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# Influence of Dispersant and Surfactant on nZVI Characterization by Dynamic Light Scattering †

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**Abstract:** The agrifood industries generate tremendous amounts of waste, with the valorization of these wastes being of the utmost importance. The aim of this work was to synthesize green zero-valent iron nanoparticles (nZVI) using hydromethanolic extracts of spent coffee grounds (SCGs) and post-distillation residues of *Cistus ladanifer* L. leaves (CLL). The synthesized nZVI were then analyzed by dynamic light scattering (DLS), and their size, polydispersity index (PDI), and zeta potential (ZP) were determined. Different dispersants (water and methanol) and the impact of a surfactant (Tween® 20) were tested for DLS analysis. nZVI dispersed in water and added with Tween® 20 displayed lower agglomeration, particle size, and PDI, but higher ZP than nZVI without the addition of surfactant and methanolic suspension. These results provide further insight into the applicability of surfactants in nZVI characterization.

**Keywords:** nZVI; green synthesis; Tween® 20; DLS



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## 1. Introduction

The remediation of water and soils contaminated with toxic chemicals has become a high priority. Zero-valent iron nanoparticles (nZVI) have been extensively studied due to their ability to remove different types of contaminants [1]. Typically, nZVI are synthesized by chemical techniques, using sodium borohydride (NaBH4) [2]. These nZVI are highly reactive but tend to agglomerate due to van der Waals forces [3]. Green synthesis is an environmentally friendlier synthesis process, using plant extracts instead of toxic chemicals [4]. The phenolic compounds and other compounds, such as caffeine, are responsible for the stabilization of nZVI and serve as a reducing and capping agent [5,6].

The agrifood sector generates significant waste, highlighting the growing importance of effectively valorizing these materials.

The coffee industry generates around 6 million tons of spent coffee grounds (SCGs) annually [7]. *Cistus ladanifer* L. (CLL), commonly known as labdanum or rockrose, is a plant widely distributed in the Mediterranean area, used in the perfume industry and for its medicinal properties [8]. Essential oils are typically extracted, with the rest of the plant being considered waste [9].

These residues have been reported as a source of phenolic compounds and can therefore be used as starting materials for the green synthesis of nZVI. Fernandes et al. [10]

obtained hydromethanolic extracts with total phenolic content (TPC) for SCGs and CLL of 134.64 ± 64 and 175.24 ± 21.82 mg gallic acid equivalent (GAE)/g dw, respectively. Pavlović et al. [11] obtained extracts from SCGs with a TPC of 398.95 mg GAE/g extract with microwave-assisted extraction (MAE), using a 80:20 H2O:EtOH (*v*/*v*) solution under just 40 s of microwave radiation (80 W). Andrade et al. [12] produced extracts from *C. ladanifer* plant and described a TPC of 334.46 ± 31.83 mg GAE/g in acetone extract and 255.19 ± 7.12 mg GAE/g in ethanolic extract.

nZVI have significantly large surface areas, and high reactivity, which are responsible for their capabilities in contaminant degradation reactions [13]. They also do, however, display a great tendency of agglomeration and sedimentation and limited mobility in aquatic environments [14]. Much research has been performed in ways to combat these issues, as well as to ensure nZVI stability and enhanced remediation activities [13,14]. The use of a surfactant has been a potential solution to some of these problems [15].

Here, green nZVI were synthesized from SCGs and from CLL post-distillation residues, and the influence of the dispersant (water or methanol), as well as the use of a surfactant (Tween® 20) on the characterization by dynamic light scattering (DLS) and zeta potential (ZP) were studied.

## 2. Materials and Methods

### 2.1. Samples

Coffee (*Coffea arabica* L. and *Coffea robusta* L. blend, 50:50)-spent coffee grounds (SCGs) were graciously donated by MoCoffee Europe (Azambuja, Portugal). Labdanum (*Cistus ladanifer* L.) leaves (LL) were kindly donated by Naturalness Essential Oil Distillery (Louriçal do Campo, Portugal). Samples were grinded, dried in a dehydrator under 41 °C until less than 10% moisture, and stored in the dark until further use.

### 2.2. Extract Preparation

Extractions were performed by using a solid:solvent ratio of 1:50 g sample/mL solvent (50:50 *v*/*v* $H_2O$:MeOH), 40 °C, 1 h. After extraction, extracts were filtered, and solvents were evaporated using a rotary evaporator. Afterwards, the samples were redissolved in 50:50 *v*/*v* $H_2O$:MeOH to a concentration of 10 mg/mL.

### 2.3. nZVI Synthesis

nZVI were synthesized by mixing 1 mL of SCGs or CLL extract with 100 µL $FeCl_3$, under rotation (100 rpm, 15 min). Solvents were evaporated in a dehydrator at 41 °C.

