

Corncob Biochar Activation by Phosphoric Acid and Hydrogen Peroxide for Enhancing Ammonium Adsorption

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Abstract:

Biochar is a multifunctional carbon-pore material that can be used as a soil amendment and an adsorbent biomaterial for water treatment. Nitrogen is one of the nutrients that causes water eutrophication in aquatic environments. In this study, corn cob biochar (CBB) characterizations were modified using phosphoric acid (P-CCB) and hydrogen peroxide (H-CCB) to improve ammonium removal efficiency from synthetic wastewater. The biochar physiochemical properties were investigated, including ash content, pH, total elements, functional groups, surface area, and morphological structure. A batch kinetic trial extended to 24 h was carried out to evaluate the adsorption efficiency of ammonium (40 mg L^{-1}) by the three biochar types; moreover, four kinetic models were tested. The results revealed that the acid oxidation process reduced ash content, pH, and total carbon content values. At the

same time, oxygen percentage and molar ratios of O/C and (O+N)/C were increased relative to the original corncob biochar. The efficiency of the activated biochars to remove $\text{NH}_4^+\text{-N}$ was higher than that of CCB, and there was not much difference between P-CCB and H-CCB. The adsorption capacity (Q_e) of $\text{NH}_4^+\text{-N}$ by CCB reached 4.47 mg g^{-1} after 24 h, whereas this amount increased due to the activation and reached 6.88 and 6.61 mg g^{-1} for P-CCB and H-CCB, respectively. The Pseudo-Second order model displayed well-fitting results to elucidate the adsorption results depending on the R^2 value (0.99–1.00). These results suggest that corncob-activated biochar by phosphoric acid and hydrogen peroxide could effectively eliminate ammonium-nitrogen from wastewater.

Keywords: Eutrophication; Ammonium pollution; Activated Biochar; Batch Adsorption; Kinetic Models

Introduction

Water is an essential natural resource for all living organisms. Correspondingly, the challenge of the twenty-first century is sustaining water of sufficient quantity and quality to fulfill the population's demands. On the other hand, agricultural activity has greatly intensified water demand due to the requirement to deliver food to the people, leading to increased water pollution. Nutrient-rich water, mainly nitrogen and phosphorus, is responsible for water eutrophication caused by excessive N and P water discharge from point and nonpoint sources in aquatic environments. As a result, dissolved oxygen levels drop, causing toxicity for fish, as well as destruction of aquatic ecosystems. (Yin et al., 2017 and Pantoja et al., 2023). The major nitrogenous substances encountered in wastewater are ammonia (NH_3) and ammonium (NH_4^+) ions. The acceptable level of NH_4^+ in surface water and groundwater is less than 3 mg L^{-1} . In contrast, a level of 0.2 mg L^{-1} may be toxic to aquatic life, especially in aquaculture systems that should be lower than 0.05 mg L^{-1} (Zhang et al., 2013; Khalil et al., 2018).

Various Physical, chemical, and biological technologies have been studied and applied to control the high levels of inorganic NH_4^+ and NO_3^- from aquatic systems. Nitrification/denitrification methods are the most common biological technologies to eliminate NH_4^+ from wastewater. However, the process effectiveness of biological technologies requires specific conditions related to C/N ratio permanency, ammonium concentration, aeration rate, growth rate of nitrifying bacteria, sensitivity of bacteria, water pH, solution temperature, seasonal conditions, and economic value (Yang et al., 1999; Kurama et al., 2010; Huang et al., 2015; Yin et al., 2017). Physical and chemical technologies have also been utilized to remove ammonium contaminants, including air stripping, adsorption, ion exchange, chemical precipitation, and chlorination (Kurama et al., 2010; Zhang et al., 2013). Among these techniques, adsorption and ion exchange techniques are widely used due to the highly effective and low-cost adsorbents, the ease of operation, and the economic viability of this approach (Zhang et al., 2013; Yin et al., 2017). The main challenge with adsorption methods is finding inexpensive and effective adsorbents (Gao et al., 2023). Numerous adsorbent materials demonstrated high removal efficiency for inorganic contaminants from wastewater, such as sepiolite, zeolite, limestone, clay mineral, ion exchange resin, activated carbon, fly ash, aluminum oxide, charcoal, and biochar (Liang

et al., 2016; Yin et al., 2017; An et al., 2021). Some materials mentioned are expensive and unavailable (Yin et al., 2017).

