Original Article

Study of the polystyrene degradation in water using nanoparticle tracking analysis (NTA)

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Abstract

Several studies describe the release of plastic materials from irregular disposal in landfills affecting soil and water qualities. Studies report that increasing plastics are released into ecosystems estimating approximately 100 million tons by 2030 and, as a consequence causing serious damage to the environment. The impact on the water resources due to contamination is a critical issue. Thus, this research used a nanoparticle tracking system method - NTA (LM20) to determine the concentrations of nanoplastics emitted in aqueous solutions. The rate of nanoplastics production is important to design methods to mitigate the contamination. The present study results showed that the concentrations emitted in samples of 500 mg and 1 g of polystyrene initially reach 0.42E8 particles.mL-1 and 2.09E8 particles.mL-1 and continuously forms new structures increase the concentration in solution and the average particle size along the time. Thus, this research carried out a systematic study of the degradation of polystyrene over 7, 14, and 28 days under 30 °C, 50 °C and 70 °C, respectively. This research concluded that up to 27% of nanoplastic release is expected due to the environment temperature variation during the seasons of tropical regions.

Keywords: Polystyrene; Nanoplastics; NTA.

1 Introduction

The exaggerated release of polymeric products combined with the inadequate disposal of urban waste is a worldwide concern, and it has been causing serious damage to the environment [1,2]. Studies report that an increasing amount of plastics are released into ecosystems estimating approximately 100 million tons by 2030, and only in the ocean, this amount reaches approximately 10 million tons [3,4]. By 2030, we will find the equivalent of 26 thousand plastic bottles in the sea for every km^2. Brazil is the fourth-largest producer of plastic waste globally with 11.3 million tons, behind only the United States, China, and India. Of this total, more than 10.3 million tons are collected (91%), but only 145 thousand tons (1.28%) are recycled or reused [4,5].

The inadequate disposal of plastic in terrestrial and aquatic ecosystems directly affects soil quality and water supply systems [6,7]. The direct impacts are due to the non-regulation of nanoparticles of plastics (nanoplastics) waste into the water treatment, causing soil contamination by these materials. In soil pollution, one of the villains is the nanoplastics coming from washing and household clothes, which are filtered in the water treatment system of cities or used as fertilizer recipients [8]. When they are not captured, these particles are released into the environment, increasing the contamination of soils and oceans [9]. In addition, these materials, being exposed to a marine environment, undergo environmental interactions and reactions due to sun exposure, different levels of oxygen, wave energy, and abrasive factors, such as sand, gravel, or rocks.

Unfortunately, these waste materials are food for many marine species causing their death and interfering in the reproductive cycle of many species. Thus, the nanoplastics in the environment are absorbed in the food chains, being consumed by humans via ingestion of salt, fish, mainly seafood, mussels, and oysters [10-12].

Studies indicate that for about every 250 bottles of water, an average of 240 bottles are contaminated with nanoplastics [4,13]. Although alarming, the long-term impacts of this human exposure are still poorly known. In multiphase systems, where the solid phase is dispersed in a fluid, it can be considered that the process of forming the nanoparticles can be described in five phases [7,14,15]: (a) the suspension can be diluted without interaction between the particles; (b)

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the suspension stabilizes; (c) the flocculate suspension; (d) the suspension is partially stable with some structure formed; (e) the suspension settles, as shown in Figure 1.

The importance of addressing this issue using a different approach is obvious. Some attempts have been carried out to address this problem using analytical methods to investigate different environmental plastic degradation [16,17]. The present study aims to propose a simple method to estimate the degradation of a specific type of plastic, polystyrene. Thus, the target was to investigate the formation process of plastic size particles, termed nanoplastic, when exposed to water under variable temperatures (30 °C, 50 °C and 70 °C), essentially simulating the nanoplastic production during the use of disposable coffee cups (polystyrene), since they release small amounts of plastic nanoparticles that can be ingested by a human being, which could cause several long-term diseases.

2 Methods

The methodology used in this research consists of investigating the formation of nanoplastics through disposable coffee cups (polystyrene). Polystyrene materials were exposed to water during the experiments, and the resulting solutions were analyzed. The methodology used the plastic size and water volume used by Lambert as an empirical reference [16,17] and adapted to this study. Initially, 500 mg of plastics were cut into a 1.0 cm^2 and produced a set of experiments. In a second set, 1 g of plastics were used and cut in the same size. Then, 100 mL of demineralized water was added and kept under vigorous agitation for 24 hours at 250 rpm. The samples were left to settle for 7, 14, and 28 days and kept at constant temperatures of 30 °C, 50 °C, and 70 °C, respectively. Table 1 summarizes the experimental conditions.

