



Potential of Using Surfactants to Enhance Ammonium and Nitrate Adsorption on Rice Husk and Its Biochar

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Abstract

Inorganic nitrogen fertilizers are widely and heavily used in agriculture. Leaching of these fertilizers is a cause of eutrophication in water bodies. This study examines the use of rice husk and its biochar, their efficiency in adsorption of ammonium and nitrate and the potential of using surfactants, sodium dodecyl benzenesulfonate (SDBS) and cetyl trimethyl ammonium bromide (CTAB), to increase adsorption. Physical and chemical properties of adsorbents were examined through BET, SEM-EDX, and CEC value, respectively. The equilibrium batch adsorption was conducted. The result showed that rice husk was lower in surface area, total pore volume, pore diameter, silica and oxygen content, and CEC value as compared to biochar. Rice husk adsorbed nitrate well while rice husk biochar adsorbed ammonium ions better. The adsorption patterns of both ammonium and nitrate were well explained by Freundlich's isotherm and are primarily attributed to chemical charge sorption. Both adsorbents could adsorb surfactants through Van der Waals forces between the long chain of surfactant and organic fraction on the surface of rice husks, exposing the charging head for ionic pollutant adsorption. Either SDBS or CTAB-modified rice husk and its biochar could enhance the adsorption of ammonium and nitrate.

Keywords: Ammonium; Adsorption; Biochar; Nitrate; Rice husk; Surfactant

Introduction

Nitrate contamination of water bodies is a worsening global problem for both environment and human health. For example, when nitrates are converted to nitrites they combine

with blood hemoglobin to form methemoglobin, which reduces the blood's ability to bind oxygen- a condition that is especially serious in babies and children under four years. Moreover, some bacteria species in the stomach

can metabolize nitrates into nitrosamines which are known mammalian carcinogens [1]. Nitrate is also the cause of eutrophication in water bodies: nitrate-driven algal blooms lead to competition for sunlight, space and oxygen, and the resulting fall in dissolved oxygen levels lead to a collapse in aquatic life. One of the main contributors to nitrate contamination in the environment is runoff from the large amounts of nitrogen fertilizer used in agriculture [2-3].

Many inorganic nitrogen fertilizers used in agriculture usually are in the form of ammonium and nitrate compounds. The ammonium generally is oxidized to nitrate by microbial groups of nitrifying bacteria. Nitrate can be easily leached from the soil having the same negative charge group as soil particles. Increasing the absorption of ammonium and nitrate into the soil could help reduce nitrate leaching into water bodies, while also reducing the cost of fertilizers for farmers.

Rice husk is one of the most common types of agricultural waste used to increase soil porosity and retain moisture. It is very durable in the soil. Rice husk biochar produced through a pyrolysis process is also used [4]. Many experimental results indicated that use of rice husk biochar can improve soil properties [5-6] and increase yields [6-7]. The rice husk and rice husk biochar have very different composition. Raw rice husk contains mostly organic substances [8] while the rice husk biochar contains higher levels of recalcitrant carbon [5] which accounts for the differences in adsorption properties. Several studies have examined the adsorption of nitrate on to rice husk including: lignocellulosic anion exchangers from sugarcane bagasse and rice husk [9], a cross-link of rice husk with epichlorohydrin [10]. However, there have been few studies exploring the use of non-toxic household materials and simple preparation methods for their use to enhance adsorption of ammonium and nitrate. Such studies could be of particular benefit for far-

mers and gardeners. Surfactants are compounds containing both the hydrophobic tail of a carbon chain and the hydrophilic head group charge [11]. Various studies have shown that surface modification of clay minerals by positive charge surfactants can enhance adsorption of anions [12-13]. Thus, modifying the surface of rice husks with charged surfactant opposite to the pollutant may enhance adsorption of the ionic pollutant.

