Kaunas University of Technology

Faculty of Chemical Technology

Microplastics in fine fraction of biologically treated waste

Master's Final Degree Project

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Kaunas, 2020

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Environmental engineering (6211EX003)

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Declaration of Academic Integrity

I confirm that the final project of mine, Hooman Ghiasvand, on the topic „Microplastics in Fine Fraction of biologically treated waste“ is written completely by myself; all the provided data and research results are correct and have been obtained honestly. None of the parts of this thesis have been plagiarized from any printed, Internet-based or otherwise recorded sources. All direct and indirect quotations from external resources are indicated in the list of references. No monetary funds (unless required by Law) have been paid to anyone for any contribution to this project.

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Summary

Recently, microplastics have become widely distributed in the environment, so its extraction and identification according to the specific type of plastics has become an important object of research. Scientists and engineers have proposed several different methods for extraction of microplastics.

In this work, microplastics were detected and identified in the small fraction of Torma landfill (Estonia), in the compost obtained at the Kaunas green waste composting facility and in the waste aerobic treatment products obtained at Kaunas waste mechanical-biological treatment facility. During the research, the methodology for the separation of different types of plastic Microparticles from waste fine fraction was improved.

Ghiasvand, Hooman. Mikroplastikai biologiškai apdorotų atliekų smulkiojoje frakcijoje. Magistro baigiamasis projektas / vadovas prof. dr. Gintaras Denafas; Kauno technologijos universitetas, Cheminės technologijos fakultetas.s

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Kaunas, 2020, 63 p.

Santrauka

Pastaruoju metu mikroplastikai yra plačiai pasiskirstę aplinkoje, todėl jų išskyrimas ir identifikavimas pagal konkrečią plastiko rūšį tapo svarbiu mokslinių tyrimų objektu. Mokslininkai ir inžinieriai yra pasiūlę kelis skirtingų mikroplastikų išskyrimo metodus.

Šiame darbe mikroplastikai buvo aptikti ir identifikuoti Tormos sąvartyno (Estija) smulkiojoje frakcijoje, Kauno miesto žaliųjų kompostavimo aikštelėje gautame komposte ir Kauno atliekų mechaninio-biologinio apdorojimo įrenginiuose gautuose atliekų aerobinio apdorojimo produktuose. Tyrimų metu buvo patobulinta skirtingos rūšies plastiko mikrodalelių išskyrimo iš atliekų smulkiosios frakcijos metodika.

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Terms:

MSW– Municipal Solid Waste

MBT_ Mechanical-Biological treatment

FTIR_ Fourier Transfer Inferred spectroscopy

MP_ Microplastics

Introduction

By improving the technology and achieving to the huge source of Plastics, the life style has changed significantly. During the last 50 years, the plastic production is almost 9 billion tones, with 8.3 % rate of increasing (R. Geye 2017). Nowadays plastics play an important role in case of packaging, instrument, life habits and etc. according to the statistics, humans are exposed to plastics through two distinct pathways which are namely direct path and indirect path. Direct one include those touchable plastics for instance, plastic bottles, pens, plates and etc., and on the other hand there are hidden plastics which are found in pharmaceuticals, make up conditioner and etc.

Among all kind of plastics and polymers which have been using recently, the most usable and proper type due to low cost and easily formation are namely, polyethylene (PE), polypropylene (PP), polystyrene(PS), polyvinylchloride (PVC) and polyethylene terephthalate (PET). (Roland Geyer 2017)An estimated shows that around 250 tone of plastics are released to the marine environment and this rate is increasing annually. By using chemical, physical and biological methods in order to recycle the plastics, a huge amount of small plastic debris are generated which classified as indirect source of plastics (German Krzysztof 2005)

Microplastics (MPs) are micro-scale plastic fractions with size of smaller than 5 mm. The term "microplastics" was first mentioned by (Thompson, et al. 2004). In addition, micro plastics can be directly produced by cosmetic manufacturing for variety kind of purposes.

Due to plastic consumption habits, terrestrial and marine environments are threatened. Any kind of extra material added to the any media will lead to thorough changes on habitat. Releasing microplastics into ocean, rivers or other aqua environment can alter the aquatic life and on the other hand bringing microplastics to the terrestrial environment like farms, lands or generally to the soil, malformed the soil habitat and also it is really good media for plants to be grown.

The second group one plastic (hidden plastic) include very small particle in the size of smaller than 5 mm. as it has been mentioned above, recently microplastics extensively detected in sea, shore, land fields, ocean and fresh water. (M.Liu 2018)

Up to now characterization, identification and extraction of microplastics in soil and terrestrial environment is a big challenge for scientist worldwide. There are several methods suggested by scientist and engineers, although they are not sufficient and efficient enough, but they can be used as beginning point.

This research is aimed to compare the quantity and type of Microplastics in fine fractions from biologically treated wasted which have been sampled from Landfill, MSW after Biological treatment of MBT plant and Green compost.

In order to accomplish the affordable and logical results from the research, following **objectives** should be addressed:

1. Literature review to analyze and evaluate the result of previous studies in the same field of identification and extraction of microplastics in both hydrosphere and terrestrial media.

2. Develop the extraction method associating with salt options for brine solution corresponding to density separation method
3. Optimize the extraction by considering the physical treatment at certain condition for sample treatment
4. Create a logic base for removal of organic content of samples without interaction and without reveres reaction to selected salt

5. Recognize and identify the microplastic and their share in different matrices

1. Literature Review

Several Scientific articles and researches were analyzed on order to synchronize our mindset with the reality of current stands of Research for MP. However, there are some hidden and blurry ideas need to be clarified and presented. In this chapter, Comprehensive view of this literature analysis is explained.

1.1. Concept and formation of Microplastics

Microplastics are known, in the simplest way, Conventional plastics with the size of smaller than 5mm. These micro-size particles are classified in two different groups of formation and they find their rout to daily life of human in two pathways.

Plastics are made by an artificial raw materials and can form into different shapes in order to meet the people's need. But plastic industry is not the only source of generating microplastics, Textile industry, Economical Activities, waste treatment plants and packaging services are also another top head sources of MP generation.

Now it would be a question how these Microplastics are grouped in case of Formation. The answer to this question, I should say there are two Classification as shown in below:

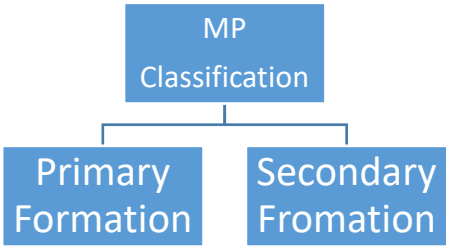


Fig. 1. Microplastics formation Group

Primary group allocate to those activities which has direct contact with plastic or raw material of plastic and polymers, for instance, in a typical factory which produces Plastic bottle, bunch of microplastics are released through the heating, shredding and etc. whereas, Secondary group is the one, which in, microplastics released to environment after manufacturing process. To give a clear example for the second group, scrubbing plastics in waste treatment, sunlight, exposing to heat and acid in daily usage of plastic generate huge amount of microplastics to the environment.

Two pathways are considered for microplastics to enter human's daily life which are namely, direct path and indirect path. The first path, as it is clear from the name, shows an entirely direct contact of people with plastics this group are also considered as secondary microplastics, in contrast the second group (primary microplastics) shows the indirect contact such as washing liquid, cosmetic products, pharmaceutical products, personal care products and etc.

Microplastics consist of carbon and hydrogen atoms bound together in polymer chains. Other chemicals, such as phthalates, polybrominated diphenyl ethers (PBDEs), and tetrabromobisphenol A (TBBPA), are typically also present in microplastics, and many of these chemical additives leach out

of the plastics after entering the environment. All other impurities effect the chemical and physical property of microplastics. (Rogers, Microplastics Particulate plastics)

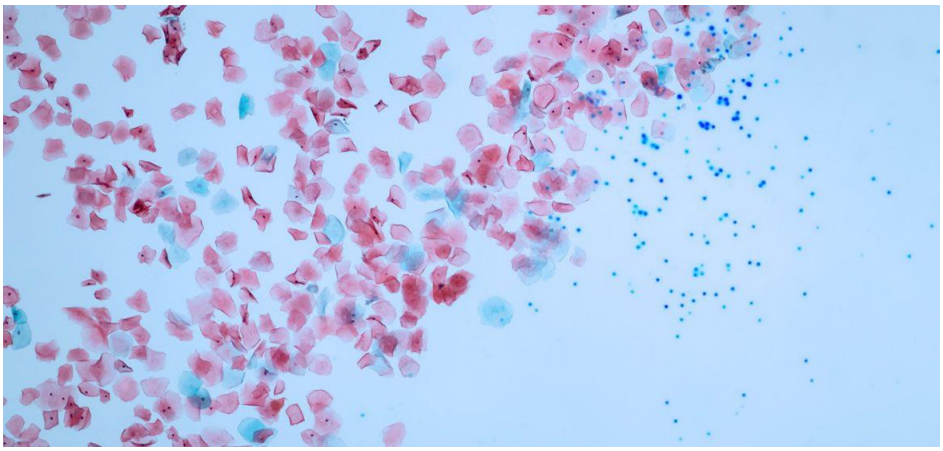


Fig. 2. Microplastics under microscope view **(Ohm 2020)**

1.2. Microplastics in different Medias

Microplastics are ubiquitous from Deep part of ocean to the soil in our garden. The term Microplastics sounds horrific for its presence in both aquatic media and soil media, additionally, variation in density and size of microplastics lead them to float on water current or get stick to different solid organic which add another value to level of horrification.

Let's move from comprehensive view to a little bit scientific and deep details of MP's variation and properties. As it has been mentioned in previous section of this chapter, Microplastics are usual plastics with smaller size and it turns our mind to the point that they should have the same physical and chemical property of conventional polymers, on the other hand their size and capability of being floated on Water or stick to surface are two strong reason to look at them quite differently.

The variation of density of microplastics let them to be settled down and sediment at the bottom of seas, or occasionally suspend in the middle of aquatic media, or even floating on the surface. Consequently, it makes extraction of microplastics difficult and also effects on sampling from oceans, lakes, etc. (H. Zhang 2017)

The major destination of microplastics after natural aquatic Medias, is Water treatment facilities. Waste water is identifies as receptor of MP pollution for its input flow contaminated with different soluble and non-soluble wastes. (Mahon, et al. 2019) This waste stream are changed to sludge at different stages of Settlement regime.

It can be a question that what effects actually presence of microplastics in Aquatic environment has? Answer to this question is

According to Van Sebile, Wilox and Lebreton (2015) only 1% to 2% of plastics ended up in Marine and aquatic media and the rest released to Terrestrial environment. By entering Microplastics to the terrestrial Media and specially soil, some consequences appear. Firstly, Microplastics occupy huge

space of between-soil[1] particles and change the soil habitat, secondly, soil structure mediates plenty of chemical, physical, and Biological processes in soil. In contrast with Aquatic media, Terrestrial environment plays a significant role on Microplastic's Accumulation and fate. It is noticeable to be mentioned that sources of microplastics in terrestrial Media are much larger than that in Aquatic environment, for instance some of these sources are Laundry dust, Car tire debris, Sewage sludge, Blown dust from landfills and paint flakes. (Abel de souza machado, et al. 2018)

Soils biota has a visible impact on transmission of Microplastics, in the other word, structure of the soil itself is involved on microplastics translocation, storage, erosion and degradation. The fact is followed by other factors which have enough influence on microplastic's behavior in soil such as Temperature, humidity and exposure to sun light. (Defu, et al. 2018)

The life cycle of plastics in the earth shows that terrestrial media give more opportunity to polymer and hard plastic to be accumulated and be translocated to the depth than Seas and Oceans. Highly exposed spots for microplastics to be found are MBTs, Landfills, Farmlands and Composting facilities.

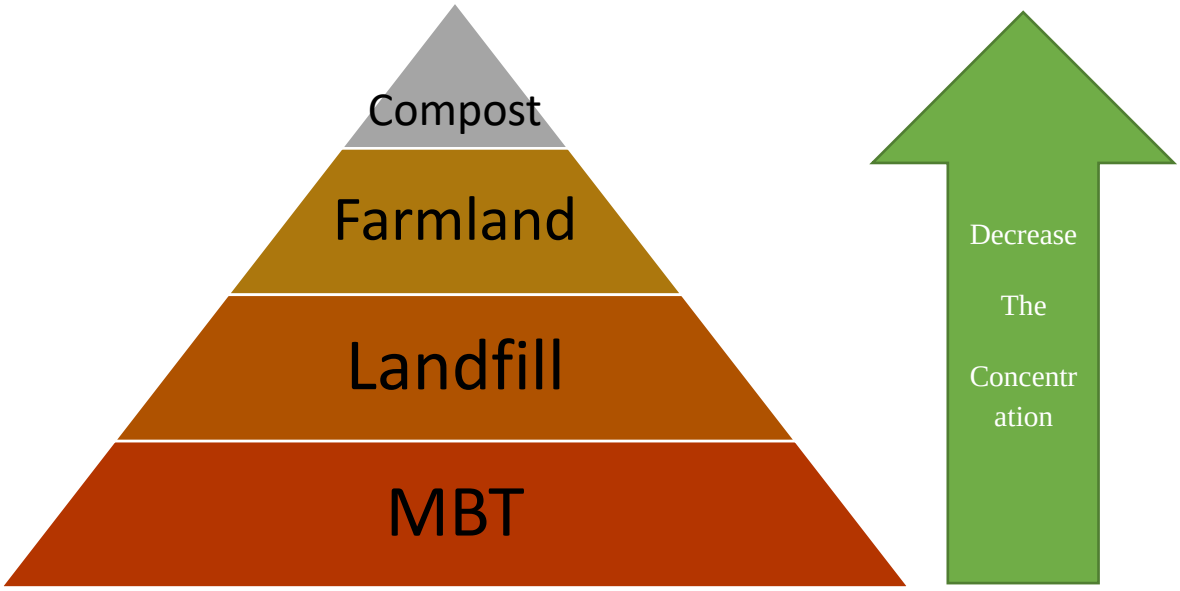


Fig. 3. Microplastics proportion in different section of terrestrial media

Microplastics can be easily transferred from soil through the plant's root to the product and leaves of herbages. Composts are often used as a fertilizer to improve the structure of soil and if it is already polluted with Microplastics then it can cause MP's translocation to plants.

Several researches have been done to evaluate the concentration of microplastics in different daily products and their effects on human's body and most significant products which humans are in exposure to, for instance, tea bags and Health care products. In conclusion, Microplastics exist in Soil and terrestrial Ecosystem has more bad effects on human health, for its straight contact and direct

[1] Normal distance between soil ingredient to circulate water, air and other organic material.

route to human's daily life. Several studies were done to proof if Microplastics can be considered as hazardous waste or not, but still this issue is under investigation (Neira 2019)

1.3. Practice of Microplastics research

Exclusive of environmental media, all investigation and research regarding Microplastics recognition and identification follow these three steps:

1- Sampling
2- Sample preparation (treatment)
3- Identifying

1.3.1. Sampling

Environmental scientists are aware of the influence of sampling on the further study and experiments, therefore, taking proper sample both temporally and spatially accurate can lead the research to high efficient result. There are two major factors should be taken into account for each sample, namely:

1- Depth of sample at both terrestrial and aquatic environment
2- Spatial selection of spots for sample

Depth of sample help the scientist to find variety types of polymer, especially if the sample is taken from aquatic environment. Not all the microplastics are floating on the surface, for their inequivalent density value. On the other hand, for low weight of microplastics they translocate among different spot, consequently, It would be really precise to take different sample from different spot by using statistical methods for modeling the media (Zhang and Liu 2018)

On other aspects of sampling, Method of sampling, using the suitable tools and reservoir to keep sample, are other important factors. Microplastics and generally plastics are sensitive to temperature, UV radiation and in case that the medium where microplastics exist in is basic or acidic then malformation and/or diffusion of microplastics can be taken place. (Mark E. Hodson 2019)

Sampling the terrestrial media for investigation of microplastics requires high accuracy and large volume of sample in order the scientist to be able to have a chance duplicating the process. It is recommended to take sample from three different depth at one particular spot (Wright and Kelly, 2017). This tip helps to have variation of microplastics not only spatially but also temporally because buried samples on the bottom belong to times ago.

