

Removal and Degradation of Microplastics Using the Magnetic and Nanozyme Activities of Bare Iron Oxide Nanoaggregates

Mohamad Zandieh and Juewen Liu*[a]

[a] M. Zandieh, Prof. Dr. J. Liu
Department of Chemistry, Waterloo Institute for Nanotechnology,
University of Waterloo
200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada
E-mail: iujw@uwaterloo.ca

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Abstract: Removal and degradation of microplastics are often carried out separately. In this work, hydrophilic bare Fe_3O_4 nanoaggregates allowed efficient removal of the most common microplastics including high-density polyethylene, polypropylene, polyvinyl chloride, polystyrene, and polyethylene terephthalate. Full extraction was achieved using Fe_3O_4 at 1% of the mass of microplastics. Hydrogen bonding is the main force for the adsorption of Fe_3O_4 . Unlike the more commonly used hydrophobically modified Fe_3O_4 nanoparticles, the bare Fe_3O_4 benefitted from the peroxidase-like activity of its exposed surface, enabling further catalytic degradation of microplastics with nearly 100% efficiency and easy recovery of the Fe_3O_4 .

50°C,^[12] this was still quite far away from the melting temperature of PET. Bare Fe_3O_4 NPs are a classic peroxidase-mimicking nanozyme.^[13] Nanozymes are attractive since they are much more stable and cost-effective than natural enzymes.^[14] In this work, we demonstrated that bare Fe_3O_4 NPs (Figure 1B) are highly efficient for removal of a variety of common microplastics, even better than hydrophobically modified ones. Moreover, the Fe_3O_4 NPs showed enhanced nanozyme activity after adsorption to microplastics and they can promote degradation of microplastics at high temperatures.

Hundreds of million tons of plastic materials are produced annually.^[1] Microplastics are generated when plastics are shredded into submillimeter pieces via chemical, microbiological or mechanical transformations.^[2] Each human being is estimated to consume ~100,000 microplastic pieces annually by means of ingestion and inhalation.^[3] Microplastics have a high surface-to-volume ratio and they can serve as a vector for invasive microorganisms, heavy metals, and other pollutants.^[4] Some of the long-term hazardous effects of microplastics include infertility, disruption of the immune system and cancer.^[5] Therefore, removal and degradation of microplastics from water resources is of vital importance.^[6] The most abundant microplastics include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET).^[7]

Magnetic separation has been extensively used due to its low energy consumption and ease of operation.^[8] In recent years, removal of microplastics via magnetic separation has also been reported.^[9] With the perception that plastics are hydrophobic, the majority of the magnetic Fe_3O_4 nanoparticles (NPs) were modified with a hydrophobic ligand (Figure 1A-i),^[9a-d] polydopamine,^[9e] carbon nanotubes,^[9f] or flay ash^[9g] to enhance adhesion to microplastics. Fe_3O_4 NPs capped with a hydrophobic layer cannot be easily dispersed in water and they are more expensive to prepare. Since many common microplastics have polar groups, especially after their oxidation and aging in the environment,^[10] we reason that hydrophilic magnetic NPs might also be adsorbed by microplastics.

To further degrade microplastics, enzymes such as PETase have been immobilized on Fe_3O_4 NPs (Figure 1A-ii). However, only a minor change in the degree of crystallinity was achieved due to limited enzyme activity and densely packed polymer chains in microplastics.^[11] While harsh conditions such as high temperature can help soften microplastics, enzymes cannot survive such conditions. Recently, a machine learning guided engineered PETase was reported. Although it could be used at

