changes in temperature and heat flow.[69] The temperature program is controlled, and the temperature ramp is linear.[67] Both endothermic and exothermic processes are monitored, and the results are commonly presented in a plot of heat flow versus temperature.

Thermogravimetric analysis (TGA) was used as one of the main characterization methods in this thesis and is one of the most common techniques in thermal analysis. Compared to DSC, TGA measures the change in the sample's mass when the sample is either heated or cooled down. The temperature program, as well as the atmosphere, is controlled. The atmosphere is created with the purge gas, which can be either inert (nitrogen, argon, helium), oxidizing (air, oxygen), or reducing. Polymers commonly undergo mass loss in TGA analysis through which information about composition, extent of cure, and thermal properties of the polymer may be yielded. The maximum temperature used for polymers in TGA analysis is typically 1000˚C.[67]

4 Adsorption as a tertiary treatment in the wastewater treatment process

The wastewater treatment process can harshly be divided into four parts; preliminary, primary, secondary, and tertiary treatment. These treatments contain physical, chemical, and biological processes that are focused on the removal of pollutants and contaminants. The wastewater treatment process has been reported to remove the majority of contaminants, for example, more than 95 % in Finland.[70] However, the problematic chemicals and substances for the wastewater treatment processes commonly listed in Finland as well as in multiple different countries are detergents and cleansers containing phosphates and chlorine compounds, various substances used as personal care products and for instance in cosmetics, finishing substances of textiles, flame retardants, different paints, varnish and stain removers, viruses, metals, microplastics

and lastly pharmaceuticals. The removal efficiencies between these groups vary, as well as the removal efficiencies inside these groups depending on the specific compound or chemical.[71] Wastewater treatment facilities have extorted and invested especially in the purification of nutrients, such as phosphorus, as well as organic matter during the last few decades and a noticeable decrease in the concentrations has been detected. The removal of nitrogen and other (organic) contaminants still varies today, and thus more efficient purification processes must be developed for the tertiary treatment phase.

Shortly, the wastewater treatment process starts with pretreatment processes that utilize different physical-chemical methods as well as mechanical methods such as sedimentation and coagulation. The primary treatment contains the treatment of pretreated effluent with physical-chemical and chemical methods including techniques like coagulation, precipitation, and flocculation. Treated effluent continues to secondary treatment and undergoes physical-chemical methods and biological treatment.[72] Biological treatment is typically based on the utilization of microbes either under aerobic or anaerobic conditions[73] with which biodegradable organic matter and solids can be removed through biological decomposition.[74] Other secondary treatment techniques are for instance filtration and adsorption.[72] The tertiary treatment process is considered the last step before water discharge. Tertiary treatment processes are advanced processes required to remove concerning contaminants, such as final nutrients and toxic compounds from the treated wastewater.[74] This last treatment process includes physical and chemical methods, and a wide range of different techniques such as different filtrations, oxidation and membrane techniques, ozonation, chlorination, and adsorption.[73] New tertiary treatment processes are continuously developed and designed for several reasons, including stringent environmental regulations, emerging contaminants, and resource recovery. Utilization of adsorption is one of the tertiary (and even secondary) methods. The experimental part of this thesis is largely based on the use of adsorption in the removal of pharmaceuticals from water samples.

Adsorption is a process in which adsorbate attaches to the surface of an adsorbent. Adsorbates are typically molecules or ions that are present either in liquid or gaseous bulks. Adsorbents, in turn, are often solids, rarely liquids, that come in contact with the adsorbates. The binding to the surface of the adsorbent can be either physical (physisorption) or chemical

(chemisorption). If the adsorbate is bound chemically, the formed interactions are strong, for example, covalent bonds. Physisorption occurs via weaker interactions between molecules, such as van der Waals interactions, hydrogen bonds, or electrostatic interactions, depending on the properties of the attending molecules.[75,76] Adsorption has been claimed to be one of the most promising purification techniques for wastewaters (effluents) and contaminated waters in general. Adsorption is not considered to be a new technique but has gained popularity due to its simplicity and the possibility to utilize it in many applications. In addition, the used adsorbents may also be recyclable and even reusable due to the reversible process of adsorption called desorption. The advantages of adsorption have been highlighted especially in the removal of the remaining pollutants after the wastewater treatment processes, such as heavy metal ions, dyes, organic macromolecules, pharmaceuticals, and even environmental gases.[76,77]

The most common, and also probably studied adsorbent for organic contaminant purification is activated carbon, and other carbon-based materials in general.[78] On the other hand, one of the most promising adsorbent materials is focused on the utilization of polymers due to their high surface area, and relatively strong affinity for multiple different contaminants. Polymers are also applicable to different environmental applications. Other materials that are used as adsorbents in water treatment include for instance zeolites, clay minerals, resins, alumina, and silica.

4.1 Carbon-based materials in adsorption

One of the most commonly used carbon materials in adsorption is activated carbon which is used as an adsorbent to remove a wide variety of contaminants from gases and liquids, such as in water treatment. Activated carbon generally has an amazing capacity to adsorb contaminants, especially emerging contaminants[79] even when used in low amounts due to its large surface area. The material is porous and can be used in a wide range of applications in physical adsorption. To be more specific, activated carbon is generally microporous adsorbent and thus will adsorb smaller molecules more effectively than larger molecules. Other carbon-based adsorbents are carbon nanotubes, graphene, and fullerene.[80]

Activated carbon is primarily used in two forms in water purification processes, powdered and granulated activated carbon. Powdered activated carbon has a greater removal capacity for

many contaminants but granulated activated carbon, in turn, has already been used in several wastewater treatment plants. This is because the regeneration and recycling of granulated activated carbon is easier than that of powdered activated carbon. The recycling of powdered activated carbon is possible but is hardly ever done these days. In addition to the challenges in the regeneration of powdered activated carbon, the desorption of contaminants from the material is difficult, and the powder also poses practical challenges in handling. Also, the recycling conditions typically require at least relatively high temperatures.[79,81] One final drawback of activated carbon in adsorption is that the removal efficiency towards some contaminants, such as certain dyes, is however low.[82]

4.2 Polymer-based adsorption

Polymer-based adsorption holds a lot of potential for future research on water purification and has already had an important role in the purification of polluted waters.[77,83] Frimodig *et al.*[84], Lahtinen *et al.*[85], Kulomäki *et al.*[86] and Tang *et al.*[87], to name a few, have successfully shown that simple polymeric materials such as polyamide can adsorb estrogen hormones, heavy metal ions, and dyes, respectively, from liquid samples.[84–87] Different additives to polymer materials, such as nanoparticles, can further increase the adsorption capacity of polymers. Altogether, these results have proved that polymeric materials can inherently, as well as together with additives, adsorb contaminants with relatively high removal efficiencies.

Both natural and synthetic polymer materials have been used in adsorption in different applications. These applications include different films, membranes, nanocomposites and nanofibers, porous materials, and hydrogels, which all may have different properties and functionalities. Recently, especially the role of nanotechnology has increased in both as its own method as well as together with adsorption.[83] One of the main advantages polymeric adsorbents hold is the numerous possibilities to modify the polymer structure. The modifications can be for example done to create a selective adsorbent for specific compounds or chemicals, such as for water contaminants. The modifications may also improve the original properties of the polymer material and thus expand the possibility of using it in different applications even in extreme or challenging conditions. The addition of functionality also generally increases the number of possible adsorption sites, and therefore further increases the adsorption capacity of

the material.[77] Especially in porous materials and hydrogels the functional groups in the material play a major role in the degree of adsorption capacity.[83] Pu *et al.*[88] have demonstrated how amidation of waste polystyrene created an efficient recyclable adsorbent for the removal of organic dyes.[88] Other factors in addition to the functional groups affecting the adsorption capacity in these different applications include the pore sizes in the porous materials, the permeability of the membrane materials, and the surface area.[83] One disadvantage that may decrease the adsorption capacity when it comes to polymeric materials is the potential cross-linking of the polymer chains. Cross-linking may cause the functional groups of the polymer chain to react with each other which in turn decreases the number of adsorption sites for the contaminants.[5]

5 Experimental

The experimental work of this master's thesis can be divided into three major phases including the functionalization of polystyrene with Friedel-Crafts acylation, characterization studies of the functionalized polystyrene material, and finally the adsorption studies including the analysis with UHPLC-MS. For the adsorption studies, selective laser sintering (SLS) 3D-printing was also utilized to print 3D-scavengers of polystyrene powder to help the performance of the adsorption studies.

The utilized reaction, Friedel-Crafts acylation, in the polystyrene functionalization was modified and optimized from the studies of Liu *et al.*[89] and Li *et al.*[90].[89,90] Functionalization of polystyrene was first done for commercial polystyrene powder which can be used as a printing material in SLS 3D-printing. Later in the study, the optimized functionalization reaction was performed for recycled material of expanded polystyrene (EPS, styrox). Characterization studies for the produced solid material were performed with different solid-state methods including NMR, FTIR, and TGA. The degree of functionality was also determined by using acid-base back titration.

Adsorption studies were conducted for two commonly used pharmaceuticals, naproxen and diclofenac. The adsorption studies aimed to demonstrate the adsorption capacity of the functionalized polystyrene material. The adsorptivity of the functionalized polystyrene was analyzed by using UHPLC-MS. Adsorption studies required solid support materials for the formed modified polystyrene powders, which were printed from unmodified polystyrene with an SLS 3D-printer. All the used reagents are presented in Table 2 and all the used equipment are shown in Table 3.

Table 2. The used reagents.

Reagent	Manufacturer
Aluminium chloride ($AlCl_3$)	Sigma-Aldrich
Dichloromethane (DCM)	AnalaR NORMAPUR
Diclofenac (2-(2,6-Dichloroanilino)-phenylacetic acid)	TCI Chemicals
Expanded polystyrene (EPS)	-
Hydrochloric acid (HCl)	Sigma-Aldrich
(+/-)-Naproxen	TCI Chemicals
Methanol (MeOH)	J.T.Baker
Phenolphthalein (Phph)	-
Polystyrene powder (PS)	Axalta Coating Systems Ltd
Sodium hydroxide solution (NaOH)	Sigma Aldrich
Succinic anhydride (SA)	Sigma-Aldrich
Ultrapure water	Elga Purelab Ultra

Table 3. The used equipment.

Equipment	Manufacturer and model	The used purpose
3D-printer	Sharebot SnowWhite SLS 3D-printer	Adsorption studies
FT-IR	Bruker Alpha Platinum-ATR	Characterization studies
NMR	Bruker AV 400 Ultrashield with CP/MAS solid-state probe	Characterization studies
Peristaltic flow rate pump	Shenchen LabV1 Flow Rate Tube Pump	Adsorption studies
TGA	Perkin Elmers STA 600 Simultaneous Thermal Analyser.	Characterization studies
UHPLC-MS	Agilent 1290 Infinity UHPLC system coupled with Agilent 6460 Triple Quadrupole -mass spectrometer	Adsorption studies

5.1 Functionalization of polystyrene

Approximately 1 g of succinic anhydride (SA) and 4 g of aluminum chloride ($AlCl_3$, catalyst) were stirred in 100 ml of dry DCM (3Å molecular sieves) for 2 hours at room temperature. The moisture intake was controlled with a condenser coupled with the used round-bottom flask and a $CaCl_2$ guard tube. The reaction mixture required rapid stirring to disperse the starting materials evenly to the used dispersing agent, and to enable as efficient reaction between the reagents as possible. Visible reaction between SA and $AlCl_3$ was seen after stirring approximately for 20 minutes. Visible change from light yellow to light beige could be detected as well as a visible change in the composition of the reaction mixture (Figure 5). 1.04 g of polystyrene powder was first dissolved in 50 ml of dry DCM (3Å molecular sieves) and added in a dissolved form to the reaction mixture to ensure the polymer's dispersion to the mixture. Rapid stirring was continued and the reaction was put under a nitrogen atmosphere. Rapid color change of the reaction mixture from light beige to bright orange occurred after the addition of the dissolved polystyrene (Figure 5). The orange color indicates the successful functionalization reaction. The reaction mixture was left to stir for approximately 1.5 hours. Figure 6 shows a scenario where polystyrene powder is not dissolved to DCM beforehand. Polystyrene clumps immediately after getting in contact with the reaction mixture, and the reaction occurs mainly on the surface of the formed polystyrene clump.

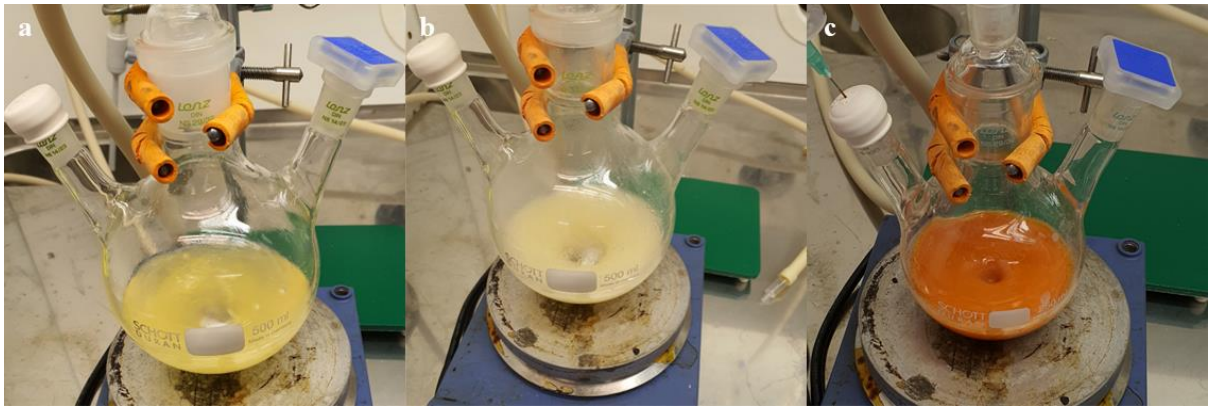


Figure 5. The functionalization of polystyrene, where a) represents reaction initiation, b) represents the reaction mixture after stirring for 20 minutes and c) shows the reaction after the addition of polystyrene.

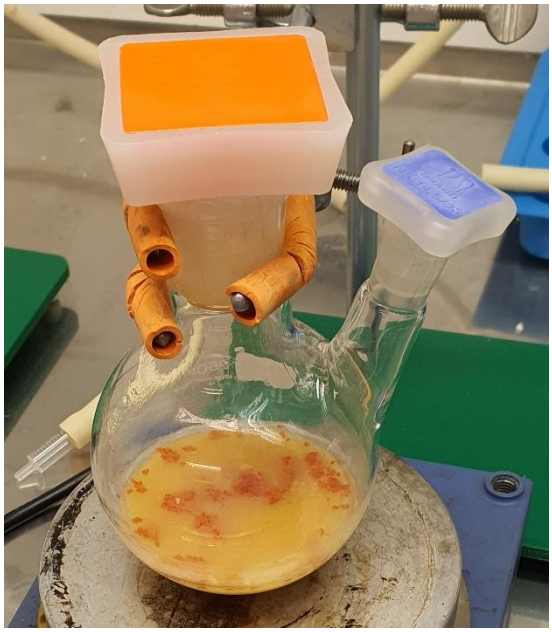


Figure 6. Polystyrene added as a solid to the reaction mixture.

