From Waste to Clean Water: Utilizing Chestnut Shell Wastes-based and Coal-based Adsorbents for Pesticide Remediation

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Introduction

Pesticides, as dichlorvos and atrazine, are widely used in agriculture for pest control. However, their widespread application poses significant environmental risks due to their toxic effects on aquatic life. Upon entering water bodies via runoff or direct application, these pesticides can contaminate aquatic ecosystems, jeopardizing the well-being of fish, insects, and other organisms. Moreover, they can disrupt the balance of aquatic ecosystems and present health hazards to humans upon consumption.

Various remediation methods, including filtration and advanced oxidation processes, are employed to alleviate their environmental impact. Notably, adsorption using activated carbon emerges as a particularly effective approach. While traditionally derived from coal-based materials like peat, bituminous, or lignite (Lladó et al., 2016) and activated through a physical process involving steam or carbon dioxide, thereby increasing the surface functionality of the activated carbon. In recent years, there has been a surge of interest in converting organic waste materials such as coconut shells and wood into activated carbon. In addition, there is a growing interest in valorizing chestnut shells into biochar and activated carbons through single or two step chemical activation with KOH (Ruiz et al., 2017). This approach not only provides a sustainable solution for waste management but also yields highly efficient adsorbents with enhanced surface functionalities.

Considering all of the above, this research focuses on the revaluation of chestnut waste into biochar and activated carbon as potential adsorbents (Ruiz et al, 2017), alongside coal-based activated carbons for pesticide removal in aqueous media. The removal effectiveness of the experimental adsorbents will be compared with that of commercial activated carbons. A comprehensive characterization of the adsorbents will be carried out to elucidate the factors that influence the pesticide adsorption process.

Methodology

A total of seven carbonaceous porous materials were used in this study: a chestnut char (CHP), a chestnut activated carbon (CHPAC), two bituminous coal-based activated carbons (BBAC), a lignite activated carbon (MAC) and two commercial activated carbons from wood (WAC) and coconut shell (YAO).

CHP was obtained from chestnut shells wastes by carbonizing in a N_2 flow of 150 ml min^{-1}. (heating rate of 5 ºC min^{-1}, up to 750 ºC and a maintenance time at this temperature of 60 min). CHPAC was sustainably obtained in a second step from CHP by chemical activation using KOH; the biochar and the activating agent were mixed in solid state (physical mixture) and the thermochemical process took place in a conventional tubular furnace at 750 ºC during 60 min and in a N_2 flow of 500 ml min^{-1} (Ruiz et al, 2017). BBACs were obtained by physical activation with carbon dioxide; the coal precursor was ground and sieved under to 425 µm; then the precursor was oxidized (270º ºC) and pyrolyzed (850 ºC); and the char obtained was activated in a vertical reactor to 850 ºC in a flow of carbon dioxide (9 cm^3 min^{-1}) and up to 51± 2% of burnt-off. The production of MAC is extended detailed in Lladó et al. (2016).

An exhaustive and complete study of the chemical, morphological and textural properties of all adsorbent materials was made. Texture of the adsorbents were characterized by N_2 adsorption at 77K. BET specific surface area (S_{BET}), the total pore volume (V_{TOT}) and the distribution of porosity, obtained by applying the density functional theory (DFT) model, were obtained from the N_2 isotherms. The adsorbents were further characterized for their elemental analysis (C, H, N, S, O), ash content, humidity, and pH.

Four different pesticides were selected according to their molecular size and physico-chemical properties: dichlorvos, atrazine, diazinon and malathion. The presence of these organic contaminants in surface and ground waters can be common, and various organizations have established guideline and maximum allowable values for these due to its dangerousness (WHO, 2019). Equilibrium adsorption studies were determined with batch experiments. Isotherms experimental data were fitted to two-parameters isotherms model Langmuir and Freundlich using MATLAB.

Results

The experimental chestnut biochar and chestnut activated carbon, coal-based activated carbons and commercial activated carbons displayed good chemical characteristics: high carbon content (82-94%), oxygen content (1-5%) and low ash content (0.5-7%). MAC stood out for its 6% of sulfur content. The textural properties showed different values of S_{BET} and pore volume depending on the obtaining process and the raw material: CHP had a S_{BET} of 101 $m^2\ g^{-1}$, CHPAC and MAC showed similar S_{BET} (around 1100 $m^2\ g^{-1}$) and a high pore volume in which more than 65% were micropores, and BBAC a S_{BET} up to 1200 $m^2\ g^{-1}$.

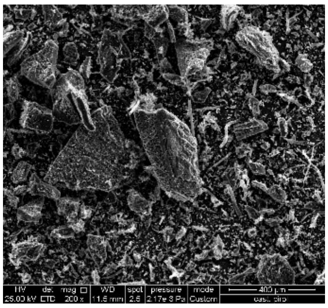

Figure 1. Chestnut Char

In the adsorption process, different results were obtained according to the different adsorbents and the pesticide adsorbed. Maximum adsorption of dichlorvos was observed on MAC, up to 0.90 mmol g^{-1}. Due to the absence of an aromatic ring, dichlorvos is not expected to undergo π-π interactions during the adsorption process. Maximum adsorption capacity of atrazine was observed on the different adsorbents respect to the rest adsorbates. In this case, acid-base nature of adsorbents can affect differently the adsorption process. The adsorption of diazinon was the lower in all adsorbents. Malathion, despite having a higher molecular weight than the rest of the adsorbates, was more adsorbed than diazinon. In addition, similar q_{max} were observed on the BBAC (approximately 0.49 mmol g^{-1}). These results suggest that malathion can be more easily adsorbed into the porous structure of the adsorbents compared to diazinon.

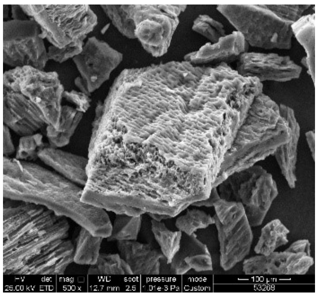

Figure 2. Chestnut Shell Waste activated.carbon

Conclusions

In this study, biochar and activated carbon were experimentally obtained from chestnut shell waste and coal-based activated carbons were also obtained, and all of them were compared with commercial adsorbents in terms of their effectiveness in adsorption processes of various pesticides in aqueous media. The chemical and textural characteristics of the chestnut activated carbon contribute to better pesticide adsorption compared to the coal-based adsorbents. These properties exerted varying effects on the adsorption process. Atrazine adsorption, for instance, was affected differently by functional groups and the pH of the adsorbents. While the adsorption of other pesticides was primarily physical due to the factors as larger molecule volumes compared to atrazine or the difficulty in forming chemical interactions like π-π interactions or hydrogen bonding. The use of chestnut shell wastes-derived adsorbents demonstrated potential for positively impacting the circular economy in the future.

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