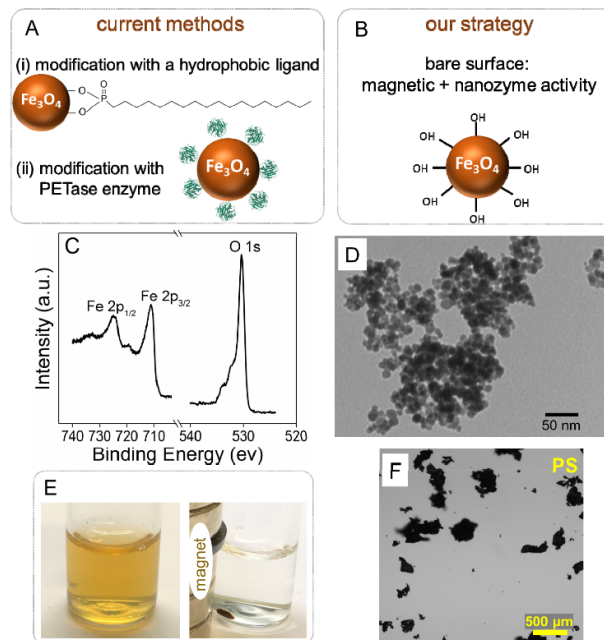


Figure 1. (A) Schemes depicting traditional methods for removal and degradation of microplastics using (i) Fe_3O_4 NPs modified with a hydrophobic ligand;^[9c, 15] (ii) Fe_3O_4 NPs with immobilized PETase enzymes.^[11] (B) Bare Fe_3O_4 NPs with peroxidase-like nanozyme activity used in this work. (C) High resolution XPS spectrum of the Fe_3O_4 NPs in the Fe and O regions. (D) A TEM micrograph of the aggregated bare Fe_3O_4 NPs. (E) Photographs of the Fe_3O_4 NPs before and after magnetic separation. (F) An optical micrograph of the PS microplastics used in this work.

Our Fe_3O_4 NPs were synthesized by mixing Fe^{2+} , Fe^{3+} and ammonia in water free of surfactants.^[16] Thus, the resulting NPs

had the bare oxide surface exposed (Figure 1B). To verify the native Fe_3O_4 surface, X-ray photoelectron spectroscopy (XPS) was performed, which showed peaks with binding energies of 710 eV, 724 eV, and 530 eV, corresponding to Fe $2\text{P}_{3/2}$, Fe $2\text{P}_{1/2}$, and O 1s, respectively (Figure 1C).^[17] The Fe_3O_4 NPs had an average size of ~ 10 nm under TEM (Figure 1D). Using dynamic light scattering (DLS), the hydrodynamic size reached ~ 300 nm (Figure S1A) suggesting aggregation. The ζ -potential of the Fe_3O_4 NPs was 5.3 mV at pH 6.5 (Figure S2). The small ζ -potential and a lack of surface ligand disallowed charge or steric stabilization, explaining the aggregation. The synthesized Fe_3O_4 nanoaggregates showed strong superparamagnetic property with a saturation magnetization of 68 emu/g from vibrating sample magnetometry (VSM, Figure S1B). The Fe_3O_4 samples were easily attracted by a magnet (Figure 1E).

Our microplastics were prepared by mechanical shredding of common plastic objects.^[18] Raman spectroscopy was used to identify the plastics to be high density PE (HDPE), PP, PVC, PS, and PET (Figure S3).^[19] Using optical microscopy, microplastics ranged from $20\ \mu\text{m}$ to $800\ \mu\text{m}$ were observed (Figure S4). Figure 1F is an optical micrograph showcasing the PS microplastic sample used in this work.

To test the capture efficiency, the five microplastics were respectively mixed with the Fe_3O_4 nanoaggregates (Figure 2A, 2B). After 5 min, all of the tested microplastics could be extracted using a magnet (Figure 2C). Figure 2D is a TEM micrograph depicting that the Fe_3O_4 NPs were densely adsorbed onto a PS microparticle, which facilitated the quick navigation of the microplastics in a magnetic field. For example, the PS microplastics were well dispersed in aqueous solutions due to their density ($1.02\ \text{g/cm}^3$) close to water. After mixing with the Fe_3O_4 and locating the sample on a magnet, the microplastics settled down within a few seconds (Video S1).

