

Adsorption of ammonium, nitrite, and nitrate onto rice husk biochar for nitrogen removal

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ABSTRACT

This study aims to investigate the adsorption capacity of ammonium NH_4^+ , nitrite NO_2^- and nitrate NO_3^- onto rice husk biochar (RHB) obtained from 550°C pyrolysis temperature in the context of using low-cost absorbent for recirculating aquaculture system (RAS). Raw RHB at its original size 5–8mm has been chosen for testing its adsorption capacity as well as several key material properties (pH_{PZC} , surface area, and elemental analysis). From surface functional group analysis, there existed the O–H group (at frequency 3443cm^{-1}), $-\text{CH}_3$ (2360cm^{-1}), and either $-\text{C}=\text{O}$ or $\text{C}=\text{C}$ group (in the range of frequency $1600\text{--}1650\text{cm}^{-1}$) as well as $-\text{COOH}$ (1456cm^{-1}) that helped enhance chemical adsorption. The experimental adsorption data has been roughly consistent with Langmuir and Freundlich models that used to calculate the maximum saturated monolayer adsorption capacity Q_{max}^0 of ammonium, nitrite, and nitrate were 0.1003, 0.2477, and 0.1290mg/g respectively. Therefore, RHB could be a potential candidate for biofilter application in both targets cost-efficient and sustainable that worth applied at scale.

1. Introduction

Ensuring food security is always on top priority in any sustainable development framework (FAO, 2020). In particular, aquaculture together with livestock and crop farming are considered as three pillars of the global food production system (Gladek et al., 2017). Nevertheless, the aquaculture industry poses many issues that need to be addressed from water quality, aquatic juveniles and feed formulations. Recirculating aquaculture system (RAS) has been developed to tackle the primary problem relating to water saving in terms of protecting aquatic animal health and decreasing environmental impact from aquaculture activities (Takeuchi, 2017; Timmons, Guerdat, & Vinci, 2018). Despite continuous improvement through years, there are still major issues within RAS themselves such as biofilter, nitrogen removal, denitrification device as well as protein skimmer which needed to research for better efficient, eco-friendly and low-cost solutions. (Badiola, Mendiola, & Bostock, 2012). On the other hand, biochar recently emerged as a green adsorbent as well as a disposal filter in biological wastewater treatment mainly for bioretention and bioremediation (Ahmed & Hussain, 2018; Crini & Lichtfouse, 2018; Ferreira, Calisto, Otero, Nadais, & Esteves, 2016; Poor & Mohamed, 2020; Wu et al., 2020). Because biochar is a stable

carbon-rich material derived from thermal pyrolysis of biomass, it has been regarded as an economical and sustainable carrier which has extensive application prospects in the field of soil improvement or wastewater treatment. Also, there have been many studies on the efficacy of biochar as a support medium during anaerobic/aerobic digestion or a support-based catalyst for biodegradation of recalcitrant contaminants (Enaime, Baçaoui, Yaacoubi, & Lübken, 2020; Lehmann & Joseph, 2015; Wu et al., 2020). Depending on pyrolysis temperatures and post-preparation methods, biochar could be engineered to obtain new valued properties such as higher surface area, micropore volume and specific functional groups that become more suitable for different inorganic/organic substances sorption even for metal immobilization (Enaime et al., 2020; Huang et al., 2016; Mohan, Sarswat, Ok, & Pittman, 2014; Wang et al., 2015). In this work, we study on the capacity adsorption of rice husk biochar (RHB) for nitrogen compounds such as ammonium NH_4^+ , nitrite NO_2^- and nitrate NO_3^- to gain more insights about mechanism behind that could be used to improve nitrogen removal process. In Vietnam, researches on biochar and its nearest relative (hydrochar) for wastewater treatment are very active that focus on the modification of biochar surface in order to increase adsorption capacity for organic species as well as heavy metal (Bui, 2016; Nguyen et al., 2021; Pham, 2016; Vu & Trinh, 2016). Several critical papers that provide us a solid explanation on the process of removing organic contaminants by adsorption mechanism of biochar including electrostatic attraction, pore-filling, π - π electron-donor acceptor interaction, H-bonding, complexes adsorption, hydrophobic interactions and so on that well-written in recent studies (Ahmad et al., 2014; Dai, Zhang, Xing, Cui, & Sun, 2019; Liang, Yu, Huang, Zhang, & Cao, 2016; Tran, You, Hosseini-Bandegharaei, & Chao, 2017; Zhang et al., 2020). Among many mathematical models have been developed for prediction and interpretation of adsorption mechanism such as isotherm equation, kinetic model, and thermodynamic constant beside calculation the effects of contact time, pH of aqueous solution as well as functional groups which caused by pre- and post-treatment methods being applied to the adsorbent, we focus on two main points that help introduce rice husk biochar into nitrogen removal application. There are to analysis the functional groups and to apply isotherm models on experimental data for estimation about either the nature of our studied biochar and maximum saturated monolayer adsorption capacity Q_{\max}^0 of ammonium, nitrite, and nitrate onto RHB that would be useful to design an economical but effective biological filtration for RAS.

