Electrically conductive carbon–sepiolite nanocomposites from citrus wastes

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INTRODUCTION

Amongst the many known adsorbents of pollutants in water, clay minerals are very attractive alternatives due to their low cost and worldwide presence (Awad et al., 2019). In spite of their hydrophilic nature, clay minerals can be modified to be employed as alternative to carbonaceous materials and biochars in the adsorption of a large variety of organic compounds, including polycyclic aromatic hydrocarbons (Lamichhane et al., 2016). A way to valorize wastes is to use them in combination with clay minerals to produce composite biochars from diverse type of wastes, which frequently offer improved adsorption properties (Sizmur et al., 2017). Clay minerals, such as sepiolite, and other silica-based substrates have been also combined with certain organic species, for instance sucrose, to produce electrically conducting composites due to the formation of graphene-like materials (Ruiz-Hitzky et al., 2011). Amongst other applications, some of these materials have been evaluated as adsorbents of organic pollutants that can be electrically regenerated (Canencia et al., 2015). In this context, we are now exploring the viability of using citrus wastes in combination with sepiolite to produce electrically conducting carbon-clay composites to produce effective and reusable adsorbents for the removal of organic pollutants in water.

EXPERIMENTAL

Sepiolite from Vallecas-Vicálvaro (Spain) was supplied by Tolsa SA (Pangel® S9) and pectin from citrus peel was obtained from SIGMA. Citrus waste was collected from the dump in Tunisia, dried in open air, then in oven at 105°C for 12 hours and then crushed and sieved (150 μm). Carbon-sepiolite nanocomposites were prepared from starting physical mixtures of citrus waste powder, pectin and sepiolite (mixtures were prepared with variable relative content in each component). The mixtures were shaped as compact cylinders and heated at 700 °C under N_2 flux for 2 h to obtain carbon-sepiolite nanocomposite foams (Fig. 1A).

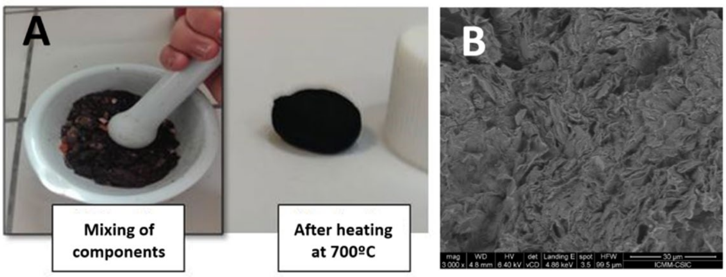

Fig 1. *A. Preparation of carbon-sepiolite nanocomposites; B. FESEM image of carbon-sepiolite nanocomposite.*

TG-DTA of components and starting mixtures provide information on events during heating. FTIR and Raman spectroscopies were used to confirm the transformation of the organic mater and the nature of the formed carbonaceous material. Electrical conductivity was analysed using electrochemical impedance spectroscopy (EIS). The textural aspect of the formed carbon-sepiolite nanocomposites was observed by FESEM. Carbon content in samples was determined from CHN chemical analysis. Preliminary studies on adsorption capacity of the carbon-sepiolite nanocomposites in the removal of aromatic compounds in water was tested using methylene blue as a model pollutant. Electrochemical regeneration was carried out in a Solartron 1480 Multistat potentiostat/galvanostat, using the dye-loaded adsorbent as working electrode and NaOH as electrolyte.

RESULTS

Heating of citrus waste-sepiolite mixtures produces carbon-clay nanocomposites that do not preserve the starting shape of the mixture. The incorporation of pectin allows the formation of carbon-sepiolite blocks that preserve the initial shape and can be easily handled. In fact, these samples show very good mechanical properties with Young's modulus values of around 23 MPa, proving ternary systems allow processing monolithic systems. According to FTIR and TG-DTA, the heating at 700ºC allows the transformation of the organic matter into carbon without dehydroxylation of the sepiolite structure. From the Raman spectra is confirmed the formation of carbonaceous materials containing both sp^2 C (G band) and sp^3 C atoms (D band), which agrees with previous results of formation of graphene-like materials with defects when biomolecules evolve to carbons in presence of sepiolite and other porous silica materials (Ruiz-Hitzky et al., 2011; Canencia et al., 2017). FESEM images of carbon-sepiolite nanocomposites (Fig. 1B) reveal the presence of flat particles organized on the surface and the interior of pores in the formed blocks, probably due to the formation of graphene-like materials in contact with the sepiolite fibers. All the prepared carbonaceous materials, with or without sepiolite, show electrical conductivity, however only those materials prepared with certain content in sepiolite preserve their shape as monoliths. In this way, we have found that carbon-sepiolite nanocomposites from starting mixtures containing 1:1:1 citrus waste:pectin:sepiolite composition show relatively good conductivity ($\approx$ 1 mS/cm) retaining a monolithic shape. Therefore, we are evaluating this carbon-sepiolite composite as adsorbent of aromatic compounds in water with the aim to remove them and regenerate the adsorbent using electrical conductivity (Canencia et al., 2017). Preliminary results show that adsorption kinetics for methylene blue in water is reached after 2h. In the studied conditions, it was possible to remove 1.4 mg of methylene blue per gram of carbon-sepiolite nanocomposite. By applying a galvanostatic cathodic method for the electrochemical regeneration of the adsorbent, it is possible to remove the adsorbed methylene blue and reuse the material in a second adsorption cycle, being able to remove 1.1 mg of pollutant per g of adsorbent.

CONCLUDING REMARKS

This study shows that it is possible to prepare electrically conducting carbon-sepiolite nanocomposites conformed as rigid blocks from citrus wastes and sepiolite using pectin as agglomeration agent. The nanocomposite blocks show good mechanical properties as well as relatively high electrical conductivity. Preliminary test of methylene blue removal from water shows promising results for using these nanocomposite blocks as biosorbents with the possibility of regeneration by applying an electrochemical process.

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