Table 1. Principles of sampling and future queries for MP **(Margaret Murphy 2017)**

Microplastics Field Sampling	Microplastics Extraction, Separation and Cleanup	Microplastics Quantification and Characterization
▪ Which sample type/matrix is relevant? ▪ What size range is relevant? ▪ Which particle/polymer types are relevant? ▪ How many samples are needed? ▪ Will samples be kept discrete, homogenized or pooled for analysis, and what does this mean for interpretation of the results? ▪ Which sampling method is appropriate? ▪ What sample volume is needed to get a representative sample? ▪ What quality assurance/ quality control (QA/QC) methods are needed? ▪ Which units will be used for the final results and what does that mean for the comparability of data? ▪ What are the detection limits of the methods used?	▪ What QA/QC methods can be used (e.g., to determine procedural recoveries or to prevent background contamination)? ▪ What are the impacts of the chosen method on the final result? Will artifacts be introduced? ▪ How can sorbed contaminants and microbes be accounted for? ▪ Which polymers/particle types are accounted for, recognizing that some particle types such as microfibers can be challenging to extract and may be lost? ▪ What are the detection limits of the methods used?	▪ What are the limitations of the methods used? ▪ Which polymers/particle types are accounted for? ▪ What are the detection limits of the methods used?

1.3.2. Sample preparation and treatment

When samples are taken, they need to be treated differently in order to let microplastics get separated from other ingredients of sample. Extraction of microplastics requires well separation method. Major method is used for microplastics distinction is Density separation by using variety types of salt.

Method of separation for both Terrestrial samples and water samples can be the same and the most important different between them is how to treat sample before separation started. There are few cautions for different samples which has an impact on effectiveness of separation are mentioned below:

a- **Sample from seas, oceans and lake**

Despite of depth and volume of sample taken from water media, it is recommended to keep sample in dark glass bottles to avoid any interaction with surface of container and also prevent sample from sunlight. Water samples need to be kept in 20 Celsius degree and should be analyzed up to 3 days after sampling, otherwise organic material in sample start to rearrange the structure and sample lost its homogenization. (Young k., et al. 2015)

b- **Sample from sludge**

Samples should better to keep in dark glass container to avoid sun light penetrate and also skip interaction with surface. Sludge samples contain large value of organic material which gives an error for extraction of microplastics, therefor, after taking sample to Laboratory it

should be keep in to big diameter tray to let redundant organics oxygenized and then sample need to be dried in 5 different steps. (Mahon, et al. 2019)

c- **Sample from Green compost**

As it is clear from the structure of the sample, Green compost samples includes a immense proportion of textile, wood, organic material and plants. Green compost is classified as wet solid sample and needs to be kept in metal container or glass container with some paths for air recirculation, also it should be kept away from sun light, for photosynthesis. Sample can be kept in room temperature for maximum 30 days.

d- **Sample from Landfills**

Landfill samples should be kept in large metal container and they should better to keep in room temperature. They last long enough.

e- **Sample from MBT plant**

Municipal solid waste after biological aerobic treatment is the target of sampling, and it requires air circulation. As samples from Landfills it needs to also keep in metal with availability of air to move in. MBT plant is also known as wet sample and for it stinks badly should be treated as soon as possible.

Fig. 4. Microplastics in water sample **(Wiss 2016)**

Fig. 5. Terrestrial sample from dried sludge **(HOgan 2015)**

Solid terrestrial samples after keeping, they need to be heated in different temperature due to character of sample. Samples are dried extensively in temperature around 105 Celsius to 120 Celsius to measure

both humidity and ashes content. All the media should be heated and dried so that it can be sieved easy into different granular metric fraction to be digested in salt solution.

Next step after drying the sample is to keep them in desiccator for 1 hour to become the room temperature and then the experiment followed by Sieving sample into different granular metric fractions. Some studies preferred to remove particles more than 5 mm and only continue process with left overs. (Margaret Murphy 2017) Other studies claim to use different granular metric fraction less than 5 mm to be more efficient of identifying different size of plastic. (Mark E. Hodson 2019)

Up to this step, sample itself has been ready, but extraction and separation of microplastics from no useful content of sample is the task of this step and most important step by far. The most operational method for separation has been used so far, is density separation by dissolving salt into water and make high density or saturated brine to be able make plastics floating on the surface and other heavy fractions settled down the bottom of container. It is noticeable that different researches provided deferent salt solutions and some extra treatment which are shortly described next.

(Mark E. Hodson 2019), suggested two distinct steps of adsorption by Zn and desorption by washing the sample using Hydrogen peroxide. In this case ingested range of Zn by Plastics is high and this function transfer microplastics into a combined material to be desorbed and washed by hydrogen peroxide. Brine solution is made by $Zn(NO_3)_2$ in electrolyte$NaNO_3$. Sample will be added to this solution and shake for 24 hours and later on filtered by Whatman filter 42[2]. They will be washed in ultrasonic bath and air dried and to desorb Zn they should be digested inHNO_3.

Salt Solution using Zinc Chloride is second option recommended by (Mahon, et al. 2019). With the same principles of digestion and removal method operating Whatman filter.

There is another method of elutriation using back washing technique either back washing by flowing air or liquid to remove low weight particles from heavy ones. The risk of this method appears one the samples are small enough to stick to organic heavy. Moreover there are humus, textiles and other organics lighter than microplastics which will be removed by air flow and still another extraction is required.

Physical treatments play important role on separation and removal of plastics from solution. Three methodology offered by previous study namely, Shaking, Centrifuge and thermal heat loss. On the next chapter we will take a broader look on how these methods work and what the advantages and disadvantages they have.

1.3.3. Identifying the extracted particles

All polymers and particles have been found in the samples need to be identified due to their type and properties such as PET,PS, PE and etc. this identification is done by two major methods namely, FTIR (furrier-Transform Inferred spectroscopy) and RAMAN spectroscopy.

[2] Type of paper filter with accurately low penetration value and low speed filtration

That would be quite difficult to identify microplastics of various sample sizes and different shapes and polymer types just by applying one method of identification, therefor, the combination of two methods are used to increase the accuracy and precision of result. This combination consists of physical characterization at first step and followed by chemical characterization at second step (W.J.Shim 2018)

Scanning electron microscopy (SEM) can clearly provide high0-magnification images of the microplastics found in the sample with high resolution quality. And Energy-dispersive X-ray spectroscopy (EDS) provide the elemental analysis of sample content based on different wavelength absorbed by them. (W.J.Shim 2018)

To figure out what other organic and inorganic materials are included (Nizzetto, Futter and Langaas 2016) suggested to use SEM-EDS analysis to observe the proportion of other content in the sample. EDS analysis should have been done before microplastics identification.

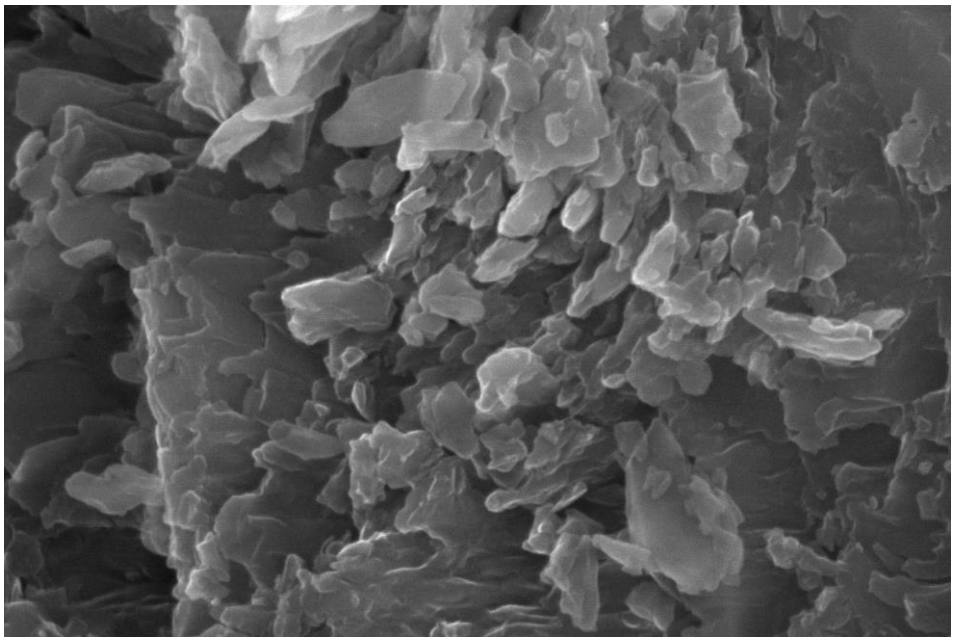


Fig. 6. SEM sample photos of silicate (Pum Dietmar 2019)

To observe the high quality images of sample, two major principles of Wavelength (corresponding of the size of sample) and washed sample with salts.

2. Research Methodology

The second chapter of the research includes all experiment and methodology used for the sample, starting with sampling and continues with methodic improvement and at last the identification techniques. The main purpose of this chapter is to make the reader more familiar with the work has been done and detailed information regarding improvement.

2.1. Research objects

2.1.1. MBT and MSW

Previous chapter talked about the literature review of current study, and more or less, it was clear that most of the studies in terms of Microplastics analysis have been managed to investigate samples from marine area and Aquatic environment. However, Microplastics exist in terrestrial and solid environment. In the other hand, Microplastics quantity represents the past utilization of plastics, or generally Polymers, n the environmental media.

Aquatic area, Hydrosphere, is defined as a platform of growth of plastics ion the earth, moreover, water and marine environment conduct the polymers, in any sizes, from one spot to another spots, in contrast, Terrestrial media accumulate polymers or let's say the general wastes in the solid and solid media (lithosphere).

MBT is a generic term used for the combination of various mechanical (grinding, separation, screening, pneumatic classification, etc.) and biological processes (occurring under aerobic and anaerobic conditions). (Garg 2014) MBT plants are used to separate mixed waste streams, typically from MSW, into a range of dry products (typically ferrous and non-ferrous metals and glass), high calorific value refuse derived fuels (RDF) suitable for incineration, and wet biodegradable slurries suitable for either composting or anaerobic digestion (AD) (DEFRA 2012b)

Main biological treatment options used in MBT include bio-drying/bio-stabilization, in-vessel composting or anaerobic digestion. Standard aerobic MBT process with RDF production is showed in the pic 7.

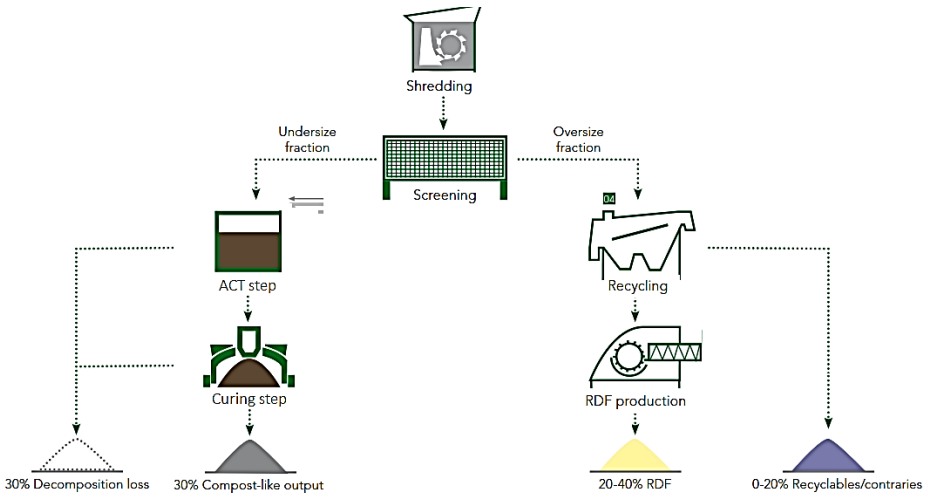


Fig. 7. MBT process schematic

The biological element of an MBT process can take place prior to or after mechanical sorting of the waste. In some processes all the residual MSW is biologically treated to produce a stabilized output for disposal to landfill and no sorting is required, but generally MSW is sorted by vibrating, trammel or disc screens into undersize fraction which is subsequently sent to biological treatment, and oversize fraction, which is used for RDF production and resources recovery.

Undersize fraction may have various grain size, which depends on technological needs and machines used in the process (Bilitewski 2011) (Marlena Debicka 2013),Most frequently, the undersize fraction is characterized by grain size below 80, 100 or 120 mm. A common feature of the undersize fraction is high content of organic and mineral waste, paper, cullet and small plastics. (Malinowski 2017)

MSW requires mechanically pre-treatment before biological, which are mainly aimed at "condition" the physical nature of waste to be biologically processed and remove non-compostable materials (Ricci- Jurgensen 2016) . First MSW is shredding. The machinery used in this phase varies in terms of its shredding effect and depends on the type of waste to be treated. Most commonly used equipment in composting sector is hammer mills. It have shredding unit made of one or more horizontal fast-rotating shafts (1.000-2.000 rpm), provided with swinging hammers or clubs (the number and shape depending on the model). These machines are particularly suitable for green waste shredding, since they are able to de-fibre wood instead of cutting it, thus increasing the contact surface between C-rich and N-rich materials (Ricci- Jurgensen 2016)If the waste is delivered in bags, the trammel screen might be equipped with blades to open the bags.

The last stage of preprocessing is usually the adjustment of moisture and C/N and the addition of a bulking agent. Typically, acceptable C/N ratios are obtained by mixing putrescible waste and lignin base organic waste in appropriate rates (50-65% putrescible; 35-50% garden waste) (Ricci-Jurgensen 2016) Mixing trammels and pug mills can be used for homogenizing and mixing of two or more feedstocks. In smaller facilities mixing is combined with other unit operations such as size reduction and screening. (Bolsrin, et al. 2010)

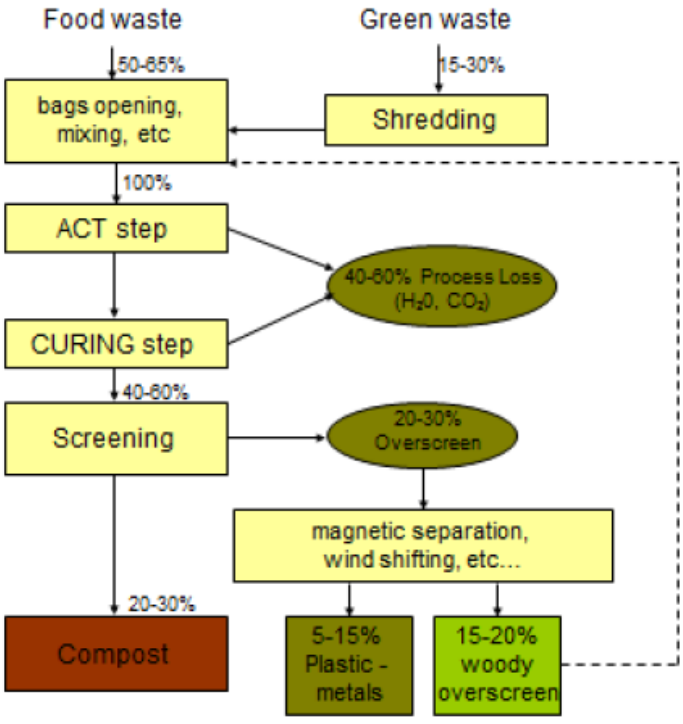


Fig. 8. Material flow of a standard composting process

Municipal waste consists to a large extent of waste generated by households, but may also include similar wastes generated by small businesses and public institutions and wastes not collected by the municipality. The content of MSW can be differ from one district to another the reason of this vast distribution depends on socio-economic structure, income level, consumption, and usage habits of people, but there are some material which are always obtained in MSW. It being said that the proportion of contents of MSW is quite important for both aeration and an aeration process, below the pie chart reveals the main content in usual percentages.

