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Impact of Pyrolysis Temperature on the Removal of Nutrients Using Coarse Rice-Husk Biochar

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ABSTRACT

Biochar is a known potential for nutrient removal in wastewater. This study focuses on the adsorption of rice-husk biochar to remove nutrients in the form of nitrate, ammonium, and phosphate in the wastewater. Two types of biochar production were used: laboratory-made biochar with variations of pyrolysis temperature and biochar made traditionally by local people. The results showed pyrolysis temperature influence the sorption capacity of nitrate and phosphate. The best nitrate sorption capacity using biochar made with low pyrolysis temperature, whereas the best phosphate sorption capacity using biochar made with high pyrolysis temperature. While the best ammonium sorption capacity by biochar made traditionally. The use of biochar with a coarse form shows nutrient sorption ability that is not inferior to the powder form compared to the other research. The use of coarse biochar forms can be selected if the powder form is impractical for field applications. The utilization of biochar variations can be selected according to the dominant nutrient removal needs in the field.

Keywords: ammonium, biochar, nitrate, phosphate, rice-husk.

INTRODUCTION

High nutrient levels in agricultural wastewater usually present in the form of ammonium (NH_4^+), nitrate (NO_3^-), and in the form of phosphate (PO_4^{3-}), which can lead to eutrophication if it enters water bodies. Eutrophication is a condition that causes abundant growth of aquatic plants due to high nutrient levels in water. This can reduce oxygen levels in the water, endanger aquatic biota, and cause poor water quality. The problem can be overcome by treating agricultural wastewater. The sorption method is considered an efficient technology in wastewater treatment. The sorption method has advantages including simple to utilize, flexible, and cost-effective so it is widely used in wastewater treatment (Plaza-Bonilla et al., 2013). The sorption method is considered an efficient technology in wastewater treatment. One material that can be used as a material for the adsorption process is biochar. Biochar is made by heating biomass that is difficult to decompose in the environment, resulting in a high carbon composition and a porous material structure. Therefore, biochar is suitable for sorption process, which is the transfer of solutes to the surface of a solid (Ahmedna et al., 1997). The use of biochar made from various raw materials derived from agricultural waste as an adsorbent for nutrient removal has been widely studied. Rice husk biochar in a powder form was proven to be effective in removing nitrate (Konneh et al., 2021; Thao et al., 2021; You et al., 2019; Zou et al., 2022), ammonium (Kizito et al., 2015; Thao et al., 2021; Zou et al., 2022), and phosphate in wastewater (Kumar et al., 2010; Zou et al., 2022). Differences in biochar pyrolysis temperature were shown to affect the removal of nutrients from wastewater. The result of Zhou (2019) found that biochar pyrolyzed at high temperatures was better at removing phosphate (Zhou et al., 2019). In contrast, ammonium removal was better using biochar pyrolyzed at lower temperatures (Chen

& Chen, 2009; Gao et al., 2015; Uchimiya et al., 2011; Zou et al., 2022). However, the use of biochar in powder form is not always applicable, therefore it is also important to study the adsorption capacity of coarse form.

Ready-made biochar from rice husks is widely available in the markets of tropical countries. The materials are usually processed using traditional methods by local people. This material is easy to utilize, flexible, and cost-effective so it will be more convenient for water purification applications. The ability of these materials to remove nutrients in the form of nitrate, ammonium, and phosphate has also rarely been studied. Therefore, the purpose of this study is to analyze the sorption capacity of the coarse form of rice-husk biochar which is traditionally made, also compared to biochar which is pyrolyzed at various temperatures to remove ammonium, nitrate, and phosphate in agricultural wastewater. This study can provide an alternative for the removal of ammonium, nitrate, and phosphate in agricultural wastewater to be able to prevent pollution in the water body.

MATERIAL AND METHODS

In this study, we analyzed the physical characteristics of biochar, the sorption capacity of biochar in removing nitrate, ammonium, and phosphate using the artificial solution and to study the sorption mechanism with the kinetics model and sorption isotherms. Desorption experiments were not available in this study.

Biochar characteristics

Surface image of biochar was observed using a Scanning electron microscope- Energy Dispersive X-ray (SEM-EDX) brand Hitachi S-3400N equipped with ion sputter brand Hitachi E-1045. While the functional groups on biochar were analyzed using Fourier Transform Infrared (FTIR) brand Perkin Elmer FT-IR spectrometer frontier L128-0099. Cation-exchange capacity measurements were performed using SW-846 Test Method 9081: Cation -Exchange Capacity of Soils (EPA, 1986).

Sorption of nutrients using biochar

For the sorption experiments, we used two types of rice husk biochar, the biochar that is made traditionally by local people using metal barrel, and the biochar which is made with a furnace in difference pyrolysis temperature in the laboratory. The designations of the rice husk biochar which was produced using a furnace at pyrolysis temperatures of 300°C, 450°C and 600°C respectively RH300, RH450, and RH600. While rice husk biochar made traditionally, was designated as RHT. The Sorption study were conducted in batch experiments in the laboratory to find the most effective biochar variant for the removal of nitrate, ammonium, and phosphate using artificial wastewater. The raw materials for sorption materials consisted of cleaned coarse rice husk with a size ±0.5 cm. The biochar pyrolysis speed was 5°C/min until it reaches the desired temperature and is allowed to stand for 2 hours. Afterward, the biochar was cooled at room temperature and washed thoroughly with distilled water before batch sorption experiments.