This study examines the mechanism and efficiency of rice husk and its biochar in the adsorption of ammonium and nitrate. Also included in the study is the potential of using the readily available, low cost surfactants sodium dodecyl-benzenesulfonate (SDBS) and cetyl trimethyl ammonium bromide (CTAB) to increase adsorption of ammonium and nitrate.

Materials and methods

1) Materials/chemicals

Rice husk was purchased from a rice mill located in Nonthaburi Province, Thailand. The low cost, readily available and biodegradable surfactants, CTAB (Figure 1a) and SDBS (Figure 1b), were used in this study as being representative of positive and negative charge surfactants, respectively. Cetyl trimethyl ammonium bromide ($\geq 96\%$) was purchased from Fluka, Sodium dodecylbenzenesulfonate was purchased from Aldrich, KNO_3 ($\geq 99\%$) and $(\text{NH}_4)_2\text{SO}_4$ ($\geq 99\%$) was purchased from Ajax Finechem.

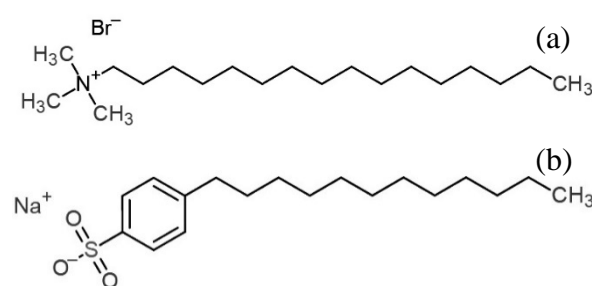


Figure 1 The chemical structure of (a) CTAB and (b) SDBS.

2) Adsorbent preparation and characterization

Two adsorbents were used in this study: rice husk (RH) and the rice husk biochar (RHB). The rice husk was cleaned by DI water to remove dirt, air dried, and preserved at room temperature. RH was prepared by grinding and sieving to the size of 0.106 to 0.600 mm. To prepare RHB, cleaned rich husk was heated to 500 °C for 2 h in a furnace and then ground to 0.106 to 0.600 mm.

The surfactant modified RH and RHB were prepared by soaking either RH or RHB with 30 mM SDBS and 90 mM CTAB at a solid: solution ratio of 1:20. These surfactant concentrations were higher than their critical micelle concentration (CMC) which are 1.6 mM [14] and 0.9-1.0 mM [15] for SDBS and CTAB, respectively. Then the samples were rinsed 3 times with DI water and then dried at 60 °C using a standard laboratory oven.

3) Adsorbent characterization

The confirmation of differences in properties of RH and RHB were analyzed: the surface and element composition by SEM-EDX model JSM-6400; surface area, total pore volume, and average pore diameter by Surface Area and Pore Size Analyzer model Autosorb-1; and CEC by the ammonium acetate method. The calculations for this study were based on dry weight of the adsorbent.

4) Adsorption experiments

The solutions of ammonium and nitrate at different concentrations (3-300 mgN L⁻¹) were prepared by serial dilution of a stock solution of 5 gN L⁻¹ of (NH₄)₂SO₄ and KNO₃, respectively. The batch equilibrium adsorption tests were carried out by shaking 20 mL solution with 2 g adsorbent in a 50 mL centrifuge tube at 250 rpm, 4 h, 25±1 °C, then filtered through Whatman filter paper no.42 to separate the supernatant. Ammonium and nitrate concentrations were determined using a WTW analyzer (Terminal

740 series), with ion selective electrode model NH 500 and NO 500, respectively. The percentage of removal was calculated using the following formula:

$$\text{Removal} = (C_i - C_e) / C_e \times 100$$

where C_i is the initial concentration and C_e is the equilibrium concentration of ammonium or nitrate. The isotherms used in this study were Langmuir, Freundlich, Redlich–Peterson, Dubinin–Radushkevich, Tempkin, as shown in Table 1. The batch equilibrium adsorption of surfactant SDBS and CTAB of 10-900 mg L⁻¹ on RH and RHB were conducted the same way. Surfactant concentration in the supernatant was determined following the method of Liu et al. [21]. Adsorption of ammonium and nitrate on surfactant-modified RH and RHB was conducted in the same way as ammonium and nitrate adsorption on RH and RHB, as previously described.

