water

Article

Measuring Microplastic Concentrations in Water by Electrical Impedance Spectroscopy

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Abstract: Plastics are vital for society, but their usage has grown exponentially and contributes to the growth of pollution worldwide. The World Health Organization, WHO, already reported that microplastics (MPs) are found everywhere, in waste and fresh water, and in the air and soil. Regarding water effluents, waste-water treatment plants only minimize the problem, trapping only larger size particles. In contrast, smaller ones remain in oxidation ponds or sewage sludges, or are even released to aquifers environment. Classic procedures for MPs detection are still quite laborious, and are usually conducted off-line, involving several steps and expensive equipment. Electrical Impedance Spectroscopy, EIS, is a technique that allows the analysis of a system's electrical response, yielding helpful information about its domain-dependent on physical-chemical properties. Due to the superficial electronegativity of MPs' particles, EIS may allow to attain the purpose of the present work: to provide a fast and reliable method to detect/estimate MPs' concentration in water effluents. Among the most common microplastics are Polyethylene, PE, and Polyvinyl Chloride, PVC. Using the developed setup and experimental data collection methodology, the authors could differentiate between MPs' suspensions containing the same concentration of the different evaluated MPs, PVC and PE, and assess PVC concentration variation, in the interval between 0.03 to 0.5 g (*w*/*w*), with an error, estimated based on the obtained impedance modulus, around or below 3% for the entire stimulus signal frequency range (from 100 Hz to 40 MHz) for the PVC particles.

Keywords: electrical impedance spectroscopy; microplastics detection; polyethylene; polyvinyl chloride

Citation: Gomes, D.; Magalhães, S.; Rasteiro, M.G.; Faia, P. Measuring Microplastic Concentrations in Water by Electrical Impedance Spectroscopy. *Water* **2024**, *16*, 3228. https://doi.org/10.3390/w16223228

Academic Editors: Muthiah Annalakshmi, Sakthivel Kumaravel and Thangaraj S.T. Balamurugan

Received: 7 October 2024
Revised: 1 November 2024
Accepted: 8 November 2024
Published: 10 November 2024

1. Introduction

The word 'plastics' has its origin in the Greek word plastikos, which refers to a material characterized by being moldable. Plastics have been used as early as 1600 BC in the form of natural rubber in ancient Mesoamerica and have, since then, become vital in society. After the finding of Bakelite (the first synthetic polymer), plastics mass production was launched in the late 1950s, due to the upgrades of modern engineering; it was followed by the introduction of at least 15 different classes of synthetic polymers, and their usage was accelerated. Plastic consumption has exponentially grown during the last decades (its application in construction, packaging, transportation, personal care products, and medicine is generalized today). This unchecked growth has led to the uncontrolled use of plastics, making it one of our most serious environmental contamination issues. Microplastics, MPs (particles that are less than 5 mm in diameter), and nano plastics, NPs (particles in the size range 1–1000 nm), are mainly formed by the fragmentation of large plastic materials [1], and an essential negative contribution arises from textile industry [2] and home washing practices [3]. Evidence shows that MPs have a negative impact on marine and aquifer environments. Although recent reports refer to their presence in the human body [4–6], human exposure risks are still not well documented [7,8]. Contrarily, environmental pollution with

NPs and MPs and the resultant unavoidable exposure of humans to these materials has raised universal concerns. Microplastics become spread in nature due to environmental factors and their inherent properties, such as density, hydrophobicity, and recalcitrance; subsequently, the consequences of plastic accumulation in nature, particularly in waters, have risen drastically in recent years. Typically, high-density MPs sink and accumulate as sediments, while the low-density ones float. Conventional wastewater and drinking water treatment systems are based on sedimentation, filtration, and biological treatments, and the existent approaches to minimize MPs dissemination are clearly deficient. In the case of wastewater, waste-water treatment plants only minimize the problem, trapping only larger-sized particles, while smaller ones remain in oxidation ponds or sewage sludges or are even released into water streams. Meanwhile, for evaluating the efficiency of the treatment procedures, the presence and quantification of MPs in wastewater and drinking water are vital [9]. For many years, scientists have been trying to deal with the complexity of MP detection and quantification, including the probability of obtaining results that are either false positives or false negatives. However, the lack of universal and validated methods led to a wide range of analytical approaches, compromising a large-scale interpretation of results. Currently, research groups may struggle with selecting the right methods for sampling microplastics due to the inexistence of a standard procedure.

According to the scientific literature, there are several types of plastics that contribute to environmental pollution [10]. Among the most common MPs are Polyethylene, PE, Polyethylene Terephthalate, PET, and Polyvinyl Chloride, PVC. These make up the largest percentage of contaminants in the environment, together making up to around 36% of the total MPs released to the environment, being among the most common pollutants in the environment. Moreover, Polyethylene (PE) and Polyvinyl Chloride (PVC) were chosen as they represent MPs with different densities and surface properties, which influence their behavior in water MPs systems. This selection strengthens the study by ensuring that the microplastics used are representative of real-world pollutants commonly found in aquatic environments.

The existing procedures for MPs detection and quantification are still quite laborious and usually involve several steps and expensive equipment. Therefore, systems that can quickly evaluate the existence/estimation of MPs in wastewater and drinking water are urgently needed. Consequently, the main purpose of the present work is to provide a fast and reliable methodology to detect/estimate MPs' concentration of Polyethylene, PE, and Polyvinyl Chloride, PVC, in aqueous effluents.

2. Classical Classification Methods

Traditional analytical techniques for MP evaluation can be grouped into physical or chemical-based characterization ones (destructive and non-destructive techniques) [10]. Physical characterization analysis of MPs can preliminarily determine the particle size, color, shape, morphology, corrosion degree, and ageing degree of MPs [11]. One of the techniques providing physical information on MPs is visual analysis. Despite this methodology's advantages including simplicity of operation, low cost, and little chemical hazard during operation, it cannot provide MPs' chemical composition and it is time-consuming and laborious. Moreover, its accuracy is relatively low once the results are easily affected by factors such as the presence of other impurities, the color and structure of MPs, etc. [12].

Non-destructive methods, such as Scanning Electron Microscopy (SEM), provide high-resolution images by scanning the particle surfaces with a focused electron beam [13,14]. These detailed images enable differentiation between particles, based on surface characteristics. However, SEM does not reveal the composition of the particles and requires intensive sample preparation, including cleaning, drying, applying a conductive coating, and mounting the sample on a stub with a conductive tape, steps that can potentially damage the MPs.