The artificial solution for each parameter used KNO_3 as the base solution for nitrate, NH_4Cl for ammonium, and KH_2PO_4 for phosphate. The biochar amount used in each variation was 0.5 g/100 ml of sample with a contaminant concentration of 10, 20, 40, and 80 mg/L (Zhou et al., 2019) and observed its sorption capacity after six hours. While for adsorption kinetic experiments was using contaminant concentration of 20 mg/L and observed at of contact time of 1, 2, 3, 4, 5, and 6 hours (Nguyen, 2015). Each experiment was performed in triplicates using an orbital shaker at 180 rpm, and the solution was filtered with filter paper prior to analysis. Nitrate analysis was performed using the cadmium reduction method at a spectrophotometer wavelength of 420 nm. Ammonium analysis was carried out according to the Nessler method of testing ammonium levels in water at a wavelength of 420 nm, while phosphate according to the ascorbic acid method at 880 nm (APHA, 2003). From this experiment, adsorption capacity q (mg/g) is calculated with Eq. 1 (Tchobanoglous, 2003):

$$q = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where: C_o – the initial nutrient concentration, C_t – the nutrient concentration at time t (mg/L), V – the volume of solution (L), m – the dry weight of biochar (g). The maximum sorption capacity obtained in the experiment was then analyzed statistically to see the significant difference using the ANOVA with IBM SPSS 24 software.

SORPTION KINETIC

Sorption kinetics were calculated to estimate the rate of sorption of a nutrient by biochar over contact time. This can be determined by measuring the change in concentration of the adsorbed substance by time to obtain the *k* value (in the form of slope). Sorption kinetics are dependent on the rate of sorption. Several adsorption kinetics models explain the adsorption mechanism (Largitte & Pasquier, 2016). In this study, adsorption kinetics will be carried out with the Pseudo 1st order, Pseudo 2nd order, and the Weber-Morris intra-particle diffusion models which formula presented in Eq. 1, Eq. 2, and Eq. 3, respectively.

$$q_t = q_e\left[1 - \exp(-k_{1p}t\right] \tag{2}$$

$$q_t = \frac{K_{2p}{q_e}^2 t}{1+K_{2p}{q_e}^2 t} \tag{3}$$

$$q_t = K_p t^{0,5} + C \tag{4}$$

where: q_t – the sorption capacity at time *t* (mg/g), q_e – the adsorption capacity at equilibrium (mg/g), k_{1p} – the pseudo-first-order rate constant (h^{-1}), K_{2p} – the pseudo-second-order rate constant (g/mg/h), K_p – the intra-particle diffusion rate constant ($mg/g/h^{0,5}$), *C* – related to the boundary layer thickness (mg/g), *t* – the contact time (h).

Sorption isotherm

Sorption isotherms were obtained from experiments with variations in the initial concentrations of nitrate, ammonium, and phosphate, which were 10, 20, 40, and 80 mg/L. The solution was stirred at 180 rpm for 12 hours until equilibrium concentrations and adsorption capacity were obtained. Sorption isotherm was calculated using the Langmuir isotherm and the Freundlich isotherm which is calculated using Eq. 5 and Eq. 6.

$$x/m = K_f(C_e)^{1/n} \tag{5}$$

where: K_f – Freundlich constant (l/g), *n* – sorption capacity and intensity, *x*/*m* – the amount of phosphate adsorbed onto 1 g adsorbent under equilibrium conditions (mg/g), C_e – contaminant concentration at equilibrium (mg/L).

The Langmuir isotherm refers to homogeneous sorption, for which each molecule has a constant enthalpy and sorption activation energy (all sites have the same affinity for the adsorbate), without transmigration of the adsorbate in the surface plane. The Langmuir isotherm equation is as follows:

$$x/m = \frac{abC_e}{1+bC_e} \tag{6}$$

where: *x*/*m* – the amount of phosphate adsorbed onto 1 g adsorbent under equilibrium conditions (mg/g), C_e – the contaminant concentration at equilibrium (mg/L*), a* and *b* – the empirical constant.

RESULTS AND DISCUSSION

Physical characteristics of the media

The surface morphology of biochar using SEM with a magnification of 2,000 times is shown in Figures 1 and 2. The numerous pores allow the sorption of contaminants on the biochar surface. The surface morphology of rice husk biochar is almost similar to that obtained by Zhang (2018) which pores are larger than 20 µm. The surface morphology of rice husk biochar in the low pyrolysis temperature has a smaller pore size compared to others, higher pyrolysis temperature biochar shows the same pore size, likewise with the traditional-made-biochar. Rice husk contain a certain amount of hemicellulose, cellulose, and lignin that play a role in the formation of biochar surface pores when pyrolyzed (Boundzanga et al., 2020). In the sorption process, the number of pores on the surface of the material is one of the factors that affect the sorption capacity. The more pores on the surface of biochar, related to the wider surface where the sorption process occurs, which can occur due to attraction force, as well as ion exchange, electrostatic interactions, and also precipitation. (Yang et al., 2019).

The results of cation exchange capacity, and element analysis of each biochar are shown in Table 1. Carbon is the main element detected in rice husk biochar is made from the pyrolysis process. The CEC measurement results showed RH450 with the highest sorption capacity, followed by RH600, and almost the same value between RHT and RH300. On the other hand, the levels of Ca, Mg, K and Na were highest in RH300 and RHT, followed by RH600 and RH450. This indicates that RH450 has more negatively charged ions available for cation adsorption, such as ammonium. The detected carbon gets larger with the higher pyrolysis temperature. Meanwhile, the