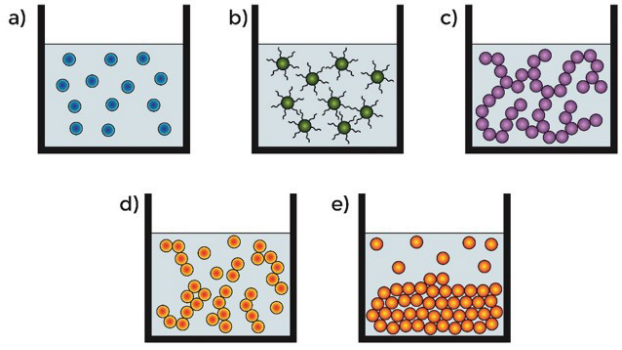


Figure 1. Mechanism of formation of nanoparticles in multiphase systems. a) The suspension can be diluted without interaction between the particles; b) The suspension stabilizes; c) The flocculated suspension; d) The suspension is partially stable with some structure formed; e) The suspension settles.

The resulting colloidal solution was analyzed using the nanoparticle tracking analyzer (NTA-LM20) to determine the concentrations and particle size distribution in the liquid samples. Three video images were captured and treated to characterize each sample in a representative way. The duration of the video image was adjusted between 30 and 60 seconds, and the temperature was specified according to the measurement setup. The video images were processed using the NTA 2.3 software. Figure 2 illustrates the measurement principle of the nanoparticle tracking analyzer method (NTA).

The Nanoparticle Tracking (NTA) analysis uses the light scattering and Brownian motion properties to obtain the particle size distribution in samples in liquid colloidal suspensions. A laser beam is passed through the sampling chamber with the particles suspended in the beam path, spreading the light to be easily viewed through a microscope with a 20x magnification over the fluid aliquot. The camera captures a video file of the particles in Brownian motion. The software tracks multiple particles individually and calculates their hydrodynamic diameter using the Stokes-Einstein Equation [18].

$$\frac{(x,y)^2}{4} = D \quad (1)$$

$$D = \frac{TK_B}{3\pi\eta d} \quad (2)$$

Where:
D: Diffusion coefficient (m^2/s);
K_B: Boltzmann constant ($1.38x10^{-6}$ ergs/K);
T: Absolute temperature (K);
d: Nanoparticle diameter (nm);
η: Colloid viscosity (Pa.s).

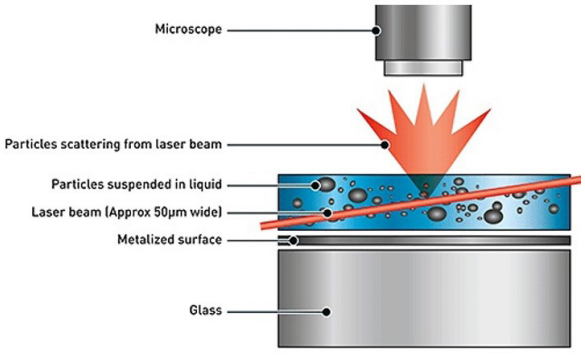


Figure 2. Principle of operation of the NTA-LM20 equipment used in this study.

Table 1. Summary of the experiment

Nanoplastic	Solution	Temperature			Time(days)		
500 mg	100 mL demineralized water	30 °C	50 °C	70 °C	7 days	14 days	28 days
1 g	100 mL demineralized water	30 °C	50 °C	70 °C	7 days	14 days	28 days

Additional measurements of pH, temperature, electrical conductivity, and ionic strength were obtained during the capture of the images. The ionic strength values were calculated from the linear relationship of ionic strength and electrical conductivity, as shown in Equation 3, as previously reported [19,20].

$$I = 0.0127 \times CE \quad (3)$$

Where I and CE represent ionic strength and electrical conductivity, respectively.

3 Results

This study investigated the formation of plastic nanoparticles during the degradation process of disposable coffee cups (polystyrene). The 500 mg and 1 g samples were exposed to constant temperatures of 30 °C, 50 °C, and 70 °C. Figure 3 describes stabilizing the 500 mg and 1 g plastic samples. The samples were subjected to a 28-days rest at room temperature.