2. Materials and methods

2.1. Biochar preparation

Rice husk biochar (RHB) was produced by putting rice husk in an inox box wrapped by aluminum foil for creating a limited oxygen condition during slow pyrolysis process in a furnace (Nabertherm) with heating rate $10^\circ\text{C}/\text{min}$ from beginning to 550°C and held for 3 hours (Fidel, Laird, & Spokas, 2018). For the purpose to use raw RHB as biofilter substrate in trickling filtration so its original size (5-8mm) was selected for adsorption experiments in awareness that this particle size may lessen adsorption efficiency if compared with powder size. To prepare RHB as adsorbent, we followed the acid-washing method (Fidel et al., 2018). Biochar after treatment was dried at 60°C for testing adsorption capacity.

2.2. Biochar characterization

The pH and EC values of raw RHB were measured by using ratio 1:20 w/v biochar and deionized water (DI water) followed IBI guidelines (International Biochar Initiative, 2015; Inyang et al., 2012). pH_{PZC} value was determined using salt addition method (Bakatula, Richard, Neculita, & Zagury, 2018). It is essential to remind that the point of zero charge (pH_{PZC}) is the pH value at which the net charge on material surface becomes zero. When $\text{pH}_{\text{PZC}} < \text{pH}$ of the solution, the

biochar surface will be negatively charged that possibly attracts cations better, likewise, when the $\text{pH}_{\text{PZC}} > \text{pH}$ of the solution, the surface becomes positively charged that might attracts anions effectively (Essandoh, Kunwar, Pittman, Mohan, & Mlsna, 2015; Herath et al., 2016). To measure surface area and observation the microscopic shape of RHB, the BET and SEM method also undertaken. The surface functional groups of RHB have been characterized by the FTIR spectroscopy (Bruker Tensor 27) for explanation the adsorption process by chemical reactions. In addition, elemental analysis of the studied RHB was conducted using SEM-EDS method. For determination of ammonium NH_4^+ , nitrite NO_2^- , and nitrate NO_3^- in the filtrates, we followed Nessler method (ASTM D1426-15), Griess assay (TCVN 6178:1996), and spectrometric method using sulfosalicylic acid (TCVN 6180:1996) respectively.

2.3. Batch adsorption experiments

2.3.1. Ammonium adsorption onto RHB

Ammonium solutions with concentration varying from 0.5-1-2-4-6 (mg NH_4^+/L) were prepared by diluted $(\text{NH}_4)_2\text{SO}_4$ in DI water. Adsorption experiments were conducted by putting 1g RHB inside a 50mL centrifuge tube containing 20mL ammonium solution accordingly. Control treatment was conducted the same procedure using DI water without adding adsorbate solution. These centrifuge tubes were shaken at 200rpm and 28°C then analyzed ammonium concentration in the filtrates using filter papers (Sartorius® 292) for each time interval 0.5-1-2-3-4-5-6-8-16-24 hours. Every ammonium concentration and time point were triplicate. From empirical data, we fitted them on isotherm equations and calculated the maximum saturated monolayer adsorption capacity Q_{max}^0 of studied adsorbate (Shukla, Sahoo, & Remya, 2019).

❖ Adsorption capacity at time:

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

where, q_t (mg/g) is the adsorption capacity at time, C_0 (mg/L) and C_t (mg/L) are the adsorbate concentrations at beginning and at time, respectively; m (g) is the mass of adsorbent used, V (L) is the volume of the adsorbate solution.

❖ Adsorption capacity at equilibrium:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

where, q_e (mg/g) is the adsorption capacity at equilibrium, C_0 (mg/L) and C_e (mg/L) are the adsorbate concentrations at beginning and at equilibrium, respectively; m (g) and V (L) were described above.

For studying on adsorption mechanism, Langmuir and Freundlich adsorption model were used with the assumptions that homogeneous surface sites or heterogeneous surface sites respectively that would be the main nature of a particular adsorbent (Wan et al., 2012).