We further tested the removal of microplastics in a wastewater sample spiked with $4\ \text{mg/mL}$ PS (Figure 2E). After introducing the Fe_3O_4 nanoaggregates, the microplastics were thoroughly captured, and the absorbance of the wastewater at $650\ \text{nm}$ dropped 95% (Figure S5). Therefore, our bare Fe_3O_4 can efficiently extract microplastics even in wastewater.^[20]

We then measured the efficiency of magnetic extraction by varying the concentration of the Fe_3O_4 . The measurements were performed on an analytical balance using vacuum dried samples, and complete drying was confirmed by thermogravimetric analysis (Figure S6). With fixed $4\ \text{mg/mL}$ PP or PS microplastics, more Fe_3O_4 yielded a higher removal percentage (Figure 3A). The data were fitted with a sigmoidal binding curve for both microplastics confirming that multiple Fe_3O_4 NPs were needed to cooperatively remove the microplastics. $40\ \mu\text{g/mL}$ of the Fe_3O_4 was sufficient to fully remove $4\ \text{mg/mL}$ PS (1% w/w), indicating a high removing efficiency. This was about 100-fold more efficient than those Fe_3O_4 NPs modified with a hydrophobic layer, where comparable weights of magnetic NPs and microplastics were mixed (Table S1).^[9a-c, 9e]

In the above experiment (Figure 3A), the adsorption time was 5 min. To understand the kinetics of adsorption, we fixed the Fe_3O_4 at $60\ \mu\text{g/mL}$ and quantified the removal at different time points (Figure 3B). The microplastic removal rate followed the order of $\text{PET} > \text{PS} > \text{HDPE} > \text{PVC} > \text{PP}$, and 5 min was enough to fully remove all of them. The order of removal correlated with the size

of the microplastics (Figure S7). Smaller microplastics could be moved by a smaller number of Fe_3O_4 NPs, which allowed faster removal. Thus, the higher efficiency of removing PS in Figure 3A can be explained by the smaller size of the PS than the PP. To further confirm the effect of size, we sieved the PP and PS microplastics and acquired two size ranges: $>250\ \mu\text{m}$ and $<250\ \mu\text{m}$. For the same microplastic material, smaller particles were indeed removed faster (Figure 3C and Figure S8).

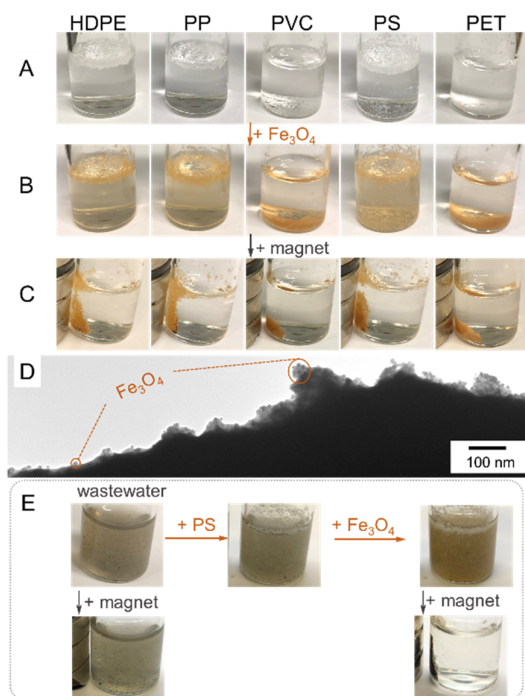


Figure 2. Photographs of $4\ \text{mg/mL}$ of the five types of microplastics (A) dispersed in water, (B) after incubation with $60\ \mu\text{g/mL}$ Fe_3O_4 , and (C) after magnetic separation. (D) A TEM micrograph depicting Fe_3O_4 NPs adsorbed to a PS microplastic. (E) Photographs depicting magnetic separation of $4\ \text{mg/mL}$ PS microplastics in wastewater using $100\ \mu\text{g/mL}$ of the Fe_3O_4 nanoaggregates.