As for the chemical characterization, Raman spectroscopy and FTIR are the most used analytical methods for determining the composition of MPs [15,16]. Both techniques rely on vibrational spectroscopy to produce a unique spectrum that can be matched and identified using reference libraries. In FTIR, infrared radiation is partially absorbed by the particle and measured in either transmission or reflection mode. In Raman spectroscopy, a monochromatic laser interacts with the sample, generating molecular vibrations that reveal its chemical composition. However, fibers made from multiple materials, or those with complex internal structures, can produce varying spectra. The presence of copolymers or composite materials requires a more efficient identification process and a careful interpretation of the spectra.

Destructive methods, such as pyrolysis-GC-MS (Pyro-GC-MS), involve thermally decomposing microplastics under inert conditions [15]. The resulting gases are cryo-trapped, separated using a chromatographic column, and then identified through mass spectrometry. While this technique provides detailed chemical characterization of individual MPs or bulk samples, it is destructive and does not offer insights into the particles' number, size, or shape [17]. Thermo-extraction and desorption coupled with GC-MS (TED-GC-MS) enhances this process by combining thermogravimetric analysis (TGA), for thermal degradation, with solid-phase extraction of plastic degradation products, which are then analyzed through thermal desorption in GC-MS [18]. This method allows for the analysis of larger sample amounts, making it suitable for complex heterogeneous matrices. It also enables the identification and quantification of polymers in environmental samples without the need for preselection [15]. Additionally, liquid chromatography, particularly size exclusion chromatography, is used to characterize polymers by employing a solvent suited to the polymer type. While these techniques improve representativeness by analyzing larger sample quantities, they remain destructive and primarily provide chemical composition information [19].

As described, existing procedures for MPs detection and quantification are still quite laborious and usually involve several steps and expensive equipment [14]. Therefore, systems that can quickly evaluate the existence/estimation of MPs in wastewater and drinking water are urgently needed.

3. Electrical Impedance Spectroscopy

Recently, efforts have started on the use of electrochemical methods, particularly on Electrical Impedance Spectroscopy, EIS, which is ideal for creating transportable devices with a faster response time, enabling real-time water sample monitoring [20]. Electrical Impedance Spectroscopy plays a fundamental role in many research and development areas, where it is an essential analytical technique for studying intricate systems' behavior [21,22]. It is a methodology that allows for characterizing the electrical behavior of systems through the measurement of their complex impedance, for which different coupled processes contribute to the overall response. When the system under evaluation is a suspension containing different particles, such as MP particles, those particles change the measured complex impedance according to their relative permittivity [23] Consequently, impedance reflects both the material properties and the size of the particles, which is why measurements should be conducted at both high and low frequencies (at low or zero frequency, the impedance change is proportional to the particle's volume).

The technique consists of applying an electrical stimulus through electrodes (a known and defined current or voltage) and analyzing the system response, assuming that the system's electrical properties are time-invariant [24]. Characterizing the suspension behavior implies using electrodes to perform the measurements [24,25]. In EIS, a two/four points measuring configuration is used, in which the same pair of electrodes is used simultaneously for applying the excitation to the media intended to be analyzed and for measuring its electrical response: the four points configuration is an extension of this approach intended to diminish the measuring electronics setup, and consequently, its influence on the impedance measurements. There is a second form of electrochemical analysis, based on a three electrodes setup, designated in the literature as Electrochemical Impedance Spectroscopy, ECIS, for which the number of literature reports is higher [26]. However, even if it sometimes displays higher selectivity and sensitivity in a laboratory environment, its usage for online measurements is limited, in contrast to a two-electrode configuration, once it involves more complex electrode preparation and suspension properties adjustment.

Different types of electrical stimuli can be used when applying EIS [27], being the most common the one in which the complex impedance is measured by applying a single-frequency voltage sinusoidal signal, after which the resulting current amplitude and phase shift are measured for that same frequency (or their respective real and imaginary parts) [28,29]. However, if instead of evaluating the response to a single frequency stimulus, a chosen set of frequencies is studied, a sweep, the obtained set of impedances can be represented in the form of a Nyquist plot (the imaginary part of the impedance as a function of the real part of the impedance), or of Bode plots (the imaginary part of the impedance as a function of frequency, along with the real part of the impedance as a function of frequency). For each frequency, the complex impedance is accessed using the generalized Ohm's Law: in it, the alternate current, AC, typically with a sinusoidal form ($I = I_m cos(wt + \varnothing)$ A, where I_m is the current maximum amplitude in Amperes, w is the angular velocity given by $w = 2\pi f$ in rad/s, and $\varnothing$ is the respective phase angle, in degrees), is applied as a stimulus, and the voltage produced at the system terminals is measured ($V = V_m cos(wt + \theta)$ V, where V_m is the current maximum amplitude in Volts, and θ is the respective phase angle, in degrees). The impedance is then calculated by dividing the measured voltage by the used current. If performed in the frequency domain, the impedance Z is given by $Z = \left(\frac{V_m}{I_m}\right) \times e^{-j(\theta - \varnothing)}$ Ω (Ohms), or in the complex form, $Z = R + jX$ Ω, where R is the resistance of the system ($Z' = R = Zcos(\theta - \varnothing)$) in Ohms, and X is the reactance ($Z'' = X = Zsin(\theta - \varnothing)$) also in Ohms. Usually, a low amplitude excitation signal is used so that the measurements are performed as close as possible to the linearity condition.

In summary, EIS can be used to assess how charges are bounded or are transferred along the suspension or the existing interfaces (for instance, solid-liquid ones) [30], once the electrical response of heterogeneous systems, like suspensions, varies and depends on the system composition, on the charge of the species, and on the electrodes' shape, placement, and type. Besides, its main advantage is that it allows the identification of each electrical phenomenon present in a system once it reaches its maximum contribution at different excitation frequencies of the applied current.