### 2.4. Dynamic Light Scattering Analysis

DLS analysis were carried out in a NanoZS (Malvern Instruments, Ltd., Worcestershire, UK) to determine nZVI size, distribution (polydispersity index—PDI), and ZP. nZVI were dispersed in ultrapure water or methanol (1:5 mg nZVI/mL solvent), and ultrasonication (10 min) was used to disperse the nZVI uniformly. Tween® 20 (0.2%) was used as a surfactant. Samples were transferred to Malvern DTS1061 cuvettes and 3 cycles of 10 runs each were applied for size and PDI measurements. For ZP, 5 cycles of 10 runs each were used. Zetasizer Software version 7.11 was used, which calculates hydrodynamic diameter from the fluctuation of intensities. The calculation is made using the Stokes–Einstein equation.

### 2.5. Statistical Analysis

The results are presented as the mean ± standard deviation based on a minimum of three replicates. An ANOVA with a Tukey post hoc test was conducted to compare nZVI

size, PDI, and ZP of different samples using GraphPad Prism (version 8.0.1). Statistical significance was set as $p < 0.05$.

## 3. Results

The results for DLS analysis are presented in Table 1.

**Table 1.** Size, PDI, and ZP of the synthesized nZVI.

| Sample | Size (nm) | Intensity (%) | PDI | ZP (mV) |
|---|---|---|---|---|
| SCG met | $514.30 \pm 135.39^{c}$ | 100 | $0.43 \pm 0.08^{b}$ | $-6.72 \pm 2.76^{c}$ |
| SCG met T | $2112.33 \pm 483.02^{a}$ | 90.1 | $0.52 \pm 0.14^{a,b}$ | $-4.23 \pm 0.19^{b,c}$ |
| SCG w | $565.60 \pm 80.84^{c}$ | 73.8 | $0.56 \pm 0.08^{a}$ | $-19.57 \pm 0.95^{d}$ |
| SCG w T | $14.64 \pm 0.76^{c}$ | 81.5 | $0.24 \pm 0.07^{b}$ | $-5.99 \pm 1.71^{c}$ |
| CLL met | $1552.00 \pm 167.77^{a,b}$ | 100 | $0.66 \pm 0.03^{a,b}$ | $17.48 \pm 0.47^{a}$ |
| CLL met T | $1436.00 \pm 340.99^{b}$ | 95.8 | $0.29 \pm 0.08^{b}$ | $-0.82 \pm 0.12^{b}$ |
| CLL w | $218.07 \pm 43.02^{c}$ | 84.0 | $0.43 \pm 0.08^{b}$ | $-4.30 \pm 1.75^{c}$ |
| CLL w T | $13.4 \pm 4.26^{c}$ | 86.4 | $0.31 \pm 0.04^{b}$ | $-5.51 \pm 0.86^{c}$ |

Abbreviations: CLL—*Cistus ladanifer* leaves; met—methanol; SCG—Spent coffee ground; T—Tween® 20; w—water; different superscript lowercase letters in the same column means statistically significant differences at $p < 0.05$.

For the SCGs, water and methanol samples displayed similar particle size when no surfactant was added. The addition of the surfactant, however, resulted in nZVI with increased average size in the methanolic suspension ($p < 0.0001$) but lower particle size in the aqueous suspension, although no statistical difference was found. In the labdanum samples, the methanolic suspension showed a slight decrease in mean particle size when the surfactant was added, while in the aqueous suspension, the average particle size decreases without statistical difference. The intensity obtained is very high in nearly every sample, with the exception of SCG w. The PDI was lower in the samples where the surfactant was used, which indicates the successful prevention of excessive agglomeration. The addition of the surfactant resulted in an increase in the ZP in the SCGs, particularly in the aqueous suspension ($p < 0.0001$). In the labdanum samples, the ZP of the methanolic suspension decreased significantly ($p < 0.0001$), while in the aqueous sample, no significant difference was found.

## 4. Discussion

The choice of dispersant can severely impact nanoparticle stability and DLS analysis. Therefore, both methanol and water were assessed as dispersants for nZVI. Methanol is less polar than water and displays lower viscosity. These can influence the interactions with the nZVI, resulting in systems with different characteristics [16,17]. The CLL methanolic suspension and the SCG met T samples displayed very high particle sizes, which indicate the presence of large agglomerates. While the use of the surfactant in the aqueous suspensions resulted in lower particle sizes, which suggest that agglomeration did not happen in these samples, the same could not be said for the methanolic suspensions, suggesting that for these nZVI, water is the better dispersant. One of the limitations of DLS is that even a few large particle sizes can mask many small particles [18]. Therefore, the intensity % is close to 100% in the methanolic dispersions with large particle sizes, as shown in Table 1. The aqueous dispersions display slightly smaller percentages in intensity, although the displayed size is still the most significant peak. Significant differences were found for ZP, both for the dispersant and surfactant. This was especially so in the aqueous SCG, where ZP changed from $-19.57 \pm 0.95$ to $-5.99 \pm 1.71$ mV, when the surfactant was added. For the CLL methanolic suspension, ZP changed from $17.48 \pm 0.47$ to $-0.82 \pm 0.12$ mV with the addition

