Analysis of Microplastic Beads and their Removal at a Municipal Wastewater Treatment Plant

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WATER AND
ENVIRONMENTAL
TECHNOLOGY CENTER

Analysis of Microplastic Beads and their Removal at a Municipal Wastewater Treatment Plant

TU-15-06

Research Team: Rupa Lamsal and Rominder Suri

Objectives:

- To develop analytical method for detection and quantification of microplastics in wastewater samples
- To determine removal efficiency of microplastics in biological wastewater treatment process

Period of Performance:

- 01/2014 – 12/2014

Accomplishments and Key Findings:

- Analytical method was developed for detection and quantification of microplastics
- Fate of microplastics was studied in municipal wastewater treatment system
- Significant removal (83+%) of microplastics at wwtp

Cost/Schedule Performance Status:

The project completed on schedule and within budget

Key Deliverables / Milestones:

- **Deliverable 1**: Analytical method development – **(Completed)**
- **Deliverable 2**: Microplastics Removal efficiency determination – **(Completed)**
- **Deliverable 3**: Research article; progress reports; presentations to IAB

Project Status:

Completed

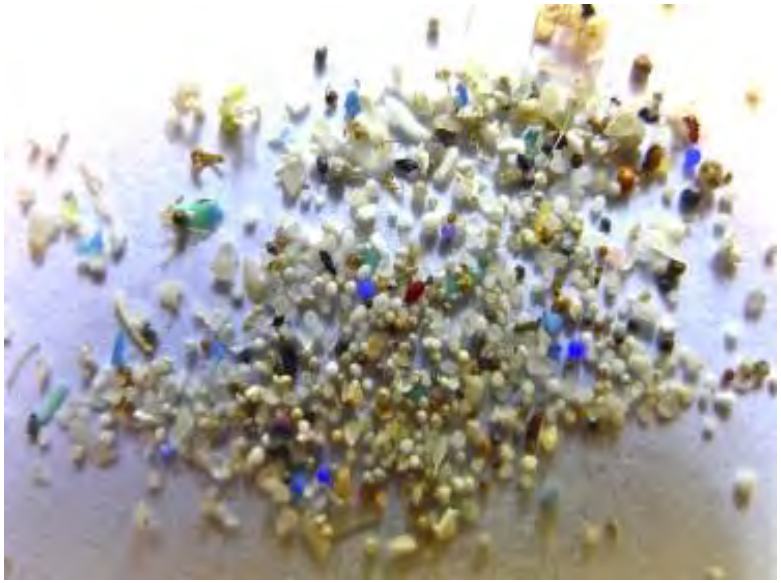
Background

- Microplastics are used in personal care products such as exfoliating scrubs, toothpastes, shower gels and shaving creams, etc.
- Persistent in environment and attract chemicals

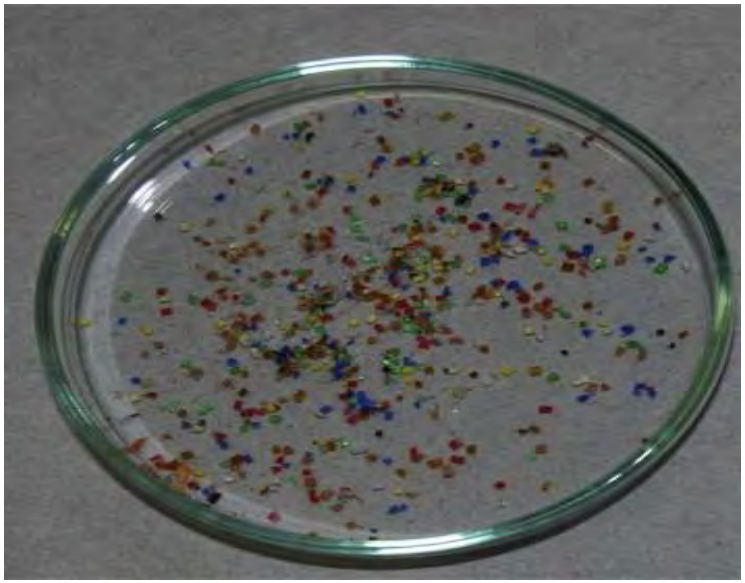
  e.g. DDT, PCBs, nonylphenol, flame retardants
- Detected in surface water (Great Lakes), marine organisms such as in fish, lobsters, mussels, oysters
- Ingested higher in the food chain

1. 5 Gyres Institute, Microplastics in consumer products and in the marine environment, Position paper, 2013
2. Eriken et. al. Microplastic pollution in the surface waters of the Laurentian Great Lakes, Marine Pollution Bulletin, 77(1-2), 2013, 177-182.

Studies in Lake Waters and Sediments



Microplastics in Great lake
Size 0.355-5 mm[1]



Synthetic microplastics isolated from lab water ; Size 0.5-1 mm[2]

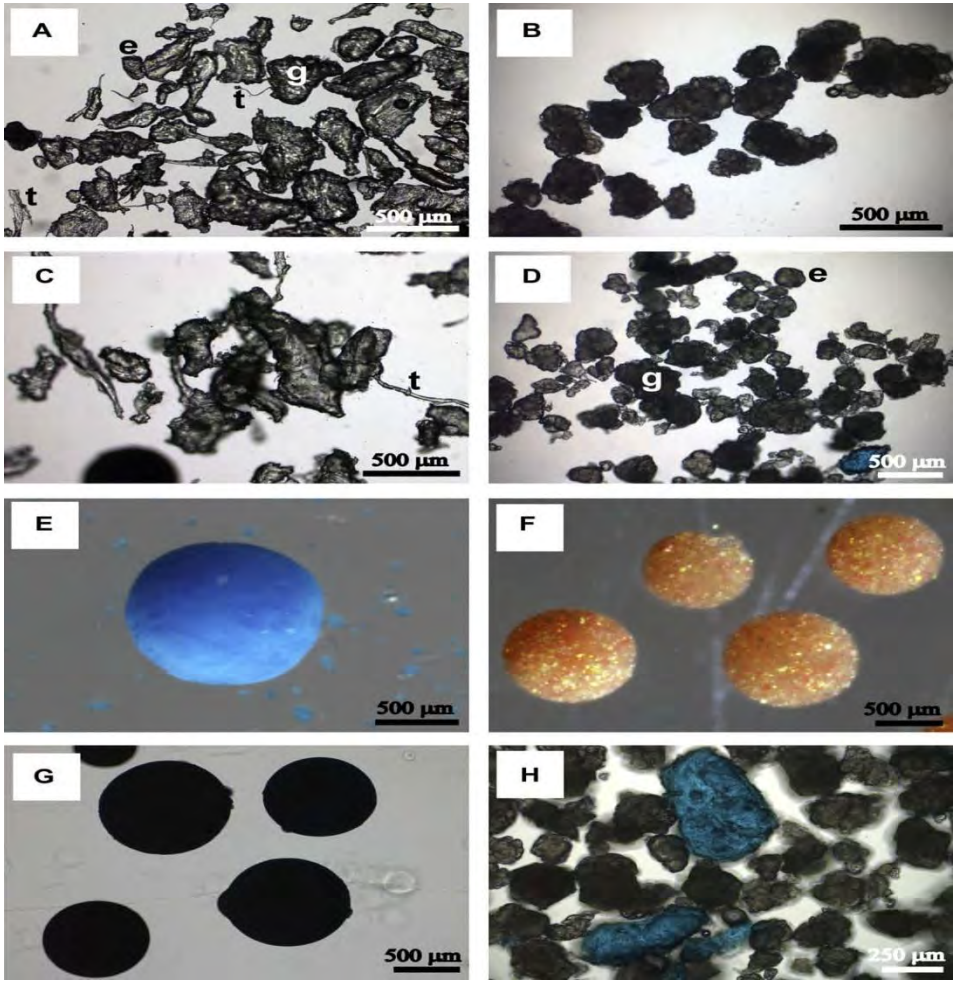
[1] Eriken et. al. Microplastic pollution in the surface waters of the Laurentian Great Lakes, Marine Pollution Bulletin, 77(1-2), 2013, 177-182.