The reaction was quenched with additions of ice water and 0.5 M HCl solution. The quenching reaction was exothermic, and the round-bottom flask was cooled down in an ice bath throughout the additions. The addition of 0.5 M HCl and ice water caused a color change from the previous orange suspension to white. In this quenched reaction mixture, there was a noticeable separation between the organic solvent layer and water-based layer, and the polymer was separately as a solid material insoluble in either phase. The polymer was separated from the liquid material by vacuum filtration and washed multiple times with ultrapure water (UPW). The purified polymer was first left to dry at room temperature overnight, and further drying was done by heating at 130˚C. After drying at room temperature, the polymer material was easily grindable to a light yellow fine powder. The overall synthesis scheme of the functionalization is presented in Figure 7.

Exactly the same synthesis was conducted for recycled expanded polystyrene (EPS). The only difference in the syntheses was that EPS was not powder but a solid block of polystyrene foam which was dissolved in DCM similarly as the commercial polystyrene powder. Both syntheses were replicated multiple times to ensure the reliability of the synthesis as well as to ensure a good amount of functionalized polystyrene for the following adsorption studies.

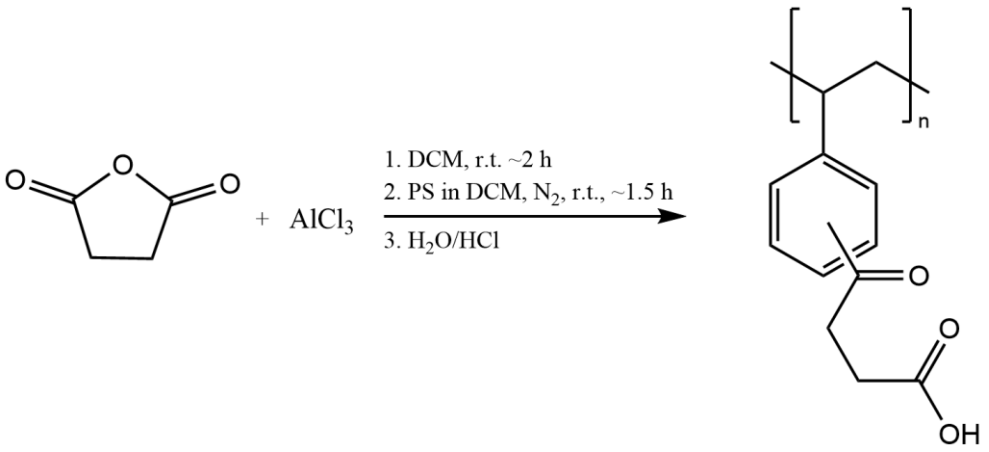


Figure 7. The synthesis scheme of polystyrene functionalization with Friedel-Crafts acylation.

The optimization of the required molar ratio of the starting materials, $AlCl_3$ (catalyst) and SA, was performed by conducting multiple different syntheses with different molar ratios of $AlCl_3$ and SA to solve the correct ratio to yield the highest degree of functionalization. The added amounts of the starting materials are presented in Table 3. The amount of added polystyrene was kept unchanged as well as the volume of the solvent which was chosen to be 50 ml of dry DCM (3Å molecular sieves).

Table 4. Starting materials ratios and approximate values of the starting materials.

[$AlCl_3$]:[SA]	Added amount of $AlCl_3$ (g)	Added amount of SA (g)
2:1	1.0	0.5
3:1	1.5	0.5
4:1	2.0	0.5
5:1	2.5	0.5
6:1	3.0	0.5

5.2 Characterization studies

The characterization studies of the functionalized polystyrene materials were based on techniques that are applicable to solids. The polymer material did not dissolve to any of the tried solvents, techniques suitable for solutions, such as ^1H proton NMR, were not applicable for this purpose. The chosen characterization techniques were NMR spectroscopy, FTIR, TGA,

and acid-base back titration. The main aim of the characterization was to determine whether the techniques could detect the added functionality, and to compare the polymer's properties before and after functionalization.

5.2.1 NMR spectroscopy and IR spectroscopy

^{13}C NMR spectroscopy was performed with Bruker AV 400 Ultrashield with CP/MAS solid-state probe. The analyzed sample was fine yellow powder yielded from the functionalization of polystyrene (see above). The NMR spectroscopy brought its challenges with this polymer material. Conventional ^{13}C NMR did not produce good results as the peaks were lost in the noise, and this technique required very long acquisition times. With the CP/MAS solid-state probe, the yielded spectra were better than with conventional ^{13}C NMR. The detected peaks were rather broad as in polymer characterization with CP/MAS typically, and the acquisition time was also relatively long. However, CP/MAS was the only NMR method that was suitable for this polymer material and could provide a good spectrum of the polymer. The packing of the material to the rotor also proved to be a crucial step in yielding a good spectrum. The parameters were optimized for this sample, and rotor speed was set to 10,000 Hz, contact time to 2 ms, and relaxation delay to 4 s. The sample was at room temperature (25˚C, 297 K) throughout the experiment. ^{13}C CP/MAS NMR was conducted for the products of multiple separate syntheses done with commercial polystyrene powder to ensure the reproducibility of the synthesis and the NMR method. No NMR experiments were conducted for the functionalized polystyrene made from expanded polystyrene (EPS). NMR experiments were performed together with laboratory technician Esa Haapaniemi.

FTIR spectroscopy was performed with Bruker Alpha Platinum-ATR spectrophotometer. FTIR was generally measured from the unmodified starting material of polystyrene powder and the spectrum was compared with the functionalized polystyrene material. Functionalized polystyrene material was synthesized by using commercial polystyrene powder as well as recycled EPS, and the FTIR spectra were also compared to ensure the addition of new functionalities to the polystyrene structure. Additionally, FTIR spectrum was a great tool together with TGA to investigate the residual water present in the polymer material. FTIR was

also measured from all the products from syntheses presented in Table 4, and compared whether the degree of functionalization was seen in the intensity of the FTIR peaks.

5.2.2 TGA

TGA measurements were performed with Perkin Elmers STA 600 Simultaneous Thermal Analyser and the used temperature program is shown in Table 5. The TGA analysis was done in an oxidizing atmosphere with air as a purge gas, with a constant gas flow of 40 ml min^{-1}. TGA was used as a characterization method to analyze the changes in the material's properties under heating, primarily to see the effect of the added functional group, as well as to see at what temperature degradation of the added functional groups occurs and when the decomposition of the polymer occurs.

Table 5. The used TGA method.

Phase	Program
1)	Hold 1 min at 22˚C
2)	Heat from 22˚C to 120˚C at 10.00˚/min
3)	Hold for 10.0 min at 120˚C
4)	Heat from 120˚C to 600˚C at 10.00˚/min
5)	Hold for 20.0 min at 600˚C

5.2.3 Acid-base back titration

Acid-base back titration was used to determine the degree of functionalization by using phenolphthalein as an indicator. Acid-base back titration was also used to choose the most efficient ratio of the starting materials, aluminum chloride, and succinic anhydride, for further bulk syntheses. The titration was based on the reaction between the acidic carboxylate group added to the polystyrene and the base (sodium hydroxide, NaOH).

To determine the degree of functionalization, functionalized polystyrene was stirred with an excess of base, and the non-reacted base was titrated with an acid. 100 mg of functionalized

polystyrene (FPS) was stirred for 15 minutes with 50 ml of 0.02 M NaOH solution in an erlenmeyer flask. A drop of the indicator solution, phenolphthalein, was added to this reaction mixture. The addition of Phph showed the alkaline conditions of the reaction mixture by turning the solution pink. The reaction mixture of the functionalized polystyrene and base was titrated with 0.02 M solution of HCl, and the equivalent point was indicated by a color change from the previous pink solution to a clear and greyish solution. It was noted that prolonged stirring time of 30 minutes of NaOH and functionalized polystyrene did not change the titration results, and neither did the refluxing of these two components before titration. The degree of functionalization was calculated as (mmol g^{-1}).

5.3 3D-printing

SLS 3D-printing was used to print solid support scavengers for the adsorption studies from polystyrene powder. The functionalized polystyrene was in a powder form, and the adsorption studies were performed in a 10 ml syringe. Thus, cylinder-shaped PS filters were printed with SnowWhite SLS 3D-printer and used in the syringes as a support under the functionalized powder. PS filters were additionally utilized to ensure sample purity before analysis with UHPLC-MS. An illustrated picture of the experiment conditions is presented in Figure 8. The weights of the printed filters fitting a 10 ml syringe in this thesis ranged between 0.45-0.55 g. One characteristic of these filters is their porosity, which can affect the filter's adsorption capacity by increasing it. This was taken into account in the adsorption studies.

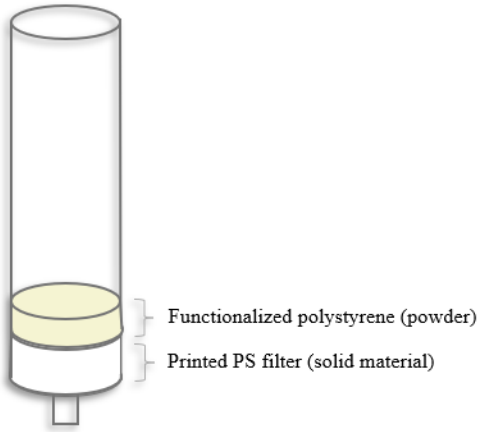


Figure 8. Illustration of the 10 ml syringe in the adsorption studies including the printed 3D-filter and functionalized polystyrene powder.

5.4 Adsorption studies

The adsorption studies were performed with 0.5 mg L^{-1} solution of naproxen and diclofenac that was made from dilution series of 1 g L^{-1} solution. The 1 g L^{-1} solution was made by weighing 50 mg of naproxen and 50 mg of diclofenac and dissolving them in 50 ml of MeOH. All the other dilutions were made in MeOH but the last dilution yielding the sample solutions (1 mg L^{-1} used for the standard curve, 0.5 mg L^{-1} for the adsorption studies) was made in ultrapure water (UPW). Pure polystyrene filters were used as a solid support for the functionalized polystyrene powder as well as used to ensure sample purity before analysis. The PS filters were first purified by pumping 3x10 ml of UPW, 3x10 ml MeOH, and finally 3x10 ml of UPW again with a flow rate of 10 ml min^{-1}. Purified filters were dried before the adsorption studies.

In general, the adsorption studies of the functionalized polystyrene were conducted by fitting the printed PS filter and functionalized powder to a 10 ml syringe according to Figure 8. These experiment conditions were used to perform a flow-through experiment with a constant flow rate of the sample solution through the filter and powder. Generally, the PS filter was used as a sintered glass filter. Shenchen LabV1 peristaltic flow rate pump was used to pump the 0.5 mg L^{-1} sample solution of naproxen and diclofenac through the functionalized polystyrene powder and the pure printed PS filter placed in the syringe with a flow rate of 1 ml min^{-1}. The

samples were collected and analyzed with Agilent 1290 Infinity UHPLC system coupled with an Agilent 6460 Triple Quadrupole -mass spectrometer. Kinetex Biphenyl (2.1 mm x 50 mm 1.7 µm) column was used in the adsorption tests and Multiple Reaction Monitoring (MRM) was used in the detection of naproxen and diclofenac. Isocratic elution was used for the mobile phase with a solvent ratio of 40:60 v/v-% where A solvent was H_2O and B solvent was 35 % acetonitrile with 65 % methanol. The flow rate was set to 0.2 ml min^{-1}.

In total, four different situations underwent the adsorption studies, including pure PS filter, pure PS filter together with unmodified commercial PS powder, pure PS filter together with functionalized polystyrene synthesized from commercial PS powder (FPS), and pure PS filter together with functionalized polystyrene synthesized from recycled EPS (FEPS). Pure PS filter and the filter together with unmodified polystyrene powder were measured to calculate the adsorption capacity of the filter itself as well as figure out how well plain polystyrene can adsorb naproxen and diclofenac in these reaction conditions. The adsorption tests for each case were conducted in triplicate to ensure reliability and repeatability, and all the samples were measured in triplicate with the UHPLC-MS. The adsorption study is illustrated in the chart presented in Figure 9.

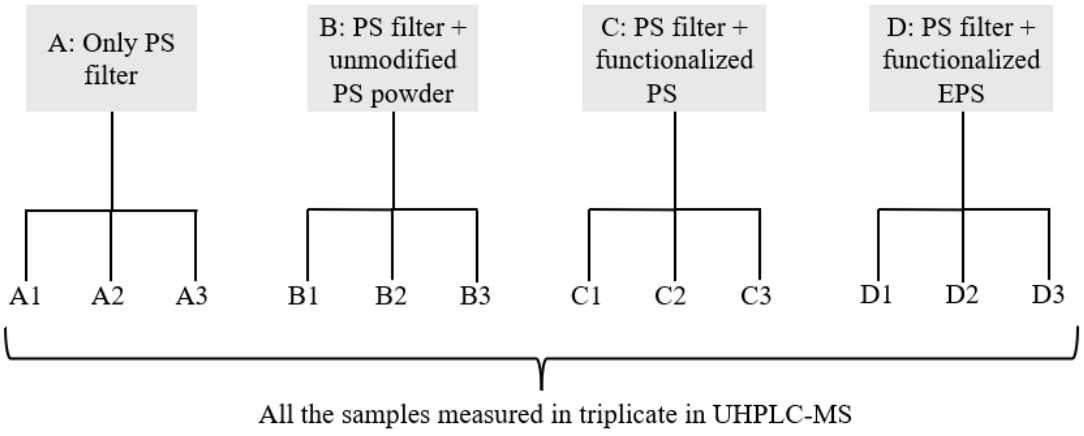


Figure 9. Chart of the samples in the adsorption studies.

6 Results and discussion

6.1 Functionalization of polystyrene

The final product from the functionalization was light yellow powder after it was dried and ground. According to Table 4, the synthesis was conducted with different molar ratios of the starting materials to discover the best and most efficient ratio to yield the highest possible degree of functionalization. All the other ratios resulted in a light yellow powder, but with [$AlCl_3$]:[SA] ratio of 2:1, the resulting powder was white. The degrees of functionalization for different ratios are presented later in the section "Acid-base back titration". The yield was only calculated as (mmol g^{-1}) because before the polymer product was dried, the material was rather elastic and was attached to the edges of the round-bottom flask where the reaction was performed. Thus, some of the polymer product was left in the reaction flask and the calculated yield (m-%) was not realistic. In addition, the length of the polymer chains was not possible to determine with the accessible equipment making the absolute weight and weight change impossible to be calculated.

The functionalized polystyrene brought its challenges with its solubility. It is known that multiple different additives may have been added to polystyrene, both commercial polystyrene powder and expanded polystyrene, to improve its properties. One possible reason for the challenges in dissolving may be due to the modified structure of polystyrene but also the fact that the synthesis and used solvent (DCM) may have dissolved additives that could improve the solubility of the polystyrene material. Functionalized polystyrene did not dissolve to any of the tried solvents, including all the solvents used in NMR experiments such as ethanol, methanol, acetone, dichloromethane (DCM), chloroform, toluene, tetrahydrofuran (THF), acetonitrile (MeCN), dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). The solubility was also attempted to improve with additions of strong acids and bases together with the solvents listed above. Also, an ultraviolet bath was applied with increased temperature for polystyrene suspended in the solvents. "Dissolving" the functionalized polystyrene to THF, and stirring for multiple days, and finally with elevated temperature did not improve the solubility either. Since none of these techniques or solvents were capable of enhancing the solubility, all the characterization methods had to be applicable to solid materials.

