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Green zero-valent iron nanoparticles synthesised using herbal extracts for degradation of dyes from wastewater

Emilio Rosales[a,b,*], M. Ángeles Sanromán[b], Celia Dias-Ferreira[a,c]

[a]*Research Centre for Natural Resources, Environment and Society (CERNAS), College of Agriculture, Polytechnic Institute of Coimbra, Bencanta 3045-601 Coimbra, Portugal, Tel. +351 239 802 940; Fax: +351 239 802 979; email: celia@esac.pt (C. Dias-Ferreira)*
[b]*Department of Chemical Engineering, University of Vigo, Isaac Newton Building, Campus As Lagoas, Marcosende 36310, Vigo, Spain, Tel. +34 986 812 304; Fax: +34 986 812 380; emails: emiliorv@uvigo.es (E. Rosales), sanroman@uvigo.es (M.A. Sanromán)*
[c]*Materials and Ceramic Engineering Department, CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

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ABSTRACT

Nano zero-valent iron (nZVI) is an effective way to degrade different compounds. The green synthesis of nZVI showed potential as an alternative to $NaBH_4$ synthesised nanoparticles. In this study, a comparison among different nanoparticles (green, bare and polyacrylic acid coated) was carried out. Based on the higher stability of green nanoparticles, new extracts obtained from herbal aromatic leaves (rooibos, lemon verbena and camphora) were evaluated for the synthesis of nZVI. Two different extraction procedures were compared: decoction and infusion. The results showed that using a constant temperature of 100°C during the extraction increases the quantity of polyphenols and antioxidants extracted. The antioxidant content was highest in green tea (*Camellia sinensis*), but reactivity of synthesised nanoparticles of zero-valent iron is higher when using rooibos (*Aspalathus linearis*) extracts. Synthesised rooibos green nZVIs have been applied to degrade a textile dye, Reactive black 5, directly and as catalyst in an electro-Fenton process, reaching a decolourisation of 90% and 70% in 60 min, respectively. The synthesised nanoparticles demonstrated a good performance in the treatment of the polluted wastewater.

Keywords: Green nZVI; Rooibos; Nanoparticles; Lemon verbena; Dye; Fenton; Zero-valent iron; Green synthesis

1. Introduction

Nanoparticles of zero-valent iron (nZVI) have attracted much attention for their potential to treat and degrade various soil contaminants, e.g., chlorinated compounds and pesticides. The use of nZVI in environmental remediation is increasing.

Production of nZVI has been tackled from different approaches: mechanical [1,2] or chemical [3]. One of the most common chemical processes is the synthesis using sodium borohydride ($NaBH_4$) [4,5]. However, the production of nZVI from $NaBH_4$ shows some disadvantages such as high cost and toxicity of iron nanoparticle production due to costly reagents, the generation of unsafe flammable gas (H_2) by-products, toxicity of sodium borohydride, tendency to form agglomerates and rapid oxidation of iron nanoparticles [6–8].

To overcome these problems, the synthesis of nZVI requires a different approach. The use of safer solvents and auxiliaries helps to design safer and greener nZVI alternatives.

These solvents and chemical products should be chosen to perform their desired function while minimizing their toxicity and cost. Moreover, the high reactivity with side

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* Corresponding author.

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reactions (Eqs. (1) and (2)) and the lack of stability of the nZVI requires a different approach.

$$2Fe^{0}_{(s)} + 4H^{+}_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \tag{1}$$

$$Fe^{0}_{(s)} + 2H_2O_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^{-}_{(aq)} \tag{2}$$

Nanoparticles have an alternative green synthesis process using natural products with high phenolic content and antioxidant capacities such as extracts of grape marc, black tea or vine leaves [7,9,10]. Among them, the use of tea extracts is highlighted due to the high concentration of caffeine/polyphenols. It is known that phenolic compounds or polyphenols have been extensively used in the food industry being labelled as "green" materials. In addition, the chemical activity of polyphenols in terms of reducing properties (as hydrogen or electron-donating agents) envisages their potential action as free-radical scavengers (antioxidants) and their capacity to act as reducing agents. More recently, polyphenols have been employed in the production of green nZVI (G-nZVI) [10–13]. According to these authors, the formation of Fe nanoparticles with polyphenols takes place via the following steps: polyphenol complexation with Fe, simultaneous reduction of Fe and capping with oxidised polyphenols. In addition to a greener synthesis process, several drawbacks such as nanoparticle aggregation and deposition are reduced by nZVI surface modification, as the polyphenol coating provides stability, biodegradability and water solubility. The use of different coating agents has been widely studied in the literature to reduce the aggregation effect and increase the stability of nZVI. The selected approach also presents an alternative to frequently used coating agents like polyacrylic acid (PAA) sodium salt that have been widely used in the coating of the nanoparticles [4,5].

