PYROLYSIS OF SOYBEAN WASTE: A ROUTE TO BIOCARBON FOR PESTICIDES CAPTURE

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ABSTRACT

Background: This study explores the potential use of biomass residues from soybean pressing via static pyrolysis to produce carbonaceous materials for pesticide adsorption. It emphasizes concerns regarding the environmental impact of agroindustrial waste and the persistent nature of pesticides in soil and water systems. Aims: To investigate the efficacy of biochar obtained from soybean waste in adsorbing pesticides. Specifically, to analyze the gas products generated during pyrolysis and characterize the obtained carbonaceous material for its adsorption capabilities. Methods: Soybean residue underwent static pyrolysis at various temperatures and durations. Gas analysis utilizing FTIR spectroscopy identified the gaseous products generated during the pyrolysis process. The obtained biochar underwent successive washes and characterization through FTIR spectra comparison with commercial activated carbon. Through absorption assays, using UV-VIS spectroscopy, investigations were conducted on the solid biocarbon fractions to evaluate their capacity for absorbing pesticides. Results: Gas Analysis: The study revealed the production of volatile organic compounds (VOCs) and highlighted the prevalence of mono-carbon compounds with increased temperature and pyrolysis time. The analysis demonstrated consistent carbon mass percentages across different reaction conditions. Characterization of Biochar: Comparison with activated carbon indicated structural similarities with heightened intensity in certain bands, suggesting the presence of incomplete cellulose cracking in the obtained biochar. Regarding the Chlorothalonil, Atrazine and Dicamba remotion, notably, the concentration of Chlorothalonil in a 7:3 water: acetonitrile solution decreases by 77 % through adsorption on the carbons. Discussion: The investigation examined the adsorption efficiency of the biochar for Chlorothalonil, Atrazine, and Dicamba from aqueous solutions. Chlorothalonil exhibited substantial retention by the biochar, while Atrazine showed comparatively lower adsorption effectiveness. Remarkably, Dicamba did not demonstrate retention by either the biochar or activated carbon. Conclusion: The study underscores the potential of pyrolyzed soybean waste for pesticide adsorption, particularly highlighting Chlorothalonil's strong affinity with the carbonaceous structure. Further research is needed to optimize adsorption properties and explores potential enhancements of these materials through additional treatment methods, offering promising avenues for environmental remediation.

Keywords: Pyrolysis, mesoporous carbons, Chlorothalonil, Atrazine, Dicamba.

1. INTRODUCTION

Many agroindustrial processes yield side-products that constitute 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 of a great amount of feedstock in short 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, using pyrolysis techniques that allow careful control of the products leaving the process is key to minimizing the environmental impact. 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 (a 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).

At present, the modern intensive agricultural practices aimed at providing food for the increasing global population raise ecological concerns. Along with this comes the massive use of pesticides, which are chemicals that serve the purpose of eradicating unwanted pests to safeguard agricultural production. Pesticides include insecticides (insects), herbicides (weeds), and fungicides (fungi), among others (Hassaan and El Nemr, 2020). The agricultural demand fuels the growth of the agrochemical industry, providing a range of chemicals distinguished by diverse structural characteristics and intended targets. Figure 1 shows the structures and uses for the pesticides essayed in this work. Each of these chemicals plays a significant role in agricultural practices but also raises concerns related to environmental impact, health effects, and management of their residues in soil and water systems.

Figure 1. Chemical structures of Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, 1), Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, 2), Dicamba (3,6-dichloro-2-methoxybenzoic acid, 3)

The persistence of pesticides refers to their ability to remain in the environment after application. It involves how long they stay active, break down, or degrade. Factors like the type of pesticide, environmental conditions, and application methods influence their persistence. Some pesticides break down relatively quickly, especially when exposed to soil sunlight, air, water, or microbial activity. Others, however, might persist for longer periods, posing risks to the environment, including water sources, wildlife, and even human health through bioaccumulation in the food chain. 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 into potential toxics byproducts in groundwater (Kiefer et al., 2020). However, 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. Moreover, the herbicide Atrazine (AT) is very persistent and does not degrade gradually (Chen et al., 2019), so it emerged as the most frequently detected contaminant in aquifers across Latin America and mirrored similar occurrences in European and United States groundwater (Mohaupt et al., 2020). Despite the herbicide ban in European countries in 2004 due to surpassing permitted drinking water limits (0.1 μg L\(^{-1}\)), its persistence in water and soil continues to result in its detection even years after prohibition.