Results and discussion

1) Adsorbent properties

Differences in physical structure and chemical composition between RH and RHB were observed. SEM images showed that the surface of RHB was rougher than RH (Figure 2). The surface areas, pore volume, pore diameter and CEC of RHB were higher than those of RH (Table 2) in agreement with the study of Saleh et al. [22] and Varela Milla et al. [7]. These could be explained by the removal of volatile organic compounds during pyrolysis, leaving only the stable structure of the rice husk fiber and resulting in the observed increase in porosity of the material [23]. The percentage of major elements found on the outer surface of both RH and RHB was similar, being 25 % carbon, 46-47 % oxygen, and 26-28 % silicon (Table 3). The carbon content of rice husk is found primarily in the form of cellulose [24] (Figure 3a). However, a significant difference in elemental composition was observed at the inner surfaces of the materials

where the percentage of silicon of RHB was 4 times higher, while the oxygen content was lower as compared to the RH. This result agreed with the results of Della et al. [25] and Varela Milla et al. [7] and this silicon con-tent

(Figure 3b) is in the form of SiO_2 [26]. Thus, the surface of RHB had a greater fraction of silica than of RH. In addition, the carbon content on the inner surface of the rice husk was higher than on the outer surface.

Table 1 Lists of adsorption isotherms models

Isotherm	Nonlinear equation	Linear equation	Plot	Reference
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	$\frac{C_e}{q_e}$ VS C_e	[16]
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	$\log q_e$ VS $\log C_e$	[17]
Redlich–Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(a_R)$	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right)$ VS $\ln(C_e)$	[18]
Dubinin–Radushkevich	$q_e = (q_s) \exp(-K_{ad} \varepsilon^2)$	$\ln(q_e) = \ln(q_s) - (K_{ad} \varepsilon^2)$	$\ln(q_e)$ VS ε^2	[19]
Tempkin	$q_e = \frac{RT}{b_T} \ln(A_T C_e)$	$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T} \right) \ln C_e$	q_e VS $\ln(C_e)$	[20]

Where A_T is Temkin isotherm equilibrium binding constant (L kg^{-1}), a_R is Redlich-Peterson isotherm constants (L kg^{-1}), b_T is Temkin constant related to heat of sorption (J mol^{-1}), C_e is the equilibrium concentration of adsorbate (mg L^{-1}), ε is Dubinin-Radushkevich isotherm constant, g is Redlich-Peterson isotherm exponent, K_{ad} is Dubinin-Radushkevich isotherm constant ($\text{mol}^2 \text{kJ}^{-2}$), K_f is Freundlich isotherm constant (mg kg^{-1}), K_L is Langmuir isotherm constant (L kg^{-1}), K_R is Redlich-Peterson isotherm constant (L kg^{-1}), n is absorption intensity, q_e is the amount of adsorbate per mass of the adsorbent at equilibrium (mg kg^{-1}), q_m is maximum monolayer coverage capacity (mg kg^{-1}), q_s is theoretical isotherm saturation capacity (mg kg^{-1}), R is gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is absolute temperature (K)

Table 2 Physicochemical properties of RH and RHB

Adsorbent	Surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume (mL g^{-1})	Pore diameter (\AA)	CEC (cmol kg^{-1})
RH	7.02	0.0246	15.5	17.6
RHB	174.80	0.1755	40.2	23.0