So far, only few studies have been developed using these greener nZVI in order to treat different pollutants. G-nZVI have been tested as Fenton catalyst to treat dyes [9,14], used directly for the removal of chromium in an effluent [11,15] and for the degradation of pharmaceutical compounds [7].

The aims of this work are: (1) to ascertain the efficiency of G-nZVI in comparison with bare and PAA-coated nZVI (P-nZVI); (2) to evaluate the extraction of polyphenols contained in different herbal aromatic extracts and (3) to test the potential of different polyphenol sources in the synthesis of the nZVI. Finally, the ability of the new G-nZVI directly and as catalyst for remediating a wastewater polluted with a model organic pollutant will be tested.

2. Experimental procedure

2.1. Reagents

Sodium borohydride (98%), PAA sodium salt 45 wt%, barium chloride and sodium alginate were purchased from Sigma-Aldrich (Germany), iron chloride hexahydrate was obtained from Merck (Germany) and hydrochloric acid (37% w/w) was purchased from Panreac (Spain). Reactive black 5 (RB5) was obtained from Aldrich and its structure and properties are shown in Table 1. All the chemicals used in the experimental procedures were reagent grade.

2.2. Herbal leaves

Green tea (GT; *Camellia sinensis*) and rooibos (RO; *Aspalathus linearis)* were obtained from commercial shops. Lemon verbena (LV; *Aloysia citrodora*) and camphora (CA) leaves (*Cinnamomum camphora*) were collected at Escola Superior Agraria de Coimbra (Portugal).

2.3. Polyphenol extraction procedure

In order to extract the polyphenols of the aromatic leaves, 6 g of leaves were added to 300 mL of distilled water. Two different extraction procedures were used: decoction and infusion. In the decoction extraction, the leaves were boiled for 5 min at 100°C, while in the infusion extraction the leaves were immersed in water at 80°C for 5 min. The obtained extracts were then filtrated/centrifuged before further use. The extract's pH was measured with a COMSOL pH meter (C830) before being used in G-nZVI synthesis.

2.4. Synthesis of zero-valent iron nanoparticles and characterisation

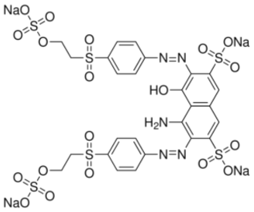
2.4.1. Green nZVI

The synthesis of the green nanoparticles was done according to Hoag et al. [9]. A solution of iron chloride hexahydrate, 0.1 M, was mixed with the different extracts solutions with a ratio 2:1 in volume. The obtained nanoparticles were centrifuged and washed three times with ethanol and distilled water prior to use.

2.4.2. Bare nZVI

The synthesis of bare nanoparticles was performed according to Wang and Zhang [16] by the reduction of iron

Table 1
Dye class, chemical structure, concentration used and wavelength at maximum absorbance of RB5

Dye	Reactive group	Structure	λ_{max} (nm)	Concentration (mg/L)
Reactive black 5 (RB5)	Vinylsulfone (diazo-dye)		597	100

chloride hexahydrate solution, 13.5 g/L with sodium borohydride, 10.63 g/L. The sodium borohydride solution was pumped (6.8 mL/min) into an iron chloride hexahydrate solution, and the mixture was mechanically mixed (200 rpm) until all the sodium borohydride was added. The obtained nanoparticles were centrifuged and washed three times with ethanol and distilled water prior to use.

2.4.3. PAA-coated nZVI

The coated nZVI particles were made in one single step based on Kanel et al. [5]. A solution containing 32.5 g/L of iron sulphate heptahydrate and 6 g/L of PAA was prepared with distilled water, previously purged with N_2. Then, sodium borohydride solution 40 g/L was pumped into the previously prepared solution at 25 mL/min. The mixture was mechanically mixed (300 rpm). The obtained nanoparticles were centrifuged and washed three times with ethanol and distilled water prior to use.

2.4.4. nZVI alginate gel beads

A new catalyst based on the green generation of nZVI in iron immobilised alginate beads (alg-G-nZVI) was prepared. Initially, iron was supported on alginate hydrogel according to the procedure described elsewhere [17]. Then, the prepared alginate beads were immersed in the corresponding herbal extract for 10 min for the reduction of the iron to take place. Following, the synthesised alg-G-nZVI were washed with distilled water and stored until their use.

