Supporting Information

Microplastics Mitigation in Sewage Sludge through Pyrolysis: the Role of Pyrolysis Temperature

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Paragraph S1 on spiked polymers pyrolysis experiment. Sludge A was dried at 105℃, fine powder < 100μm was collected after crushing and sieving. For each sample, 0.2 g of polymer spheres (with a minimum diameter of 300 μm) was spiked into 2 g of dried sludge powder then pyrolysis as the procedure mentioned in the material and methods. The preliminary experiment showed that the pyrolysis of ground sludge only would generate residue particles < 100 μm, as shown in Figure S7. In contrast, the pyrolysis of sludge with spiked polymers would generate particles > 100 μm (Figure S7). Thus, the big particles were considered as originated from the spiked polymer. After pyrolysis, the mixture was sieved with a mesh size of 100 μm to remove most of the sludge powder. Then particles originated from the spiked polymers were picked out under a stereomicroscope with tweezers and inoculation needles. The selected particles were rinsed with filtered ethanol and DI water, dried at ambient temperature, and stored in 2 mL PP centrifuge tubes until analyzed.

Paragraph S2 on density separation. The pyrolyzed sludge samples were transferred into 50 mL silicate centrifuge tube, then 30 mL $ZnCl_2$ solution (density=1.1 g/mL) was added to each tube. The tube was vigorously vortexed and centrifuged at 1000 rpm (134.16 g) for 10 min. The supernatant containing the microplastics was vacuum filtered through a 0.45μm nitrocellulose filter. The extraction step was conducted in triplicate to ensure that all potential microplastic particles could be separated from the sample. It should be noted that some plastic polymers may be wrapped by other compounds in the sludge after pyrolysis and are unable to be isolated. Since the environmental effects of microplastics appear to be mainly associated with their physical parameters (such as shapes, sizes and hydrophobicity), [1] these particles lose the major characteristics of microplastics. Therefore, only free microplastics were investigated and analyzed in this study.

Paragraph S3 on peroxidation. 10mL of sewage sludge firstly transferred to a 1L beaker and dried at room temperature. Before the reaction, the beaker was previously placed in a cold-water bath (10°C) to prevent violent boiling and heating damage to the microplastics. Then the sludge sample was treated by 50mL of 0.05M Fe (II) (in a pH=3 solution) together with 50mL of 30% hydrogen peroxide. After the boiling subsided, heat the beaker to 60°C for 30min. The peroxidation procedure was repeated 1-2 times until the solution became clear, and no organic matter was visible. Then the mixture was filtered through a 10um stainless steel mesh sieve, following with 500mL filtered deionized water to wash off the Fenton's reagent.[2] Particles on the mesh sieve were transferred to 50mL silicate centrifuge tube, then the density separation steps were performed as mentioned above.

Paragraph S4 on Raman Spectroscopy. Specifically, the analyses were carried out under a 532 nm wavelength and performed using a 50x magnification objective with a numerical aperture of 0.75. Grating with 600 grooves/mm was applied. The confocal hole width was set to 400 μm and the confocal slit width was 100 μm. To prevent sample destruction and increase the signal/noise ratio, laser power applied to the samples ranged from 2 to 20 mW, depending on the nature of the particles. Raman spectra were recorded in a range from 150 to 3500 cm^{-1}.[3] Identification was conducted in two replicates at least on individual spots of each particle for validation. All particles presented were analyzed for most of the filters. However, the filters with microplastics extracted from the untreated sludge and sludge pyrolyzed under 150 ^{o}C were analyzed for 1/4 of the total area as too many particles are presented.

Table S1. Main characteristics of the collected sludge

Sludge	pH	Total Solids (TS)	Volatile Solids (VS)	Total Chemical Oxygen Demand (TCOD)	Soluble Chemical Oxygen Demand (SCOD)
A	6.8±0.1	26200±64 mg/L	16246±46 mg/L	19100 ± 650 mg/L	306 ± 27 mg/L
B	7.1±0.1	41058±110 mg/L	15072±37 mg/L	40965 ±821mg/L	404±52 mg/L