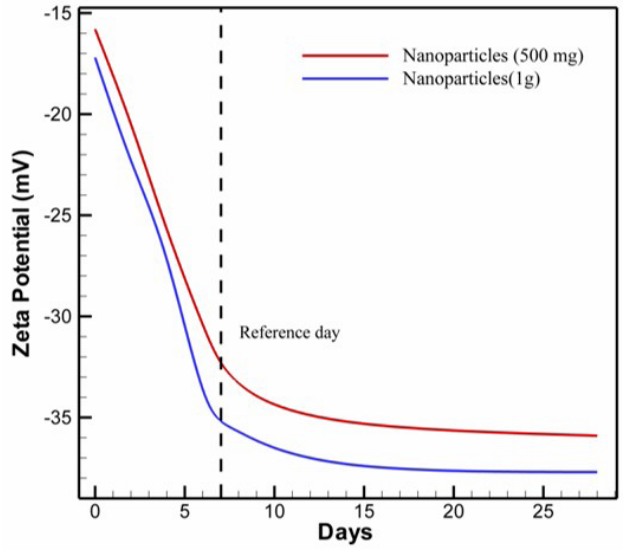


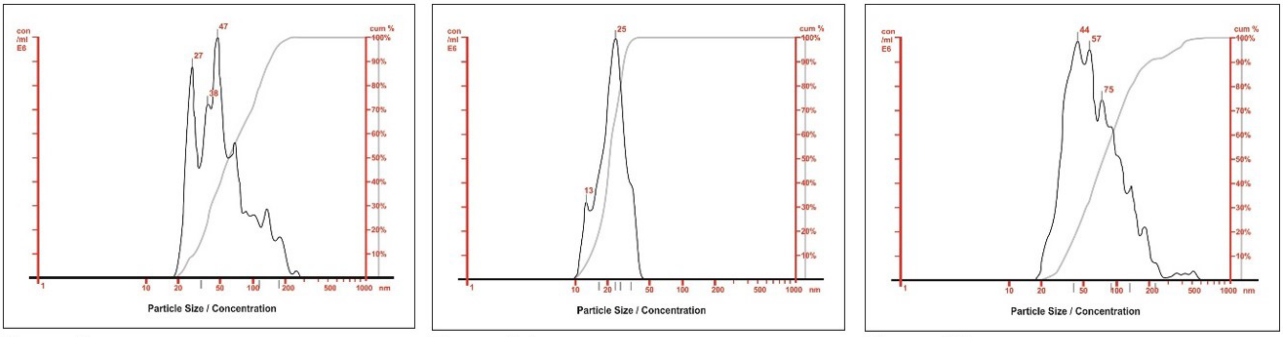
Figure 3. Stabilization of the liquid colloid.

The curves exemplify the phenomenon of migration between the positive and negative charges present in the colloidal suspension, resulting in a high zeta potential after the seventh day of exposure. Thus, the study of the formation of nanoplastics began on the seventh day of rest, after the stability of the colloidal suspensions.

The following figures represent the formation of nanoplastics during 7, 14, and 28 days, respectively, obtained using the Nanosight platform data acquisition. The profiles presented in Figure 4 suggest an average growth of 54% in the particle size from the solution stabilization process. The measured concentration growth values in this study agree with those previously discussed in the literature [16,17]. The increase in the concentration of nanoplastics is even more evident in the particle size distributions in the saturated samples of nanoplastics represented in the profiles in Figure 5, indicating that the particles present in the system are aggregating over short distances, thus proving that the samples of plastic nanoparticles are positively charged, and their stability is related to the electrostatic effect.

The primary samples of nanoplastics of 500 mg and 1 g (temperature of 30 °C) present an average of 1.35E8 and 2.83E8 particles.mL^{-1}. However, a considerable increase in their concentrations is observed when submitting these samples to an increase in temperature (50 °C and 70 °C), as shown in Figures 6 and 7. This phenomenon is attributed to the interaction between positively charged nanoparticles, causing the release of nanoplastics for the samples and, thus, contributing to the formation of new structures. However, other factors must be taken into account to evaluate the release intensity of the nanoplastics for the samples, such as pH and ionic strength.