Biochar, a green environmental biomaterial, is one of the critical, economical, and highly efficient bio-sorbents that effectively eliminate organic and inorganic pollutants from polluted water (An et al., 2021). Biochar is a recalcitrant, solid, porous, carbon-rich product generated by a low pyrolysis process at a temperature higher than 300 °C in inert atmospheric conditions. Generally, biochar gains multifunctional advantages as a soil enhancer and an effective environmental adsorbent in water treatment. The main advantages of biochar usage are its simplicity of supplement and availability, inexpensive and high adsorptive material for multipollutant (El-Gamal et al., 2023).

Biochar has a high ability to adsorb $\text{NH}_4^+\text{-N}$ from polluted water. It is a low-cost and eco-friendly beneficial potential alternative material (An et al., 2021). However, the primary physiochemical characteristics of biochar determine its ability to adsorb ammonium-nitrogen depending on the surface and morphological structures of biochar. Some studies reported that the pyrolysis conditions are the main reason that affected the biochar characterizations and, subsequently, the adsorption efficiency (Wang et al., 2023). The lower ability of biochar to adsorb ammonium significantly depends on the low specific surface area, porosity, and low variety of surface functional groups via the oxidation process with acid agents (Khalil et al., 2018). Therefore, the activation process to modify biochar properties by increasing the content of oxygen-containing functional groups is necessary to improve its adsorption capacity. Enhancing adsorption capacity of biochar requires activating, altering, and increasing oxygen-containing functional groups (Gao et al., 2016; Fdez-Sanromán et al., 2020; Wang et al., 2023).

This research aimed to study the influences of phosphoric acid (H_3PO_4) and hydrogen peroxide (H_2O_2) activation process on the corncob biochar characterizations and to evaluate the activation process on the adsorption efficiency of $\text{NH}_4^+\text{-N}$ using inactivated and activated corncob biochar.

Materials and Methods

Biochar Production, Modification, and Characterization

The air-dried corncob (CC) residues were carbonized to generate biochar using a slow pyrolysis muffle furnace at $500\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ with a residence time of 30 min under a limited condition of oxygen based on Saleh et al., 2012. The generated biochar (CCB) was cooled under environmental lab conditions ($25\text{ }^{\circ}\text{C}$). The biochar sample was ground, passed through a 0.5 mm sieve, and stored in plastic bags for further use. To produce modified biochar (P-CCB), the powdered biochar (10 g) was immersed in 100 ml concentrated H_3PO_4 (85%) or H_2O_2 (30%) for 24 h, then the products were thoroughly rinsed with tap water, followed by deionized water until the rinsing liquid is neutral; finally, the generated biochars were dried for 24 h at $80\text{ }^{\circ}\text{C}$. The derived biochars were called CCB, P-CCB, and H-CCB for corncob, phosphoric acid modification, and hydrogen peroxide modification, respectively. The physicochemical characterizations of obtained biochars are shown in Table 1.

The pH value of CCB and its modification (P-CCB and H-CCB) was measured in a suspension of 1:100 (biochar: deionized water) after stirring at $90\text{ }^{\circ}\text{C}$ for 20 min, according to Masulili et al. (2010). The ash percentage of the three biochar types (CCB, P-CCB and H-CCB) was determined by dry combustion at $600\text{ }^{\circ}\text{C}$ for 12 h. After reaching ambient temperature, the remaining residue was weighted to calculate the ash content according to El-Gamal et al. (2022):

$$\text{Ash, \%} = \left(\frac{A}{B}\right) \times 100 \quad (1)$$

Where *A* and *B* are the weight of residue (ash) after combustion (g) and biochar before combustion (g), respectively.

The main elemental compositions of biochars (C, H, N, and S) were measured using CHNS Elemental Analyzer (Vario MACRO cube, Elementar, Germany), while the following equation calculated oxygen content:

$$O, \% = 100 - \Sigma(C + N + H + S + \text{ash}) \quad (2)$$

The surface area of the three biochar types and their pore diameter and pore volume were determined by Brunauer–Emmett–Teller (BET) method equation using the N_2 adsorption-desorption isotherm at 77 K on a gas sorption analyzer (Micro-trac MRB BELSORP-mini X, Japan). The techniques of FT-IR (FT/IR-5300, JASCO Corporation, Japan) and SEM

(SEM, JEOL, Model JSM – IT200, Japan) determined the biochar functional groups and morphological structure, respectively. The details of these analyses can be found in El-Gamal et al. (2017).