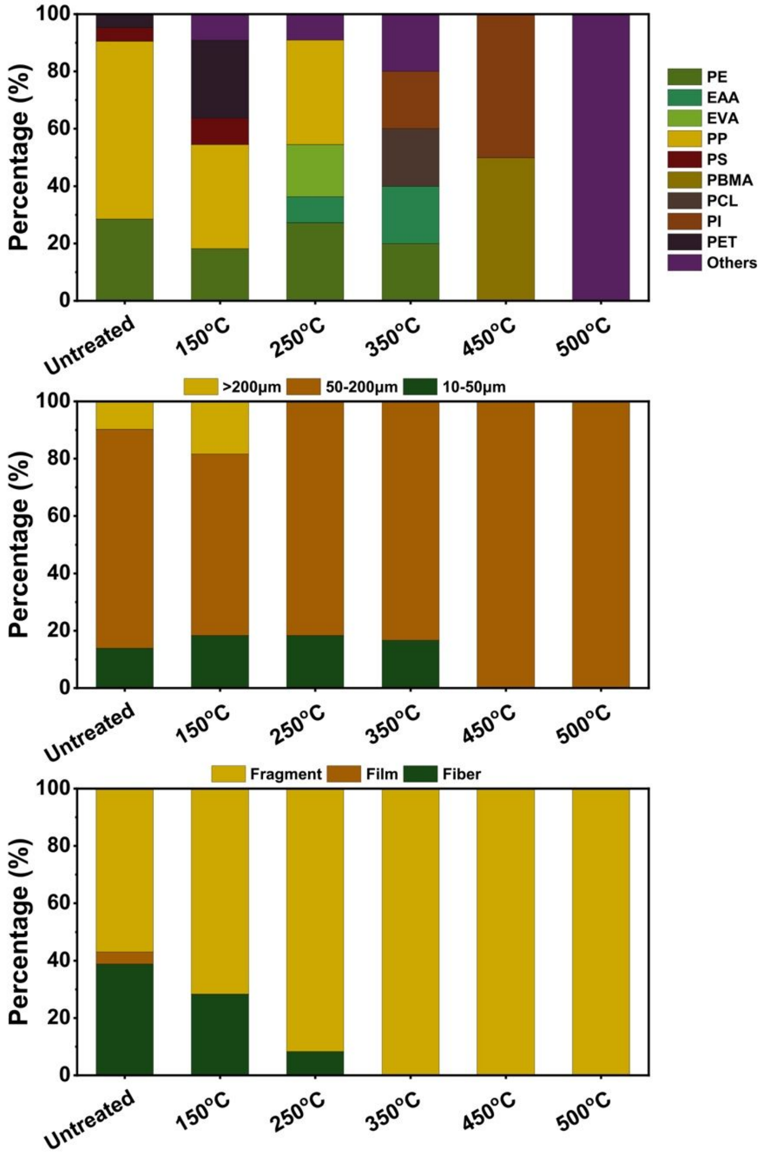

Figure S1 Characterization of microplastics in untreated Sludge B and Sludge B samples pyrolyzed at different temperatures. A: Proportion of different polymer types in sludge B. PE: polyethylene, EAA: poly (ethylene-co-acrylic acid), EVA: poly (ethylene-co-vinylacetaste), PP: polypropylene, PS: polystyrene, PBMA: poly(n-butylameth-acrylate) , PCL: polycaprolactone, PI: polyisoprene, PET: polyethylene terephthalate. Others include polyamide (PA), polytetrafluoroethylene (PTFE), poly (polyphenylene terephthalmide) (Kevlar 49). B: Proportion in different sizes in sludge B. C: Proportion of different shapes in sludge B.