2.4.5. Scanning electron microscopy

The produced nanoparticles were analysed by scanning electron microscopy (SEM) and energy-dispersive spectroscopy using a FEI Quanta 200.

2.5. Decolourisation experiments

2.5.1. Direct nZVI decolourisation

The decolourisation experiments were carried out in a cylindrical reactor with a working volume of 0.1 L under magnetic stirring for 1 h. RB5, 100 mg/L, was used to evaluate the decolourisation. Moreover, the effect of the solution initial pH was evaluated by adjusting pH to the considered initial values with HCl or NaOH.

2.5.2. Electro-Fenton and electrochemical decolourisation

The experiments were performed in 250 mL reactor with a working volume of 150 mL and a RB5 concentration of 100 mg/L. Na_2SO_4 (0.01M) was added as electrolyte and the pH was adjusted to 2 with HCl or NaOH. A voltage of 5 V was applied with a power supply using graphite sheet as anode and cathode. G-nZVI or G-nZVI alginate beads (alg-G-nZVI) were added as catalyst in electro-Fenton experiment. In order to favour the H_2O_2 generation continuous saturation of air at atmospheric pressure was ensured by bubbling air (1 L/min) onto the solution.

2.6. Determination procedures

2.6.1. Phenol index at 280 nm

This method comprises a direct measurement of the sample absorbance at a wavelength of 280 nm. Dilutions of the samples were done in order to reach a consistent value.

2.6.2. Total phenol content

The total phenol content of the various extracts was determined using the Folin–Ciocalteu's reagent [18]. The results were expressed in mg of gallic acid equivalents per mL of extract (as mean of three replicates).

2.6.3. Antioxidant activity (ferric reducing antioxidant power)

The ferric reducing antioxidant power (FRAP) of samples was determined by using the potassium ferricyanide–ferric chloride method [19]. The FRAP of the samples was estimated in terms of ascorbic acid antioxidant capacity in $mM/L_{\text{ascorbic acid}}$ (as mean of three replicates).

2.6.4. Nano zero-valent iron reactivity determination

The reactivity of the G-nZVI was evaluated through the produced H_2 gas volume when they react with acid.

A gas volumetric setup was build according to the method described by de Boer [20] and based on Elion and Elion [21]. A vial containing G-nZVI was placed in the setup, and 5 mL of 37% HCl (Panreac) solution was added to the vial through a Sterican (B-Braun, Germany) needle with a 10 mL plastic syringe. The total moles of zero-valent iron were calculated from the volume of water displaced by the hydrogen gas. The displaced water volume is assumed to be equal to the produced H_2 gas volume [21], according to Eq. (3):

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{3}$$

Eq. (3) shows the production of H_2 due to the reaction with an acid. It shows that the total number of H_2 molecules produced is equal to the number of Fe^0 molecules consumed. From the mass of elementary iron in the dried suspension, the weight ratio of nZVI to total iron was calculated. From this ratio, the real concentration of zero-valent iron in the suspension can be determined, and the variation of the Fe^0 concentration is used as an indication of the reactivity.

2.6.5. Dye determination

The dye content was measured spectrophotometrically based on the constructed calibration curves at maximum absorption wavelength (Table 1). The sample was diluted with distilled water if the absorbance exceeded the range of the calibration curve. The results are shown as mean/standard deviation of two replications.

2.6.6. Decolourisation kinetics

The dye concentration profiles permit to evaluate the kinetic behaviour of the reactions. The decolourisation kinetics were evaluated according to the zero-, first- and second-order kinetic model and the regression coefficients were calculated.

3. Results and discussion

3.1. Reactivity with time of different nZVI: bare, PAA-coated and green

Three types of iron nanoparticles: bare nZVI (B-nZVI), P-nZVI and G-nZVI were prepared. G-nZVI were prepared using GA polyphenols as reducing agent. It is commonly known that the reactivity of the synthesised nZVI varies widely with time due to the side reactions that happen when in contact with air or water. For this reason, the variation of the reactivity with time of the different synthesised nanoparticles was studied (considered as concentration of Fe^0 at a given time compared with the initial Fe^0 concentration) and the data are displayed in Fig. 1.

Reactivity of B-nZVI reduces sharply with time, reaching a 40% decrease in 7 d. The absence of coating in theses nanoparticles facilitates their reaction with air and reduces the reactivity due to the oxidation of the iron by side reactions (Eq. (1)). This explanation is also reinforced by the progressive appearance of an external layer of Fe oxide, with the nanoparticle surface changing colour from black to brown/orange. Later, this outer oxide layer may act as a coating oxide which protects the inner of the particles and avoids complete oxidation.