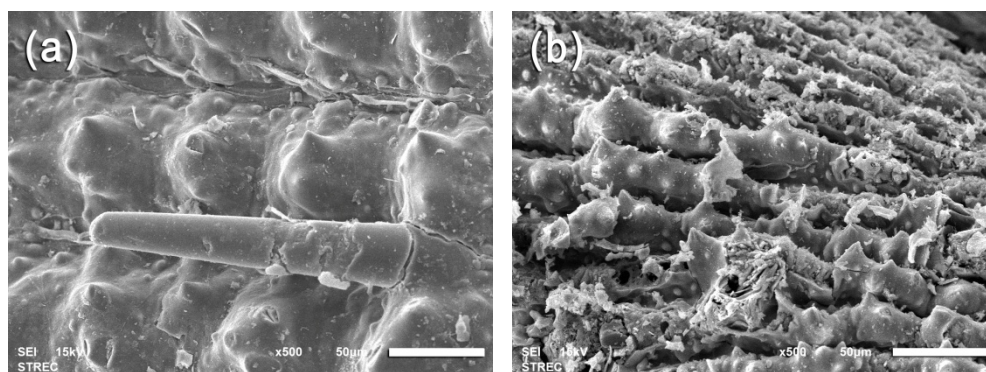
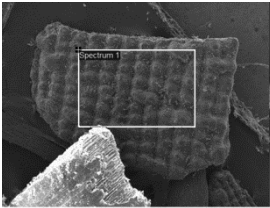
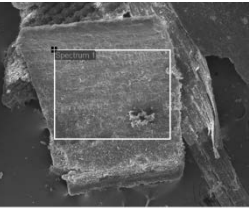
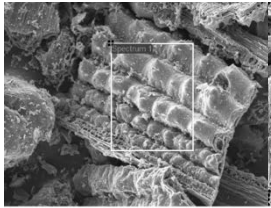
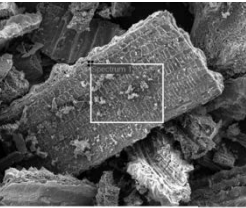


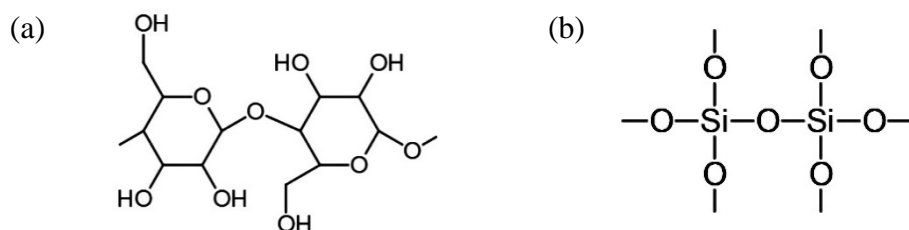
Figure 2 SEM images of (a) RH and (b) RHB, the marker is 50 μm .

Table 3 Elemental composition of rice husk and its biochar

Element	Rice husk (% wt)		Rice husk biochar (% wt)	
	Outside surface	Inside surface	Outside surface	Inside surface

	600 μm	700 μm	300 μm	400 μm
C	25.8	53.7	25.5	52.2
O	47.5	41.4	46.2	29.8
Si	26.7	3.8	28.1	17.2
K	-	0.4	-	0.3
Ca	-	0.7	0.2	0.5
Totals	100.0	100.0	100.0	100.0

**Figure 3** Structure of (a) cellulose (b) silica.

2) Adsorption of ammonium and nitrate

In the adsorption of ammonium and nitrate on RH and RHB, the isotherms of Langmiur, Freundlich, Redlich–Peterson, Dubinin–Radushkevich, and Tempkin were applied (Figure 4). From the R^2 values, ammonium adsorption onto RH could be well explained by Langmiur and Freundlich, while ammonium adsorption onto RHB fitted well with Langmiur, Freundlich, and also Redlich–Peterson's isotherm (Table 4). The Langmiur and Fruendlich isotherm of biochar shown in this study was coincide with many studies [22, 27]. From Langmiur isotherm, the maximum adsorption capacity of ammonium in RH and RHB was 286 mgN kg^{-1} (0.367 mg g^{-1}) and 476 mgN kg^{-1} (0.617 mg g^{-1}), respectively. As compared to the other studies, the adsorption of ammonium sulfate on biochar of rice husk and peanut hull was 4.46, and 9.4 mg g^{-1} , respectively, at concentrations of 2,000