Relevant information about the stability of the samples was obtained by monitoring the pH as a function of time. Therefore, the change in pH may be an indication of polymer degradation. The 500 mg and 1g samples had an average pH variation of 7.1 – 8.2 and 7.2 – 8.4, respectively.

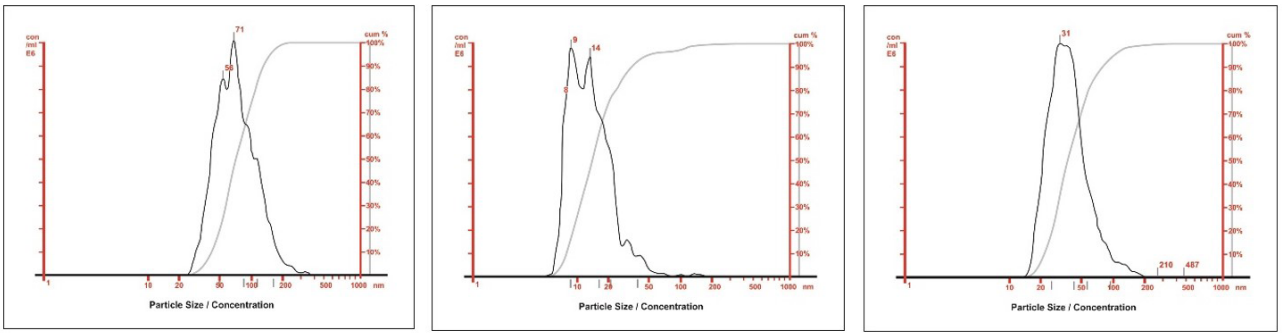


Days: 7
Concentration:
0.42 E8 particles.mL^{-1}

Days: 14
Concentration:
1.14 E8 particles.mL^{-1}

Days: 28
Concentration:
1.76 E8 particles.mL^{-1}

Figure 4. 500 mg plastic solution at 30 °C.

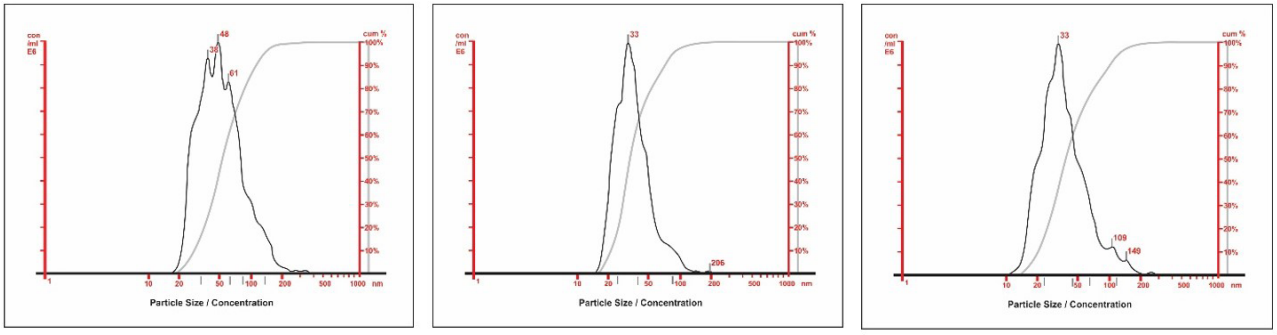


Days: 7
Concentration:
2.09 E8 particles.mL^{-1}

Days: 14
Concentration:
2.98 E8 particles.mL^{-1}

Days: 28
Concentration:
4.00 E8 particles.mL^{-1}

Figure 5. 1g plastic solution at 30 °C.