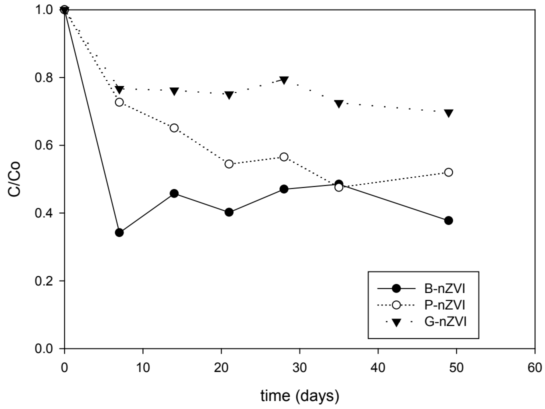


Fig. 1. Evolution of reactivity (concentration of Fe^0/initial concentration of Fe^0) for the synthesised nanoparticles: B-nZVI, P-nZVI and G-nZVI.

P-nZVI showed a higher stability along time than B-nZVI (Fig. 1), with a reduction of reactivity of approximately 50% after 21 d. This means that the longevity of these coated nZVI is higher. Similarly, the reactivity of G-nZVI reduced initially to 80% and then the value remained almost constant during the whole period of the experiment (50 d). The use of coating agents protects the inner surface of the nZVI creating a protective layer that reduces exposition to external conditions and the side reactions. This fact is in accordance with those exposed by Quina et al. [22], who reported that the presence of the coating origins a more disperse nanoparticle distribution that the B-nZVI and the size of nZVI is also smaller for G-nZVI and P-nZVI than for B-nZVI.

The obtained results confirm that B-nZVI need to be synthesised immediately before use to be effective, presenting a short shelf life, whereas coated nZVI (P-nZVI and, especially, G-nZVI) presented a good reactivity along time, allowing their storage and use later on.

3.2. Green nZVI synthesis

According to the results obtained in the previous section, green nanoparticles remain reactive for longer periods and could therefore be an alternative to B-nZVI and P-nZVI. Therefore, the synthesis of green nanoparticles using alternative herbal extracts (other than GA) has been evaluated, as discussed next.

3.2.1. Antioxidants and polyphenols extraction

Four different herbal extracts obtained from GT, RO, LV and CA have been used in the synthesis of the green nanoparticles. Two different extraction systems have been studied: decoction (extraction using boiling water) and infusion. The amount of antioxidants and polyphenols extracted from the aromatic herbs using both processes is shown in Table 2.

Table 2
Total phenolic content of the extracts used in G-nZVI synthesis

Sample	Extraction method	Initial pH	Phenol index (280 nm)	Total phenolic content (mg GAE/L)[a]	Total antioxidants (mg AAE/L)[b]	Synthesis[c]	Fe^0 content
Green tea	Decoction	5.20	103.92	1,280.62 ± 15.06	2,033.56	+	32.41%
(GT)	Infusion	5.23	75.36	1,003.61 ± 19.22			
Rooibos	Decoction	5.13	59.10	234.36 ± 43.49	1,597.34	+	43.47%
(RO)	Infusion	4.87	49.44	188.97 ± 22.92			
Lemon	Decoction	7.18	43.08	191.57 ± 16.50	389.19	+	21.52%
verbena (LV)	Infusion	7.14	27.24	52.82 ± 5.01			
Camphora	Decoction	5.26	15.6	44.39 ± 8.25	–	–	–
(CA)	Infusion	5.20	–	Not detected			

Note: The results are shown as mean/standard deviation of three replications.
[a]GAE = gallic acid equivalent.
[b]AAE = ascorbic acid equivalent.
[c]Successful = "+", failed = "–"; infusion at 80°C for 5 min.

As can be observed in Table 2, the decoction process increases the release of polyphenols contained in the aromatic herbs and the phenol index, with values about 20% higher than those obtained with infusion for GT and RO. It is also remarkable the increase in the phenolic content of the LV in 400% when decoction extraction is used. These results are in good agreement with those reported by Gião et al. [23]. Due to the higher levels of polyphenol obtained using decoction, this procedure was selected for the remaining work.

For the decoction extracts, the highest values of total polyphenols were obtained with the GT extract, reaching values 5 times higher than RO, 6 times higher than LV and more than 24 times higher than CA. However, when the total antioxidants were analysed a significant increase of the extract content was detected for RO. Total antioxidant levels on GT extract were only 1.3 times higher than those detected in RO.