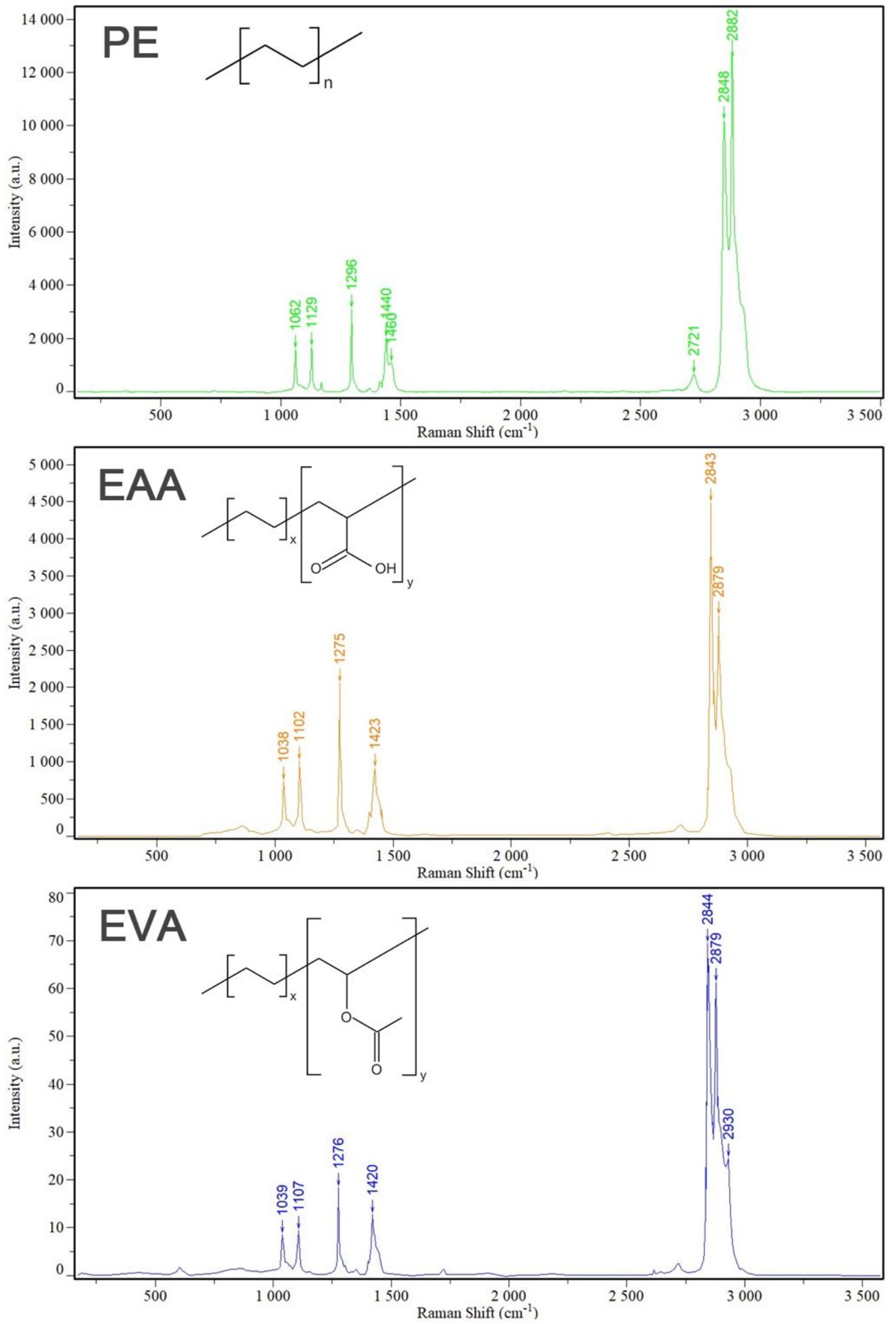

Figure S2: Raman spectra of the references for PE, EVA, and EAA (Measurement parameters: 532nm, 600grotves/mm, hole 400, slit 100, acquisition time 3 × 2s, objective 50 × , laser power ~0.2mW/2.0mW/6.4mW at the sample, intensity correction applied baseline corrected, normalized by maximum). The references were obtained from KnowItAl Informatics System, HORIBA Edition, Bio-Rad

Laboratories, Inc.