However, regarding microplastic particles assessment, this is a recently "born" approach, and consequently, the literature reports are scarce but highly promising. For instance, Meiler et al. [31], combined EIS with machine learning (support vector machines, SVMs) for detecting microplastics. Electrical measures were carried out in resting water samples containing different plastic concentrations in a cylindrical measuring cell, in the frequency range from 20 Hz to 2 MHz (prepared samples contained plastic mass fractions varying from 0 to 10 g in steps of 1 g). The plastics tested were polypropylene, PP, a polyolefin, PO, and a mixture of different plastics, mainly consisting of low-density polyethylene. The classification task, consisting of distinguishing different plastic materials and particle sizes, was achieved with a success accuracy of over 98%. They also conducted measurements at 2 MHz with water flows carrying microplastic particles of different materials and sizes, to investigate the dynamic capabilities of the measurement method: for this case, the classification accuracy achieved was of 85%. Another dynamic approach was conducted by Colson and Michel [32]. In a rectangular channel with a pair of measuring electrodes, they demonstrated the use of an EIS-based flow-through sensing for the identification of microplastics directly in water. They were able to quantify polyethylene MPs particles based on their dimension (sizes ranges of 212–250, 300–355, 425–500, 500–600, 600–710, and 850–1000 µm were used in the experiments). MPs were reliably detected, sized, and differentiated from biological materials, with a false positive rate of misidentifying the biological material as plastic of 1%. So, the advantage of the present work methodology is that it enables real-time analysis of the effluent without the need for sample treatment. By directly introducing the sensor into the medium, it can immediately detect the presence or absence of microplastics, eliminating the need for any pre-processing, in comparison with the mandatory multistep procedures needed for laboratorial analysis of samples using FTIR or RAMAN, such as the use of alkaline compounds to remove organic matter, the use of acid compounds to remove inorganic matter, peroxide to remove bacterial compounds, washing and filtering, among others, overall highly time consuming procedures, which use expensive techniques.

4. Materials and Methods

The experimental work involved using polyvinyl chloride (PVC) particles is sourced from Cires, Portugal, with an average particle size ranging from 20 to 30 µm. Additionally, polyethylene (PE) was also used with three distinct particle sizes corresponding to 35, 60, and 125 mesh, obtained from Goovean Fibres, Lda, in the United Kingdom, with the exception of the 60 mesh PE, which was prepared in the laboratory from recycled plastic water bottles. These bottles were processed using a knife mill (Thomas Scientific, Chadds Ford Township, PA, USA) equipped with a 60-mesh sieve size screen to achieve a uniform particle size of approximately 250 µm.

Laser diffraction spectroscopy (LDS) was used in a Mastersizer 2000 (Malvern Instruments, Malvern, UK) and a Hydro 2000 module to assess the size distribution of MPs. The device's pump was set to 1500 rpm. MP samples were introduced into the dispersion unit until the obscuration level reached 7–8%, ensuring an optimal signal-to-noise ratio. Laser Diffraction Spectroscopy is a technique widely used for micrometric particles characterization, including plastic particles [33]. Data analysis was conducted using the Mastersizer 2000 software, applying the Mie Theory, to obtain the particle size distribution from the scattering.pattern. The particle size is reported as the volume-equivalent sphere diameter.

The zeta potential of MP particles (PE and PVC) in suspension was measured using the Zetasizer NanoZS from Malvern Instruments, UK. Each sample was tested six times, with 15 sub-runs per measurement, across a pH range from 2 to 12. To prepare the samples, a dispersion was created by mixing 0.1 g of MPs in 30 mL of water, and the pH was adjusted to the desired level. The suspensions were then transferred to the capillary measuring cell, and zeta potential measurements were conducted at 25 °C, following a 60-s thermal equilibrium period.

Using the same sample preparation procedure as for zeta potential analysis, additional samples with varying microplastic concentrations were prepared for the EIS tests. The final PVC concentrations were 0.03, 0.06, 0.1, 0.2, 0.3, and 0.5 g/mL (w/v), while for PE, the concentrations were 0.06, 0.1, and 0.5 g/mL (w/v).

An immersible device was fabricated to carry the complex impedance evaluation, allowing for its usage and easy positioning inside the suspensions without disturbing them: the idealized prototype scheme can be seen in Figure 1a). The constructed device is shown in Figure 1b), and its main body is an acrylic made U-shaped structure (length, depth and width all equal to 19, 20, and 16 mm, respectively): a part of the bottom of the U form structure was removed (a square with a width of 15 mm) to facilitate the device displacement/placement in the suspensions, simultaneously avoid interfering as much as possible with the particle distribution in the suspension. A pair of gold circular electrodes with a 10 mm radius was placed on opposite sides of the U-shaped structure. A gold wire with a 1 mm section was soldered to each electrode; those wires were used to connect the device to the electrical impedance analyzer. For all assessments carried both at the top and bottom of the suspensions for each type of plastic type, concentration, and pH level, three acquisition runs were conducted: the depicted data in the Nyquist plots are the average values all three runs.

The impedance analyzer used during the experimental work was an Agilent 4294A. The frequency interval used for the evaluation ranged between 100 Hz and 40 MHz, with a voltage difference potential possessing an amplitude of 500 mV (0 V bias). The electrical voltage signals possessing varying frequency generated by the impedance analyzer were applied through the gold wires to the electrodes: the equipment measured simultaneously the developed electrical current flowing through the suspension between the pair of electrodes, which was transmitted to the impedance analyzer through the gold wires. Electrical evaluation was carried out by placing the measuring device inside the vessels containing the suspensions, near the suspensions' surface and at the bottom, after intense agitation for 30 s.

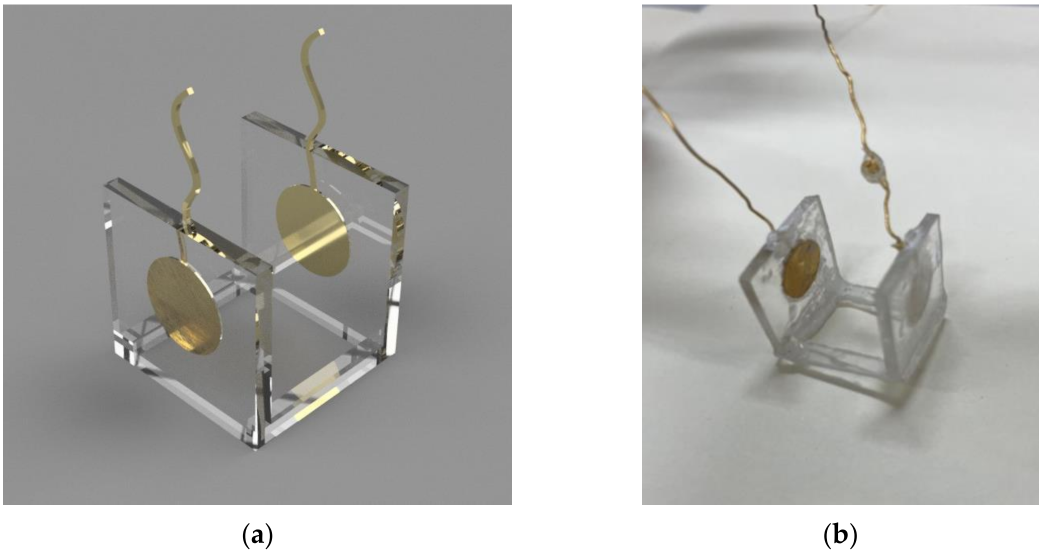

(**a**) (**b**)

Figure 1. Immersible device idealized: (**a**) 3D schematic; (**b**) prototype photograph.

