Phosphorus Fraction in Hydrochar from Co-Hydrothermal Carbonization of Swine Manure and Rice Straw: An Optimization Analysis Based on Response Surface Methodology

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Abstract: Livestock manure and crop residues are significant sources of phosphorus. However, the ineffectiveness of current processing technologies often leads to the suboptimal recovery of this phosphorus, causing considerable resource wastage and environmental pollution. Recently, global research has increasingly been focused on the resource recovery of organic waste materials using hydrothermal carbonization technology. This study investigated variations in phosphorus forms in the hydrochar produced from swine manure and rice straw, employing diverse hydrothermal carbonization conditions and applying the Box–Behnken response surface methodology and Hedley’s phosphorus fractionation method. The results indicated that inorganic phosphorus predominates in the hydrochar, with organic phosphorus comprising 5–30% of the total phosphorus. Furthermore, the available phosphorus content, as measured by NaHCO$_3$ extraction, decreased as the reaction time and temperature of the hydrothermal carbonization process increased. The concentrations of H$_2$O-P and NaHCO$_3$-P fractions decreased with increasing reaction times and temperatures but increased with a higher swine manure-to-straw ratio. Conversely, the concentrations of NaOH-P and HCl-P fractions showed an increasing trend with rising reaction temperature, prolonging reaction time, and using a high swine manure-to-straw ratio. Consequently, this study offers vital theoretical and practical insights into the resource utilization of livestock manure and crop straw, significantly contributing to the challenges of waste management and environmental sustainability in agriculture.

Keywords: phosphorus; hydrochar; sustainable development; hydrothermal carbonization; response surface methodology; circular economy

1. Introduction

With the development of livestock and agricultural industries continuing, there has been a corresponding increase in swine manure, other animal waste emissions, and crop residue production [1,2]. Improper waste management can lead to severe ecological pollution, posing a threat to human health, and considerable resource wastage, as observed...
Notably, swine manure is rich in essential nutrients like N, P, and K, and crop residues including straw contain various nutritional elements; therefore, both are highly suitable for recycling [4–6]. Consequently, the transformation of livestock waste and straw into valuable resources has emerged as a prominent research topic [1,7]. This approach not only facilitates effective resource conservation but also promotes global sustainable development.

Presently, a range of methods, including aerobic composting, anaerobic digestion, and thermochemical treatments, are used to treat and recover resources from agricultural and livestock waste [8–10]. Thermochemical treatment approaches, including combustion, pyrolysis, gasification, and biochar production, are notable for their rapid reaction times, enabling efficient conversion of waste into various useful products [1]. Recently, the hydrothermal carbonization method, in particular, has attracted significant attention [11,12]. This method involves combining biomass with water under specific temperature conditions using thermochemical conversion technology, resulting in a variety of high-value products, primarily hydrochar [13,14]. When compared to alternative techniques, hydrothermal carbonization can be applied to wet samples such as fresh manures and provides substantial advantages in terms of resource recovery, energy conversion efficiency, and environmental friendliness, presenting a novel approach to the sustainable management of agricultural and livestock waste [15,16].

In biological systems, phosphorus is a fundamental element that is essential for the growth and development of both flora and fauna. The global scarcity of phosphorus resources makes its recovery and reuse not only urgent but also critically important [17,18]. With the development of urban industrialization, a large amount of phosphorus is discharged into natural water bodies, causing serious damage to natural systems and forming non-point source pollution, such as the eutrophication of oceans and lakes. Maintaining the ecological balance of phosphorus is challenging. Additionally, the global shortage of phosphate resources poses a threat to the supply of phosphate fertilizers [19]. Livestock manure and straw can be converted via suitable recycling processes into valuable “secondary phosphorus mines”, forming a crucial route for phosphorus resource recovery [20,21]. The effective utilization of these agricultural wastes not only helps mitigate environmental pollution but also provides a potent strategy for addressing phosphorus shortages [22,23]. Consequently, the comprehensive investigation and implementation of these resource utilization technologies are of profound significance for environmental protection and sustainable resource recycling.

Employing hydrothermal carbonization technology to process livestock manure and straw, particularly for phosphorus recovery, is at the forefront of current research in environmental science and engineering. Khosravi et al. [24] demonstrated that increasing the hydrothermal reaction temperature enhances the phosphorus content in the solid phase of swine manure hydrochar. In contrast, Song et al. [4] found that acidic conditions accelerate organic matter degradation, reducing the total organic carbon (TOC) content in hydrochar. Additionally, it has been shown that both acidic and alkaline conditions can enhance the solubility of nutrients, such as phosphorus, leading to a reduced concentration in the solid phase of hydrochar. In an attempt to enhance the bioavailability of phosphorus in hydrochar, significant efforts have been undertaken recently to optimize the process parameters in hydrothermal conversion. Fu et al. [25] showed that high reaction temperatures in the hydrothermal process promoted the transformation of various forms of phosphorus into calcium-bound phosphorus, thereby increasing the proportions of HCl-P fractions. Huang et al. [26] found that the forms of phosphorus in hydrochar were closely linked to the metal ion content of hydrochar. They also demonstrated that altering the chemical composition of hydrochar, e.g., by adding iron salts, can alter phosphorus composition, increase vivianite content, and facilitate the transformation of stable phosphorus (i.e., hydroxyapatite) into a moderately stable form (i.e., vivianite). Studies have shown that incorporating lignocellulosic biomass, like straw, into animal manure can result in significant synergistic effects during the hydrothermal carbonization process. The sugars
generated from the hydrolysis of carbohydrates in straw interact with the amino acids produced from the hydrolysis of proteins in swine manure, a phenomenon known as the Maillard reaction [27]. The combination of the two can increase the yield, energy, and carbon recovery rate of hydrochar and also reduce the ash content [28].