With the different extracts obtained, the addition of a filtration and/or centrifugation process as a previous step in order to remove higher size particles from the extracts was evaluated. Both centrifugation and filtration of the extracts allow improving the synthesis reaction, without any detected effect in the amount of polyphenols or antioxidants available in the extract. As conclusion, and based on the obtained values, it may be possible to use these extracts as reducing agent in the synthesis of G-nZVI.

3.2.2. Green nano zero-valent iron particles synthesis and reactivity/ageing

The previously obtained extracts were then used for the synthesis of G-nZVI. As shown in Table 2, the synthesis process was successful for GT, RO and LV extracts, but did not succeed when CA extracts were used. This fact may be explained by the low total polyphenolic contents and the absence of antioxidants on the CA extract.

The obtained G-nZVI were characterised by SEM microscopy, and Fig. 2 shows the nanoparticles obtained using GT extracts.

The composition of the different synthesised nanoparticles was analysed by energy-dispersive X-ray (EDX) spectroscopy and a homogeneous distribution of the iron was observed when the mapping was done (Fig. 3). Moreover, the results showed the presence of Fe, C, O and Cl in the green capped nanoparticles. Those data are in accordance with the results reported by Paul et al. [24] and Genuino et al. [25].

Finally, the concentration of Fe^0 in the G-nZVI was quantified (Table 2). The higher Fe^0 content was determined when RO extracts were used for the synthesis (43.47%), reaching the lowest value with LV extract (21.52%) and an intermediate value when nanoparticles were synthesised from GT extracts (32.41%).

3.3. nZVI decolourisation studies

3.3.1. Screening of green nZVI

Initially, synthesised G-nZVI particles were directly applied as reducing agents in the treatment of a coloured simulated effluent and the results are presented in Fig. 4.

According to the obtained results, the highest performance was obtained with G-nZVI synthesised using RO extracts, reaching values near 60% in 30 min. LV and GT nZVI showed a decolourisation degree of approximately 36% and 48%, respectively. G-nZVI obtained from RO extract showed the best performance and were selected for further studies and the optimisation of the operational parameters such as pH.

3.3.2. Effect of pH on decolourisation

The results of the decolourisation of RB5 dye at different pH (acidic, slightly basic and basic) using green RO nZVI are depicted in Fig. 5, showing there is a marked increase of the dye decolourisation at lower pH values.

For pH 4.5 the decolourisation efficiency reached almost 90% after 60 min. The obtained results are consistent with those reported by Satapanajaru et al. [26]. These authors obtained a decolourisation degradation of 100% in 120 min using bare nZVI. The use of pH 8.5 and 10.5 lead to a significant decrease in the efficiency of treatment, and the final decolourisation (after 60 min) was approximately 50% and 23%, respectively.

The decolourisation kinetic for pH 4.5 was studied, and the kinetic parameters were calculated based on first-order (Eq. (4)) and second-order (Eq. (5)) kinetics, following the expressions:

$$\mathrm{d}C/\mathrm{d}t = -k_1 \cdot C \qquad (4)$$

$$\mathrm{d}C/\mathrm{d}t = -k_2 \cdot C^2 \qquad (5)$$

where C is the concentration of dye (mg/L); t is the reaction time (min); k_0 is the kinetic coefficient for the order-zero reaction (mg/min/L); k_1 is the kinetic coefficient for the first-order reaction (min^{-1}) and k_2 is the kinetic coefficient for the second-order reaction (L/mg/min).

The obtained rate constant values and the statistical correlation parameters are described in Table 3. As it is shown,

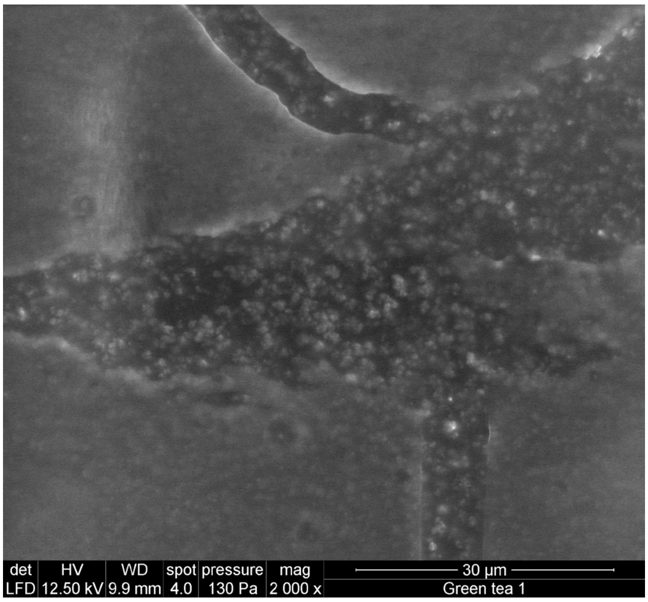


Fig. 2. SEM image of the synthesised green tea coated nanoparticles.