Kinetic Adsorption Experiments:

The adsorption of ammonium (NH₄⁺-N) on the corncob (CCB) and its modified biochars (P-CCB and H-CCB) were investigated by adding 0.125 g (oven-dry equivalent) to 25 ml of NH₄Cl solution (1:200, suspension ratio). The initial concentration of NH₄⁺-N was 40 mg L⁻¹ added in different bottles, which were agitated at 200 rpm (25 ± 5 °C) for varying contact times extended from 5 minutes to 24 hours. After each time, the supernatant was filtered via filter paper (Whatman no. 42), and the amount of NH₄⁺-N was determined by the Vapodest 30s Gerhardt Kjeldahl distillation unit (Keeney and Nelson, 1982). The result data were measured in triplicate by calculating average values. The adsorbed amount at time T (Q_t , mg g⁻¹) and equilibrium (Q_e , mg g⁻¹) and removal efficiency (RE, %) of NH₄⁺-N were calculated as following equations:

$$Q_t = \frac{(R_o - R_t)A}{M} \quad (3)$$

$$Q_e = \frac{(R_o - R_e)A}{M} \quad (4)$$

$$RE = \frac{(R_o - R_e)100}{R_o} \quad (5)$$

Where R_o , R_t , and R_e are the NH₄⁺-N concentration (mg L⁻¹) of initial, time T, and equilibrium, respectively. M is the adsorbent weight (g), and A is the solution volume.

The kinetics of the NH₄⁺-N biosorption data on biochar surface were analyzed and described using different kinetic models such as Elovich, Fractional Power, Pseudo-First order, and Pseudo-Second order mathematical models in the linear forms as given below:

The Pseudo-First order kinetic model depends on the quantity of free active sites in a sorbent material directly correlating with the sorption rate.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

Pseudo-Second order model presumes that the sorption rate of sorbant is regulated by chemisorption behavior on active sites.

$$t/Q_t = 1/k_2 Q_e^2 + 1/Q_e t \quad (7)$$

The Elovich model has been used extensively to analyze chemisorption kinetics data, which is more applicable for heterogeneous adsorbing surfaces.

$$Q_t = \beta \ln(\alpha\beta) - \beta \ln t \quad (8)$$

Fractional Power is a Freundlich equation modified model version

$$\ln Q_t = \ln a - b \ln t \quad (9)$$

Where Q_t (mg g^{-1}) is the adsorption capacity at time t (min), Q_e (mg g^{-1}) is the adsorption capacity at equilibrium, and t is the contact time (min). The Pseudo-First- and –Second order adsorption rate constants are k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$), respectively. α ($\text{mg g}^{-1} \text{min}^{-1}$) is the initial sorption rate; β (g mg^{-1}) is the Elovich model adsorption constant, while a (mg g^{-1}) and b (min^{-1}) are the Power Function model constants.

Result and Discussion

Characterization of original and modified Corncob Biochar

Table (1) displays the selected physicochemical characteristics of generated corncob biochar (CCB) at a temperature of 500 °C for 30 min and the modified form of phosphoric acid (P-CCB) and hydrogen peroxide and (H-CCB). The ash content of CCB (9.13 %) was higher about 2.54 and 1.42 times relative to P-CCB (3.59 %) and H-CCB (6.44%), respectively. It is well known that the acid treatment leads to remove and dissolve the salts constituting biochar ash. The same result was confirmed by Wang et al., 2020; they found that the ash content of peanut shell biochar decreased from 32.5% to lower than 10% after H_2O_2 , HCl, and H_2SO_4 treatments. The pH values of corncob biochar was slightly alkaline (7.80, Table 1) that reduced and declined to neutral range after activation treatments with a difference value of 0.78 unit for P-CCB and 0.84 unit for H-CCB. This may be due to an oxidation reaction on the surface of the biochar and formation of more acidic functional groups (e.g. COOH). It is reported that the pH of pinewood biochar (7.16) decreased to 5.66 after H_2O_2 modification (Huff and Lee, 2016 and Tan et al., 2019). Additionally, Wang et al. (2020) observed that the pH of alkaline peanut shell biochar became acidic after the modification with different acids.