Multiple studies have shown that hydrothermal processes can modulate the phosphorus nutrient composition in hydrochar [29–31]. The hydrothermal carbonization process under different conditions affects the form of phosphorus in the product’s hydrothermal carbon, enriches phosphorus elements, converts the non-point source pollution of phosphorus elements into resource recycling, establishes a good phosphorus cycle, realizes the utilization of agricultural waste, and reduces phosphorus loss. However, research into the relationship between hydrothermal reaction conditions and phosphorus components in hydrochar is still required. We hypothesize about generating hydrochar with the co-hydrothermal carbonization of straw and manure and using response surface methodology (RSM) [32,33] to verify our hypothesis and ultimately gain insight into the fundamental mechanisms that optimize phosphorus fractions. This study primarily investigates the co-treatment of straw and manure under various hydrothermal carbonization conditions, analyzing phosphorus forms in the resulting hydrochar. The Hedley fractionation method is employed to categorize phosphorus components, and the RSM is utilized to optimize process conditions (time, temperature, and the ratio of swine manure to rice straw). Consequently, this facilitates the construction of an interaction model between process conditions and phosphorus forms. Therefore, the process conditions for preparing hydrochar with varying properties were optimized, leading to efficient phosphorus utilization. This optimization provides technical support for the recovery and utilization of phosphorus.

2. Materials and Methods

2.1. Sampling of Swine Manure and Rice Straw

Air-dried swine manure samples were collected from a pig farm located in the suburbs of Beijing, China. The manure was thoroughly mixed for homogeneity and following the drying process, and the solid particles were ground using a crusher and then sieved through a 50-mesh stainless steel sieve. Processed samples were stored in zip-lock bags and preserved in a refrigerator at 4 °C for subsequent use. The basic physicochemical properties of these samples are shown in Table S1. Rice straw was collected from Lianyungang City, Jiangsu Province, China. Similar to the swine manure, the rice straw was also ground and sieved through a 50-mesh stainless steel sieve. Table S2 displays the fundamental physicochemical characteristics of these samples. This methodical approach to sample preparation is crucial for ensuring the consistency and reliability of subsequent experimental analyses.

2.2. Experiments and Measurements

RSM is a statistical method that can investigate the influences of individual factors and their interactive influences [34,35]. In this research, RSM was applied to evaluate the relative significance of hydrothermal process factors and the interactive effects of phosphorus forms in hydrochar. This study utilized the RSM with Design Expert 13, adhering to the Box–Behnken experimental design principles. As outlined in Table S3, a three-factor, three-level experimental design was implemented. The independent variables considered were reaction temperature, reaction time, and the swine manure-to-rice straw ratio. Measured responses included the available phosphorus content in hydrochar (g/kg) and the concentrations of \( \text{H}_2\text{O-P} \), \( \text{NaHCO}_3\text{-P} \), \( \text{NaOH-P} \), and \( \text{HCl-P} \) (mg/g). The experimental design and results are shown in Table S4. An 8 g mixture of swine manure and rice straw was placed in a hydrothermal reactor, to which 80 mL of deionized water was added, forming a 1:10 mixture. This mixture was processed in a 150 mL stainless steel hydrothermal reactor. The sealed reactor was then placed in an oven to facilitate the reaction. Each experimental condition was replicated three times. The resulting hydrochar was oven-dried at 105 °C for 24 h, ground into a fine powder, weighed, and finally sieved through a 50-mesh sieve. The sieved material was stored in sealed bags at 4 °C.
2.3. Analysis of Basic Parameters

The following basic parameters of the collected swine manure and rice straw samples were determined in replicates (n = 3) for each sample to ensure the reliability of the results:

1. **pH measurement**: A 0.50 g sample of dried hydrochar was mixed with 10.0 mL of deionized water and agitated at 25 °C and 1500 r/min for 24 h. The glass electrode was implemented to measure the pH of the sample suspension [36].

2. **Electrical conductivity (EC) determination**: A 0.50 g sample of dried hydrochar was combined with 5.00 mL of deionized water and agitated at 25 °C and 1500 r/min for 24 h. The sample suspension was then used to determine the EC value using an EC meter [37].

3. **The solid yield calculation**: Calculating the solid yield (SY) is crucial for understanding the efficiency of the carbon production process. SY is defined as the ratio of the mass of the obtained hydrochar to the mass of the raw material. The following equation was employed to calculate the SY.

\[
SY(\%) = \frac{M_2}{M_1} \times 100\%
\]  

where \(M_2\) represents the hydrochar mass (g) and \(M_1\) indicates the combined mass of swine manure and rice straw (g). This distinction in the solid yield of different samples is crucial for understanding the compositional dynamics within the system.

2.4. Analysis of P Fraction

Dried hydrochar samples were prepared to determine available phosphorus [38] and phosphorus fractions according to the procedure described by Hedley et al. [39]. This process involved measuring concentrations of the available phosphorus and the sequential fractionation of \(H_2O-P\), \(NaHCO_3-P\), \(NaOH-P\), and \(HCl-P\) fractions.

