Detection of microplastics in water using electrical impedance spectroscopy and support vector machines

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Abstract

The detection of microplastics in water currently requires a series of processes (sample collection, purification, and preparation) until a sample can be analyzed in the laboratory. To shorten this process chain, we are investigating whether electrical impedance spectroscopy (EIS) enhanced by a classifier based on support vector machines (SVM) can be applied to the problem of microplastics detection. Results with suspensions of polypropylene (PP) and polyolefin (PO) in deionized water proved promising: The relative permittivities extracted from measured impedances agree with literature data. The subsequent classification of measured impedances by SVM shows that the three classes “no plastic”, “PP”, and “PO” can be distinguished securely and that the microplastics concentration can be estimated quantitatively. We conclude that machine-learning-enhanced EIS (MLEIS) appears to be a promising approach for in-situ microplastics detection and certainly warrants more research activities.

1 Introduction

Microplastics are plastic particles ranging in size from 1 µm to 5 mm [1]. As plastic production has been growing by about 8.7 % every year since the 1960s and at the same time the plastic is not recycled for a number of reasons, 8 million metric tons of plastic now enter the oceans every year [2, 3]. As a consequence, plastic particles are increasingly found in human food [4] and subsequently in the human body [3-5]. To be able to control the microplastic concentration in the environment and to keep it as low as possible, one must be able to measure the concentration. The state of the art for this is to take water and soil samples and to analyze them in batches, usually in laboratories.

To date, expensive, time-consuming, and material-intensive measurement methods like Raman spectroscopy or FTIR spectroscopy are necessary to investigate water bodies [6]. Easily applicable, cost-effective and yet reliable in-situ measurement methods are not available in practice [7]. Here, we address the application of electrical impedance spectroscopy (EIS) as a cheap, fast, and simple measurement method and its suitability for in-situ microplastics detection.

In some cases, it may suffice to detect the presence of plastics without actual concentration measurement; in other cases, it may be necessary to quickly determine the microplastics concentration quantitatively. The first task calls for mere classification rather than measurement. A classification method known from machine learning and based on statistical analysis is the support vector machine (SVM). As it can also be used for regression, it was deemed suitable for evaluation of EIS data [8]. We therefore investigated the performance characteristics of EIS enhanced by SVM in the context of in-situ microplastics detection and concentration measurement. It is our goal to shed light on the merits and drawbacks of such a machine-learning-enhanced EIS variant (MLEIS).

2 Measurement setup

We worked with suspensions of two types of plastics, polypropylene (PP) and polyolefin (PO), in deionized water. The aim was to find out how well the MLEIS approach is able to determine (i) the presence of microplastics in the sample, (ii) the type of particles present, and (iii) the microplastics concentration. A cylindrical capacitor was used as a measuring cell as shown in Fig. 1 (height: 10 cm; electrode spacing: 0.6 cm; electrode material: aluminum). The space between the electrodes was filled with deionized water, to which PP or PO particles were added in steps of 1 g. The electrodes were contacted via two RG 174 AU coaxial cables.

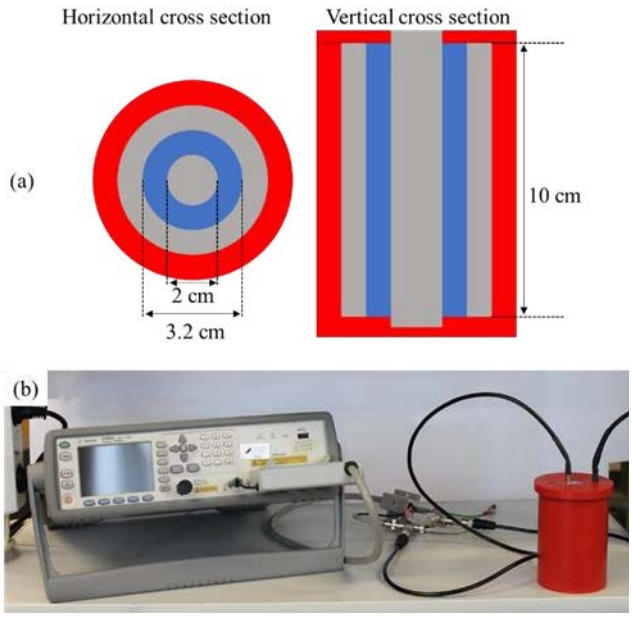

Figure 1. Measurement setup. (a) Scheme of the measuring cell [9]. (b) Photograph of the physical setup.

