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PYROLYSIS OF SOYBEAN WASTE: A ROUTE TO ACTIVATED CARBON FOR FUNGICIDE CHLOROTHALONIL CAPTURE

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ABSTRACT

Soybean residues were transformed through static pyrolysis carried out at temperatures between 250 °C and 350 °C. The gaseous fraction analysis showed that the gases emanated in the pyrolysis are mainly CO₂ and CO. Furthermore, it was proved that this methodology constitutes a simple way to obtain useful carbons for the capture of pesticides present in an aqueous matrix. For example, the concentration of Chlorothalonil in a 7:3 water: acetonitrile solution decreases by 76-77 % through adsorption on the carbons obtained.

Keywords: *Thermal reaction, mesoporous carbons, pesticide*

1. INTRODUCTION

Many agroindustrial processes yield side-products that constitute an organic waste. Due to the high volumes of biomass produced this way, chemists have been intensively working to revalorize these residues. The techniques applied to transform the biomass are biochemical or thermochemical. The latter allows processing a greater amount of feedstock in shorter periods. In particular, biomass pyrolysis meets the conditions to generate high-energy-density bio-oil or biochar (Wang *et al.*, 2021).

The open burning of biomass undoubtedly releases carbon dioxide and other volatile organic compounds into the atmosphere. Therefore, the use of pyrolysis techniques that allow careful control of the products leaving the process is a key to minimizing the impact on the environment. To this end, static pyrolysis under vacuum conditions is presented as an advantageous technique for the study of volatile and non-volatile fractions of the pyrolysate (Pepino *et al.*, 2014; Firpo *et al.*, 2019).

In addition to the production of bio-oils and biochar, the transformation of biomass also produces coals that have multiple uses in the agricultural environment itself. For example, activated carbons obtained from pyrolysis can be

used for industrial pollution abatement as an adsorbent for toxic pollutants in wastewater. In structure, activated carbons are highly microporous carbons with high internal surface area and porosity. Commercially, they are the most common adsorbents used to remove organic compounds from air and water streams. They are also often prepared from coal (non-renewable source) or specially dedicated biomass such as bamboo wood. However, any material with high carbon and low inorganic content can be used as a raw material for activated carbon production (Lewoyehu, 2021).

It is also an ecological issue the persistence of fungicides in the environment. For instance, the fungicide Chlorothalonil (CT) was banned in the United States and the European Union because of its permanence in humic acids and its transformation in potential toxic byproducts in groundwater (Kiefer *et al.*, 2020). But, besides this, it is still widely used in developing countries. In this way, primarily solutions involve the photochemical transformation of the pesticide into more soluble byproducts with less toxicity.

Figure 1. Chlorothalonil structure.

As part of our study of gaseous products emitted to the atmosphere by burning industrial biomass residues from soybean pressing, it was reported here the obtention and utilization of carbons from soybean waste static pyrolysis to retain the fungicide Clorotalonil from an aqueous matrix.

2. MATERIALS AND METHODS

The soybean residue used is the solid left-over obtained after the pressing of soybeans in the oil production process. This residue was ground to particle sizes of less than 1 mm. Subsequently, 500 mg of this material was placed in a Pyrex glass ampoule and evacuated for 2 minutes until a pressure of 10^{-2} mbar was reached. They were then sealed and subjected to static pyrolysis reactions at different times (10-60 min) and temperatures (250°C - 350°C) in an electrical furnace (ORL-T40400). The gas composition was transferred and analysed by IR spectroscopy using a Fourier transform infrared spectrometer (Bruker IFS 28) following the temporal variation of reactants and products for all the reactions performed. All spectra were recorded in the range $500\text{--}4000\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} . The remaining solid was subjected to successive washes in a Soxhlet apparatus (3 x 120 mL ethanol, 98%) 3 hours each time. Then, the same procedure was performed but with acetonitrile (ACN, HPLC 99.5%, Sintorgan). Finally, the recovered solid was dried at atmospheric pressure until a constant weight was achieved.