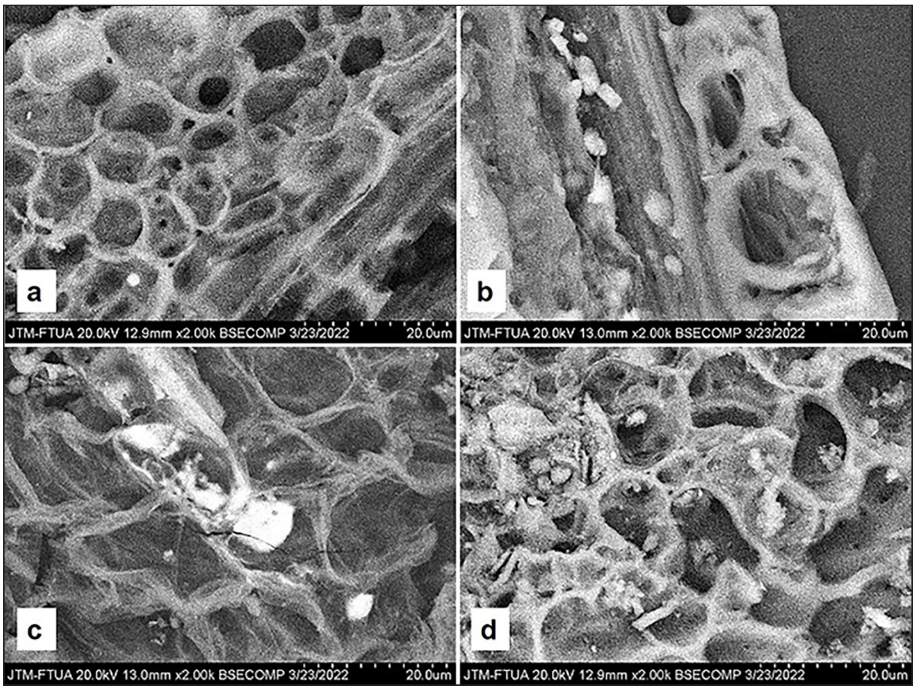

Figure 1. Surface morphology of rice husk biochar (a) RH300, (b) RH450, (c) RH600, and (d) RHT

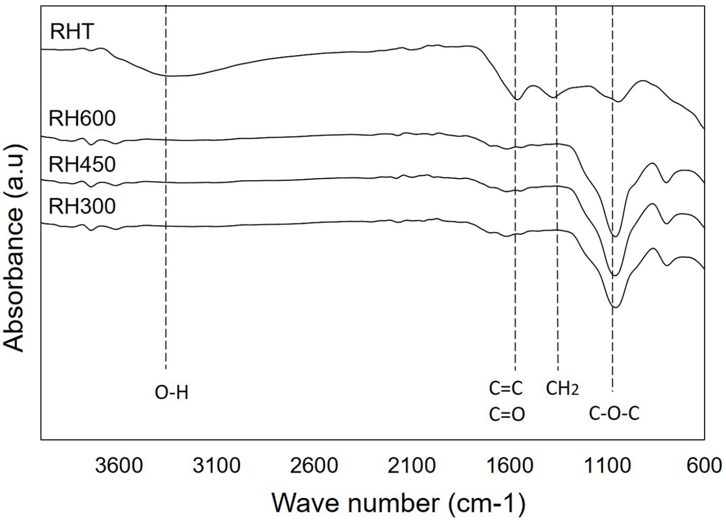

Figure 2. Biochar functional groups

carbon in traditional-made-biochar (RHT) percentage almost resembles RH450. In addition to carbon, silica detected is oxygen in all biochar variations. Silica is contained in the raw rice husk (Real et al., 1996). From the results of the study by Bakar (2016), silica found lower levels in pyrolysis above 500°C (Bakar et al., 2016). In this study, lower silica levels were found in biochar with a pyrolysis temperature of 600°C. The percentage of O and Si decreased with the lower pyrolysis temperature. Figure 2 shows the functional groups in the biochar material. Various spectra were found in the drum-made biochar, namely -OH stretching (3500–3200 cm^{-1}) caused by hydrogen-bonded hydroxyl groups, CH_2 (1375.52 cm^{-1}), aromatic C=C and C=O stretching of conjugated ketones and quinones (1613 cm^{-1}), and C-O-C (1049 cm^{-1}) (Janu et al., 2021). Rice husk biochar made using a furnace have less functional groups of C-O-C, C=C and C=O. Traditional-made-biochar formation with barrel is usually performed with a slower process that produces biochar with more functional groups due to more complex chemical reactions during combustion.

Table 1. Cation exchange capacity and element content in biochar

Biochar	CEC (T(cmol(+)/kg)	Ca (%)	Mg (%)	K (%)	Na (%)	*C (%)	*O (%)	*Si (%)
RH300	104.7	0.24	0.64	0.11	0.31	64.96	31.24	2.34
RH450	215.9	0.09	0.32	0.05	0.13	57.52	32.08	9.27
RH600	129.2	0.18	0.42	0.10	0.23	69.08	26.05	2.47
RHT	104.8	0.15	0.52	0.15	0.35	67.42	28.64	3.26

While biochar made with a furnace is usually a faster combustion process that results in certain functional groups being removed.

Functional groups are an important factor in sorption, as they can function as sites for ion exchange between ammonium (NH_4^+), nitrate (NO_3^-), and phosphate (PO_4^{3-}). Removal efficiency is positively correlated with the number of acidic and basic functional groups (Z. Wang et al., 2015). Acidic functional groups (hydroxyl, phenol, and carboxyl groups) and basic functional groups (amides, aromatic amines, and pyridine groups) provide cation and anion exchange sites for NH_4^+, NO_3^- and PO_4^{3-}, respectively. In particular, the acidic functional groups of biochar are negatively charged due to hydrogen ionization in the solution. The positively charged NH_4^+ is electrostatically attracted and exchanged with H^+ (Yin et al., 2017). The positively charged biochar basic functional groups and hydroxide ions exist simultaneously to neutralize the solution. While the negatively charged NO_3^- is electrostatically attracted and anion exchange will occur between NO_3^- and OH^- (Zeng et al., 2013). In addition, Zeng et al (2013) found that aliphatic C=O, C=C, and C-O-C functional groups were lost on biochar after ammonium was adsorbed, which means that the functional group plays a role in ammonium adsorption in solution.

