SYNTHESIS OF THIN SHELL CARBON-ENCAPSULATED NZVI FROM OLIVE MILL WASTEWATER AND APPLICATION TO ADVANCE OXIDATION OF POLLUTANTS

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Introduction

Nanoscale zerovalent iron (nZVI) particles have proven in the last two decades to be a powerful tool for water treatment[1]. Recent studies show that nZVI can be encapsulated inside micro-carbon spheres via hydrothermal carbonization (HTC) using as carbon source an organic compound, such as glucose or sucrose[2]. In addition, the organic material acts as reductant agent, transforming iron oxides to zero valent iron. The use of organic wastes as substitute of glucose could be an interesting alternative for nZVI production. In this context, Spain is the main world producer of olive oil with 37.5% of the total production worldwide[3]. The waste generation in the olive oil industry is nearly 75% of the total mass harvested, which entails a high impact on the environment due to its high phytotoxicity. One of the waste streams from the olive oil production is the olive mill wastewater (OMW).

In the present work OMW was used as a raw material to produce nZVI through HTC, with the purpose of using its reducing properties to maximize the amount of nZVI and the percentage of iron in the final material. This synthesis method could help dealing with the waste from the olive oil industry, and at the same time would produce a high-quality nanomaterial able to treat polluted water sources. Synthesized nZVI has been applied as heterogeneous catalyst for the elimination of 2,4-D by Fenton oxidation

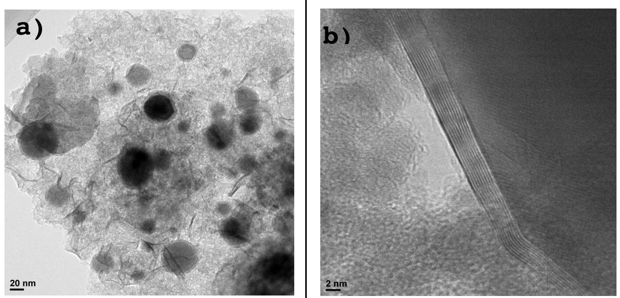
Materials and Methods

The experimental procedure followed was based on Sun et al.'s (2012) work [5], in which iron (III) nitrate nonahydrate is reduced by means of a hydrothermal reaction with glucose. However, the glucose was replaced by olive mill wastewater and slight modifications were performed. Briefly, 300 mL of clarified OMW were mixed with 0.057 mol of Fe(NO3)3·9H2O for 1 h. Then, the mixture was transferred to a 1 L HTC reactor and was heated to the required temperature during 3 h. After filtration, the samples were thermally treated at high temperatures under anaerobic conditions in order to increase their zero-valent iron content (post-treatment).

2,4-D degradation tests were carried out in a laboratory reactor equipped whit a UV lamp. Experiments started with the addition of the desired amounts of nZVI and H_2O_2 to 100 ppm water solution of 2,4-D (500 mL). The natural pH of the 100 ppm solution of 2,4-D was 3.4, and no pH adjustment was performed unless specified. 2,4-D concentration was determined by high pressure liquid chromatography (HPLC).

Results and Discussion

High quality carbon-encapsulated iron nanoparticles have been obtained using OMW. CE-nZVI particles had surface areas up to 220 m2/g and as shown in Figure 1a, consisted of ~ 40 nm nanoparticles surrounded by a thin layer of carbon (< 2 nm).



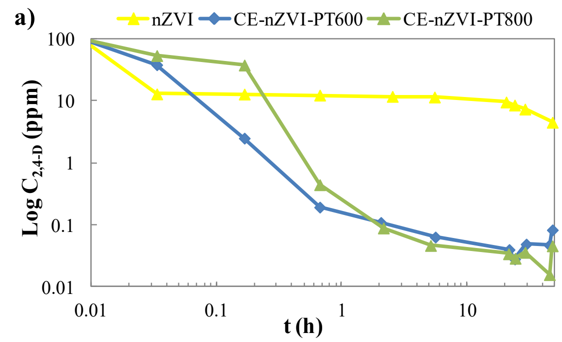


Figure 1. TEM images of CE-nZVI samples from OMW prepared using HTC

Figure 2. 2,4-D degradation using heterogeneous photo-Fenton reaction with different materials.

Photo-Fenton experiments of 2,4-D degradation showed higher activity of CE-nZVI compared with standard nZVI (Figure 2.). Encapsulatednanoparticles, activated at 600 ºC and 800 ºC, showed efficiencies above 99.9 % at the reaction end. Besides the higher efficiencies, encapsulated nanoparticles released much lower iron to the solution (2 ppm) in comparison with conventional nanoparticles, which produced an iron concentration of 20 ppm.

Conclusions

In this study, it has been demonstrated that OMW can be used as a raw material for the synthesis of high quality thin layer carbon-encapsulated iron nanoparticles by the hydrothermal carbonization method. The nanomaterial presented improved properties compared to other studies which usually employ glucose or sucrose as a feedstock. The OMW-CE-nZVI synthesized in this work consisted of nanoparticles of small sizes (40nm) surrounded by a thin layer of carbon (< 1nm).

Regarding CE-nZVI for the oxidation of the herbicide 2,4-D, the material showed better degradation efficiencies than conventional nZVI. Furthermore, and more importantly, the encapsulated nZVI protected the iron of being released to the solution, and thus the dissolved iron concentration at the reaction end was much lower than when using nZVI. This effect was further enhanced with the use of UV-light.

Acknowledgment

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References

1. Yan, W.; Lien, H.; Koel, B. E.; Zhang, W.(2013), Iron nanoparticles for environmental clean-up: Recent developments and future outlook. Environ. Sci. Process. Impacts, 15, 63– 77
2. L. Wei, M. Sevilla, A.B. Fuertes, R. Mokaya, G. Yushin, (2011), Hydrothermal carbonization of abundant renewable natural organic chemicals for high-performance supercapacitor electrodes, Adv. Energy Mater. 1 ,356-361
3. A. Roig, M.L. Cayuela, M.A. Sánchez-Monedero (2006), An overview on olive mill wastes and their valorisation methods, Waste Manage. 26 960-969