Scientific contribution/Original research

Oil Extraction of Microplastics from Communal Dewatered Sludge

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Abstract:
Microplastics (MPs) as solid particles are found all over in the environment. Plastic particles, smaller than 5 mm are defined as MP and smaller than 1 μm as nanoplastic. One of main sources are communal wastewater treatment plants (WWTPs), that contribute to releasing MPs into the environment. Through outlet, MPs continue their way into surface waters and groundwaters or come in environment with sewage sludge that is disposed on farmland or other surfaces. There is still no standardized method for extracting plastic particles from environmental samples, so we investigated efficiency of oil extraction protocol (OEP). Since sludge consists of organic matter and it needs to be pre-treated before an extraction, Fenton's reagent was used to reduce organic matter. Before and after the extraction, particles were analysed with Fourier-transform infrared spectroscopy (FT-IR), where we discovered that a washing step after the extraction with 96% ethanol removes oil traces and other interferences. A recovery rate of MP particles was assessed by counting spiked plastic particles on filters after a vacuum filtration. The results showed that with OEP the recovery rate was on average 10% higher in pre-treated samples in comparison with samples without pre-treatment. We determined the highest recovery rate for bigger particles (1-5 mm) of polypropylene (PP), (86% ± 16% with OEP and 99% ± 4% with pre-treatment). The results reveal that the oil extraction can offer a cost-efficient, rapid and simple extraction method for MPs with high recovery rate especially for plastic particles with lower densities as PP and polystyrene (PS).

Keywords: Microplastics, communal wastewater treatment plants, sludge, oil extraction, pre-treatment, organic matter

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Introduction

Microplastics (MPs) as solid particles of anthropogenic origin are due to their lasting persistence and small weight found all over in the environment. Mainly, plastic particles, smaller than 5 mm are defined as MP and smaller than 1 µm as NP (Blair et al., 2019). MP is also classified into primary and secondary MP, where primary is intentionally made in small dimensions and being in those sizes also used, while secondary MP breaks down from bigger plastic waste, during its usage or after physical, chemical or biological processes (Carr et al., 2016; Talvitie et al., 2017). MP could pose a serious risk to environment. It could negatively affect aquatic environment and as persistent small size pollutant can be fast and easily transferred on long distances, where it can physically and chemically impact many organisms and it could be also transferred through food chain to humans (Anderson et al., 2016; Corradini et al., 2019). Particles of MP could be found in cosmetic and other products for personal hygiene, textile products and in many industrial processes (Carr et al., 2016). One of significant sources of MPs is a communal wastewater treatment plant (WWTP) (Sun et al., 2019), where MPs from households through outlet can continue their way mostly into surface waters and groundwaters or on farmland with sewage sludge disposal (Ngo et al., 2019).

Since MP could reach environment, not only with wastewater through the outlet, but also with sewage sludge, quantification and qualification of MP in the sludge, that is a complex mixture, reach with organic compounds, is highly important (Hurley et al., 2018). Various different procedures of MP extraction found in literature (Hurley et al., 2018; Lares et al., 2019) aggravate comparison between results. Despite many different procedures and results reported in the literature, main steps of procedures after sampling usually involve pre-treatment, extraction, identification and characterization (Hurley et al., 2018). High content of organic matter in waste sludge could hamper the efficiency of extraction of MPs and samples need to be pre-treated (Hurley et al., 2018; Li et al., 2020). Organic matter, microorganisms and other inorganic matter that are tied together by biopolymers make sludge samples additionally more difficult to process as for example soil samples (Zhang et al., 2020).

Different chemical methods for pre-treatment have several disadvantages; nitric acid (HNO_3) could physically and chemically change surface of MP and pre-treatment could take a long time (Li et al., 2020), alkaline digestion with sodium hydroxide (NaOH) and potassium hydroxide (KOH) could change size and shape of some type of plastics (PET) due to high pH (Dehaut et al., 2016; Cole et al., 2014). One of other possible methods is enzyme digestion that is expensive and could take days (Hurley et al., 2018; Cole et al., 2014; Mintenig et al., 2017). One of common pre-treatment methods is oxidation, using hydrogen peroxide (H_2O_2) that could lead to degradation of some polymers of MP and could change colour of MP, that could affect visual recognition (Nuelle et al., 2014). The alternative of H_2O_2 is Fenton's reagent. Presence of iron catalyst ($FeSO_4$), together with H_2O_2, allows rapid digestion of organic matter (Hurley et al., 2018; Dyachenko et al., 2017).