[2] Nuelle et. al. A new analytical approach for monitoring microplastics in marine sediment, Environmental Pollution 184, 2014, 161-169.

Microplastic in Facial Cleansers

- Microplastic in different brand of facial cleansers

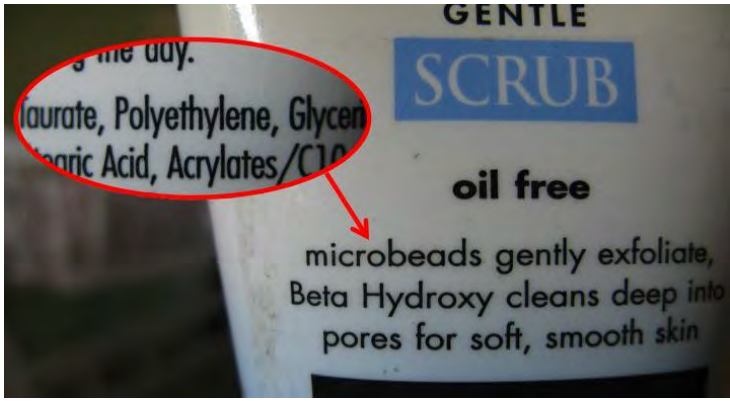
Particle size = 0.5-5mm (*Fendall & Sewell et al., 2009)*[1]



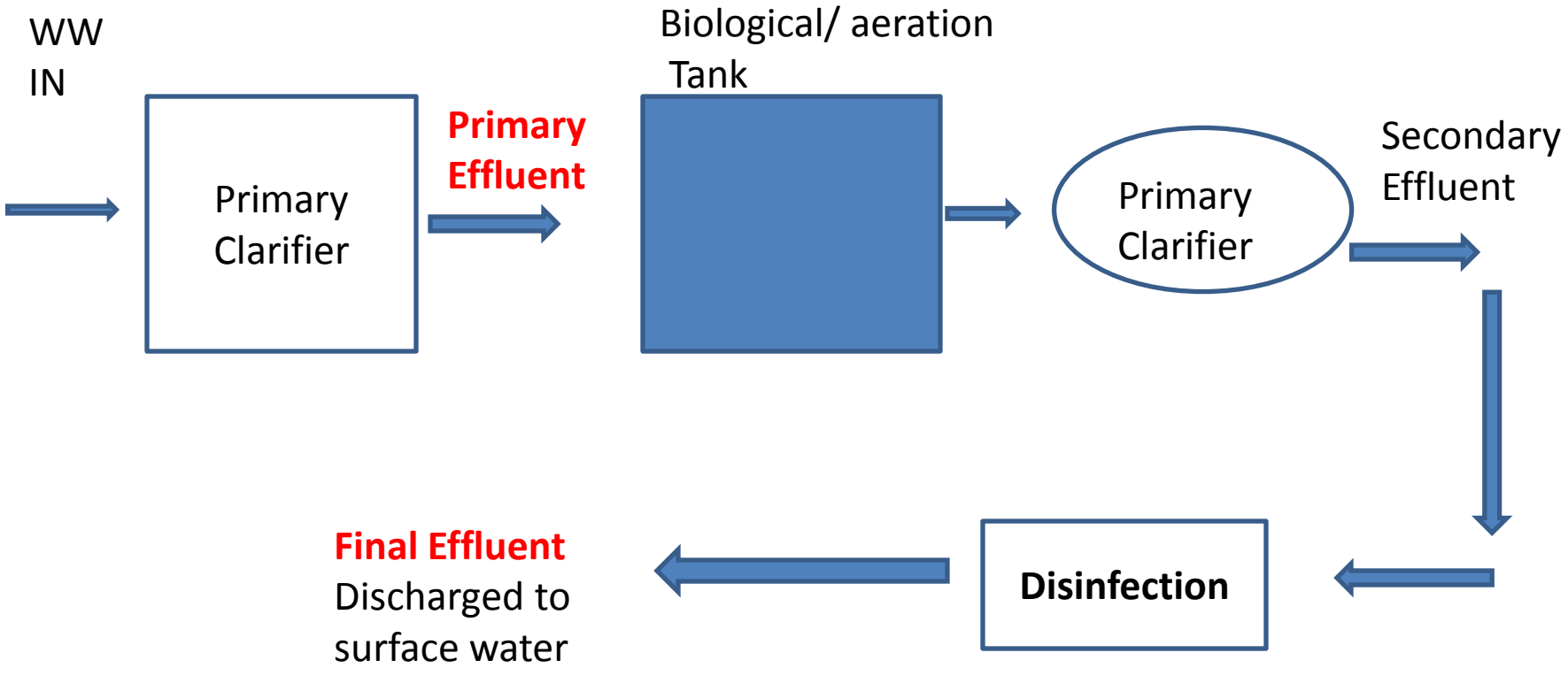
[1] L. S. Fendall and M. A .Sewell Contributing to marine pollution by washing face: Microplastics facial cleansers, Marine Pollution Bulletin, 58, 2009, 1225-1228.