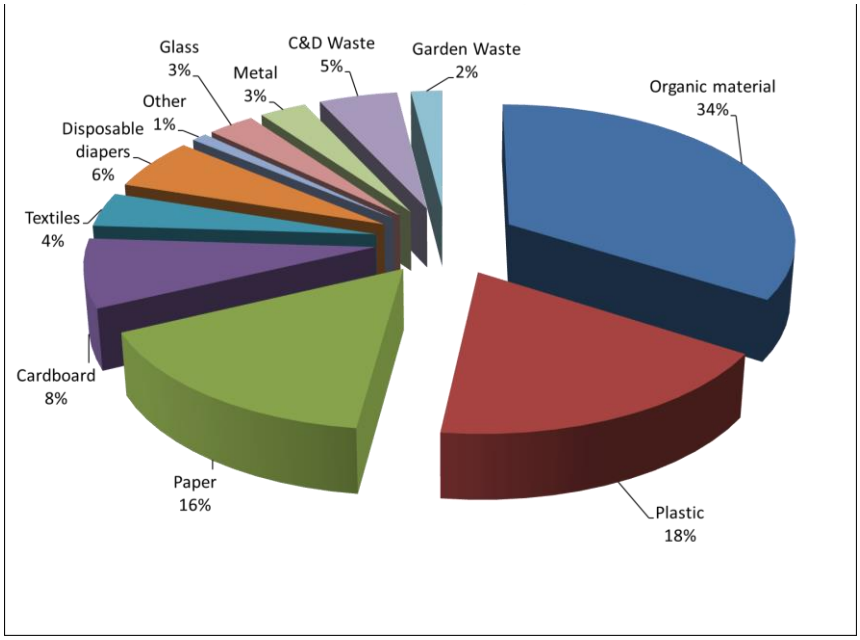


Fig. 9. Content of MSW **(https://ya-webdesign.com/image/landfill-drawing-municipal-solid-waste/1117273.html 2015)**

2.1.2. Landfills

Disposing wastes to the landfills (open area waste storage) has become approachable since middle of 60's. By improving the technology of waste recycling and reusing, quantity of waste deposed has b been decreasing noticeably. Landfills are not designed to break down trash, often to bury it. That's because they contain minimum quantity of oxygen and moisture, which prevents trash from degrade and break rapidly. So landfills are carefully filled, monitored and maintained while they are active and for up to 30 years after they are closed.

Landfills are divided into two groups namely, active facility and passive facility. The load of waste on the place annually differentiates the active from passive.

Due to variety types of regulations and prevention, landfills are structured to minimize the impacts on the soil, ground water and also gaseous to atmosphere. It should be mentioned that, the structure of landfills are varied from country to country, for different ambient factors, temperature and moisture, effecting the potential degradation and breaking down of waste.

Fig. 10. Landfill and accumulated waste **(Vine 2017)**

This prevention and structure is described below:

The following cross-section shows the different layer and technologies used for a conventional landfill based on standard of Waste management organization. The arrows indicate the flow of leachate from new waste added to the oldest ones on the bottom. The basic and fundamental sections of landfills re:

1. Bottom liner system: this part is responsible for separation of leachate from ground water to avoid any contaminates released to the ground water and under layers.
2. Cells (from old to new, bottom to top), are the places where trashes are stored
3. Storm water drainage system is the auxiliary system which conduct water rain to another storage place to avoid leachate and density water which leads to bad odors.
4. Leachate collection system is accumulative tank or pool which collects all leachates and drainages
5. Methane collection tank is another capsule which stores methane is formed by the waste during the aeration reaction.

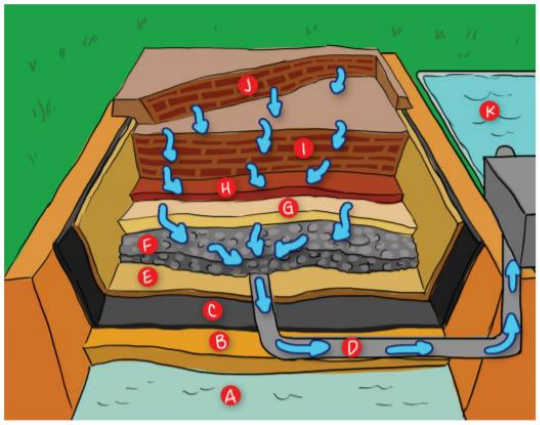


Fig. 11. Landfill's structure **(Freudenrich 2016)**

Sampling from landfills is quite complicated if the scientist needs special depth and location. Landfills and their operation are monitored by different sensors and are captured using drone and other instruments. There are few new methodologies provided to monitor the landfill's operation and its prevention.

2.1.3. Green compost facility

The average household produces tons of green wastes which are suitable to be converted to fertilizer. General views of composts include Brown mix and Green mix, and the quantity of nitrogen and protein is a term which differentiate these two terms.

In contrast to brown mix, green mix heat the pile up due to the activation and operation of microorganisms, and on the other side of card, brown mix is the one contains carbons and carbohydrates material. Brown mix plays a role as a food for organisms to break down the entire waste in the pile. Brown mix material are woods and dry particles such as Pine needle, straw and hay, cotton fabrics, etc.

Keeping the suitable ratio of the Green to brown mix is always recommend by specialist in order to avoid both not oxidizing the waste and also not slow down the process of breaking down. Without a good ratio of green and brown compost mixture, either the compost will never heat up or it will take a long time to break down into usable compost and it means the final result will not have the suitable properties of fertilizer. A usual and proper ratio is 4:1 browns (carbon) over greens (nitrogen).

Temperature is a factor which needs to be monitored continuously to keep the compost's operation under control, for high sensitivity of nutrient to temperature. Heat and productions of Composts, step by step, are handed forward. In order To activate Micro-organism with the highest potential efficiency, temperatures must remain between 90 and 140 degrees Fahrenheit. Heat may cause any destroy on ingredients and seeds. at certain and ensured temperature of heating the compost s performed perfectly and high quality of product plus quickest way. Compost not heating up to proper temperatures will result in a smelly mess or a pile that takes forever to break down.

Fig. 12. Compost waste before compile **(Walatka n.d.)**

The indoor and outdoor compost are two terminology used to define the whole process of composting due to high technology tips used.

Indoor composting refers to households which produce and separate their own green wastes from others and try to extract the benefit of it. This benefit is mostly called Fertilizer which will be returned back to the house gardens or other uses. However, the green compost has high level of effects on recycling globally, but maintenance and monitoring the process requires accuracy and patient. On the other hand, those household which obtaining the green product from their land, can use this methodology for its low custody and significant help to recycle.

Outdoor compost is a term which mostly uses for those big landlord who are not able to provide or effort indoor composting, for either having not enough place to set up the facility or huge load of green wastes monthly or even annually. Outdoor compost facilities is a huge property with large capacity of compiling the wastes under operation and monitor. The result is mostly sold out to costumer with affordable price.

Each individual factors mentioned which have effect on compost process are discussed right down below:

Moisture content:

Ideal moisture needs to be operate for normal compost is around 60%. The initial moisture content stands between 40 to 60percent with corresponding to the type of the sample. If the moisture content decreases less than 40%, microbiological activity slows down. If the moisture content goes beyond 60%, decomposition decent and odor from anaerobic decomposition is emitted. it shows that the composting condition is really sensitive to moisture range and if the moisture content exceed the mentioned interval, then the composting will turn to unconditional situation.

Temperature:

During the oxidizing activity of bacteria and other types of microorganisms the heat is produced and transferred through decomposing system organic material. The ideal temperature range within the compost for it to be efficient varies from 32°C to 60°C. If the temperature is outside this range, the activity of the microorganisms slows down, or might be destroyed. (Haggar 2010)Bacteria and microorganisms activity depends on the ambient temperature and also system temperature.

Oxygen (aeration):

A continuous supply of oxygen through aeration is a must to guarantee aerobic fermentation (decomposition). Proper aeration is needed to control the environment required for biological reactions and achieve the optimum efficiency. Different techniques can be used to perform the required aeration according to the composting techniques. The most common types of composting techniques are natural composting, forced composting, passive composting, and vermi-composting. (Haggar 2010)

The content of compost is shown below at normal and conventional ratio of both indoor and outdoor packages.

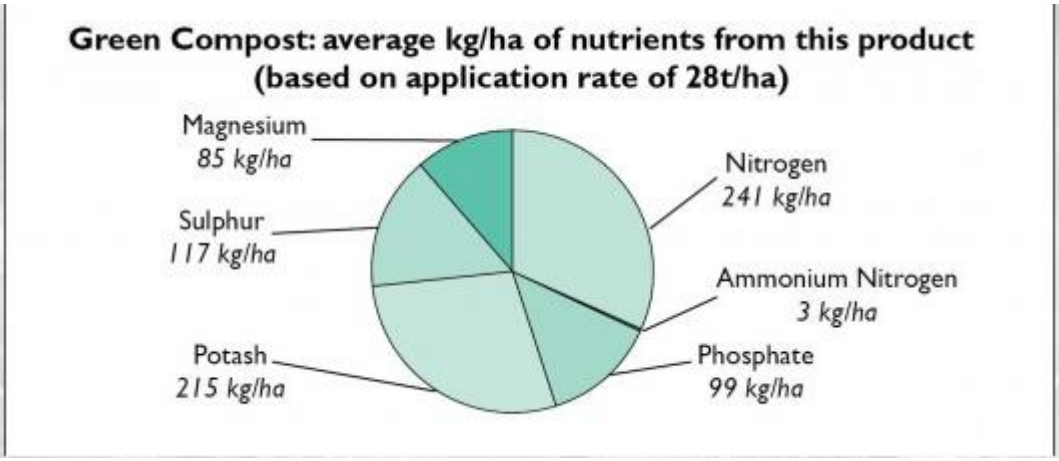


Fig. 13. Green compost nutrient **(flyer n.d.)**

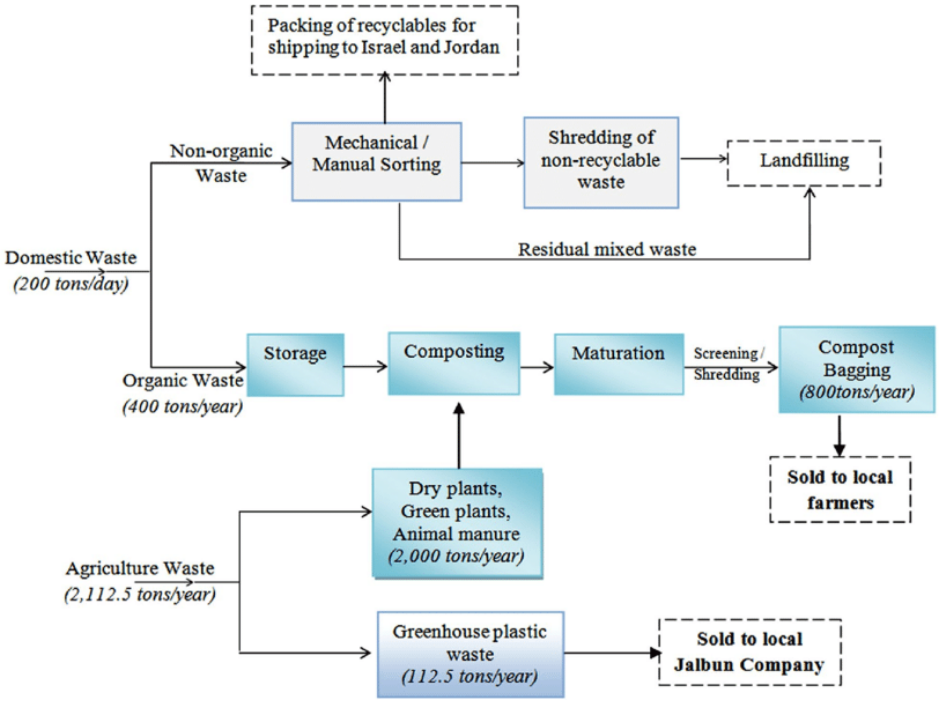


Fig. 14. Scheme of Composting in conventional waste processing for Recycling in Palestine **(Bonoli, Zanni and Aware 2019)**

2.2. Sampling

Each environmental scientist is aware of the importance of Sampling before any other processes begin. Firstly, it would be really great if we could take a short and comprehensive look on why sampling is really important and what the principals are. Secondly, the essay will continue with samples have been taken for the current study considering preservation and post prevention of sample.

Without proper and suitable sampling the rest of the experiment either will never proceed or the result will face with high errors. Samples and the quality of sample ensure that minimal requirements for experiments are met and if the practical part executes undergoes the defined and tested methodology, then final result has got something to claim.

First step of sampling is recognition of the study itself. Scientist should be aware of nutrient, content and broader view of project in order to be able to take proper sample. This recognition becomes clear one the scientist assure about raw material he or she needs. Then second step is to find a place and time to take sample. Spatial and temporal factors indicate the quality of sample due to the age of sample and periodical changes.

Samples taken from aquatic environment for instance, River, lake and etc. the depth of water and also spots on surface are important, for the turbulent flow of the water and mixture of dissolved material in water. For example, the place where the effluents are released to the water has significant amount of pollution than kilometers far away than that spot and also if the effluent is released twice per day at right particular period, temporal factor also should better to be taken into account, in order to not missing time interval.

Spatial and Temporal factors used terrestrial media have different meaning than it has had in aquatic environment. Here we will describe each of these factors for each particular sample we have taken.

Landfills are known as mountains of trashes which are bounded together and that's clear that the more button layer is observed, the older the samples are. In this case temporal factor is hardly related to the depth of the place where the sample is taken. It needs to be considered that due to non-homogeneous trashes distributed in landfills and also mechanical prevention of the facility, samples are in subordinate layer could be broken down or might have changed in physical and chemical aspects. On the other hand, spatial factor defined as thorough investigation of the land using different tools and software to monitor the temperature, density of trashes and geological indications. Samples from the landfills are more unlikely taken by grabber and keep in containers closed with top head and in this case study, samples kept in plastic container.

Fig. 15. Sampling container made by Glass with top head, **(JP n.d.)**

Several types of gaseous are generated by trashes and in the picture above we can see a tank with a suction to remove the gas from sample as much as possible to make sure sample will not have any chemical reaction or passive reaction with gases.