Our data demonstrated that bare magnetic Fe_3O_4 NPs can effectively adsorb to all these microplastics. Thus, no hydrophobic modifications were necessary. To examine the nature of the adsorption, the Fe_3O_4 NPs and the PS or PP microplastics were incubated for 5 min. Then, various agents were added to induce desorption of the Fe_3O_4 NPs. The desorption was tracked visually (Figure 3D) as well as by UV-vis spectroscopy of the supernatants (Figure S9). As a control, when water was added to the preadsorbed Fe_3O_4 , the supernatant remained clear indicating no release of the Fe_3O_4 . Then, $5\ \text{M}$ urea was added to probe hydrogen bonding (urea is a hydrogen bonding disruptor), where $\sim 50\%$ desorption occurred suggesting a significant contribution of hydrogen bonding. Hydrogen bonding likely occurred between the C-H and O-H bonds on microplastics as donors and the $-\text{OH}$ on iron oxide as acceptors.

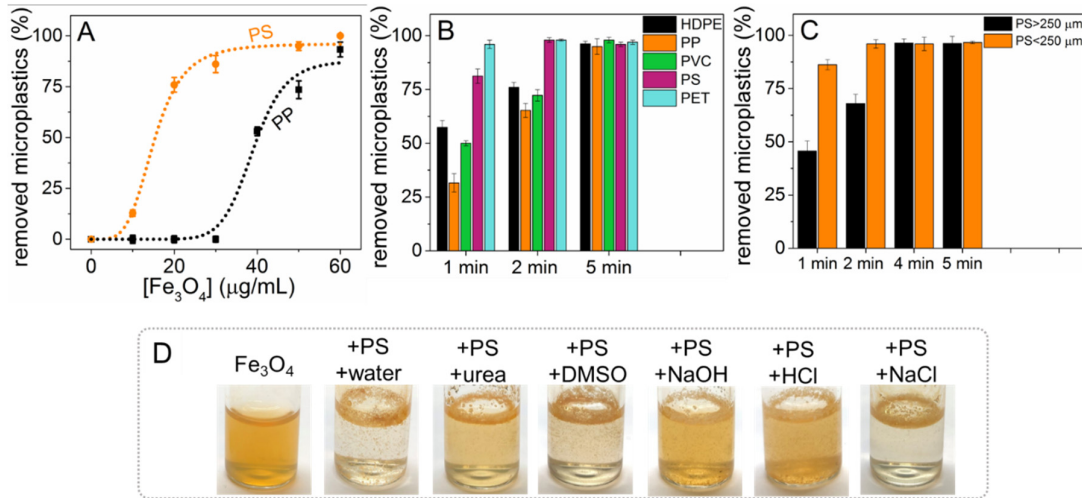


Figure 3. (A) Removal of the PP or PS microplastics by different concentrations of the Fe₃O₄ NPs. (B) Removal of the different microplastics by 60 µg/mL of the Fe₃O₄ NPs after different incubation times. (C) Removal of the PS microplastics with two size ranges by 60 µg/mL of the Fe₃O₄ NPs at different time points. (D) Desorption of Fe₃O₄ NPs from 4 mg/mL PS microplastics induced by 5 M urea, 50% DMSO, 10 mM NaOH, 10 mM HCl, or 3 M NaCl.