Project Objectives

- Develop analytical method for detection and quantification of polyethylene microplastic beads (PEMB) in wastewater samples
- Determine removal efficiency of PEMB at a municipal wastewater treatment plant



Typical Layout of a Municipal WWTP (simple)



Experimental

- Samples of polyethylene microplastic beads (PEMB) were obtained from a Pharmaceutical and Personal Care Product Company
- PEMB size – approximately 200 to 600 micron
- Used as a standard

Analytical Methods

- Several methods were examined in the lab for the detection and quantification of PEMB
  - Weighing method: Filter water and weight the mass of PEMB on the filter paper
  - Scanning electron microscope (SEM) method to observe particle morphology and size
  - Particle counting method using a Hemocytometer
  - Aerate wastewater samples, filter and weigh/count PEMB on filter paper
  - Flow Cytometry
  - **Filter wastewater sample and count particles using microscope (40X power)**
  - **FT-IR Imaging**

What Size Range of MPB should be Considered to Analyze Wastewater Samples?

- Upper limit: 5 mm
- Lower limit: ???

300 µm often used for practical reason

300 µm is standard mesh size in a plankton net used for sampling of zooplankton

Experimental Work

- Filter wastewater samples (primary and final effluents) through 1000, 600 and 90 µm mesh size sieves, respectively
- Digest biomass in the sieves by rinsing with hydrogen peroxide five and ten times for PE and FE, respectively
- Visualize particles in Stereomicroscope with 40X power and count
- Analyze chemical composition of those particles in FT-IR and confirm microplastics based on FT-IR spectra

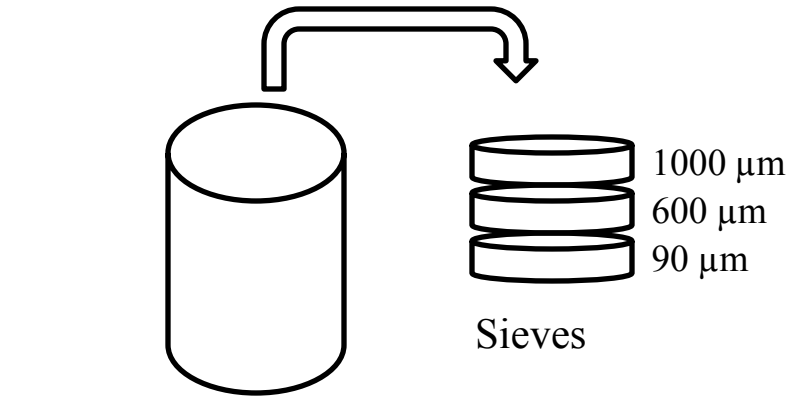
FT-IR Imaging system

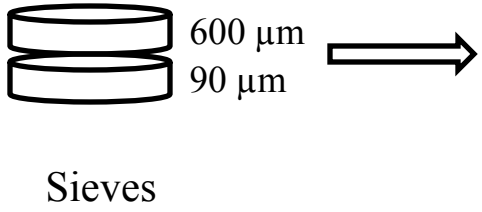
Wastewater Samples

- Wastewater samples were collected from a local wastewater treatment facility
- The plant receives domestic waste from about 50,000 residence, and trucked wastewater from some companies
- 24 hours composite samples (10 L) of primary effluent (PE) and final effluent (FE) were collected
- (Three samples - April, May, July 2014)
- 1 L of primary influent and 5 L of final effluent samples were processed

Analytical Method Development

***Primary Effluent - Sample Processing**





Cleaning with Milli-Q water

H_2O_2 (10%) cleaning to digest biomass **(10 times)**

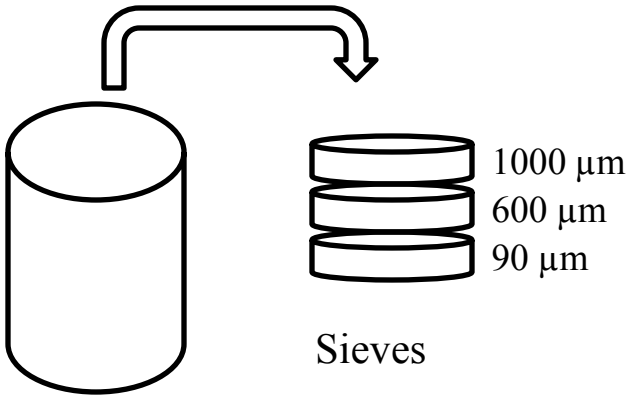

Particles Sorting


Viewing morphology of particles

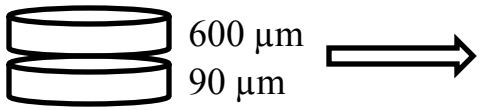
FT-IR analysis

Analytical Method Development

***Final effluent - Sample Processing**



5 L Final Effluent



Cleaning with Milli-Q water

H_2O_2 (10%) cleaning to digest biomass **(5 times)**

Particles Sorting

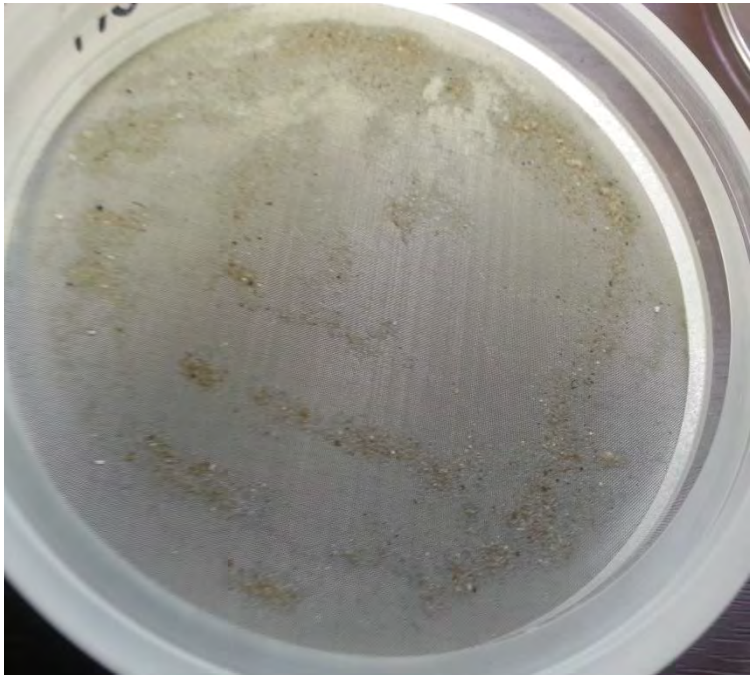
Viewing morphology of particles

FT-IR analysis

FT-IR Analysis

- FT-IR Conditions: spectral resolution of 8 cm^{-1}, 50 µm pixel size and 32 co-added scan per pixels
- FT-IR spectra of particles were compared with available standard microplastic (polyethylene microplastic bead)
- Additional spectra were compared with other polymer spectra from literatures and FT-IR spectra database
- **Polyethylene microplastic bead (PEMB) is mostly of focus in this study**