Table 1- The main physicochemical characterization of the original corncob biochar (CCB) and acid-activated biochar by phosphoric acid (P-CCB) and hydrogen peroxide (H-CCB).

Parameter	Unit	CCB	P-CCB	H-CCB
Ash		9.13	3.59	6.44
pH		7.80	7.02	6.96
Total Elements Analysis				
N	%	0.75	0.81	0.65
C	%	69.82	64.66	65.94
H	%	3.58	3.65	3.49
S	%	0.98	0.27	0.32
O	%	19.74	27.02	23.16
N/C	Molar ratio	0.010	0.011	0.008
H/C	Molar ratio	0.648	0.673	0.631
O/C	Molar ratio	0.225	0.314	0.264
(O+N)/C	Molar ratio	0.235	0.324	0.272
P	%	0.20	0.44	0.19
Ca	%	0.408	0.241	1.150
Mg	%	0.116	0.030	0.117
K	%	0.261	0.094	0.129
Na	%	0.522	0.249	2.304
Total Surface Area (BET)	m ² g ⁻¹	107.48	35.01	130.51
Average Pore Diameter	nm	23.06	147.24	19.23

The carbon content in both activated biochars was lower than that of original corncob biochar, which decreased about 7.39 and 5.56% for P-CCB and H-CCB, respectively. Notably, there a slight increase in N, H, and O contents due to the H₃PO₄ activation that led to increase the of H/C, O/C, and (O+N)/C molar ratios as compared to inactivated biochar and H₂O₂ activation. Additionally, P percentage of P-CCB increased about 120% relative to CCB. In contrast of the P content in P-CCB, the S, Ca, Mg, K, and Na elemental compositions were decreased about 72.45, 40.93, 74.14, 63.98 and 52.30%, respectively. The elemental analysis of H-CCB biochar represented that the nitrogen, hydrogen, and potassium contents were decreased. While the calcium and sodium contents had the highest values relative to CCB and P-CCB. Phosphorus and magnesium displayed no significant different change between CCB and H-CCB.

In this study, The P-CCB surface area decreased about three times, and the average pore diameter became broader relative to the original corncob without activation. Phosphoric acid activation could increase the pore volume of macropores compared to mesopores and micropores. In contrast, H-CCB had the highest surface area and the lowest

average pore diameter compared to CCB and P-CCB. The mesoporous and macroporous structures of H-CCB decreased due to the treatment with hydrogen peroxide, which destroyed these pores. The described result corresponds with most of the previous study conclusions (Yakout et al., 2015; Wang et al., 2020). It is generally recognized that micropores have a huge surface area because of their tremendous quantity and depth (Yakout et al., 2015).

The main functional groups of the original corncob biochar (CCB) and acid-activated biochar by phosphoric acid (P-CCB) and hydrogen peroxide (H-CCB) were displayed in Figure (1). FT-IR is a vital tool to detect the bonding mechanisms of contaminants on biochar surfaces to recognize the different functional groups necessary for the adsorption of pollutants. The FTIR spectra of CCB, P-CCB, and H-CCB are shown in Figure 1 in the 4000–500 cm^{-1} range. The O-H stretching bands of the broad spectrum were observed between 3730 and 3210 cm^{-1} , indicating the existence of phenols, alcohols, and carboxylic acids compounds (El-Gamal et al., 2017; Gupta et al., 2018). Narrow bands between 2350 and 2319 cm^{-1} are associated with the carbonyl functional group ($\text{O}=\text{C}=\text{O}$), demonstrating the presence of alkynes (Gupta et al., 2018). A strong peak at 1573 cm^{-1} is assigned to stretching vibrations of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ in aromatics, alkenes, and amines functional groups. This peak became less instance and shifted to 1569 and 1562 cm^{-1} in P-CCB and H-CCB, respectively, due to the activation process rather than its original corncob biochar before activation. The weak peak around 1365 cm^{-1} detected for CCB indicates the aromatic CH and carboxyl-carbonate groups (Wang et al., 2020); this peak disappeared in P-CCB due to H_3PO_4 treatment. The bonds of $\text{C}-\text{O}-\text{C}$ of polysaccharides and $\text{C}-\text{O}-\text{H}$ stretching were observed at 1071 and 1042 cm^{-1} . The peaks around 874 to 746 cm^{-1} correspond to C-H stretching aromatic functional, alkyl halides (C-Br stretch) groups and/or the presence of inorganic compounds such as KCl and CaCl_2 (Claoston et al., 2014). The biochar surface, in general, comprises huge oxygen-containing functional groups, and oxidative treatment is expected to increase the P-CCB and H-CCP oxygen-containing functional groups. However, the modification process of H_3PO_4 or H_2O_2 has little impact on the oxygen functional groups of biochar. The same results were confirmed by Wang et al (2020).