The selected solids were used to perform adsorption experiments with the pesticide Chlorothalonil. The process was monitored by UV-VIS spectroscopy on an Agilent 8354 spectrophotometer ($xL=3.65 \times 10^{-2}$ absorbance units) using a quartz cell with an optical path of 1 cm. The Chlorothalonil was purified from a commercial sample (compressed powder 82.5% w/w) by extraction with ethyl acetate followed by purification via chromatographic column using mixtures of n-hexane and dichloromethane.

For each assay, 20 mg of the carbonaceous solid was placed in disc extraction cartridges (3M Empore - Fischer Scientific, octadecyl, 10mm/6mL). The solution passage was always performed in 2 mL aliquots using a flow

rate of 2 mL every 5s. In the first stage, the carbons were washed with 20 mL (10 x 2 mL) of water: acetonitrile solution (7:3). Then, 2 mL of a solution of 1.4 mM CT in water: acetonitrile (7:3) was passed over the carbon under study.

3. RESULTS AND DISCUSSION:

3.1. Gas Analysis

In all the performed reactions, it was found that the most significant proportion of the gases corresponds to CO_2 (85 - 97 %), while CO was the second-largest gas present (2 - 9 %). In addition, it was also observed the formation of various volatile organic compounds (VOCs), whose presence and proportion depends on the temperature and time of pyrolysis: methane, propane, butane, ethylene, methanol, acetone, methyl, and ethyl acetate, among others.

It was determined that the formation of mono-carbon compounds is favored by the increase of temperature and pyrolysis time because the cracking processes were promoted and produced thermodynamically more stable compounds.

Figure 1. Characterization of the gas fraction by IR spectrum at 350°C .

3.2. Carbon obtaining

The percentages of solid crude oil recovery at each temperature and time are shown in Graph 1. It can be seen that the mass recovered in each pyrolysis reaction (corresponding to coal and non-volatile compounds) tends to remain constant as the temperature increases (47-58%). This trend is more evident in Graph 2, where the mass percentages of carbon mass at both 300°C and 350°C are very close. Likewise, when comparing the mass percentages of carbon at the three

reaction times studied, it is evident that this mass is independent of the reaction time. In other words, the amount of carbon initially formed in the process remains practically unchanged through the static pyrolysis of biomass.

Graph 1. Mass percentage of non-volatile fraction obtained in the static pyrolysis of soybean waste at different times and temperatures.

Graph 2. Mass percentage of carbon fraction obtained in the static pyrolysis of soybean waste at different times and temperatures.

The carbons obtained at the maximum working temperature (350 °C) and at times of 10 and 60 min (labelled as C10min and C60min respectively) were selected to perform the Chlorothalonil adsorption tests. The maximum absorption wavelength of the CT is 233 nm, as can be seen in graph 3 (red line). From the analysis of the spectral curves of the solution after passage over the C10min and C60min carbons, it was found that the concentration of CT decreases by 76 and 77% (green and blue lines).

Graph 3. Spectral curves show the adsorption of CT by the carbons obtained at 350 °C at 10 min (C10min, green line) and 60 min (C60min, blue line).

When comparing the behavior of C10min and C60min with commercial activated carbon, it is evident that the latter is very efficient in adsorbing CT and produces a decrease of its concentration by 94%. However, considering that the carbons obtained in this work did not have any chemical activation, the effectiveness shown is acceptable and could be improved by further treatment.

4. CONCLUSIONS:

The production of several VOCs of potential atmospheric impact from the burning of biomass soybean residues was evidenced. In addition, it was determined that the formation of mono-carbon compounds is favored by the increase in temperature and pyrolysis time because the cracking processes are promoted.

The carbonaceous solids obtained in this work were also effective retention agents for the pesticide Chlorothalonil in an aqueous solution. It is expected that the thermal or chemical activation of the carbonaceous solids studied will further improve their compound adsorption properties. It would also be of great interest to test the carbons with aqueous matrices containing other pesticides or mixtures thereof.

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