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MAGNETIC NANOPARTICLES FOR MONITORING MICROPLASTICS POLLUTION IN THE SURFACE WATERS

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Abstract

The accumulation of plastic waste in the world's oceans is a growing public concern, under the action of water and solar radiation, the macroscopic plastic objects break down into micro- and nano-sized particles. The amount of microplastics in natural waters is currently unknown because of the difficulties of their quantification in water. It is proposed to use the method of the preconcentration of micro- and nano- plastic particles in water using two main approaches, such as the addition of composite magnetic nanoseeds that form aggregates with detectable plastic particles, and the subsequent separation of these hetertoaggregates from water by magnetic separation. In order to concentrate polyethylene (PE, 20-100 µm) and polyethylene terephthalate (PET, 10-20µm) particles from water, the magnetic Fe-C-NH$_2$ nanoseeds (10 nm) were added to the water, afterward, the magnetic sedimentation of the formed heteroaggregates in a gradient magnetic field was conducted. The effect of magnetic nanoparticles concentration in suspension, the time expose for the heteroaggregation on the efficiency magnetic preconcentration have been investigated.

Keywords: nanoparticles, microplastics, preconcentration, aqueous suspensions, magnetic sedimentation.

I. Introduction

The production and consumption of huge amounts of the products from artificial polymeric materials lead to the release of the plastics into the surface water bodies. Plastic bottles and packaging, fishing nets, etc. are collected in large agglomerates floating along the banks of rivers, lakes, and on the surface of the oceans [1, 2, 3]. Under the action of water and solar radiation, the macroscopic plastic objects break down into micro- and nano-sized particles. Such particles are the most dangerous for ecosystems, as they enter the food chains of aquatic organisms and may eventually end up in the human body [4]. At high dilution, the concentration of microplastics in the seas and large rivers waters is small but can be significant in the small lakes and rivers with

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slow water exchange.

The amount of microplastics in natural waters is currently unknown because of the difficulties of their quantification in water [5], especially for the small particles. It is proposed to use the method of the preconcentration of micro- and nano- plastic particles in water using two main approaches, such as the addition of composite magnetic nanoseeds that form aggregates with detectable plastic particles, and the subsequent separation of these hetertoaggregates from water by using magnetic field [6, 7, 8]. The preconcentration will allow quantitative determining of the microplastics in water by the instrumental methods (for example, by an optical method using a standard spectrophotometer). Controlling the formation of the heteroaggregates from the magnetic and plastic particles is a non-trivial task and it requires detailed studies [9, 10]. The added nanoseeds should have a surface capable of binding small plastic particles due to electrostatic interactions and contain a magnetic material that allows them to be manipulated in an external magnetic field. The aggregate formation is influenced by a number of conditions, among them the chemical composition and pH of the aqueous medium, the value of the particle surface charges (zeta potential), and the magnetic nanoseeds concentration.

In this work, the magnetic preconcentration of the microparticles from the most common plastics such as polyethylene (MPE) and polyethylene terephthalate (MPET) [11, 12] in aqueous solutions by using composite nanoparticles as magnetic seeds was studied. The nanoseeds have a magnetic core of iron with high specific magnetization and a carbon shell with attached amino groups, Fe@C-NH$_2$ (FNP). The carbon shell with attached amino groups provides the formation of aggregates with the plastic particles in the water due to the electrostatic attraction. The resulting heteroaggregatesare separated (concentrated) by magnetic sedimentation. To determine the concentration of the plastic particles, the resulting sediment was analyzed by the spectrophotometry method together with the PLS spectrum processing algorithm [13, 14]. An important advantage of this method is a possibility to determine the concentration of the plastic particles in heteroaggregates, avoiding the stage of the magnetic nanoseeds separation, which simplifies the analysis.

II. Methods

Aqueous suspensions of PE and PET microparticles with a solid phase concentration of 0.1 g / l were used. The average hydrodynamic diameter of the plastic particles in PE suspensions was 20-100 μm, in PET suspensions it was 10-20 μm.

Magnetic carbon coated Fe@C nanoparticles were prepared by the gas condensation method [15]. For a surface modification of the composite Fe-C particles, the method suggested in [16] was applied. The synthesis of Fe@C-NH$_2$ composite nanoparticles with a core-shell structure was performed as described earlier [17, 18]. The average size of the synthesized composite nanoparticles was about 10 nm. The saturation magnetization of the Fe@C-NH$_2$ nanopowders was 60 A·m^2/ kg.