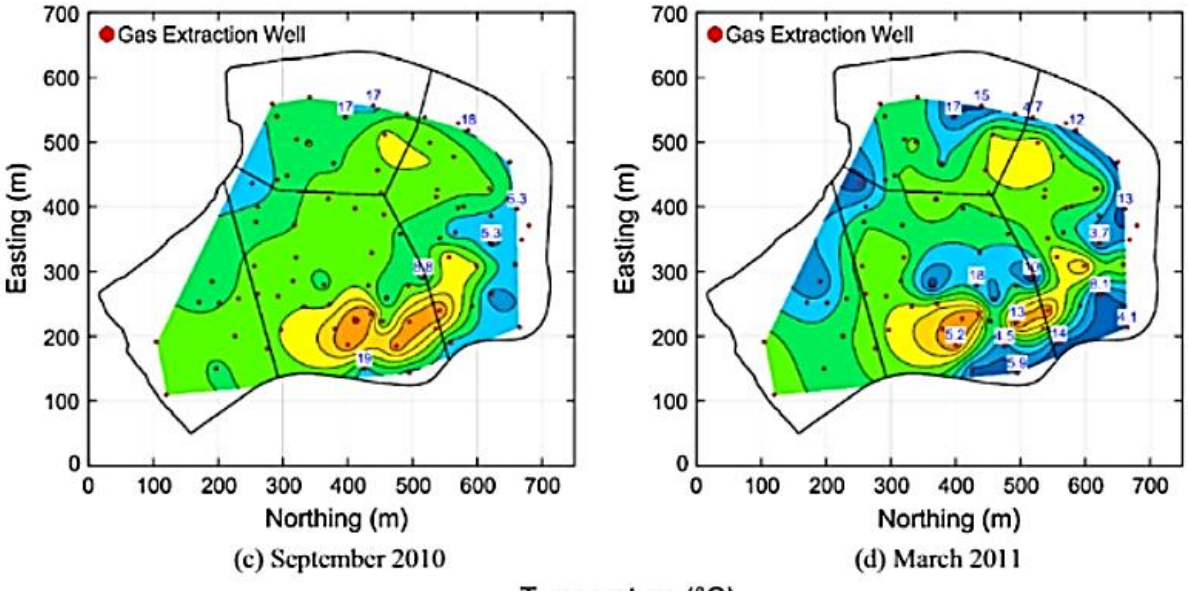


Fig. 16. Temperature analysis of a landfill **(Navid h. Jaffari 2016)**

The red pars show high temperature and high dense of trash and by moving toward the blue both temperature and density decrease. Drone is a useful tool to take a wide range photos merged with thermos-analyzer. These photos help scientist to figure out which spatial coordinators should be marked for sampling and also in which depth high level of gases obtained.

Second sample is Municipal solid waste after biological treatment. The process of mechanical and biological treatment is done daily in special treatment continuously it actually indicates that the person who is responsible for sampling of MSW needs to be aware of biological treatment of local MBT plant to have enough time to catch sample if the time plays an appropriate role in his or her study. And the spatial training of the sampling comes to the point once it is important for scientist to take sample before they have contact with air or right after aerobic treatment. Samples we have taken from MBT in Kaunas was from the last step of separation and biological treatment. The have kept into plastic container with top head door in order to decrease ambient humidity penetrate into sample mixture. Furthermore, they have kept in room temperature and in closet to avoid sun spectrum.

Table 2. Basic content of MSW

Name (assortment)	Measure units., t, m3, units, etc.	Volume per year
metals	Kg/capita	73 kg/casita
Material for cultivation of Landfill	Kg/capita	101 kg/capita

glass and plastics	Kg/capita	137 kg/capita
Biogas	m3	
RDF (refused derived fuel)	Kg/capita	

Fig. 17. Municipal solid waste in reservoir (Tenys n.d.)

Third sample is green compost which has been taken from the composting facilities. Temporal factor is defined by amount of carbon inside the compost after treatment. And spatial factor is recommended by using random spot using statistical measures. Green compost is used s fertilizer, consequently, it is important for scientist to choose the most temporal factor to eliminate any other impact of substances which indicates the quality of compost such as nitrogen and carbon and also amount of organics.

Fig. 18. Green compost facility

2.3. Description of the methodology used

In the literature review we have seen that variety kind of methods are recommended from sampling until the treatment step. We have made a conclusion that which of these methods are mostly suitable and we have tried to improve the methods in order to accomplish higher efficiency. Later on, the developed content of method and techniques we have used will be described briefly.

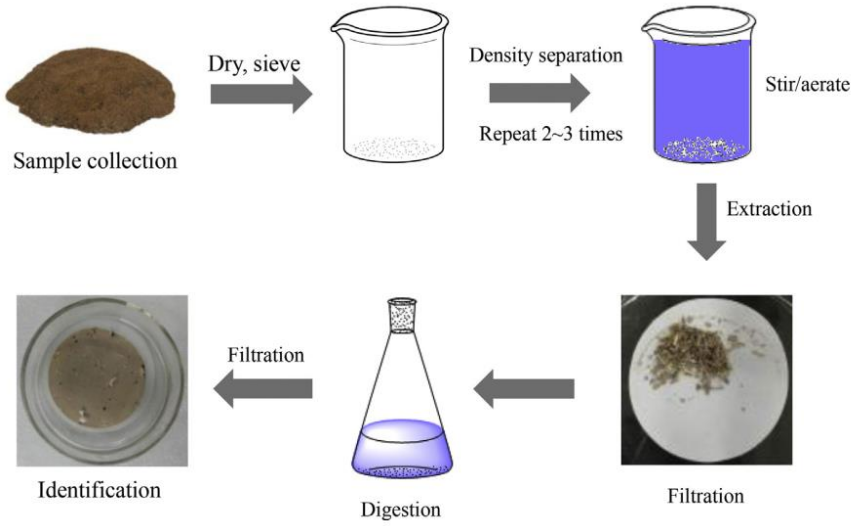


Fig. 19. Scheme of entire analysis and method **(Young k., et al. 2015)**

The diagram above shows each the flow of experiment step by steps from the sampling until the identification by FTIR, next section we will take a look deeply and with more details about each step's scope and reason.

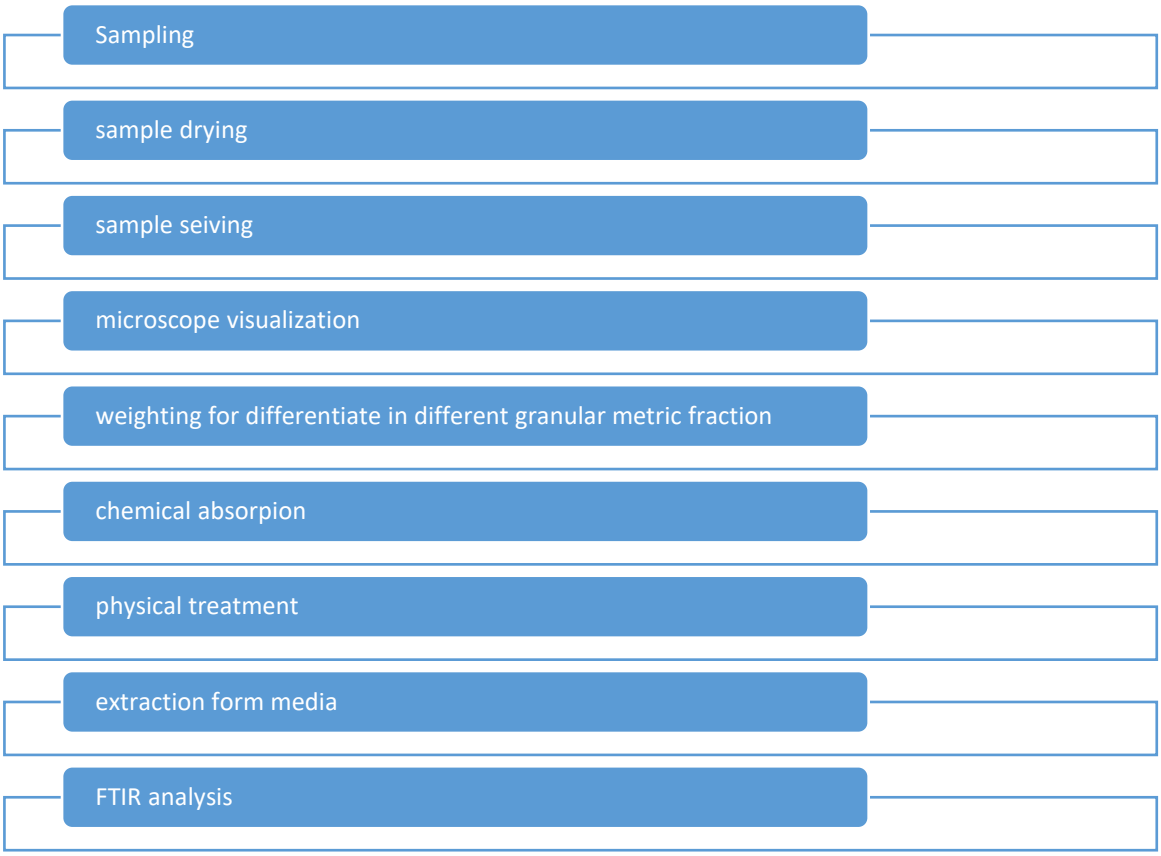


Fig. 20. diagram of the method step-by-step

2.4. Sample primary treatment

The flow chart in previous section mentioned about the step of sample drying. After sampling, all samples need to be dried at two steps with distinct thermal condition to find out both moisture content and ashes content. The process of heating is described afterward:

a. Heat the sample in the furnace at 105 Celsius for 45 minutes

b. Keep the sample in desiccator for 30 minutes (to cool down the sample to room temperature and avoid effect of ambient factors on sample)
c. Second round of heating at 95 Celsius for 30 minutes
d. Keep the sample in the desiccator for 30 minutes
e. Third round of heating at 70 to 75 Celsius, depends on type of sample, to measure moisture content
   - The temperature is asked to be monitored during heating to keep it remain at defined value to avoid any noises and thermos shock specially for samples from compost which are known as high combustibility material.

Fig. 21. Typical device used for drying **(brand 2010)**

Fig. 22. Typical desiccator to avoid ambient moisture

These values are quite important, for effects of moisture on weight. Furthermore, moisture content of sample has an impact on its absorption in the salt solution. Table below show the moisture and ashes content of each sample separately. The formula to calculate it can be found down below.

$$Moisture = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

- W_2 is the weight of the sample after heating

- W_1 is the actual weight of the sample before heating

Table 3. table of moisturea and ashes content

Sample type	Moisture Content
Torma Landfill	24.14 %
Kaunas MBT sample	42.1%
Kaunas green compost	49.6 %

All the values calculated above complied with statistical estimation of process and average value set as final value. It is clear composts had the highest amount of moisture which it is assumed as burnt of low heat organics like leaves and petals. Samples from landfill obtained the lowest value of moisture.

For importance of the size of microplastics we have decided to divide them into different granular metric fractions by sieving them. This step let us know how each fraction reacts to the salt solution for digestion. Moreover, we have had a chance to see samples under microscope visually in case if the sample contains colorful polymers. Following tables show the result of each fraction's weight and size.

Table 4. granular metric fraction of MBT sample

Sieve size	Weight (gr)	Weight proportion (%)
>1.5mm	11.7	33.4 %
>1.2 mm	3.1	8.85%
>1 mm	6.98	19.94%
>0.75 mm	5.45	15.57%
< 0.75mm	9.77	27.91%

Table 5. Granular metric fraction of Green compost

Size	Weight (gr)	Weight proportion (%)
>1.5mm	6.56	64.88%
>1.2 mm	0.61	6.03%
>1 mm	0.18	1.78%
>0.75 mm	0.46	4.54%
< 0.75mm	1.79	17.70%

Table 6. Granular metric fraction of Landfill samples

Size	Weight (gr)	Weight proportion (%)
>1.5mm	18.017	79.04
>1.2 mm	1.243	5.45

>1 mm	0.434	1.9
>0.75 mm	0.687	3.01
< 0.75mm	1.792	7.86

Fig. 23. Sample after drying

Samples are ready for chemical and physical treatment analysis according to the literature review.

2.5. Salt solution and its importance

Principle of extraction and separation of microplastics is based on density separation and we know that each polymer has different molecular weight and respectively it has different density.

Table 7. Density of some popular polymers **(German Krzysztof 2005)**

Plastic Symbol	Name	Density (gr/cm3)	Utilization
PP	Polypropylene	0.9-0.92	Plastic ware
LDPE	Low Density Polyethylene	0.91-0.93	Squeezable bottles
HDPE	High Density Polyethylene	0.94-0.96	Milk bottle and bags
PS	Polystyrene	1.03-1.38	Egg carton packing
PETE	Polyethylene Terephthalate	1.35-1.38	Water bottle
PVC	Polyvinyl Chloride	1.32-1.42	Cling wrap
O	Often Polycarbonate or Acrylonitrile butadiene styrene (ABS)	1.3-1.06	Auto body part of machinery

As it is clear from the table, some of the mostly used plastics have the density lower than the density of water and let them to be floated on the water and in contrast some others, PETE and PVC and PS,

have the density higher than water density and it allow them to sediment on bottom layers or in some aquatic medias, Salty water, they are suspended.

This physical-chemical property of polymer let them to stick to different material in soil and other terrestrial environment and easily transport from one side to another side, on the other word, microplastics can move to different layer of soil, for their small size.

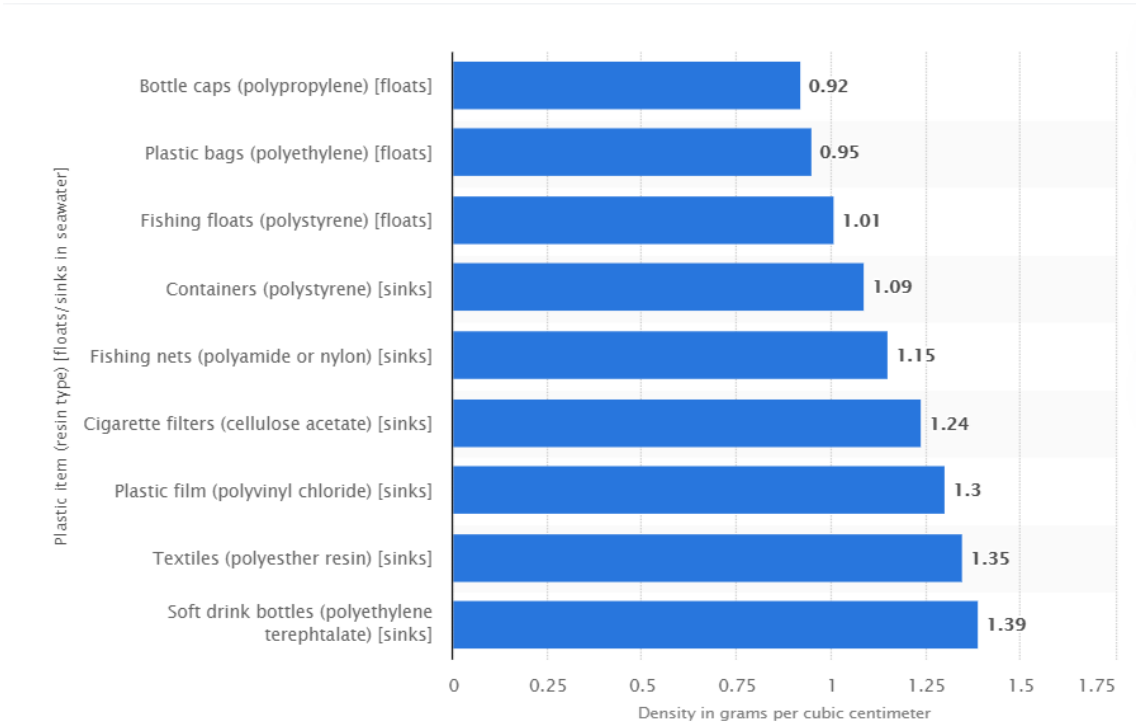


Fig. 24. desperation of microplastic in aquatic media based on density **(departemnt 2016)**

From another aspects of the Density of microplastics, it allowed us to make an improvement on the salt solution and salt selection for different types of polymers could be found in samples. Among all other indications mentioned. Selection of the proper salt for solution and digestion of sample plays the most significant role in this study. Based on the method of density separation, different salt can make the solution high density so that particles with lower density float to surface.