Most often used methos for MP extraction is separation based on difference of density, where MP float on the surface of solutions. Supernatant, together with MP is then filtrated (Hanvey et al., 2017). Solutions like sodium chloride (NaCl), zinc chloride ($ZnCl_2$) and sodium iodide (NaI) (Zhou et al., 2018; Han et al., 2019) are usually used, but are environmentally unfriendly, often hazardous and can be expensive (Nuelle et al., 2014; Imhof et al., 2012). As simple, fast and efficient method is also oil extraction procedure (OEP), due to lipophilic properties of plastics (Gies et al., 2018). Some researchers used olive, canola and castor oil for MP extraction from soil, where olive oil was the most efficient with the strongest affinity towards different types of polymers (Scopetani et al., 2020). It utilizes lipophilicity properties of plastics. By adding oil to organic matter MP can be efficiently extracted from sludge (Crichton et al., 2017).

The aim of the study was to develop rapid, easy and cost-efficient extraction method, that achieves high recovery rate in separating MP particles from sludge samples. The method was tested by counting MP particles on filter, that are after identified by FT-IR analysis. The hypothesis was that different types and sizes of MP can impact the recovery rate of OEP prior the pre-treatment of sample with Fenton's reagent.

1. Methods

2.1 Sample collection and preparation

Sewage sludge samples were collected from WWTP after dewatering. Collected samples were stored in dark and cold place until further analysis. In comparison with other protocols and research, we did not dry sludge samples prior extraction, because drying turned dried sludge into a solid agglomerate, possibly because of high content of organic matter (Vermeiren et al., 2020). Target weight of dewatered sludge were 40 g of sample. For each experiment, sludge was added into a clean glass jar and spiked with prepared MP particles. We added 100 mL of deionized water and left it on the stirrer at 700 rpm and 40 °C for 10-15 min or until sample was homogenized. Three replicates were done for each experiment (n=9).

2.2 Spiking of microplastics

Sludge samples were spiked with MP particles in order to evaluate the MP recovery rate. MP particles were mechanically fragmented and sieved on small particles (smaller than 1 mm) and bigger particles (sized between 1 mm and 5 mm). We used polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET), since most of them are one of the most common types of MP that are produced and found in the environment [27]. Particles were cut manually from PET bottle and PP and PS pot, while PVC particles were of industrial origin. Each particle of MP was picked by hand and carefully transferred into the sample. 10 pieces of each type and size of polymer was added in the sample, prior analysed by FTIR. Specific densities of selected types are listed in **Table 1**.

Table 1. Specific densities of selected polymers (Crichton E M, et al, 2017; Vermeiren P, et. al. 2020)

	PVC	PS	PP	PET
Density [g/cm³]	1.3-1.45	1.05	0.83-0.85	1.37

PVC: polyvinyl chloride, PS: polystyrene, PP: polypropylene, PET: polyethylene terephthalate

2.3 Removal of the organic matter

Since sludge contain high amount of organic matter, we used Fenton's reagent to reduce organic matter before the extraction procedure to increase recovery rate. As suggested by Vermeiren P, et. al. 2020, 20 mL of Fenton's reagent and 20 mL of 30% H_2O_2 was added in sample of 40 g with spiked MPs. The temperature was regulated with ice bath to avoid thermal degradation. Solution of catalyst was made of 3, 6 g of iron (ll) sulfate heptahydrate ($FeSO_4 \times 7H_2O$), 250 mL of deionized water and 1 mL of sulfuric acid (H_2SO_4). Three replicates were done (n=9).

2.4 Oil extraction protocol

Each sludge sample with spiked MP, after homogenization or after oxidation in case of pre-treatment, was transferred into separatory funnel (**Figure 1**). We added 100 mL of deionized water and shake by hand for 30 s. After that, we added 10 mL of olive oil to each sample. Funnel was sealed and shaken for 60 s by hand to ensure that sludge sample with spiked MP got into contact with olive oil thorough mixing of the sample. To ensure, that all MP particles and sample stays in the mixture, walls and lid of the funnel were rinsed with 200 mL of deionized water. After settling for 15 minutes, the lower aqueous and solid phase was let out from separation funnel into other clean separation funnel where 5 mL of oil was added, sealed and shaken by hand for 60 s. After settling and solid phase removal, oil layer, that remained in both funnels, was filtered using a vacuum filtration with Whatmann filters GF/C 47 mm. Lid and walls of the funnel were rinsed with

100 mL of deionized water and 100 mL of ethanol (EtOH, 96 %). Filters were carefully transferred to Petri dishes, covered and stored at 4 °C.