❖ Langmuir adsorption isotherm equation (Bolster & Hornberger, 2007; Ghosal & Gupta, 2017; Langmuir, 1918; Tran et al., 2017)

$$q_e = \frac{Q_{\text{max}}^0 \times K_L \times C_e}{1 + K_L \times C_e} \quad (3)$$

where, q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the adsorbate concentration at equilibrium, Q_{\max}^0 (mg/g) is the maximum saturated monolayer adsorption capacity of an adsorbent, K_L (L/mg) is the Langmuir constant related to the affinity between an adsorbent and adsorbate. When the experimental equilibrium data are adequately described by the Langmuir model, it is necessary to calculate the separation factor (Foo & Hameed, 2010).

$$R_L = \frac{1}{1 + K_L \times C_0} \quad (4)$$

where, R_L is a constant separation factor (dimensionless) of a solid-liquid adsorption system, K_L (L/mg) is the Langmuir equilibrium constant, and C_0 is the initial adsorbate concentration. The isotherm shape was used to predict whether the adsorption system was favorable, unfavorable, linear, or irreversible according to R_L value shown in Table 1.

❖ Freundlich adsorption isotherm equation (Appel, 1973; Freundlich, 1907; Tran et al., 2017; Van der Bruggen, 2015)

$$q_e = K_F \times C_e^{1/n} \quad (5)$$

where, q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the adsorbate concentration at equilibrium, K_F is the constant characterizes the strength of adsorption between an adsorbent and adsorbate, n is a dimensionless intensity parameter.

Table 1

Relationship between isotherm parameters and isotherm shapes (Tran et al., 2017; Worch, 2012, p. 52, p. 76)

Freundlich exponent	Separation factor	Isotherm shape	Remark
$1/n = 0$	$R_L = 0$	Irreversible	Horizontal
$1/n < 1$	$R_L < 1$	Favorable	Concave
$1/n = 1$	$R_L = 1$	Linear	Linear
$1/n > 1$	$R_L > 1$	Unfavorable	Convex

Note: $1/n$ calculated from (5); R_L calculated from (4)

Source: The researcher's data analysis

2.3.2. Nitrite adsorption onto RHB

Nitrite solutions with concentration varying from 0.1-1-3-6-10 (mg NO_2^-/L) were prepared by diluted NaNO_2 in DI water. Experiment setup was followed the same ammonium adsorption procedure described in 2.3.1.

2.3.3. Nitrate adsorption onto RHB

Similarly, nitrate solutions with concentration varying from 3-3.5-4-8-10 (mg NO_3^-/L) were prepared by diluted KNO_3 in DI water. Experiment setup was followed the same ammonium adsorption procedure described in 2.3.1.

2.4. Statistical analysis

Adsorption data was stored and calculated by Excel then fitted using OriginPro for Langmuir and Freundlich models.

3. Results and discussions

3.1. Rice husk biochar properties

Biochar derived from rice husk after pyrolysis at 550°C has pH and EC values before and after acid-washing around 10.10 ± 0.03 and 0.28 ± 0.01 mS/cm in compared with 6.11 ± 0.05 and 0.11 ± 0.01 mS/cm respondingly. From this result, acid-washing is an effective approach for neutralizing biochar for getting accuracy in applied for adsorption experiment (Fidel et al., 2018). The pH_{PZC} of this studied RHB was 6.8 also being similar with the result of Herath et al. (2016). Our biochar has surface area $42.22 \text{ m}^2/\text{g}$ that was higher than other RHBs in related studies (Kizito et al., 2015; Milla, Rivera, Huang, Chien, & Wang, 2013). Morphology of biochar at scale $\times 3000$ has clearly shown that it was a rich-porous material with many macro and micropores that obviously enhance the pollutant adsorption by both physical and chemical process. From surface functional group analysis, there existed the O–H group (at frequency 3443 cm^{-1}), $-\text{CH}_3$ (2360 cm^{-1}), and either $-\text{C}=\text{O}$ or $\text{C}=\text{C}$ group (in the range of frequency $1600\text{--}1650 \text{ cm}^{-1}$), $-\text{COOH}$ (1456 cm^{-1}) as well as CO_3^{2-} (1098 and 795 cm^{-1}). Elemental analysis of the studied RHB was C (10.19%), O (52.74%), Al (0.38%), Si (36.16%), and K (0.53%). A number of aromatic functional groups in biochar structure also appeared after pyrolysis that will contribute to adsorption capacity (Brewer, Schmidt-Rohr, Satrio, & Brown, 2009).

