ZIF-8@Graphene Oxide / PEI composite Aerogel for heavy metal capture in water

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1. Introduction

Water pollution is one of the key challenges humanity is facing in this century.[1] Due to the fact that most of the natural water sources are contaminated with high amounts of pollutants, such as heavy metals and organic compounds (pharmaceuticals and pesticides), the development of technologies for the recovery and recycling of water has become a major topic of research. Developing new materials, based on green technologies, that are able to capture or degrade these contaminants, namely mercury and lead among others, seems a fair approach to fight this problem. A promising candidate is found in metal-organic frameworks (MOFs).[2] MOF properties are optimal for heavy metal capture, since the tailor-made structure of the MOF can increase the selectivity for any given contaminant. However, MOFs are usually manufactured in the form of powders, and, as such, they present the typical challenges of these type of materials, for instance, the difficulty to recover them after exposure to a liquid sample in water remediation processes. At this point, graphene oxide (GO) aerogels come as a potential solution for the immobilization of active species/nanoparticles for water remediation. GO, with their unique structure of exfoliated and heavily functionalized flakes, can serve as a support for the MOF particles, as well as for other components that act synergistically in the common objective. It has been previously reported that cryogels of graphene oxide coated with polyethyleneimine (PEI)[3] have been used for the capture of mercury (the third most toxic element) in different water matrixes, with very promising results. However, the synthetic procedure of most aerogels or cryogels of GO involves the requirement of high energy demanding processes and/or the usage of toxic or "non-green" solvents. Alternatively, it has been previously reported in our research group at ICMAB a green and low energy demanding approach using supercritical CO_2 working at mild temperatures to produce GO aerogels,[4] as well as aerogels of GO decorated with other materials, such as MOFs or magnetic nanoparticles.[5] The aim of this research is to prepare a novel GO/PEI/MOF aerogel. The chosen MOF was ZIF-8, a hydrophobic MOF with proved capacity for lead removal from wastewaters.[6] This multifunctional nanocomposite should promote the sorption of heavy metals (*e.g.*, mercury (Hg (II)) and lead (Pb (II)) cations).

2. Materials and Methods

GO/PEI/ZIF-8 aerogels were prepared mixing a solution of PEI in water with a commercial dispersion of GO in water. A multi-step solvent exchange is followed to obtain a dispersion of GO/PEI in ethyl acetate with a concentration of *ca*. 8 mgmL^{-1}. Then, $Zn(acac)_2$ and Hmim, the constituents of ZIF-8, were added to this dispersion. 2 mL glass tubes were loaded with 1 mL aliquots of the mixture and were placed inside a non-stirred high-pressure reactor of 200 mL. A supercritical CO_2 drying method was carried out at 40 ºC and 200 bar. Two grey aerogels with a cylindrical shape were isolated (Fig. 1). The mercury sorption behaviour studies were carried out through batch experiments, adding 10 mg of the composite aerogel to 1L water bottles spiked with 50 ppb of Hg.


Figure 1. Macroscopic picture of the recovered ZIF-8@GO / PEI aerogel.

3. Results and discussion

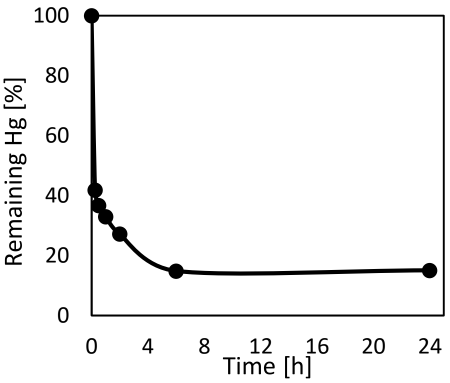

Figure 2. Normalized concentration of Hg in solution during contact time.

Figure 2 displays the evolution of the concentration of mercury in in presence of the GO aerogel composite. After the first sharp decrease in Hg concentration during the first 6 h, the curve reaches a plateau with a removal of *ca.* 85 wt%. This is the typical behavior of mercury adsorption curves where a capturing threshold is present at very low concentrations. Despite this graphic, other experiments, such as sorption isotherms analysis, suggested that the material is in fact, not saturated, and can capture higher quantities of this and other heavy metals.

The presence of the hydrophobic ZIF-8 is justified in this composite by two different points of interest. On one hand, the increase in dimensional stability, that allows the material to remain as a whole piece in water even under stirring. On the other hand, the ability to capture other metals such as Pb (II) (preliminary results, not shown), which is not a possibility with GO/PEI alone.

Figure 3 depicts a Box-Behnken optimization test performed on this material when taking into account some variables such as pH, salinity and initial Hg concentration. The best conditions (pH 8 and null salinity) gives a Hg capture of ca. 97 wt%, that remains well over 60 wt% when salinity is increased to 30 gL^{-1}, thus implying that this material can become a very interesting option for heavy metals recovery in all types of water, including sea water.

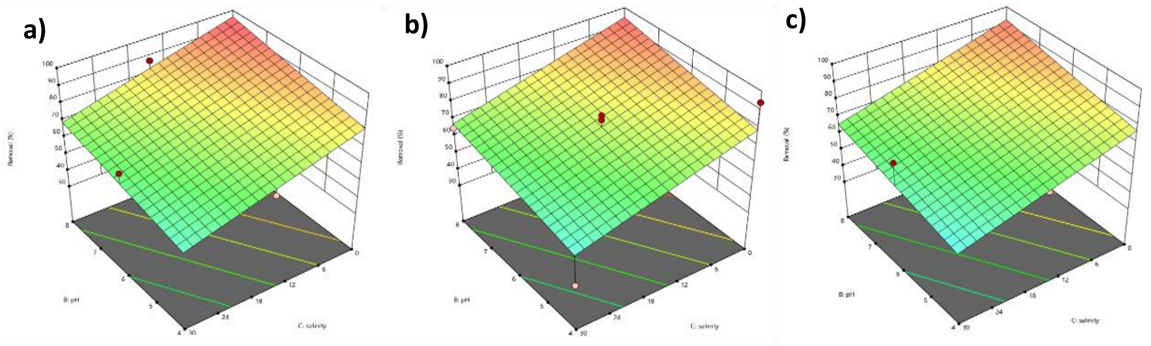

Figure 3. Box-Behnken plotting varying pH, and salinity for: a) 50 ppb, b) 175 ppb, and c) 300 ppb of Hg.

4. Conclusions

ZIF-8@GO/PEI composite aerogels were synthetized following a one-pot straightforward method using supercritical CO_2. They were tested for the capture of heavy metals in water. Preliminary results suggest a high performance on bimodal capture with possible application on real waters. This material serves as another proof-of-concept of the supercritical CO_2 assisted methodology for the preparation of composite aerogels of GO.

References

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