6.2 Characterization studies

6.2.1 NMR

The expected positioning of succinic anhydride in the electrophilic aromatic is the *para* -position to the aromatic ring of polystyrene (Figure 10), resulting in *para* product. *Ortho* product is not probably favored due to steric hindrance. Another feasible product is the *meta* product but due to the attached alkyl chain and its characteristic of being *ortho-, para-* director, *para* product is still the most probable.

NMR spectrum of functionalized polystyrene is presented in Figure 10. ^{13}C NMR (100 MHz): δ 210.9, 181.0, 164.6, 134.4, 117.4, 111.3, 23.6.

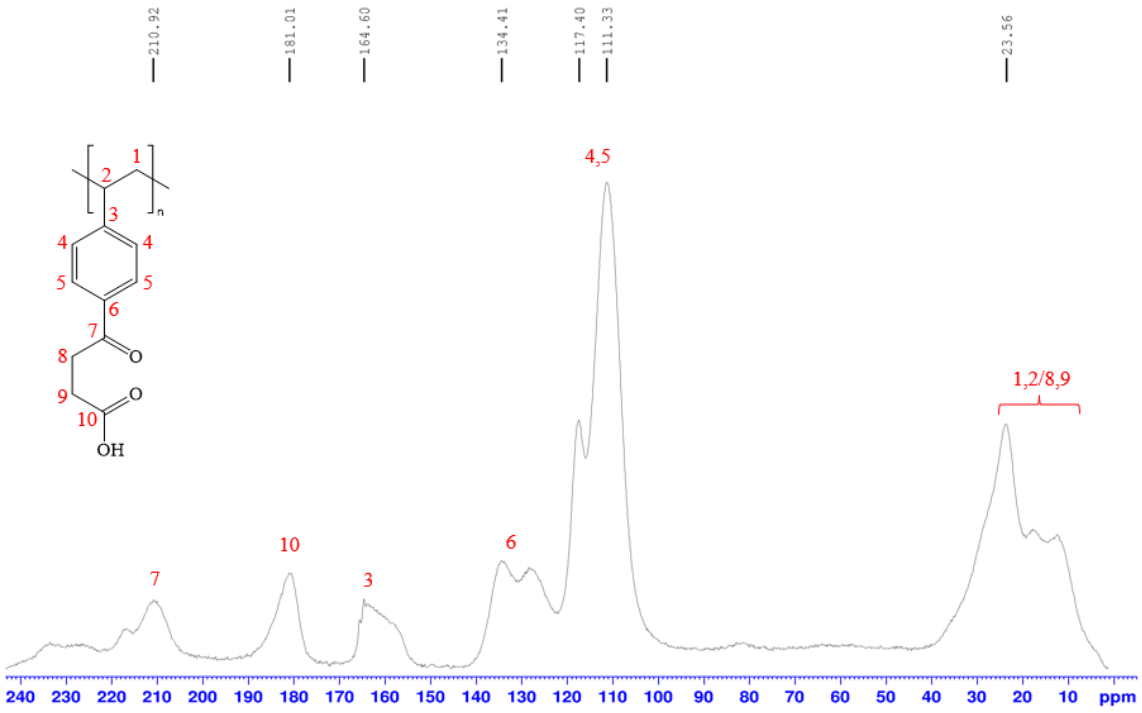


Figure 10. NMR spectrum of the functionalized polystyrene.

6.2.2 FTIR

The comparison between the unmodified polystyrene powder and functionalized recycled expanded polystyrene is shown in Figure 11. As seen in Figure 12, there is no difference in the FTIR spectra between the functionalized polystyrene whether commercial polystyrene powder or recycled expanded polystyrene has been used as a starting material in the functionalization reaction. As the final aim of the functionalization of polystyrene was the possibility of using recycled materials as starting materials in the synthesis, FEPS has been used in Figure 11 as a comparison.

Figure 11 shows the FTIR spectrum of the functionalized expanded polystyrene (FEPS) as well as the changes in the spectrum after the functionalization has occurred. The peak area around 3000 cm^{-1} has broadened a lot after the functionalization and most probably results from carboxylic acid stretching. The broad peak of a carboxylic acid is typically quite centered around the wavenumber 3000 cm^{-1} as seen in the spectrum. However, water is normally also detected around this area but the measured polymer materials were well dried before the measurement, and TGA was used to ensure that the materials were almost completely dry. Medium peaks around 3000 cm^{-1} are also detected in the unmodified polystyrene, which most likely results from the C-H stretching either from the polystyrene backbone or the stretching of =C-H of the aromatic ring. New strong and sharp peaks at around 1710 cm^{-1} and 1680 cm^{-1} are due to the presence of carbonyl groups at the functionalized polystyrene from both the carboxylic acid and ketone and are caused by the C=O stretch. The peaks between wavenumbers 1570-1000 cm^{-1} have enhanced after the functionalization. The bending of the hydroxylic group (OH) in carboxylic acid typically causes medium peaks between the area 1400-1000 cm^{-1}. Also, the functionalization has added more C-H groups to the polystyrene structure, and the C-H bendings very likely enhance the peaks around this area. The benzene ring present in the normal structure of polystyrene also shows effects of C=C stretching around the wavenumbers 1500-1400 cm^{-1}. In the unmodified polystyrene, there is a very strong and sharp peak at 750 cm^{-1} and 690 cm^{-1}. These are identified as the =C-H bending from the aromatic ring which are clearly suppressed after the functionalization when the succinic anhydride has substituted the hydrogens. In both spectra, there is also “noise” around the wavenumber 2000 cm^{-1} which is recognized as the overtone bands that are typically due to the presence of an aromatic ring.

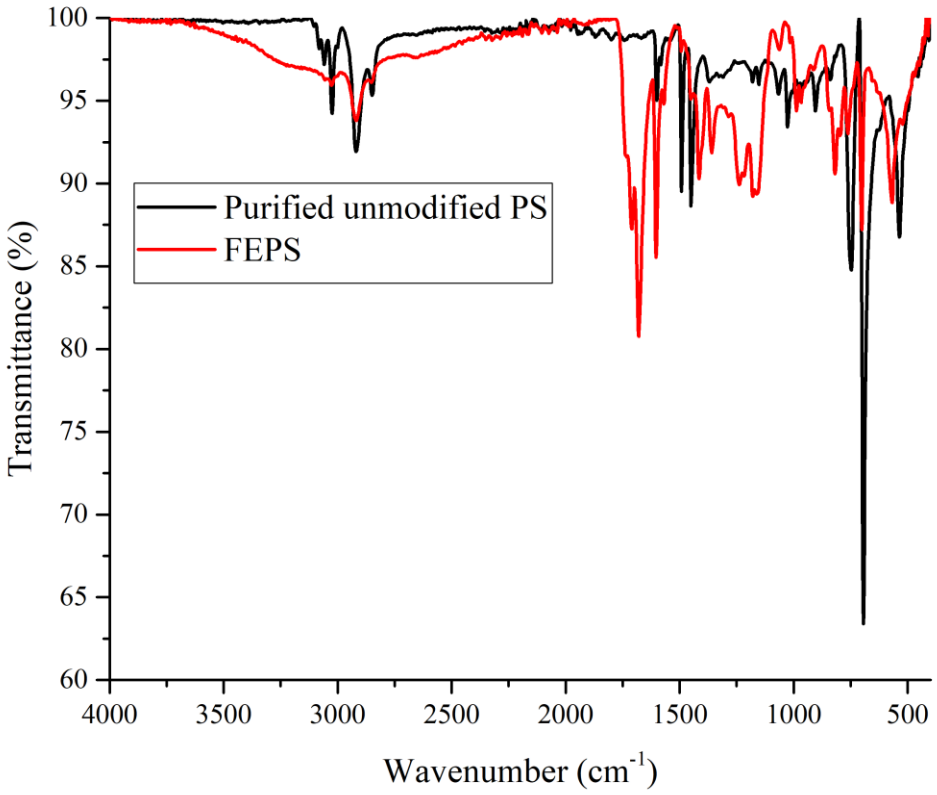


Figure 11. Comparison between unmodified and purified PS powder and functionalized polystyrene from recycled expanded polystyrene (FEPS).

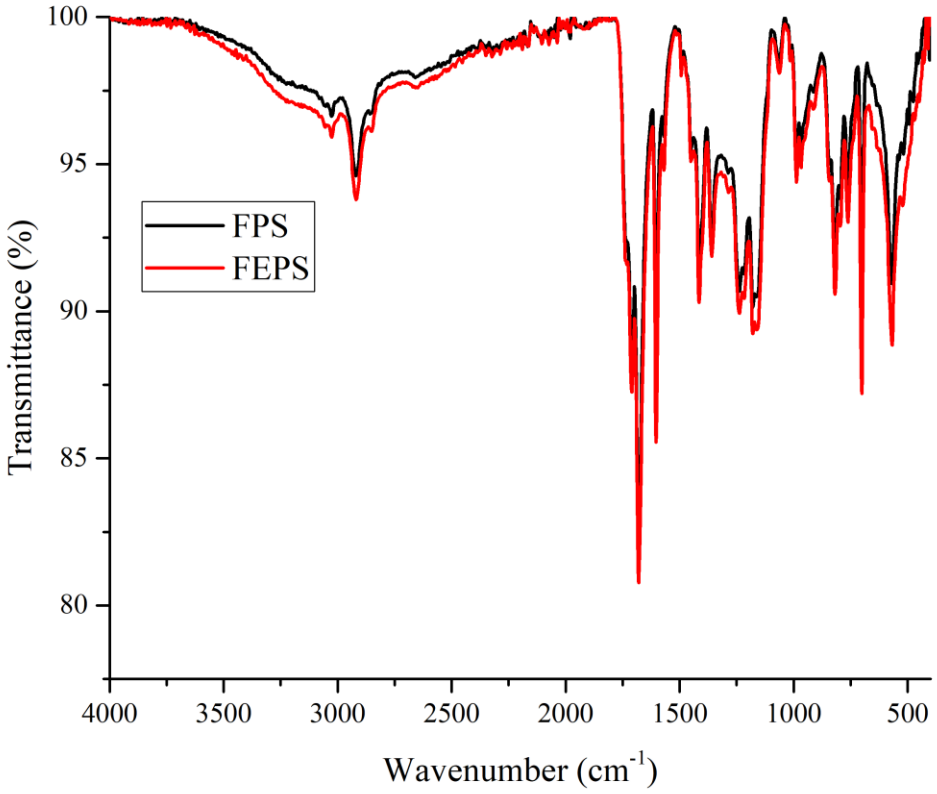


Figure 12. Comparison between functionalized polystyrene from commercial powder (FPS) and recycled expanded polystyrene (FEPS).

The functionalization was performed with different ratios of the starting materials according to Table 4 to find the most efficient ratio for the reaction. The FTIR spectra of these different reactions are presented in Figure 13. No drastic changes were detected with FTIR. However, as in Figure 13, it can be seen that the peak typical for the carbonyl group around 1700 cm^{-1} becomes stronger when the ratio increases yielding the strongest peaks with [$AlCl_3$]:[SA] ratio of 4:1, 5:1, and 6:1. Also, the suppression of the peak around 700 cm^{-1} increases as the ratio increases. Both of these changes indicate that the degree of functionalization improves as the ratio of [$AlCl_3$]:[SA] increases. The change becomes noticeable already with the ratio 3:1 but is clearly improved with the ratio 4:1, which was also chosen as the used ratio for the bulk syntheses.

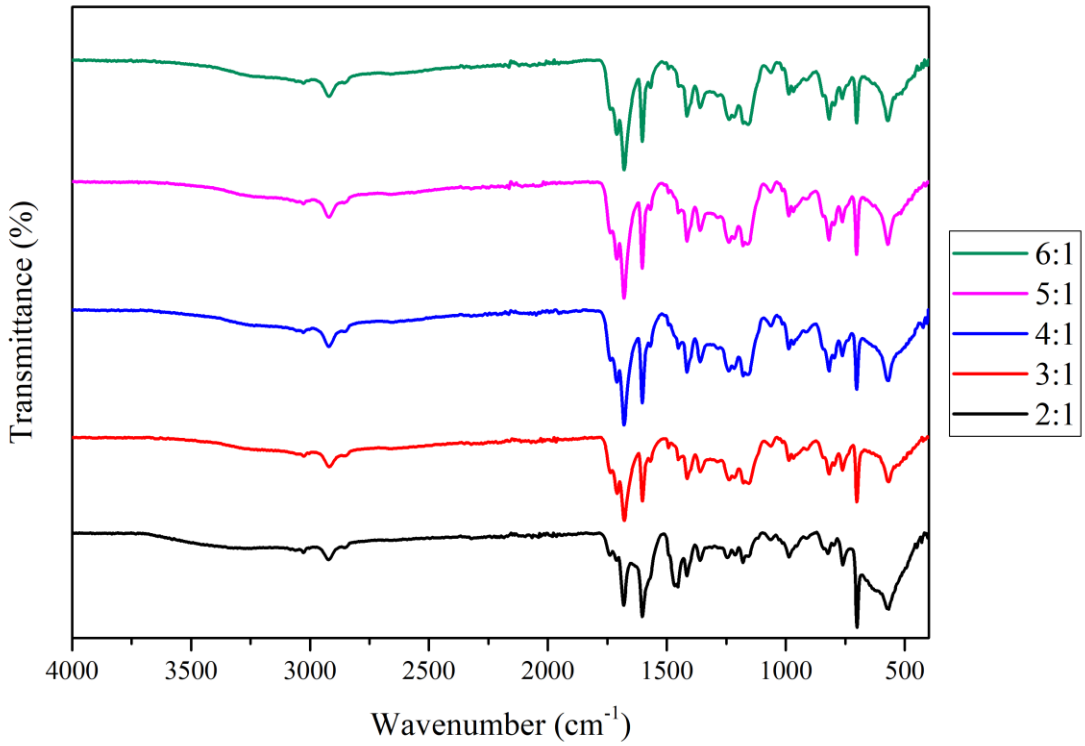


Figure 13. Comparison between syntheses from different ratios of $AlCl_3$ and SA.

6.2.3 TGA

The temperature program and used method for TGA is seen in Table 5. All the products from syntheses using different molar ratios of [$AlCl_3$]:[SA] according to Table 4 were measured in duplicate. From the TGA, the aim was to determine the mass change of the functionalized polystyrene as a function of temperature. The total change in mass percentage was between 97.4-98.4 % for all the other molar ratios than 2:1. The percentages of mass change with the molar ratio of 2:1 were 92.0 % and 92.3 % respectively. This indicates that with the molar ratio of 2:1, the amount of unburned inorganic material in the polymer material was the highest. From this observation and together with other used characterization methods, it could be said that with the molar ratio of 2:1, there is not a sufficient amount of the aluminum chloride catalyst to perform the functionalization reaction efficiently. All the other molar ratios showed similar results in TGA and showed workable and effective functionalization reactions. All the TGA curves are presented in Appendices 1-10.