to 100,000 $\text{mg NH}_4\text{-N kg}^{-1}$ of biochar with 1:200 solid: solution ratio [22], and biochar of rice husk was 2.6 mg g^{-1} at 5 to 200 mgN l^{-1} [27] which is about ten times higher than found in this study. This might be due to the properties of raw rice husk material, in which the per-centages of carbon, hydrogen, oxygen, and nitrogen could vary from 37.9 to 43.1 %, 5.6 to 6.3 %, 40.5 to 55.3 %, and 0.4 to 4.3 %, respectively [28-30]. Pyrolysis conditions too can affect the chemical and physical properties of the resulting biochar produced [31]. In addition, rice varieties differ in physicochemical structure, as demonstrated in the chemical synthesis of silica from sticky, red, and brown rice in the study of Sankar et al. [32], which found differences in particle size, surface area, and surface morphology. The n values in the Freundlich isotherm for both RH and RHB were higher than 1, indicating that the adsorption of

ammonium is favorable [27]. Regarding nitrate adsorption, even the R^2 value of Redlich–Peterson's isotherm of RHB was near unity, however, the g value was negative thus the adsorption of nitrate on both RH and RHB were well fitted by only the Freundlich isotherm. Therefore, both ammonium and nitrate adsorption could be explained well by Freundlich's isotherm.

Ammonium was efficiently absorbed on RHB ($n = 2.26$, $K_f = 41.70$) as compared to RH ($n = 1.79$, $K_f = 13.19$) while nitrate was better adsorbed on RH ($n = 0.94$, $K_f = 17.45$) rather than RHB ($n = 0.73$, $K_f = 6.07$). Since surface area, total pore volume, and pore diameter of RHB were higher than in RH, these could promote the physical adsorption of ammonium onto RHB [33]. However, some studies have showed that the surface area is not the important factor influencing ammonium

sorption on to biochar [34]. In addition, the CEC value of RHB was higher than that of RH and could promote the chemical adsorption of positive charge of ammonium onto RHB. This CEC value confirmed that it plays a major role in ammonium adsorption [33, 35]. In addition, the higher fraction of silica on RHB surface could form H-bond with ammonium [36]. Nitrate was adsorbed better in RH rather than RHB, even though surface area, total pore volume, and pore diameter of RHB was higher than for RH. However, the adsorption may also be explained by the CEC value that the RH having lower in CEC value, lower in negatively charged silica content, was higher in adsorption of negatively charge nitrate as compared to RHB. Thus, it is concluded that ammonium and nitrate adsorption on both RH and RHB were mainly controlled by a chemical charge mechanism.

Table 4 Adsorption isotherm of ammonium and nitrate onto RH and RHB

Isotherm	Parameter	NH_4^+		NO_3^-	
		RH	RHB	RH	RHB
Langmiur	q_m	286	476	-5000	-1000
	K_L	0.02	0.04	0.00	-0.01
	R^2	0.950	0.955	0.358	0.416
Freundlich	n	1.79	2.26	0.94	0.73
	K_f	13.19	41.70	17.45	6.07
	R^2	0.969	0.988	0.990	0.995
Redlich–Peterson	g	0.46	0.73	-0.12	-0.81
	a_R	4.77	1.29	1.32	5.66
	K_R	6.1	107.0	63.3	212.4
	R^2	0.175	0.959	0.255	0.984
Dubinin–Radushkevich	K_{ad}	2.0E-06	2.0E-07	1.0E-06	4.0E-06
	q_s	103	157	311	381
	R^2	0.645	0.482	0.514	0.695
Tempkin	b_T	55.76	41.40	6.76	5.50
	A_T	0.50	1.67	0.41	0.27
	R^2	0.900	0.886	0.640	0.703