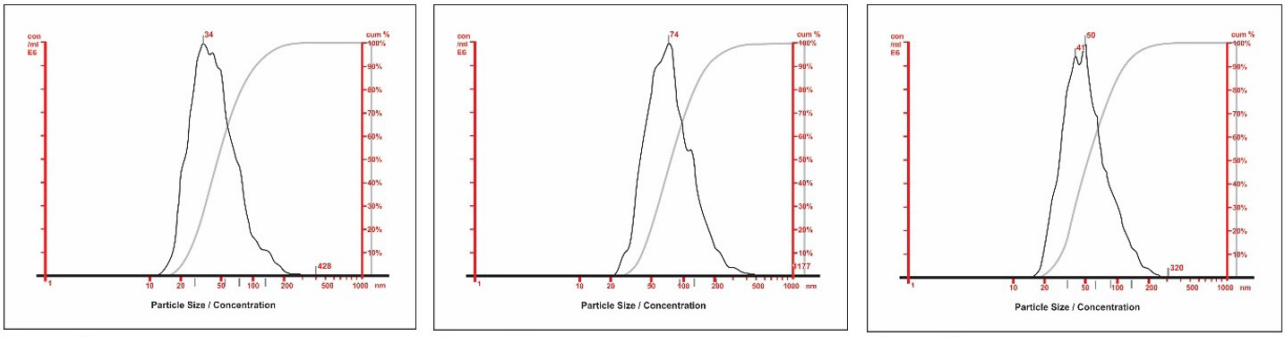


Days: 7
Concentration:
4.00E8 particles.mL^{-1}

Days: 14
Concentration:
4.78E8 particles.mL^{-1}

Days: 28
Concentration:
5.67E8 particles.mL^{-1}

Figure 6. 500 mg plastic solution at 50 °C.



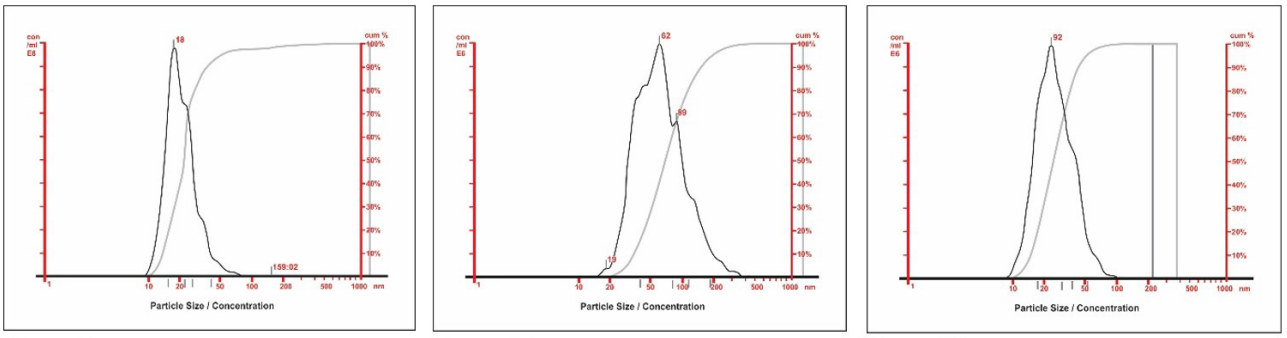
Days: 7
Concentration:
6.83 E8 particles.mL^{-1}

Days: 14
Concentration:
7.79 E8 particles.mL^{-1}

Days: 28
Concentration:
8.55 E8 particles.mL^{-1}

Figure 7. 1g plastic solution at 50 °C.

Figure 8 indicated that the samples under study have an ionic strength below 0.001 M so that the medium can be considered sufficiently diluted. However, the formation of ionic pairs is evident and can be due to the action of electrostatic forces of the electrically charged species in the solution. Thus, the greater the ionic strength, the greater the concentration of nanoplastics released in the liquid samples. The data obtained demonstrate a high emission of nanoplastics when the samples are exposed to higher temperatures, which could be potentially hazardous to human health [20-22], as shown in Figures 9 and 10.