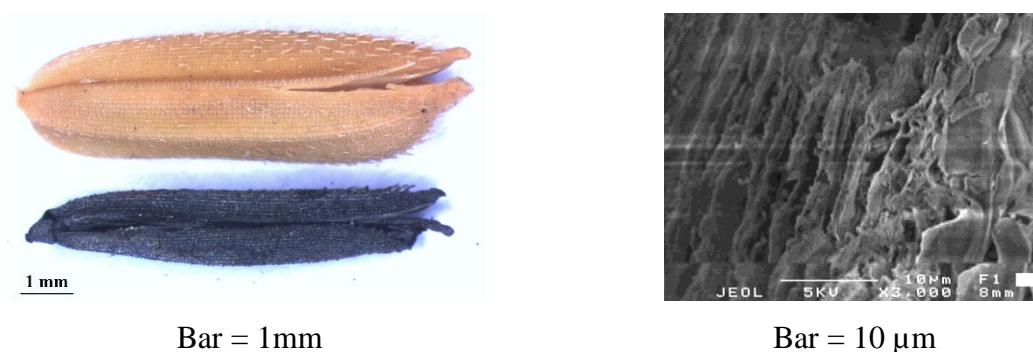


Figure 1. Left: Image of rice husk and its biochar under stereo microscope
Right: SEM image of RHB

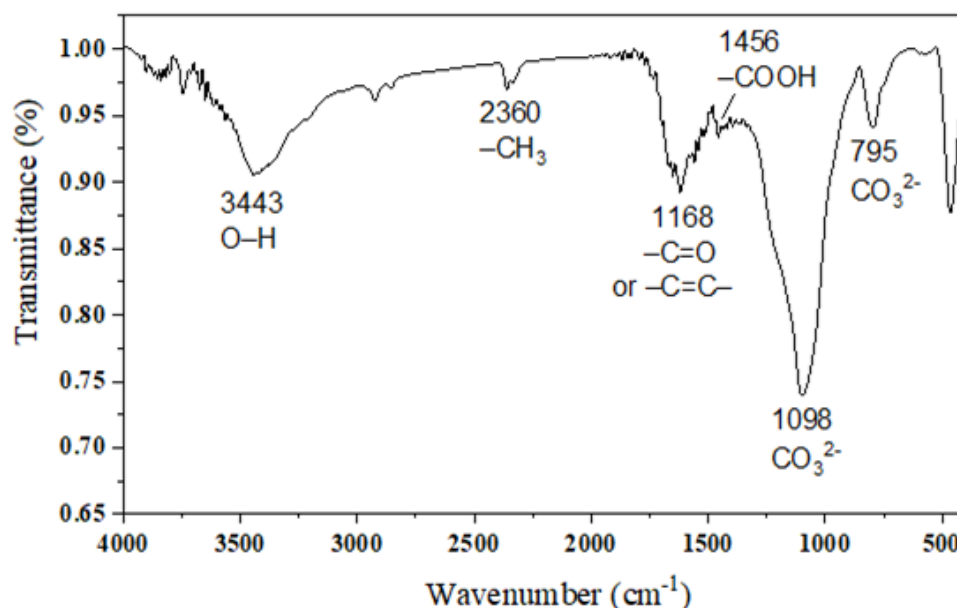


Figure 2. FTIR spectrum of the studied RHB

For ammonium adsorption, it is solely influenced by cation exchange, surface complexation with oxygen-containing functional groups as described by Cui, Hao, Zhang, He, and Yang (2016). Additionally, ammonium adsorption is pH-dependent with optimum values 7-7.5 (Fidel et al., 2018). Freundlich equation has been found that more suitable for describing the ammonium adsorption mechanism than Langmuir equation that implies there is heterogeneous adsorption of the multi molecular layer (Gai et al., 2014; Hu et al., 2020; Kizito et al., 2015; Liang et al., 2016). Nitrite and nitrate adsorption are anions that could be adsorbed to positively charged surface by electrostatic attraction when pH of aqueous solution $< \text{pH}_{\text{PZC}}$. Functional groups such as $-\text{COOH}$ and $\text{O}-\text{H}$ linked with phenolic groups or metals that attached on biochar were identified the main mechanism for chemical adsorption of nitrite and nitrate onto biochar (Afkhami, Madrakian, & Karimi, 2007; Hafshejani et al., 2016; Yakout & Mostafa, 2014; Zhang et al., 2020).

3.2. Adsorption isotherm

3.2.1. Ammonium adsorption

When increasing the initial ammonium concentration, there was a trend that adsorption capacity increases accordingly and reached an equilibrium around 16-hour contact time. Table 1 was used to check the validity of isotherms. The separation factor (R_L) of Langmuir equation ranged 0.66-0.96 and Freundlich exponent ($1/n$) was 0.81 that means both isotherms suitable for explaining the ammonium adsorption onto RHB. R^2 (0.9762) of Freundlich equation was higher than R^2 (0.9716) of Langmuir equation so that the behavior of the ammonium adsorption of this studied RHB followed the heterogeneous adsorption of the multi molecular layer rather than mono layer (Kizito et al., 2015).