The molar ratio of 4:1 was chosen for the bulk syntheses and the TGA plot for this molar ratio is presented in Figure 14. Between temperatures 250˚C and approximately 320˚C weight loss of 7.6 % can be observed. Typically residual water is evaporated in temperatures between 100-200˚C in TGA. However, the polymer structure of the functionalized polystyrene, and plausible cross-linking and voids in the structure, can trap both the residual water as well as the residual solvent to the structure which has not been evaporated by previous heating of the polymer at 130˚C. Water and the solvent can interact with each other as well as with the polymer matrix, and these interactions may affect the evaporation kinetics and the rate of decomposition. Thus, the weight loss of 7.6 % can be expected to be due to the evaporation of water and solvent. The second weight loss of 36.3 % can be detected between temperatures 320-430˚C. This weight loss can be expected to be from decarboxylation from the added side group. The final weight loss of 53.7 % is due to thermal decomposition of the polystyrene which occurs above 430˚C leading to complete degradation at approximately 520˚C. From the TGA results it can be stated that functionalized polystyrene has relatively good thermal stability as changes to the structure of the material occur only at temperatures above 350˚C.

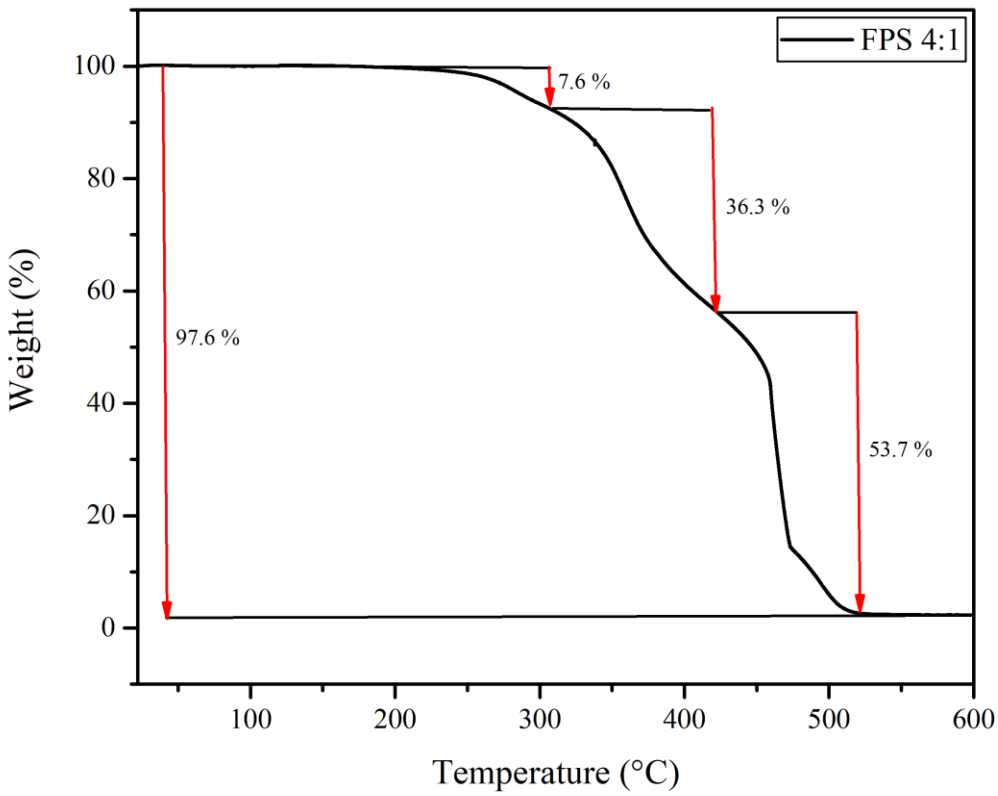


Figure 14. The TGA curve analysis for the molar ratio of 4:1 [$AlCl_3$]:[SA] (a).

6.2.4 Acid-base back titration

The main aim of acid-base back titration was to ascertain the best molar ratio of aluminum chloride catalyst and succinic anhydride to ensure the highest possible degree of functionalization for further bulk syntheses. The results are presented in Figure 15 and the numerical values are presented in Table 6. As seen in Figure 15, the ratio 2:1 shows the best degree of functionalization, and a relatively high drop in the functionalization is detected when the molecular ratio is 3:1. However, as seen in other characterization studies, including FTIR and TGA, the molecular ratio 2:1 does not show the best degree of functionalization but is rather the weakest. FTIR (Figure 13) presented the weakest peaks in the wavenumber region 1700 cm^{-1} which indicates the presence of the carbonyl group. TGA, respectively, showed a mass change of only approximately 92 % which again indicates that in syntheses with a molar ratio of 2:1, there are the highest amounts of residual mass in the structure which probably

results from unreacted starting materials, most likely from aluminum chloride. Thus, it can be suggested that in the acid-base back titration, some of the unreacted starting materials falsify the titration results and the degree of functionalization is not reliable in this case. According to the titration results, as well as other characterization methods, it can be verified that the highest degree of functionalization is reached with a molar ratio of 4:1 of [$AlCl_3$]:[SA] reaching approximately the functionalization of 4.6 mmol/g.

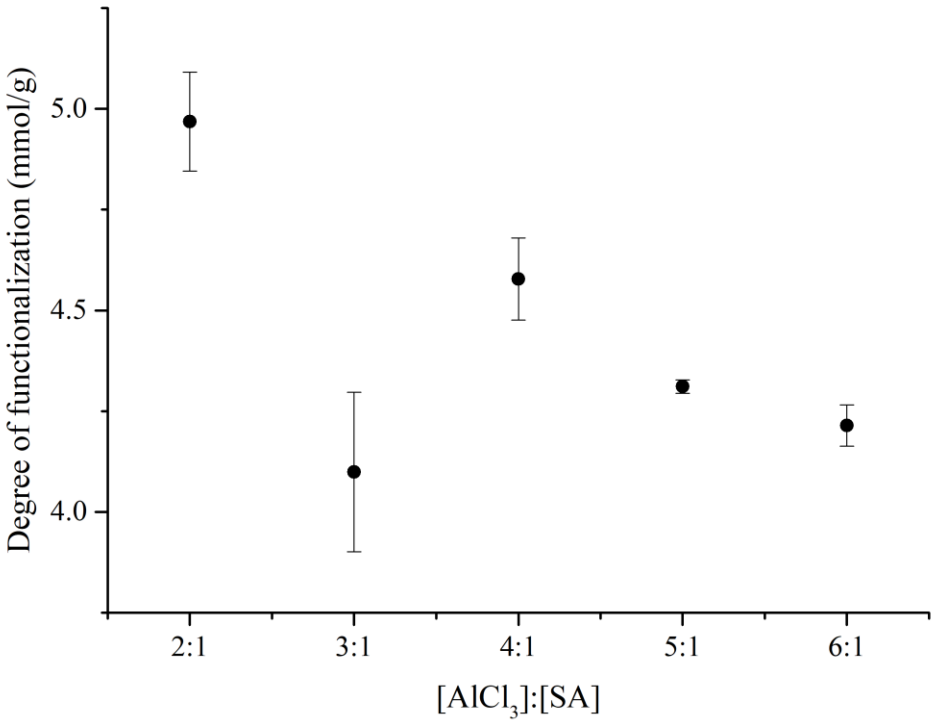


Figure 15. The degrees of functionalization for different ratios of AlCl3 and SA. Presented in the form of average ± SD.

Table 6. The numerical values for degrees of functionalization from Figure 15. Presented in the form of average ± SD.

Ratio	Degree of functionalization (mmol/g)
2:1	4,97 ± 0,12
3:1	4,10 ± 0,20
4:1	4,58 ± 0,10
5:1	4,31 ± 0,02
6:1	4,21 ± 0,05

6.3 Adsorption studies

The calibration from 50-1000 µg L^{-1} for naproxen showed good linearity of $r^2 > 0.999$. The linearity of diclofenac was poorer, being only $r^2 > 0.98$ probably due to the faster degradation of the compound. The adsorption capacities are presented in Figure 16 as well as in Table 7. As seen in the results, unmodified polystyrene powder itself can adsorb approximately 18 % of both pharmaceuticals, naproxen and diclofenac. Unmodified polystyrene has a benzene ring in its structure, and so does naproxen and diclofenac, and for example, π-π stacking is a plausible interaction causing little adsorption between polystyrene and these pharmaceuticals. However, it is seen that with functionalization with succinic anhydride, the adsorption capacity of polystyrene increases remarkably. When the functionalization is performed with commercially available polystyrene powder, the adsorption capacity reaches values of 55 % for naproxen and 76 % for diclofenac. Even higher adsorption capacities are reached when the functionalization is performed with recycled expanded polystyrene (styrox) when the adsorption of naproxen reached 75 % and for diclofenac, the adsorption was complete with an adsorption capacity of 99 %. Figure 16 presents only the adsorption capacity of unmodified polystyrene powder (PS powder) which is comparable with the functionalized polystyrene powder (FPS). Best adsorption capacities were yielded with functionalized expanded polystyrene (FEPS), and no equivalent values of unfunctionalized expanded polystyrene are presented. Recycled expanded polystyrene was a solid block of foamed polystyrene that was not directly usable in adsorption studies in that form. Therefore, no comparable adsorption test for unmodified recycled EPS is presented in Figure 16.

Naproxen and diclofenac both have benzene rings in their structures, as mentioned before. Both pharmaceuticals also have carboxylic acid residues. The pH of the environment highly affects the form in which the carboxylic acid residues, and other functionalities, are in the pharmaceuticals. The adsorption tests were performed with solutions where naproxen and diclofenac were first dissolved to methanol and the final dissolution was always done in ultrapure water. Thus, the pH of the environment for the pharmaceuticals was approximately neutral. pK_a-values for both, naproxen and diclofenac, are approximately 4 leading to the situation where the carboxylic acid residues may have been in the deprotonated form in the adsorption studies. However, as detected, the adsorption capacities were high and it is reasonable to propose that electrostatic forces as well as hydrogen bonding played a crucial role in the adsorption process. Naproxen and diclofenac can both also interact with hydrogen bonding through other functionalities present in the structures. Naproxen has an ether bridge attached to the other benzene ring, and diclofenac has a -NH -group between two benzene rings.

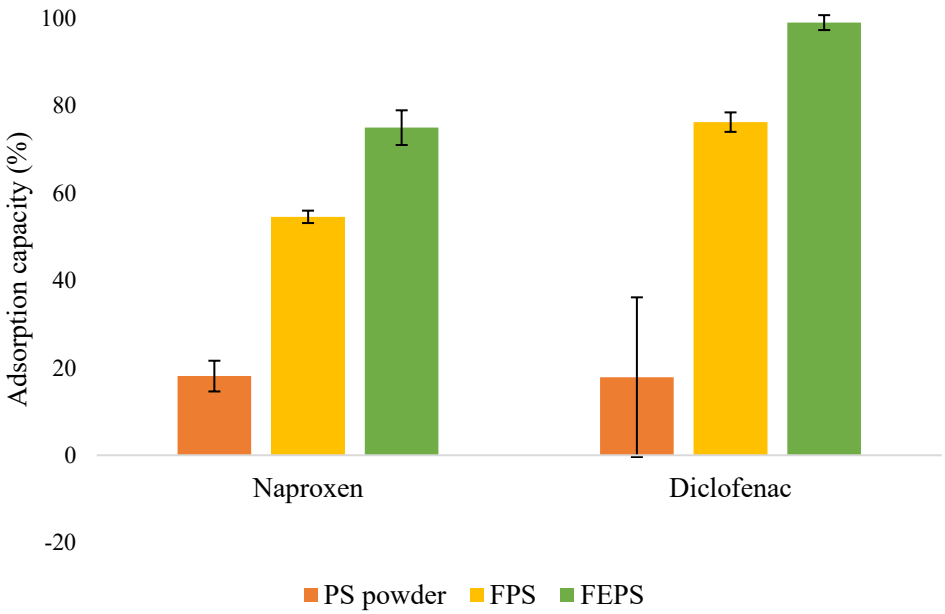


Figure 16. Adsorption capacity of unmodified PS powder, functionalized polystyrene from commercial polystyrene powder (FPS), and functionalized polystyrene from recycled expanded polystyrene (FEPS). Results presented in the form of mean ± SD.

Table 7. Adsorption capacities from Figure 16 presented in the form of mean ± SD.

	Naproxen (%)	Diclofenac (%)
PS powder	18.1 ± 3.5	17.8 ± 18.3
FPS	54.6 ± 1.4	76.2 ± 2.2
FEPS	75.0 ± 4.0	99.0 ± 1.7

7 Conclusions

This thesis demonstrates the remarkable enhancement of polystyrene's adsorption capacity towards two widely used pharmaceuticals, naproxen and diclofenac, through simple structural modifications. An important advantage is the utilization of recycled expanded polystyrene (styrox) in the synthesis process, enabling the upcycling of polystyrene material. Functionalized expanded polystyrene showed even higher adsorption capacities towards naproxen and diclofenac compared to functionalized polystyrene from commercial polystyrene powder, reaching the adsorption capacities of nearly 80 % of naproxen, and 100 % of diclofenac.

The emerging issue of organic contaminants, and especially the ever-increasing use of pharmaceuticals presents a growing threat to the environment. The current wastewater treatment processes must be improved to answer the needs of our environment and to ensure that water contamination caused by emerging organic contaminants can be minimized. While considerable research has already focused on emerging organic contaminants and their occurrence, sources, and environmental fate, further investigation is still needed especially into their impacts on aquatic life and human health. Fortunately, regulatory efforts, particularly in the EU region, are currently in progress to address this emerging challenge.

Traditional approaches to polymer recycling and upcycling have often relied on costly and energy-demanding processes. For example, widely studied and used post-polymerization modifications typically involve the use of reactive monomers that have undergone energy-intensive monomerization. The required modifications for future applications are performed after the polymerization process. One futuristic topic in polymer modification involves

upcycling polymer materials without the energy-demanding monomerization or chemical bond cleavage. This thesis presents a feasible method for polymer upcycling that bypasses the need for monomerization, offering an efficient polymer-based material for contaminant adsorption. As known, polymer materials inherently adsorb metals, and further enhancement of adsorption capacity is expected with added polymer functionality. Functionalized polystyrene offers potential not only for organic contaminants but also for future research in metal adsorption applications.

References

1. Pal, A.; Gin, K. Y. H.; Lin, A. Y. C. ja Reinhard, M., Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects, *Science of The Total Environment*, **2010**, *408*, 6062–6069.

2. Patterson, C. L. ja Haught, R. C., Regulatory considerations to ensure clean and safe drinking water, *Handbook of Water Purity and Quality*, **2021**, 93–135.

3. Gogoi, L.; Narzari, R.; Chutia, R. S.; Borkotoki, B.; Gogoi, N. ja Kataki, R., Remediation of heavy metal contaminated soil: Role of biochar, *Advances in Chemical Pollution, Environmental Management and Protection*, **2021**, *7*, 39–63.

4. Fleeger, J. W.; Carman, K. R. ja Nisbet, R. M., Indirect effects of contaminants in aquatic ecosystems, *Science of The Total Environment*, **2003**, *317*, 207–233.

5. Kyzas, G. Z. ja Bikiaris, D. N., Recent Modifications of Chitosan for Adsorption Applications: A Critical and Systematic Review, *Mar Drugs*, **2015**, *13*, 312.

6. Kumar, R.; Qureshi, M.; Vishwakarma, D. K.; Al-Ansari, N.; Kuriqi, A.; Elbeltagi, A. ja Saraswat, A., A review on emerging water contaminants and the application of sustainable removal technologies, *Case Studies in Chemical and Environmental Engineering*, **2022**, *6*, 100219.

7. Guo, W.; Pan, B.; Sakkiah, S.; Yavas, G.; Ge, W.; Zou, W.; Tong, W. ja Hong, H., Persistent Organic Pollutants in Food: Contamination Sources, Health Effects and Detection Methods.