DO and pH during sorption experiment

During the sorption experiments, we also observed changes in dissolved oxygen and pH at varying initial nutrient concentrations, which are shown in Figure 3. The range of dissolved oxygen in the ammonium, nitrate and phosphate removal experiments respectively is 5.56 to 6.34 mg/L, 5.98 to 6.57 mg/L, and 6.57 to 7.06 mg/L. Dissolved oxygen in the experiment showed a decrease with higher initial nutrient concentrations. This can be caused by the high nutrient concentrations that can affect the solubility of oxygen in the water. It could also be due to the dominating nutrient levels in the solution, thus reducing the availability of oxygen in the water. This trend was observed for each variation of biochar with varying pyrolysis temperature, which showed that the variation of biochar pyrolysis temperature did not have a significant effect on the dissolved oxygen in the solution (Kermorvant et al., 2023).

The pH trend shows a similar trend in the experiments using variations in the initial concentration of ammonium and phosphate. The range of pH in the ammonium, nitrate, and phosphate removal experiment respectively is 4.7 to 6.6, 4.4 to 6.6, and 4.5 to 6.6. There is a decrease in pH along with the high initial concentration of nutrients. This can be caused because the chemicals used for ammonium and phosphate solutions can release hydrogen ions in the solution, making it acidic. The pH level in the solution with biochar variations showed almost the same value, which means that in this study biochar variations did not affect the acidity of the solution.

The maximum sorption capacity and isotherms of each biochar variation are shown in Table 2. Each biochar shows different sorption capacity in the removal of ammonium, nitrate, and phosphate. In the removal of ammonium, RHT followed by RH450 shows the best maximum sorption capacity compared to the others, followed by RH600, and RH300. The sorption capacity of RHT can be supported by the functional groups that play a role for ammonium removal by biochar. While for biochar with pyrolysis temperature variation, the results somewhat different from Gao et al. (2015) on ammonium removal with various biochar feedstocks with varying pyrolysis temperatures also showed higher removal using biochar with pyrolysis at lower temperatures (300°C). Other studies have also found that biochar with pyrolysis at lower temperatures has a surface with oxygen-containing functional groups that allow its interaction with cations such as ammonium in solution (Chen & Chen, 2009; Uchimiya et al., 2011). For nitrate removal, RH300 showed the best maximum capacity for