5. Results and Discussion

After preparing an initial set of suspensions containing the same concentration of PVC particles with different acidity levels, their electrical response was assessed by EIS using the developed prototype. The objective was to determine which pH levels would be used during the study. The EIS spectra obtained can be seen in Figure 2. From the plots, it is easy to see that as the pH of the suspension increases, the overall shape of the impedance spectra changes (the area below the curve changes): it starts to increase up to a pH level equal to 6 and then continuously decreases. A lower overall impedance is synonymous of a higher conductivity of the suspension, which is an indication that it will be harder to distinguish between Nyquist plots of suspensions containing plastic particles with different concentrations or sizes, i.e., lower sensitivity of the measuring system. Indeed, once charge conduction paths along the suspensions are abundant, the opposition to their transportation diminishes, drastically reducing the effect of the variations in the number of particles and their sizes in the suspension. So, it was decided that pH levels equal to 4 and 10 would not be considered in this study. Moreover, pH levels in the range from 6 to 8 are more typically found in the environment, so they were chosen for the remaining experimental work.

Before preparing the suspensions containing the PVC particles with the different concentrations and chosen pHs, their size distribution was accessed by LDS. The LDS data plot can be seen in Figure 3. From it, the estimated mean particle size was around 22.55 ± 1.29 μm. Moreover, an evaluation of the particle's surface charge under the two pH levels was also performed: the measured Zeta Potentials are given in Table 1. From these values, it is possible to predict that pH will play an essential role in microplastic particle detection and differentiation. Indeed, once the mean surface charge is different, and once the conduction process is dominated by ion transportation, varying surface charges over the particle's surface will determine the conduction paths contributing to the overall found impedance of the suspensions.

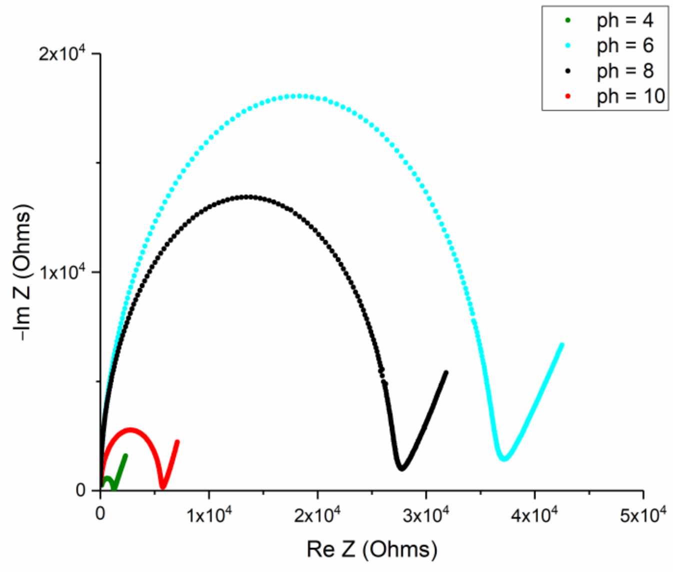


Figure 2. Nyquist plots of suspensions containing 0.1 g of PVC particles for different pH levels.