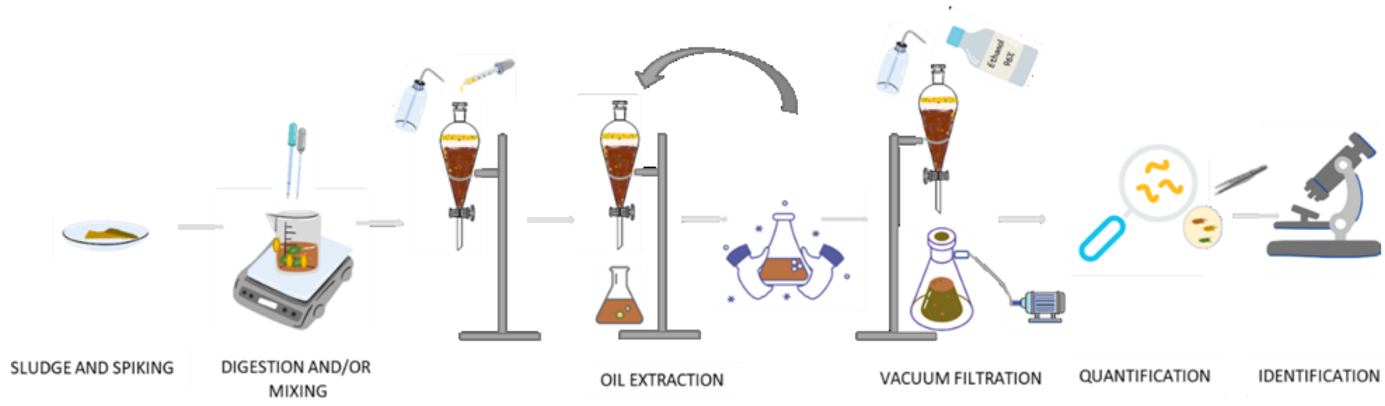

Figure 1. Steps of oil extraction procedure.

2.5 Quantification and identification

The extracted MP particles were visually quantified with magnifying lens and microscope Olympus CX43 on four times magnification. Visual identification of polymers is preliminary identification and it is the first step of polymer characterization. Particles were after extraction analysed with FTIR.

2.6 Details of sample characteristics

For dewatered sludge we determined moisture content and content of organic matter. Moisture content was established through the percentage loss while drying the sample at 105 °C for 12 h and content of organic matter through loss on ignition, while samples were heated to 550 °C for 4 h. Three replicates were done with 10 g of sludge and average value was calculated.

2. Results

After we counted and identified polymers, we determined the average recovery rate for samples that were oxidated with Fenton's reagent before OEP and samples where only OEP was done, for each type of MP and size. In the case that any other particle of MP was found in the sample it was not included in calculation of recovery rate. Recovery rate was higher for samples where oxidation of samples was performed before OEP for all types and sizes of MP. Average recovery rate with oxidation with Fenton's reagent prior OEP was on average 10% higher than OEP alone. Average recovery rate of all small polymer types (< 1 mm) reached 78% ± 17% with OEP and with additional oxidation 86% ± 9% while for bigger polymers (1-5 mm) 65% ± 32% with OEP and 75% ± 34% with oxidation. PVC with the highest density, had the lowest recovery rate. For bigger particles when only OEP was used it reached 19% ± 10%, while with oxidation, the recovery rate was higher, but still low (24% ± 12%) in comparison with plastics, that have lower densities. Small PVC particles reached higher average recovery rate 54% ± 30% with OEP and 77% ± 12% with pre-treatment. PP particles, with the lowest density, had the highest recovery rate for bigger particles and reached 99% ± 4% with oxidation and 86% ± 16% with only OEP. Small particles PP reached 93% ± 8% with OEP and 97% ± 5% with additional oxidation. Average recovery rates with SD are shown on **Figure 2**.

