A case study of identification and classification of microplastics using aluminium sulfate in wastewater treatment facility on the university campus

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Abstract: This study is to identify the Microplastics in the effluent of the treatment plant on the University campus. The plastic with less than 5 (five) mm size is universally considered as Microplastics. Volume reduced sampling method is used and for sample concentration, Aluminium sulfate as the coagulant is used. A sample was concentrated as the liquid and solid powder. One micron filter paper is used. Visual identification was done using the dissecting microscope, For particles smaller than 40X magnification scanning electron microscope (SEM) we used. For Identification of polymers Fourier Transform Infrared Spectroscopy (FT-IR) was used. In FT-IR test results all the liquid samples were negative in a result, and all the solid samples were positive that, it showed the presence of polymer in the sample, the plastics identified are Polyethylene, polystyrene, Polyvinyl chloride, Polyamide (nylon) in the solid sample.

1. Introduction
1.1 About the University:
KalasalingamDeemed to be University is located in southern Tamil Nadu in a virudunagar district with more than 8000 students both the day scholar and hostellers, 600 staff members, University has a water demand of 0.8MLD. In the campus a separate wastewater treatment plant in running to recycle the water. The plant is as per the conditions stated by state pollution control board. Treated water is reused to maintain the landscapes inside the campus.

1.2 Microplastics:
Plastic polymers are considered to be non reactive and not dangerous to human health. (Galloway, 2015). Monomers are synthesized into polymers that are plastics with the additional chemicals as catalysts, initiators, and solvents etc. These substances could leach out of the plastics and contaminate the environment and health (Galloway, 2015). A plastic particle with its longest dimension is between 5 mm to 1 μm is called Microplastic, size less than 1 μm is called nano plastic. (Crawford, et al., 2017)

MPs classified as Primary and Secondary. Intentional manufactured particles to be used in Cosmetic care products are called primary microplastics. Unintentionally created particles, results of degradation of larger particles because of environmental causes such as UV light from the sun and also use mechanical means such as wind force and Tidal waves (Crawford, et al., 2017). Like any analysis, the analysis of Microplastics in the aquatic environment starts with the sample collection. In a large water body like ocean and lakes, Manta net collection techniques are used globally (Crawford, et al., 2017). For smaller water bodies surface water collection using various collecting vessels used. When it comes to the wastewater treatment plants samples were collected at the overflow of clarifying tanks or at the intake of maturation ponds. S.M. Mintenig et al took the sample pump with PVC hose connected. The connected a membrane at the filter made up of stainless steel cartridge. (Mintenig,
al., 2017). We used a similar setup in this study and manual volume reduced sampling was followed. For contamination by microorganism mitigation, 30% of the hydrogen peroxide solution used and purification can with the addition of sodium dodecyl sulfate (5% w/vol). Samples were incubated at 70°C for 24 hours (Mintenig, et al., 2017). But in the present study to avoid microorganism contamination samples were kept in a freezer in 4°C in an attempt increase the cost-effectiveness of the process and the ultimate objective of the study to identify the MPs not to calculate its quantity. Generally based on density MPs are classified in to High, Medium and Low. In this research work its assumed that MPs are present in two density conditions, MPs with high density will settle down in fresh water when it comes to the salty water denser particle will float. MP with moderate or medium density will float with the colloidal in the wastewater (Crawford, et al., 2017).

Aluminium sulfate is being one of the common coagulant used in the waste water treatment process, we took aluminum sulfate powder and used in the rate of 1g/l with respect to the above-said assumption. Alum is cheap and it's commonly used in the effluent treatment plant for its versatility. So alum is chosen to mimic the process being followed in the treatment plant. For the separation process used only one 1µ size filter paper used, unlike in (Crawford, et al., 2017). For manual identification Dissecting microscope with 40X magnification is used and for more clarity in size of the particle, scanning electron microscope is used in this study. To classify Microplastics FT-IR and Raman spectroscopy is used widely (Crawford, et al., 2017). In this study, we used Attenuated total reflection (ATR) based FT-IR. The methodology for the study followed is as follows; the sample was collected manually, the sample was prepared in the form of liquid and solid sample using alum, dissecting microscope was used visual analyze and FT-IR analysis to classify the type of plastic polymer.