ISBN 978-3-8007-5835-7

Impedance spectra were recorded with Agilent's LCR meter E4980A [10] in a frequency range from 20 Hz to 2 MHz (200 measurement points per frequency sweep, measuring time per frequency sweep: approx. 1 min). The measurement itself was controlled by a LabView program on a PC, which was connected to the LCR meter via a USB cable. The apparent impedance $|\underline{Z}|$ and the impedance phase φ were recorded at each frequency point. The cell was filled three times with each suspension, or material under test (MUT). Each filling was measured five times impedimetrically. This resulted in 15 repeated measurements per MUT. A completely filled measuring cell held about 49 g of water. With the addition of 10 g PP or PO it respectively contained 30.3 g and 26.3 g of water to completely fill the inter-electrode gap. MATLAB was used for the signal and data processing.

3 Measurement data analysis

3.1 Plausibility of measured impedances

The plausibility of the obtained impedance spectra was checked by determining the relative MUT permittivity ε_r at a frequency of 100 kHz. To obtain ε_r, the empty theoretical capacitance $C_{e,t}$, the empty measured capacitance $C_{e,m}$ and the filled measured capacitance $C_{f,m}$ of the measuring cell are required. The values for $C_{e,m}$ and $C_{f,m}$ were determined from the respective measured $\underline{Z}$ [11]:

$$\underline{C}(\omega) = \frac{1}{j\omega\underline{Z}(\omega)} . \qquad (1)$$

It was assumed that the fringing fields at the capacitor ends are approximately constant, independent of the material filling of the measuring cell. Their influence could then be modelled by a constant capacitance parallel to the actual measuring cell capacitance. The value for ε_r follows by

$$\varepsilon_r = \frac{C_{f,m} - C_{e,m} + C_{e,t}}{C_{e,t}} . \qquad (2)$$

With each microplastics concentration, the mean permittivity observed in the 15 repeated measurements was computed. The results also serve to validate the EIS setup. Pure deionised water has an ε_r of approx. 78.2 in the investigated frequency range [12]. Plastics have a relative permittivity between 2 and 3 [13]. With increasing plastics content, ε_r should therefore decrease from the initial value of 80. This assumption is confirmed by the experimental findings presented in Fig. 2. A linear dependence between ε_r and the added plastic mass is observed for both PP and PO suspensions.

3.2 Impedance locus as function of PP or PO concentration

As usual, the measured impedance spectra are visualized as locus in the complex impedance plane (Nyquist-type diagram) [14]. Figure 3 presents the mean curves that were obtained from the 15 repeated measurements. A certain systematic trend is clearly visible. In general, as the amount of plastic in the mixture increases, the radius of the

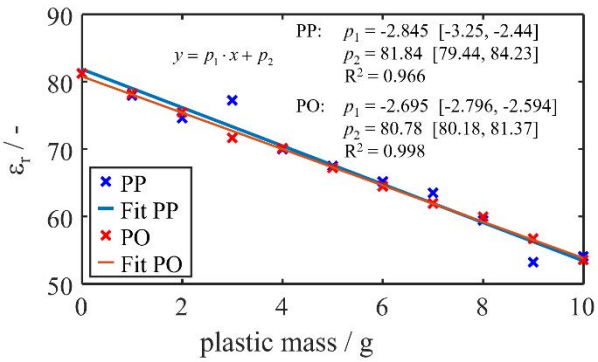

Figure 2. Measured changes in relative permittivity ε_r due to the addition of plastics (symbols) and linear fits (lines). Based on impedances measured at 100 kHz.