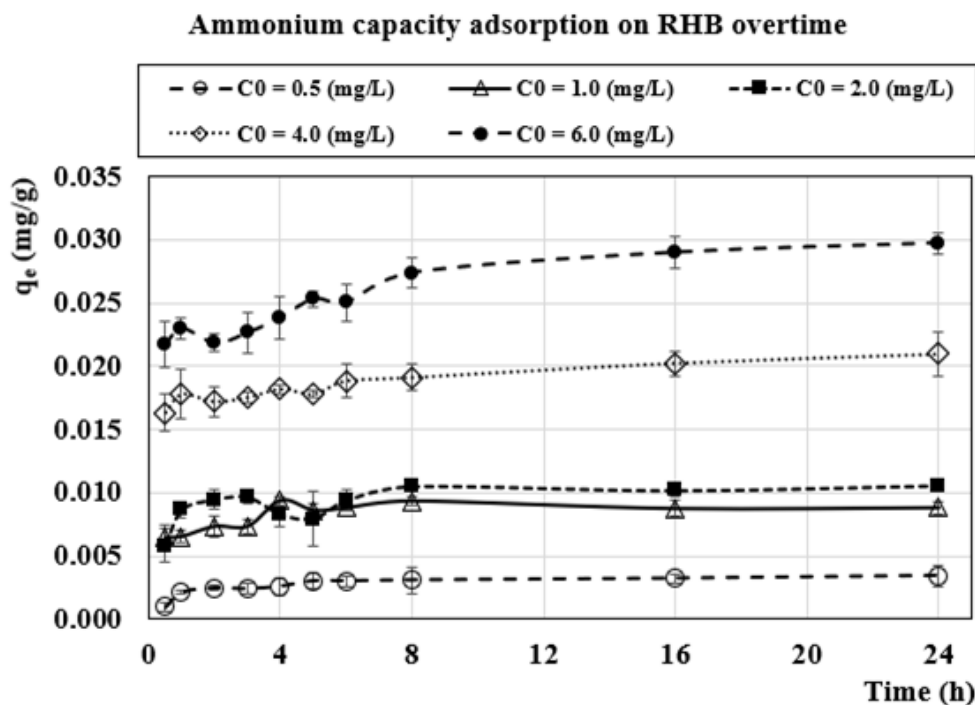


Figure 3. Effect of contact time and initial concentration to ammonium adsorption capacity onto RHB

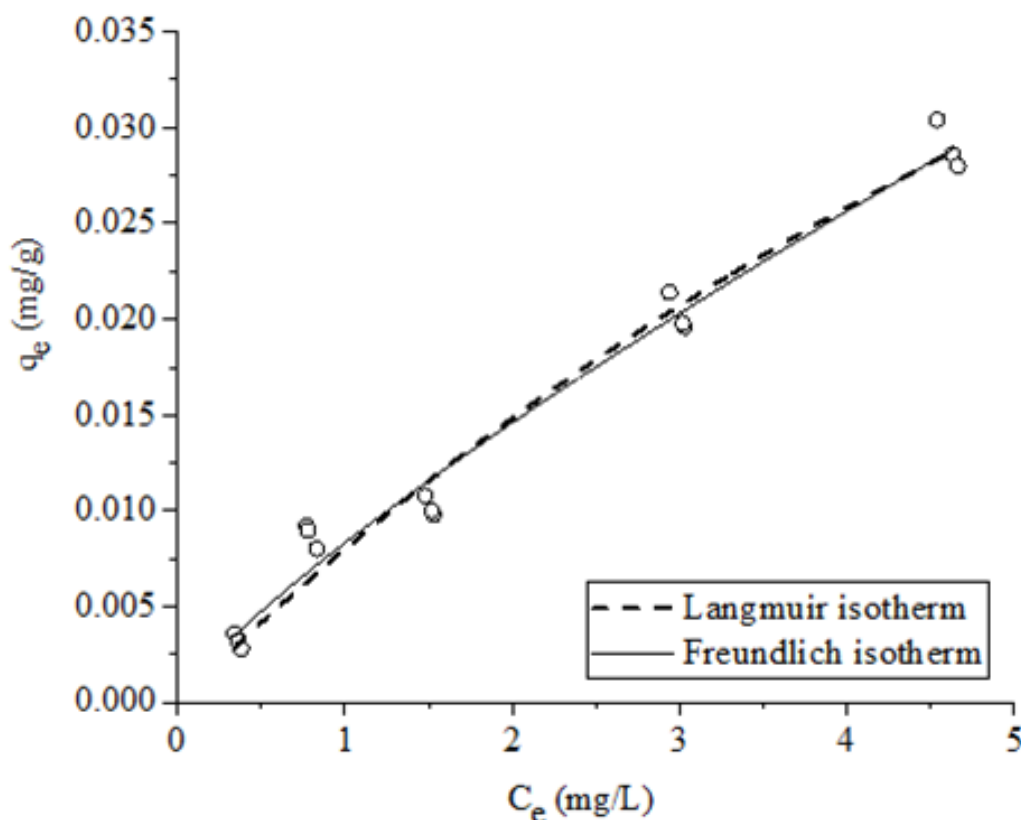


Figure 4. Langmuir and Freundlich isotherms for ammonium adsorption onto RHB

Table 2

Langmuir and Freundlich parameters for ammonium adsorption onto RHB at 28°C

Langmuir isotherm			Freundlich isotherm		
Q_{\max}^0 (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
0.1003	0.0867	0.9716	0.0083	1.2325	0.9762