2. Sampling
Sampling method influences the type of sample and originality of the sample, (Crawford, et al., 2017) suggested three sampling methods recover MPs from the environment. Namely volume reduced, selective and bulk sampling. In this study we adopted volume reduced sampling method. Volume reduced sampling technique is used because it reduces the sample till item of interest, in our case Microplastics. The main demerit of this method is also its merit, this method dispose of large quantities of water, with the risk of potential loss of Microplastics in the sample. (Crawford, et al., 2017). Volume reduced sampling method was adopted in the study; Initially, 5 L of raw sewage was collected manually on the top layer of sedimentation tank near the inlet of the tank, during peak usage hours of the university hostels. And 5 L of a treated water sample is also collected manually. In order to prevent the formation of microorganisms, samples were kept in the freezer under 5°C within half an hour of collection. Further down on the line, for filtration sample was reduced to 20ml, and for FT-IR analysis 2ml of the sample was taken. The sample was collected manually within the 15cm of depth in the primary settling tank from the top surface.

3. Sample preparation
To separate the floating MPs in the study we used Aluminium sulfate generally called alum. Alum is a usual substance used for coagulation in the wastewater treatment plant. Al₂(SO₄)₃.16H₂O is used in the study. Alum was used in the rate of 1g/l, 2g/l, and 3 g/l. for both raw and treated wastewater. For separation of floating particle 4.75mm sieve was used during the sample collection. In the volume reduction process, 20ml sample was separated and 1µ filter paper was collected.

4. Details of analysis and results
Generally Microplastics have physical and chemical characteristics, so identification of Microplastics requires more than one method for reliable results, therefore the combination of two analytical methods is used widely, for Physical analysis microscopy is used, in our study dissecting microscope with a magnification of 40X and scanning electron microscope is used. To analyze the chemical characteristics generally spectrosopes used widely (Crawford, et al., 2017). In this study to identify the polymers using its chemical characteristics, FT-IR is used.
5. Visual identification
For visual identification only dry sample was taken, using a Dissecting microscope, to measure the size of the particle in this stage, image analysis software called Motic Images plus 3.0 is used. Three numbers of dry filtered samples taken with the range of 1g/l, 2g/l, and 3g/l alum added. MPs were not separated from the filter paper, used directly in the microscope. Since the size measurement of the particle will not be accurate, an average of the measured value was taken. In this stage, we couldn’t possibly classify the particle. But MPs were identified as polymers based on the literature study (Masura, et al., 2015). In this stage, we couldn’t trace any microbeads. So for further visual identification, SEM was used. Figures 1 show the polymers identified in the dissecting microscope. Figure 3 shows the polymer identified in the SEM. Table 1 and 3 shows the size of the particle measured in visual identification.

6. FT-IR
Fourier-transform infrared spectroscopy is widely used for polymer identification. This technique is reliable, accurate and straightforward in the identification. The technique uses highly specific infrared spectra which contains distinct band patterns, which differentiate the plastic and natural materials. This technique relies on the actuality that most of the molecules absorb light in the infrared region of the electromagnetic spectrum (Crawford, et al., 2017). In the study, an analysis was carried using SHIMADZU’s IR TRACER 100 based on single reflection ATR technology. The IR tracer-100 features the highest SN ratio in its class, 0.25cm-1 resolution, and high-speed scanning capable of 20spectra/second. For each raw and treated effluent, three samples were analyzed both in dry and liquid form. Figure 2 shows the results obtained in FT-IR. Table 2 represents the types of plastic polymers identified.

7. Result and discussion
The length of the Microplastic fibers was measured both in raw and treated water samples. In the raw samples maximum length measured was 18.35 mm, and minimum thickness was 0.0933 mm. When it comes to the treated sample maximum length of measured was 4.2 mm and thickness was 0.0833, from this result it is evident that there is a possibility of the deterioration of the microplastic fibers during the treatment process. And also a number of fibers identified also very low compare to raw water in the treated water, Which indicate MPs could settle down in the sludge. In the SEM analysis, microplastics with the size of 10-20 micron is identified in both the samples, which indicates a very limited number of Microplastic particles travels after the treatment process also. This proofs the assumption that MPs were present in Low and high-density conditions.