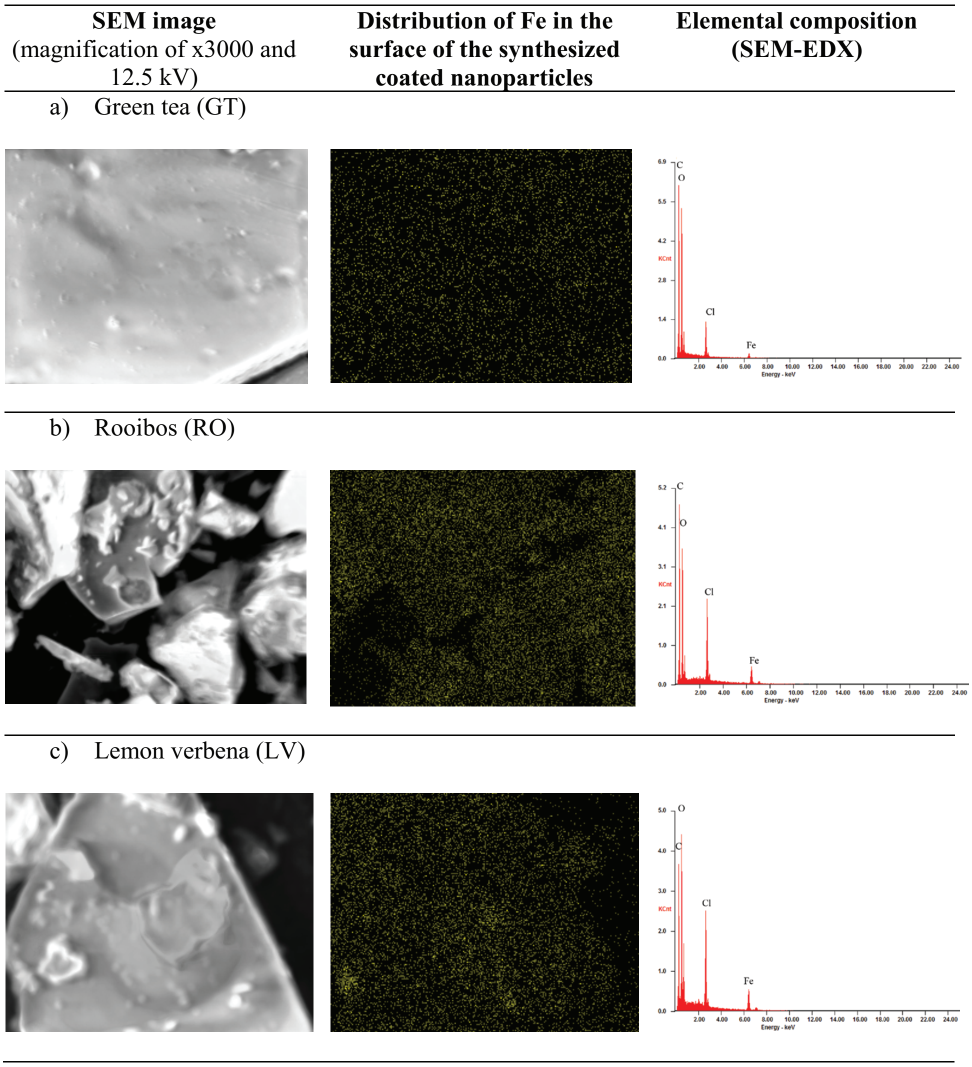


Fig. 3. SEM image, Fe-distribution at the surface and SEM–EDX elemental composition of the three types of synthesised G-nZVI.