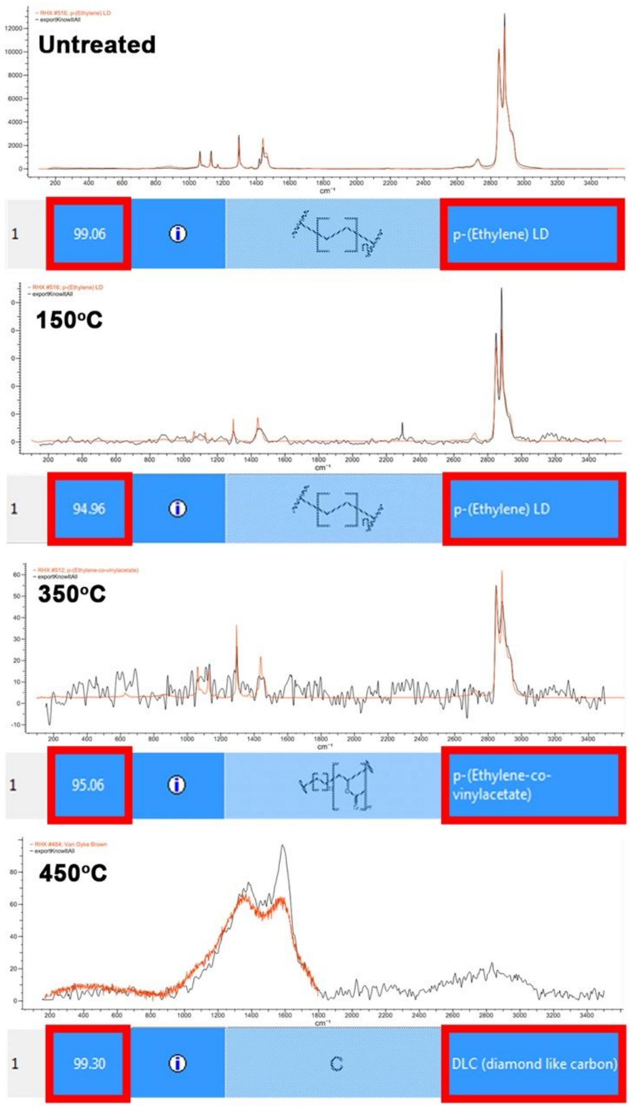

Figure S3. Raman spectra and matching results of virgin PE particles and spiked PE particles pyrolyzed after 150 °C, 350 °C, and 450°C.

