Synergistic effect of the Parameters Affecting Morphological and Magnetic properties of Magnetic Activated Carbons from Chestnut Industrial Wastes

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Keywords: Chesnut shell wastes; Magnetic activated carbons; Design of experiments; Circular economy
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Introduction

The escalating environmental challenge of waste generation, intensified by diverse industries, underscores the need for sustainable solutions. Among the often-overlooked byproducts contributing to this concern are chestnut shell. In 2021, Europe produced 319516.48 tons of chestnut, with the peeling process alone generating about 4.5% of wastes, predominantly in the form of shells (FAOSTAT; Squillaci et al., 2018). Recognizing the environmental threat, innovative approaches are imperative for the revalorization of chestnut shell waste. A noteworthy example is the development of magnetic activated carbons, offering a promising avenue for transforming this agricultural byproduct into a valuable resource with potential applications in various sustainable initiatives.

Efforts to address chestnut shell waste center on a streamlined one-step activation process with $FeCl_3$, emphasizing efficiency and reduced environmental impact. This transformative process yields activated carbons characterized by exceptional microporous structures with some grade of mesoporosity (Rodriguez-Sánchez et al., 2021), significantly enhancing adsorption capacities. The microporous and magnetic attributes of these materials play an important role in selective filtration and adsorption of pollutants, suggesting a promising way for sustainable waste management and environmental conservation. In this context, it is necessary to study the influence of the activation process parameters and optimize them to produce tailored adsorbents for specific applications.

In recent years, the application of statistical design of experiments (DoE) has been a crucial methodology, aiming for efficient designs while minimizing experiments number, particularly beneficial when exploring multiple variables.

The objective of this work is to delve into the synergistic influence of two activation process parameters, the activation temperature and the amount of activating agent, on the chemical, textural, and magnetic properties of magnetic activated carbons derived from chestnut industrial wastes. In addition, different mathematical models will be developed to predict density, textural, chemical and magnetic properties for the production of future new activated carbons.

Methodology

In this study a total of eighteen Magnetic Activated Carbons (MACs) from previous works (Rodriguez-Sánchez et al., 2019, Rodriguez-Sánchez et al., 2021) were used. The MACs were sustainably obtained through a single-step thermochemical process by chemical activation using different amount of activating agent ($FeCl_3$) and activation temperatures (from 220 ºC to 800 ºC). The raw chestnut shell waste (CH) and the activating agent were physical mixed; the mixture was placed in a conventional tubular oven and heated at a heating rate of 5ºC min^{-1} from room temperature to the activation temperature at which it remained for one hour.

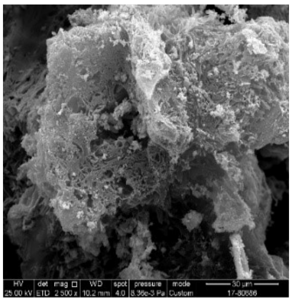

Figure 1. $FeCl_3$ Chestnut Shell waste activated carbon

A comprehensive analysis was conducted to thoroughly analyze the chemical, magnetic, morphological, and textural characteristics of the different MACs. Density of the samples was obtained by helium pycnometry on a Micromeritics AccuPyc 1330 pycnometer. The textural properties of the materials were characterized from N_2 adsorption isotherms at 77 K (BET specific surface area (S_{BET}) and total pore volume (V_{TOT})) and CO_2 adsorption isotherms at 273 K (ultramicropore volume: W_0). A vibrating sample magnetometer, VSM, (Microsense EV-9) was used to measure magnetic properties by means of the M(H) magnetization hysteresis curve in the field range from −20 to 20 kOe at RT (M_S: Saturation magnetization and M_R: Remanence). Furthermore, the adsorbents were characterized for their elemental analysis (C, H, N, and Fe), and ash content. To develop this study, a design of experiments (DoE) was carried out using the ''Design Expert 7.0'' software from Stat-Ease based in the analysis of variance (ANOVA) (Montgomery, 1991). The statistic design chosen was Historical data design based on Response Surface Methodology (RSM) that allows a further optimization of the process. The factors under consideration were $FeCl_3$ addition from 20% to 50% (from 0.25:1 to 1:1 of $FeCl_3$:CH ratio), and activation temperature from 220ºC to 800ºC. The responses studied were density (g/cm_3), BET surface area (m^2/g), V_{TOT} and W_0 (cm^3/g), remanence (M_R) and saturation magnetization (M_S) (emu/g), percent of chemical elements (C, H, N and Fe) and ash content. For developing the mathematical models 18 experiments were studied.

Results

Mathematical models were obtained for all responses, leading to the generation of response surface plots that can explain the behavior within the specific limits of the factors. The models obtained were significant with p-values <0.0001 and R squared values above of 0.8271.

Activation temperature is the main factor that affects significantly on the responses. This effect is positive on density, BET surface, V_{TOT} and W_0, the increase in temperature leads to obtaining superior results. The percentage of $FeCl_3$ added has a positive effect on the responses, although it has a significant effect but to a lesser extent than temperature. By increasing the amount of activating agent, higher values of density, BET surface, V_{TOT} and W_0 were obtained. However, for W_0 this effect can be considered insignificant, probably due to the collapse of nearby pore walls due to the increasing of the $FeCl_3$ content. In the same way as temperature, this factor affects positively. In Figure 2 is depicted the surface plot of density as a function of $FeCl_3$ and temperature.

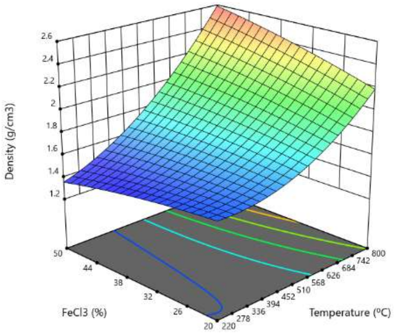

Figure 2. Surface plot of density as function of activating agent and activation temperature

Regarding magnetic parameters, linear mathematical models were obtained for M_S and M_R. Although the addition of $FeCl_3$ induces magnetization in the samples, it has been observed that varying the $FeCl_3$ ratio from 20% to 50% yields minimal changes in the magnetic parameters. Otherwise, temperature is the critical factor affecting positively on magnetic responses, its variation affects more significantly: increasing temperature increases M_S and M_R. This can indicate that a higher temperature, there are the formation of magnetic phases such as metallic iron. Equation (1) shows the quadratic equation for Density in terms of actual factors with R squared of 0.9861:

$$Density = 1.8979 - 0.0018\,T - 0.006806\,FeCl_3 + 0.000035\,T \cdot FeCl + 2.17 \cdot 10^{-0.6}\,T^2 \quad (1)$$

Where T is Temperature in ºC and $FeCl_3$ is the ratio in % of activating agent added.

Conclusions

In this study, the effect of the parameters affecting chemical, morphological and magnetic properties of chestnut waste activated carbons were analyzed depending on temperature and activating agent addition. For all responses studied the relationship between factors and mathematical models were obtained being temperature the main factor that affects significantly on all the responses. While varying the $FeCl_3$ ratio affects significantly on density, S_{BET} and V_{TOT}, but has little effect on W_0. For the magnetic parameters studied, once the activated carbon is magnetized, increases in the $FeCl_3$ ratio do not have a significant effect on the final responses.

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