8. García, J.; García-Galán, M. J.; Day, J. W.; Boopathy, R.; White, J. R.; Wallace, S. ja Hunter, R. G., A review of emerging organic contaminants (EOCs), antibiotic resistant bacteria (ARB), and antibiotic resistance genes (ARGs) in the environment: Increasing removal with wetlands and reducing environmental impacts, *Bioresour Technol*, **2020**, *307*, 123228.

9. Robles-Molina, J.; Gilbert-López, B.; García-Reyes, J. F. ja Molina-Díaz, A., Monitoring of selected priority and emerging contaminants in the Guadalquivir River and other related surface waters in the province of Jaén, South East Spain, *Science of The Total Environment*, **2014**, *479–480*, 247–257.

10. Rasheed, T.; Bilal, M.; Nabeel, F.; Adeel, M. ja Iqbal, H. M. N., Environmentally-related contaminants of high concern: Potential sources and analytical modalities for detection, quantification, and treatment, *Environ Int*, **2019**, *122*, 52–66.

11. Geissen, V.; Mol, H.; Klumpp, E.; Umlauf, G.; Nadal, M.; van der Ploeg, M.; van de Zee, S. E. A. T. M. ja Ritsema, C. J., Emerging pollutants in the environment: A challenge for water resource management, *International Soil and Water Conservation Research*, **2015**, *3*, 57–65.

12. Noguera-Oviedo, K. ja Aga, D. S., Lessons learned from more than two decades of research on emerging contaminants in the environment, *J Hazard Mater*, **2016**, *316*, 242–251.

13. Gavrilescu, M.; Demnerová, K.; Aamand, J.; Agathos, S. ja Fava, F., Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation, *N Biotechnol*, **2015**, *32*, 147–156.

14. Valdez-Carrillo, M.; Abrell, L.; Ramírez-Hernández, J.; Reyes-López, J. A. ja Carreón-Diazconti, C., Pharmaceuticals as emerging contaminants in the aquatic environment of Latin America: a review, *Environmental Science and Pollution Research 2020 27:36*, **2020**, *27*, 44863–44891.

15. Rivera-Utrilla, J.; Sánchez-Polo, M.; Ferro-García, M. Á.; Prados-Joya, G. ja Ocampo-Pérez, R., Pharmaceuticals as emerging contaminants and their removal from water. A review, *Chemosphere*, **2013**, *93*, 1268–1287.

16. Adsorption of Pharmaceuticals as emerging contaminants from aqueous solutions on to friendly surfaces such as activated carbon: A review - ProQuest, https://www.proquest.com/docview/2124409411?pq-origsite=gscholar&fromopenview=true&sourcetype=Scholarly%20Journals (14.2.2024).

17. Maculewicz, J.; Kowalska, D.; Świacka, K.; Toński, M.; Stepnowski, P.; Białk-Bielińska, A. ja Dołżonek, J., Transformation products of pharmaceuticals in the environment: Their fate, (eco)toxicity and bioaccumulation potential, *Science of The Total Environment*, **2022**, *802*, 149916.

18. Araujo, L.; Villa, N.; Camargo, N.; Bustos, M.; García, T. ja de Jesus Prieto, A., Persistence of gemfibrozil, naproxen and mefenamic acid in natural waters, *Environ Chem Lett*, **2011**, *9*, 13–18.

19. European Federation of Pharmaceutical Industries and Associations, The Pharmaceutical Industry in Figures, **2022**.

20. OECD Studies on Water, OECD (2019), Pharmaceutical Residues in Freshwater: Hazards and Policy Responses, Paris, 2019.

21. Gadupudi, C. K.; Rice, L.; Xiao, L. ja Kantamaneni, K., Endocrine Disrupting Compounds Removal Methods from Wastewater in the United Kingdom: A Review, *Sci 2021, Vol. 3, Page 11*, **2021**, *3*, 11.

22. Tyumina, E. A.; Bazhutin, G. A.; Cartagena Gómez, A. d. P. ja Ivshina, I. B., Nonsteroidal Anti-inflammatory Drugs as Emerging Contaminants, *Microbiology (Russian Federation)*, **2020**, *89*, 148–163.

23. Li, W.; Zheng, X.; Tu, G.; Zhang, S. ja Zhang, P., Novel aqueous biphasic system based on ionic liquid for the simultaneous extraction of seven active pharmaceutical ingredients in aquatic environment, *Environmental Science and Pollution Research*, **2021**, *28*, 17853–17864.

24. Zhou, Y.; Lin, J. yuan; Bian, Y.; Ren, C. jie; Xiao-li, N.; Yang, C. yu; Xiao-xue, X. ja Feng, X. song, Non-steroidal anti-inflammatory drugs (NSAIDs) in the environment: Updates on pretreatment and determination methods, *Ecotoxicol Environ Saf*, **2023**, *267*, 115624.

25. Rastogi, A.; Tiwari, M. K. ja Ghangrekar, M. M., A review on environmental occurrence, toxicity and microbial degradation of Non-Steroidal Anti-Inflammatory Drugs (NSAIDs), *J Environ Manage*, **2021**, *300*, 113694.

26. Puckowski, A.; Mioduszewska, K.; Łukaszewicz, P.; Borecka, M.; Caban, M.; Maszkowska, J. ja Stepnowski, P., Bioaccumulation and analytics of pharmaceutical residues in the environment: A review, *J Pharm Biomed Anal*, **2016**, *127*, 232–255.

27. Schwaiger, J.; Ferling, H.; Mallow, U.; Wintermayr, H. ja Negele, R. D., Toxic effects of the non-steroidal anti-inflammatory drug diclofenac: Part I: histopathological alterations and bioaccumulation in rainbow trout, *Aquatic Toxicology*, **2004**, *68*, 141–150.

28. Xu, C.; Niu, L.; Guo, H.; Sun, X.; Chen, L.; Tu, W.; Dai, Q.; Ye, J.; Liu, W. ja Liu, J., Long-term exposure to the non-steroidal anti-inflammatory drug (NSAID) naproxen causes thyroid disruption in zebrafish at environmentally relevant concentrations, *Science of The Total Environment*, **2019**, *676*, 387–395.

29. Almeida, Â.; Solé, M.; Soares, A. M. V. M. ja Freitas, R., Anti-inflammatory drugs in the marine environment: Bioconcentration, metabolism and sub-lethal effects in marine bivalves, *Environmental Pollution*, **2020**, *263*, 114442.

30. Puckowski, A.; Mioduszewska, K.; Łukaszewicz, P.; Borecka, M.; Caban, M.; Maszkowska, J. ja Stepnowski, P., Bioaccumulation and analytics of pharmaceutical residues in the environment: A review, *J Pharm Biomed Anal*, **2016**, *127*, 232–255.

31. Ojoghoro, J. O.; Scrimshaw, M. D. ja Sumpter, J. P., Steroid hormones in the aquatic environment, *Science of The Total Environment*, **2021**, *792*, 148306.

32. Azizi-Lalabadi, M. ja Pirsaheb, M., Investigation of steroid hormone residues in fish: A systematic review, *Process Safety and Environmental Protection*, **2021**, *152*, 14–24.

33. Almazrouei, B.; Islayem, D.; Alskafi, F.; Catacutan, M. K.; Amna, R.; Nasrat, S.; Sizirici, B. ja Yildiz, I., Steroid hormones in wastewater: Sources, treatments, environmental risks, and regulations, *Emerg Contam*, **2023**, *9*, 100210.

34. Bradley, P. M.; Battaglin, W. A.; Clark, J. M.; Henning, F. P.; Hladik, M. L.; Iwanowicz, L. R.; Journey, C. A.; Riley, J. W. ja Romanok, K. M., Widespread occurrence and potential for biodegradation of bioactive contaminants in Congaree National Park, USA, *Environ Toxicol Chem*, **2017**, *36*, 3045–3056.

35. Liu, J.; Lu, G.; Xie, Z.; Zhang, Z.; Li, S. ja Yan, Z., Occurrence, bioaccumulation and risk assessment of lipophilic pharmaceutically active compounds in the downstream rivers of sewage treatment plants, *Science of The Total Environment*, **2015**, *511*, 54–62.

36. Water Framework Directive - European Commission, https://environment.ec.europa.eu/topics/water/water-framework-directive_en (20.2.2024).

37. Halleux, V., BRIEFING EU Legislation in Progress.

38. Reducing pollution in EU groundwater and surface waters | News | European Parliament, https://www.europarl.europa.eu/news/en/press-room/20230911IPR04917/reducing-pollution-in-eu-groundwater-and-surface-waters (20.2.2024).

39. Caban, M. ja Stepnowski, P., How to decrease pharmaceuticals in the environment? A review, *Environmental Chemistry Letters 2021 19:4*, **2021**, *19*, 3115–3138.

40. Bușoi, C.-S.; Sidl, G.; Huitema, J.; Rivasi, M.; Baldassarre, S.; Kopcińska, J. ja Konečná, K., MOTION FOR A RESOLUTION.

41. Fauvelle, V.; Castro-Jiménez, J.; Schmidt, N.; Carlez, B.; Panagiotopoulos, C. ja Sempéré, R., One-single extraction procedure for the simultaneous determination of a wide range of polar and nonpolar organic contaminants in seawater, *Front Mar Sci*, **2018**, *5*, 396611.

42. Lukač Reberski, J.; Terzić, J.; Maurice, L. D. ja Lapworth, D. J., Emerging organic contaminants in karst groundwater: A global level assessment, *J Hydrol (Amst)*, **2022**, *604*, 127242.

43. Jiang, J. J.; Lee, C. L. ja Fang, M. Der, Emerging organic contaminants in coastal waters: Anthropogenic impact, environmental release and ecological risk, *Mar Pollut Bull*, **2014**, *85*, 391–399.

44. Meffe, R. ja de Bustamante, I., Emerging organic contaminants in surface water and groundwater: A first overview of the situation in Italy, *Science of The Total Environment*, **2014**, *481*, 280–295.

45. Parolini, M., Toxicity of the Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) acetylsalicylic acid, paracetamol, diclofenac, ibuprofen and naproxen towards freshwater invertebrates: A review, *Science of The Total Environment*, **2020**, *740*, 140043.

46. Świacka, K.; Michnowska, A.; Maculewicz, J.; Caban, M. ja Smolarz, K., Toxic effects of NSAIDs in non-target species: A review from the perspective of the aquatic environment, *Environmental Pollution*, **2021**, *273*, 115891.

47. Mukhopadhyay, A.; Duttagupta, S. ja Mukherjee, A., Emerging organic contaminants in global community drinking water sources and supply: A review of occurrence, processes and remediation, *J Environ Chem Eng*, **2022**, *10*, 107560.

48. Chaturvedi, P.; Shukla, P.; Giri, B. S.; Chowdhary, P.; Chandra, R.; Gupta, P. ja Pandey, A., Prevalence and hazardous impact of pharmaceutical and personal care products and antibiotics in environment: A review on emerging contaminants, *Environ Res*, **2021**, *194*, 110664.

49. Global Chemicals Outlook | UNEP - UN Environment Programme, https://www.unep.org/explore-topics/chemicals-waste/what-we-do/policy-and-governance/global-chemicals-outlook?_ga=2.260920205.1630203610.1707832663-792568335.1707832662 (19.2.2024).

50. Saldívar-Guerra, E. ja Vivaldo-Lima, E., Handbook of Polymer Synthesis, Characterization, and Processing, *Handbook of Polymer Synthesis, Characterization, and Processing*, **2013**.

51. Shrivastava, A., Introduction to Plastics Engineering, *Introduction to Plastics Engineering*, **2018**, 1–246.

52. Osswald, T. A., *Tim A. Osswald - Understanding Polymer Processing_ Processes and Governing Equations-Hanser (2017)*, 1390.

53. Obi, B. E., Polymer Chemistry and Synthesis, *Polymeric Foams Structure-Property-Performance*, **2018**, 17–40.

54. Theato, Patrick. ja Klok, H.-Anton., Functional Polymers by Post-Polymerization Modification : Concepts, Guidelines, and Applications., **2013**, 606.

55. Nagae, H.; Akebi, S. Y.; Matsushiro, S.; Sakamoto, K.; Iwasaki, T.; Nozaki, K. ja Mashima, K., Chain Transfer Approach for Terminal Functionalization of Alternating Copolymerization of CO2and Epoxide by Using Active Methylene Compounds as Chain Transfer Agents, *Macromolecules*, **2022**, *55*, 9066–9073.

56. Blasco, E.; Sims, M. B.; Goldmann, A. S.; Sumerlin, B. S. ja Barner-Kowollik, C., 50th Anniversary Perspective: Polymer Functionalization, *Macromolecules*, **2017**, *50*, 5215–5252.

57. Gauthier, M. A.; Gibson, M. I. ja Klok, H. A., Synthesis of Functional Polymers by Post-Polymerization Modification, *Angewandte Chemie International Edition*, **2009**, *48*, 48–58.

58. Hamad, K.; Kaseem, M. ja Deri, F., Recycling of waste from polymer materials: An overview of the recent works, *Polym Degrad Stab*, **2013**, *98*, 2801–2812.

59. Guselnikova, O.; Semyonov, O.; Sviridova, E.; Gulyaev, R.; Gorbunova, A.; Kogolev, D.; Trelin, A.; Yamauchi, Y.; Boukherroub, R. ja Postnikov, P., "Functional upcycling" of polymer waste towards the design of new materials, *Chem Soc Rev*, **2023**, *52*, 4755–4832.

60. D. Campbell, R.A. Pethrick, J. R. W., *Polymer Characterization - Physical tecniques*, 2000.

61. Alvarez-Ordóñez, A. ja Prieto, M., Fourier transform infrared spectroscopy in food microbiology, *Fourier Transform Infrared Spectroscopy in Food Microbiology*, **2012**, 1–55.

62. ATR-FTIR Spectroscopy, FTIR Sampling Techniques | Agilent, https://www.agilent.com/en/product/molecular-spectroscopy/ftir-spectroscopy/atr-ftir-spectroscopy (25.4.2024).

63. Apperley, D. C.; Harris, R. K. (Robin K. ja Hodgkinson, Paul., Solid-state NMR : basic principles & practice, **2012**, 276.

64. ’Wesdemiotis, C. ’Williams-Pavlantos, K. N. ’ ’Keating, A. R. ’ ’McGee, A. S. ’Bochenek, C., Mass spectrometry of polymers:A tutorial review, *Mass Spectrom Rev*, **2023**, 1–50.

65. Guo, Q., Polymer morphology : principles, characterization, and processing.

66. Polymer Surface Characterization, *Polymer Surface Characterization*, **2014**.

67. Menczel, J. D. ja Prime, R. B., Thermal Analysis of Polymers: Fundamentals and Applications, *Thermal Analysis of Polymers: Fundamentals and Applications*, **2008**, 1–688.

68. Investigation of Polymers with Differential Scanning Calorimetry.

69. Gill, P.; Moghadam, T. T. ja Ranjbar, B., Differential Scanning Calorimetry Techniques: Applications in Biology and Nanoscience, *J Biomol Tech*, **2010**, *21*, 167.

70. Jätevedenpuhdistamolla tapahtuu | Vesi.fi, https://www.vesi.fi/vesitieto/jatevedenpuhdistamolla-tapahtuu/ (9.4.2024).

71. Finnish Water Utilities Association ja Helsinki Region Environmental Services Authority, Finnish Industrial Wastewater guide, 2018.