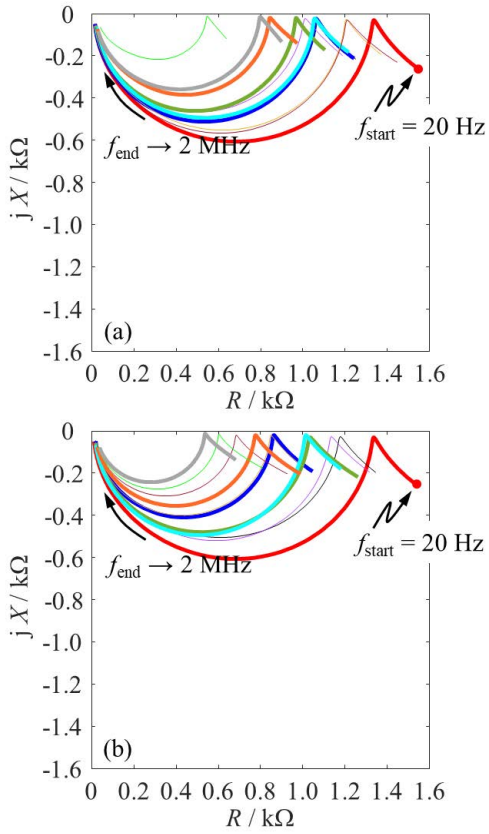

Figure 3. Measured mean impedance locus for (a) PP and (b) PO in deionized water. The colors indicate the plastic mass content in the measuring cell: 0 g (red, bold), 1 g (black), 2 g (blue, bold), 3 g (violet), 4 g (green, bold), 5 g (yellow), 6 g (turquoise, bold), 7 g (burgundy), 8 g (orange, bold), 9 g (light green), and 10 g (gray, bold).

quasi-semicircle of the impedance locus decreases. However, this trend is not unique for each mixture, which makes it difficult to unambiguously assign a plastic concentration to each curve. In field environments, the disturbing influence of, e. g., salinity, temperature fluctuations, mineral particles etc. would render the situation even more complicated. One concludes that classical signal processing of the impedance locus would not allow one to estimate the plastic concentration, at least not with the practically required

ISBN 978-3-8007-5835-7

insensitivity to influence quantities. This motivates the investigation of machine learning methods, specifically SVM, as signal processing tools for microplastic-dependent impedance spectra.

3.3 Classification and regression results

A first SVM classifier was implemented to determine whether microplastics are present and, if so, what type (PP or PO). Subsequently, in case the presence of microplastics is detected, a regression is performed by a second SVM stage to determine the concentration (Fig. 4).

The measured impedance spectra—200 triples of the form $(|\underline{Z}|_i, \varphi_i, f_i)$ with f_i being the i-th measurement frequency—serve as input data to the SVM. A Gaussian function was used as the SVM kernel and a "one-vs-one" approach was selected to enable the discrimination of three classes [6]. The box constraint is derived from the cost parameter C and was set at the default setting of 1, as this prevents overfitting [7]. We used the tools "Classification Learner" and "Regression Learner" from the Deep Learning Toolbox in Matlab 2021a [15].

We followed a two-step strategy to generate the regression SVMs. In the first step, the parameter values were the same as the ones used by the classification SVM. As this did not lead to optimum regression results, the parameter values were then modified to improve the situation. Table 1 summarizes the final (optimum) parameter values for the three SVMs (classifier, PP content estimator, and PO content estimator).

70 % of the measurement data were used to train the SVMs. With the remaining 30 % of the data, the generated SVM system was tested. A 10-fold cross-validation was also carried out with the training data.

Table 2 lists the obtained results. The correctness of the SVM classification, defined as the proportion of correctly assigned class memberships (no plastic, PP, and PO), exceeds 90 %. This is convincing, but of course it also means that the classifier is wrong in almost 10 % of the cases. Whether or not this is acceptable in practice cannot be decided once and for all—it is a matter of judgement.

Table 1. Parameterization of the three SVMs. C-SVM and R-SVM respectively denote classification and regression SVMs.