Source: The researcher's data analysis

3.2.2. Nitrite adsorption

When increasing the initial nitrite concentration, there was a trend that adsorption capacity increases accordingly and reached an equilibrium at 16-hour contact time. Table 1 was used to check the validity of isotherms. The separation factor (R_L) of Langmuir equation ranged 0.08-0.90 and Freundlich exponent ($1/n$) was 0.56 that means both isotherms suitable for explaining the nitrite adsorption onto RHB. R^2 (0.9090) of Langmuir equation was higher than R^2 (0.8804) of Freundlich equation so that the behavior of the nitrite adsorption of this studied RHB followed the homogeneous adsorption of the mono molecular layer.

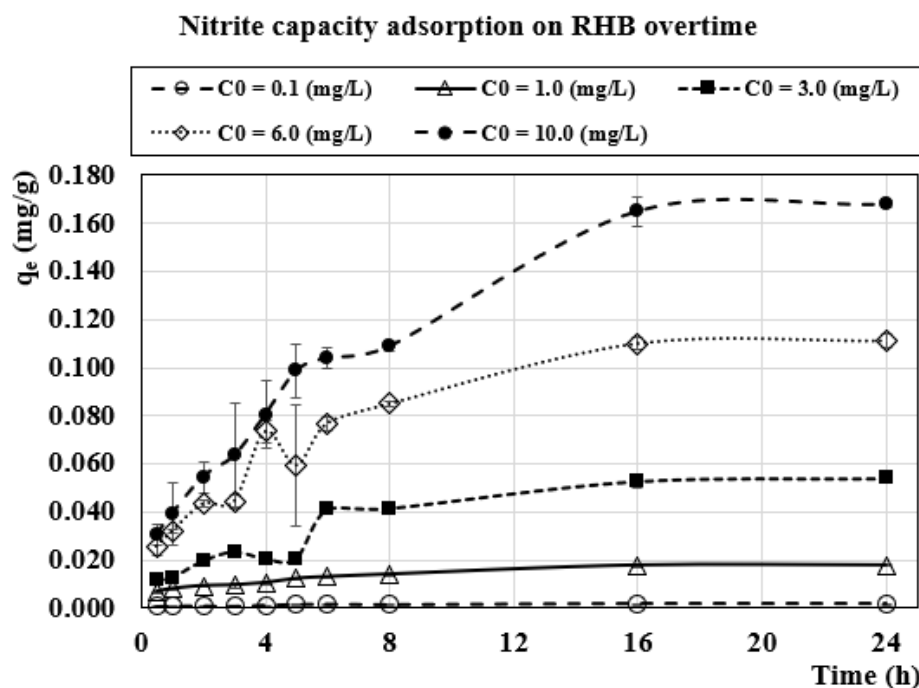


Figure 5. Effect of contact time and initial concentration to nitrite adsorption capacity onto RHB