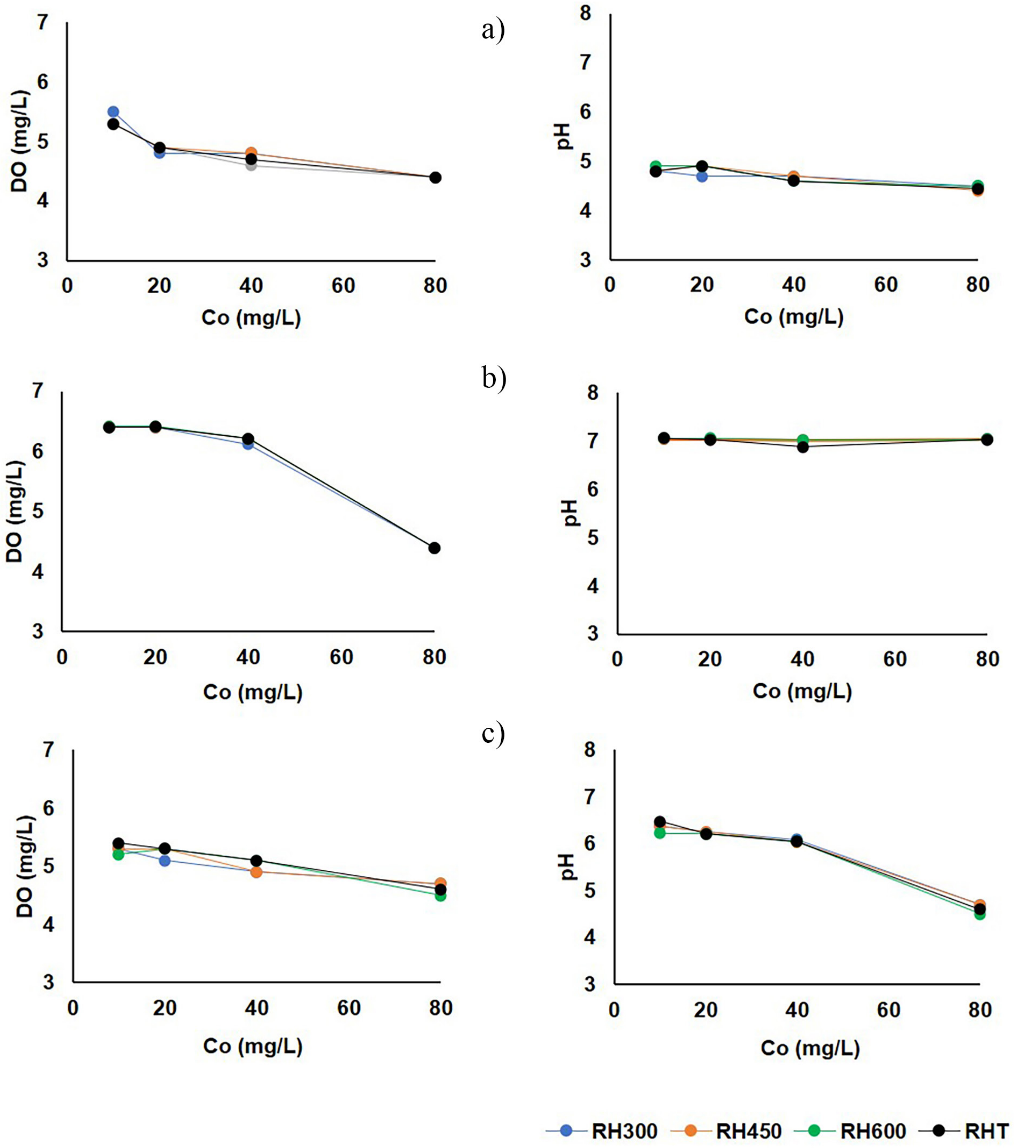

Figure 3. DO and pH changes in sorption experiment using rice husk biochar (a) ammonium removal (b) nitrate removal (c) phosphate removal

nitrate sorption followed by RH450, RH600, and RHT. The sorption capacity of rice husk biochar in removing nitrate is inversely proportional to the pyrolysis temperature of the biochar. Biochar with high pyrolysis temperature has almost the same ability as traditionally made biochar. Compared to high-temperature pyrolysis procedures, low-temperature pyrolysis uses less energy. This increases the energy efficiency and environmentally friendly in biochar manufacturing.

In phosphate removal, RH600 showed the best sorption ability, followed by RH450, RH300 and RHT. The study of Muoghalu (2023) found that higher temperatures can increase the specific surface area of adsorption material. At higher production temperatures, this might be attributable to an increase in anion exchange sites and a rise in surface positive charge (Zhang et al., 2017).

Overall, all coarse biochar variations are capable to remove ammonium, nitrate, and phosphate. RH450 showed better ammonium sorption ability than the others. This is supported by the CEC measurement results of RH450 which is higher than the other biochar variations. While in the nitrate removal experiment, the best biochar variation is RH300, and it is recommended to use RH600 for phosphate removal. The alternative for rice-husk biochar used can be determined by the dominant nutrients exist in the agricultural wastewater. Table 3 present the best-fit isotherms for nutrient removal using biochars in this study. It appears that all K_L and n coefficients are in the

Table 2. Best fit isotherm for nutrient removal

Biochar	Langmuir			Freundlich		
	Q_{max} (mg/g)	K_L	R^2	n	K_F	R^2
Ammonium removal						
RH300	8.07	0.22	0.92	1.61	1.41	0.97
RH450	11.27	0.13	0.98	1.48	1.35	1.00
RH600	11.21	0.13	0.98	1.49	1.34	1.00
RHT	20.74	0.03	1.00	1.27	0.80	1.00
Nitrate removal						
RH300	19.73	0.03	0.97	0.72	0.46	0.90
RH450	9.46	0.05	0.99	0.63	0.26	0.84
RH600	1.78	0.08	0.96	0.34	0.01	0.86
RHT	1.89	0.09	0.62	0.39	0.03	0.85
Phosphate removal						
RH300	8.84	0.20	0.95	1.63	1.46	0.99
RH450	10.14	0.15	0.96	1.47	1.30	0.99
RH600	11.61	0.12	0.99	1.50	1.36	1.00
RHT	4.63	0.11	0.87	0.57	0.41	0.87

range of 0 to 1 which means favorable adsorption (Patel, 2020). From the correlation coefficient (R^2), the removal of ammonium, nitrate, and phosphate with rice husk biochar is better described by the Freundlich isotherm. The Freundlich isotherm describes non-ideal and reversible adsorption, not limited to monolayer formation. While the Langmuir isotherm assumes monolayer adsorption, with adsorption capable of adsorbing only one molecule of adsorbate for each molecule of adsorbent, it is assumed that there is no interaction between the adsorbed molecules.

ANOVA statistical analysis is used to examine the effect of biochar variation, dissolved oxygen, and also pH on sorption capacity in this study is presented in Table 3. From the ANOVA analysis, it was found that dissolved oxygen and pH did not affect the sorption capacity of ammonium, nitrate and phosphate in this study. While biochar variations affect the capacity of ammonium and phosphate. Nitrate sorption capacity with biochar variations was found to be non-significant based on the results of statistical calculations.

Comparison of sorption capacity using biochar variation

Comparison of the maximum adsorption capacity of ammonium, nitrate and phosphate using biochar with variations in pyrolysis temperature and material form are shown in Tables 4, 5 and 6 respectively. The comparison of adsorption capacity is also analyzed based on the form of biochar powder and coarse. In this study, the experiment was conducted using biochar in coarse form, and therefore the maximum capacity was compared with biochar from other studies. In field applications, the use of powdered materials can be impractical, because if they are used as filter media they can cause clogging, or rapidly changing flow velocities can cause shear in the media. To avoid this, a material with a larger size is required. For this reason, in this study, an experiment was conducted using rice husk biochar in coarse form.