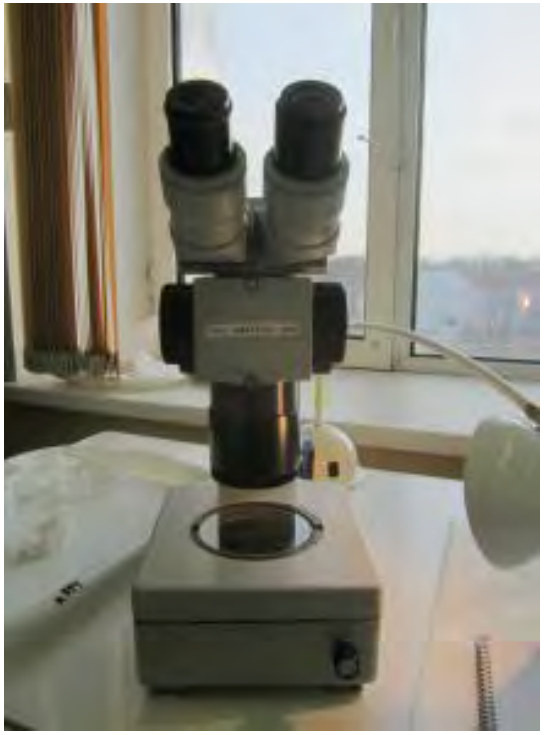
First Set of Composite Samples (April 24-25, 2014)



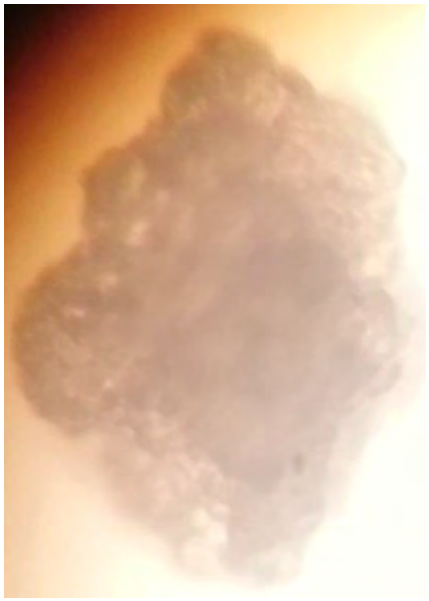
Particles collected in 90 µm sieve
(1L of Primary Effluent sample)

Particles collected in 90 µm sieve
(5L of Final Effluent sample)

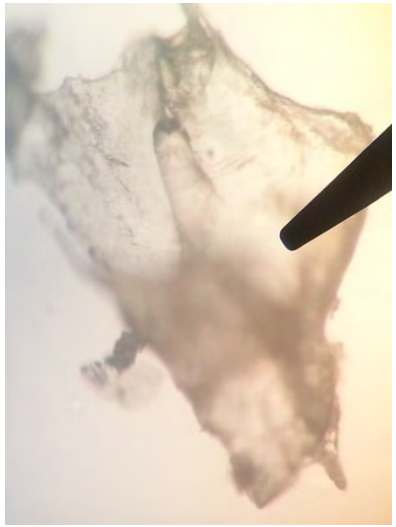
Microplastic Pictures in Microscope (40X power)



