



# Low cost and easy rice husk modification to efficiently enhance ammonium and nitrate adsorption

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## Abstract

**Purpose** This research aimed to study the adsorption of ammonium and nitrate by simply modifying the surface of the rice husk using slow pyrolysis and surfactants modification.

**Methods** Rice husk biochar was prepared by slowly pyrolyzing at 500 °C, 2 h. The rice husk and its biochar were modified by cetyltrimethylammonium bromide or sodium dodecylbenzenesulfonate. FTIR, BET and zeta potential measurements were used to characterize the obtained adsorbents.

**Results** Slow pyrolysis increased the specific surface area and decreased the surface charge of rice husk while surfactant clogged the pore but could change the charge of a surface. Adsorption of both ammonium and nitrate on rice husk, its biochar, and their modification with surfactants fitted Freundlich and Langmuir isotherms, indicating heterogeneity in adsorption. Slow pyrolysis gave the highest ammonium removal with maximum adsorption capacity of 44 mgN/g and it was a physical process. The cetyltrimethylammonium bromide modification gave a significant nitrate removal on both rice husk and its biochar with maximum adsorption of 278 and 213 mgN/g, respectively, which is higher than a commercial adsorbent.

**Conclusions** These two modification techniques gave great adsorption enhancement with cost-effectiveness as compared to other reviewed methods which could use as a nitrogen-rich fertilizer and fertilizer retainment in crop production.

**Keywords** Ammonium · Nitrate · Rice husk · Pyrolysis · Surfactant

## Introduction

Nitrogen contamination of water bodies is a worsening global problem causing eutrophication of water which is toxic to aquatic life. Ammonium and nitrate are major causes of the problem, especially from the agricultural sector. There are many techniques used to remove nitrogen including adsorption. Rice husk, one of the major agricultural wastes, is a more cost-effective adsorbent compared to commercial adsorbents. It also enhances growth of the plants (Mustafa et al. 2016). Natural materials, however, may not adsorb a

certain pollutant efficiently. Accordingly, surface modification normally is applied to increase the adsorption efficiency and capacity of the biomass. There have been several studies on improvement of biomass adsorption of nitrogen as with pyrolysis (Zeng et al. 2013), NaOH pre-treatment (Liu et al. 2016), carboxylic acid modification (Halim et al. 2013), acid treatment (Gai et al. 2014), and cross linking with epichlorohydrin (Wang et al. 2007).

From the various techniques used, pyrolysis is especially interesting since it is simple, practical, and is a well-known technique. Zeng et al. (2013) showed that the adsorption of ammonium on pyrolyzed phytoremediation plants could be varied depending on pyrolysis temperature. Kizito et al. (2015) indicated that around 60% of ammonium from piggery manure could be removed by rice husk and wood biochar. Biochar also offers a mechanism for developing slow release fertilizers (Hou et al. 2016). Another attractive technique is surfactant modification since it can provide positive and negative charges to the modified surface. Mathurasa and Damrongsiri (2017) showed that surfactant could be adsorbed onto rice husk

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and rice husk biochar through Van der Waals force and had a potential to increase the adsorption of ammonium and nitrate. In addition, many surfactants are common, readily available household chemicals; so the know-how and techniques are readily transferred to the farmer. There are some further studies which attempt to modify clay minerals with cationic surfactants to improve nitrate adsorption (Aroke et al. 2014; Ozcan et al. 2005).

Combining surfactant modification and pyrolysis of biomass is a new approach which may enhance the adsorption of nitrogen. The focus of this research is, therefore, to investigate the adsorption of ammonium and nitrate using rice husk and its biochar following surface modification using positive- and negative-charged surfactants.

## Materials and methods

### Materials/chemicals

Rice husk was purchased from a mill in Nonthaburi Province, Thailand. Two low cost and biodegradable surfactants were used. Cetyltrimethylammonium bromide (CTAB), a positive-charge surfactant, and sodium dodecylbenzenesulfonate (SDBS), a negative-charge surfactant, were purchased from Fluka and Aldrich, respectively.  $\text{KNO}_3$  ( $\geq 99\%$ ) and  $(\text{NH}_4)_2\text{SO}_4$  ( $\geq 99\%$ ) were purchased from Ajax Finechem.