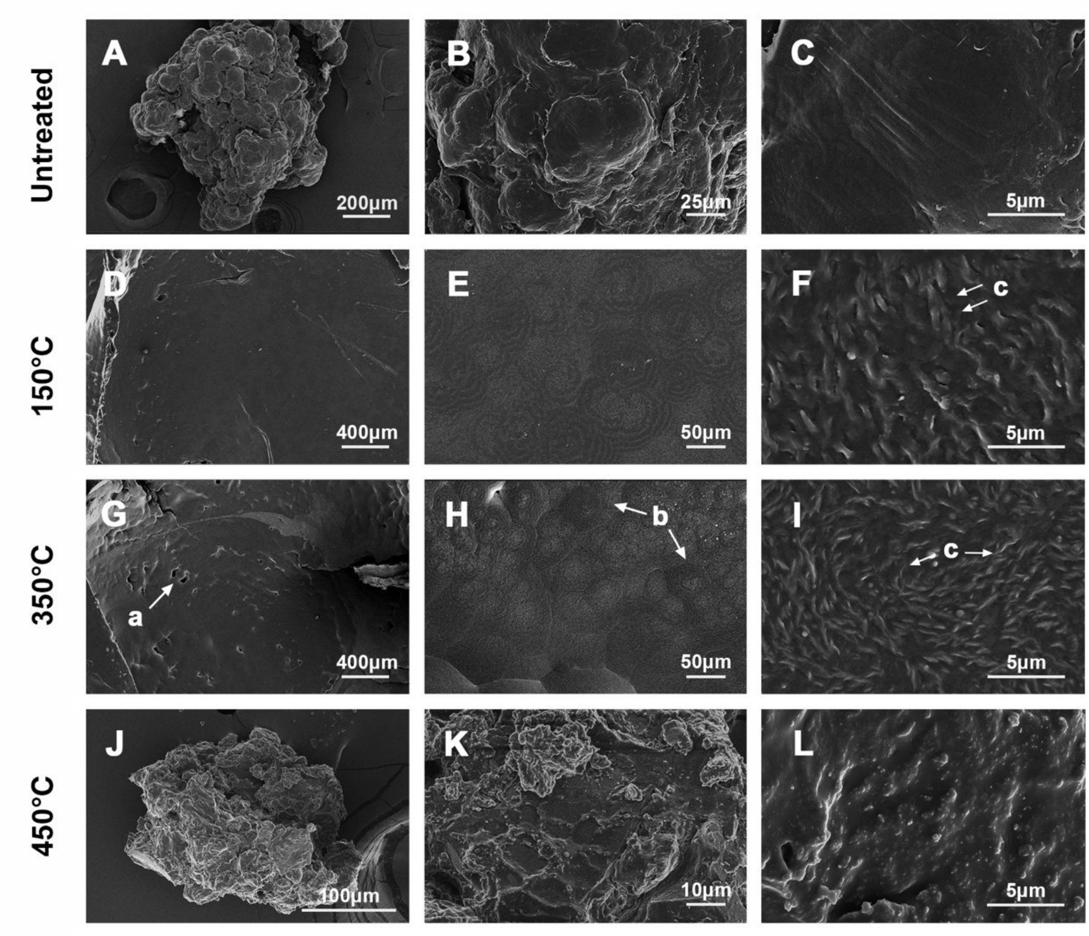

Figure S4 Scanning electron images of untreated PE particle (A-C), and pure PE particle after pyrolysis at 150 ^{o}C (D-F), 350 ^{o}C (G-I), and 450 ^{o}C (J-L). The presence of cracking (arrow a), blistering effect (arrow b), and irregular deformation lines (arrow c) were shown on the pyrolyzed polymer surface. After pyrolysis at 150 ^{o}C and 350 ^{o}C, the pyrolyzed PE particles resolidified, and particle size was increased. The surface was relatively smooth compared to spiked particles in the sludge. After pyrolyzed at 450 ^{o}C, the particle size reduced significantly, and the surface characteristics were similar to that of spiked particles.

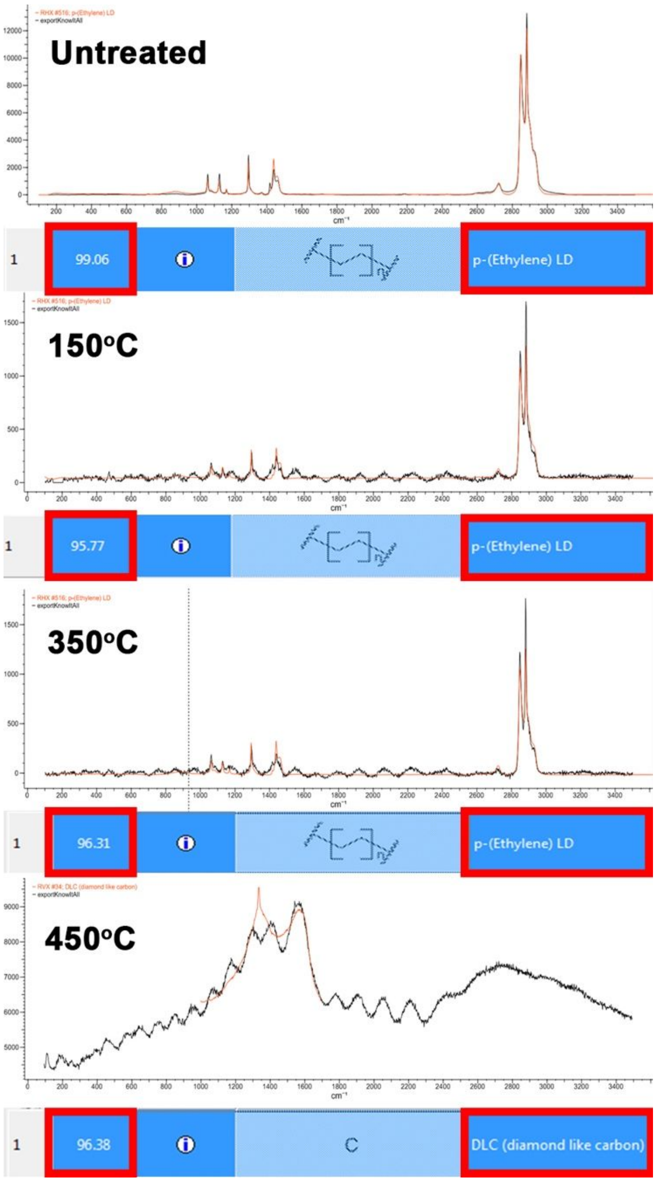

Figure S5 Raman spectra and matching results of pure PE particles after pyrolysis at 150 °C , 350 °C, and 450 °C.