Stereomicroscope



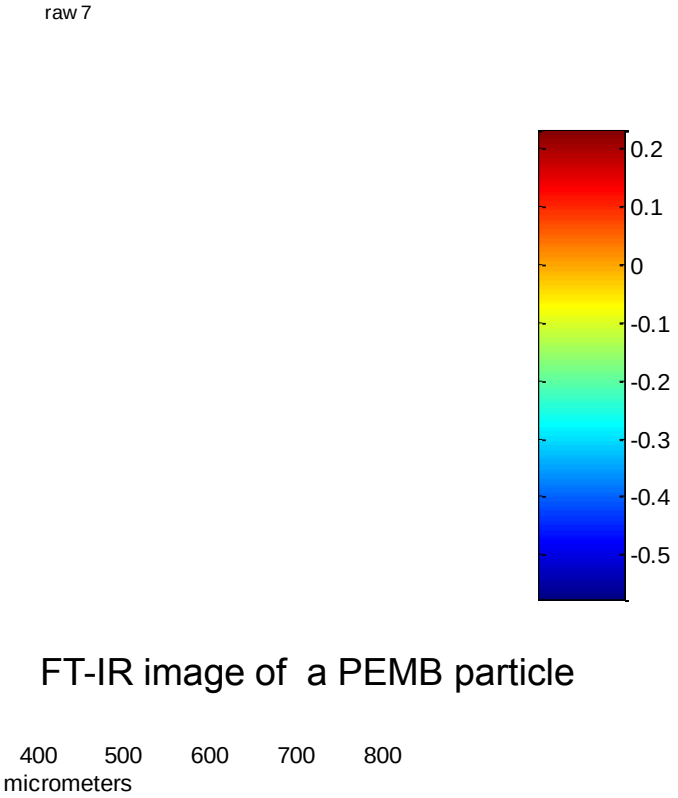
Standard PEMB



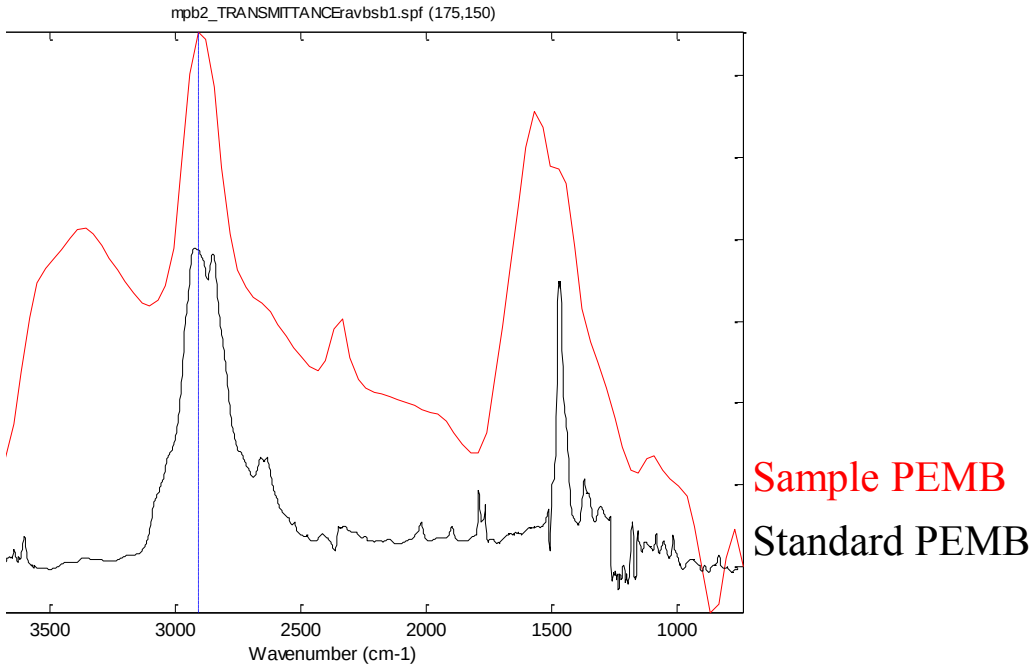
Possible micoplastic in Final effluent

FT-IR Analysis-Primary Effluent

***Note: Total of 55/L particles detected out of which 23/L were PEMB**



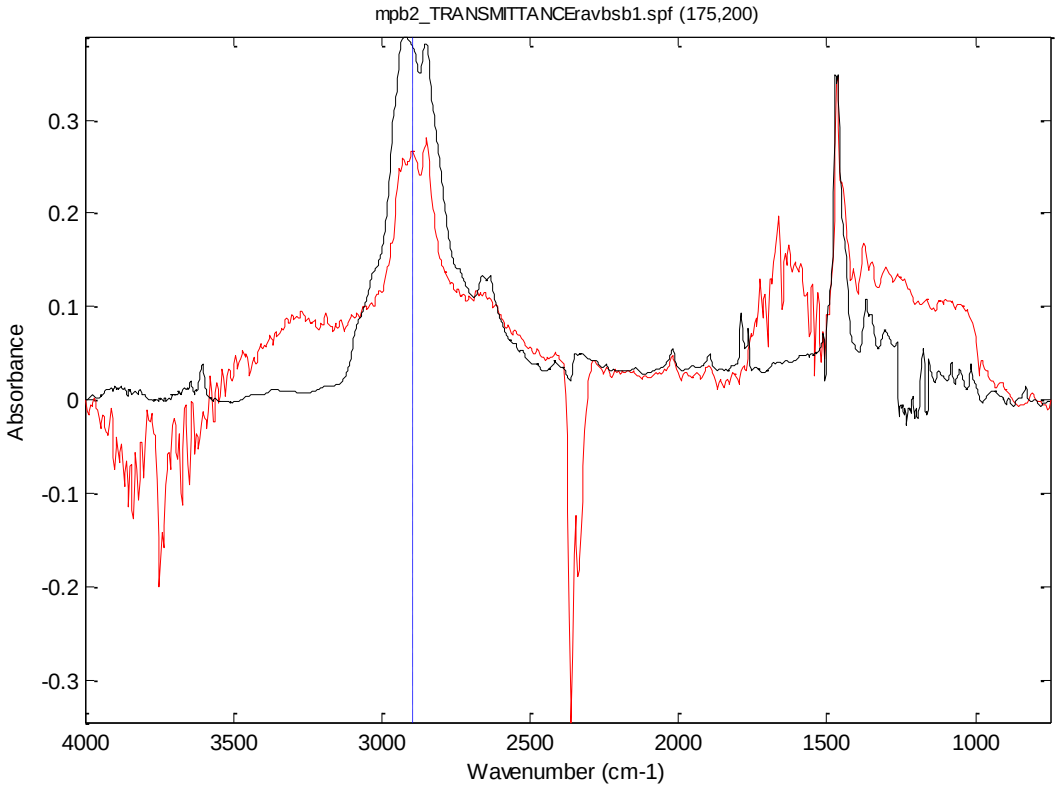
FT-IR image of a PEMB particle



FT-IR spectra of standard and sample PEMB

FT-IR Analysis-Final Effluent

***Note: Total of 30 particles detected out of which 3/L were PEMB**



Standard PEMB

Sample PEMB

FT-IR spectra of standard and sample PEMB

Removal efficiency of PEMB in April 24 = 87 %

First Set of Composite Samples (April 24-25, 2014)

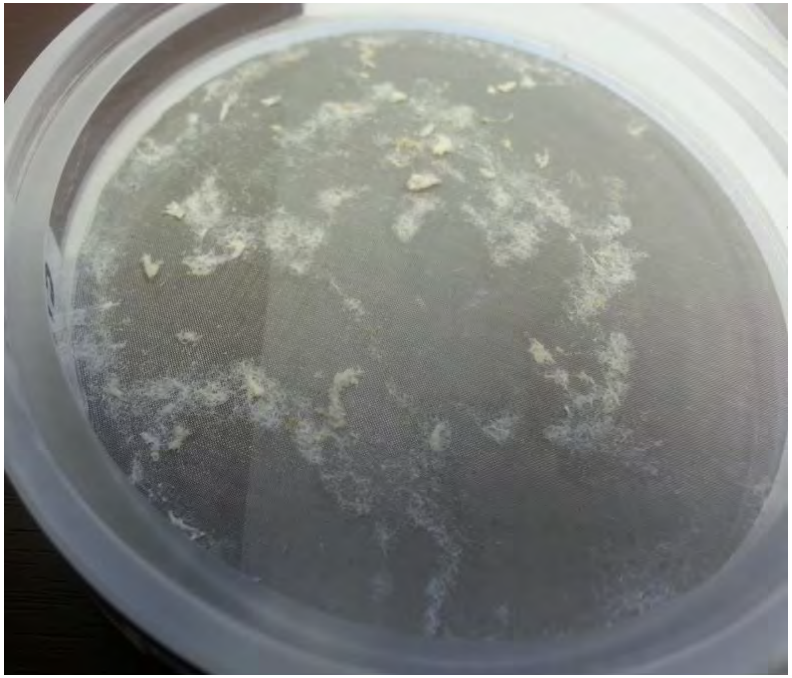
Primary Effluent sample volume = 1L

Final Effluent sample volume = 5L

Primary Effluent	Number of Fibers	Number of particles	Number of PEMB	Average number of particles
First analysis	**Numerous**	**55 particles/L (55 total particles)**	**23/L**	49/L
Second analysis	Numerous	43 particles /L (43 total particles)	NA	

Final Effluent	Number of Fibers	Number of particles	Number of PEMB	Average number of particles
First analysis	**Numerous**	**6 particles/L (30 total particles)**	**3/L**	5 /L
Second analysis	Numerous	4 particles/L (20 total particles)	NA	

Second Set of Composite Samples (May 21-22, 2014)