1. **For determining the available phosphorus**: 0.25 g of each hydrochar sample was mixed with 30 mL of 0.5 mol/L \(NaHCO_3\) solution. The mixture was agitated for 30 min at 25 °C and 150 r/min, followed by the separation of liquid and solid phases and an analysis of the filtrate to determine the available phosphorus concentration.

2. **Sequential fractionation**: For \(H_2O-P\) determination, 0.25 g from each hydrochar sample was mixed with 30 mL of deionized water. The mixture was agitated for 16 h at 25 °C and 150 r/min, then centrifuged at 4500 r/min for 10 min to separate the supernatant. Two tests were conducted, i.e., the filtrate was mixed with 2,4-dinitrophenol and 4 mol/L \(NaOH\) until it turned yellow; then, 0.9 mol/L sulfuric acid was added until the yellow faded to measure the concentration of \(H_2O-Pi\) fractions, and in the second test, 5 mL of the filtrate was mixed with 0.5 g of ammonium persulfate and 10 mL of 0.9 mol/L sulfuric acid. This was then boiled at 121 °C for 1 h. After boiling, 1 drop of 2,4-dinitrophenol was added to the filtrate; then, 4 mol/L \(NaOH\) was added until it turned yellow, followed by 0.9 mol/L sulfuric acid until the disappearing of the yellow color, and ultimately, the concentration of \(H_2O-Pt\) fractions was measured.

For \(NaHCO_3-P\) determination, the previously separated solid phase was further processed by adding 30 mL of the 0.5 mol/L \(NaHCO_3\) solution. The mixture was agitated for 16 h at 25 °C and 150 r/min, then centrifuged at 4500 r/min for 10 min to separate the supernatant. Two distinct measurements were performed on the supernatant. Initially, the filtrate was treated with 2,4-dinitrophenol and then 4 mol/L \(NaOH\) solution until it turned yellow. The yellow color was neutralized with 0.9 mol/L sulfuric acid, allowing for the determination of \(NaHCO_3-Pi\) in the sample. For \(NaHCO_3-Po\) determination, the filtrate was mixed with 0.5 g of ammonium persulfate and 10 mL of 0.9 mol/L sulfuric acid. After boiling at 121 °C for 1 h, one drop of 2,4-dinitrophenol was added, followed by 4 mol/L \(NaOH\) until a yellow color was formed. The yellow color was then neutralized with 0.9 mol/L sulfuric acid, enabling a comprehensive analysis of both \(NaHCO_3-Pi\) and \(NaHCO_3-Pt\) in the sample.
For NaOH-P determination, the solid phase from the previous step was further processed. Initially, 30 mL of 0.1 mol/L NaOH solution was added to the solid, followed by agitation for 16 h at 25 °C and 150 rpm. The mixture was then centrifuged at 4500 rpm for 10 min to separate the supernatant. This step is crucial for the following dual measurement processes. In the first measurement, the filtrate was mixed with 2,4-dinitrophenol, then gradually with 4 mol/L NaOH solution until it turned yellow. The yellow color was then neutralized by adding 0.9 mol/L sulfuric acid until it faded. This procedure determines the concentration of NaOH-Pi in the sample. For the second measurement, 0.4 g of ammonium persulfate and 10 mL of 0.9 mol/L sulfuric acid were added to the filtrate. The mixture was heated at 121 °C for 1.5 h. The resulting filtrate was treated with 2,4-dinitrophenol, then 4 mol/L NaOH until it turned yellow, and neutralized with 0.9 mol/L sulfuric acid to determine the NaOH-Pt concentration. This methodical approach ensures the precise quantification of NaOH-Pi and NaOH-Pt, providing comprehensive insight into the sample’s characteristics.

For HCl-P determination, the solid phase from the previous step was treated with 30 mL of 1 mol/L HCl solution and agitated for 16 h at 25 °C and 150 r/min. The mixture was then centrifuged at 4500 r/min for 10 min to separate the supernatant for two distinct assays. In the first assay, the filtrate was mixed with 2,4-dinitrophenol, and a 4 mol/L NaOH solution was added dropwise until it turned yellow. An aliquot of 0.9 mol/L sulfuric acid was then added dropwise until the yellow color faded, allowing for HCl-Pi measurement in the sample. The second assay was performed for the determination of HCl-Pt. The filtrate was treated with 0.6 g of ammonium persulfate and 10 mL of deionized water, then boiled at 121 °C for 1 h. An aliquot of 1 mL of the boiled filtrate was mixed with a drop of 2,4-dinitrophenol, and then 4 mol/L NaOH solution was added dropwise until it turned yellow, followed by 0.9 mol/L sulfuric acid until the yellow color disappeared.

3. Results and Discussion

3.1. Basic Parameters

The solid yield of hydrochar decreased with increasing reaction times and temperatures (Figure S1). Specifically, at a reaction time of 1 h and a temperature of 180 °C, the solid yield was approximately 64.9%. However, as the temperature was elevated to 210 °C, the yield dropped to around 53.8%; further increasing the temperature to 240 °C resulted in a further reduction in the yield to approximately 49.7%. When the reaction time was extended to 3 h, the solid yields at the reaction temperatures of 180 °C, 210 °C, and 240 °C were reduced to 56.3%, 51.4%, and 44.7%, respectively. This may be because as the reaction temperature increases and the reaction progresses, the moisture content initially decreases, followed by the volatilization of some volatile compounds, resulting in a decrease in weight [40]. Consequently, it was observed that hydrochar with a higher proportion of straw generally exhibited higher yields compared to those with a higher proportion of swine manure.