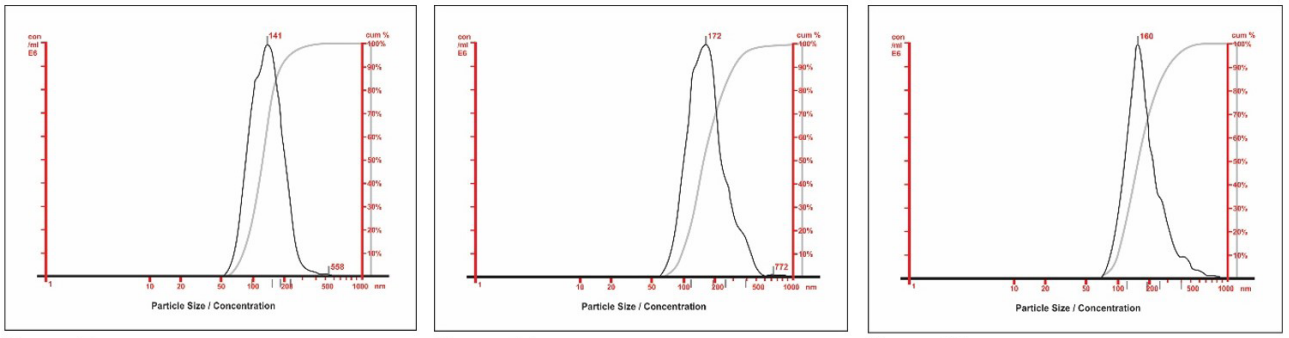


Days: 7
Concentration:
10.52 E8 particles.mL^{-1}

Days: 14
Concentration:
13.51 E8 particles.mL^{-1}

Days: 28
Concentration:
16.19 E8 particles.mL^{-1}

Figure 8. 500 mg of plastic samples in contact with water at 70 °C.



Days: 7
Concentration:
20.82 E8 particles.mL^{-1}

Days: 14
Concentration:
23.58 E8 particles.mL^{-1}

Days: 28
Concentration:
28.61 E8 particles.mL^{-1}

Figure 9. 1g of plastic in contact with water at 70 °C.

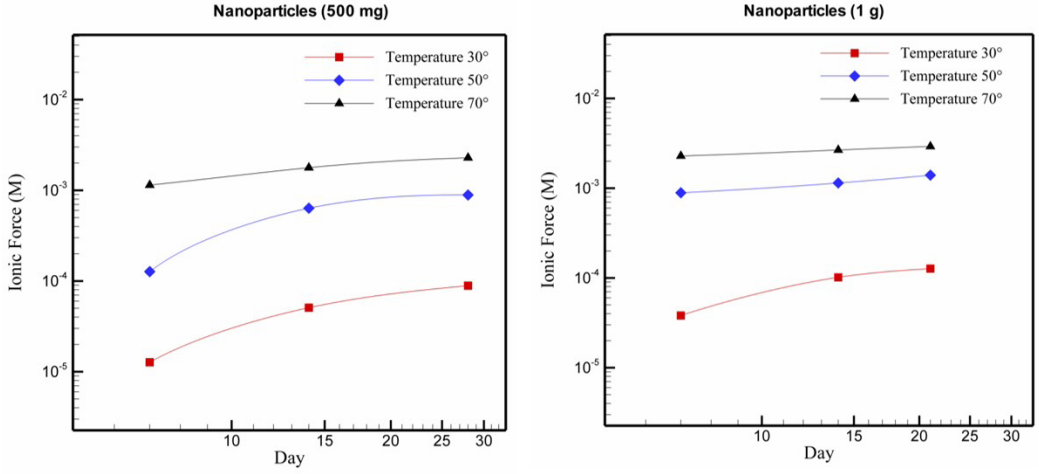


Figure 10. Effects of temperature on the ionic force of the liquid colloids.

In this case, the energy absorbed by the particles in the samples under study can accelerate the disintegration and degradation of the plastics immersed in the liquid, leading to the fragmentation of smaller particles of the polymer resulting in the release of nanoplastics to the liquid forming colloids, in order to increase the concentration in the liquid allowing the formation of new structures, causing an increase in the average particle size.

The exposure conditions used in this research simulate real conditions, where plastics present in disposable cups are

exposed to temperatures from 30 °C to 70 °C, this phenomenon is influenced by the degree of thermal expansion in which the plastic samples are submitted, as shown in Figures 9 and 10. As can be observed, the temperatures strongly affect the total amount of nanoplastic released due to the exposure of the plastic samples to the water during the exposure time. With these data, we can estimate the amount of nanoplastic contamination from the polystyrene under usage conditions and disposal.

4 Conclusions

The aim of this study was to quantitatively evaluate the nanoplastics that are formed during the use of disposable coffee cups (polystyrene) under varying temperatures. In all samples, an increasing number of plastic nanoparticles were observed. Nevertheless, as evidenced by the results, the increase in temperature accelerates the disintegration and degradation of polystyrene. The variability presented by the pH in solution and the ionic strength are strong indicators of the gradual degradation of the polystyrene. An increase of about 27% in the concentration of nanoplastics was observed, taking as reference the daily release (1.021 E8 particles.mL^{-1}), corroborating the inherent risk to human health.

The temperature variation in the range of seasonally observed in tropical regions strongly enhances the rate of releasing nanoplastics to the environment with the potential to impose severe consequences on the living species.

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