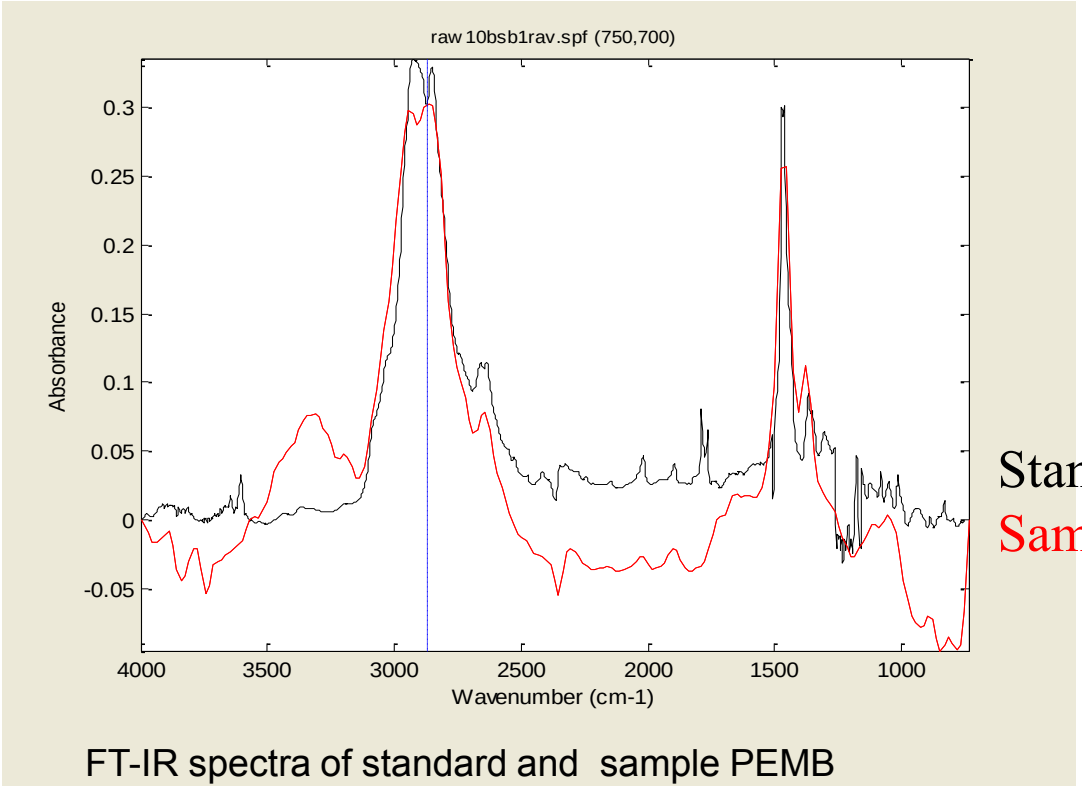


Particles collected in 90 µm sieve
(1L of Primary Effluent sample)

Particles collected in 90 µm sieve
(5L of Final Effluent sample)

FT-IR Analysis –Primary Effluent (May 21-22, 2014)

***Note: Total of 38/L particles detected; 6/L were confirmed as PEMB**



FT-IR spectra of standard and sample PEMB

PEMB in the final effluent = 0

Removal Efficiency of PEMB in May 21 = 100 %

Second Set of Composite Samples (May 21-22, 2014)

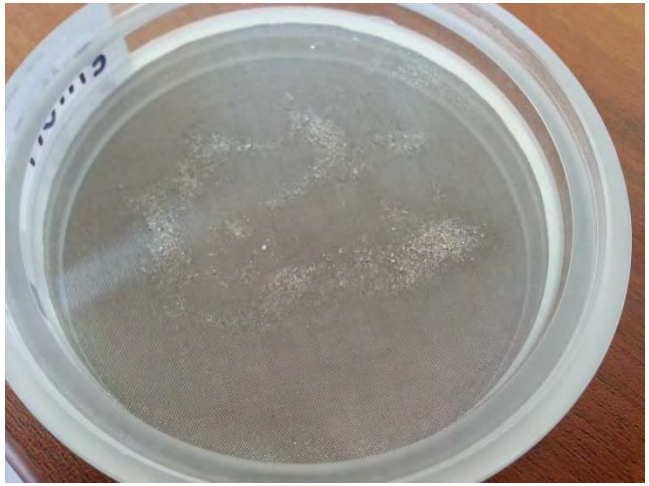
Primary Effluent sample volume = 1L

Final Effluent sample volume = 5L

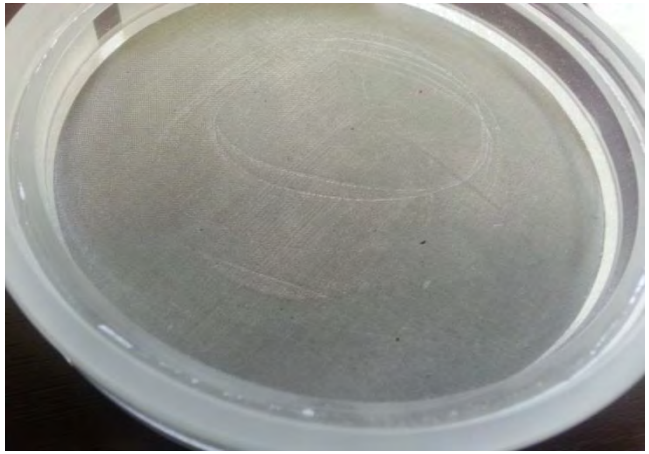
Primary Effluent	Number of Fibers	Number of particles	Number of PEMB	Average number of particles
First analysis	**Numerous**	**38 particles/L (38 total particles)**	**6/L**	54 particles/L
Second analysis	Numerous	69 particles/L (69 total particles)	NA	

Final Effluent	Number of Fibers	Number of particles	Number of PEMB	Average number of particles
First analysis	**Numerous**	**2 particles/L (10 total particles)**	**0/L**	3 particles/L
Second analysis	Numerous	4 particles/L (20 total particles)	NA	

Third set of Composite Samples (July 7-8, 2014)

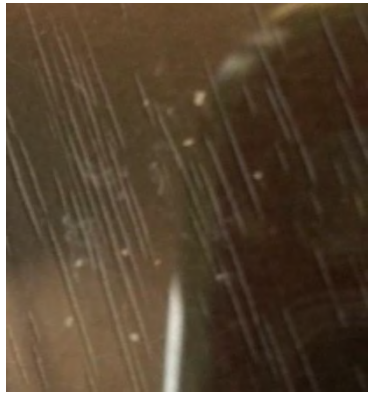


Particles collected in 90 µm sieve
(500 mL of Primary effluent sample)



Particles collected in 90 µm sieve
(5 L of Final effluent sample)