Figure S2 shows the results of the pH measurements. Specifically, when the swine manure-to-straw ratio was 0.5, the corresponding pH value of the hydrochar remained consistent within a narrow range of 5.8 to 6.0. However, as the ratio increased to 1.25, the fluctuation in the pH value of the hydrochar became significantly more pronounced, with measured values ranging from 5.9 to 6.3. Conversely, at a swine manure-to-straw ratio of 2, the pH value of the hydrochar stabilized and maintained a consistent range of 6.1 to 6.2. These findings are in close alignment with the results of Yu et al. [41] concerning the pH values of swine manure-derived hydrochar.

Figure S3 demonstrates the notable differences in the EC among different hydrochar combinations. A higher ratio of swine manure-to-straw increased the EC value of the hydrochar, while a lower reaction temperature resulted in a higher EC value of the hydrochar. Likewise, a shorter reaction duration correlated with an increased EC value. In hydrochar with more swine manure, the impact of the reaction temperature and the reaction time on the EC values was more observed, with a gradual slowdown in the declining trend in the
EC values. Xiong et al. [42] investigated the variations in the EC value of swine manure-derived hydrochar at different temperatures. He confirmed that the EC value decreased with increasing reaction temperatures. Similarly, in the hydrothermal carbonization of swine manure, Gascó et al. [40] observed comparable results.

3.2. Available Phosphorus

Following the application of RSM for data fitting, a regression equation (Equation (2)) was performed for the available phosphorus content in the hydrochar derived from swine manure and rice straw. The ANOVA results are presented in Table S5. The results indicate that the model fits commendably within the studied range (p-value < 0.05, the lack-of-fit p-value > 0.05). The R² value of 0.9835 (surpassing the 0.95 threshold) reflects a high correlation between the model and the data. Additionally, the adjusted R² was 0.9539, with a predictive R² of 0.7713. The discrepancy between these two R² values, which was less than 0.2, further implies the effective elucidation of process variations by the regression model.

\[
\text{Olsen} - P = 1.01 - 0.4505A - 0.7671B + 0.0636C + 0.3022AB - 0.0738AC - 0.0885BC + 0.1600A^2 + 0.1623B^2 - 0.2228C^2
\]

(2)

where \( A \) represents the reaction time (h), \( B \) indicates the reaction temperature (°C), and \( C \) represents the swine manure-to-straw ratio.

The available phosphorus, which was readily absorbable and utilizable by plants, served as an indicator for assessing phosphorus nutrient supply levels. In soil, Olsen-P is used to estimate the content of available phosphorus in alkaline soil, which is an important indicator for assessing soil fertility. Figure 1a illustrates how the available phosphorus content in the hydrochar increased with decreasing reaction temperature and reaction time. This aligned with Yu et al. [41], who observed a reduction in the available phosphorus content in swine manure hydrochar with longer reaction times and higher temperatures. Therefore, increasing the reaction temperature and prolonging the reaction time seem conducive to reducing the available phosphorus content in the hydrochar. Lang et al. [43] found that adding calcium oxide during hydrothermal carbonization promotes the conversion of phosphorus into stable forms. During the hydrothermal carbonization process, calcium ions in swine manure easily combine with phosphorus. As the reaction temperature increased and the reaction time prolonged, water-soluble phosphorus, Fe/Al oxides, or hydroxides in the available phosphorus are converted into stable forms of Ca-P, resulting in a decrease in the content of available phosphorus in hydrothermal carbonization [25]. On the other hand, in high-temperature environments, the crystallinity of phosphate minerals in hydrothermal carbonization increased, forming more stable phosphorus [44]. Therefore, by adjusting different process conditions, various forms of phosphorus can be converted into stable hydroxyapatite, which is greatly beneficial for recovering phosphorus from organic waste. Figure 1b,c show the response of surface and contour lines, within the range of a 0.5 to 2 swine manure-to-straw ratio as the swine manure-to-straw ratio increased; the content of available phosphorus in hydrochar first increased and then decreased. This means that when the ratio of swine manure to straw is either too high or too low, it will result in a decrease in the effective phosphorus content of hydrochar. This may be because when the ratio of swine manure to straw is high, the calcium ions and phosphorus with more hydrothermal carbon gather, and when the ratio of swine manure to straw is high, some organic acid extracellular enzymes in the straw promote phosphorus mineralization. An optimal swine manure-to-straw ratio maximizes the effective phosphorus content in the hydrochar. The data suggest that the optimal available phosphorus content in the hydrochar was achieved at a reaction temperature of 180 °C, a reaction time of 1 h, and a swine manure-to-straw ratio of 1.632. Consequently, this optimal ratio was crucial for enhancing phosphorus content, though the specific mechanisms behind this enhancement justify further investigation.
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Figure 1. Response surface and contour map of the available phosphorus in the hydrochar (a) at different temperatures and time points (swine manure-to-straw ratio = 1.25); (b) at different swine manure-to-straw ratio and time points (temperature = 210 °C); and (c) at different swine manure-to-straw ratio and temperatures (time = 2 h).