To probe hydrophobic interactions, we added 50% DMSO. Less than 20% of the Fe₃O₄ NPs were desorbed (Figure S9), confirming that hydrophobic interactions were insignificant for the adsorption of the bare hydrophilic Fe₃O₄. The effect of pH was then investigated by adding 10 mM NaOH or 10 mM HCl, both of which turned the supernatants dark yellow suggesting desorption of the Fe₃O₄ NPs (Figure 3D and Figure S9). At high pH, both the Fe₃O₄ and the microplastics were highly negatively charged (Figure S2) thereby repelling each other (Figure S10). At low pH, the Fe₃O₄ NPs were positively charged, whereas the microplastics were close to charge neutral (Figure S2), resulting in no electrostatic attraction. Protonation of hydrogen bond acceptors (-OH on the Fe₃O₄ NPs) at low pH can disrupt hydrogen bonding to induce desorption (Figure S10). Moreover, we screened the charge interactions by adding 3 M NaCl, but negligible desorption happened suggesting that electrostatic interactions were less important than hydrogen bonding for the adsorption. Thus, hydrogen bonding was the main force responsible for the adsorption of the bare Fe₃O₄ NPs at neutral pH.

After demonstrating the excellent removal efficiency, we then investigated the degradation of microplastics. Bare Fe₃O₄ NPs can function as a peroxidase-like nanozyme, accelerating the oxidation of organic substrates in the presence of H₂O₂.^[13a, 13d, 14e, 14f] We reason that our Fe₃O₄ NPs might retain a high catalytic activity to degrade the adsorbed microplastics. To test this, we first used an organic dye, rhodamine B (RhB), as a model

substrate. RhB was added to the mixtures containing the Fe₃O₄ nanoaggregates and different microplastics in the presence of H₂O₂. Degradation of RhB was followed by its absorption peak at 555 nm. After 6 h and 24 h, the 555 nm peak decreased remarkably for all the samples (Figure 4A, 4B, Figure S11), confirming the nanozyme activity of the Fe₃O₄. Interestingly, the extent of RhB degradation was higher in the presence of the microplastics. Attaching polymers such as DNA to nanozymes have been shown to enhance their activities,^[21] and the microplastics appeared to have a similar boosting effect.

A main challenge of enzymatic degradation of plastics is that enzymes can hardly access polymer chains. While melting plastics can expose polymer chains, most enzymes cannot survive such high temperatures. In contrast, nanozymes are often more active at higher temperatures.^[22] Taking advantage of this property, a few samples were heated at different temperatures for degradation. In this experiment, the mass of the microplastics was 5-fold higher than that of the Fe₃O₄. Nearly 100% degradation was achieved when the microplastics were heated close to their melting ranges.^[23] On the other hand, no degradation occurred at temperatures below the melting ranges (Figure 4C). In a control experiment, we showed that combining Fe₃O₄ and H₂O₂ resulted in higher degradation than using them individually (Figure S12). In addition, accelerated degradation was also achieved when the samples were heated beyond their melting range (Figure S12B).