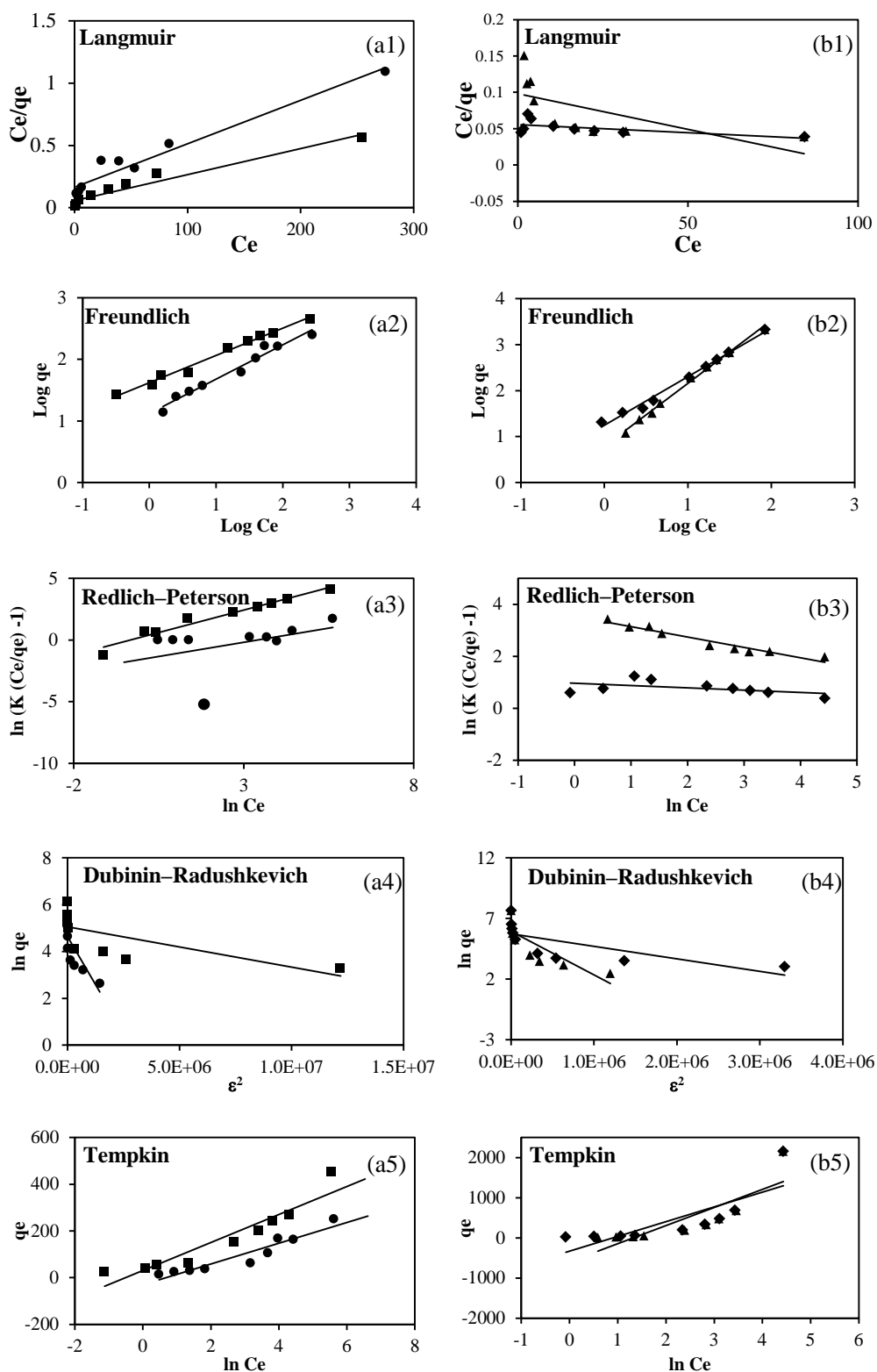


Figure 4 Isotherm of (●) ammonium adsorption on RH, (■) ammonium adsorption on RHB, (◆) nitrate adsorption on RH, and (▲) nitrate adsorption on RHB at 25±1 °C, initial pH of 7.0±0.5.