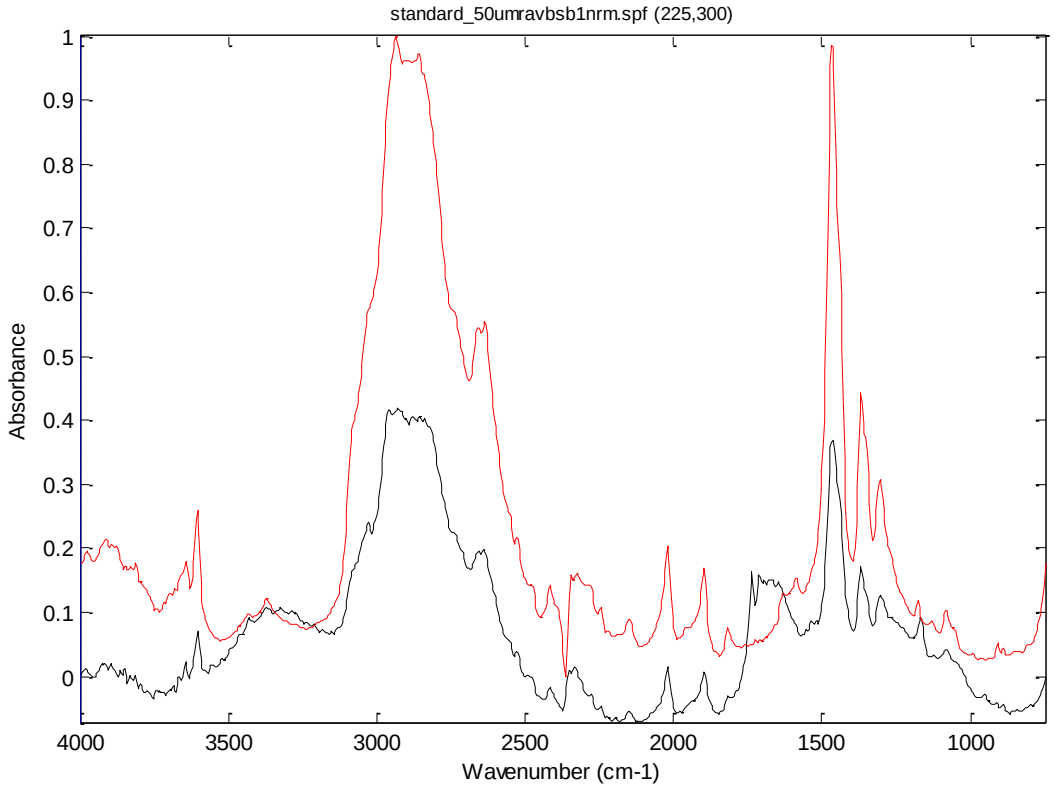
Picked particles for FTIR analysis



Picked particles for FTIR analysis

FTIR of First Analysis of Final Effluent- 3rd sample

Note: Total of 23/L particles; 1/L particle was confirmed as PEMB

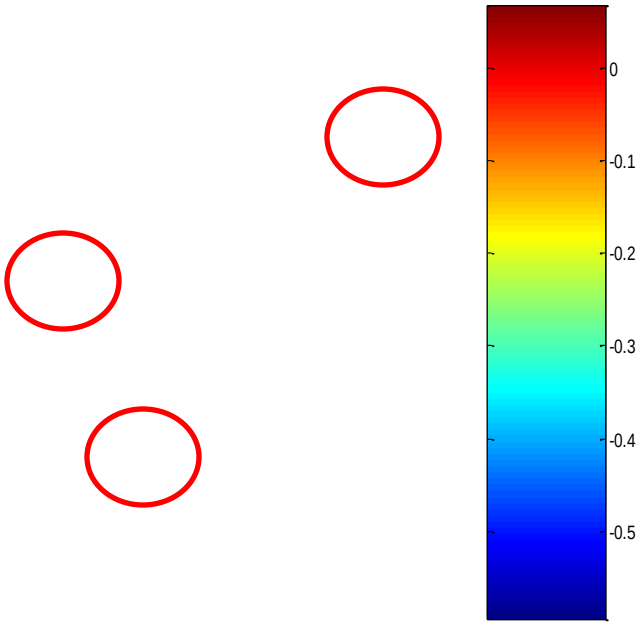


Standard PEMB
Sample PEMB

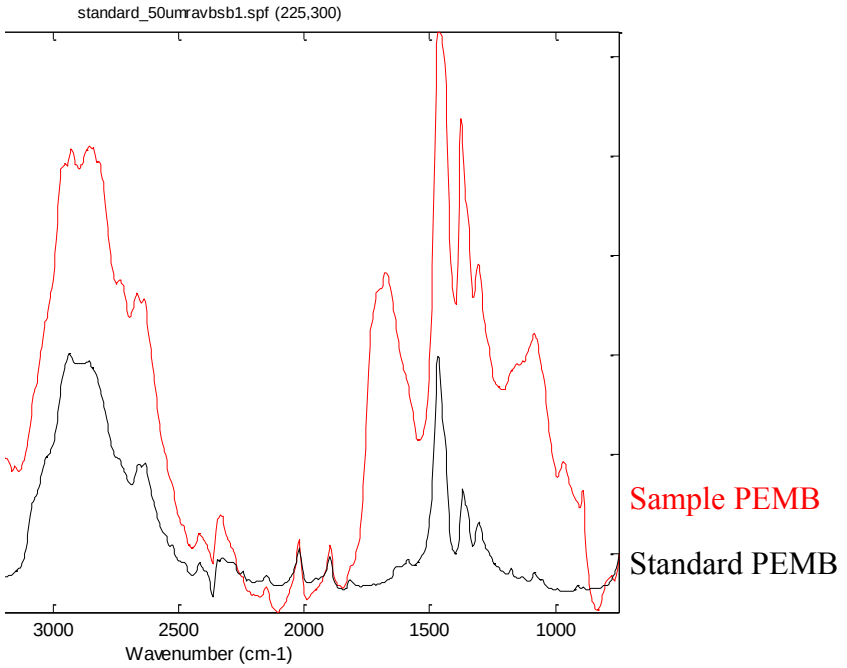
FT-IR spectra of standard and sample PEMB

FT-IR of Second Analysis of Final Effluent – 3rd sample

s are confirmed as PEMB



FT-IR Image of particles; particles with red circles are confirmed as PEMB



FT-IR spectra of standard and sample PEMB

First Analysis of Primary Effluent Particles – 3rd sample

- Total of 112 particles of which 60 particles were analyzed on FTIR
- **Spectra of PEMB was not observed**
- 6 particles had spectra similar to poly (vinyl alcohol)
- 23 particles had spectra similar to polyamide
- 4 particles had spectra similar to polyvinylchloride
- 27 particles yet to be identified (unknown spectra)

Second Analysis of Primary Effluent Particles – 3rd sample

- Total of 86 particles of which 60 particles were analyzed on FTIR
- **Spectra of PEMB was not observed**

Third set of Composite Sample (July 7-8, 2014)

Primary Effluent sample volume = 500 mL

Final Effluent sample volume = 5L

Primary Effluent	Number of Fibers	Number of particles	Number of PEMB	Average number of particles
First analysis	4 /L	224 particles/L	**0**	198 particles/L
Second analysis	10 /L	172 particles/L	**0**	

Final Effluent	Number of Fibers	Number of particles	Number of PEMB	Average number of particles
First analysis	0	23 particles/L	**1/L**	18 particles/L
Second analysis	1/L	13 particles/L	**3/L**	