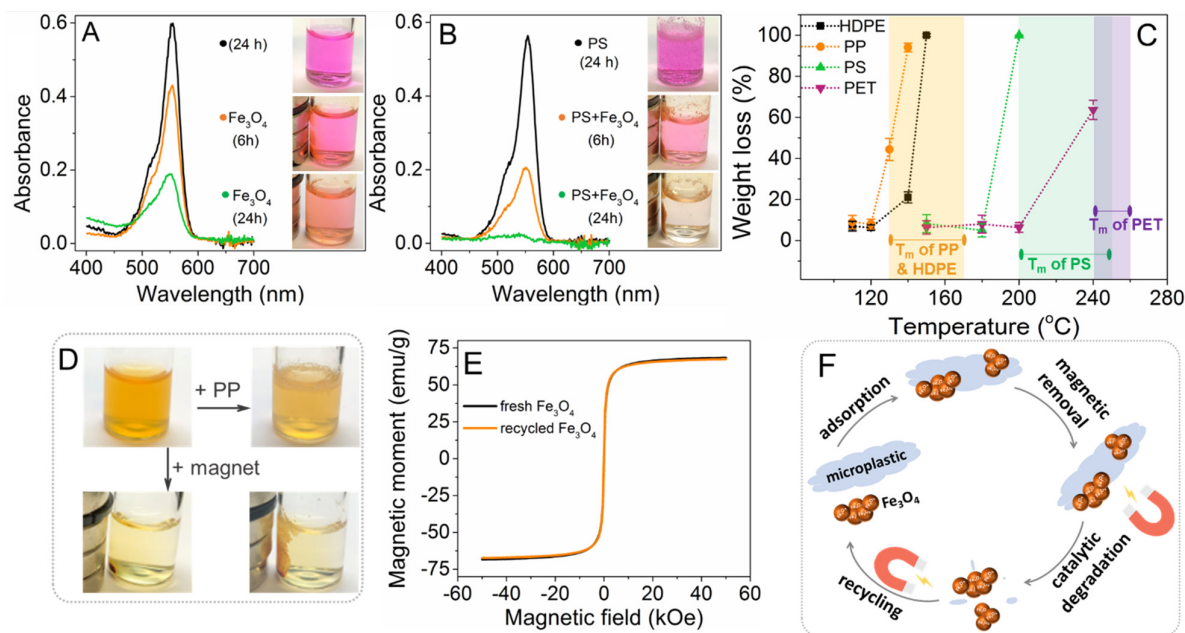


Figure 4. UV-vis spectra and photographs illustrating the degradation and decolorization of 10 μM RhB by 60 $\mu\text{g/mL}$ (A) the free Fe₃O₄ NPs, and (B) the Fe₃O₄ NPs adsorbed to 4 mg/mL PS microplastics in the presence of 200 mM H₂O₂ in 20 mM acetate buffer, pH 4. (C) Degradation and weight loss of 1 mg/mL of the microplastics heated at different temperatures in the presence of 200 $\mu\text{g/mL}$ of the Fe₃O₄ and 200 mM H₂O₂ for 12 h. The melting range is $\sim 130\text{--}170^\circ\text{C}$ for HDPE and PP, $\sim 200\text{--}250^\circ\text{C}$ for PS, and $\sim 240\text{--}260^\circ\text{C}$ for PET. (D) Photographs depicting magnetic microplastic removal by the Fe₃O₄ recycled after the degradation experiment. (E) VSM magnetization curves of the fresh Fe₃O₄ NPs and the Fe₃O₄ NPs recycled after the degradation experiment. The curves were almost the same and no hysteresis was observed suggesting that both NPs had similar superparamagnetic properties. (F) The recycle of Fe₃O₄ nanoaggregates for removal and degradation of microplastics.

After the degradation experiments, the Fe₃O₄ samples were collected and washed with water. The collected Fe₃O₄ still retained the same superparamagnetic property (Figure 4D, E). Moreover, the surface morphology was unchanged (Figure S13A), and they could still remove the microplastics with the same efficiency as the freshly prepared Fe₃O₄ NPs (Figure S13B). Therefore, the Fe₃O₄ NPs were robust and reusable after microplastic degradation at high temperature. The cyclic use of the bare Fe₃O₄ nanoaggregates is shown in Figure 4F.

In summary, we combined the strong superparamagnetic and nanozyme activities of bare Fe₃O₄ NPs to extract and degrade a variety of common microplastics in water and wastewater. Different from previous works using hydrophobically modified Fe₃O₄ NPs, we demonstrated here that bare Fe₃O₄ can adsorb to all major microplastics via hydrogen bonding. The bare Fe₃O₄ surfaces allowed the peroxidase-like nanozyme activity to degrade organic pollutants. At elevated temperatures close to the melting range of plastics, efficient catalytic degradation of microplastics was achieved. The Fe₃O₄ NPs can be readily recycled thanks to their magnetic properties and excellent stability. Together, this study highlights the use of nanozymes for efficient, simple and low-cost removal and degradation of microplastics, which may inspire more explorations of nanomaterials for solving environmental problems.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: microplastics • iron oxide nanoparticles • nanozymes • water treatment • plastic degradation

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