3) Adsorption of surfactant

The adsorption of CTAB and SDBS onto RH and RHB was examined. The adsorption of surfactant onto the surface could be attributed to electrostatic interaction between the ionic surfactant head and the surface charge of RH and RHB as well as by Van der Waals force from the long tail of the surfactant [11]. The results showed that both CTAB and SDBS were better adsorbed in RHB than RH (Figure 5 and Table 5) and complied better with the larger surface area of RHB than RH. This evident adsorption of both CTAB and SDBS did not rely solely on the ionic charge of the surfactant head. Thus, it was conducted by the non-ionic part of the surfactant. By this mechanism, the non-ionic part of surfactant was turned to the surface of adsorbent, while the ionic head was turned to the aqueous phase. In the case of CTAB, electrostatic interaction through H-bonding between the positive head of the quaternary ammonium cation and the negative charge of silica, especially of the RHB surface, could be attributed to adsorption [36]. This is similar to the adsorption of CTAB on the negatively charged surface of zeolite in the study of Taffarel and Rubio [37] in which a bilayer of CTAB could form at high concentration, giving the surface a positive charge. In contrast, adsorption could be diminished by the negative head of SDBS. However, greater K_f of SDBS than CTAB points to adsorption by the force from their tail being dominated, conforming to the larger molecular structure of SDBS than CTAB. The study of Hosseinnia et al. [38] showed that the adsorption of sodium alkyl benzene sulfonate on rice husk ash was due to Van der Waals

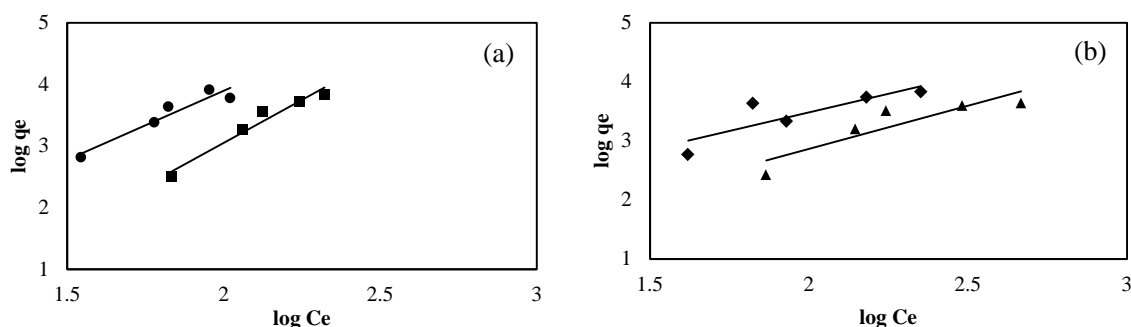
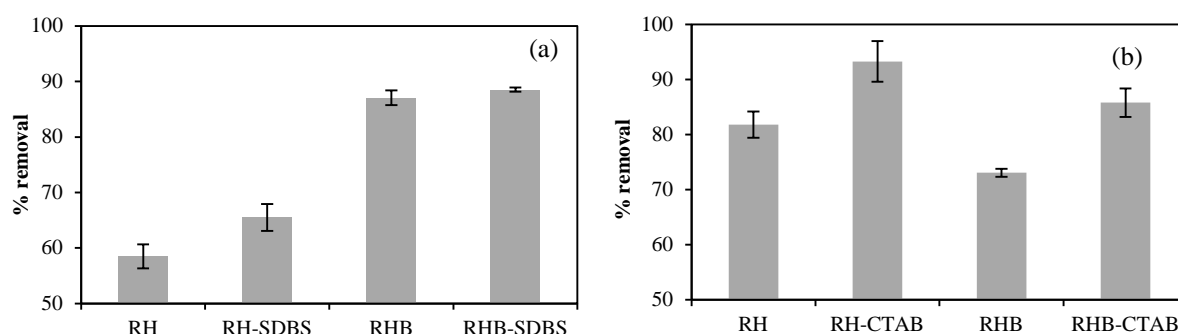
forces between the long chain of surfactant and cellulosic fraction on the surface of rice husk ash. This adsorption of the alkyl chain of surfactant onto the hydrophobic part of surface was also found in other studies [37, 39]. With this modification, the surface of RH and RHB was altered. The charge of the surface was modified via the charge of adsorbed surfactant.