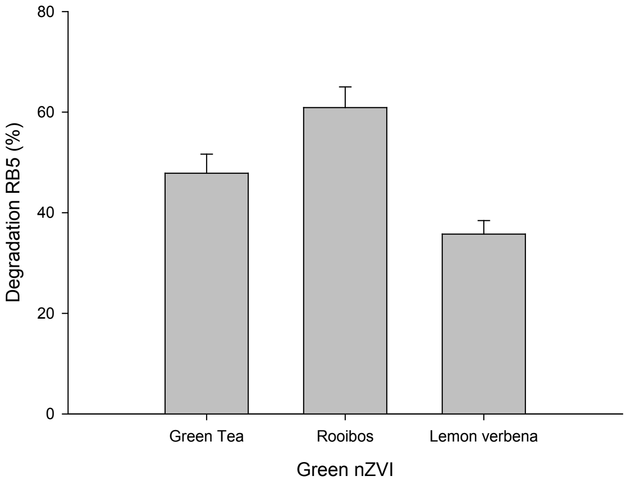


Fig. 4. Direct degradation of RB5 (100 mg/L) using different green nZVI (*t* = 30 min).

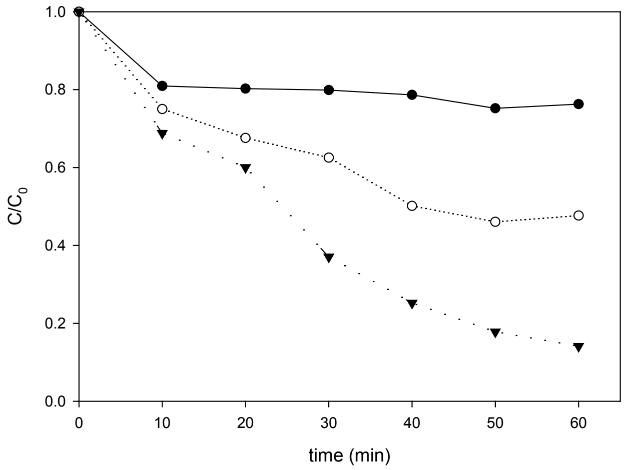


Fig. 5. Effect of time in the direct decolourisation of RB5 (C_0 = 100 mg/L) by rooibos G-nZVI at different pHs: (▼) 4.5, (O) 8.5 and (●) 10.5.

the results indicate that the decolourisation of RB5 at pH 4.5 could be quantitatively described by a first-order-kinetic equation with respect to the dye concentration. These results are in agreement with the reported by Lin et al. [27] for the removal of another dye, AB24, using nZVI.

3.4. Green nZVI as catalyst in electro-Fenton decolourisation studies

An alternative application of the G-nZVI based in RO extract is proposed, consisting in the use of the synthesised RO G-nZVI as catalyst in electro-Fenton process. The synthesised RO G-nZVI presented the advantage of providing two types of Fe (Fe^0 and Fe^{2+}) available for the reactions according to Eqs. (6) and (7):

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + \cdot OH + 2OH \quad (6)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (7)$$

The results of RB5 decolourisation by electro-Fenton and RO G-nZVI are displayed in Fig. 6.

The electro-Fenton process was compared with a reference electrochemical treatment. The decolourisation data showed an increase in the efficiency around 9% at 15 min in comparison with the electrochemical treatment. After 60 min an improvement of 15% in the efficiency of the treatment can be observed when RO G-nZVI was used.

The kinetics of the decolourisation processes were also evaluated and the results are shown in Table 3. In the selected treatments (electrochemical and electro-Fenton) the decolourisation process followed a pseudo-first-order kinetics. It can be observed that the kinetic constant increased 28% when the RO G-nZVI were used as catalyst in electro-Fenton process reaching a value of 0.0235 min^{-1}. The performance of the treatment was therefore improved when the selected RO G-nZVI were used.

3.5. Electro-Fenton treatment using G-nZVI immobilised

Once the feasibility of the RO G-nZVI as catalyst in an electro-Fenton process was demonstrated, the application of the synthesis procedure for the preparation of a heterogeneous catalyst was evaluated. Therefore, the immobilisation of RO G-nZVI in alginate beads was evaluated. Fig. 7 shows the prepared alg-G-nZVI and the reduction of the iron present in the alginate beads by the use of the RO extract.

The decolourisation profiles achieved are shown in Fig. 6. As referred above (section 3.4), an improvement of 15% in the efficiency of the treatment could be observed after 60 min when electro-Fenton treatment was performed using RO G-nZVI as catalyst, compared with standard electrochemical treatment. The results in this section show that heterogeneous catalyst alg-G-nZVI presents a similar decolourisation profile as RO G-nZVI. However, the kinetic constant determined is 0.0215 min^{-1} (pseudo-first-order kinetic model), being therefore, a little lower than that obtained for the RO G-nZVI electro-Fenton treatment. The appearance of diffusional problems in order to generate the powerful ·OH oxidant can be one of the reasons of this constant diminishment. Nevertheless, the use of the immobilised green nanoparticles opens new perspectives in the development of continuous treatments with the possibility of catalyst regeneration using the RO extract, instead of the continuous addition of catalyst required in the other alternative.