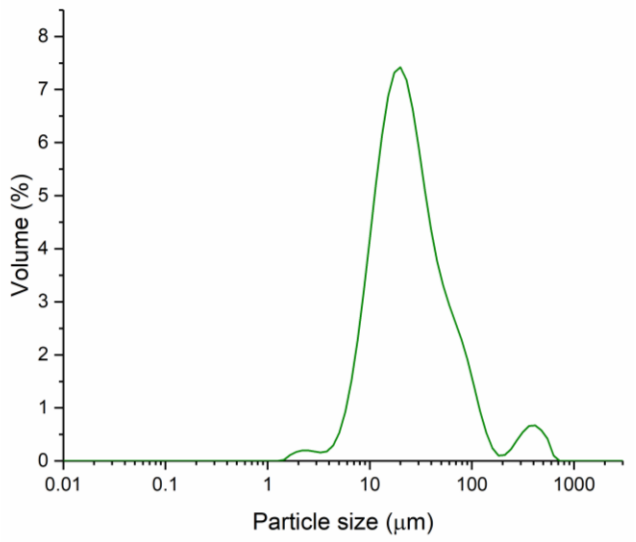


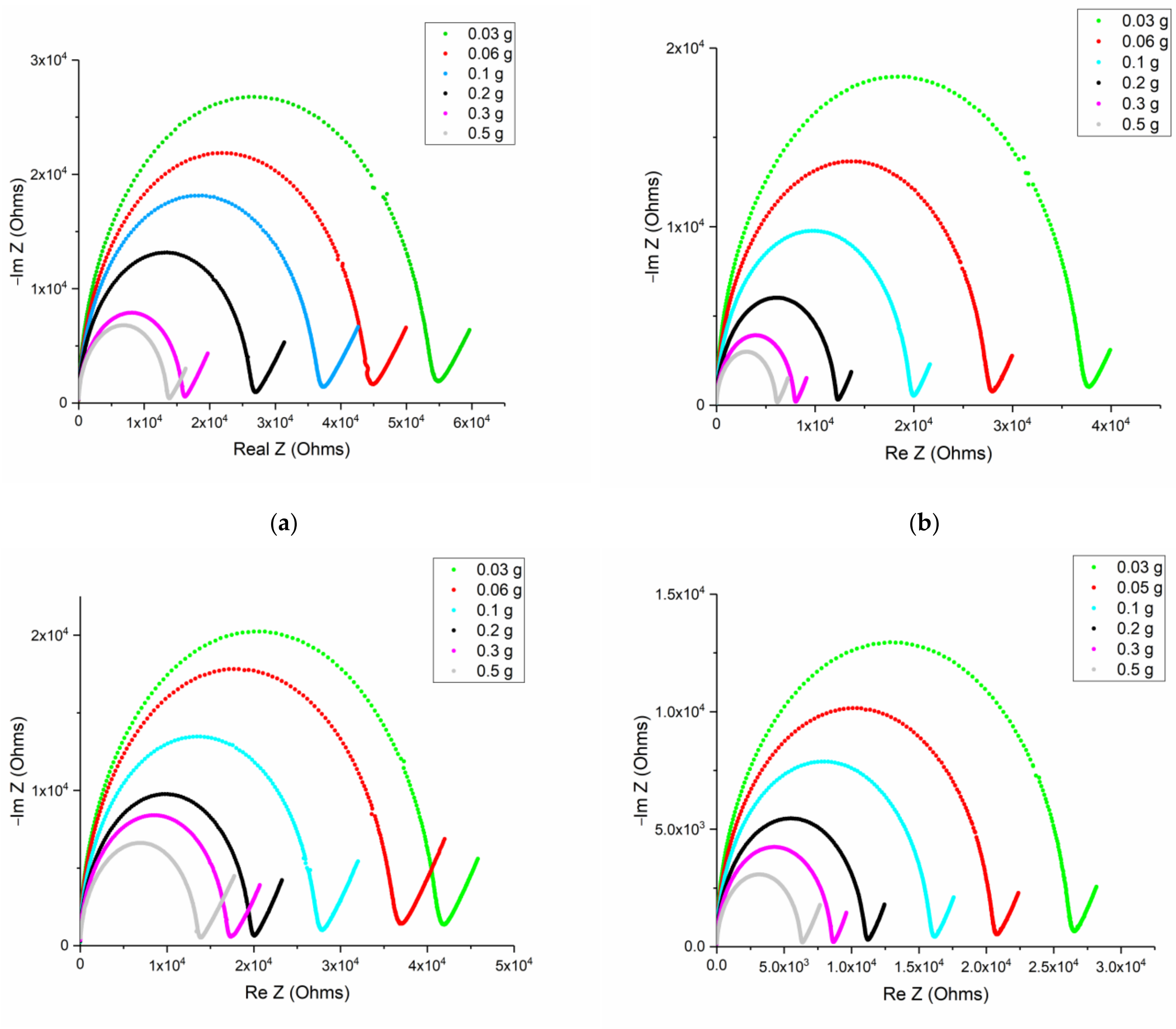
Figure 3. PVC size distribution obtained by LDS.

Table 1. PVC and PE MP particles zeta potential for different pH levels.

Plastic	Zeta Potential (mV)	
	pH 6	pH 8
PVC	−59.65 (±1.52)	−79.23 (±3.14)
PE	−10.84 (±1.80)	−15.13 (±3.98)

After preparing the PVC-containing suspensions with different concentrations and pH levels, they were evaluated by EIS using the developed prototype. As described, each suspension was intensely agitated for 30 s before completely immersing the device near the surface and bottom of the jars.

The obtained EIS Nyquist plots are presented in Figure 4. From them, it can be concluded that the measuring system can distinguish PVC suspensions containing different concentrations of PVC, both near the surface and the bottom of the jars and for the two pH levels. Indeed, for both pH levels and suspensions' inspection placements (i.e., near the surface and bottom of the jars), it is possible to observe that as PVC particle concentration increases, the overall area of the circumscribed impedance spectra diminishes. Indeed, as the number of superficially charged particles increases, there is an increment in the possible conduction ion transfer paths, and so a consequent increase in the conductivity of the suspension (with subsequent decrease in the impedance). Moreover, it can also be retrieved from the plots that for all concentrations and both studied pHs, the overall area of the circumscribed impedance spectra obtained near the surface of the jars is higher than the one found near the bottom: this fact is also in accordance with the known higher sedimentation velocity of the PVC particles when compared with other types of plastics, and as a consequence, the presence of larger quantities of particles, even after agitation, is expected at the bottom, and thus the number of superficial charges increases with an increment of the possible ion conduction paths, resulting in the increase in the conductivity of the suspension.



(**a**) (**b**)

(**c**) (**d**)

Figure 4. Nyquist plots for the different PVC suspensions obtained for pH 6 near the jar surface, (**a**), pH 6 near the jar bottom, (**b**), pH 8 near the jar surface, (**c**), and pH 8 near the jar bottom, (**d**).

Additionally, the measuring strategy reliability was also primarily assessed. As can be seen in the Figure 5, as an example, the standard deviations estimated from the impedance modulus for the data obtained for PVC with pH equal to 6 at the bottom of the jars, the measuring approach shows to be very reliable and consistent, presenting, for all concentrations, an error around or lower than 3%. Moreover, it is observable that the error tends to be invariable in the lower frequency range up to 100 kHz (above that frequency, in the high frequencies domain, the variations observed are due to geometric capacitance charging time connected to the geometry of the device, and so does not contain useful information about charges transportation within the device, i.e., it can be disregarded in this case).

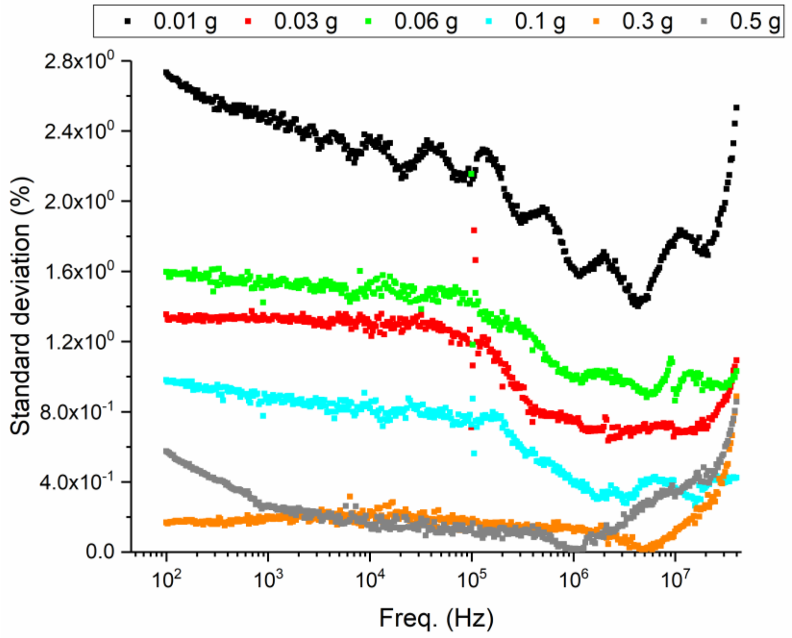


Figure 5. Estimated standard deviation for pH equal to 6 while varying PVC concentration.