3.3. H2O-P

In phosphorus fractionation extraction, the phosphorus detected with water as a solvent is categorized as soluble phosphorus. Soluble phosphorus is abundant in natural water bodies and is easily utilized by aquatic plants. Figure 2 shows that water-extracted phosphorus primarily comprises inorganic phosphorus (constituting 85.1% to 99% of the total P), while organic phosphorus accounts for only 1% to 14.9% of the total P. The H2O content in hydrothermal carbon under different process conditions is relatively low, typically around 2 g/kg.
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By utilizing RSM, a regression analysis of water-soluble phosphorus content in the hydrochar resulted in Equation (3). The results of the analysis of variance are shown in Table S5. The significance of this model is evident, as indicated by a p-value less than 0.05, while a p-value greater than 0.05 indicates a poor fit within the study area. The R² value is 0.9894 (exceeding 0.95), the adjusted R² value is 0.9704, and the predicted R² is 0.8464, indicating a strong correlation between the measured and predicted values.

\[
\begin{align*}
H_2O - P &= 2.72 - 0.8883A - 1.58B + 0.6226C + 1.02AB - 0.3753AC \\
&\quad - 0.6760BC + 0.0472A^2 + 0.3397B^2 - 0.3823C^2
\end{align*}
\]

(3)

where A represents the reaction time (h), B indicates the reaction temperature (°C), and C represents the swine manure-to-straw ratio.

Figure 3a shows that the H₂O-P content in the hydrochar gradually increased in response to the decreasing reaction time and temperature. The trend of decreasing H₂O-P content in hydrochar with increasing reaction time weakened with increasing reaction temperature, while the trend of decreasing H₂O-P content in hydrochar with increasing reaction temperature became weaker with increasing reaction time. Figure 3b,c illustrate that a higher swine manure-to-straw ratio correlates with increased soluble phosphorus content in the hydrochar. The steeper response surface in Figure 3c compared to Figure 3b suggests a more substantial influence of the reaction temperature on the soluble phosphorus content. When the reaction temperature decreased, the trend of soluble phosphorus content increasing with the increase in swine manure-to-straw ratio was more evident. This may be because swine manure contains a higher amount of soluble phosphorus. At lower temperatures, prolonging the reaction time led to a reduction in the H₂O-P content, while at high temperatures, it gradually increased with longer reaction times. This phenomenon might be attributed to the rapid decomposition of organic matter in the initial stages of the hydrothermal reaction, causing phosphorus to transform into orthophosphate and a transition from the solid to the liquid phase. In the later stages of the reaction, as the environment becomes more alkaline, the liquid phase phosphorus is combined with calcium to form Ca-P precipitates, immobilizing it in the hydrochar [45]. Consequently, at high temperatures and longer reaction times, the solubility of phosphorus in the hydrochar exhibited a declining trend. Xiong et al. [42] studied the variation of the soluble phosphorus content in the hydrochar derived from swine manure to changes in the reaction temperature. They found that the soluble phosphorus content significantly decreased with increasing reaction temperatures, which is consistent with our data. Consequently, the optimal conditions were determined as a reaction time of 2.494 h, a reaction temperature of 180.000 °C, and a swine manure-to-straw ratio of 2.000; the content of H₂O-P is 4.438 g/kg.

Figure 2. Organic and inorganic phosphorus content in the H₂O-P of hydrochar.
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**Figure 3.** Response surface and contour map of the H₂O-P in the hydrochar (a) at different temperatures and time points (swine manure-to-straw ratio = 1.25); (b) at different swine manure-to-straw ratio and time points (temperature = 210 °C); and (c) at different swine manure-to-straw ratios and temperatures (time = 2 h).

### 3.4. NaHCO₃-P

The phosphorus recovered from the water, NaHCO₃-P, is considered unstable phosphorus [39]. In nature, it exists as an exchangeable form of phosphorus, comprising mainly inorganic and organic forms. Inorganic forms of phosphorus primarily consist of phosphorus adsorbed on the soil surface, while organic phosphorus is soluble phosphorus that is easily mineralized. Exchangeable phosphorus is relatively easy to release and is more readily utilized by plants. Figure 4 unequivocally shows that the majority of the exchangeable phosphorus, as measured by the NaHCO₃ extraction in the hydrochar, is inorganic. Under most process conditions, the exchangeable phosphorus in hydrothermal carbon is relatively low, typically below 2 g/kg. Significant differences in NaHCO₃-extractable
phosphorus content were observed among different groups. However, the proportion of organic phosphorus consistently remained below 30%. Table S5 shows the variance analysis of the regression equation for NaHCO$_3$-P, which was derived from the hydrochar using RSM, Equation (4). In addition, similar to the previous analysis of variance, the slight difference between the adjusted $R^2$ (0.9706) and the predicted $R^2$ (0.8369) due to the lack of fitting $p$-value (>0.05) is less than 0.2. This indicates that the model effectively explains this process.

$$\text{NaHCO}_3 - P = 1.98 - 0.7761A - 1.04B + 0.8417C + 0.6510AB - 0.4266AC - 0.5549BC + 0.1561A^2 - 0.4266B + 0.8417C + 0.6510AB - 0.4266AC - 0.5549BC + 0.1561A^2$$

where $A$ represents the reaction time (h), $B$ indicates the reaction temperature (°C), and $C$ represents the swine manure-to-straw ratio.