### Adsorbent preparation

The rice husk was prior cleaned with DI water, and air dried before use. A rice husk adsorbent (RH) was prepared by grinding and sieving the cleaned rice husk to the size of 0.600–0.106 mm. A rice husk biochar (RHB) was prepared by slowly pyrolyzing rice husk at 500 °C, 2 h, in a furnace and then ground to the same size as RH. The pH of RH and RHB were  $6.5 \pm 0.5$  and  $7.8 \pm 0.5$ , respectively. The CTAB-modified RH or RHB (C-RH or C-RHB) and SDBS-modified RH or RHB (S-RH or S-RHB) were prepared by soaking 1 g of solid per 20 ml of 30 mM SDBS or 90 mM CTAB. These surfactant concentrations ensured the saturation of surface (Mathurasa and Damrongsiri 2017). The samples were rinsed 3 times with DI water and then dried at 60 °C using a standard laboratory oven. The properties of each adsorbent were analyzed as follows: the specific surface area, total pore volume, and average pore diameter using BET technique model Autosorb-1; zeta potential by zetasizer model ZSP; and surface functional by FTIR model Nicolet 6700. All calculation was based on the dry weight of the adsorbent.

## Adsorption experiments

The working solutions of ammonium and nitrate at different concentrations, 30–3000 mgN/l, were prepared from the stock solution of 5000 mgN/l of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{KNO}_3$ , respectively. The equilibrium batch adsorption was carried out by shaking 20 ml solution with 2 g adsorbent in a 50 ml centrifuge tube at 250 rpm for 4 h at  $25 \pm 1$  °C, then filtered through Whatman filter paper no. 42 to obtain an aqueous phase. The aqueous phase was determined using a WTW analyzer, model Terminal 740 series, with an ammonia probe for ammonium and nitrate probe for nitrate. The amount of ammonium or nitrate ion adsorbed ( $q_e$ ) was calculated using Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where  $q_e$  is the adsorbed concentration (mgN/g),  $C_i$  is the initial concentration (mgN/l),  $C_e$  is the equilibrium concentration (mgN/l),  $m$  is the mass of adsorbent based on dry weight (g),  $V$  is the volume of solution (l). The  $q_e$  and  $C_e$  were analyzed for the isotherm of Langmuir, Freundlich and Dubinin–Radushkevich and the fitness was observed by its  $R$  square. The Langmuir isotherm assumes that adsorbate, ammonium or nitrate ion, is adsorbed homogeneously at a specific site on the surface of adsorbent without interaction between the adsorbed molecules (Langmuir 1916). The linearized Langmuir isotherm is as Eq. (2):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2)$$

where  $q_m$  is the maximum monolayer coverage capacity (mgN/g) and  $K_L$  is Langmuir isotherm constant (l/mgN). The Freundlich adsorption can be applied to uneven distribution of adsorption energy on heterogeneous surface or multi-layer adsorption on non-ideal surface as natural biomass (Freundlich 1906). A linearized form of the Freundlich adsorption isotherm is expressed as Eq. (3):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where  $K_f$  is Freundlich isotherm constant (mgN/g). The  $n$  value indicates heterogeneity of the surface. A value greater than 1 implies favourable conditions for a sorption or chemisorption process and  $n$  lower than 1 indicates unfavourable conditions for cooperative adsorption. If the adsorption follows the Langmuir assumption, then  $n$  is equal to 1. The physical and chemical adsorption also tested using the Dubinin–Radushkevich isotherm which is generally applied to express the adsorption mechanism on heterogeneous surfaces (Dubinin and Radushkevich 1947). A linearized form of the Dubinin–Radushkevich isotherm is as Eq. (4):

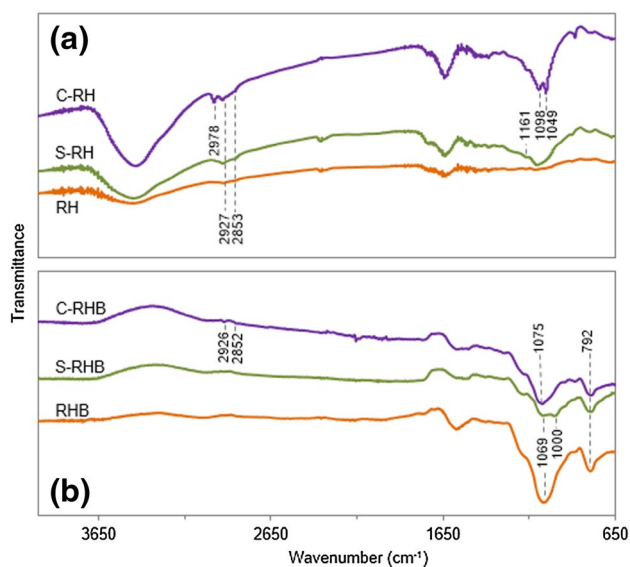
$$\ln(q_e) = \ln(q_s) - (K_{ad}\epsilon^2) \quad (4)$$

