Conversion of corncob into high-performance biochar: pyrolysis conditions, activation methods, and adsorption capabilities

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The improper disposal of agricultural waste contributes significantly to greenhouse gas emissions, environmental degradation, and health risks(Wakudkar & Jain, 2022). Among agricultural biomasses, corncob (CC), a byproduct of corn production, is one of the world's most diffused and extensive crops (the global production in 2019/2020 peaked at 1,11641 million metric tons)(X. Liu et al., 2014; Wang et al., 2022). The high organic carbon content (45-50%) in its layered structure makes it a promising candidate for biochar production through slow pyrolysis. Biochar's properties, such as porosity, pH, and adsorption capacity, are influenced by biomass characteristics and pyrolysis operative conditions and can be enhanced through functionalization methods like chemical activation(Jayakumar et al., 2023; Sandoval-Rangel et al., 2024).
The present study investigates the conversion of corncob into biochar through slow pyrolysis by analyzing the operative conditions and testing the most promising biochar for adsorption tests. Pre- and post-activation processes are examined to enhance biochar's physicochemical properties. Absorption tests with methylene blue (MB) are conducted to assess the effectiveness of both pyrolysis and activation and to compare the results with existing literature. The study's novelty lies in exploring the activation effects not only on CC but also on the derived biochar.
The adopted research approach is described as follows. The biochar is produced via slow pyrolysis using a horizontal fixed-bed pyrolysis reactor. 15-20 g of CC is divided into three crucibles and inserted into a stainless-steel chamber. 0.4 ml/min nitrogen flowrate (is sent to the reactor throughout the process to guarantee an inert environment. Pyrolysis is performed at 500 °C and 700 °C with a heating rate of 10 °C/min and a residence time of 30 min. The condensable and non-condensable gases (not investigated in this context) are piped into a condensation unit. The obtained samples are called BC500 and BC700, respectively. Chemical activation, concerning pre- and post-activation with base and acid, represents the strategic point of the study. Pre-activation is performed following the one-step procedure by (He et al., 2023)with some modifications. It consists of a dry mixing of chemical reagent (KOH or H_3PO_4) and biomass, with a 1:1 impregnation ratio, directly into the crucible, followed by pyrolysis at 500 and 700 °C, respectively. The obtained biochar is washed until pH =7, filtered, and dried overnight at 60 °C. The obtained samples are CC-KOH-OS or CC-H3PO4-OS, and pyrolysis temperature is specified for each sample name. Post-activation is performed following the procedure by (L. Liu et al., 2019) where CC is first pyrolyzed at 500 °C and then activated in a solution containing KOH or H_3PO_4 with a 1:1 impregnation ratio under stirring for 24 h and then thermally activated with a second pyrolysis at 700 °C. Neutralization and drying overnight are the final steps. The obtained samples are called BC-KOH and BC-H_3PO_4. Commercial active carbon (CAC) has been chosen as a control for comparative purposes. The produced samples have been characterized through nitrogen physisorption at 77 K to evaluate the specific surface area (SSA) and the pore size distribution, FT-IR spectroscopy to evaluate functional groups, and elemental analysis to evaluate the amount of carbon, nitrogen, hydrogen, and, consequently, H/C ratio, and proximate analysis to measure the moisture, volatile matter, ashes and fixed carbon. Methylene blue (MB) adsorption tests are performed on the best-performing biochar samples, considering their physicochemical properties, Precisely, 20 g/l of MB solution has been prepared as a stock solution for subsequent experiments. Experiments are conducted using biochar concentrations equal to 0.5 g/l and 1 g/l in 100 ml of solution stirred at 200 rpm at room temperature. The absorbance measurements are conducted after 10, 20, 30, 40, 60,120,180, and 1440 min to monitor the variation of MB concentration. The absorbance of MB solutions is measured with a UV-vis spectrophotometer at a wavelength of 660 nm. The absorption capacity (q_t) at any time is calculated with the equation 1:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

Where C_0 is the initial MB concentration (mg/l), C_t is the MB concentration at any time (mg/l), m is the amount of the adsorbate (g) and V is the volume of the diluent(l).

Preliminary results concern the biochar yields and physic-chemical properties. Experimental results (**Table 1**) show that biochar's yield decreases with temperature increase since more volatile compounds enrich the liquid and gaseous fractions. Additionally, both pre- and post-activations result in higher yields, cause the enhancement of SSA. However, pre-activation leads to a mesoporous structure, while post-activation results in a microporous structure. Among all samples, CC-H_3PO_4 resulted in the best one in terms of physicochemical properties, thus showing the highest surface area (682.18 m^2/g), the highest hydrophilic nature (H/C= 0.073), and the highest MB removal efficiency even if the concentration is halved. This is probably due to the introduction of acid-functional groups that enhance the interaction with MB cationic molecules via both hydrogen bond formation and electrostatic attraction. It can be also noticed that pre-activation of corn cob with KOH at 500 °C results in low SSA (44.50 m^2/g) and then pre-activation at 700 °C is required to obtain a SSA comparable with the one related to acid pre-activation. Nevertheless, CC-KOH-OS-500 possesses higher MB removal efficiency than CC-KOH-OS7-00 both in terms of kinetics and concentration, thus drawing to the conclusion that the mechanism of absorption is not only physical but also chemical.

Sample	**Yield [%]**	**H/C**	**SSA [m^2/g]**	**Pore volume [cm^3/g]**
BC500	25	0.043	0.198	-
BC700	24	0.065	4.55	0.001
BC-KOH	39	0.056	243.95	0.13
BC-H_3PO_4	40	0.073	298.73	0.16
CC-KOH-OS-500	60	0.034	44.50	0.05
CC-KOH-OS-700	51	0.035	489.43	0.26
CC-H_3PO_4-OS-500	53	0.063	682.18	0.41
CAC	-	0.044	927.56	0.79

Table1: preliminary experimental results

Future developments will include a deeper insight into the properties of samples produced through more characterizations with a synthesis optimization. Acid pre-activation of corn cob at 700 °C in one step pyrolysis will be performed for comparative purposes as well as acid and basic pre-activation of corn cob at 500 and 700 °C in a two step process involving preliminary impregnation of the biomass and subsequent pyrolysis. Moreover, physical activation with CO_2 will be investigated and finally, MB absorption tests will be performed at higher MB concentrations and the kinetic and thermodynamic will be investigated.

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