4) Adsorption of ammonium and nitrate of surfactant modified RH and RHB

Charged surfactant could change the surface charge properties of the adsorbent [40]. The RH and RHB modified surface by positive charge surfactant CTAB was used to adsorb negative charge nitrate. RH and RHB modified by negative charge SDBS were used to adsorb positive charge ammonium in equilibrium batch experiments. The result showed that the ammonium adsorption of RH and RHB modified by negatively charge SDBS could increase the removal by 7 ± 4 % and 2 ± 1 %, respectively. A small increase in the removal efficiency of modified RHB could be due to nearly a hundred percent removal (Figure 6). The adsorption of nitrate by CTAB modified RH and RHB could increase the removal by 11 ± 3 % and 13 ± 2 %, respectively, as compared to un-modified RH and RHB. Thus, using surfactants to modify the surface charge of RH and RHB to have opposite charge to ammonium and nitrate could increase adsorption of both ammonium and nitrate. This result coincided with the result of Xi et al. [13], who showed that the positive charge head group of surfactant on the surface of the adsorbent could increase adsorption of negative charged nitrate ions.

Table 5 Adsorption isotherm of CTAB and SDBS onto RH and RHB

Isotherm	Parameter	CTAB		SDBS	
		RH	RHB	RH	RHB
Freundlich	n	0.36	0.45	0.68	0.79
	K_f	0.003	0.262	0.871	9.264
	R^2	0.957	0.914	0.803	0.715

**Figure 5** Freundlich adsorption isotherm of surfactant (■) CTAB on RH, (●) CTAB on RHB, (▲) SDBS on RH, and (◆) SDBS on RHB**Figure 6** Percentage of removal of 10 mgN L⁻¹ of (a) ammonium and (b) nitrate on RH and RHB compared to their surfactant modification at 25±1 °C, initial pH of 7.0±0.5.

Conclusions

Pyrolysis of rice husks at 500 °C for 2 h increases the surface area, total pore volume, pore diameter, and CEC value of the resulting biochar. The adsorption of ammonium and nitrate onto rice husk and its biochar was well explained by Freundlich's isotherm. Adsorption of ammonium and nitrate were highest on RHB and RH, respectively, with electrostatic attraction identified as the major mechanism governing adsorption. Surfactant could be adsorbed on both adsorbents by Van der Waals forces between the long carbon chain of the surfactant and the organic fraction on the surface of rice husk, exposing the charging head for ionic pollutant adsorption. Thus, using

opposite charge surfactants for surface modification of rice husk and rice husk biochar can increase adsorption of ammonium and nitrate, and this is likely attributable to changes in charge on the rice husk and rice husk biochar. However, the percentage removal of ammonium and nitrate appears to depend on their respective initial concentrations. Further study on ammonium and nitrate adsorption onto surfactant modified rice husk or rice husk biochar is necessary, particularly at higher initial concentrations. Nevertheless, the present research application could be highly beneficial for farmers to reduce fertilizer costs while preventing eutrophication of water bodies due to leaching of nitrogen from the soil.

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