of the surfactant. Typically, dispersions with ZP between ±0 and 10 mV are considered unstable, between ±10 and 20 mV being relatively stable, while values between 20 and 30 mV are considered moderately stable, and ± 30 mV being highly stable. This has been disputed, as ZP depends on van der Waals attractive forces, as well as electrostatic repulsive forces. While ZP provides information on the latter, it does not provide information on the former. It is not uncommon to find stable dispersions with low ZP and vice versa [17]. Several previous studies assessed the influence of the addition of surfactants and stabilizers on DLS measurements. For instance, Mahmoud et al. [19] synthesized nZVI from cloves and green coffee. The synthesized nZVI were analyzed by DLS and displayed size distributions of 892 and 1884 nm, as well as PDI of 0.263 and 0.563, for clove and green coffee, respectively. The ZP of the nZVI was −43 and −30 mV, respectively. Ruiz-Torres et al. [20] synthesized nZVI in a non-aqueous reduction medium, with methanol as solvent, in an attempt to reduce size distribution and increase nZVI stability, by reducing oxidation. The authors also used ethylene glycol (EG) as a stabilizer. The DLS results indicated a particle size of 6.5 and 265.1 nm in EG-stabilized and non-stabilized nZVI, respectively. Furthermore, the ZP was 16.3 and −13.0 mV, respectively. This corroborates the influence of the surfactant on the ZP of the synthesized nZVI. Kocur et al. [21] assessed the viability of nZVI stabilized with sodium carboxymethylcellulose (CMC) in a field scale test. nZVI were successfully transported 1 m to a monitoring well, and DLS analysis of the nZVI size changed from 624.8 nm to 562.9 nm 1 day after injection. Ibrahim et al. [22] synthesized CMC-stabilized nZVI under different pH and ionic strength (IS) of the background electrolyte solution. The hydrodynamic size of the nZVI ranged between 131.2 ± 12.5 nm and 71.3 ± 8.5 nm, with pH 7 resulting in lower particle size, and IS decreasing from 0.01 to 0.001 resulted in a size decrease from 76.1 ± 9.4 nm to 71.3 ± 8.5 nm. The ZP was also assessed, ranging from −16.8 ± 1.2 mV in the pH 5, IS 0.01 sample, to −20.3 ± 0.9 mV in the pH 7, IS 0.001 sample. Soukupova et al. [15] stabilized nZVI with Tween® in a highly concentrated aqueous dispersion (20% (*w*/*w*)) and analyzed the stability of the nZVI. The modified nZVI displayed far lower aggregation behavior than the bare nZVI, with the latter increasing in mean size from 300 nm to 650 nm after 70 days, while in the former, the average size remained almost constant. Moura et al. [23] synthesized nZVI using rhamnolipids of microbial origin as a stabilizer. The green nZVI were synthesized by either adding the rhamnolipids prior to nZVI synthesis (1) or by immersing the synthesized nZVI in a solution with rhamnolipids (2) after synthesis. The nZVI displayed mean particle sizes of 42, 50, and 60 nm. These correspond to method 2, bare nZVI, and method 1, respectively. Furthermore, the ZP was also analyzed, with bare nZVI displaying the highest value (37.2 mV), followed by method 1 and method 2 (35.1 mV and 6.3 mV, respectively). Despite the lower ZP result, the authors stated that the coating of the magnetic core by the rhamnolipids resulted in a compound with steric stability.

## 5. Conclusions

The type of dispersant and the use of a surfactant can have a significant impact on the characteristics of synthesized nZVI. Here, the use of Tween® 20 in aqueous and methanolic dispersions was assessed. Aqueous dispersion, with Tween® 20, resulted in lower average particle size (decreasing from 565.60 ± 80.84 nm to 14.64 ± 0.76 nm and from 218.07 ± 43.02 nm to 13.40 ± 4.26 nm in SCG and CLL, respectively) and lower PDI (decreasing from 0.56 ± 0.08 to 0.24 ± 0.07 and from 0.43 ± 0.08 to 0.31 ± 0.04 in SCG and CLL, respectively). The use of a surfactant can also greatly impact the ZP, as seen in the aqueous dispersion of SCG, where ZP increased from −19.57 ± 0.95 mV to −5.99 ± 1.71 mV, and methanolic CLL dispersion, where ZP decreased from 17.48 ± 0.47 mV to −0.82 ± 0.12 mV.

This study provides further information into the optimization of synthesis and analytical measurements of green nZVI.

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