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Nitrogen activation of carbon-encapsulated zero-valent iron nanoparticles and influence of the activation temperature on heavy metals removal

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Abstract. Nanoparticles of zero-valent iron (nZVI) represent a promising agent for environmental remediation. This is due to their core-shell structure which presents the characteristics of both metallic and oxidised iron, leading to sorption and reductive precipitation of metal ions. Nevertheless, nZVI application presents some limitations regarding their rapid oxidation and aggregation in the media which leads to the delivery of the ions after some hours (the "aging effect"). To address these issues, modifications of nZVI structure and synthesis methods have been developed in the last years. The aging problem was solved by using nZVI encapsulated inside carbon spheres (CE-nZVI), synthetized through Hydrothermal Carbonization (HTC). Results showed high heavy metals removal percentage. Furthermore, CE-nZVI were activated with nitrogen in order to increase the metallic iron content. The aim of this study was to test CE-nZVI post-treated with nitrogen at different temperatures in heavy metals removal, demonstrating that the influence of the temperature was negligible in nanoparticles removal efficiency.

1. Introduction

Urban wastewater contains a variety of organic and inorganic substances from domestic and industrial sources. This means that wastewater reuse is associated with certain risks. Even if toxic materials are not present in concentrations likely to affect humans, they might well be at phytotoxic levels and this would limit their agricultural reuse [1, 2]. Agricultural reuse concerns mainly tertiary treated effluents. However, recent research has shown that micropollutants such as pharmaceuticals, heavy metals and other emerging pollutants are variably removed by wastewater treatments and thus, they can be found in treated wastewater even after advanced secondary and tertiary treatments.

In the last two decades nanoparticles of zero-valent iron (nZVI) have proven to be effective at the sequestration of heavy metals from aqueous solutions [3, 4, 5, 6], thanks to both reducing (metallic iron in the core) and adsorbing (iron oxides in the shell) properties [7]. In general, the states of the metals on the nZVI surface exhibit three distinctive responses, depending on their standard oxidation-reduction potential (E^0) [8]:

- Sorption only: for metal cations with E^0 more negative than or close to $E^0(Fe)$; e.g. Zn^{2+}, Cd^{2+}, Ba^{2+};
- Sorption + reduction: for metal cations with E^0 slightly more positive than $E^0(Fe)$; e.g. Ni^{2+}, Pb^{2+};
- Reduction only: for metal cations with E^0 substantially higher than $E^0(Fe)$; e.g. Ag^+, Cu^{2+}, Hg^{2+}.

Nevertheless, nZVI application presents some limitations: they rapidly age in water (oxidation reactions) [9, 10] and, as consequence, a thicker and crystalline shell originates [11]. This structural change leads to a decrease in removal efficiency and metals ions re-dissolve after some hours [9].

To address this issue, a new way of using nZVI is in combination with carbon materials by encapsulation of them (5-10 nm) inside micro- or nano-carbon spheres (6-8 μm) through Hydrothermal Carbonization (HTC) from a moist biomass. HTC is a thermal treatment of an aqueous solution or dispersion of a carbon-containing organic material at moderate temperatures and under pressure, which produces a carbon-rich black solid as an insoluble product [12].

An alternative source to produce carbon substrate is biomass waste, making the synthesis green, sustainable and also inexpensive. A previous research [13] reported the synthesis of carbon-encapsulated nZVI (CE-nZVI) from olive mill waste (OMW) and compared nZVI and CE-nZVI in heavy metals removal. Results showed that using CE-nZVI there was no delivery of heavy metals again to the water. It can be supposed that using CE-nZVI the carbon matrix blocked the delivery and so heavy metals remained adsorbed onto the nanoparticles surface.

The aim of this study was to synthetize CE-nZVI via HTC and activate them with nitrogen at different temperatures in order to increase the Fe(0) content. The synthetized particles were characterized, determining the iron content, the zero-valent iron content, the surface area, the morphology and the crystallinity. The influence of the activation temperature on nanoparticles removal efficiency was investigated.