Adsorption presents a viable method for extracting contaminants from water, holding significant promise, particularly when leveraging biomass or agricultural remnants for valorization, known as bio-based adsorption. This environmentally benign technique proves non-
invasive, ensuring elevated efficacy, straightforward operation, and convenient regeneration (Vievard et al., 2023). Because of its simplicity and cost-effectiveness, adsorption was discovered to be the most preferred technique (Rani et al., 2017).

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 leftover obtained after pressing 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, 30, and 60 min) and temperatures (250 °C, 300 °C, and 350 °C) in an electrical furnace (ORL-T40400). Completed the pyrolysis step, the ampoule was connected to a glass vacuum line equipped with a capacitance pressure gauge (0-760 Torr, MKS Baratron). Once the ampoule opened, the total pressure of formed gases was measured and then transferred to a 210 mm-path gas cell placed inside the sample compartment of a Fourier transform infrared (FTIR) spectrometer (Bruker IFS-28). The composition of the gas mixture was performed for all the reactions. All spectra were recorded in the range 500-4000 cm⁻¹ with a resolution of 2 cm⁻¹.

For the identification and quantification of each component, reference spectra and the corresponding calibration curves of different gases were obtained under the same experimental conditions. The remaining biochar was subjected to successive washes in a Soxhlet apparatus (3 x 120 mL ethanol, 98%) for 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 Chlorothalonil, Atrazine, and Dicamba. The process was monitored by UV-VIS spectroscopy on an Agilent 8354 spectrophotometer (xL=3.65*10⁻² absorbance units) using a quartz cell with an optical path of 1 cm.

Chlorothalonil was purified from a commercial sample (compressed powder 82.5% w/w) by extraction with ethyl acetate, followed by chromatographic column purification using n-hexane and dichloromethane. Atrazine was obtained in a pure form by its isolation from a commercial sample of Atrazine TC 97%. Finally, Dicamba 96.4% (Riedel de Haën) was used without any further purification.

For each essay, 20.0 mg of the carbonaceous solid was placed in a disc extraction cartridge (3M Empore - Fischer Scientific, octadecyl, 10mm/6mL). Prior to the essay, the biocarbons were washed several times with water: acetonitrile solution (7:3) in 2 mL aliquots, following the process by UV-VIS spectroscopy. The washing process was concluded once the spectral curve of the aliquots showed no further changes. Subsequently, 2 mL of a freshly prepared solution of the pesticide in water: acetonitrile (7:3), was passed over the carbon under study. The solution flow was always performed in 2 mL aliquots using a flow rate of 0.4 mL/s.

3. RESULTS AND DISCUSSION:

3.1. Gas Analysis

A typical gas phase spectrum resulting from the FTIR analysis is presented in Figure 2.

A glance at the spectra allows the identification of signals corresponding to the generation of carbon dioxide (broad signal at around 2350 cm⁻¹ and sharp peak at 667 cm⁻¹) and carbon monoxide (bands centered at 2140 cm⁻¹) as majority reaction products. Quantitative analysis revealed CO₂ values ranging between 17 and 81%, while CO ranged from 0.4 to 2.4%, depending the pyrolysis assay conducted. Furthermore, the observation of various volatile organic compounds (VOCs), whose presence and proportion are contingent upon the temperature and time of pyrolysis, was noted. Graphs 1 and 2 illustrate the general trends in the analysis of gaseous products for the 10 min reactions at 250 ºC, 300 ºC, and 350 ºC.
Higher temperatures and prolonged pyrolysis times favored the formation of mono-carbon compounds. This phenomenon occurs due to a significant rise in cracking events with increasing temperatures, producing thermodynamically more stable compounds.

3.2. Carbon obtaining

Graph 3 illustrates the percentages of solid crude oil recovery at each temperature and reaction time. Observably, the recovered mass in each pyrolysis reaction, representing coal and non-volatile compounds, tends to stabilize within a range of 47-58% as the temperature rises. This trend is more evident in Graph 4, which displays remarkably similar carbon mass percentages at 300°C and 350°C. Yet another noteworthy consideration is the consistent similarity in carbon mass percentages obtained at each temperature, regardless of the reaction times. In other words, the amount of carbon initially formed in the pyrolysis process remains unchanged throughout the experiment.