In the FT-IR analysis, dry sample results show the presence of the Microplastics namely Polyethylene, polystyrene, Polyvinyl chloride, Polyamide (nylon). However liquid samples show no absorbance of the spectrum by the sample, theoretically, we can conclude that there are no polymers present in the sample. However, there could be polymers, which do not absorb the spectrum present in the sample. Apart from that only 2ml of the sample was taken, which is very low compared to the original sample volume, on the other hand using of the coagulant might have used the colloidal and drag the suspended MPs into the sludge, the positive result of the sludge also supports this argument. The main source of the Microplastics is the garments used by the hostel in the campus, and cosmetic good used by the inmates also could contribute a little. As a continuation of this work, quantification of the result can be done and comparison of the polymers identified and confirmation of the source could be done.
Figure 1: Polymer fibers identified in raw water sample

Sample with 1g/l of alum

Sample with 2g/l of alum

Sample with 3g/l of alum

Figure 2: FT-IR results of raw water-solid sample
Table 1: Dimensions of the MP fiber in raw water.

| S.No | Sample Name | Length (mm) | Thickness (mm) | Color (mm) | Average Length (mm) | Average Thickness (mm) |
|------|-------------|-------------|----------------|------------|---------------------|------------------------|
| 1    | R1          | 6.30        | 0.10           | Black      | 7.0666              | 0.11                   |
|      | R2          | 6.48        | 0.11           | Dark green |                     |                        |
|      | R3          | 8.42        | 0.12           | Red        |                     |                        |
|      | R4          | 12.70       | 0.05           | Black      |                     |                        |
| 2    | R5          | 19.06       | 0.16           | Black      | 12.343              | 0.33                   |
|      | R6          | 5.27        | 0.12           | Black      |                     |                        |
|      | R7          | 19.05       | 0.08           | Red        |                     |                        |
| 3    | R8          | 17.43       | 0.08           | Dark green | 18.3566             | 0.0933                 |
|      | R9          | 18.59       | 0.12           | Black      |                     |                        |

Table 2: Polymer identification and range of the particle.

| Raw water | Treated water |
|-----------|---------------|
| Liquid (Abs) | Frequency cm^-1 | Polymer type | Solid (Abs) | Frequency cm^-1 | Polymer type | Liquid (Abs) | Polymer type |
| 0.3 | - | - | 1.75 | 3398.7 | Polyethylene | 0.3 | - | - | 1.6 | 979.84 | Polyethyleneterephalate |
| 0.3 | - | - | 1.65 | 611.43 | Polystyrene | 0.3 | - | - | 1.8 | 594.08 | Polystyrene |
| 0.3 | - | - | 2.70 | 3496.94 | Polyethylene | 0.3 | - | - | 2.2 | 3458.37 | Polyethylene |
| 0.3 | - | - | 2.20 | 1126.43 | Polyvinylchloride | 0.3 | - | - | 2 | 574.79 | Polyvinylchloride |
| 0.3 | - | - | 1.2 | 1651 | Polyamide (nylon) | 0.3 | - | - | 1.2 | 1120.6 | Polyvinylchloride |
| 0.3 | - | - | 1.8 | 1107.4 | Polyvinylchloride | 0.3 | - | - | 1.1 | 611 | Polyvinylchloride |

Table 3: Dimensions of the MP fiber in treated water.

| S.No | Sample Name | Length (mm) | Thickness (mm) | Color (mm) | Average Length (mm) | Average Thickness (mm) |
|------|-------------|-------------|----------------|------------|---------------------|------------------------|
| 1    | T1          | 3.04        | 0.05           | Black      |                     |                        |
| 2    | T2          | 3.55        | 0.06           | Black      | 4.2066              | 0.0866                 |
| 3    | T3          | 6.03        | 0.15           | Red        |                     |                        |
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