Parameter	C-SVM 1	R-SVM 2a	R-SVM 2b
Model type	Fine Gaussian	Polynomial	Fine Gaussian
Cross-validation	10-fold	10-fold	10-fold
Kernel	Gaussian	2. polynomial	Gaussian
Box constraint level	1	78.9293	681.8977
Kernel scale mode	Automatic	1	972.764
Epsilon mode	-	0.007596	0.02625
Multiclass method	One-vs-One	-	-
Standardize data	True	True	False

Table 2. Performance characteristics of the generated SVM.

	Classification correctness / %	R^2 of regression	
		PP	PO
Validation	90.05	0.96	0.97
Test	91.49	0.99	1.00

The goodness of the SVM regression, defined as the coefficient of determination R^2 between the true and the estimated microplastics content, is above 0.96. Such a value is usually considered very good.

The overall high goodness of the classification and estimation results suggests that MLEIS can be a powerful tool. At least in the case considered, SVMs help to evaluate EIS data that at first glance do not reveal unambiguous systematics.

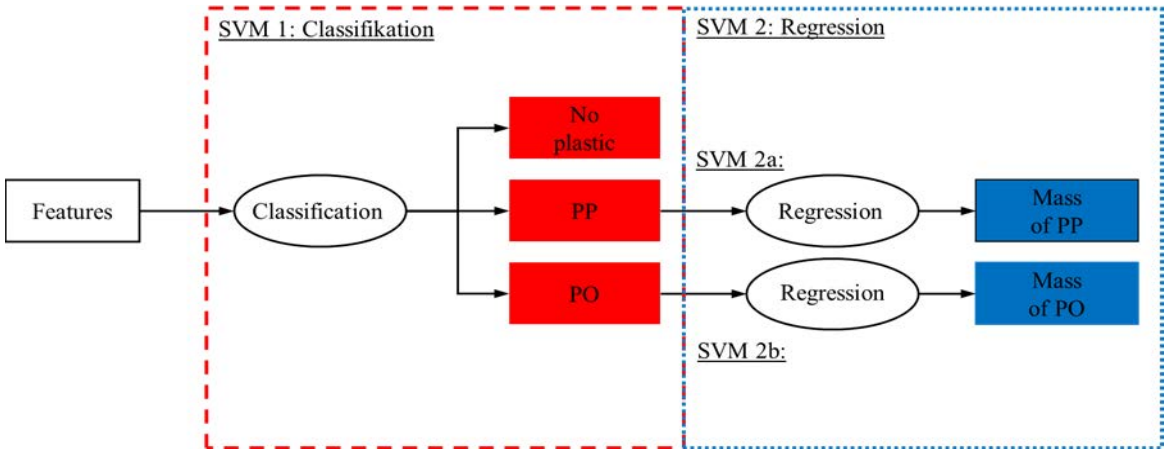

Figure 4. Schematic representation of the SVM cascade. A first SVM classifies the incoming data into three classes (subsystem with dashed red frame). This is followed by a regression SVM for each of the two classes PP and PO (subsystem with dotted blue frame). The mass of the respective plastic in the water-plastic mixture is the output variable.

4 Conclusion

With EIS, a possible alternative measurement method is available in the field of microplastics detection, which is fast and relatively inexpensive compared to the current conventional laboratory analysis methods. Measurements indicate that it is suitable for the task in principle in that impedance spectra show many features varying with the microplastics content in aqueous solutions. Whether this feature richness can be used to unambiguously estimate concentrations from the impedance spectra is not easy to decide. Nyquist plots do not reveal such unambiguous relationships at first glance. This is especially true when influence quantities affect the measurements.

We could demonstrate that the situation improves when machine learning methods are used to process the impedance spectra. The results listed in Table 2 justify our hope that EIS as a measurement method in combination with SVM-based classification and estimation is suitable for the rapid in-situ monitoring of microplastics in water.

Based on these encouraging results, the effects of influence quantities such as water conductivity and temperature and the path from static to dynamic MLEIS will be investigated in the future.

5 Literature

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