The zeta potential of the particles in the water was detected by Dynamic Light Scattering method (DLS, NanoZS, Malvern, UK). For that, a He-Ne laser beam of λ=633 nm was used, operating in the back-scattering mode at the angle of 173°.

Particle images were obtained by scanning electron microscopy (SEM) using an Inspect F (FEI) instrument.

The absorption spectra of the mixed suspension samples were monitored and were processed mathematically using the PLS algorithm [13]. This procedure allowed to determine the partial concentrations of the MPE and FNP or MPET and FNP components in water. The UV–visible absorbance spectra were collected at the interval of wavelengths of 190 – 1100 nm using the SF-102 spectrophotometer (Fig. 1), for that, an aqueous suspension sample was placed in a quartz cell (12.5× 12.5×45 mm^3). The calculations were performed using the R-language [19] and the PLS

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package [20]. The suspension samples of different compositions were prepared in the range of 0–0.1 g / l. The concentration values as detected from the absorption spectra for 32 PE and for 46 PET samples were used as a calibration set, and the other 15 concentration values were used for a test set. The relative standard error for single components is 7% both for PE and for PET. It was shown that the minimum detectable concentration for MPE and MPET was 0.002 g / l.
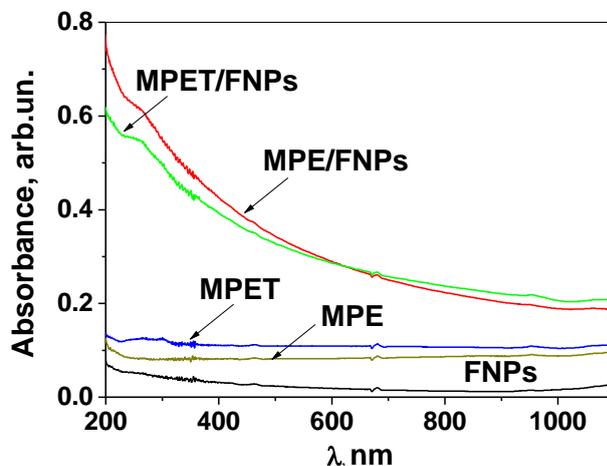
Figure 1: *Absorption spectra of aqueous suspensions of FNPs (0.01 g / l), MPE and MPET (0.1 g / l) and their mixture for the mass concentration ratio 1 : 10.*

The Magnetic Preconcentration Efficiency (MPCE) was determined from the change in the residual concentration of MPE, and MPET particles in water:

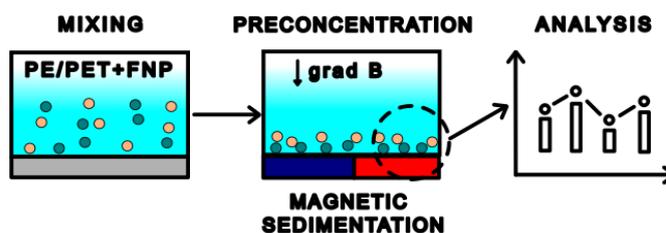$$MPCE = \frac{c_0 - c}{c_0} \cdot 100\% \qquad (1)$$

where c_0 is the initial concentration, c is the residual concentration of particles in water, g / l.

III. Results and discussion

At the first step, the magnetic FNPs were added to suspensions of MPE or MPET. At the second step, magnetic sedimentation of the MPE/FNP and MPET/FNP aggregates was carried out in the aqueous suspension. Finally, the resulting precipitate, consisting of the mixture of the plastic and magnetic particles, was analyzed by the UV–Visible Spectrophotometry method together with the PLS spectrum processing algorithm. Preliminarily, the precipitate was redispersed in the water.

Since the heteroaggregation of the plastic and the composite magnetic particles is caused by their electrostatic attraction, the necessary condition is that the initial particles have high values of the electric surface charges of opposite signs. The magnitude and the sign of the surface charge of the particles in water suspensions are characterized by the zeta potential [21]. In order to evaluate the possibility of the interaction of the plastic particles with magnetic seeds and the formation of heteroaggregates, as well as to estimate the amount of the needed added magnetic particles, the zeta potential of the particles in aqueous suspensions was monitored.

It was measured at all pH values, MPE and MPET are negatively charged (-17±2 and -29±2 mV, respectively), which is consistent with the data of the other researchers [22]. In aqueous suspensions, FNPs have a high positive zeta potential (30±2 mV) in the region of pH < 7 opposite to the plastic particle's charge. Thus, the pH range of 6-7 was chosen for the heteroaggregation process. When the plastic particles interact with added magnetic particles (seeds) of opposite charge, MPET/FNP and MPE/FNP heteroaggregates were formed (Fig. 3).