Finally, it is also possible to observe the influence of the suspension pH on the sensitivity of the measuring system. Indeed, and as predicted by the initial evaluation carried (see Figure 2, from which it was observed that a higher sensitivity in distinguishing plastic particles if the pH was equal to 6), the suspension pH for which higher differences between the Nyquist spectra's for the different concentrations tested was detected, was pH 6 (see Figure 4), which allows to detect the plastic particles more easily. In fact, for the same particle concentration in the suspension, the overall area of the circumscribed impedance spectra obtained for pH 6, is always higher than the one obtained for a pH equal to 8.

After this set of results, the authors decided to move on and check if their approach could also differentiate varying concentrations of other types of microplastics. PE was the chosen material, considering its high predominance in many effluents. The particle size distribution of the PE powder obtained by LDS can be seen in Figure 6. From these results, the average particle size of PE was estimated at around 259.49 ± 25.63 µm. For both the PVC and the PE particles, an assessment of the particle's surface charge under the two pH levels was performed, and the Zeta Potentials are presented in Table 1.

After preparing the PE suspensions for the different concentrations and pH, EIS evaluated them using the developed prototype, once again. Again, and as already described, each suspension was intensely agitated for 30 s before completely immersing the device near the surface and bottom of the jars. The obtained EIS Nyquist plots are presented in Figure 7. From them, it can be concluded that the measuring system can distinguish between PE-suspended particles with diverse concentrations, with similar trends observed for PE, both when concentration and pH change, as the ones observed for PVC. However, the sensitivity of the measurement is lower than the one observed for the PVC suspensions. That is, from the author's point of view, mainly due to the lower superficial electrical charge present in the PE particles: indeed, when comparing the Zeta potentials (see Table 1), the

PVC particle's surface potentials for both studied pH levels are much higher than the ones measured for the PE particles. Consequently, the sensitivity regarding the detection of variations in PE particles' concentration diminishes.

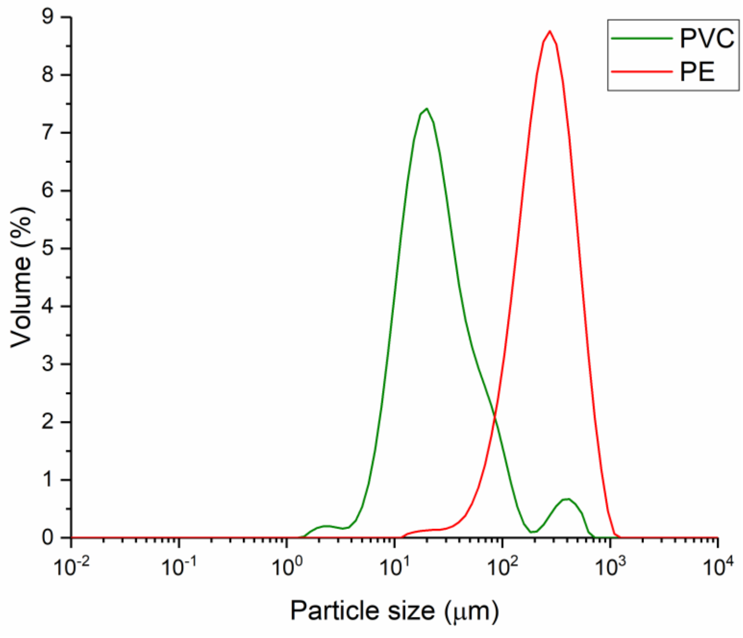


Figure 6. PE and PVC particle size distributions obtained by LDS.

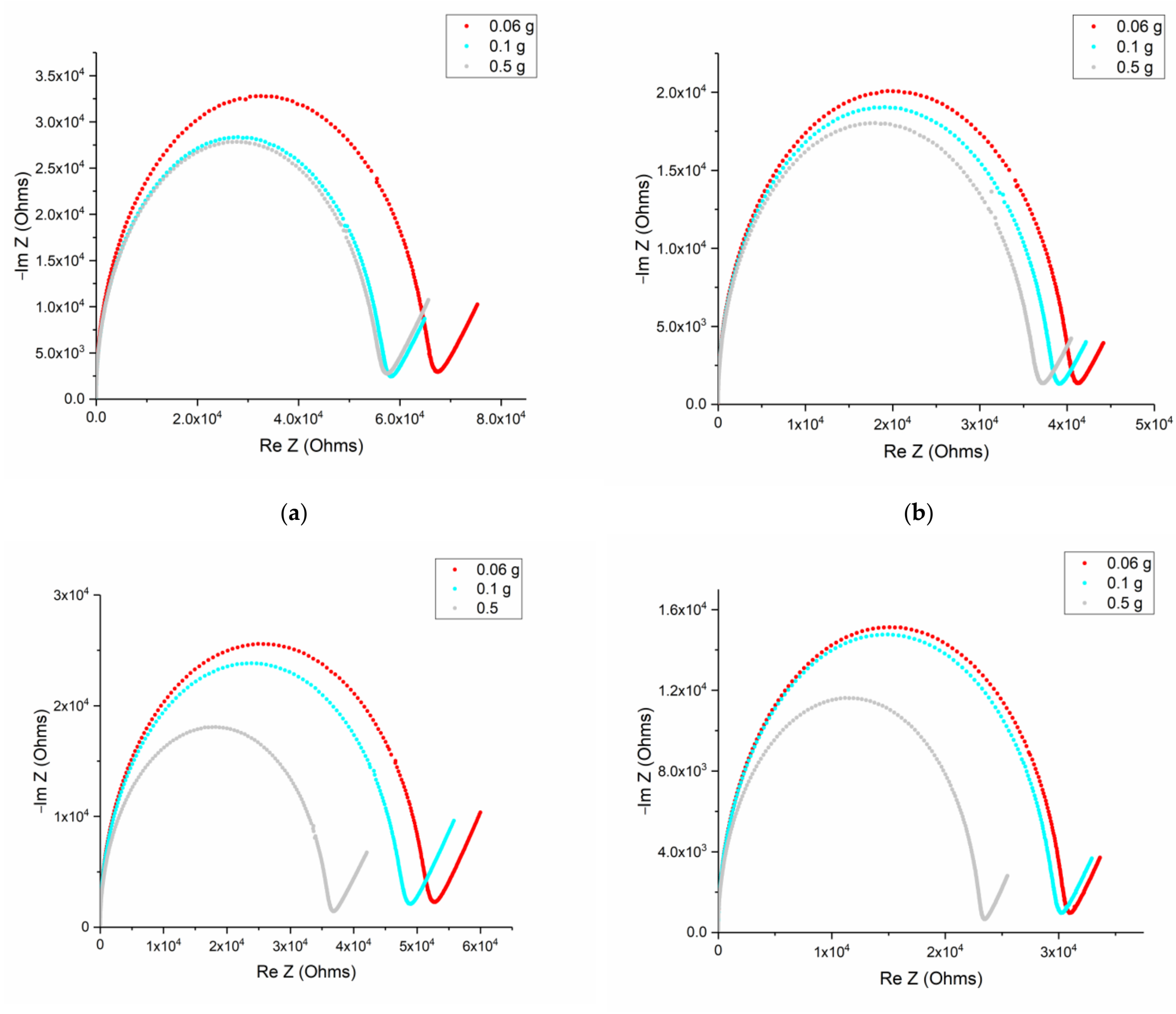
Nevertheless, when comparing suspensions containing PE and PVC particles with similar concentrations (see Figure 8), the capacity of the adopted measuring strategy to differentiate them (both near the surface and the bottom of the jars) is clear.