72. Crini, G. ja Lichtfouse, E., Advantages and disadvantages of techniques used for wastewater treatment, *Environ Chem Lett*, **2019**, *17*, 145–155.

73. Laitinen, J.; Nieminen, J.; Saarinen, R.; Saijariina, J. ja Ympäristöministeriö, T., Yhdyskuntien jätevedenpuhdistamot.

74. Topare, N. S.; Attar, S. J. ja Manfe, M. M., SEWAGE/WASTEWATER TREATMENT TECHNOLOGIES : A REVIEW, *Sci. Revs. Chem. Commun*, **2011**, 18–24.

75. Artioli, Y., Adsorption, *Encyclopedia of Ecology, Five-Volume Set*, **2008**, *1–5*, 60–65.

76. Miao, M.; Lu, Q.; Wang, X.; Zhang, Y.; Wong, N. H.; Sunarso, J.; Xiao, C. ja Li, N., Removal of micro-organic contaminants from wastewater: A critical review of treatment technology, *Next Materials*, **2023**, *1*, 100016.

77. Gkika, D.; Liakos, E. V.; Vordos, N.; Kontogoulidou, C.; Magafas, L.; Bikiaris, D. N.; Bandekas, D. V.; Mitropoulos, A. C. ja Kyzas, G. Z., Cost Estimation of Polymeric Adsorbents, *Polymers 2019, Vol. 11, Page 925*, **2019**, *11*, 925.

78. Gwenzi, W.; Chaukura, N.; Muisa-Zikali, N.; Musiyiwa, K. ja Teta, C., Occurrence and behaviour of emerging organic contaminants in aquatic systems, *Emerging Contaminants in the Terrestrial-Aquatic-Atmosphere Continuum: Occurrence, Health Risks and Mitigation*, **2022**, 67–86.

79. Snyder, S. A.; Adham, S.; Redding, A. M.; Cannon, F. S.; DeCarolis, J.; Oppenheimer, J.; Wert, E. C. ja Yoon, Y., Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, *Desalination*, **2007**, *202*, 156–181.

80. Dehghani, M. H.; Ahmadi, S.; Ghosh, S.; Othmani, A.; Osagie, C.; Meskini, M.; AlKafaas, S. S.; Malloum, A.; Khanday, W. A.; Jacob, A. O.; Gökkuş, Ö.; Oroke, A.; Martins Chineme, O.; Karri, R. R. ja Lima, E. C., Recent advances on sustainable adsorbents for the remediation of noxious pollutants from water and wastewater: A critical review, *Arabian Journal of Chemistry*, **2023**, *16*, 105303.

81. Soni, R.; Bhardwaj, S. ja Shukla, D. P., Various water-treatment technologies for inorganic contaminants: current status and future aspects, *Inorganic Pollutants in Water*, **2020**, 273–295.

82. Lee, J. ja Patel, R., Wastewater Treatment by Polymeric Microspheres: A Review, *Polymers 2022, Vol. 14, Page 1890*, **2022**, *14*, 1890.

83. Alipoori, S.; Rouhi, H.; Linn, E.; Stumpfl, H.; Mokarizadeh, H.; Esfahani, M. R.; Koh, A.; Weinman, S. T. ja Wujcik, E. K., Polymer-Based Devices and Remediation Strategies for Emerging Contaminants in Water, *ACS Appl Polym Mater*, **2021**, *3*, 549–577.

84. Frimodig, J.; Autio, A.; Lahtinen, E. ja Haukka, M., Recovery of 17b-Estradiol Using 3D Printed Polyamide-12 Scavengers, *3D Print Addit Manuf*, **2023**, *10*, 1122–1129.

85. Lahtinen, E.; Hänninen, M. M.; Kinnunen, K.; Tuononen, H. M.; Väisänen, A.; Rissanen, K. ja Haukka, M., Porous 3D Printed Scavenger Filters for Selective Recovery of Precious Metals from Electronic Waste, *Adv Sustain Syst*, **2018**, *2*.

86. Kulomäki, S.; Lahtinen, E.; Perämäki, S. ja Väisänen, A., Preconcentration and speciation analysis of mercury: 3D printed metal scavenger-based solid-phase extraction followed by analysis with inductively coupled plasma mass spectrometry, *Talanta*, **2022**, *240*.

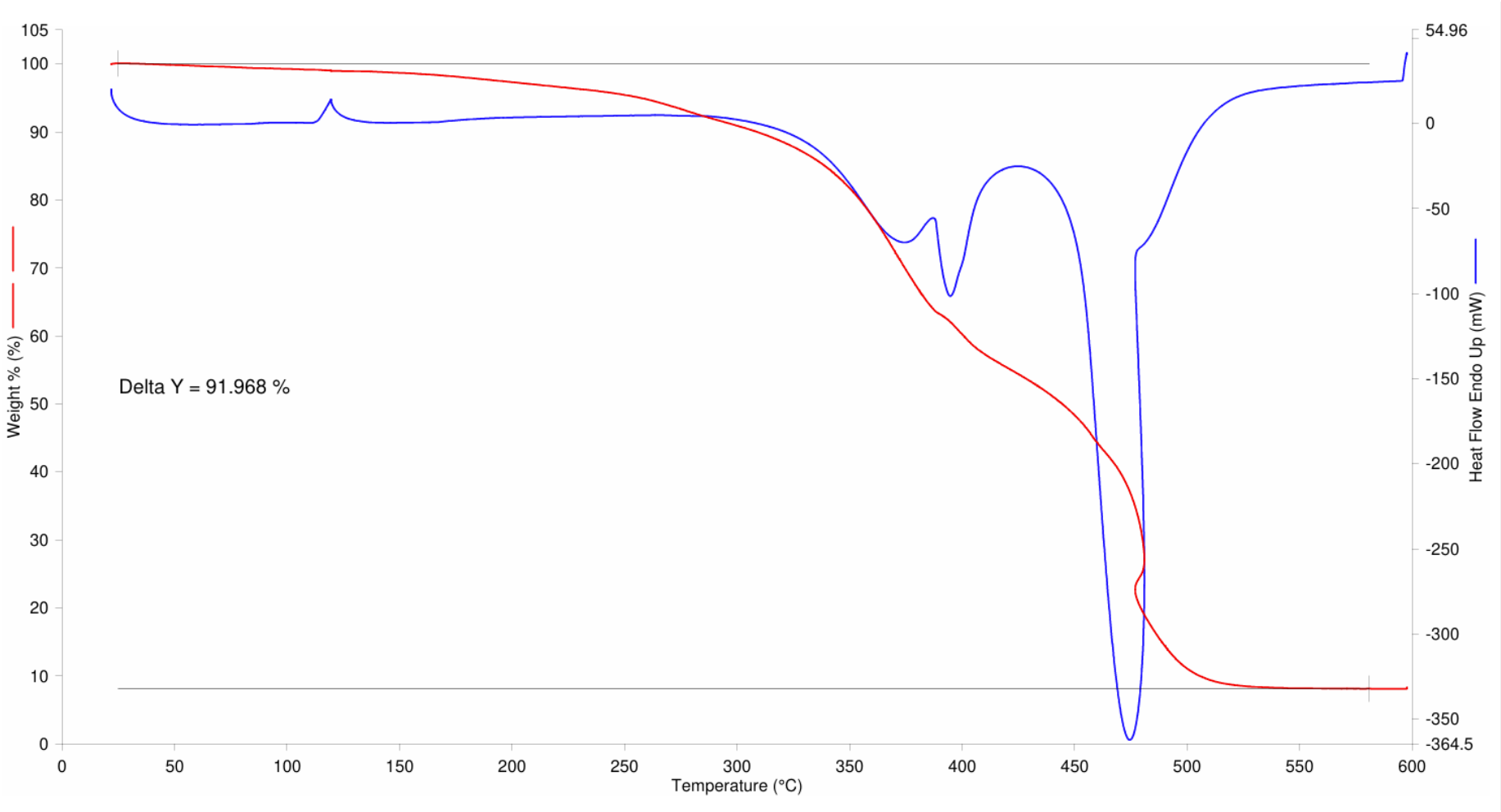
87. Tang, S.; Yang, X.; Zhang, T.; Qin, Y.; Cao, C.; Shi, H. ja Zhao, Y., Adsorption mechanisms of metal ions (Pb, Cd, Cu) onto polyamide 6 microplastics: New insight into environmental risks in comparison with natural media in different water matrices, *Gondwana Research*, **2022**, *110*, 214–225.

88. Pu, Y.; Xie, Z.; Ye, H. ja Shi, W., Amidation modified waste polystyrene foam as an efficient recyclable adsorbent for organic dyes removal, *Water Science and Technology*, **2021**, *83*, 2192–2206.

89. Liu, M.; Xie, Z.; Ye, H.; Li, W.; Shi, W.; Liu, Y. ja Zhang, Y., Waste polystyrene foam – Chitosan composite materials as high-efficient scavenger for the anionic dyes, *Colloids Surf A Physicochem Eng Asp*, **2021**, *627*, 127155.

90. Li, J. ja Li, H. M., Functionalization of syndiotactic polystyrene with succinic anhydride in the presence of aluminum chloride, *Eur Polym J*, **2005**, *41*, 823–829.