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Figure 2: *Scheme of the determination of concentrations of MPE and MPET in water using the preconcentration by magnetic sedimentation.*
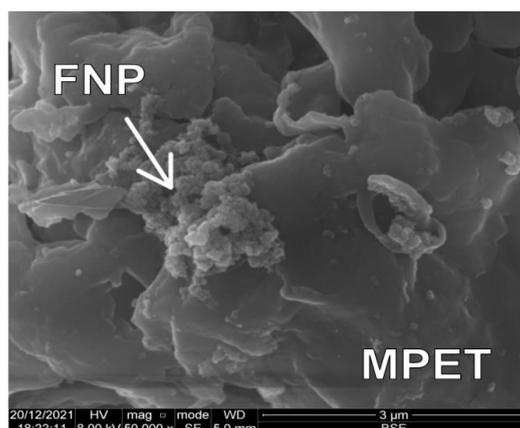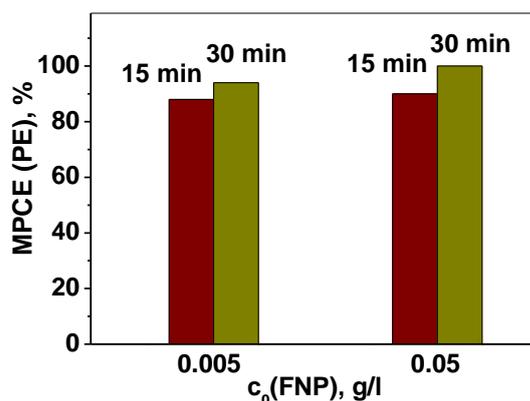

Figure 3: *SEM images of MPET/FNP heteroaggregates from aqueous suspensions (c_0(MPET) = 0.1 g / l, c_0(FNP) = 0.005 g / l).*

In order to carry out the magnetic separation of the plastic particles from the water suspensions, it is necessary that the zeta potential of heteroaggregate in the suspension is close to zero. Under this condition, the suspension becomes unstable and the magnetic sedimentation of heteroaggregates occurs very quickly. Therefore, the conditions for the compensation of the surface charge for various particles compositions ratios were studied. For the MPET/FNP mixed suspensions (with c_0(MPET) = 0.1 g / l), heteroaggregation should proceed most efficiently in the range of c(FNP) = 0.001–0.005 g / l. For the MPE/FNP mixed suspensions (with c_0(MPE) = 0.1 g / l), the zeta potential values close to zero are achieved at the concentration range of c(FNP) = 0.005–0.05 g / l. Thus, it is possible to control the required amount of magnetic particles that must be added to fully interact with the plastic particles.

Figure 4 shows the Magnetic Preconcentration Efficiency of MPE for various contents of the added magnetic particles in water and for various heteroaggregation exposure times. For c_0(FNP) = 0.005 g / l, it is about 85%, and it is not changed significantly by the increase in the time exposure from 15 to 30 minutes. Raising the concentration of magnetic seeds up to 0.05 g/l improves the MPE extraction even with the aggregation time of 15 minutes. The longer exposure (up to 30 minutes) allowed to reach the MCE value of about 100%.

It had been determined that the separation of MPE and MPET from water was close to 100% with the addition of optimal concentrations of the added magnetic nanoparticles and the heteroaggregation time of 30 minutes.

Using the plastic particles preconcentration followed by the magnetic separation lets to achieve a range of measurable concentrations of plastics in the water. Thus, for example, at a preconcentration of 100 times, the plastic concentrations up to 0.00002 g / l can be determined by this technique.

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Figure 4: *MPCE (PE) for two concentrations of FNPs (c₀ = 0.005 and 0.05 g / l) and for heteroaggregation exposure times 15 and 30 minutes*

IV. Conclusion

This study provides a scientific basis for the use of composite magnetic nanoparticles for the preconcentration of plastic microparticles in water, and the subsequent determination of its concentration in the process of monitoring pollution of natural waters. The range of problems that need to be solved for the wide application of this method is determined. Among them is the search for composite magnetic nanoseeds with the maximum ability to selective capture microplastics in water, and the creation of portable magnetic systems for the magnetic separation of the concentrate from water. The next step is to apply portable, easy-to-handle devices that allow obtaining quantitative information on the plastics pollution of water bodies, processing it, and transmitting it to database centers.

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