For ammonium removal, the trend of pyrolysis temperature variation showed different results from other studies. In other studies, the sorption

Table 3. ANOVA of biochar variation, dissolved oxygen and pH to sorption capacity

No	Effect to sorption capacity	P-value		
		Ammonium removal	Nitrate removal	Phosphate removal
1	Biochar variation	0.018	0.148	0.010
2	Dissolved oxygen	0.994	0.984	0.975
3	pH	1.000	1.000	0.997

Tabel 4. Comparison of ammonium removal using various kind of biochar

Biochar	Material form	Pyrolysis temperature (°C)	Q_{max} (mg/g)	Reference
Rice husk	Coarse	550	0.10	(Thao et al., 2021)
Corncob	Powder	400	15.30	(Liu et al., 2014)
Corncob	Powder	600	12.80	(Liu et al., 2014)
Wheat straw	Powder	400	7.33	(Gai et al., 2014)
Wheat straw	Powder	500	4.68	(Gai et al., 2014)
Wheat straw	Powder	600	3.16	(Gai et al., 2014)
Wheat straw	Powder	700	0.63	(Gai et al., 2014)
Coconut shell	Powder	300	12.80	(Zou et al., 2022)
Coconut shell	Powder	500	14.20	(Zou et al., 2022)
Coconut shell	Powder	700	15.50	(Zou et al., 2022)
Tea tree	Powder	400	1.52	(Salimova et al., 2020)
Rice husk	Coarse	300	8.07	This study
Rice husk	Coarse	450	11.27	This study
Rice husk	Coarse	600	11.21	This study
Rice husk	Coarse	300 (traditional)	20.74	This study

Tabel 5. Comparison of Nitrate removal using various kind of biochar

Biochar	Material form	Pyrolysis temperature (°C)	Q_{max} (mg/g)	Reference
Coconut shell	Powder	-	9.70	(You et al., 2019)
Rice husk	Powder	700	12.32	(Konneh et al., 2021)
Coconut husk	Powder	700	12.97	(Konneh et al., 2021)
Coffee husk	Powder	700	12.08	(Konneh et al., 2021)
Rice husk	Coarse	550	0.129	(Thao et al., 2021)
Coconut shell	Powder	300	78.1	(Zou et al., 2022)
Dates	Coarse	300	0.22-0.42	(Alsewaileh et al., 2019)
Dates	Coarse	700	1.46-2.82	(Alsewaileh et al., 2019)
Rice husk	Coarse	300	19.73	This study
Rice husk	Coarse	450	9.46	This study
Rice husk	Coarse	600	1.78	This study
Rice husk	Coarse	300 (traditional)	1.89	This study

capacity of biochar increased with the higher pyrolysis temperature of biochar. However, in this study, biochar made with a pyrolysis temperature of 450°C showed the highest sorption capacity compared to biochar made with pyrolysis temperatures of 300°C and 600°C. This is confirmed by the results Sof CEC analysis at RH450 which is higher than other variations, so that it can absorb ammonium better than other variations. On the other hand, traditionally made biochar showed the best sorption capacity compared to other variations in this study. In addition to the role of sorption on the surface of biochar, this can also be influenced by functional groups on biochar is not just lost during the manufacture of biochar. These functional groups can play a role for the exchange of ammonium ions. The ammonium sorption capacity in this study is higher than the study of Thao et al. (2021) who also used rice husk biochar in powder form with almost similar pyrolysis temperature. This shows that the coarse biochar form does not reduce its sorption capacity to nutrients. On the other hand, the maximum sorption capacity of ammonium with rice husk biochar in this study was lower than using other biochars such as corncob (Liu et al., 2014), and coconut shell (Zou et al., 2022). Muoghalu et al. (2023) found that feedstock type can influence the sorption capacity of nutrients which can affect the elemental composition and pore structure of biochar. Compared

Tabel 6. Comparison of phosphate removal using various kind of biochar

Biochar	Material form	Pyrolysis temperature (°C)	Q_{max} (mg/g)	Reference
Rice straw	Powder	700	5.41	(Zhou et al., 2019)
Phragmites communis	Powder	300	7.75	(Zhou et al., 2019)
Phragmites communis	Powder	500	3.27	(Zhou et al., 2019)
Sawdust	Powder	300	3.86	(Zhou et al., 2019)
Sawdust	Powder	500	3.39	(Zhou et al., 2019)
Egg shell	Powder	700	6.08	(Zhou et al., 2019)
Peanut shell	Powder	700	6.01	(Jung et al., 2015)
Rice husk	Coarse	300	8.84	This study
Rice husk	Coarse	450	10.14	This study
Rice husk	Coarse	600	11.61	This study
Rice husk	Coarse	300 (traditional)	4.63	This study

to other studies, rice husk biochar prepared at high pyrolysis temperature showed a lower nitrate maximum adsorption capacity than using coconut shell, rice husk and coffee husk biochar from Konneh et al. (2021) and the study of Zou et al. (2022).

The trend of adsorption capacity with phosphate is also directly proportional to the pyrolysis temperature of biochar in this study. Traditionally made biochar showed lower adsorption capacity than rice husk biochar with variation of pyrolysis temperature. Phosphate sorption capacity using rice husk biochar in this study showed a better capacity than using biochar with other raw materials in other studies such as *Phragmites communis* biochar, sawdust (Zhou et al. 2019), and peanut shell (Jung et al., 2015). It can be concluded that pyrolysis temperature affecting the nutrients sorption capacity of coarse-rice-husk-biochar, which can affect the number of pores as a physical nutrient sorption site. In this study, pyrolysis temperature affected the maximum sorption capacity of nitrate and phosphate. Nitrate sorption was higher using biochar pyrolyzed at a higher temperature, while phosphate sorption capacity was higher using biochar made at a lower pyrolysis temperature. Highest sorption capacity of ammonium observed when using traditionally-made biochar. Even in coarse form, biochar is still able to remove nutrients. The results of this