However, one last issue still required further attention to validate the proof of concept presented here: could the changes observed in the Nyquist plots, when comparing PVC and PE suspensions, be mainly due to the particle mean size differences and not primarily dependent on the different surface charge of the two materials? So, PE suspensions containing the same particles' concentration of 0.1 g, but using powders with three different mean sizes, around 500, 250, and 100 μm (see Figure 9 and Table 2 for the particle size distribution), were prepared for a pH level of 6, named batches n°1, 2 and 3, respectively (Table 2).

Table 2. PE microplastic batches mean size.

PE Mean Size (μm)		
Batch n°1	**Batch n°2**	**Batch n°3**
194.37 (±23.85)	259.49 (±25.63)	541.60 (±32.14)

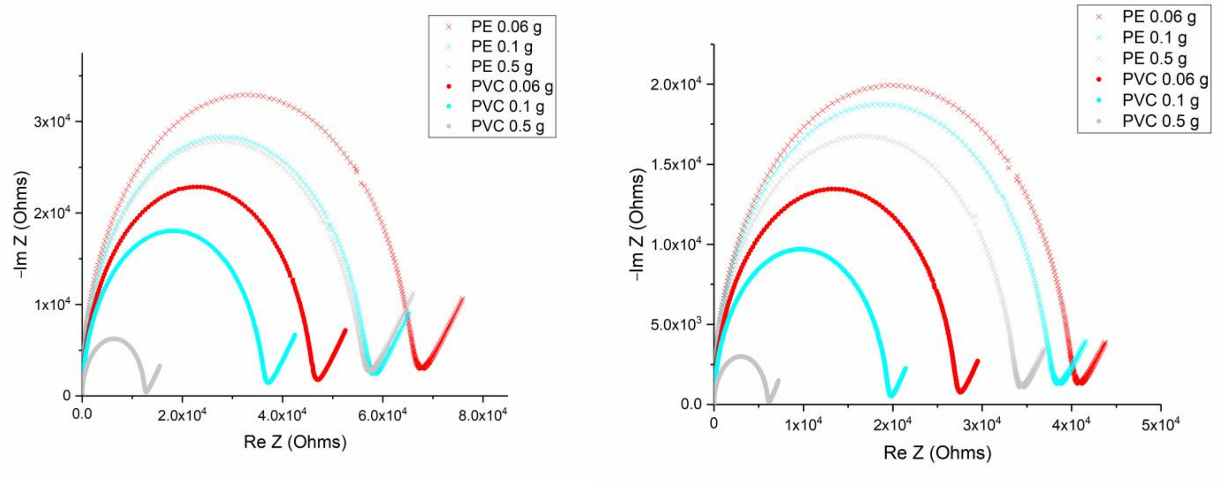
The PE suspensions, with the different particle sizes, were then evaluated by EIS using the prototype developed (each suspension was intensely agitated for 30 s before completely immersing the device near the surface or bottom of the jars). The obtained EIS Nyquist plots are presented in Figure 10. Indeed, the particle mean size changes are also detectable by EIS; however, the differences in the area below the Nyquist plots curves are much smaller when compared to the changes due to the variation in particle type, even if the area decreases as the particle size decreases: indeed, near the surface and bottom the estimated impedance variations due to the change in particle size are around 1 and 0.5 kΩ, respectively, while the changes due the modification of suspended particle type also near the top and bottom of the jars are around 2.5 and 1.5 kΩ, respectively (that is around three times higher).



(**a**) (**b**)

(**c**) (**d**)

Figure 7. Nyquist plots for the different PE suspensions obtained for pH 6 near the jar surface, (**a**), pH 6 near the jar bottom, (**b**), pH 8 near the jar surface, (**c**), and pH 8 near the jar bottom, (**d**).



(**a**) (**b**)

Figure 8. Nyquist plots comparing three different PE and PVC suspension concentrations for pH 6 near the jar surface, (**a**), for pH 6 near the jar bottom, (**b**).