It may work with any type of salt and the result can be different time to time. The wrong salt leads the experiment to give an error because of low separation ratio and malformation happening while physical treatment is happening. Below we try to announce the researcher about salt selection.

It may be a question how to find the proper salt for corresponding sample type, the answer is complicated because of non-homogenized ingredient. Additionally we made a table for terrestrial samples after redoing all experiment and comparing the result. It is also really important if the microplastics are recognized in water and aqua media because of natural organic salt contained in water. Recently, there are some research done in order to figure out the content of microplastics in sea salt and mine salts from different elements. The occurrence of microplastics (< 5 mm) in coastal and oceanic environments has gained global recognition due to their threats to the marine environment and ecology (Van Sebile, Wilox and Lebreton, 2015).

A recent study has developed an extraction method for light density plastics such as PE and PP from soils by distilled water, with advantages of simple and cost-effective. (Zhang and Liu 2018)

Table 8. Salts recommended for terrestrial environemnt

no	Salt	Description	Corresponding sample
1	NaCl	Normal distribution in sample media with highly adjustable bound with organic compound	Landfill
2	$ZnCl_2$	Hardly adsorbed by inorganic material	Biologically treated MSW
3	$CaCl_2$	Trap humus content and help them to settle down	Compost

NaCl (Sodium Chloride): it is known as casual salt for separation of low density plastics, it has chosen for samples from Landfill. Landfills contain more light plastic.

$ZnCl_2$ (Zinc Chloride): it helps the washing of microplastics from sample integrated becomes easier and has lower reaction with hydrogen peroxide.

$CaCl_2$ (Calcium Chloride): it has less effect to organics such as humus and wooden ingredients than other salts and will not destroy the structure of sample.

At the first experiment, we have used all types of salt solutions mentioned above and the result could not make us satisfied because after identification the number of particles and their types. Major problem was that this digestion mix with physical treatment made the sample hardly stick together and filtration became difficult.

Fig. 25. Sample from landfill less than 1 mm fraction

To increase the efficiency of separating microplastics from the introduced hub sample, it was decided to use a new and efficient method. The proposed method consists of several separate steps, so that each step separate different type of polymer according to the salt which is used for particular density. Each step is distinguished from the other by Purification.

Since samples are digested in different salt solution, the salt and chemical used as an agent media are partially merged with organics and need to be separated. This separation is called purification which we will clarify it later about the process and chemicals used.

The list below shows the type of salt used, their density, their target polymer, and instruction of preparation are shown.

Table 9. Salt and agent used for separation

Salt	Chemical name	Density (g/cm^3)	Sediment	Polymer target	Purification Agent
NaI / $ZnCl_2$	Sodium Iodide/ Zinc Chloride	3.67 / 2.91	Sand/dust	All polymer	H_2O /H_2O_2
$CaCl_2$	Calcium chloride	1.35	PET,PVC	PP, LDPE, HDPE,PS,PC	H_2O_2
NaCl	Sodium chloride	1.20	PET,PVC,PC	PP, LDPE, HDPE,PS	H_2O
H_2O	Mineral water	1.001	PET,PVC,PC,PS	PP, LDPE, HDPE	--------
MeOH 25%	Methanol	0.9592	PET,PVC,PC,PS,HDPE	PP, LDPE	H_2O_2
Ethanol 60%	Ethanol	0.8927	PET,PVC,PC,PS,HDPE,LDPE	PP	H_2O_2

Each step needs to be washed by purification agent for several times to remove all leftovers of salt and make sure that the next salt solution will not interact with previous one. This improvement is quite time consuming method because each steps needs 10 to 12 hours to be washed and also physical treatment for each step takes 4 to 6 hours. Table below shows the positive and negative features of this methodology.

Table 10. Pros and Cons of Method

Advantage	Disadvantage
• High separation for each particular polymer • Capable to be implemented for any sample • Less disturbance with organic material	• Time consuming • No more than 5 hours delay between steps, otherwise malformation will occur • Unlikely the sample to be defused

As it is clear from the table above, it might be a problem if the time interval between each step is delayed to more than 5 hours approximately, for direct contact of sample with other variety chemicals. Extraction of microplastics is performed by using Whatman filter 42D which is suitable for filtration

at Micro size. Later on we will explain briefly how to use Whatman filter and how to operate physical treatment for each sample size and sample type.

The following diagram shows the scheme of the improved methodology in a simple way.

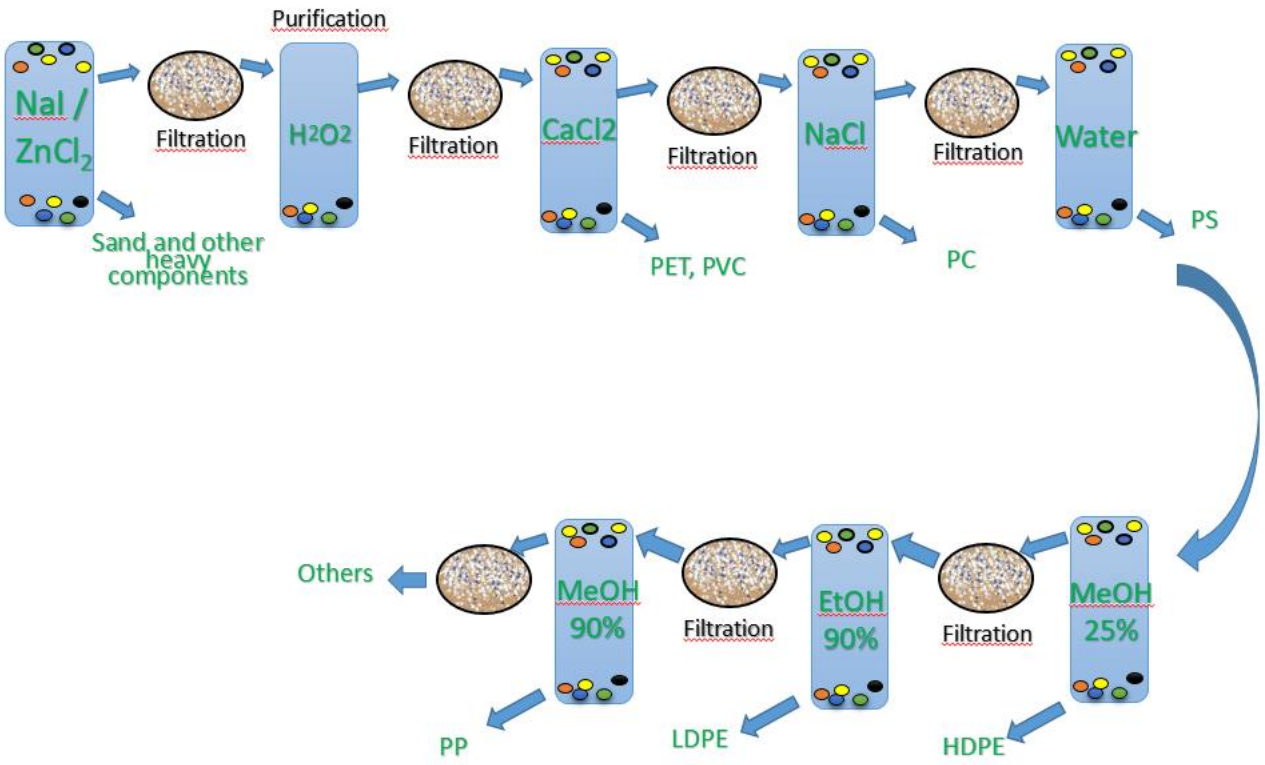


Fig. 26. schematic of imroved methodology of sparation

Consequently, salt selected for density separation plays the most significant role and if it does not choose carefully there might be some consequences happening right after digestion or via physical treatment. For instance, some plastics are sensitive to Calcium chloride and corrosion happens for them.

2.5.1. KI salt solution

Potassium iodide is another salt agent with relevant high density on saturated mode which can separate microplastics from the sample and it is useful because of its high execution with organics. This hypothesis is structured as it the same method was described previously using salt solution and then separation and finally purification with Hydrogen peroxide. But Iodide reacts with Hydrogen peroxide significantly and emit gas. This reaction is that harmful for sample which can totally demolish sample and its structure then sample will become shapeless.

Care should be taken handling 30% or more hydrogen peroxide – it is significantly corrosive to the skin, eyes and respiratory tract and causes irritation on mouth. Do not stand over the reaction – steam and oxygen are quickly produced (recommended to proceed the reaction under air hood conditioner). Potassium iodide is slightly toxic. Safety goggles and gloves should be worn during the demonstration.

Potassium Iodide is a metal halide composed made of two elements potassium and iodide. With molecular weight of 166.003 g/mol and exact mass of 165.86 g/mol. In addition, this agent acts as an expectorant by increasing secretion of respiratory fluids resulting in decreased mucus viscosity. To prepare the saturated KI solution 37.2 gr of KI is added to 100 ml of distilled water. The agent is not neither exothermic nor endothermic and without color and smell.

Fig. 27. KI solution prepared

To avoid this reaction the sample is washed by distilled water for 3 to 5 times depend on the volume of sample. After extraction the materials from sample and pour it through the Whatman filter each 15 minutes 2 ml of distilled water need to be added on the top so that the sample is totally washed.

2.5.2. Fenton Agent and organic removal

Fenton's reagent is an advanced oxidation process using H_2O_2 in the presence of a catalyst (Fe^{2+}) and Fenton's reagent could enable the analysis of microplastics in other sample types that are challenging to analyses such as soils or compost-like output (CLO). (program 2015)

The purpose of this case study lead us to also use other improved method to separate microplastics from the sample using Fenton agent under particular conditions which are mentioned below. This technique is much more affordable that the previous one, for its less time consumption and at this point we have needed to separate whole microplastics from the major sample and identification is done by spectroscopy. Initial conditions for Fenton agent is described below:

1) Iron (Fe(II)) solution (0.05 M) should be prepared by adding 7.5 g of FeSO4°7H20 (= 278.02 g/mol) to 500 mL of water and 3 mL of concentrated sulfuric acid.
2) Then 20 mL of aqueous 0.05 M Fe(II) solution should be added to the beaker containing the fraction of collected solids
3) Add 20 mL of 30% hydrogen peroxide or 40 mm if big amount of organic presented in sample
4) Let mixture stand on lab bench at room temperature for five minutes prior to proceeding to the next step.

5) Add a stir bar to the beaker and cover with a watch glass
6) Heat to 70-75^{o}C on a hotplate
7) As soon as gas bubbles are observed at the surface, remove the beaker from the hotplate and place it in the fume hood until boiling subsides. If reaction appears to have the potential to overflow the beaker, add distilled water to slow the reaction.
8) Heat to 70-75^{o} C for an additional 30 minutes. If natural organic material is visible, add another 20 mL of 30% hydrogen peroxide.
9) Repeat until no natural organic material is visible.

A ice bath is required because this process is exothermic and it might lead to formation of organic, time by time once the bubble are throwing up from the beaker, it needs to be moved from heater to ice bath to decrease temperature and continue the process.

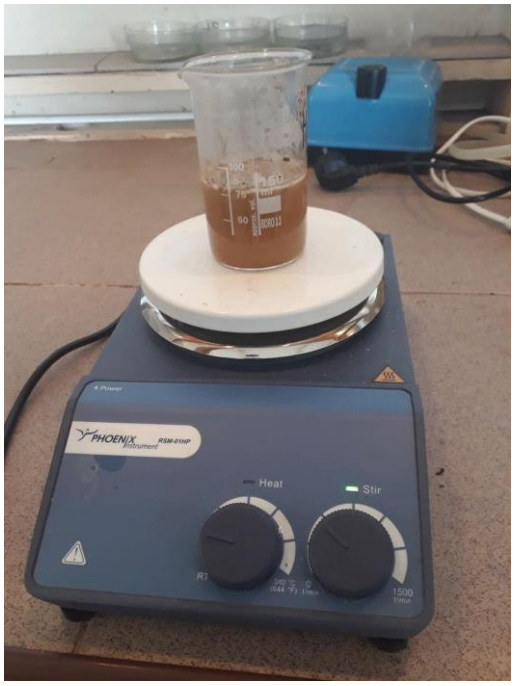


Fig. 28. Sample stirring on heater at presence of Fenton agent

2.6. Physical Treatment

Right after Chemical treatment and sample preparation, Physical treatment is required to stabilize the media for polymers and other light particles to be floating at solution. There are variety kind of physical treatment which help the scientist to observe the most accurate result of separation.

2.6.1. Thermal separation

This method is used mostly for aquatic sample taken from Sea, rivers, sludge and so forth. The thermal extraction is carried out using the Gas chromatography mass spectroscopy GC-MS with auto sampler at the normal balance of the weight symbolizing. Sample re weight in the ratio of1:10. For each ml of the sample 10 ml of solution (aluminum oxide) and heated up at 600 Celsius for 10 to 13 minutes. The out layer material are collected from the other side of the apparatus in gas tube with diameter of 4.5 mm to 6 mm. the gas tube is affixed with stainless steel sieves. (Baruk, Pul Eisentraut and Baannik 2017)

The potential reference plastics could be extracted via this method are namely, PP, PE, PS and Pa due to high resonance against the heat at presence of Aluminum.

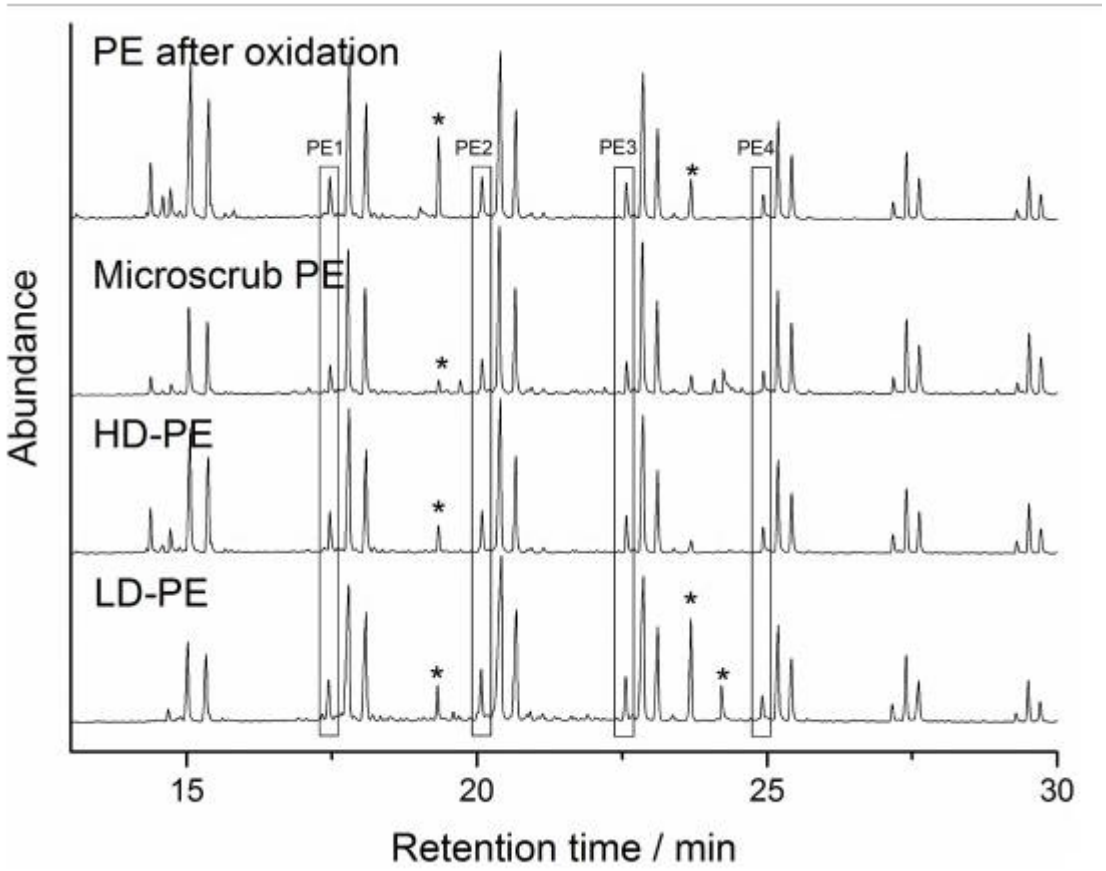


Fig. 29. Comparison of different PE types of polymer with thermal method

Three major disadvantage of this method is that, method is highly costly, complex structure of mobile fluid preparation and finally limited value of temperature and polymer extraction.