4. Conclusions

Different natural extracts presenting high polyphenols contents were evaluated for the synthesis of G-nZVI. RO extracts demonstrated a great potential for the synthesis of

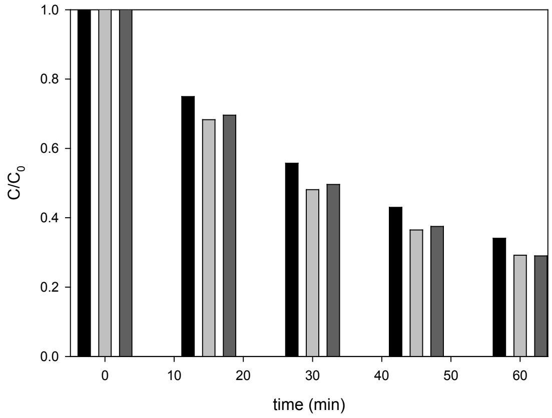


Fig. 6. Comparison of electro-Fenton treatment of RB5 (100 mg/L) using RO G-nZVI 2.68 mM (gray), 2.68 mM alg-nZVI (dark gray) as catalyst and electrochemical treatment (black).

Table 3
Kinetics parameters for RO G-nZVI and electro-Fenton alg-G-nZVI catalysed decolourisation of RB5

Treatment	pH	RB5 concentration (mg/L)	Kinetics	k_i	r^2
RO G-nZVI	4.5	100	First order	0.0315	0.9934
			Second order	0.00089	0.9086
Electrochemical (standard)	2	100	First order	0.0175	0.9962
			Second order	0.00051	0.8970
Electro-Fenton G-nZVI	2	100	First order	0.0235	0.9939
			Second order	0.00037	0.9875
Electro-Fenton alg-G-nZVI	2	100	First order	0.0215	0.9921
			Second order	0.00027	0.8987

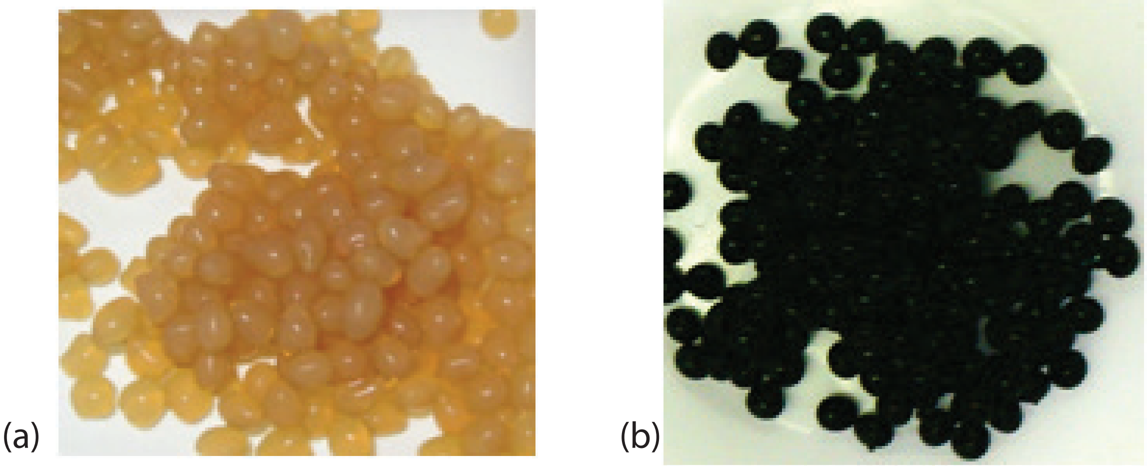


Fig. 7. Green alginate nZVI beads (b) prepared from initial Fe-alginate beads (a).

nano zero-valent iron, increasing the reactivity of the particles in comparison with the more studied GA nZVI. RO application for the treatment of polluted effluents like dyes, directly or as catalyst in Fenton-based process demonstrated to be successful and the obtained results showed an improvement on the performance of this RO G-nZVI in comparison with the more studied GA G-nZVI. Moreover, the immobilisation of the RO G-nZVI in alginate beads was evaluated and the viability of their reuse has been proved. The potential of the new synthesised G-nZVI based on RO extracts to treat effluents polluted with organic compounds has been demonstrated.

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