Appendices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Temperature (°C)
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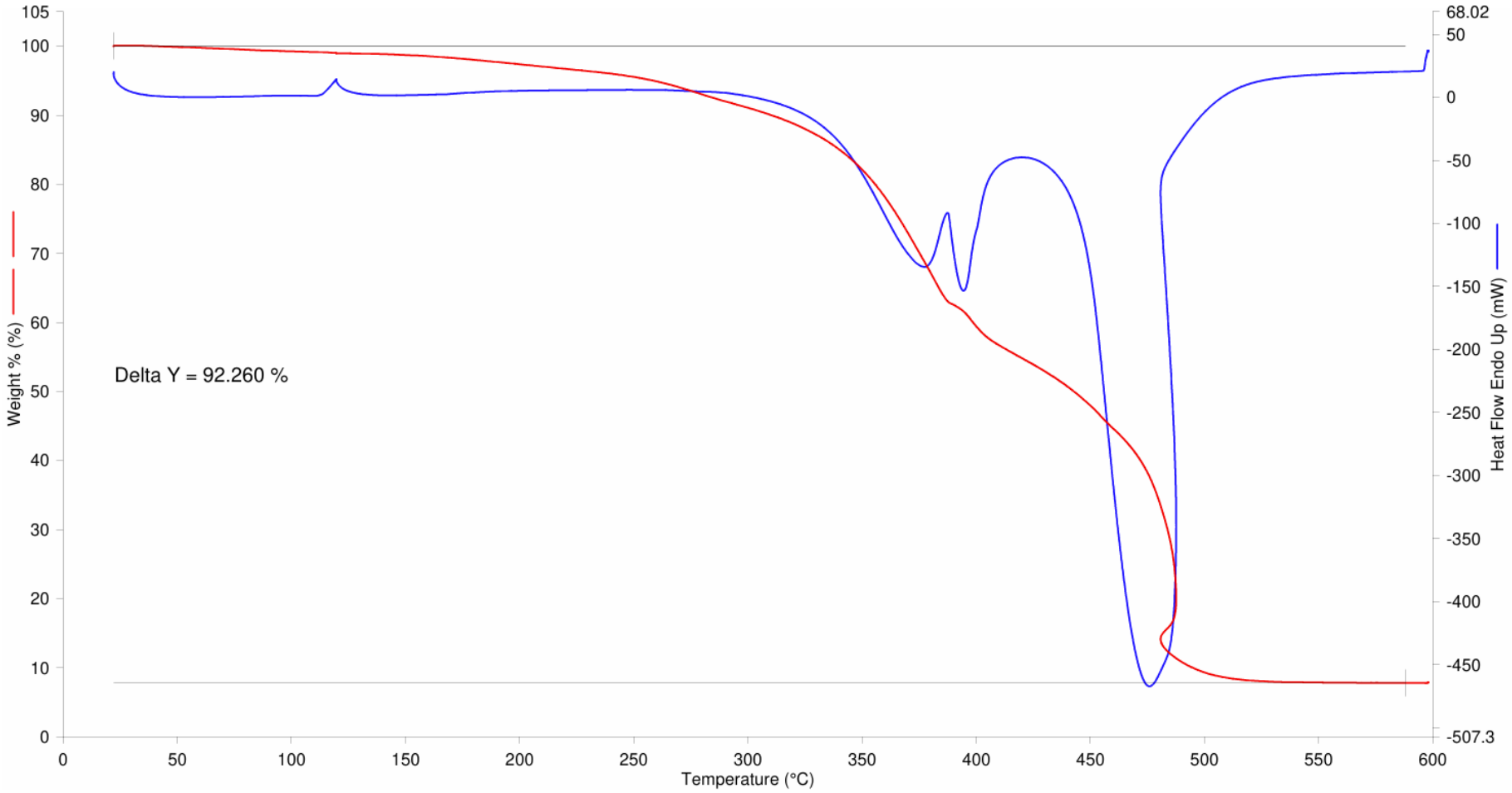
105
100
90
80
70
60
50
40
30
20
10
0
54.96
0
-50
-100
-150
-200
-250
-300
-350
-364.5
0
50
100
150
200
250
300
350
400
450
500
550
600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Temperature (°C)
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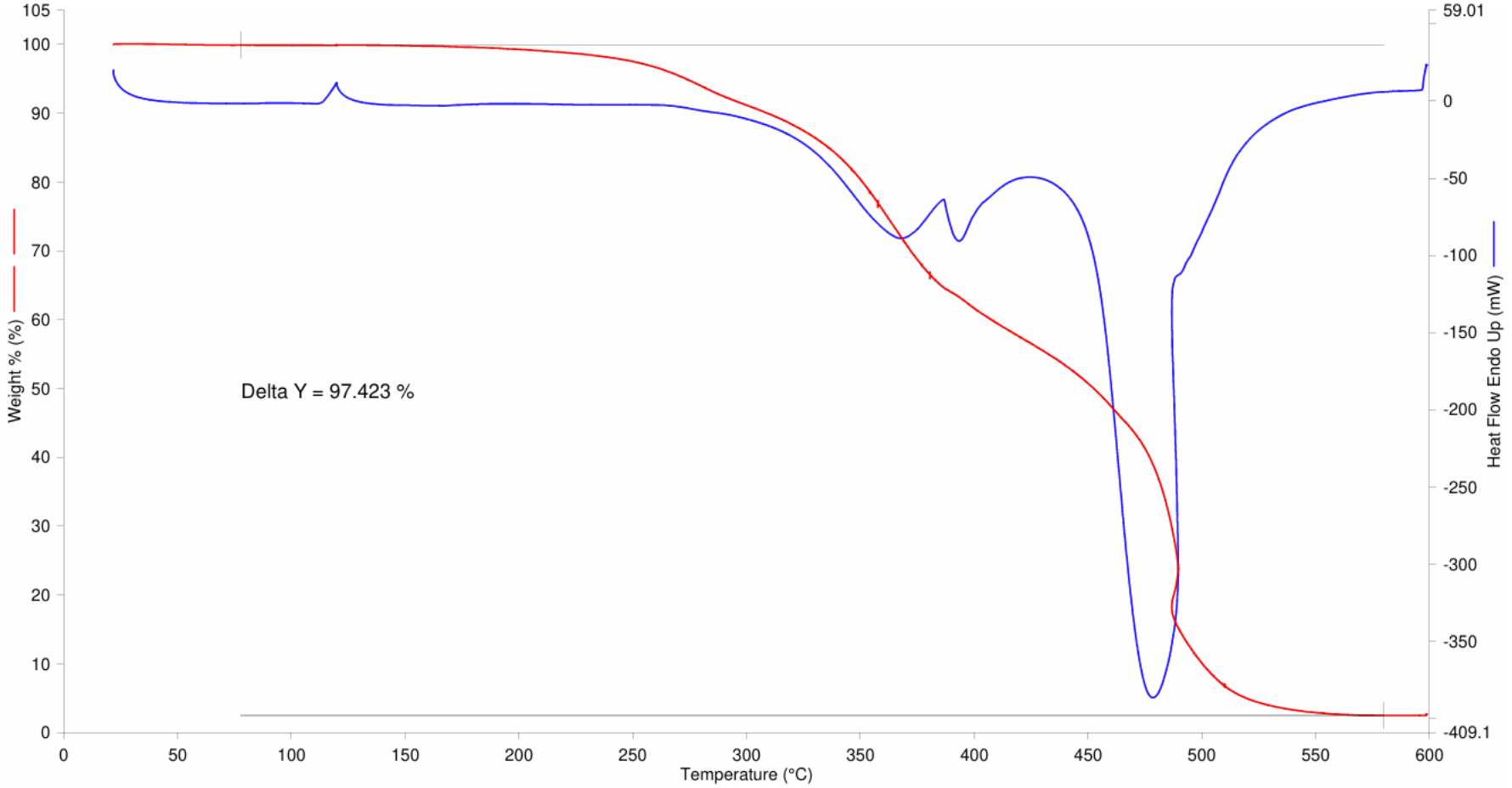
100
90
80
70
60
50
40
30
20
10
0
68.02
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-507.3
0
50
100
150
200
250
300
350
400
450
500
550
600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Temperature (°C)
Delta Y = 97.423 %
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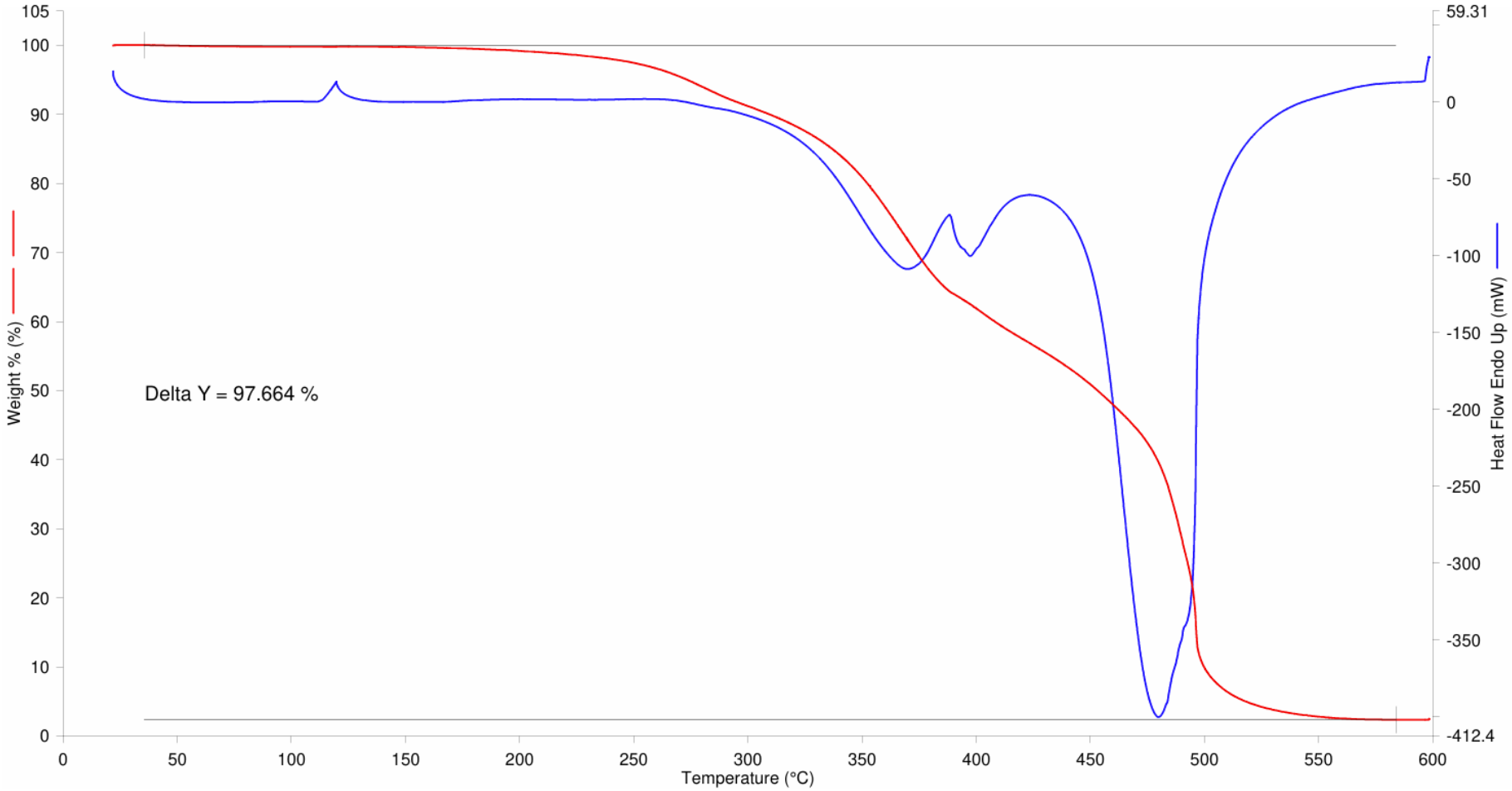
100
90
80
70
60
50
40
30
20
10
0
59.01
0
-50
-100
-150
-200
-250
-300
-350
-409.1
0
50
100
150
200
250
300
350
400
450
500
550
600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Heat Flow Endo Up (mW)
Temperature (°C)
Delta Y = 97.664 %
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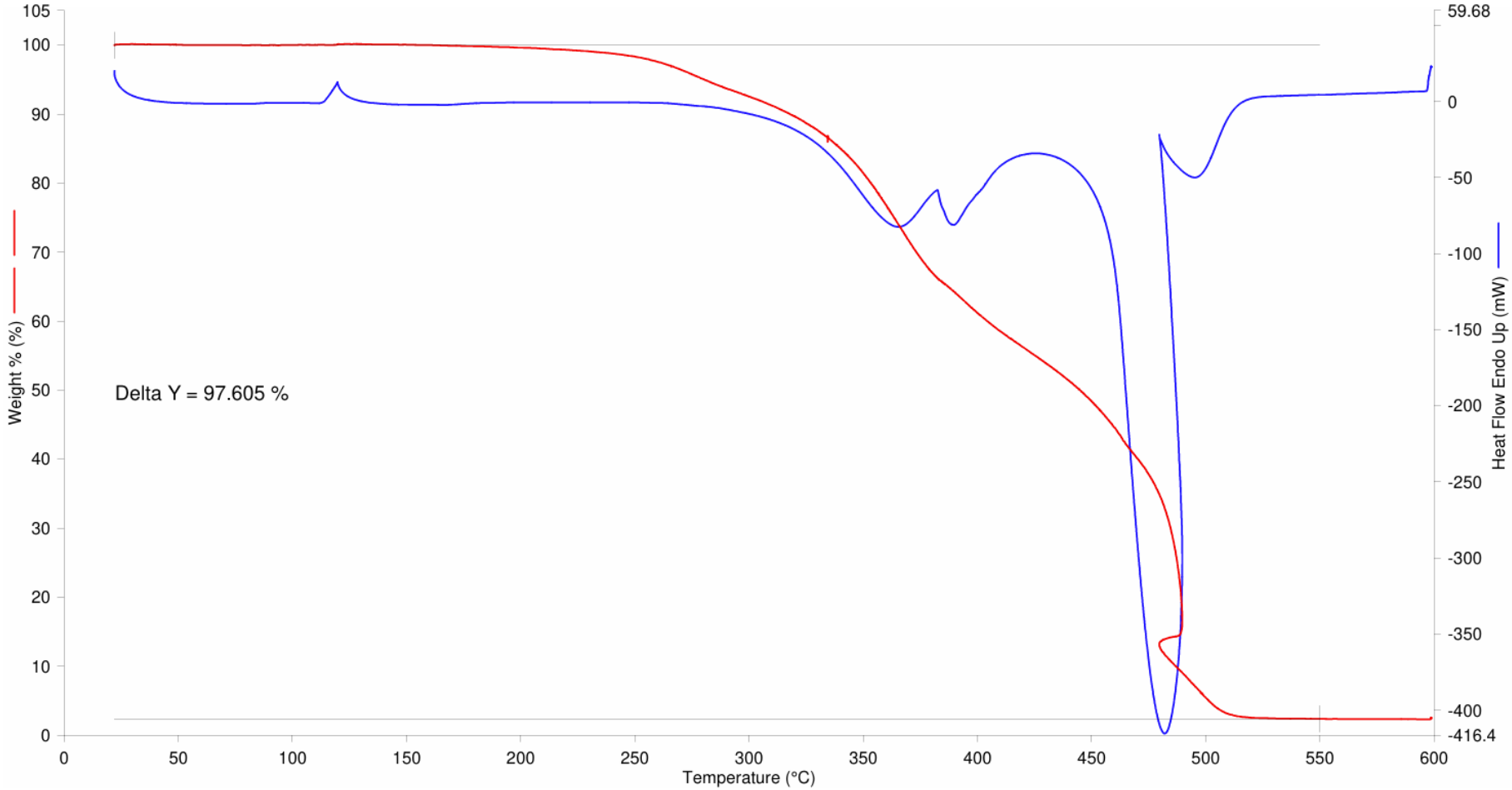
100
90
80
70
60
50
40
30
20
10
0
59.31
0
-50
-100
-150
-200
-250
-300
-350
-412.4
0
50
100
150
200
250
300
350
400
450
500
550
600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Heat Flow Endo Up (mW)
Temperature (°C)
Delta Y = 97.605 %
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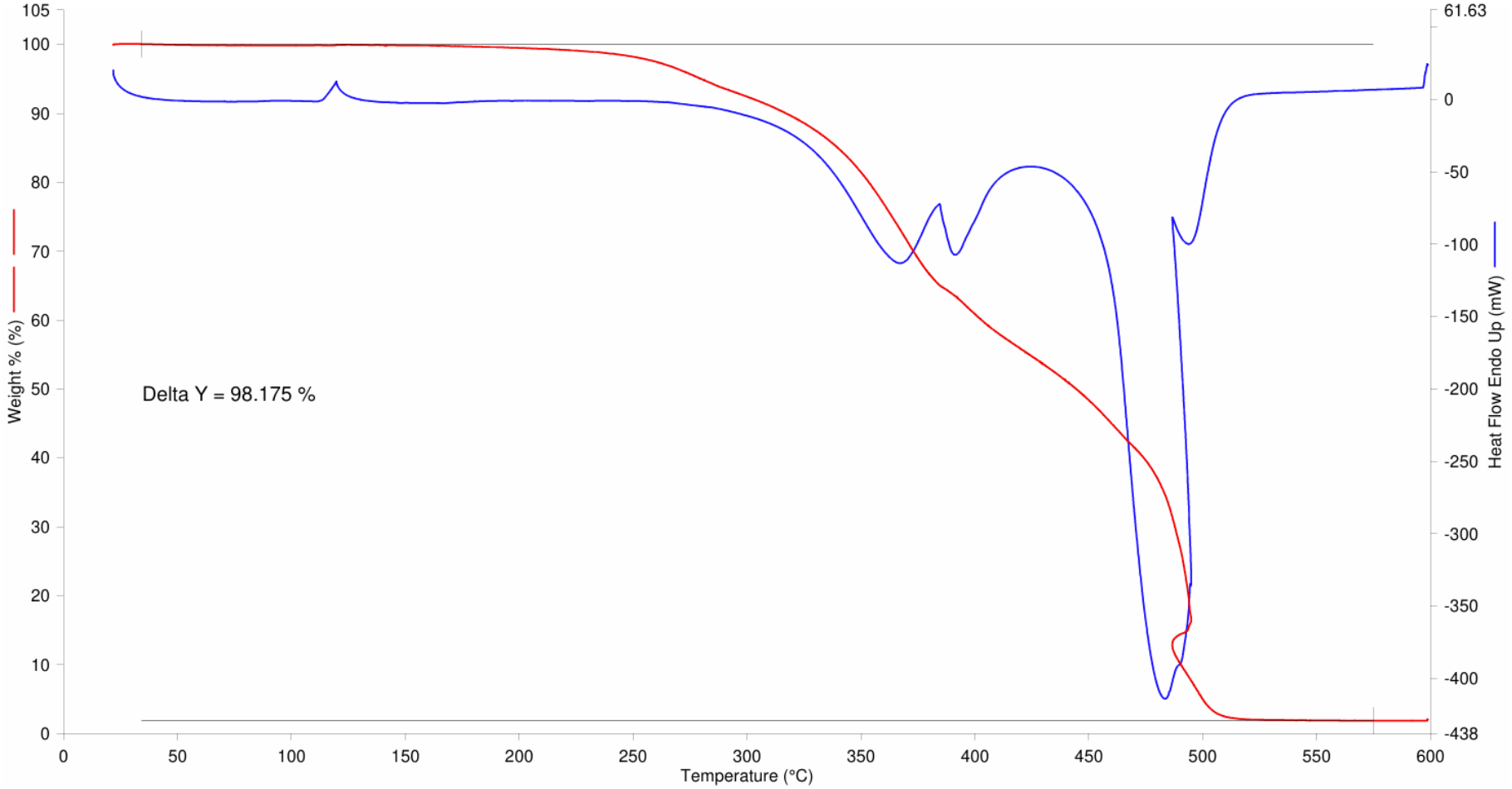
100
90
80
70
60
50
40
30
20
10
0
59.68
0
-50
-100
-150
-200
-250
-300
-350
-400
-416.4
0
50
100
150
200
250
300
350
400
450
500
550
600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Temperature (°C)
Delta Y = 98.175 %
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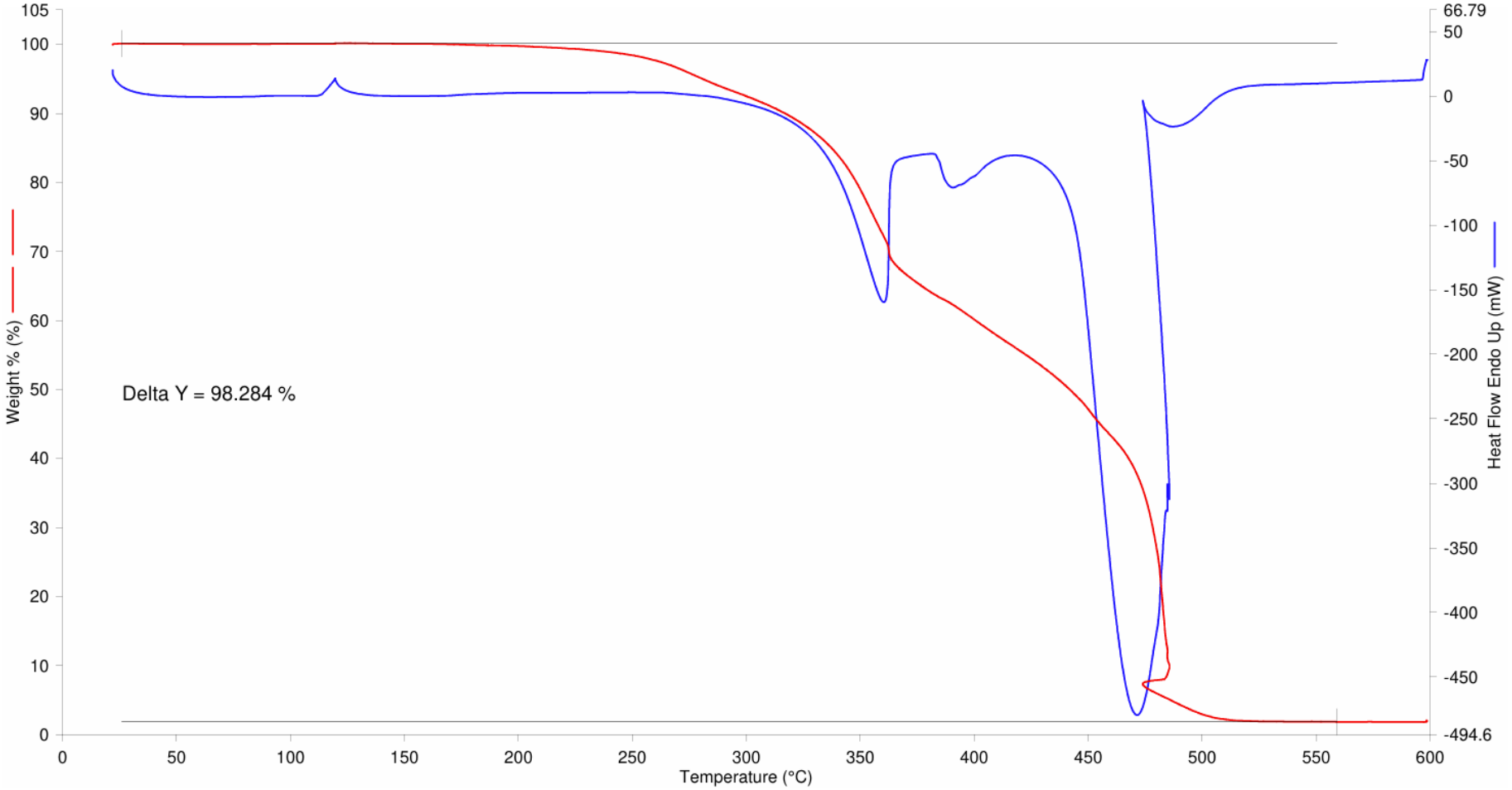