2.6.2. Centrifuge and spinner centrifuge

In the case that sample is divided into different granular metric fractions, particles less than 1 mm are mostly suitable to be treated by centrifuge. This idea complies with the rule of mass transfer. The turbulence mixture which happens while the sample is rotating and help the sample to create the bed for organics and plastic to float and move from the sides to the center.

It should be noticed that, samples are treated with centrifuge should be extracted not longer than 15 to 30 minutes after they are taken out form centrifuge apparatuses, for their highly stabilization. We have experienced that the sample less than 0.75 mm were treated by centrifuge and it became hard and not possible to extract.

The conventional way to extract and remove material from the sample is to use siring (metal body) with large diameter to be able to remove material. The other way is to use Filter with method of wet adsorption. But it should be used for big plates and only for sample which are visible, if the media is

dull then filtration with wet adsorption will not be efficient. Furthermore, liquid should have the enough depth to use filter.

Fig. 30. Centrifuge with normal machinery

Other hypothesis for the centrifugal extraction is using spinner centrifuge with high demand velocity and siring installed above the tank. This apparatuses used by mean of sensitive extraction and it is highly efficient. Sample must be prepared in special container and then placed inside the central pin of machine, the top head of the container is closed and a siring is installed above the top head and is controlled by an electro-handle. Once the container starts to spin with exact rotational velocity, then user can see the physical condition of sample and is allowed to use controller to conduct siring in the center of container ad extract all materials in the center of media.

Siring diameter and length is adjustable, and also siring can move from 1 to 55 mm radially from the center in order to collect all suspension.

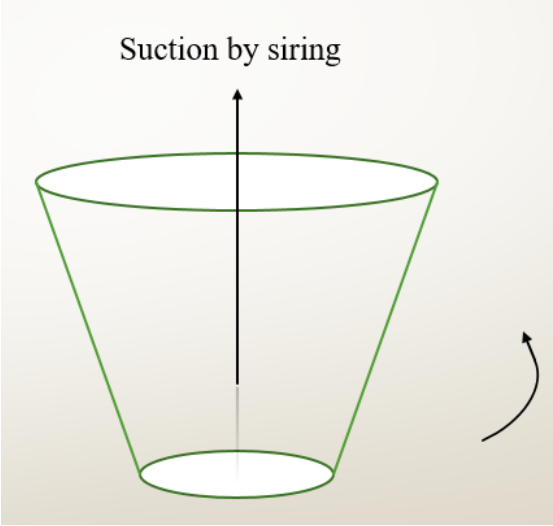


Fig. 31. Scheme of spinner centrifuge

Most important advantage of this spinner is the high extraction efficiency based on mass transfer and some disadvantages are expected such as cost of the apparatuses and another negative point is that, if

the fraction less than 0.75 mm is used, huge amount of dust re going to be observed after filtration and might give an error within EDS analysis.

2.6.3. Flat-bed shaker

Flat-bed shaker is also knows as a linear mixture method which helps the solution and contained ingredients to be mixed based on linear fluid shock. We have decided to use this methodology to mix all our samples. However this technique obtains mostly good result but time plays a significant role on the final mixture as well as velocity does. Here we will describe briefly how these two terms influence the result.

a. Time interval: if the sample contains salts with soft chemical property which has less interaction with physical movement like NaCl, in this case, time can be set from 6 to 24 hours with average velocity. In contrast if hard chemical such as $ZnCl_2$ is used as base solution, due to sensitivity to movement and lack of stability, sample should be treated 4 to 10 hours at low speed.
b. Shaking speed: for sample with volume of less than 50 ml it is recommended to use low speed in order to avoid harsh mixture. If high speed is used then salt inside the solution will trap the small content and make them floating or suspending. In the other hand, for large volume size sample, high speed is required to ensure if target content is treated well.

In this case study, all sample were placed in flat-bed shaker for 24 hours with average speed of 1800 RPM.

Fig. 32. Flat-bed shaker

2.7. Identification of Microplastics by FTIR and other methods

There are few methods recommended by previous studies and researches to observe the type of polymers such as FTIR, RAMAN spectroscopy, EDS- AFX analysis and thermos-spectroscopy by X-ray.

FTIR stands for Fourier transform infrared, the mostly preferred technique of infrared spectroscopy. When IR radiation is passed through a sample (material, in this case polymers), some radiation is absorbed by the sample and some passes through (is transmitted). The resulting signal at the detector is a spectrum which represents a molecular 'fingerprint' of the particular sample. The usefulness of infrared spectroscopy arises because variety chemical structures (molecules) produce different spectral fingerprints. (NANCY Birkner 2020)

FTIR can be used as a single purpose tool or a highly flexible research apparatuses. With the FTIR configured to use a specific sampling device – transmission or ATR for example – the spectrometer can provide a vast range of data information: (NANCY Birkner 2020)

- Most commonly, the identification of an unknown
- Quantitative information, as additives or contaminants
- Kinetic information through the growth or decay of infrared absorptions
- Or more complex information when coupled with other devices for advance analysis such as TGA

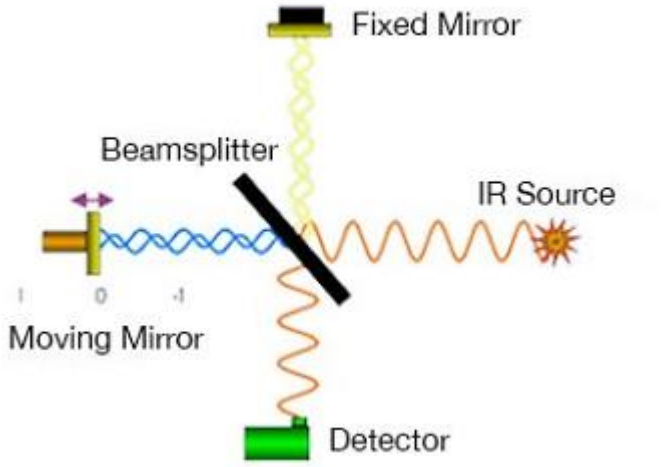


Fig. 33. How FTIR works schematically

Microplastics quantification is often performed visually using Microscope or even with naked eyes. (Free Cm 2014) (Lechner A 2014).However, visually identification of polymer especially microplastics alone using morphological criteria of sample will lead to overestimating of substances in vide range with large magnitude of error. (Dekiff JH 2014)

After analysis of the FTIR three major steps will appear which are namely DATABASE, DATA Processing and Image analysis. (Primpke, et al. 2017)

Database: The database has been setup early and been transferred from the name of the polymer (chemical name or conventional name) to numbers for an automated analysis. Therefore, a number was assigned to each polymer to be known for interpretation. In the measured region PTFE has no signal and was eliminated from the database. (J. P. Harrison 2012)

Data processing: processing of the data requires the high quality and fast processor computer with configuration of , 8 GB RAM, casual 5450 Graphic card for visualization.

Image analysis: images of the FTIR can be analyzed both by previous database and by mathematical methods using Python Code to read the image sector by sector and matches with source of polymer.

Therefore, visual identification of microplastics is some inaccurate, and should be combined with other physical or chemical technologies. In addition, the SEM is also used for identification of microplastics, and provides high magnification and clearer structural images of microplastics. (Won Joon shim 2017)

It might be a case to know how to interpret the FTIR result, if this is a case so, the x-axis or horizontal axis represents the infrared spectrum, which plots the intensity of infrared waves. The peaks, which are also are known as absorbance bands, correspond with the various vibrations of the sample's atoms when it's exposed to the infrared emission of the electromagnetic spectrum. For mid-range IR, the wave number on the infrared spectrum is plotted between 4,000 to 400 cm-1. The y-axis or vertical axis represents the amount of infrared light absorbed or transmitted by the content material being analyzed under the mentioned condition. Typically, absorbance bands are grouped within two types: Group frequencies and fingerprint frequencies. (Jennifer Mathias 2017)

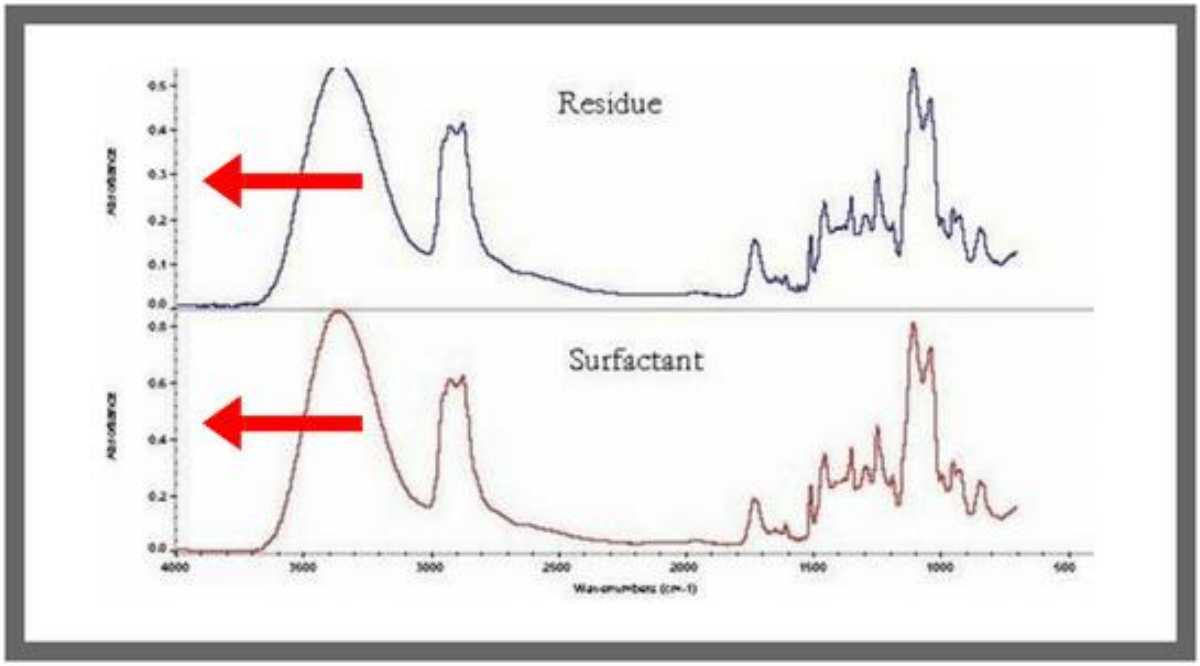


Fig. 34. FTIR final result sample

Any apparatus used for analysis has some weaknesses and strength which should better to be considered. Different kind of material can be analyzed by FTIR but regarding our topic, mostly polymers and carbonated material are analyzed.

Table 11. Advantages and disadvantages of FTIR

Advantages
Solids, Liquids, gases, semi-solids, powders and polymers are all analyzed
The peak positions, intensities, widths, and shapes all provide useful information
Fast and easy technique
Sensitive technique (Micrograms of materials can be detected routinely)
Inexpensive

Disadvantages
Atoms or monatomic ions do not have infrared spectra
Homonuclear diatomic molecules do not posses infrared spectra
Complex mixture and aqueous solutions are difficult to analyze using infrared spectroscopy

However, SEM detection takes a lot of time and is relatively expensive. In addition, SEM requires other coatings in the early preparation, which may result in inaccuracies for identifying surface texture and color of microplastics. (Defu He 2018)

In general, infrared microscopy is one of the most widely available techniques in chemical identification of microplastics.
Similar non-destructive vibrational techniques include m-FT-IR, attenuated total reflectance (ATR), and (micro-) Raman spectrometry. These have advantage of one individual instruments and scanning which is merged with spectroscopy techniques. There are different spatial distinguishability between of m-FTIR and m-Raman. Assay size limit of m-Raman can reach as low as 1 mm, while mFTIR can only detect microplastics larger than 10e20 mm. additionally, both m-FTIR and m-Raman techniques must cover the answer of question regarding the organic maters in the sample and their impact on the final result of the sample preparation, which may interfere with the signal of spectrometer. (Baruk, Pul Eisentraut and Baannik 2017) In the case that m-Raman spectroscopy, the signal of organic matters can partly degrade through a highly fluorescent background; however it may exceed the magnitude of the polymer signal. Although m-FTIR and mRaman can provide reliable identification information for microplastics, the process will take a lot of time. Another technique, macroscopic dimensioned near-infrared (NIR) spectroscopic analysis in combination with chemo metrics can overcome the disadvantage of time-costing, and rapidly assesse chemical composition of microplastics without any chemical pretreatment. A recent study showed that hyperspectral imaging technology was a potential technique to determine and visualize the microplastics with particle size from 0.5 to 5 mm on soil surface directly. Another study developed a method of thermal extraction desorption gas chromatography mass spectrometry (TED-GC-MS) to performed precise and efficient quantification of PE, PET, PP, and PS. (Defu, et al. 2018)

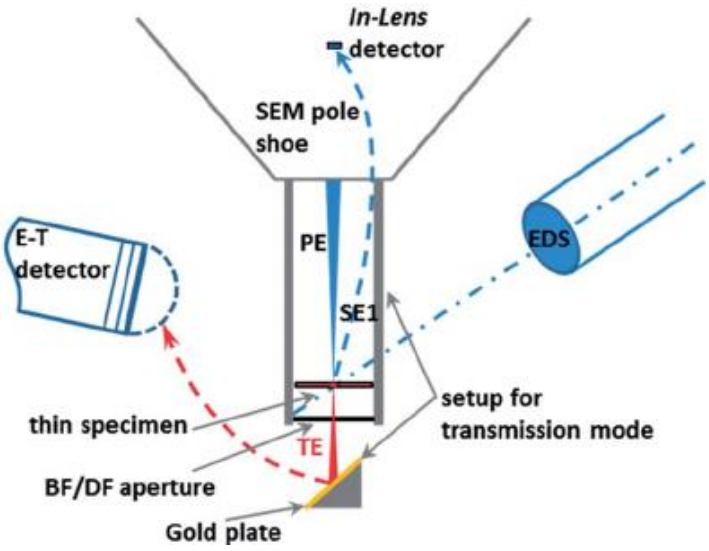


Fig. 35. SEM schematic

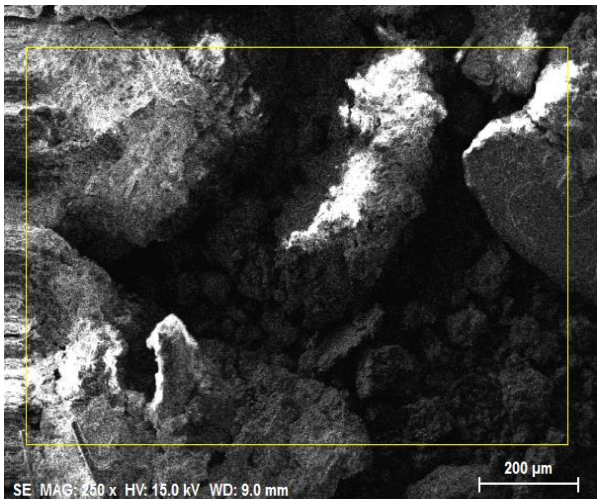
3. Research Result

3.1. Result obtained for Torma Landfill

3.1.1 SEM-EDS analysis for dry sample

The result of SEM analysis shows the organic and inorganic contents of samples, not really useful data can be detected and investigated the only thing which we needed to have out of this section is finding the carbon content. Some SEM images are shown below.