Soxlet equipment utilizing ethanol and acetonitrile as solvents was employed to wash the reaction crude and extract the solid carbons. An interesting observation was made: with increasing reaction temperature, the cleaning solution exhibited reduced coloration, indicating a lesser presence of organic residues adhering to the solid
material. This phenomenon can be attributed to the increased occurrence of biomass fragmentation at higher temperatures. This leads to a higher production of volatile compounds that are effectively eliminated during the reduced pressure drying of the solid carbons obtained.

The FTIR spectra of the biocarbons were compared with a commercial activated carbon sample (AC), analyzing the appearance, disappearance, or reduction of bands (Figure 3). In the activated carbon, distinct bands at approximately 1450 cm\(^{-1}\) correspond to C-C vibrations in aromatic rings, while bands around 1500 cm\(^{-1}\) indicate C=C stretching vibrations within the plane. Similarly, the biocarbons exhibit bands within the same range, validating the presence of C=C and C-C skeletal bonding. A distinguishing feature of these biocarbons was the heightened intensity of bands between 2900-3100 cm\(^{-1}\) associated with C-H stretching, indicating a higher degree of incomplete cellulose cracking.

Consistent patterns emerge across all reaction durations and temperatures when comparing the biochars among themselves. Considering this, the carbons obtained at 350°C for 60 minutes (labeled as C60min) were chosen for the adsorption tests due to their easier washing properties.

### 3.3 Pesticide adsorption tests

The molar absorption coefficient at the corresponding maximum absorption wavelengths obtained for three pesticides were Chlorothalonil: \(\varepsilon_{233\text{nm}} = 66400 \text{ M}^{-1} \text{ cm}^{-1}\); Atrazine, \(\varepsilon_{222\text{nm}} = 34386 \text{ M}^{-1} \text{ cm}^{-1}\) and Dicamba: \(\varepsilon_{205\text{nm}} = 35306 \text{ M}^{-1} \text{ cm}^{-1}\).

After examining the spectral curves of the pesticide solution following its filtration through the C60min biocarbon, a significant decrease by 77% of its concentration was observed (Graph 3). AC also achieved good adsorption with 94% retention.

In the case of Atrazine, its adsorption was found to be not very effective, achieving only 18% retention by the C60min (Graph 4). Likewise, AC did not achieve near complete retention as it had with Chlorothalonil and showed a 62% decrease in Atrazine concentration.

The pesticide Dicamba exhibited distinct behavior, as it was not retained by either the C60min or the activated carbon. Upon a thorough analysis of spectral curves, it is evident that the transit of the Dicamba solution through the disc extraction cartridge housing C60min or activated carbon triggers an elevation in absorbance, presumably attributed to an augmented baseline. Essentially, it is conceivable that Dicamba facilitated the extraction or dissolution of carbon, potentially resulting in a cleansing effect.
Based on the findings, it is evident that CT demonstrates a stronger affinity towards the carbonaceous structure. This propensity could be attributed to its higher proportion of chloro substituents, which provide the molecule with an apolar character that facilitates an effective interaction between the solid material and the pesticide. Conversely, AT that also bears chloro groups shows a weaker interaction with the biocarbon. This can be explained by the more polar feature of the molecule due to the triazine ring and the secondary amine moieties, which reduce the AT engagement with the biocarbon. Lastly, DC, characterized by its acidity and being the most polar among the series, exhibits no retention, displaying a greater inclination towards the aqueous solvent system (water:acetonitrile, 7:3).

4. CONCLUSIONS:

The production of several VOCs of potential atmospheric impact from burning 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 study displayed notable efficacy in retaining pesticides like Chlorothalonil and Atrazine within aqueous solutions. Considering that these carbons underwent no chemical activation, their demonstrated effectiveness is regarded as promising and suggests potential for enhancement via supplementary treatment methods. The thermal or chemical activation of the carbonaceous solids studied is expected to further improve their compound adsorption properties. Exploring these carbons in aqueous matrices containing different pesticides or mixtures thereof would also be a valuable avenue for future research.

5. DECLARATIONS

5.1. Study Limitations

The study is limited to the sample size and the methods employed.

5.2. Acknowledgements

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5.3. Funding source

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5.4. Competing Interests

The authors declare no conflict of interest.

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ACKNOWLEDGMENTS:

6. REFERENCES:


Figure 3. FTIR spectra comparison of commercial activated carbon (AC) and Biocarbons obtained at 350 °C at different reaction times.