where  $q_s$  is theoretical isotherm saturation capacity (mgN/g),  $K_{ad}$  is Dubinin–Radushkevich isotherm constant ( $\text{mol}^2/\text{kJ}^2$ ), and  $\epsilon$  is Polanyi potential, which is expressed as Eq. (5):

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (5)$$

where  $R$  is universal gas constant (8.314 J/mol K) and  $T$  is absolute temperature (K). The constant  $K_{ad}$  in Dubinin–Radushkevich isotherm is indicative of the mean adsorption energy ( $E$ ) (kJ/mol) of adsorption per mole of the adsorbate (Mahmoud 2015). It can be calculated as Eq. (6):

$$E = \frac{1}{\sqrt{2K_{ad}}} \quad (6)$$



**Fig. 1** FTIR spectra of **a** rice husk (RH) and **b** rice husk biochar (RHB) and their modification with CTAB (C-) and SDBS (S-)

**Table 1** Specific surface area, total pore volume, average pore diameter, and zeta potential of each adsorbent

Adsorbent	Specific surface area ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cm}^3/\text{g}$ )	Average pore diameter (Å)	Zeta potential (mV)
RH	7.02	0.025	15.5	$0.21 \pm 0.36$
S-RH	28.71	0.061	85.0	$-4.75 \pm 0.91$
C-RH	2.78	0.065	938.1	$1.70 \pm 1.46$
RHB	174.80	0.176	40.2	$-36.57 \pm 2.05$
S-RHB	3.67	0.119	1299.0	$-28.37 \pm 1.50$
C-RHB	105.10	0.098	37.2	$-27.33 \pm 4.37$

## Results and discussion

### Properties of adsorbent

The FTIR results of RH and RHB were different (Fig. 1a, b). The peak between 2852 and 2927  $\text{cm}^{-1}$  of RH corresponds to an aliphatic C–H stretching vibration which was not noticeable in RHB indicating the labile aliphatic compounds had decreased in RHB (Abdulrazzaq et al. 2014). Moreover, the peak between 1000–1260  $\text{cm}^{-1}$  and at 792  $\text{cm}^{-1}$  of RHB indicated Si–O bonds (Tian et al. 2010) and Si stretching (Lippincott et al. 1958), respectively, showed the increase of silica content in RHB as compared to RH (Alvarez et al. 2014). A broad band at 3250–3500  $\text{cm}^{-1}$  of C-RH (Fig. 1a) corresponds to the N–H stretching vibration while the peaks at 2978, ~2927, and ~2853  $\text{cm}^{-1}$  were due to C–H stretching of a terminal methyl group, anti-symmetrical stretching, and the symmetrical stretching of the methylene group of the aliphatic surfactant tail, respectively. The peaks at 1250–1020  $\text{cm}^{-1}$  indicate the vibration of the C–N bond, confirming the presence of CTAB on C-RH. The results for C-RHB (Fig. 1b) were similar with the characteristic peaks found at 2926, 2852 and 1075  $\text{cm}^{-1}$ . These characteristic peaks of CTAB are consistent with the results of Taffarel and Rubio (2010), Quan et al. (2015) and Ramimoghdam et al. (2012). A peak at 1161  $\text{cm}^{-1}$  of S-RH (Fig. 1a) indicates the S=O group of sulfonic acid and a peak at 1000  $\text{cm}^{-1}$  of S-RHB (Fig. 1b) indicates the S–O group of sulfonate, signifying the presence of SDBS.