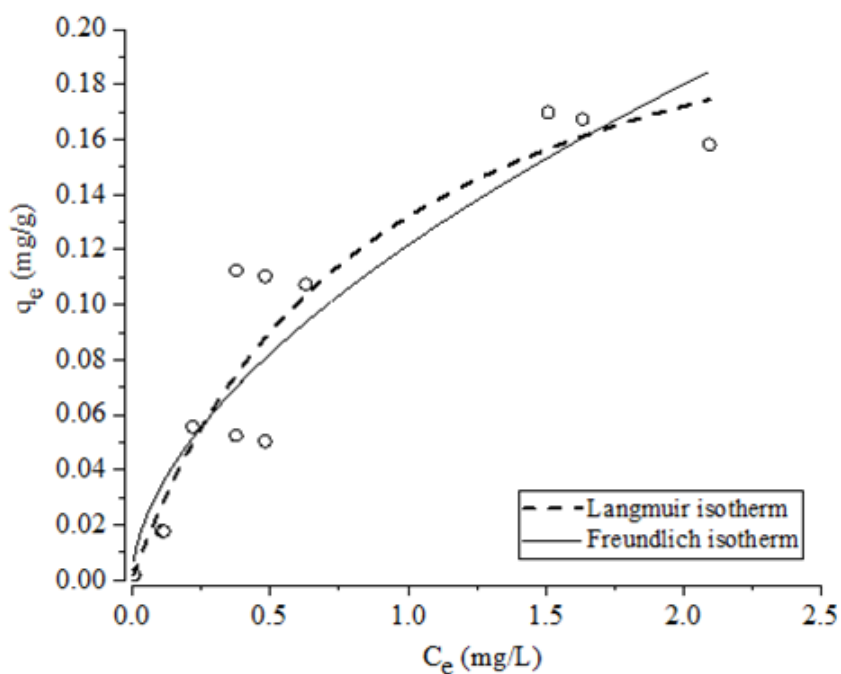


Figure 6. Langmuir and Freundlich isotherms for nitrite adsorption onto RHB

Table 3

Langmuir and Freundlich parameters for nitrite adsorption onto RHB at 28°C

Langmuir isotherm			Freundlich isotherm		
Q_{\max}^0 (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
0.2477	1.1381	0.9090	0.1215	1.7655	0.8804

Source: The researcher's data analysis

3.2.3. Nitrate adsorption

When increasing the initial nitrate concentration, there was a trend that adsorption capacity increases accordingly and reached an equilibrium at 8-hour contact time. Table 1 was used to check the validity of isotherms. The separation factor (R_L) of Langmuir equation ranged 0.14-0.35 and Freundlich exponent ($1/n$) was 0.44 that means both isotherms suitable for explaining the nitrate adsorption onto RHB. R^2 (0.9380) of Freundlich equation was higher than R^2 (0.9140) of Langmuir equation so that the behavior of the nitrate adsorption of this studied RHB followed the heterogeneous adsorption of the multi molecular layer rather than mono layer (Kizito et al., 2015).

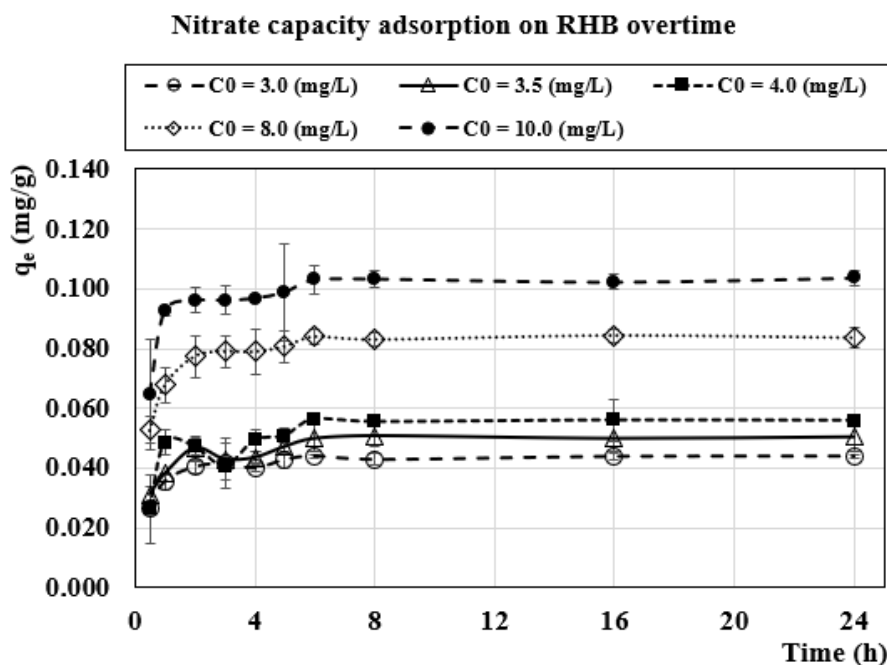


Figure 7. Effect of contact time and initial concentration to nitrate adsorption capacity onto RHB