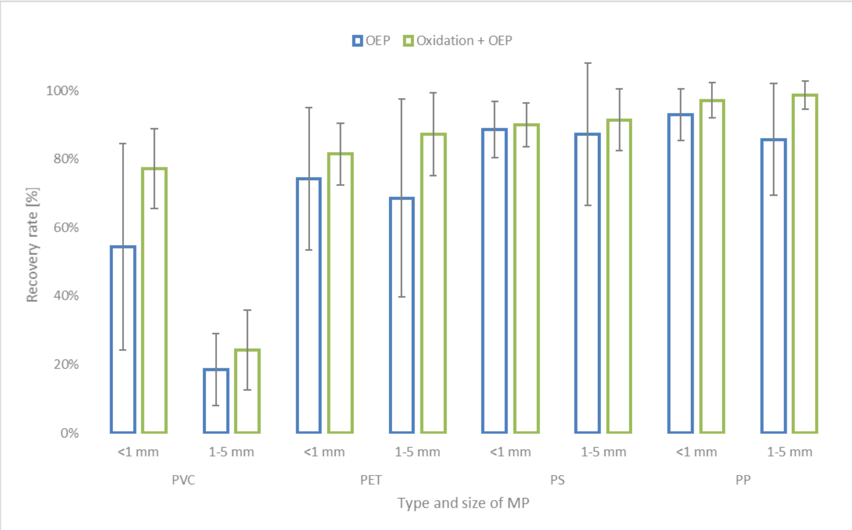

Figure 2. Recovery rate (mean + SD; n=9) of OEP with and without oxidation with Fenton's reagent

3.2 FTIR analysis

FT-IR analysis prior and after extraction have confirmed, that no chemical change occurred during the procedure (Figure 3, PVC polymer). It seems, that Ethanol efficiently removes oil from particles and does not affect FTIR spectra from polymers.

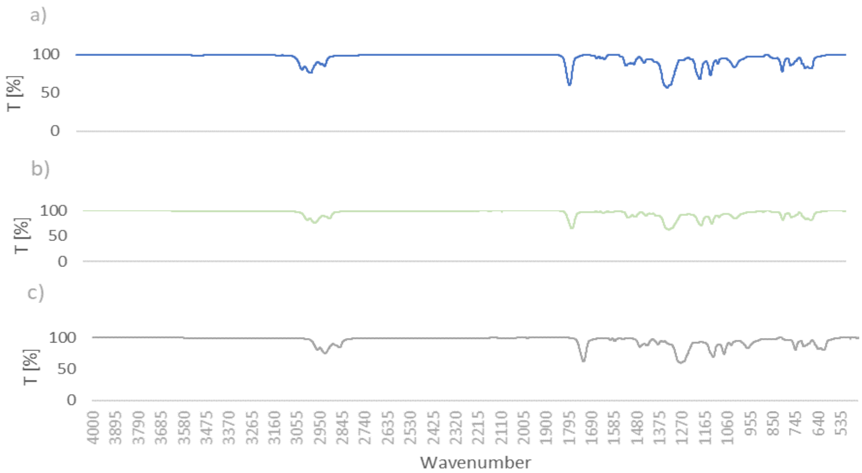

Figure 3. FTIR spectra from samples for PVC sample a) before extraction, b) after olive oil extraction c) after oxidation, followed by oil extraction protocol.

3. Discussion

Oxidation with Fenton's reagent improves recovery rate for all types of MP and it seems, that size of particles does not have impact on higher recovery rate, except with particles, that have higher densities as is PVC. Oxidation was shown as an important pre-step for oil extraction of MP in sludge samples with reducing organic matter and helps to avoid clogging the vacuum filters, slowing down the filtration and also quantification and identification of polymers is easier to miss, when oxidation is involved in the procedure.

No marked difference in recovery rate was discovered between different sizes of polymers, except with PVC, where the recovery rate was much higher (in average 36% with OEP and 53% with oxidation) with particles smaller than 1 mm. However, for polymers with higher densities, further experiments need to be done, since those polymers can be easily overseen because of small size and colours of MP with this approach. In the usage of OEP it is important, that the mixture is well mixed, so that all polymers got into the contact with oil. The method is suitable for smaller particles than is the size of the outlet of the funnel, since it restricts the maximum size of MP and bigger particles could also clog the funnel as high content of organic matter. This is the reason, why pre-treatment is an important step prior OEP.

4. Conclusion

OEP is simple, reliable, rapid and cost-effective method for separation of polymer particles in environmental samples. It is a promising extraction method, since it reaches high recovery rate and is harmless to environment and humans. Nevertheless, further research needs to be done with particles of higher densities and bigger sizes than 1 mm. Currently there is no standardised procedure of treatment of environmental samples as it is sludge. Efficient and standardised extraction method of MP from sludge could unify results of further research and ensure comparable results between different research studies.

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