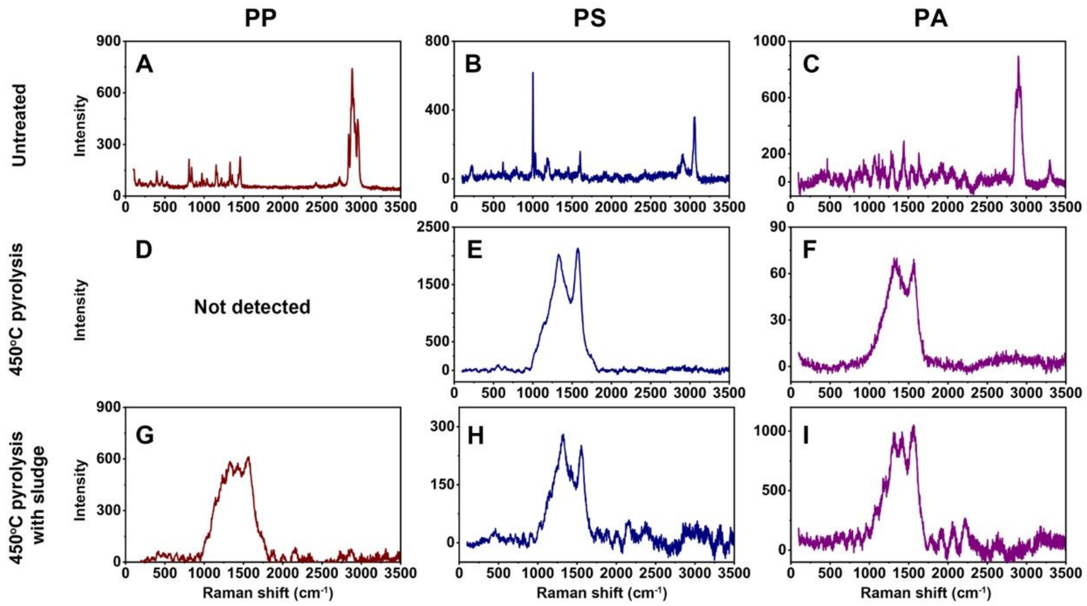

Figure S6 Raman spectra of PP, PS, PA virgin particles (A-C), pyrolysis at 450 ^{o}C (D-F), co-pyrolysis with sludge at 450 ^{o}C (G-I). The residues of PP particles pyrolysis after 450 ^{o}C were not detectable by micro-Raman spectroscopy due to high fraction of oil.

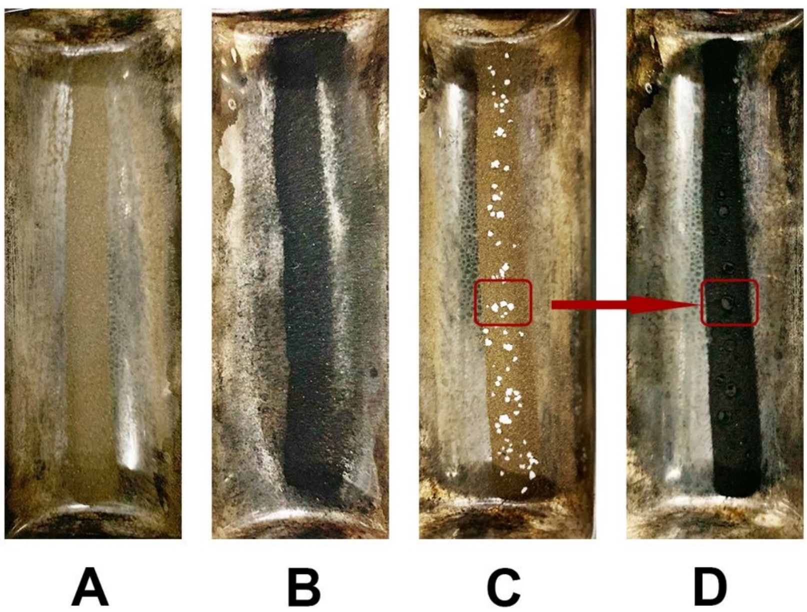

Figure S7 A: Dried sludge powder (size < 100 μm). B: Dried sludge powder (size < 100 μm) after pyrolysis at 450 ^{o}C for 30 min. C: Dried sludge powder (size < 100 μm) with spiked PE particles (size > 300 µm). D: Dried sludge powder (size < 100 µm) with spiked PE particles (size > 300 µm) after pyrolysis at 450 °C for 30 min. Arrow: Spiked PE particles combined with sludge after pyrolysis.

References

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2. Tagg, A. S.; Harrison, J. P.; Ju-Nam, Y.; Sapp, M.; Bradley, E. L.; Sinclair, C. J.; Ojeda, J. J., Fenton's reagent for the rapid and efficient isolation of microplastics from wastewater. *Chem Commun (Camb)* **2016,** *53*, (2), 372-375. https://doi.org/10.1039/c6cc08798a
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