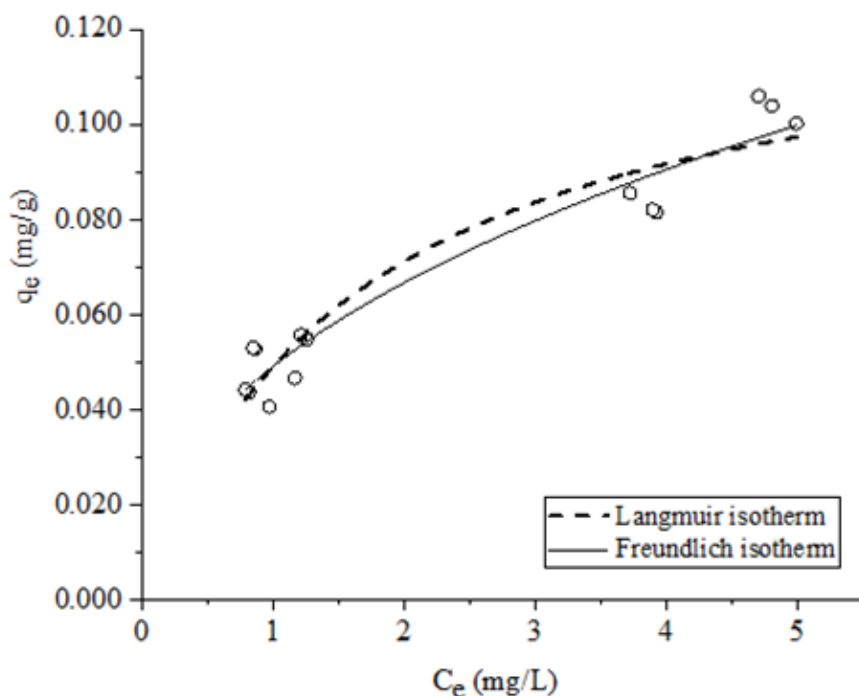


Figure 8. Langmuir and Freundlich isotherms for nitrate adsorption onto RHB

Table 4

Langmuir and Freundlich parameters for nitrate adsorption onto RHB at 28°C

Langmuir isotherm			Freundlich isotherm		
Q^0_{\max} (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
0.1290	0.6142	0.9140	0.0491	2.27	0.9380

Source: The researcher's data analysis

The studied RHB has a low adsorption capacity to ammonium, nitrite, and nitrate in comparison with other adsorbents as shown in Table 4. It could be explained that its original size (5-8mm) was selected for adsorption experiments. This is a trade-off in order to reduce the clogging when uses raw RHB as biofilter substrate in trickling filtration. Nevertheless, with a moderate adsorption capacity for nitrite (0.2477mg/g), RHB would be a better choice to replace activated carbon for minimizing nitrite toxicity in aquaculture water thanks to its economical and environmental aspects.

Table 5

Comparison of RHB's adsorption capacity in this study with other biochar-based adsorbents

Adsorbate	Adsorbent	Particle size (mm)	Pyrolysis temperature (°C)	Pyrolysis time (h)	Adsorption temperature (°C)	Maximum saturated monolayer adsorption capacity Q^0_{\max} (mg/g)	Reference
NH_4^+	Rice husk biochar	5–8	550°C	3	28	0.1003	This study
	Pitaya peel biochar	Powder	400°C	2	25	2.65	(Hu et al., 2020)
	<i>Thalia dealbata</i> biochar	< 0.5	500°C	2	25	1.91	(Cui et al., 2016)
	Rice husk biochar	0.25–1.25	600°C	10	25	39.8	(Kizito et al., 2015)
	Rice husk charcoal	-	300°C	-	25	2.60	(Han, Zhao, Dou, Jing, & Zhu, 2013)
NO_2^-	Rice husk biochar	5–8	550°C	3	28	0.2477	This study
	Hydrotalcite	-	-	-	25	46.3	(Ogata et al., 2018)
	Rice straw-derived activated carbon	-	650°C	1	25	1.24	(Hamed, Yakout, & Hassan, 2013)

Adsorbate	Adsorbent	Particle size (mm)	Pyrolysis temperature (°C)	Pyrolysis time (h)	Adsorption temperature (°C)	Maximum saturated monolayer adsorption capacity Q^0_{\max} (mg/g)	Reference
	Calcined hydrotalcite	0.149	-	-	25	37.17	(Wan et al., 2012)
	Wood-derived activated carbon	< 0.125	-	-	29	2.19	(Shabir, 2010)
NO_3^-	Rice husk biochar	5–8	550°C	3	28	0.1290	This study
	Hydrogel-rice husk biochar	Powder	500°C	1	25	1.53	(Afjeh, Marandi, & Zohuriaan-Mehr, 2020)
	Rice husk biochar	-	600°C	0.5	25	0.497	(Shukla et al., 2019)
	Corn stover biochar	< 0.5	600°C	2	-	1.5	(Fidel et al., 2018)
	Sugarcane bagasse biochar	-	600°C	4	22	11.56	(Hafshejani et al., 2016)

Note: the minus sign means not shown in literature

Source: The researcher's data analysis

4. Conclusions

Biochar has been received great attention recent years due to its novel structure and characteristics that let it become a promising candidate for bioremediation in both targets cost-efficient and sustainable (Lu et al., 2020). The findings in this paper that raw RHB can be used for nitrogen removal because its adsorption capacity towards ammonium, nitrite, and nitrate ranging from 0.10-0.24mg/g that adequately satisfies for controlling water quality in RAS. Nevertheless, raw biochar is not recommended as a silver bullet unless it should be engineered for specific application that can unlock fully its potential. It means the continuation of biochar research would focus on integration biotic and abiotic agents on biochar matrix to make it more effective in different operation settings.

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