Tabel 7. Adsorption kinetic

No	Material	Pseudo 1st order			Pseudo 2nd order			Intra-particle diffusion		
		K	q_e	R^2	K	q_e	R^2	K	C	R^2
		(/h)	(mg/g)		(/h)	(mg/g)		(/h)	(mg/g)	
Ammonium removal										
1	RH300	0.560	1.366	0.527	0.073	3.108	0.432	1.065	0.744	0.716
2	RH450	0.505	1.472	0.501	0.071	3.115	0.420	1.065	0.774	0.701
3	RH600	0.482	1.292	0.430	0.063	3.314	0.394	1.016	0.783	0.676
4	RHT	0.435	2.122	0.570	0.152	0.617	0.617	1.278	0.544	0.819
Nitrate removal										
1	RH300	1.475	6.294	0.843	2.767	1.681	0.882	1.421	0.543	0.762
2	RH450	0.920	4.556	0.865	2.475	2.115	0.918	1.155	0.279	0.829
3	RH600	1.318	2.665	0.941	0.189	2.189	0.689	1.349	0.387	0.909
4	RHT	0.921	2.996	0.969	0.354	2.096	0.839	1.317	0.036	0.968
Phosphate removal										
1	RH300	0.672	2.133	0.755	0.106	2.802	0.563	1.097	0.574	0.805
2	RH450	0.627	1.996	0.786	0.109	2.736	0.571	1.134	0.566	0.832
3	RH600	0.789	3.025	0.936	0.254	2.298	0.816	1.207	0.183	0.950
4	RHT	0.428	3.270	0.877	0.727	2.579	0.812	1.017	0.204	0.846

study show that for applications that do not allow powder material, the coarse form can also function well in removing nutrients from wastewater.

Sorption kinetics

The sorption kinetic in this experiment is shown in Table 2 and Figure 5. From the correlation coefficient obtained, the removal of ammonium, and phosphate was better explained by the intra-particle diffusion model. The intraparticle diffusion model describes that the adsorption mechanism works on the internal part of the solid by diffusion to the inside of the adsorbent (Yagub et al., 2014). In this model, there are about four stages in the adsorption process, which are the movement of molecules to the surface of the adsorption medium, diffusion through the surface boundary layer of the adsorption medium, adsorption on the surface of the medium and intra-particle diffusion into the adsorption medium. Nitrate adsorption with biochar is better described by the model of Pseudo 1st order (Table 7). This model is an empirical equation that is frequently used to describe the kinetics of solute adsorption at solid/solution interfaces. On the assumption that the rate of adsorption is proportional to the difference between the amount of solute adsorbed at any given time and the amount of solute adsorbed at equilibrium. This model is a limiting form of the kinetic equations created by assuming both surface reaction kinetic models and diffusional models (Revellame et al., 2020; Wang & Guo, 2020).

CONCLUSIONS

The adsorption capacity of coarse rice husk biochar in removing nitrate, ammonium, and phosphate from wastewater was tested in the laboratory in batch experiments, and the mechanism was examined using rate kinetics and isotherm models. Biochar with pyrolysis temperature variation shows different sorption capacity trends. Ammonium sorption capacity is best shown by biochar made traditionally, while based on pyrolysis temperature, ammonium sorption capacity is best using biochar made at 450°C because it has a higher cation exchange capacity than biochar with other pyrolysis temperature variations. The order of biochar from the highest ammonium sorption capacity is RHT>RH450>RH600>RH300. For nitrate removal, the maximum capacity is best using biochar with low pyrolysis temperature, whereas for phosphate removal using biochar with high pyrolysis temperature. The order of biochar with nitrate sorption capacity from the highest is RH300>RH450>RHT>RH600, while for phosphate removal RH600>RH450>RH300>RHT. The selection of biochar to be used for application can consider the type of dominant nutrient to be removed. So that, major findings in this study that pyrolysis temperature affects the sorption of phosphate as well as nitrate, also the coarse form of biochar proved to be able to remove nutrients in wastewater, and has the potential to be applied to treatments that do not allow the use of powder materials. While the presence of other contaminants in agricultural wastewater will possibly interfere with nutrient adsorption by biochar, which is not investigated in this study. For this reason, further research can be carried out to obtain the effect of other contaminants in agricultural wastewater on nutrient adsorption on biochar.

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REFERENCES

1. Alsewaileh, A.S., Usman, A.R., Al-Wabel, M.I. 2019. Effects of pyrolysis temperature on nitrate-nitrogen (NO 3− -N) and bromate (BrO 3−) adsorption onto date palm biochar. Journal of Environmental Management, *237*(February), 289–296. https://doi.org/10.1016/j.jenvman.2019.02.045
2. An, T., Nguyen, H. 2015. Removal and Recovery of Phosphorus From Municipal Wastewater By Adsorption Coupled With Crystallization. June. https://opus.lib.uts.edu.au/handle/10453/38985
3. APHA. 2003. Standard Methods For The Examination of Water and Wastewater, 23rd Edition (A.D.E.EW. Rice, R.B. Baird (ed.)). American Water Works Association.
4. EPA. 1986. SW-846 Test Method 9081: Cation-Exchange Capacity of Soils (Sodium Acetate).
5. Gai, X., Wang, H., Liu, J., Zhai, L., Liu, S., Ren, T., Liu, H. 2014. Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. PLoS ONE, 9(12), 1–19. https://doi.