![Figure 4](image_url)

**Figure 4.** Organic and inorganic phosphorus content in the NaHCO$_3$-P of hydrochar.

The RSM analysis revealed a similar trend in NaHCO$_3$-P and H$_2$O-P variations, with parallel mechanisms of change. The key distinction lay in the varying degrees of influence that the reaction temperature and time had on the NaHCO$_3$-P content. Figure 5 illustrates that as the reaction time extended, the NaHCO$_3$-P content in hydrochar decreased. This trend became more pronounced as the reaction temperature decreased. Conversely, the NaHCO$_3$-P content decreased as the reaction temperature increased, but this trend weakened with longer reaction times. The reduction in NaHCO$_3$-P content may be attributed to the formation of non-apatite and apatite at high temperatures [43]. Figure 5b shows that extending the reaction time from 1 to 3 h and decreasing the swine manure-to-straw ratio from 2 to 0.5 resulted in a significant reduction in the NaHCO$_3$-P content from more than 4 g/kg to less than 1 g/kg. As the ratio of pig manure to straw increased, the content of NaHCO$_3$-P in hydrochar also increased. This trend is more pronounced in shorter reaction times. Furthermore, increasing the reaction temperature from 180 °C to 240 °C resulted in a decrease in the NaHCO$_3$-P content from nearly 5 g/kg to less than 1 g/kg; at lower temperatures, the trend of NaHCO$_3$-P content in hydrochar increased more significantly with the increase in the swine manure-to-straw ratio. (Figure 5c). This indicated that the content of NaHCO$_3$-P in the hydrochar decreased in response to increasing the reaction time and decreasing the ratio of swine manure to straw. Xiong et al. [46] observed a continuous decrease in the NaHCO$_3$-P content in swine manure hydrochar with increasing reaction temperatures, which is consistent with our results. The optimal conditions that yielded the highest NaHCO$_3$-P content comprised a reaction time of 1.296 h, a reaction temperature of 180.428 °C, and a swine manure-to-straw ratio of 1.719; the content of NaOH is 5.453 g/kg. As a result, it can be concluded that higher reaction temperatures resulted in
reduced NaHCO₃-P content. However, maximizing NaHCO₃-P content involved a balance of longer reaction times and higher temperatures, necessitating the careful consideration of these factors.

Figure 5. Response surface and contour map of the NaHCO₃-P in the hydrochar (a) at different temperatures and time points (swine manure-to-straw ratio = 1.25); (b) at different swine manure-to-straw ratios and time points (temperature = 210 °C); and (c) at different swine manure-to-straw ratios and temperatures (time = 2 h).

3.5. NaOH-P

In research on phosphorus fractionation, NaOH extraction from the hydrochar facilitated the chemical adsorption separation of organic and inorganic phosphorus from iron-aluminum compound surfaces. The NaOH extraction process mainly separated Fe-P and Al-P [39]. NaOH-P is insoluble phosphorus and belongs to mineral phosphorus, which is difficult for plants to absorb and utilize. In soil, it is a potential source of phosphorus. In
nature, iron (Fe) is susceptible to external interference and changes its form, which, in turn, affects the fixation or dissolution of phosphorus by iron. Therefore, NaOH-P is the main active phosphorus component in sediments and plays a significant role in the cycling of phosphorus at the sediment–water interface. The data show that inorganic phosphorus predominates in NaOH-P, comprising a significant proportion of 7% to 36% in most cases. Meanwhile, overall, groups 1 to 4 with lower levels of pig manure straw had lower levels of NaOH-P content in their hydrochar, while groups 5 to 15 with higher levels of pig manure straw had higher levels of NaOH-P content in their hydrochar. This may be related to the presence of more metal ions in pig manure, leading to the formation of more NaOH-P (Figure 6). This proportion was notably higher than the percentage of organic phosphorus found in soluble and exchangeable forms of phosphorus.

![Figure 6](image-url). Organic and inorganic phosphorus content in the NaOH-P of hydrochar.

Table S5 shows the analysis of variance results for the regression Equation (5) performed using the RSM for NaOH-P in the hydrochar. The p-value of less than 0.05 indicated its statistical significance. The R² value of 0.9822 (exceeding the threshold of 0.95) indicates a strong correlation. The slight difference between the adjusted R² (0.9503) and the predicted R² (0.7525) suggests the model’s effectiveness. Therefore, the findings suggest that the model significantly explained the hydrothermal carbonization process, though further research is needed to achieve a comprehensive understanding.

NaOH – P = 3.74 + 0.7295A + 1.28B + 0.9861C + 0.1137AB + 0.2256AC + 0.1989BC − 0.2819A² + 0.0206B² − 0.3003C²  

(5)

where A represents the reaction time (h), B indicates the reaction temperature (°C), and C represents the swine manure-to-straw ratio.