The surfactants binding was also confirmed by specific surface area, total pore volume, average pore diameter and zeta potential value of the adsorbent RHB, S-RHB, and C-RHB as shown in Table 1. Surfaces modified with surfactant showed decreased specific surface area and total pore volume while increasing zeta potential value. The specific surface area of the adsorbent RHB decreased from 174.80 to 3.67  $\text{m}^2/\text{g}$  and 105.10  $\text{m}^2/\text{g}$  after modification with SDBS (S-RHB) and CTAB (C-RHB), respectively. This is consistent with the results of Xi et al. (2010) who showed that CTAB decreased the specific surface areas of clay minerals. The total pore volume of 0.176  $\text{cm}^3/\text{g}$  of adsorbent RHB

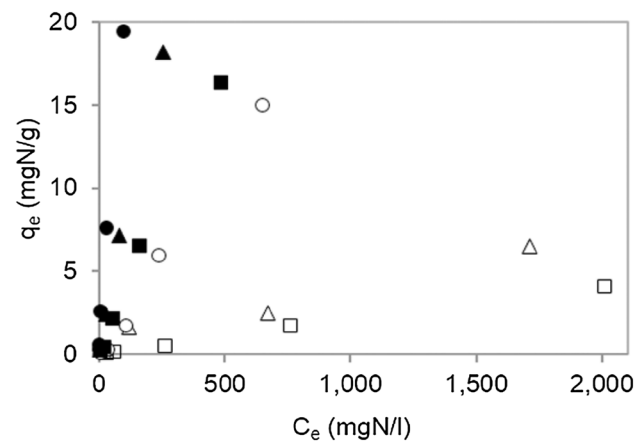


reduced to 0.119 and 0.098 cm<sup>3</sup>/g for adsorbent S-RHB and C-RHB, respectively. These decreases in the specific surface area may result from the pore filling by surfactant (Berthod and Garcia-Alvarez-Coque 2000). The pore diameter also changed: the average pore diameter of the S-RHB was greater than of RHB while the average pore size of C-RHB was slightly decreased as compared to RHB. The zeta potential indicating surface charge also increased after modified with surfactants. These changes indicated that CTAB and SDBS surfactant clogged the small pore on the surface of RHB and creating a new surface.

Analysis of the surface of RH as compared to S-RH and C-RH, found that surfactant broadened the average pore diameter from 15.5 Å to values of 85.0 Å and 938.1 Å, respectively (Table 1). A surfactant could either increase or decrease the surface area of rice husk; the specific surface area of S-RH rose from 7.02 m<sup>2</sup>/g of RH to 28.71 m<sup>2</sup>/g while the specific surface area of C-RH was 2.78 m<sup>2</sup>/g. These results are consistent with those of Wang et al. (2004) who studied the effect of absorbing surfactants, tetramethylammonium chloride and hexadecyltrimethylammonium bromide, on the pore structure of Ca-montmorillonite. They reported that the cationic surfactant could make the surface area, pore volume, pore size and surface fractal dimension *D* of the adsorbent greater or lesser depending on the size, the molecular arrangement, and degree of hydration of the exchanged ion in the clay. The zeta potential values of S-RH and C-RH were decreased and increased as compared to RH, respectively. These confirmed that surfactants could modify the surface charge of material.

## Adsorption of ammonium

Data of ammonium adsorption on rice husk, rice husk biochar and their modification with SDBS and CTAB surfactants (Fig. 2) could be fitted well with Freundlich and Langmuir isotherm (Table 2). This is in general agreement with many studies using wood and rice husk biochar (Kizito et al. 2015), giant reed biochar (Hou et al. 2016), wheat



**Fig. 2** Adsorption of ammonium 30–3000 mgN/l onto RH (open circle), RHB (filled circle), C-RH (open square), C-RHB (filled square), S-RH (open triangle), and S-RHB (filled triangle) at 25 ± 1 °C, initial pH of 7.0 ± 0.5

straw (Ma et al. 2011), barbecue bamboo charcoal (Zhou et al. 2015), acid-treated zeolite (Dong and Lin 2016), and acid-treated bentonite (Angar et al. 2017) as adsorbents.

The  $K_L$  values indicated that RHB was more efficient than RH and the modification with SDBS was more efficient than CTAB, indicating that the surface charge may also play role in the adsorption of ammonium. This is in contrast to the results of Song et al. (2014) who showed that the sediment modified with CTAB had better adsorption of ammonia–nitrogen, nitrate–nitrogen, and phosphorus in seawater as compared to SDS and TX-100. These may due to the effect of salt in seawater. However, RHB is better than S-RHB in terms of both capacity ( $q_m$ ) and efficiency ( $K_f$ ) as the specific surface area of RHB was higher than of S-RHB and zeta potential values of RHB were more negative than S-RHB. The adsorption capacity ( $q_m$ ) showed the following behavior: RHB > S-RHB ~ S-RH ~ RH > C-RH B > C-RH which follows the increase of surface area and the decrease of zeta potential values. This confirms that the surface charge and area affect the adsorption of ammonium.