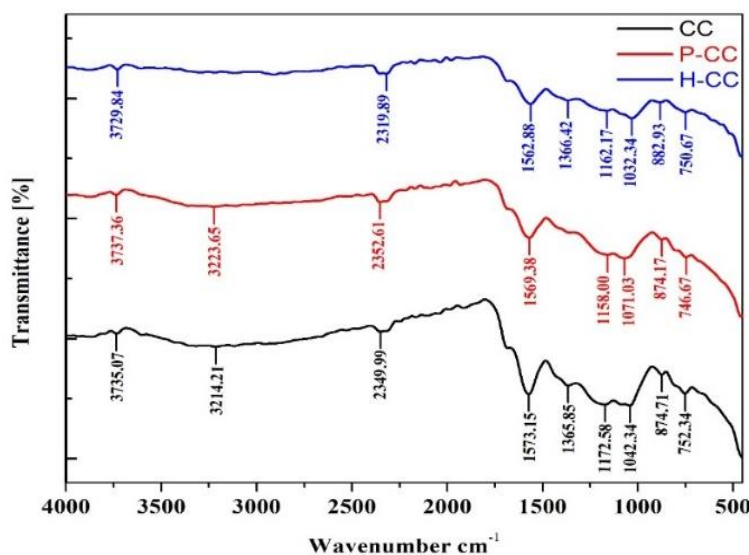


Fig. 1. FTIR of the corncob biochar (CCB) and its activation by H_3PO_4 (P-CCB) and H_2O_2 (H-CCB).

The SEM image (Fig. 2) shows that CCB biochar produced at 500 °C under controlled conditions of oxygen and the modified biochars after emerging in H_3PO_4 (P-CCB) or H_2O_2 (H-CCB). The porous structure could be observed clearly with a highly complex network with different channels and pores. However, the unique surface was changed due to the treatment of H_3PO_4 , and the caves became wider and larger than unmodified biochar, which led to a decrease in the surface area and an increase in the average pore diameter (Table 1). Generally, the structure of CCB was not much different from that of activated biochar (P-CCB). The H_2O_2 -modified CCB gained more pores with a thick wall. Additionally, the Pores numbers were developed, which led to the increase in the surface area (BET).

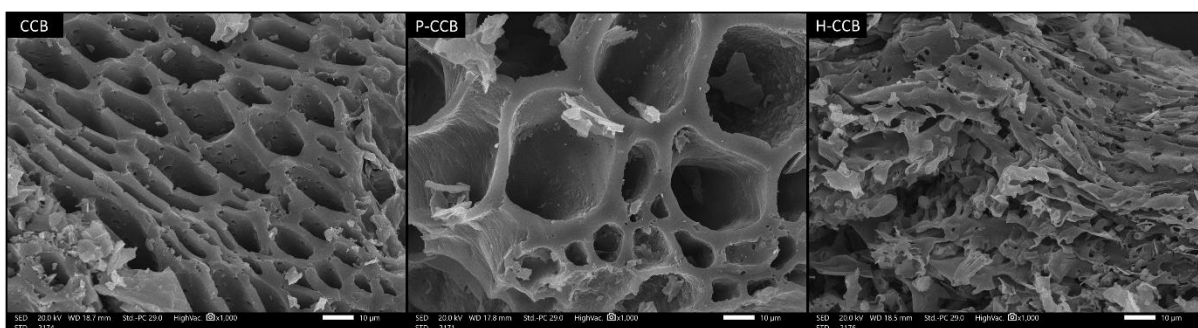


Fig. 2. Scanning electron microscopy images of the corncob biochar (CCB) and its activation by phosphoric acid (P-CCB) and hydrogen peroxide (H-CCB).