Figure 7a shows a gradual increase in the NaOH-P content in the hydrochar in response to rising reaction temperatures. Similarly, a longer reaction time resulted in an increased NaOH-P content. Among these factors, the rise in temperature had a more pronounced effect on the increase in the NaOH-P content through hydrothermal reaction. This phenomenon was attributed to phosphorus binding to iron and aluminum ions mainly in the later stages of the hydrothermal reaction [41]. Elevated reaction temperatures provided a homogeneous environment for inorganic ions, enhancing reactivity and promoting adsorption, complexation, and precipitation reactions [47]. Consequently, this led to increased Fe-P and Al-P contents in the solid phase of the hydrochar. Xiong et al. [46] found that the NaOH-P content in the hydrochar increased with a reaction temperature ranging from 200 to 240 °C, which is aligned with our results. However, they demonstrated a decrease in the NaOH-P content at a reaction temperature ranging from 260 to 280 °C. With increasing reaction temperatures, Fe/Al cations may be replaced by calcium ions,
forming hydroxyapatite phosphorus or becoming encapsulated by calcium phosphate, thereby leading to a decrease in NaOH-P content [48]. Figure 7b,c show that an increase in the swine manure-to-straw ratio was associated with an increase in the NaOH-P content. And, at higher temperatures, the increase in the ratio of swine manure to straw had a more significant effect on the increase in the NaOH-P content in hydrochar. This may also be attributed to the fact that swine manure contains more iron and aluminum ions, and metal ions at high temperatures tend to bind with phosphorus [44]. Three response surface plots indicated that the NaOH-P content varied (decreasing from 5 g/kg to less than 2 g/kg) in response to changes in the different studied conditions. The optimal reaction conditions for maximum NaOH-P content reached were identified as a reaction time of 2.981 h, a reaction temperature of 227.940 °C, and a swine manure-to-straw ratio of 1.974; the content of NaOH-P is 6.028 g/kg.

![Response surface and contour map of the NaOH-P in the hydrochar](image1)

![Response surface and contour map of the NaOH-P in the hydrochar](image2)

![Response surface and contour map of the NaOH-P in the hydrochar](image3)

**Figure 7.** Response surface and contour map of the NaOH-P in the hydrochar (a) at different temperatures and time points (swine manure-to-straw ratio = 1.25); (b) at different swine manure-to-straw ratios and time points (temperature = 210 °C); and (c) at different swine manure-to-straw ratios and temperatures (time = 2 h).
3.6. HCl-P

In the phosphorus fractionation extraction study, HCl-extracted phosphorus from hydrochar primarily consisted of Ca-P. HCl-P, also known as apatite-type phosphorus, is a calcium-bound form of phosphorus. In calcareous soils, HCl is commonly used to extract apatite-type phosphorus. Its properties are inert and have low environmental risks, but it is also not easily utilized by plants. As shown in Figure 8, in hydrochar, the primary component of HCl-P was inorganic phosphorus, while organic phosphorus constituted between 5 and 18%. The first, fifth, and twelfth groups are under conditions of low reaction temperature and time (a reaction temperature of 180 °C, a reaction time of less than or equal to 2 h), and the inorganic and organic phosphorus contents in HCl-P of hydrochar are low. The ratio of swine manure to straw in groups 1 to 4 is 0.5, while the ratio in groups 5 to 11 is 1.25, and the ratio in groups 13 to 15 is 2. The overall trend in HCl-P in hydrochar increased with the increase in the swine manure-to-straw ratio. Compared with other forms of phosphorus, the content of HCl-P is significantly higher. Using the RSM, the regression equation (Equation 6) for HCl-P extraction from hydrochar was obtained (Table S5). The analysis results indicate that the p-value of the model is less than 0.05, which is statistically significant. A p-value greater than 0.05 indicates a lack of fitting terms, suggesting that the model fits well. The slight difference between the adjusted R² value (0.9657) and the predicted R² value (0.8303) suggests a correlation between the two, indicating a good correlation between the model’s predicted value and the actual value.

\[
\text{HCl-P} = -94.89141 + 16.02784A + 0.632359B - 7.78335C - 0.051671AB + 1.67688AC + 0.138719BC - 0.522981A^2 - 0.000952B^2 - 5.26772C^2
\]  

(6)

where A represents the reaction time (h), B indicates the reaction temperature (°C), and C represents the swine manure-to-straw ratio.

![Figure 8. Organic and inorganic phosphorus content in the HCl-P of hydrochar.](image)

The Ca-P obtained primarily from HCl extraction was stable hydroxyapatite, which was challenging for plants to utilize when applied to the soil [26]. In the later stages of the hydrothermal process, a significant amount of amorphous phosphorus is combined with calcium to form hydroxyapatite [49]. Consequently, this increase in Ca-P content can impact the availability of phosphorus for plants. Therefore, controlling the Ca-P content during the preparation of hydrochar was crucial to maintaining its phosphorus release capability. Figure 9 shows that with the extension of reaction time and the increase in
reaction temperature, the amount of Ca-P in hydrochar will increase. This phenomenon may be attributed to the fact that at elevated temperatures, during the advancement of the reaction, phosphorus and calcium ions in the solid phase continue to amalgamate to create Ca-P. Decreasing the reaction duration and reducing the reaction temperature can effectively diminish the Ca-P concentration, thus regulating the Ca-P content and enhancing the phosphorus release of hydrochar [44].

Figure 9. Response surface and contour map of the HCl-P in the hydrochar (a) at different temperatures and time points (swine manure-to-straw ratio = 1.25); (b) at different swine manure-to-straw ratios and time points (temperature = 210 °C); and (c) at different swine manure-to-straw ratios and temperatures (time = 2 h).