2. Materials and methods

2.1. Chemicals

The reagents used for CE-nZVI synthesis were Fe(III) as source of iron (22.83 g iron(III) nitrate nonahydrate salt) and clarified olive mill waste (OMW) as source of carbon (300 mL) (CE-nZVI with molar ratio 0.05 nFe/nC).

In order to simulate wastewater conditions, this study was performed with a solution containing a mixture of five heavy metals ions (Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+} and Cr(VI); 10 ppm each). All the solutions were prepared using purified water.

2.2. nZVI synthesis

During the HTC process, the mixture of iron salts and OMW was heated in a high-pressure reactor at relatively low temperatures (200°C) for 3 hours under inert atmosphere. When the reactor had reached the HTC operating temperature (50 minutes/1 hour), measurement of the residence time (3 hours) began.

The reaction products were gases (mainly carbon dioxide, carbon monoxide, hydrogen, methane, ethane and propene) and a mixture of solid and liquid solution mechanically easy to separate on filter paper (0.2 μm cellulose acetate filter) under vacuum.

Then the filtered part was washed 2 times with a 50/50 ethanol-water solution. After washing, the sample was transferred to an oven (under inert atmosphere to avoid oxidation of Fe(0)) and allowed to dry at 80°C until all water was removed. After being taken out of the oven, the sample was ground into a fine powder.

2.3. Post-treatment with nitrogen

About 1.5 g of sample were put in a quartz tube and blocked with glass wool, then positioned inside a tubular oven and, after having reached the desired temperature (about 1 hour), the nanoparticles were heated under a nitrogen atmosphere (500 mL/min) for 3 hours. The presence of the nitrogen gas created a reducing atmosphere, leading to the reduction of Fe(III) / Fe(II) to Fe(0). Furthermore, the post-treatment also caused the evaporation of tars that may block the pores of the carbon matrix.

After the reaction, zero-valent iron became very reactive and it suddenly burnt in contact with air. Therefore, when the sample was taken out from the oven (after cooling), it was immediately wetted with water in order to protect the zero-valent iron by formation of a thin oxide layer on it.

In this work, temperatures of post-treatment of 600°C, 700°C and 800°C were investigated.

2.4. Batch tests

The post-treated CE-nZVI were added to 700 mL solution containing the mixture of the five metals. About 2 mL of sample from the reaction mixture were taken at different times and filtered through a 0.2 µm cellulose acetate filter (about 20 samples, with a decreasing rate, in about 220 hours, in total). At last nitric acid was added until 2-3% acid concentration to avoid the formation of solid particles.

2.5. Analytical methods

CE-nZVI were characterized using different techniques: zero-valent iron content determination (based on the measurement of hydrogen gas volume, which is evolving during the redox reaction of zero-valent iron and hydrochloric acid), thermogravimetric analysis (to determine the total iron content), X-ray diffraction (to determine the crystalline structure), transmission electron microscopy and scanning electron microscopy (to determine the size, the aggregation and the composition of the nanoparticles and the iron location within the carbonaceous structure) and surface area determination.

The concentration of heavy metals in aqueous samples was determined by inductively coupled plasma-mass spectrometry.

3. Results and discussion

3.1. CE-nZVI characterization

The non-post-treated sample showed a high surface area and a high Fe(0) percentage (4.46%), thanks to the presence of polyphenols in OMW having reducing properties (Table 1). All these features led to an improving of adsorption and reduction mechanisms in heavy metals removal. Furthermore, the total iron percentage was also high (Table 1), index of a good work of encapsulation by carbon from OMW.

The post-treatment with nitrogen proved to increase the Fe(0) content. Results showed that the reduction of the iron increased with the increase of the temperature of the post-treatment (Table 1); however, at 800°C the surface of the nanoparticles became highly crystalline and iron formed agglomerations that led to a decrease in surface area. No great differences were shown in samples post-treated at 600°C and 700°C, both in Fe(0) content and surface area (Table 1). Thus the temperature of 600°C is preferred as it requires less energy and, as a consequence, less costs.