Adsorption Efficiency of NH_4^+ -N on Corncob Biochar

The effect of contact time on ammonium adsorption efficiency by original CCB biochar and its modifications of P-CCB and H-CCB is displayed in Fig. 3. The experiment was extended to 24 h to evaluate the three mentioned biochar types to remove $\text{NH}_4^+\text{-N}$ (40 mg L^{-1}) from synthetic wastewater. Notably, the adsorption of $\text{NH}_4^+\text{-N}$ by the three tested biochar can be divided into three stages. The first one is rapid adsorption that occurred within the first two hours, while the second stage is a slow adsorption process that extended from 2 to 6 h. The second has a low rate of adsorption (Wang et al. 2020). A stable adsorption curve and slow adsorption rates characterize the latest stage. During the second stage, the adsorption curve tends to be stable and the adsorption rate became low. After that, the equilibrium was achieved due to the saturation of the adsorption site. After 6 h, the adsorption capacity of ammonium-nitrogen reached the maximum saturated adsorption. Wang et al. (2023) concluded the same results, who confirmed that the adsorption of $\text{NH}_4^+\text{-N}$ by different modified biochars was achieved after 360 min, and insignificant changes were observed in the adsorption capacity. The quick initial adsorption was encouraged by the large number of free-occupied adsorption sites at the initial stage of the adsorption phase. The interactions between negatively charged surface anion groups (such as COO^- and OH^-) and NH_4^+ ions may promote rapid adsorption. After the two hour, the adsorption rate slowed, indicating that the ionic equilibrium between the adsorbent and the ammonium solution had been reached (Yang et al., 2018; Ismail and Hameed 2014).

Generally, the efficiency of the activated biochars to remove $\text{NH}_4^+\text{-N}$ was higher than CCB, and there is not much difference between P-CCB and H-CCB. That means activated corncob biochar had a better adsorption performance for ammonium than inactivated corncob biochar. However, it is observed that the adsorption efficiency of CCB was achieved after 6 h (Fig. 3), which reached 51.00 % and the adsorption capacity (Q_t) of 4.08 mg g^{-1} . At the same time, this percentage of $\text{NH}_4^+\text{-N}$ by P-CCB and H-CCB was raised to 61.59% and 60.82% at the same contact time, respectively. When contact time was further increased, the ammonium adsorption capacity by CCB did not rise considerably with time increasing from 6 h to 24 h (54.03%). Subsequently, the adsorption capacity exhibited approximately no discernible difference. Despite this result, the adsorption efficiency of ammonium by P-CCB and H-CCB increased significantly with increasing contact time and reached 84.44% (Q_t , 6.88 mg g^{-1}) and 81.94% (Q_t , 6.61 mg g^{-1}) after 24 h, respectively.

These data indicate that the adsorption efficiency of both modified biochar materials was higher than that of CCB. Interestingly, the adsorption performance of both modified biochar for $\text{NH}_4^+\text{-N}$ was 30.41% (P-CCB) and 27.91% (H-CCB) higher than unmodified biochar.

Adsorption kinetics of different Corncob Biochar

A fundamental aspect of assessing the adsorption process is adsorption kinetics. Pseudo-First order, Pseudo-Second-order, Elovich, and Fractional Power kinetic models were used to study the adsorption mechanism of ammonium on corncob biochar and its modifications. According to kinetic parameters, the correlation coefficients (R^2) of the kinetic model for $\text{NH}_4^+\text{-N}$ adsorption on CCB and modified biochar (P-CCB and H-CCB) are gained from Fig. 4 and Table 2 that listed the fitting parameters of investigated kinetic linear models. The Pseudo-Second order model is an effective model to describe the adsorption process due to the higher calculated determination coefficients (R^2 , 0.99-1.00) than the other kinetic models.