Figure 9b,c show that the reduction in the swine manure-to-straw ratio was associated with the reduction in the Ca-P content. At 210 °C, the reduction in the swine manure-to-straw ratio from 2 to 0.5 and the reduction in the reaction time from 3 h to 1 h led to a reduction in the Ca-P content from about 40 to less than 15 g/kg. Similarly, with a
fixed reaction time of 2 h, reducing the swine manure-to-straw ratio from 2 to 0.5 and the reaction temperature from 240 °C to 180 °C resulted in a reduction in the Ca-P content from more than 40 to less than 10 g/kg. This should be attributed to the high content of calcium ions in swine manure. When the swine manure-to-straw ratio is relatively large, calcium ions and phosphorus in the hydrochar can form more Ca-P [50]. This finding aligns with Li et al. [51]—who investigated phosphorus components in swine manure and corn cob co-hydrothermal carbonization—and Fu et al. [25]—who studied swine manure and cattle manure-derived hydrochar. Both studies demonstrated an increase in the Ca-P content with rising reaction temperatures. Ultimately, the optimal preparation conditions were identified as a swine manure-to-straw ratio of 1.930, a reaction time of 2.894 h, and a reaction temperature of 226.741 °C; the content of HCl-P is 43.047 g/kg.

4. Conclusions

This study examined phosphorus fractions in the hydrochar produced from the co-hydrothermal carbonization of swine manure and rice straw under different process conditions (temperature, time, swine manure-to-straw ratio), utilizing RSM optimization analysis.

In the hydrochar, inorganic phosphorus predominated, while organic phosphorus accounted for 5–30% of the total phosphorus content. Increasing the reaction time and temperature resulted in a reduction in the available phosphorus content.

An increase in the proportion of swine manure-to-straw resulted in highly soluble phosphorus in the hydrochar. As the reaction temperature increased and the reaction time was prolonged, the H_2O-P content decreased. Notably, the impact of the reaction temperature on the soluble phosphorus was more significant than that of the reaction time. Consequently, the optimal preparation conditions that maximized the soluble phosphorus were identified as a reaction time of 2.494 h, a reaction temperature of 180.000 °C, and a swine manure-to-straw ratio of 2.000.

As the reaction time was prolonged and the reaction temperature increased, the content of NaHCO_3-P decreased. As the ratio of swine manure-to-straw increased, the content of NaHCO_3-P also increased. Therefore, the optimal preparation conditions were identified as a reaction time of 1.296 h, a reaction temperature of 180.428 °C, and a swine manure-to-straw ratio of 1.719.

The NaOH-P content increased in response to rising reaction temperatures, extending reaction times, and increasing swine manure-to-straw ratios. Therefore, optimal reaction conditions were identified as a reaction time of 2.981 h, a temperature of 227.940 °C, and a swine manure-to-straw ratio of 1.974.

The HCl-P content increased with rising reaction temperatures, extending the reaction times, and using higher swine manure-to-straw ratios. The optimal conditions were determined to be a swine manure-to-straw ratio of 1.930, a reaction time of 2.894 h, and a reaction temperature of 226.741 °C. By changing the process conditions of hydrothermal carbonization, it is possible to modify the phosphorus form and composition in hydrochar, resulting in the production of hydrothermal carbon with suitable performance characteristics. The phosphorus in hydrochar can be transformed into fertilizers or industrial raw materials for phosphate production, thereby enhancing the recovery and utilization rate of phosphorus. Therefore, exploring the phosphorus fractionation extraction process conditions of hydrochar is of great significance for the recovery and utilization of phosphorus.

In general, by adjusting the hydrothermal carbonization treatment under different process conditions, the proportion of water-soluble phosphorus and stable phosphorus can be increased, the migration rate of phosphorus in hydrochar can be reduced, phosphorus loss can be minimized, and the non-point source pollution of phosphorus can be alleviated. At the same time, the composition of hydrochar and phosphorus forms can be adjusted to create an organic fertilizer that achieves a certain balance between protecting the soil environment and improving plant absorption efficiency. During the hydrothermal carbonization process, the liquid phase produced is weakly acidic, and the main form of nitrogen in the liquid phase is nitrate. Nitrate nitrogen can be rapidly utilized by plants
and is a good nitrogen fertilizer. Additionally, the form of nitrogen will also change under the influence of different reaction temperatures, times, and raw materials. Therefore, based on the design of this experiment, further research can be conducted on the nitrogen forms in hydrochar under different process conditions in the future. By controlling different process conditions for hydrothermal carbonization treatment, nitrogen elements can be enriched to convert nitrogen into stable forms or adjust the ratio of active nitrogen to stable nitrogen. This is of great help in promoting plant absorption, alleviating soil pollution, and producing organic fertilizers.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w16152208/s1: Figure S1: the solid yield of hydrochar as affected by different treatments; Figure S2: hydrochar pH as affected by different treatments; Figure S3: the EC of hydrochar as affected by different treatments; Table S1: basic physicochemical properties of swine manure samples; Table S2: basic physicochemical properties of the rice straw samples; Table S3: Box-Behnken design of the levels and factors; Table S4: experimental design for the Response Surface Methodology; Table S5: analysis of variance for Olsen-P, H₂O-P, NaHCO₃-P, NaOH-P and HCl-P in the hydrochar.

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