100
90
80
70
60
50
40
30
20
10
0
61.63
0
-50
-100
-150
-200
-250
-300
-350
-400
-438
0
50
100
150
200
250
300
350
400
450
500
550
600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Heat Flow Endo Up (mW)
Temperature (°C)
Delta Y = 98.284 %
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100
90
80
70
60
50
40
30
20
10
0
66.79
50
0
-50
-100
-150
-200
-250
-300
-350
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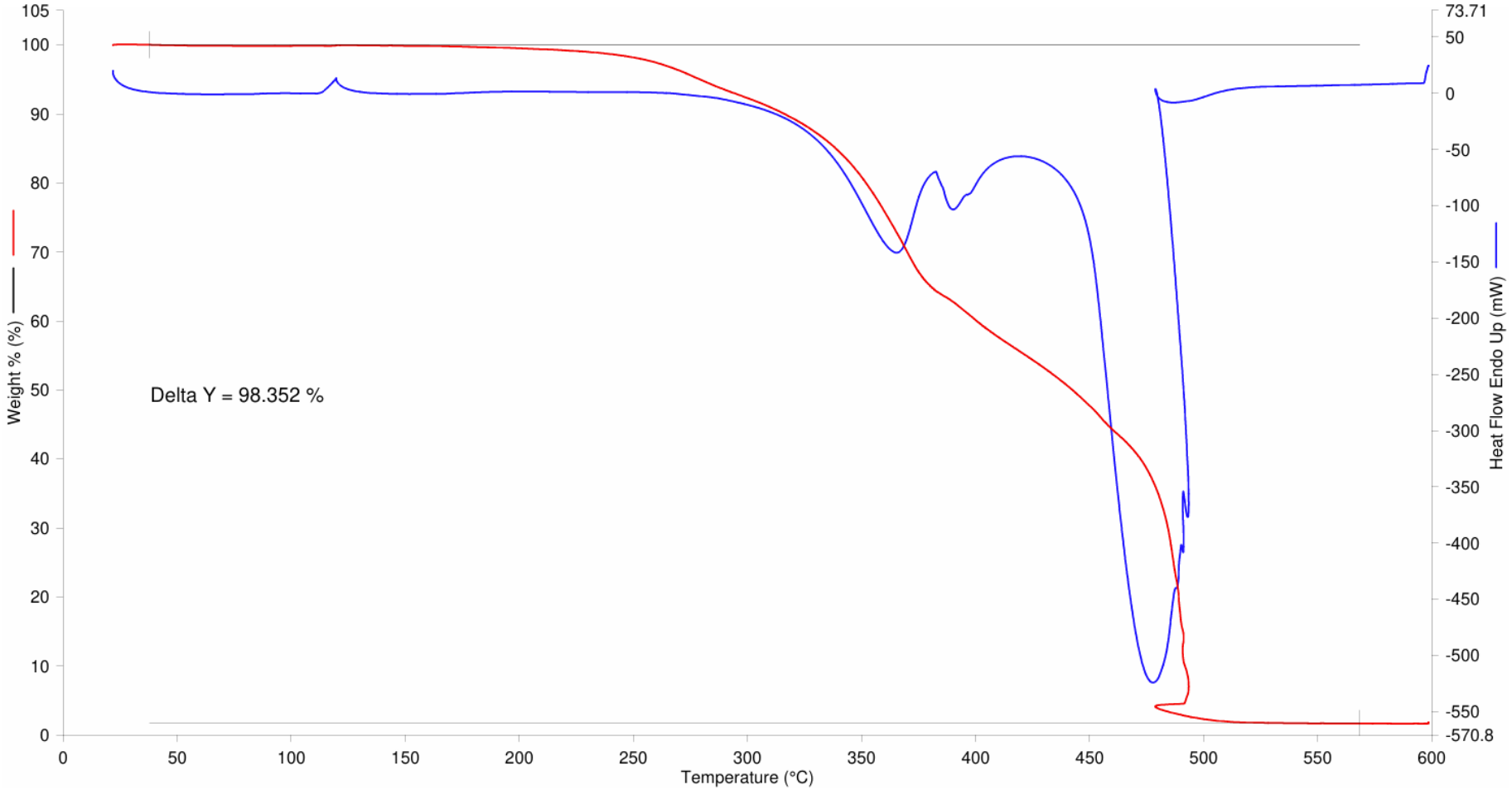
-450
-494.6
0
50
100
150
200
250
300
350
400
450
500
550
600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Heat Flow Endo Up (mW)
Temperature (°C)
Delta Y = 98.352 %
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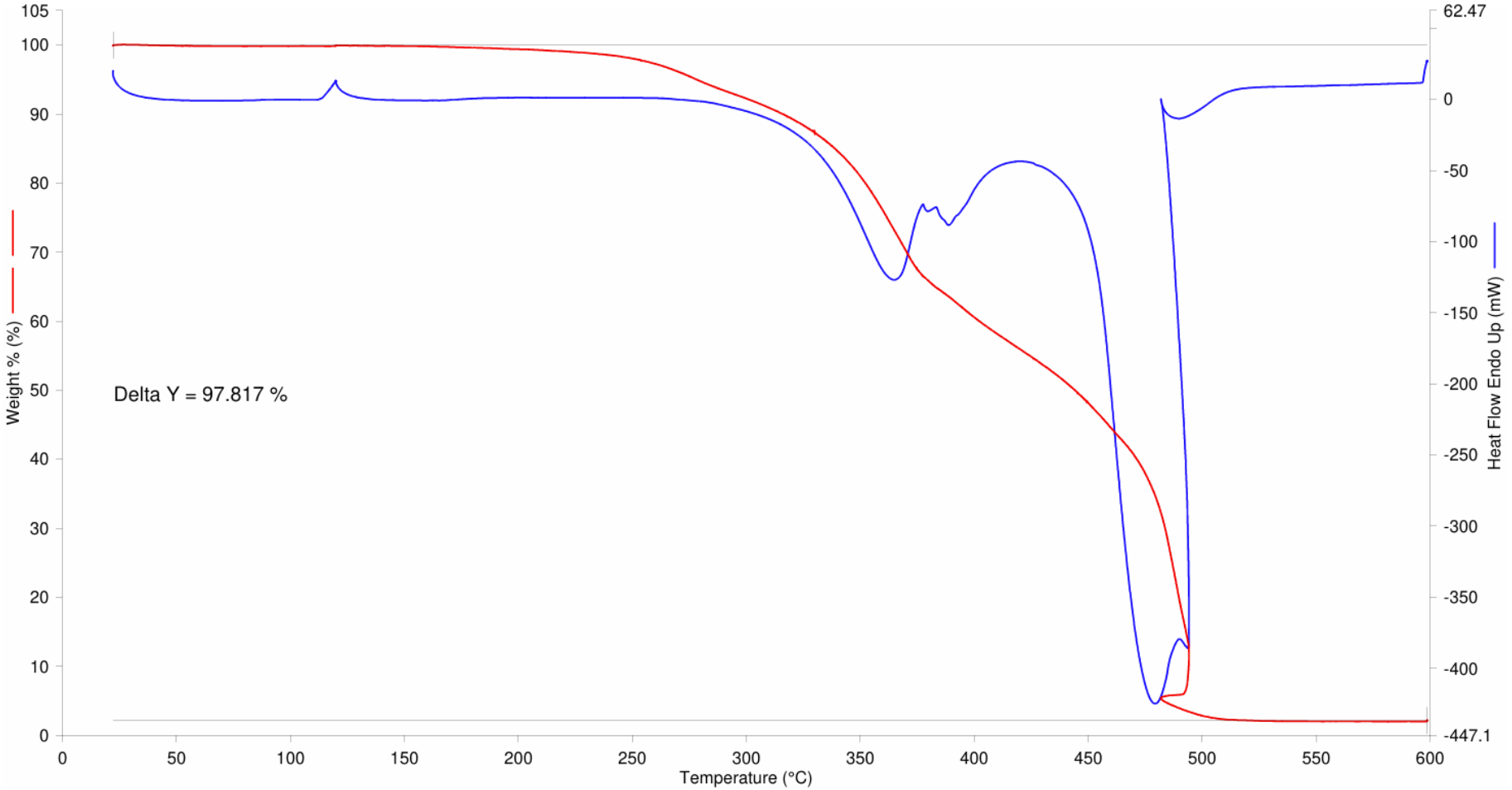
100
90
80
70
60
50
40
30
20
10
0
73.71
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-500
-550
-570.8
0
50
100
150
200
250
300
350
400
450
500
550
600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Temperature (°C)
Delta Y = 97.817 %
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100
90
80
70
60
50
40
30
20
10
0
62.47
0
-50
-100
-150
-200
-250
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-350
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-447.1
0
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100
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200
250
300
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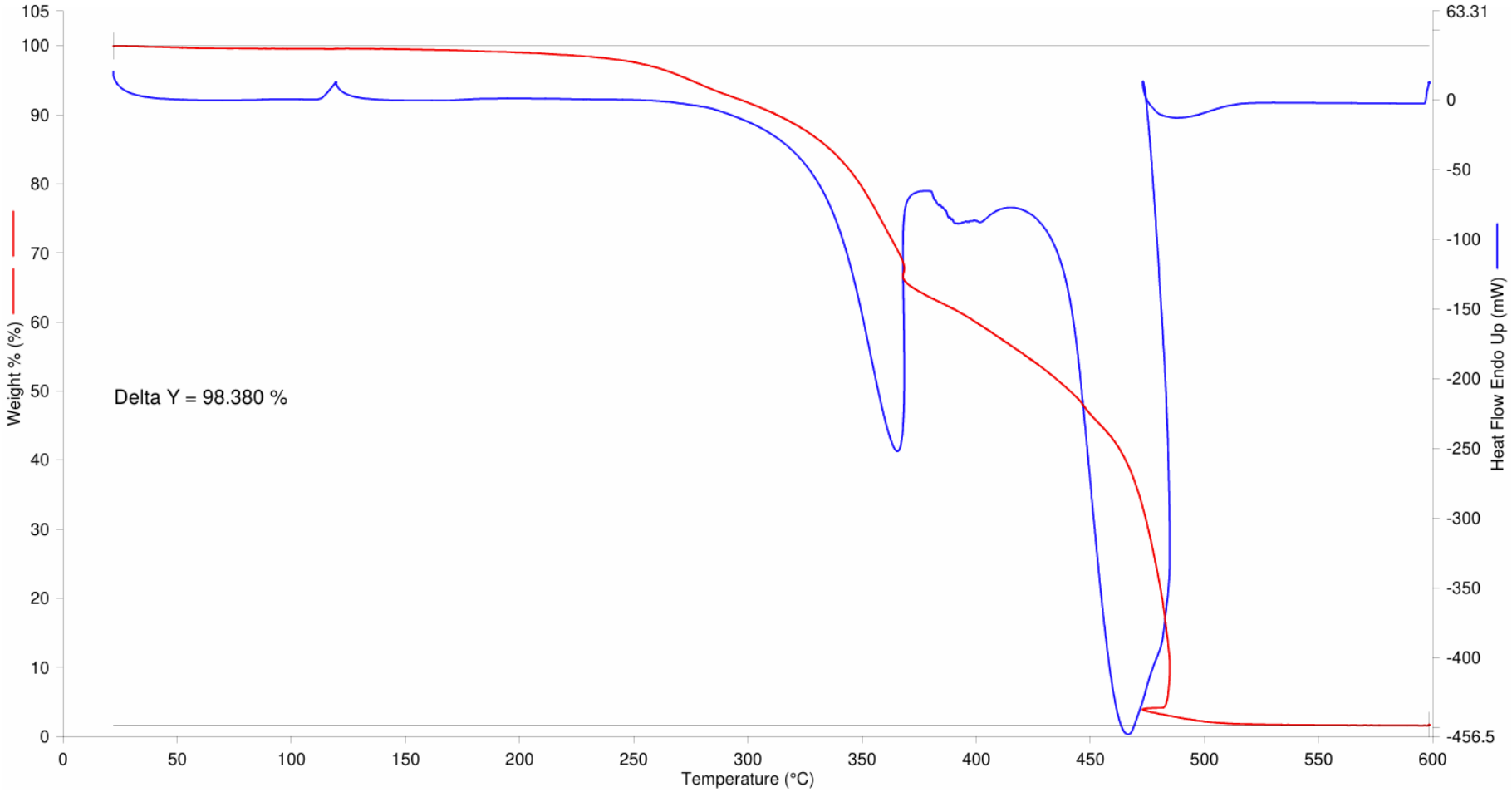
400
450
500
550
600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Heat Flow Endo Up (mW)
Temperature (°C)
Delta Y = 98.380 %
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100
90
80
70
60
50
40
30
20
10
0
63.31
0
-50
-100
-150
-200
-250
-300
-350
-400
-456.5
0
50
100
150
200
250
300
350
400
450
500
550
600