org/10.1371/journal.pone.0113888

6. Janu, R., Mrlik, V., Ribitsch, D., Hofman, J., Sedláček, P., Bielská, L., Soja, G. 2021. Biochar surface functional groups as affected by biomass feedstock, biochar composition and pyrolysis temperature. Carbon Resources Conversion, 4(January), 36–46. https://doi.org/10.1016/j.crcon.2021.01.003
7. Jung, K. W., Hwang, M. J., Ahn, K. H., Ok, Y. S. 2015. Kinetic study on phosphate removal from aqueous solution by biochar derived from peanut shell as renewable adsorptive media. International Journal of Environmental Science and Technology, 12(10), 3363–3372. https://doi.org/10.1007/s13762-015-0766-5
8. Kermorvant, C., Liquet, B., Litt, G., Mengersen, K., Peterson, E. E., Hyndman, R. J., Jones, J. B., Leigh, C. 2023. Understanding links between water-quality variables and nitrate concentration in freshwater streams using high frequency sensor data. Plos One, 18(6), e0287640. https://doi.org/10.1371/journal.pone.0287640
9. Konneh, M., Wandera, S.M., Murunga, S.I., Raude, J.M. 2021. Adsorption and desorption of nutrients from abattoir wastewater: modelling and comparison of rice, coconut and coffee husk biochar. Heliyon, 7(11), e08458. https://doi.org/10.1016/j.heliyon.2021.e08458
10. Largitte, L., Pasquier, R. 2016. A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. Chemical Engineering Research and Design, 109, 495–504. https://doi.org/10.1016/j.cherd.2016.02.006
11. Liu, X., Zhang, Y., Li, Z., Feng, R., Zhang, Y. 2014. Characterization of corncob-derived biochar and pyrolysis kinetics in comparison with corn stalk and sawdust. Bioresource Technology, 170, 76–82. https://doi.org/10.1016/j.biortech.2014.07.077
12. Revellame, E.D., Fortela, D.L., Sharp, W., Hernandez, R., Zappi, M.E. 2020. Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: A review. Cleaner Engineering and Technology, 1(December), #100032. https://doi.org/10.1016/j.clet.2020.100032
13. Salimova, A., Zuo, J., Liu, F., Wang, Y., Wang, S., Verichev, K. 2020. Ammonia and phosphorus removal from agricultural runoff using cash crop waste-derived biochars. Frontiers of Environmental Science and Engineering, 14(3), 1–13. https://doi.org/10.1007/s11783-020-1225-1
14. Stensel, G.T.F.L.B.H.D. (2003). Wastewater Engineering: Treatment Disposal Reuse-3rd edition (B.J.C. and J.M. Morries (ed.); 4th ed.). McGraw-Hill, Inc.
15. Thao, V.T.M., Canh, N.T., Hang, N.L.N., Khanh, N.M., Phi, N.N., Niem, P.T.A., Anh, T.T., Nguyen, N.T.H., Duc, N.T. (2021). Adsorption of ammonium, nitrite, and nitrate onto rice husk biochar for nitrogen removal. Engineering and Technology, 11(1), 30–44. https://doi.org/10.46223/hcmcoujs.tech.en.11.1.1622.2021
16. Wang, J., Guo, X. 2020. Adsorption kinetic models: Physical meanings, applications, and solving methods. Journal of Hazardous Materials, 390(January), #122156. https://doi.org/10.1016/j.jhazmat.2020.122156
17. Wang, Z., Guo, H., Shen, F., Yang, G., Zhang, Y., Zeng, Y., Wang, L., Xiao, H., Deng, S. 2015. Biochar produced from oak sawdust by Lanthanum (La)-involved pyrolysis for adsorption of ammonium (NH4+), nitrate (NO3-), and phosphate (PO43-). Chemosphere, 119, 646–653. https://doi.org/10.1016/j.chemosphere.2014.07.084
18. Yang, X., Wan, Y., Zheng, Y., He, F., Yu, Z., Huang, J., Wang, H., Ok, Y.S., Jiang, Y., Gao, B. 2019. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review. Chemical Engineering Journal, 366(January), 608–621. https://doi.org/10.1016/j.cej.2019.02.119
19. Yin, Q., Zhang, B., Wang, R., Zhao, Z. 2017. Biochar as an adsorbent for inorganic nitrogen and phosphorus removal from water: a review. Environmental Science and Pollution Research, 24(34), 26297–26309. https://doi.org/10.1007/s11356-017-0338-y
20. You, H., Zhang, Y., Li, W., Li, Y., Ma, Y., Feng, X. 2019. Removal of NO3-N in alkaline rare earth industry effluent using modified coconut shell biochar. Water Science and Technology, 80(4), 784–793. https://doi.org/10.2166/wst.2019.321
21. Zeng, Z., Zhang, S. Da, Li, T. Q., Zhao, F. L., He, Z.L., Zhao, H.P., Yang, X.E., Wang, H.L., Zhao, J., & Rafiq, M.T. 2013. Sorption of ammonium and phosphate from aqueous solution by biochar derived from phytoremediation plants. Journal of Zhejiang University: Science B, 14(12), 1152–1161. https://doi.org/10.1631/jzus.B1300102
22. Zhang, H., Voroney, R.P., & Price, G.W. 2017. Effects of Temperature and Activation on Biochar Chemical Properties and Their Impact on Ammonium, Nitrate, and Phosphate Sorption. Journal of Environmental Quality, 464, 889–896. https://doi.org/10.2134/jeq2017.02.0043
23. Zhou, L., Xu, D., Li, Y., Pan, Q., Wang, J., Xue, L., Howard, A. 2019. Phosphorus and nitrogen adsorption capacities of biochars derived from feedstocks at different pyrolysis temperatures. Water (Switzerland), 11(8), 1–16. https://doi.org/10.3390/w11081559
24. Zou, G., Shan, Y., Dai, M., Xin, X., Nawaz, M., Zhao, F. 2022. Comparative effectiveness of biochar derived from tropical feedstocks on the adsorption for ammonium, nitrate and phosphate. Archives of Environmental Protection, 48(4), 25–34. https://doi.org/10.24425/aep.2022.143706