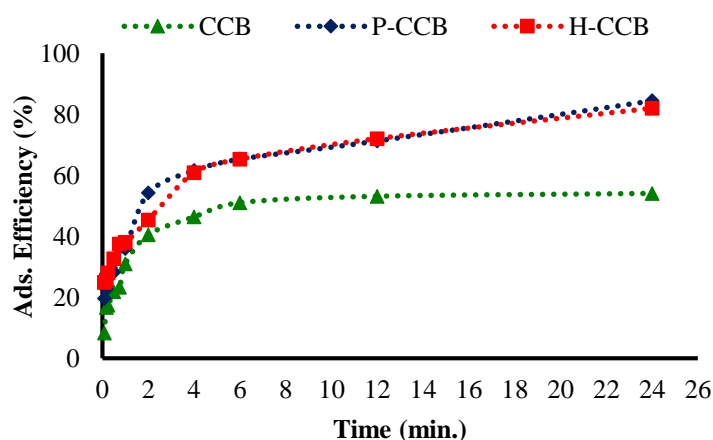


Fig. 3. Removal efficiency (RE, %) of ammonium ions from synthetic wastewater using corncob biochar (CCB) and its activation by phosphoric acid (P-CCB) and hydrogen peroxide (H-CCB).

Additionally, the calculated adsorption capacity from the Pseudo-Second order kinetic model ($Q_{e,cal}$) was remarkably close to the empirical equilibrium capacity results ($Q_{e,exp}$) (Table 2). Although R^2 of Pseudo-First order is relatively close to Elovich and Fractional Power, the calculated $Q_{e,cal}$ values for Pseudo-First order are ineffective in describing the adsorption process of ammonium by the three tested biochar types due to the calculated $Q_{e,cal}$ results were invalid to empirical values ($Q_{e,exp}$). However, it is observed that there is an insignificant influence between the P-CCB and H-CCB on the q_e values. The obtained data from the Pseudo-Second order model

provided that the rate-limiting step in the sorption of $\text{NH}_4^+\text{-N}$ on different corncob biochar materials is chemical sorption. Generally, Pseudo-Second order depends on the sharing and exchanging of electrons between pollutants and adsorbent, meaning the adsorption is a chemical process. In comparison, the Pseudo-First order presupposes that the number of adsorbate molecules might adsorb onto the same number of biosorbent active sites.

As shown in Table 2, the result of Elovich's initial rate sorption (α , $\text{mg g}^{-1} \text{min}^{-1}$) of H-CCB was the highest ($1.02 \text{ mg g}^{-1} \text{min}^{-1}$) rather than P-CCB; the better adsorption mechanism is demonstrated that chemisorption is the rate-limiting process (Wang et al., 2020 and Fawzy et al., 2022). Subsequently, the order of this value could be summarized as $\text{H-CCB} > \text{CCB} > \text{P-CCB}$. Furthermore, the low Elovich constant value (β) suggests that the activation energy for chemisorption is low, and many mechanisms govern the adsorption process. β is a constant associated with the extension of surface coverage. The surface area of P-CCB ($35.01 \text{ m}^2 \text{g}^{-1}$) was found to be relatively low compared to CCB ($107.48 \text{ m}^2 \text{g}^{-1}$) and H-CCB ($130.51 \text{ m}^2 \text{g}^{-1}$), implying that P-CCB adsorption may occur more through functional groups. The internal- and hidden-functional groups of biochar pore cavities were thought to be tightly bound and sank for NH_4^+ ions (Saleh et al., 2012). According to the adsorption rate of the Fractional power model (a , mg g^{-1}), H-CCB had the highest ammonium adsorption rate (1.23 mg g^{-1}) followed by P-CCB (0.99 mg g^{-1}). In contrast, CCB recorded the lowest adsorption rate (0.57 mg g^{-1}). Additionally, the fractional power constant value (b , min^{-1}) of the studied biochars was less than one, indicating that this model may adequately describe the adsorption kinetics data (Inyinbor et al., 2016).