Table 1. CE-nZVI characterization.

T of post-treatment (°C)	Tot Fe content (%)	Fe(0) in tot Fe (%)	Fe(0) in sample(%)	Surface area (m^2/g)
Non-post-treated	42.46	10.51	4.46	168.268
600	52.99	12.72	6.74	194.581
700	56.43	19.49	11.00	219.281
800	73.12	21.05	15.39	161.087

3.2. Influence of CE-nZVI activation temperature in heavy metals removal.

The test aimed to assess how different temperatures of post-treatment with nitrogen could influence the nanoparticles application; the assessed temperatures were 600°C and 800°C. For comparison, the total iron concentration was about the same in both samples (1.018 g/L in 600°C-CE-nZVI and 1.017 g/L in 800°C-CE-nZVI).

Results did not show significant differences, both in heavy metals concentration and in removal rate (Figures 1a, b). To be more precise, there was a slightly higher removal percentage using nanoparticles post-treated at 600°C. This was probably due to the more crystalline surface of 800°C-CE-nZVI, which led to a decrease in adsorbing capacity.

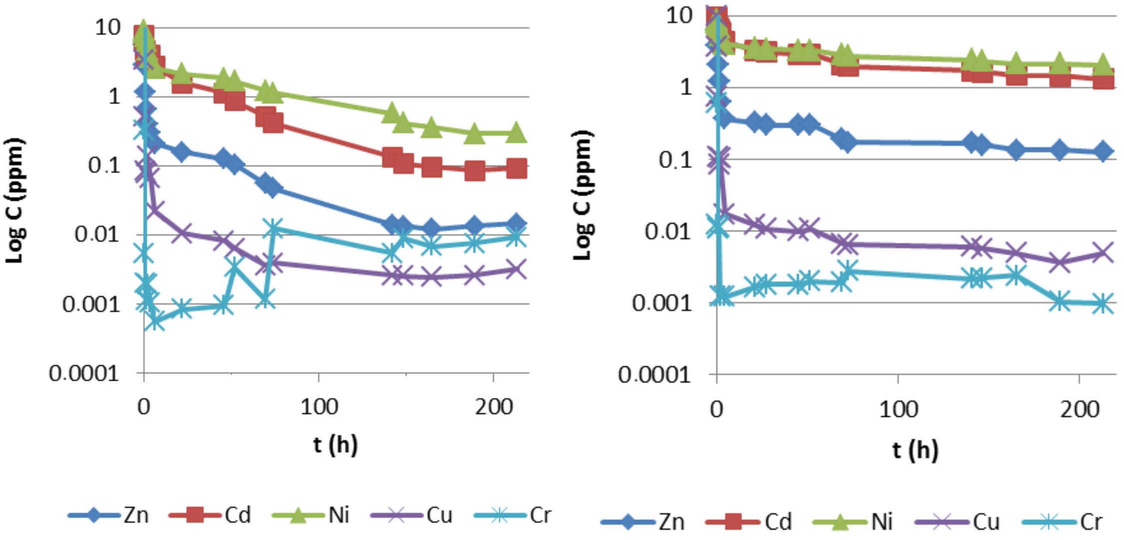

Figure 1. Heavy metals removal using (a) 600°C and (b) 800°C post-treated CE-nZVI.

4. Conclusion

In conclusion, the effectiveness of CE-nZVI in the elimination of heavy metals contaminants has been successfully demonstrated at lab-scale.

The temperature of CE-nZVI post-treatment with nitrogen slightly influenced the removal performance. Even if both satisfactory, the removal percentages using nanoparticles post-treated at 600°C presented slightly higher values, probably due to the more crystalline surface of 800°C CE-nZVI, which led to a decrease in adsorbing capacity. Thus the use of nanoparticles with post-treatment at 600°C is preferred, also because it involves lower synthesis costs, thus economic benefits.

The utilization of Fe-C nanomaterials for the treatment of secondary and tertiary treated effluents is a new technological concept for wastewater remediation, which reflects the originality and the innovative technological character of the project.

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