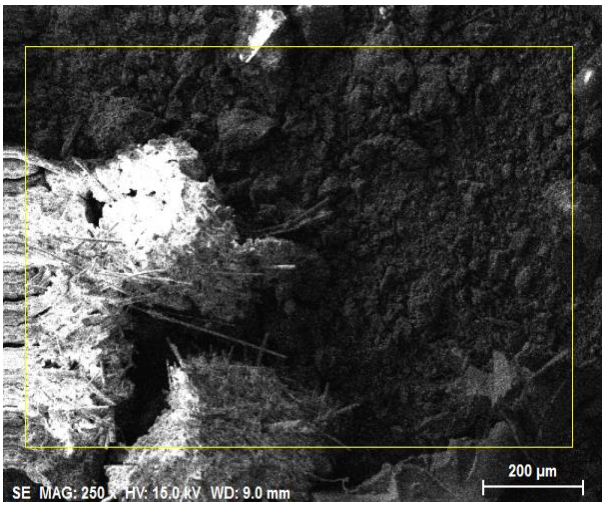
a)1.5 mm sample



Spectrum:

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	19.85	22.07	32.97	8.14
Oxygen	K-series	41.11	45.70	51.24	14.92
Sodium	K-series	0.60	0.67	0.52	0.21
Magnesium	K-series	0.64	0.72	0.53	0.19
Aluminium	K-series	2.07	2.30	1.53	0.38
Silicon	K-series	5.51	6.13	3.92	0.78
Sulfur	K-series	1.75	1.95	1.09	0.28
Potassium	K-series	0.87	0.97	0.45	0.18
Calcium	K-series	9.42	10.48	4.69	0.95
Titanium	K-series	0.33	0.37	0.14	0.13
Iron	K-series	7.14	7.94	2.55	0.77
Chlorine	K-series	0.33	0.37	0.19	0.12
Phosphorus	K-series	0.29	0.33	0.19	0.12
	Total:	89.94	100.00	100.00	

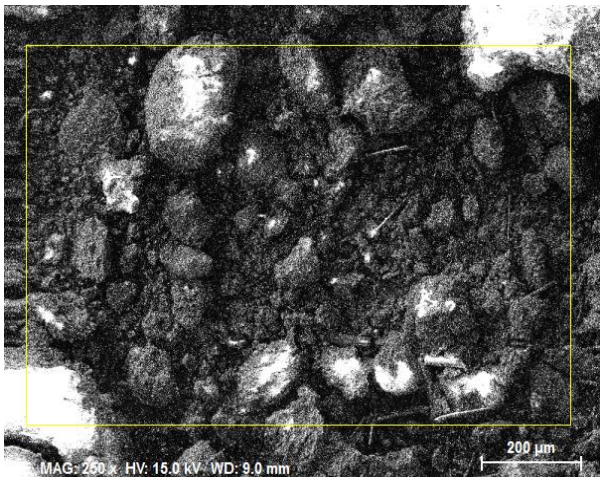
b) 1.2 mm sample



Spectrum:

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	19.37	21.28	31.89	8.21
Oxygen	K-series	40.22	44.19	49.70	14.88
Sodium	K-series	0.77	0.85	0.67	0.24
Magnesium	K-series	0.86	0.94	0.70	0.23
Silicon	K-series	10.18	11.18	7.17	1.36
Sulfur	K-series	1.11	1.21	0.68	0.21
Potassium	K-series	1.32	1.45	0.67	0.22
Calcium	K-series	10.86	11.93	5.36	1.08
Titanium	K-series	0.36	0.40	0.15	0.14
Iron	K-series	3.35	3.68	1.19	0.44
Phosphorus	K-series	0.24	0.26	0.15	0.12
Aluminium	K-series	2.06	2.26	1.51	0.38
Chlorine	K-series	0.32	0.35	0.18	0.12
	Total:	91.01	100.00	100.00	

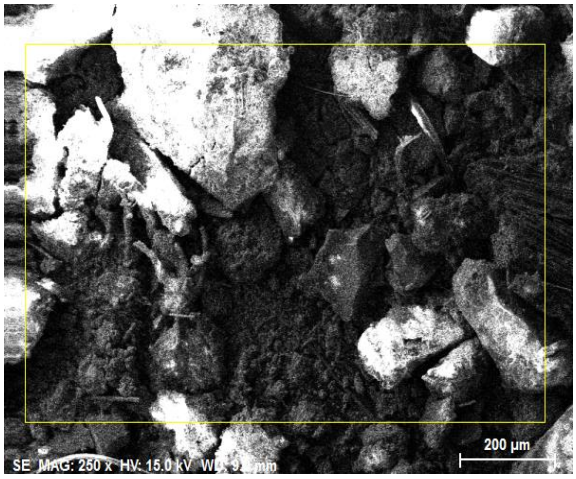
Sample of 1mm



Spectrum:

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	28.07	28.34	40.13	11.44
Oxygen	K-series	42.25	42.66	45.35	16.04
Sodium	K-series	0.82	0.82	0.61	0.26
Magnesium	K-series	1.03	1.04	0.73	0.26
Aluminium	K-series	1.94	1.96	1.24	0.37
Silicon	K-series	7.79	7.87	4.76	1.07
Potassium	K-series	1.23	1.24	0.54	0.22
Calcium	K-series	11.29	11.40	4.84	1.12
Iron	K-series	2.89	2.92	0.89	0.41
Sulfur	K-series	1.05	1.06	0.56	0.21
Chlorine	K-series	0.41	0.42	0.20	0.14
Phosphorus	K-series	0.28	0.28	0.15	0.12
Total:		99.04	100.00	100.00	

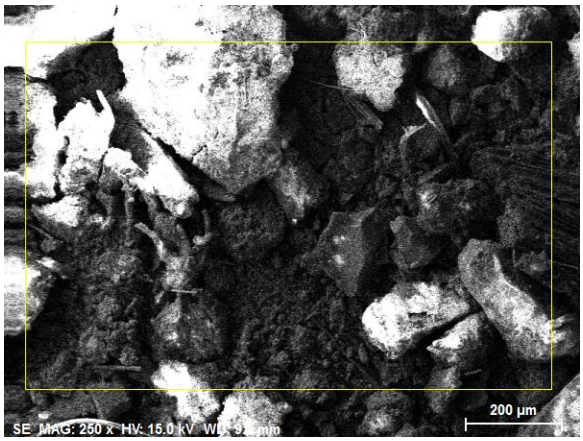
sample of >0.75



Spectrum:

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	27.92	28.68	41.03	11.17
Oxygen	K-series	40.26	41.36	44.42	15.03
Sodium	K-series	0.87	0.89	0.67	0.26
Magnesium	K-series	0.95	0.98	0.69	0.25
Silicon	K-series	7.26	7.45	4.56	1.00
Phosphorus	K-series	0.46	0.47	0.26	0.14
Sulfur	K-series	1.31	1.35	0.72	0.24
Chlorine	K-series	0.44	0.45	0.22	0.14
Potassium	K-series	1.07	1.10	0.48	0.20
Calcium	K-series	9.48	9.74	4.18	0.96
Titanium	K-series	0.31	0.32	0.11	0.13
Iron	K-series	5.72	5.88	1.81	0.66
Aluminium	K-series	1.30	1.34	0.85	0.27
Total:		97.34	100.00	100.00	

Sample of <0.75



Spectrum:

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	27.92	28.68	41.03	11.17
Oxygen	K-series	40.26	41.36	44.42	15.03
Sodium	K-series	0.87	0.89	0.67	0.26
Magnesium	K-series	0.95	0.98	0.69	0.25
Silicon	K-series	7.26	7.45	4.56	1.00
Phosphorus	K-series	0.46	0.47	0.26	0.14
Sulfur	K-series	1.31	1.35	0.72	0.24
Chlorine	K-series	0.44	0.45	0.22	0.14
Potassium	K-series	1.07	1.10	0.48	0.20
Calcium	K-series	9.48	9.74	4.18	0.96
Titanium	K-series	0.31	0.32	0.11	0.13
Iron	K-series	5.72	5.88	1.81	0.66

Fig. 36 shows the SEM image for sample from compost with different size and the table of EDS content

The tables and their corresponding images have been carried out from SEM-EDS analysis for Torma Landfill samples to clarify the organic compound and content of sample. By the size increased the

content of Carbon is rising up and other content almost remain the same. Iron and Calcium fluctuating by the size increase.

It is clear from the below graph that the samples contain high level of organic compounds specially Carbon content. It can be also Humus compound or textile pieces.

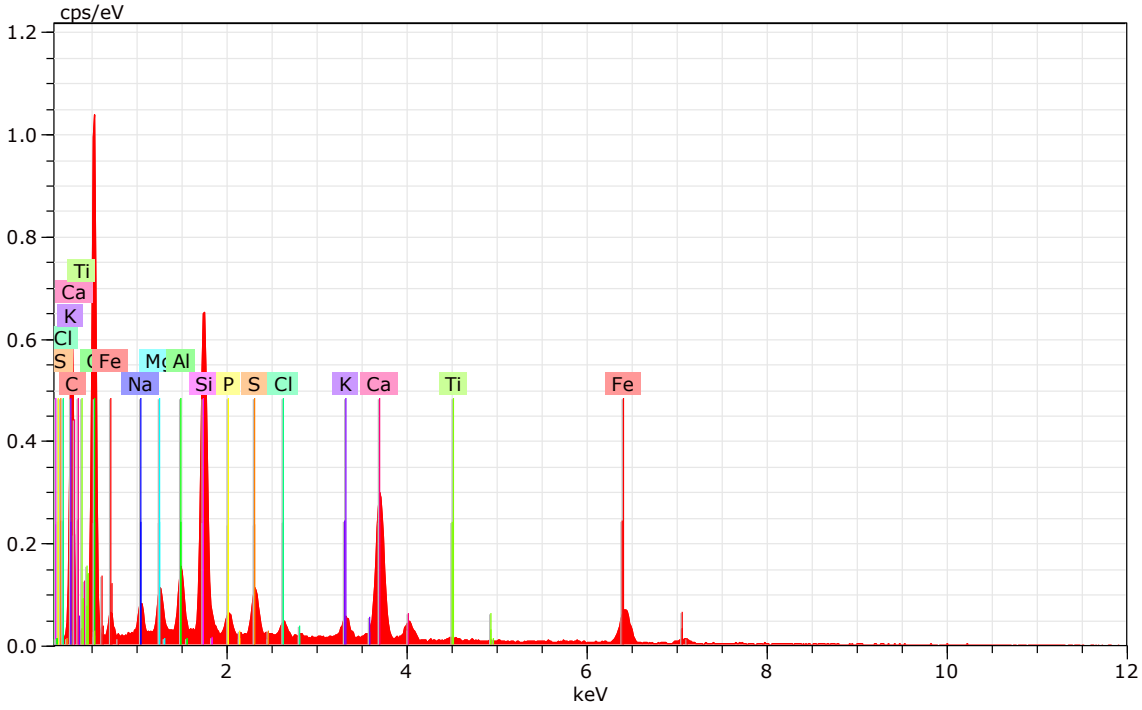


Fig. 37. Substances pick at EDS result

The content figured out by EDS analysis are quite differ and it is because of the high contaminated sample taken from the Landfill and it was expected to observe different elements with different density and chemical property. Mostly Humus as an organic material such as textile and papyrus material are contained.

3.1.2 FTIR analysis for extracted microplastics

For Polymer identification, FTIR was the next and last step. The result of the FTIR are shown down below and the result compare with true database from the library of polymer. It should be mentioned that for FTIR analysis we have mixed all extracted particles together and sent to laboratory.