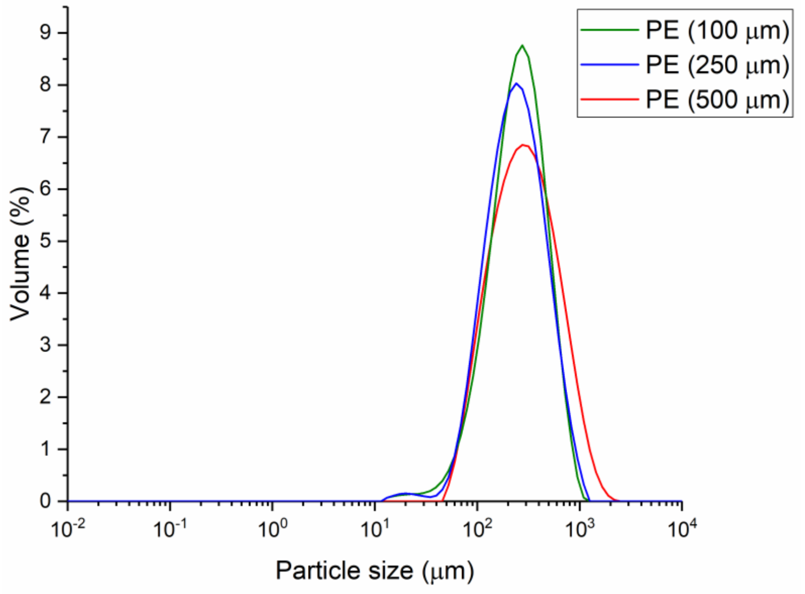
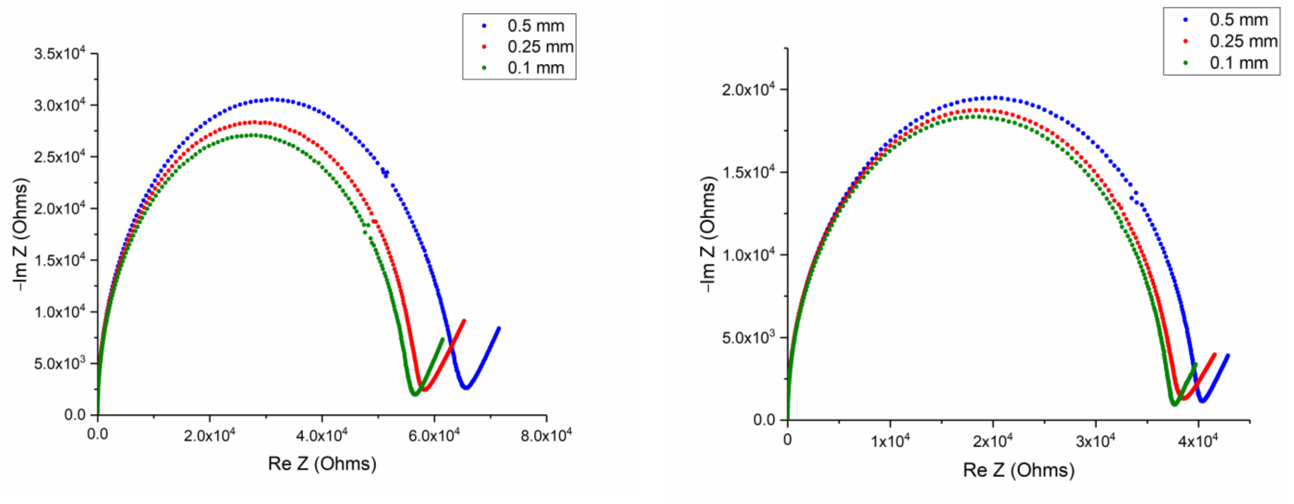


Figure 9. PE particle size distribution obtained by LDS for the three PE batches evaluated.



(**a**) (**b**)

Figure 10. Nyquist plots for the different PE suspensions containing the same 0.1 g concentration of plastic particles but with different mean sizes obtained for pH 6 near the jar surface, (**a**), and pH 6 near the jar bottom, (**b**).

In summary, the determining factor for distinguishing plastic particle types or assessing particle concentration variation is their electrical surface charge, for which electrical impedance spectroscopy can be an extremely powerful tool.

6. Conclusions and Future Perspectives

In the present work, a new measuring strategy that combines a submersible device with Electrical Impedance Spectroscopy was developed and used to inspect microplastic particle suspensions. The evaluation was carried out using PVC and PE particles, and in the case of PE, using powders with different mean sizes.

The measuring system could differentiate between suspensions containing particles with different concentrations of identical plastic-type and suspensions with particles of different types of plastic with similar concentrations. Moreover, particle size differences were also distinguishable. The results confirmed that the main factor determining the differentiation capacity of the strategy developed, between microplastic types and concentrations is plastic particles' superficial charge. Nevertheless, the approach exhibits higher sensitivity when the plastic particles' suspensions possess a neutral pH (pH near 7), as usually happens in wastewater treatment plants.

Finally, electrical impedance spectroscopy was confirmed to be an extremely powerful tool for detecting microplastic particles. The developed submersible device, combined with the evaluation strategy (agitation, which tries to mimic some of the conditions found in wastewater treatment plants, especially in the zones of treated effluent release), showed to be highly promising in terms of future use (easy to deploy).

Future work will have to be conducted to enlarge the detection capacity of the overall system, such as tests at laboratory scale of suspensions containing other types of plastic particles (such as polystyrene and polyethylene terephthalate, which are also among the most common MPs released to the environment), suspensions containing simultaneously plastic particles of different types, and also testing the effect of adding to the suspensions organic compounds (such as bacteria, as some of them are known to degrade plastic particles and, consequently, it is also quite important to evaluate the influence of the degradation process in the detection capacity). The major limitation envisaged by the authors, in the case of suspensions containing multiple materials/contaminants, is related to the fact that the electrical charges interaction between them will also play a role in the final measured impedance, an aspect that still has to be evaluated. Consequently, there is still a significant path to be pursued until a portable and totally reliable sensing device is available commercially. Still, the results already achieved and described in the present work present strong evidence that the approach being followed has a high potential to be upscaled and used in the future for MPs detection in real field systems.

Author Contributions: All authors contributed in equal parts to this article. Conceptualization, P.F. and M.G.R.; formal analysis D.G.; investigation, D.G. and S.M.; data curation, D.G.; writing—original draft preparation, P.F.; writing—review and editing, M.G.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author/s.

Acknowledgments: This research was sponsored by Portuguese funds through FCT—Fundação para a Ciência e a Tecnologia, under the project UIDB/00285/2020. Solange Magalhães also acknowledges FCT for the PhD grant 2020.07638.BD (DOI: https://doi.org/10.54499/2020.07638.BD). This work was supported by national funds from FCT—Fundação para a Ciência e a Tecnologia, within the project UIDB/00102/2020 (DOI: 10.54499/UIDB/00102/2020 and DOI: 10.54499/UIDP/00102/2020).

Conflicts of Interest: The authors declare no conflicts of interest.

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