**Table 2** Adsorption isotherm of ammonium 30–3000 mgN/l onto rice husk, rice husk biochar, and their modification with CTAB and SDBS surfactant at 25 ± 1 °C, initial pH of 7.0 ± 0.5

Isotherm	Parameter	RH	S-RH	C-RH	RHB	S-RHB	C-RHB
Langmuir	$q_m$	13.95	14.49	4.43	44.05	14.73	9.30
	$K_L$	0.0008	0.0009	0.0004	0.0046	0.0051	0.0029
	$R^2$	0.935	0.979	0.979	0.980	0.970	0.926
Freundlich	$n$	0.80	1.46	0.95	0.97	0.97	0.90
	$K_f$	0.0048	0.0387	0.0014	0.2031	0.0673	0.0186
	$R^2$	0.979	0.952	0.996	0.987	0.988	0.972
Dubinin–Radushkevich	$K_{ad}$	0.0255	0.0195	0.0497	0.0030	0.0063	0.0139
	$q_s$	5.81	3.47	1.70	9.07	7.45	6.38
	$E$	4.43	5.06	3.17	12.91	8.91	6.00
	$R^2$	0.751	0.912	0.809	0.835	0.785	0.741



**Table 3** Comparison of surface modification technique on increasing adsorption capacity of ammonium

Modification technique	Adsorbent	$q_m$ (mgN/g)	Ratio of increasing capacity ( $q_m/q_m^*$ )	References
Pyrolysis	<i>S. rosthornii</i> Seemen at 500 °C	3.31*	–	Zeng et al. (2013)
	<i>S. rosthornii</i> Seemen at 600 °C	7.43	2.24	
	<i>S. rosthornii</i> Seemen at 700 °C	6.61	2.00	
	<i>T. dealbata</i> at 500 °C	7.49*	–	
	<i>T. dealbata</i> at 600 °C	11.20	1.50	
	<i>T. dealbata</i> at 700 °C	17.60	2.35	
	<i>V. zizanioides</i> at 500 °C	1.87*	–	
	<i>V. zizanioides</i> at 600 °C	3.12	1.67	
	<i>V. zizanioides</i> at 700 °C	4.36	2.33	
	<i>Phragmites</i> sp. at 500 °C	2.21*	–	
	<i>Phragmites</i> sp. at 600 °C	2.43	1.10	
	<i>Phragmites</i> sp. at 700 °C	5.43	2.46	
	Wheat straw at 400 °C	7.33*	–	Gai et al. (2014)
	Wheat straw at 500 °C	4.68	0.64	
	Wheat straw at 600 °C	3.16	0.43	
	Wheat straw at 700 °C	2.64	0.36	
	Corn straw at 400 °C	15.46*	–	
	Corn straw at 500 °C	12.05	0.78	
	Corn straw at 600 °C	8.62	0.56	
	Corn straw at 700 °C	7.17	0.46	
	Peanut-shell at 400 °C	10.52*	–	This study
	Peanut-shell at 500 °C	9.92	0.94	
	Peanut-shell at 600 °C	7.78	0.74	
Peanut-shell at 700 °C	4.01	0.38		
RH	13.95*	–		
RHB at 500 °C	44.05	3.16	Liu et al. (2016)	
NaOH pre-treatment	Peanut shells biochar	200.43*		–
	NaOH treated peanut shells biochar	258.51		1.29
	Corncoobs biochar	179.04*		–
	NaOH treated corncoobs biochar	307.26		1.72
	Cotton stalks biochar	166.76*		–
	NaOH treated cotton stalks biochar	427.33		2.56
	Basanites	0.06*	–	Choi et al. (2014)
10% NaOH treated basanites	3.30	55.00		
20% NaOH treated basanites	5.38	89.67		
40% NaOH treated basanites	3.48	58.00		
Sodium acetate-microwave	Natural zeolite	4.79*	–	Dong and Lin (2016)
	Sodium acetate and microwave treated zeolite	6.56	1.37	
Carboxylic acid modification	Activated carbon	1.75*	–	Halim et al. (2013)
	Carboxylic acid modified activated carbon	7.52	4.30	
Acid treatment	Wheat straw biochar	0.33*	–	Gai et al. (2014)
	H <sub>2</sub> SO <sub>4</sub> washed wheat straw biochar	0.27	0.82	
	Corn straw biochar	0.92*	–	
	H <sub>2</sub> SO <sub>4</sub> washed corn straw biochar	0.45	0.49	
	Peanut-shell biochar	0.54*	–	
	H <sub>2</sub> SO <sub>4</sub> washed peanut-shell biochar	0.43	0.80	