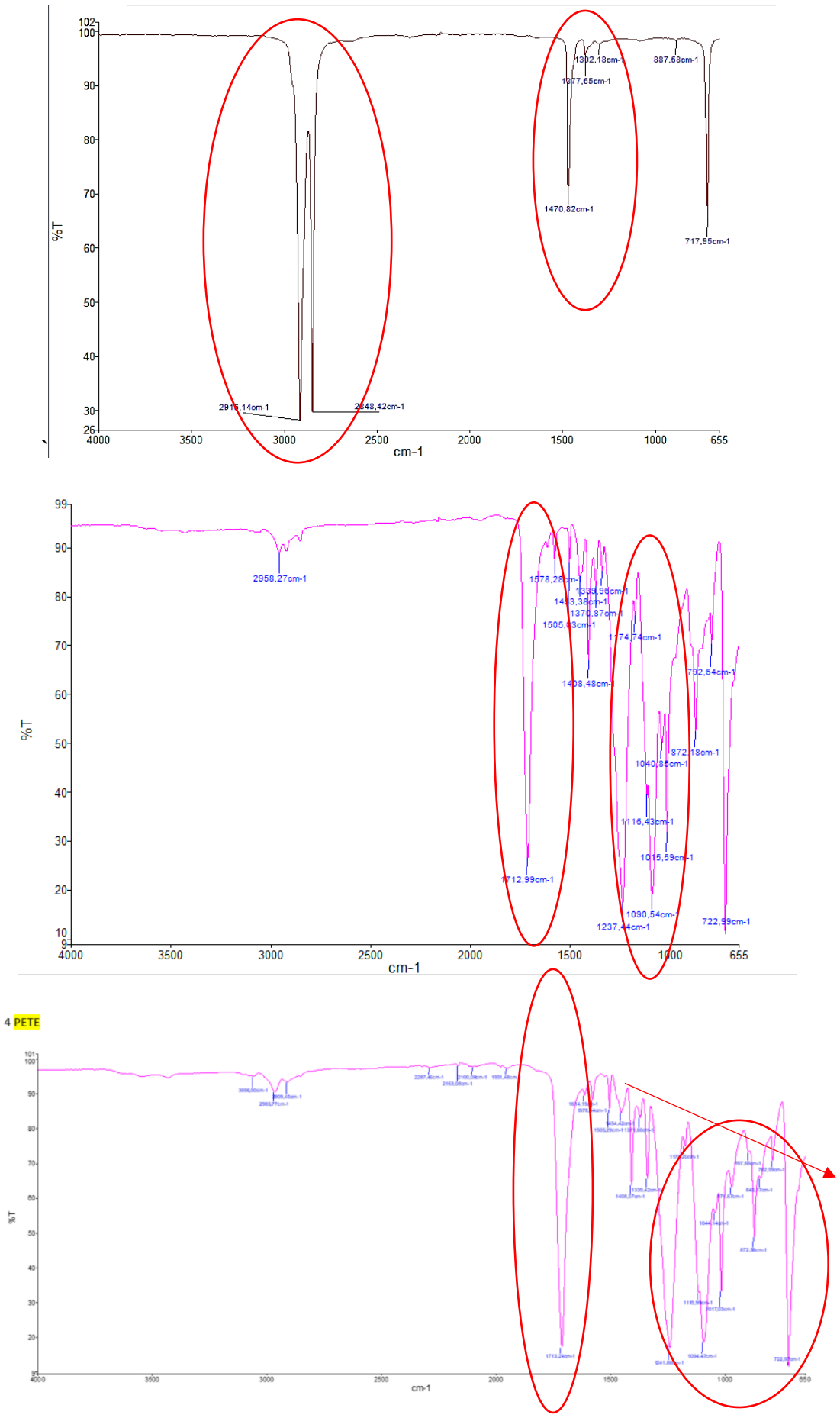


Fig. 38. FTIR for Torma Landfill

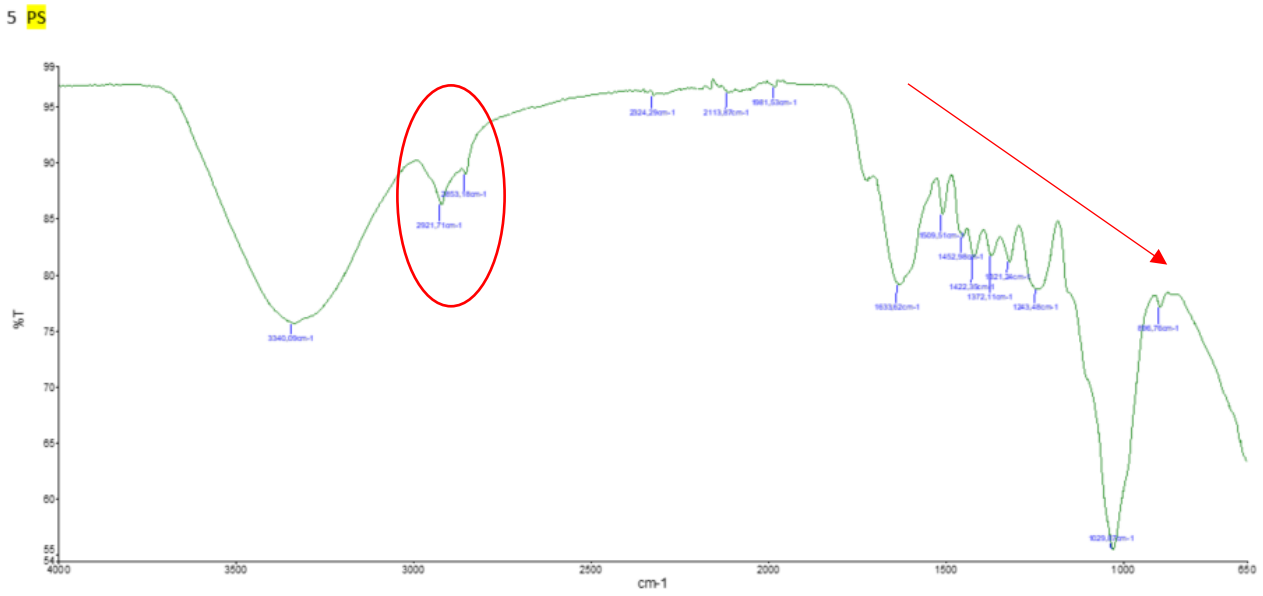
By a comparison and matching the picks in the graphs and relevant source, PS, PE and PET were observed mostly in the Landfill environment.

3.2. Results obtained for MBT sample

3.2.1 FTIR analysis for extracted microplastics

MBT samples after Biological treatment contains wet particles and mostly mediocre density particles. Here there are two types of polymers observed for MBT samples. 14 small particles were found with same morphology and structure under microscope.

Municipal solid waste is treated both mechanically to remove hard and bid shape particle and then biological treatment is performed at two stages. The compost waste after MBT contains the following polymers.



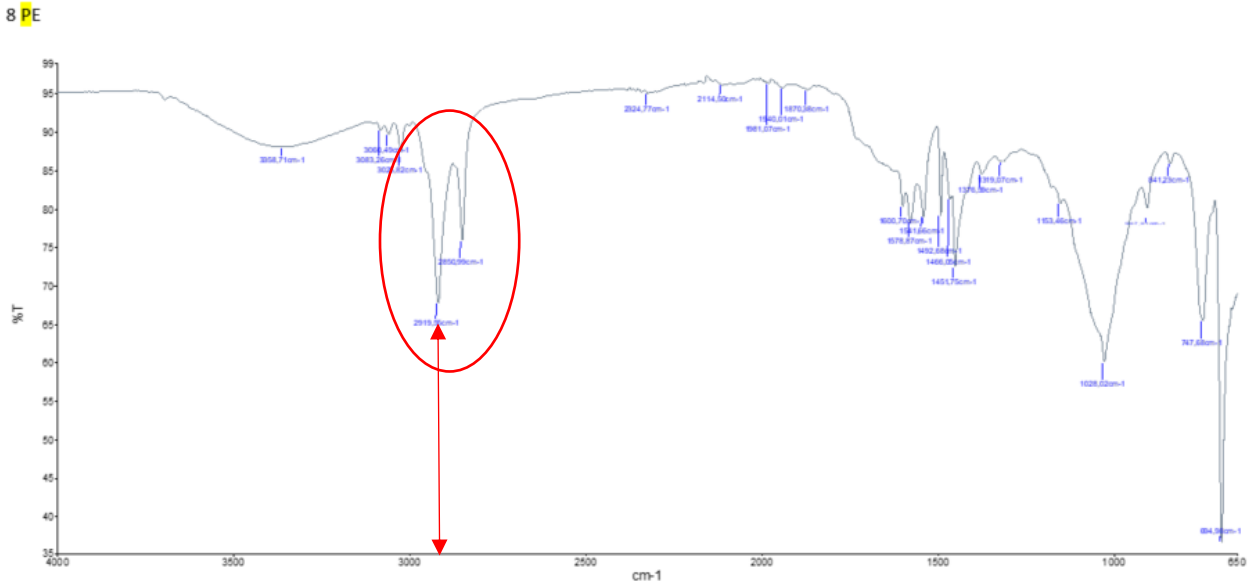


Fig. 39. FTIR result for MBT sample

Plastics are found in nondurable products, such as disposable tissue diapers, bags, cups, utensils, medical devices and medical packaging and household items like such as shower curtains. The plastic food service items and their packaging are generally made of foamed polystyrene, while trash bags are made of high-density polyethylene (HDPE) or low-density polyethylene (LDPE). But none of these polymers were observed in the sample.

3.3. Results obtained for Green compost

3.3.1 FTIR analysis for extracted microplastics

Green compost sample contained different types of polymers, surprisingly. In contrast to our expectation, 7 small particles obtained for the green Compost sample the structure and color of the particle was more or less similar but the FTIR helped us to differentiate them.

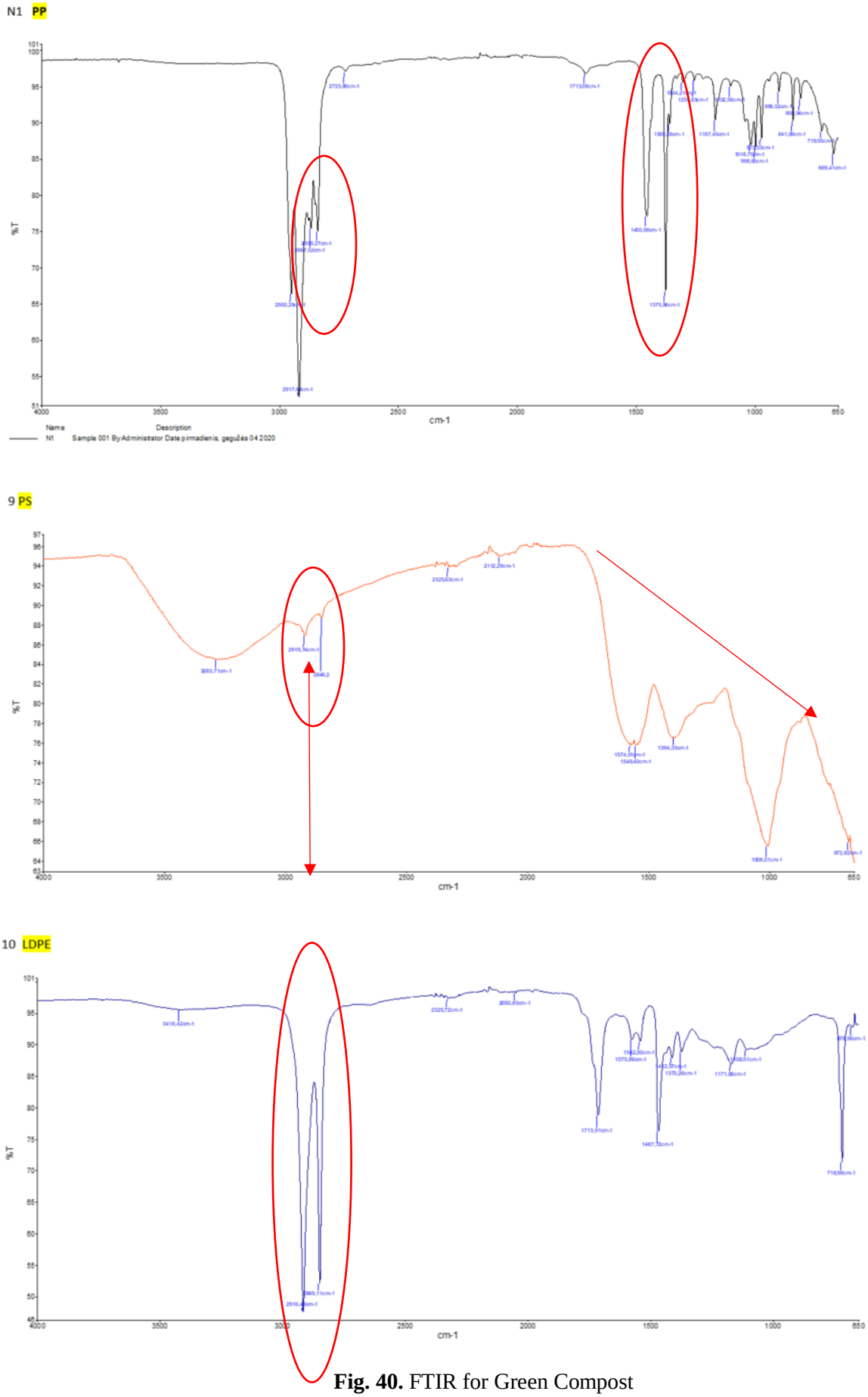


Fig. 40. FTIR for Green Compost

Except PP and PS we can see that LDPE was observed during spectroscopy which means green compost is contaminated to plastics as well.

3.4. Comparison

Since, statistical methodology and logics have been taken into account for samples which have been taken from the media, and normal dispersion is mostly considered. The amount of microplastics in Landfill experienced the largest quantity of 28 Particles then MBT sample followed the trend with 14 particle, and the last category of Green Compost obtained 7 particles.

Polystyrene, Polypropylene and Polyethylene are three types of plastics which were found in all samples the most and Low density Polyethylene also found in green compost. Following images show the shape and size of microplastics were found in each sample.

With Length of 4.67 mm * 4.35mm

With Length of 4.93 mm * 5.03 mm

With length of 4.02 mm * 2.085 mm

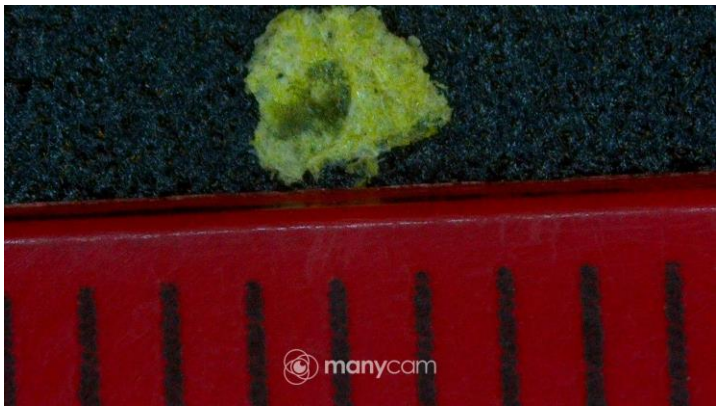
Fig. 41. Microplastics from Green compost

With Length of 5.95 mm* 3.68 mm

With Length of 5.86 mm * 4.37 mm

With Length of 1.756 mm *1.63 mm

Fig. 42. Microplastics from biologically treated MSW



With Length of 2.09 mm * 2.16 mm

With Length of 1.83 mm * 1.59 mm

With Length of 0.95 mm * 1.21 mm

Fig. 43. Microplastics from Torma Landfill

From the images above which have been taken Microscope equipped with Camera, it is clear that Compost contains plastic with the size larger than them from Landfill and MBT. The morphology of particles in MBT and Landfill are similar eventually but in compost, even the shape and morphology of particles are quite different.

It is quite challenging to directly make a comparison between the microplastics concentrations reported in this case-study with each other. Overall, it was noted that the microplastics concentrations found in MBT samples from Kaunas plant were comparable to those reported in the Torma Landfill and they both are denser than microplastics found in Green compost.

Conclusions

Within this study, a critical comparison between FTIR spectroscopy for microplastics identification in terrestrial samples of biologically treated waste (landfill fine fraction, compost, biologically treated MSW) was attempted.

Interestingly, Polyethylene, Polystyrene, and Polypropylene are main types of polymers have been found in all fractions and it means due to their source they are ubiquitous. And it was observed that PP, PE and PE are highly accumulated in Municipal solid waste biological treated and Landfill, than Compost; and on the other hand, Low Density Polyethylene was observed with some additives on green compost samples. Except all polymers mentioned, PET (Polyethylene Terephthalate) is mostly disposed to Landfill.

a. The first approach, the results of extraction were compared with regard to number, type and size of recognized microplastics as well as measurement peak. We highlight that FTIR imaging are excellent method to analyze the smaller microplastics fraction directly on filters and also upon the hard particles. Moreover, for the first time, a validation of the two spectroscopic SEM and FTIR approaches was performed. Density separation coupled with physical treatment was the major methodology used for several researches. NaCl, CaCl2, ZnCl2 were the salts which have been used the most, and additionally Hydrogen Peroxide assigned for desorption of organic matters. Consequently, the current research obtained the density separation as a core method plus physical treatment.
b. According to the several tests have been done and analysis of polymer's structure while reacting with high density salt, the decision was made to use Potassium Iodide for brine solution with high capability of separation.
c. Flat-bed shaker was chosen to be the main apparatus for physical treatment due to physical features of linear mixing rather than centrifugal mixing with certain period of 24 hours and 1800 RPM as a constant speed.
d. With a comprehensive and thorough evaluation of miscellaneous agents for Organic removal, Fenton solution was selected to remove organics at the presence of Hydrogen peroxide and certain condition of constant temperature at 70 Celsius and consistently stirring.
e. The size, type and quantity of polymers which were identified in each sample were compared together to find out the source and significant values.

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