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REDUCED GRAPHENE OXIDE – SUPPORTED NANOSCALE ZERO VALENT IRON FOR THE REMOVAL OF THE MYCOTOXIN PATULIN FROM WATER

Craig R. McKerlie[1], Blanca Calderón[1], Ignacio Aracil[1], Andrés Fullana[1]*

[1] *Institute of Chemical Process Engineering, University of Alicante, 03080 Alicante, Spain*

*Presenting author's e-mail: andres.fullana@ua.es

Introduction

One challenge that has recently become evident in the water treatment industry is the remediation of micropollutants, which can be difficult to remove with conventional water treatment technologies. The use of nanotechnology has shown to be an emerging area of study for the removal of these pollutants from water[1]. This work assessed the suitability nanoscale zero valent iron decorated on reduced graphene oxide (nZVI/rGO) for this purpose. The study included the synthesis of the material using an anaerobic wet synthesis method, its subsequent characterisation and finally several performance tests for the removal from water of the mycotoxin patulin –which is a toxin commonly found in apple based products, particularly apple juices– using both Fenton and photo-Fenton oxidation.

Materials and Methods

nZVI/rGO was synthesised following Li et al.'s method[2], with a final ratio of 0.15:1 of GO to iron. Firstly, the required mass of GO was added to water and put in a sonication bath for 1 hour. After this, it was put under ultrasonication for 2 hours, while under stirring and in an ice bath to prevent evaporation. The sample was then allowed to sit for one hour. On the other hand, a $FeCl_3 \cdot 6H_2O$ and polyvinylpyrrolidone (PVP) solution in water was prepared and then added to the GO suspension and stirred for 30 min. Then, a $NaBH_4$ solution was added dropwise to the mixture under constant stirring and nitrogen atmosphere, to avoid oxidation. The obtained mixture was then left for 6 hours under stirring in order to ensure maximum reduction. Finally, the solid was separated by magnetic filtration and washed 3 times with ethanol. The synthesised material was characterised using TEM, Raman Spectroscopy and physisorption analysis.

In order to assess the effectiveness of the synthesised nZVI/rGO, 800 mL of a 400 ppb patulin solution was placed in a vessel along with 40 mL of 10 mM H_2O_2 solution, to allow for the Fenton oxidation to occur. HPLC was used to determine the effectiveness of the treatment by monitoring patulin concentration, and ICP-MS was used to test for iron leaching in the medium.

Results and Discussion

Figure 1 shows a TEM image of the synthesised nZVI/rGO. A good distribution of the nZVI nanoparticles across the rGO was observed, which is the desired as this maximises the active sites available for the material to interact with the contaminant to remove. The iron nanoparticles were found to form long chains varying in length from around 200 nm to as long as 2μm.

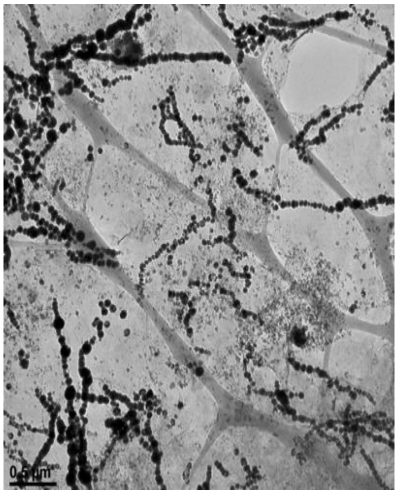

Figure 1. TEM image of nZVI/rGO showing the particle distribution (scale bar: 0.5 µm)

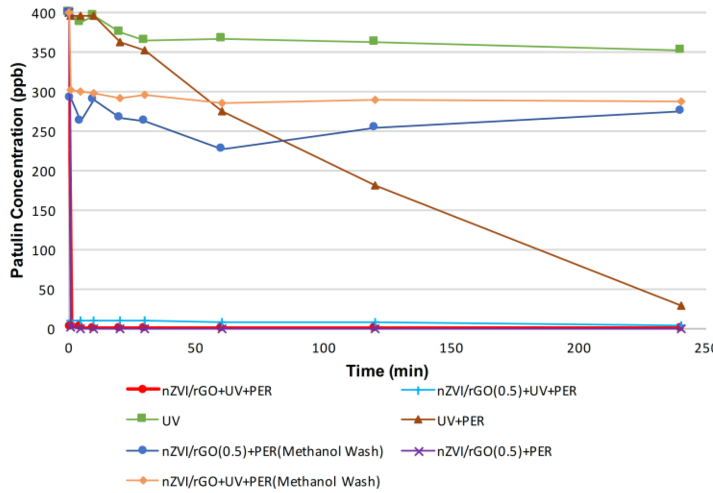

Figure 2. Remediation profile comparison for all treatment combinations (where PER means H_2O_2)

A comparison of the remediation tests can be seen in Figure 2. It was found that patulin was successfully removed through both Fenton and photo-Fenton (with UV-C) oxidation. A removal yield up to 99.9% in the presence of nZVI/rGO and H_2O_2 was reached, thus bringing the patulin concentration below the recommended limit of 25 ppb. nZVI/rGO performed properly except when methanol was used to wash the synthesised material instead of ethanol. The high removal rate was upheld even when not in the presence of UV-C. ICP-MS analysis was also carried out to determine if any iron leaching into the medium was occurring, showing that the iron content was always below 300 ppb, which is 10% of the world health organisation's limit of 3000 ppb.

Conclusions

The nZVI showed to be very effective to remove patulin from water by acting as a slow delivering source of ferrous iron required for Fenton hydroxyl radical formation, while the reduced graphene oxide helped this to occur at non-acidic pH, as graphene coupling promotes electron transfer which improves the action of Fenton mechanism. Theoretically, the use of UV-C further helps promote Fenton mechanism by recovering ferrous iron from complexes such as $Fe(OH)^{2+}$, but no differences were observed in this work with and without UV-C. The results showed lots of promise for the future of nZVI and graphene-based materials in water treatment.

Acknowledgment

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References

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