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BOOK OF FULL ABSTRACTS

Jointly Meeting of the Italian Zeolite Association (AIZ) Czech-Italian-Spanish (CIS) Conference Italian Interdivisional Catalysis Group (GIC)







XVI National Congress of Zeolites Science and Technology



8th Czech-Italian Spanish Conference on Molecular Sieves and Catalysis



XXI National Congress of Catalysis

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Book of Abstracts

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Jointly Meeting of the Italian Zeolite Association (AIZ) Czech-Italian-Spanish (CIS) Conference Italian Interdivisional Catalysis Group (GIC) 11-14th June 2019 - Amantea (CS) - ITALY

ONE-STEP DEPOSITION METHOD FOR THE SYNTHESIS OF A NANOCOMPOSITE MEMBRANE BASED ON REDUCED GRAPHENE OXIDE/ZEOLITE-A FOR ADSORPTION OF METAL IONS WITH ENHANCED ANTIBACTERIAL PROPERTIES

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To purify water for various sources, such as sea water, produced water, industrial waste water and other polluted waters, the use of membrane filtration is an economical way to raise the emerging problem of a clean water shortage. During the last few decades, improvements in membrane science and technology have been important and membranes have been developed to improve the energy efficiency of filtration.¹ But, when it comes to the removal of small molecules, such as salt ions in sea water (desalination), the problem remains unresolved. In this work, a novel design strategy is proposed to remove metal ions from water by a nanocomposite membrane based on reduced graphene oxide (r-GO) and zeolite A. Our motivation in utilizing graphene oxide (GO) and its oxide derivatives stems from the presence of functional groups such as carboxyl, epoxy, and hydroxyl groups providing possible functionally reactive sites and imparting hydrophilic properties to the membrane. In addition, they would ensure a large negative zeta potential, which should also decrease biofouling process of attachment of bio-foulants and their accumulation on the membrane surface.² As far as concerns zeolites, these microporous materials contain nm-sized channels and cavities which can selectively pass throughout the membrane water molecules and exclude other molecules. Consequently, the water flux increases and most other small competitors (such as ammonium and heavy metals) are rejected, thus improving both membrane permeability and selectivity.² In order to develop this nanocomposite membrane, zeolite 3A (UOP) was chosen (Si/Al=1) for its affinity towards metal ions (Na⁺, NH₄⁺, K⁺, Ca^{2+} , Mg^{2+}), its highly hydrophilic character, high thermal stability and because it was readily available, at low cost and with a high degree of purity and crystallinity. Graphene oxide was synthesized from natural graphite (Aldrich) according with modified Hummers method.³ This and the nanocomposite membrane were prepared in the MackGraphe Research Center laboratories. All materials were characterized by



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SEM, AFM, FT-IR, XRD, TGA and WCA. The proposed synthesis method, with low energy consumption, involved the deposition on a nylon substrate by vacuum filtration (Uniglas - phox boro 3.3, 1000 ml) starting from a graphene oxide and zeolite A homogeneous mixture (2:1 ratio) dispersed in aqueous solution. Firstly a colloidal zeolite 3A "milky solution" was prepared by ultrasonic processor (UP400S - Hielscher), by diluting 50 mg of zeolite in 100 ml of deionized water. The nylon filter paper (Nylon 66 Membranes - Supelco, 0.22 µm porosity and 47 mm diameter) was used as a substrate for the deposition, and then a treatment with NaOH⁻ (0.5M) was performed for 10 minutes was in order to increase surface hydroxyl groups as well as facilitate the crystals adhesion by Van der Waals and H interactions. Reduced graphene oxide (r-GO) was obtained by reducing dispersed GO in the resultant homogeneous GO solution using hydrazine (N₂H₄, Sigma-Aldrich) for 10 minutes, in order to compact the structure and force the water flow into functionalized pores thus increasing the adsorption/rejection capacity. The nascent membrane (GO/ZEOA) was then washed with deionized water, kept at 79.9°C for 72 hours and then stored in a dryer. Figure 1 shows the prepared GO/ZEOA membranes and surface roughness, as estimated by SEM (Fig. 1a) and AFM (Fig. 1b).



Figure 1. Photographs of freestanding GO/ZEOA membrane by SEM (a) and AFM (b).

In addition, series batch tests for GO/ZEOA membrane adsorption performances toward common cations, particularly Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺ (always ubiquitous in natural water and wastewater effluents) were performed. These highlighted a strong selectivity to Mg²⁺ thus attesting that functional groups exhibited strong metal–ligand interaction ion in aqueous solutions. Finally, the bactericidal properties of the membrane were tested in liquid medium, against four multi-drug resistant clinical isolates, representative both for Gram-positive (*Staphylococcus aureus Sa2*) and Gram-negative (*Escherichia coli APN1, Pseudomonas aeruginosa PaPh32 and AC12a*) species. In conclusion, these results suggested that GO/ZEOA membranes are a promising approach for the development of novel antimicrobial membranes, environmentally compatible, efficient in water purification technologies for waste water and industrial waste. Additionally, our results suggest that functionalization of thin-film composite membranes with r-GO and zeolite is a promising approach for the development of novel antimicrobial membranes.

References

¹ Zhao, M.; Huang, Y.; Peng, Y.; Huang, Z.; Ma, Q.; Zhang, H. Chem. Soc. Rev. **2018**, 47 (16), 6267-6295.

² Szunerits, S.; Boukherroub, R. J. Mater. Chem. B **2016**, 4 (43), 6892-6912.

³ Hummers Jr, W.S.; Offeman, R.E. J. Am Chem. Soc. **1958**, 80 (6), 1339-1339.