Development of porous microwave-acid treated sepiolite /ZnO nanocomposite particles for potential ethylene scavenger application

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Ethylene scavengers have been used to adsorb or decompose ethylene, a phytohormone responsible for inducing biochemical, physiological, and structural changes during the fruit ripening, in order to prolong the fruit shelf-life [1]. Natural porous clays, such as sepiolite, have been addressed as ethylene adsorbing matrices [2]. However, their low adsorption activity still compromise their broad application. Recently, an acid treatment of natural clays has been applied to increase their porosity [3]. On the other hand, ZnO has already demonstrated to have ethylene chemisorption activity [4]. Combination of acid treted clays and ZnO particles may enhance the ethylne adsorption kinetics and pave the way for different applications. In this work, the feasibility of using a microwave (MW)-assisted acid treatment to modify sepiolites and further assembling ZnO nanoparticles on their structure was explored. The influence of MW-assisted acid treatment and nano co-precipitation of ZnO on chemical, tructural, morphological, and ethylene scavenging properties of sepiolite was studied. Untreated sepiolite was used as control.

Sepiolite was chemically composed of SiO_2 76.7 %, MgO 7.2%, K_2O 3.2%, P_2O_5 3.0%, CaO 2.4%, and Al_2O_3 1.7% (wt%). MW-acid treatment caused the depletion of Mg^{2+} from sepiolite octahedral sheets, which was confirmed by the progressive loss of FTIR bands attributed to magnesium species coordinated with -OH and H_2O, and the decrease of MgO content (3.2%) determinated by X-ray fluorescence. The modification of sepiolite sheets increased its specific surface area from 337 m^2/g to 519 m^2/g and pore volume from 0.404 cm^3/g to 0.769 cm^3/g. The posterior synthesis of ZnO on MW-acid treated sepiolite surface generated sepiolite/ZnO nanocomposite particles. X-ray fluorescence confirmed the presence of 17.1% ZnO, as expected by the amount of added ZnO precursors. STEM images revealed that ZnO nanoparticles synthetized on MW-acid treated sepiolite showed a size between 1.0 nm and 2.5 nm, similar to the ones synthesized without any clay support. The assembly of ZnO decreased the specific surface area (423 m^2/g) and pore volume (0.613 cm^3/g) of MW-acid treated sepiolite. These chemical and morphological changes affected the ethylene scavenging activity of sepiolite. Therefore, the simultaneous modification of sepiolite by MW-assisted acid activation and ZnO assembly revealed to be a suitable approach for obtained porous nanocomposite materials with higher specific surface areas than the commercially available, enhancing their potential for food packaging application.

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References

[1] Alver BE, Sakızcı M., *Adsorption Science & Technology*, 30 (2012)265-273.
[2] Vilela C, Kurek M, Hayouka Z, et al., *Trends in Food Science & Technology*, 80 (2018) 212-222.
[3] Venaruzzo JL, Volzone C, Rueda ML, Ortiga J., *Microporous and Mesoporous Materials*, 56 (2002) 73-80
[4] Kesavulu V, Narayana D, Lal J., *The Journal of Physical Chemistry*, 74(1970)4150-4155.