**Table 3** (continued)

Modification technique	Adsorbent	$q_m$ (mgN/g)	Ratio of increasing capacity ( $q_m/q_m^*$ )	References
Surfactant modification	RH	13.95*	–	This study
	S-RH	14.49	1.04	
	C-RH	4.43	0.32	
	RHB	44.05*	–	
	S-RHB	14.73	0.33	
	C-RHB	9.30	0.21	

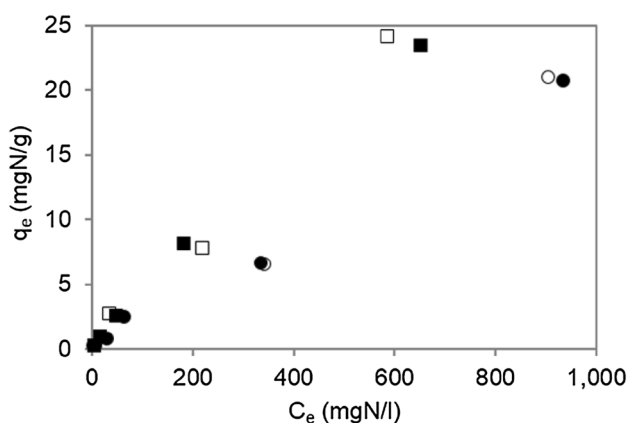
\* is unmodified material

The thermodynamics indicate the adsorption mechanism. If the value of  $E = 8\text{--}16$  kJ/mol then the adsorption process flows by chemical ion-exchange, and if  $E < 8$  kJ/mol the adsorption process is physical in nature; whereas if the value is more than 16 kJ/mol, the adsorption process is chemisorption in nature (Youssef et al. 2008). The adsorption free energy of ammonium on RHB (12.91 kJ/mol) and S-RHB (8.91 kJ/mol), therefore, indicates an ion exchange, while C-RHB tends to be physical sorption. This result is in agreement with the results of Clough et al. (2013) in their study of ammonium adsorption on biochar, and of Hou et al. (2016) whose results indicate that ion exchange was the main mechanism of ammonium adsorption on giant reed biochar.

Surface modification of rice husk using pyrolysis was a more effective method for increasing ammonium adsorption than using a surfactant modification technique, as the pyrolysis technique results in a greater negative charge value and surface area while the surfactant decreases surface area.

Comparing the adsorption capacity of RHB (44.05 mgN/g), the best ammonium adsorbent, with other studies, showed a lower result than that of Kizito et al. (2015) who examined the use of rice husk biochar to adsorb

ammonium at 1400 mgN/l ( $q_m$ , 71.9 mgN/g). However, the results were in the range of other biochar studies (Table 3). There have been only limited studies on both unmodified and modified adsorbent. However, they are very useful for considering feasible modification techniques to increase the ammonium adsorption of an adsorbent. It has been shown that modifying the surface by pyrolysis could increase adsorption capacity of adsorbent material up to a maximum of 3 times; NaOH pre-treatment could increase adsorption by 55–90 times for mineral material, however, only around 2 times for biomass adsorbent; sodium acetate pre-treatment followed by microwave barely increases adsorption capacity (by 1.4 times); carboxylic acid modification leads to a small increase by 4 times, while  $\text{H}_2\text{SO}_4$  acid treatment could decrease  $q_m$  value; and surfactant modification, as shown in this study, especially cationic could also decrease the ammonium adsorption capacity through decreasing the specific surface area. These show that pyrolysis gives comparable ammonium adsorption efficiency with a greater cost-effectiveness.