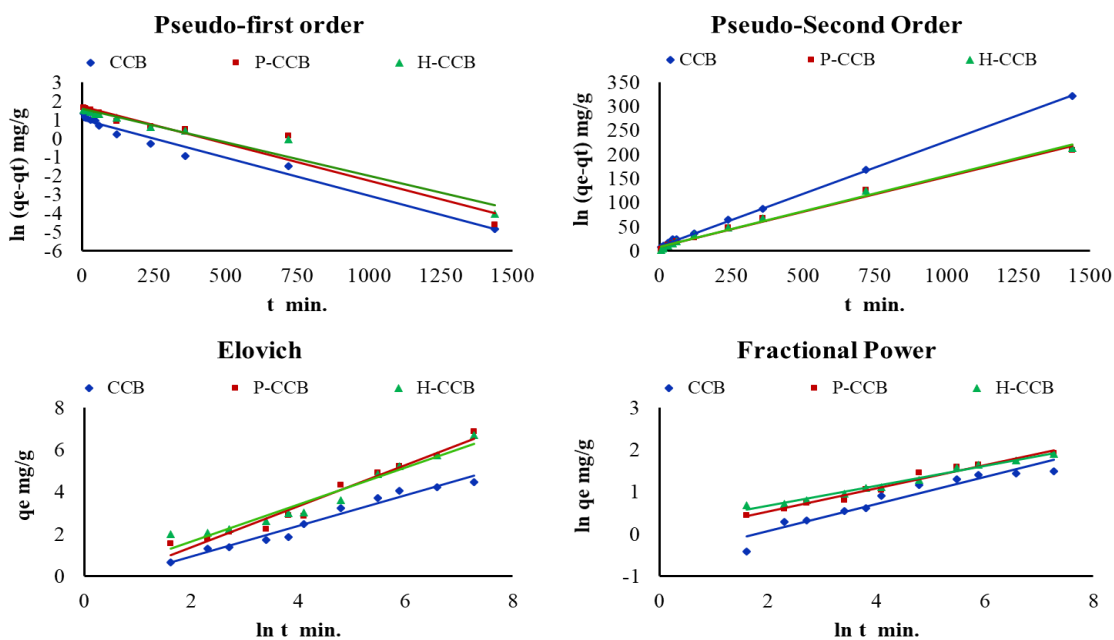


Fig. 4. Linear kinetic models of Pseudo-First order, Pseudo-Second order, Elovich, and Power fraction for $\text{NH}_4^+\text{-N}$ on corncob biochar (CCB) and its activation by phosphoric acid (P-CCB) and hydrogen peroxide (H-CCB).

Table 2- Adsorption kinetic parameters for ammonium ion ($\text{NH}_4^+\text{-N}$) adsorption on corncob biochar and its phosphoric acid (P-CCB) and hydrogen peroxide (H-CCB) activations.

Kinetic Model	CCB	P-CCB	H-CCB
$Q_{e,exp}$ (mg g^{-1})	4.47	6.88	6.71
Pseudo-First order			
$Q_{e,cal.}$ (mg g^{-1})	2.82	5.55	4.99
K_1 (min^{-1})	-0.0041	-0.0039	-0.0036
R^2	0.97	0.93	0.96
Pseudo-Second order			
$Q_{e,cal.}$ (mg g^{-1})	4.59	6.91	6.77
K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.0048	0.0022	0.0024
R^2	1.00	0.99	0.99
Elovich			
α ($\text{mg g}^{-1} \text{min}^{-1}$)	0.67	0.58	1.02
β (g mg^{-1})	0.73	0.97	0.88
R^2	0.97	0.96	0.95
Fractional Power			
a (mg g^{-1})	0.57	0.99	1.23
b (min^{-1})	0.32	0.28	0.24
R^2	0.91	0.98	0.98

Conclusion:

This study concluded that the two activated corncob biochars by phosphoric acid and hydrogen peroxide demonstrated favorable characteristics for effectively removing ammonium-nitrogen from synthetic wastewater. Generally, the activation process reduced ash content, pH, and total carbon content values, whereas oxygen percentage and molar ratios of O/C and (O+N)/C were increased relative to the original corncob biochar. The BET surface area, mean pore diameter and porous structure characteristics showed different behaviors than corncob biochar; however, the opposite trends were observed for both activated corncob biochar. The kinetic adsorption efficiency of both activated biochars to remove ammonium-nitrogen was higher than corncob biochar, and there is not much difference between phosphoric acid and hydrogen peroxide activation on the removal efficiency. That means activated corncob biochar had a better adsorption performance for ammonium than inactivated biochar. The adsorption behavior for ammonium-nitrogen followed the Pseudo-Second order model, suggesting that chemical adsorption is the rate-limiting step in the sorption of ammonium-nitrogen on different corncob biochar materials.

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