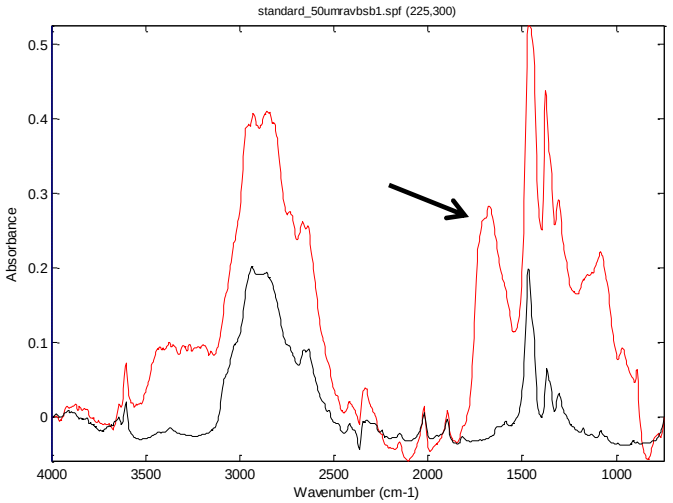
Number and Removal Efficiency of PEMB in Wastewater Treatment Plant

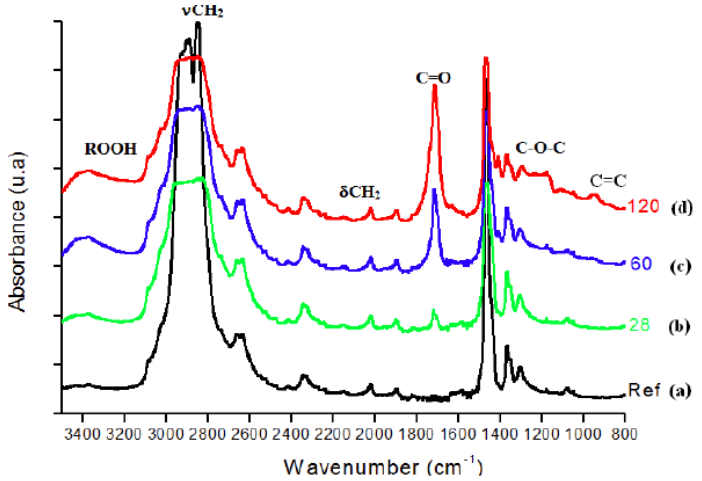
	Sample 1 (April)	Sample 2 (May)	Sample 3 (July)	Average
PEMB in primary effluent	23/L	6 /L	0	9.7 /L
PEMB in final effluent	3 /L	0	2 /L	1.7 /L
Removal efficiency of PEMB	87 %	100 %	*	83 %

Overall average removal of PEMB for 3 sampling events was 83%

Comparing Standard and Sample PEMB

- Additional peak was observed around 1700 cm^{-1}
- This may be due to c=o carbonyl group stretching (oxidation of polymer due to peroxide) or oxidation of polymer in wastewater treatment plant



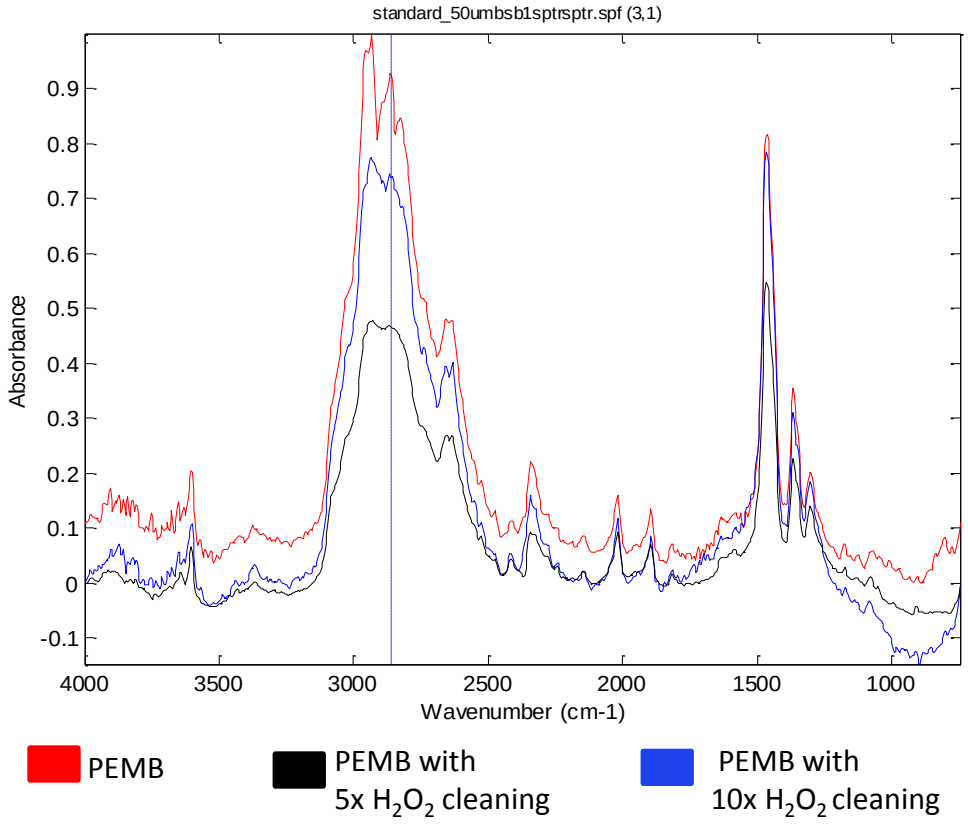


a) FT-IR spectra of reference UHMWPE and UHMWPE oxidized for b) 28 days c) 60 days and d) 120 days (*Rocha et al., 2009*)*

*M. Rocha, A. Mansur and H. Mansur, 2009. Characterization and accelerated ageing of UHMWPE used in Orthopedic prosthesis by peroxide. *Materials,* **2009**, *2*, 562-576; doi:10.3390/ma2020562.

Effect of H_2O_2 Cleaning during Sample Processing

- Cleaning with H_2O_2 during sample processing (both 5X and 10X) did not show the oxidation of standard PEMB
- There may be some oxidation of polymer occurring in wastewater treatment plant



FT-IR spectra of standard PEMB and PEMB washed with H_2O_2

Conclusion

- Polyethylene microplastic beads were successfully detected, isolated and enumerated in the primary effluent and final effluent samples from wwtp
- Reliable results were observed from FT-IR spectra to determine whether the collected particle is PEMB
- **Overall average removal of PEMB for 3 sampling events was 83%**

Thank You!

Questions?

Background

- Some studies have suggested that wastewater treatment plant acts as a point source for microplastics *(Browne et. al., 2011; McCormick et. al., 2014)*

- There is no comprehensive study on fate of microplastics at wastewater treatment plant