**Fig. 3** Adsorption of nitrate 30–3000 mgN/l onto RH (open circle), RHB (filled circle), C-RH (open square), and C-RHB (filled square) at  $25 \pm 1$  °C, initial pH of  $7.0 \pm 0.5$

**Table 4** Adsorption isotherm of nitrate 30–3000 mgN/l onto rice husk, rice husk biochar, and their modification with CTAB surfactant at  $25 \pm 1$  °C, initial pH of  $7.0 \pm 0.5$

Isotherm	Parameter	RH	C-RH	RHB	C-RHB
Langmuir	$q_m$	5.68	277.78	22.12	212.77
	$K_L$	0.0111	0.0002	0.0014	0.0003
	$R^2$	0.989	0.998	0.996	1.000
Freundlich	$n$	1.25	1.10	1.09	1.10
	$K_f$	0.079	0.073	0.038	0.070
	$R^2$	0.987	0.985	0.987	0.998
Dubinin–Radushkevich	$K_{ad}$	0.0060	0.0071	0.0109	0.0071
	$q_s$	5.58	7.48	6.12	7.45
	$E$	9.13	8.39	6.77	8.39
	$R^2$	0.689	0.760	0.736	0.769



**Table 5** Comparison of surface modification technique on increasing adsorption capacity of nitrate

Modification technique	Adsorbent	$q_m$ (mgN/g)	Ratio of increasing capacity ( $q_m/q_m^*$ )	References
Acid treatment	Red mud	26.03*	–	Cengeloglu et al. (2006)
	HCl-treated red mud	82.01	3.15	
	Wheat straw biochar	0.021*	–	Gai et al. (2014)
	H <sub>2</sub> SO <sub>4</sub> washed wheat straw biochar	0.037	1.76	
	Corn straw biochar	0.032*	–	
	H <sub>2</sub> SO <sub>4</sub> washed corn straw biochar	0.058	1.81	
	Peanut-shell biochar	0.024*	–	
	H <sub>2</sub> SO <sub>4</sub> washed peanut-shell biochar	0.042	1.75	
Acid thermoactivation	Palm kernel shell	13.58*	–	Adebayo et al. (2016)
	Acid thermoactivation pulverized palm kernel shell	19.36	1.43	
Surfactant modification	Clinoptilolite-rich zeolite	42,000.00*	–	Guan et al. (2010)
	CTAB modified clinoptilolite-rich zeolite	336,000.00	8.00	Aroke et al. (2014)
	Kaolin-clay	0.0002*	–	
	Bilayer CTAB modified Kaolin-clay	0.0278	123.00	
	Monolayer CTAB modified Kaolin-clay	0.0061	27.00	Ozcan et al. (2005)
	Natural sepiolite	– 10.60*	–	
	Dodecylethyltrimethylammonium modified sepiolite	32.90	~ 33.00	
	RH	5.68*	–	
	C-RH	277.78	48.90	
	RHB	22.12*	–	
C-RHB	212.77	9.62		
Impregnation	Lignite granular activated carbon	2.03*	–	Khan et al. (2011)
	ZnCl <sub>2</sub> impregnated lignite granular activated carbon	2.30	1.14	
Cross link with epichlorohydrin	Chitosan	12.71*	–	Jozwiak et al. (2014)
	Glutaraldehyde cross-linked chitosan	34.99	2.75	
	Epichlorohydrin cross-linked chitosan	38.47	3.03	
	Wheat residue	0.28*	–	Wang et al. (2007)
	Epichlorohydrin cross-linked wheat residue	29.12	104.00	
	Chitosan beads	20.48*	–	Chatterjee et al. (2009)
	Epichlorohydrin cross-linked chitosan beads	23.28	1.14	

\* is unmodified material

## Adsorption of nitrate

As the surface charge did not affect the adsorption of the positively charged ammonium ion, only a positively charged surfactant, CTAB, was applied in the adsorption experiment of the negatively charged nitrate. As indicated, data of nitrate adsorption on rice husk, rice husk biochar and their modification with CTAB surfactant (Fig. 3) could be fitted well with Freundlich and Langmuir isotherms (Table 4). The  $K_f$  values indicated that RH was more efficient than RHB. This was similar to the results of Gai et al. (2014) that ammonium was greater adsorbed on biochar than nitrate. As the  $q_m$  values were C-RH ~ C-RHB > RHB ~ RH, this indicated

that the modification with CTAB could increase the adsorption capacity for both raw rice husk and rice husk biochar. This result agrees with the results of Aroke et al. (2014) and Baker (2016) which showed that CTAB modified clay and zeolite could increase the adsorption capacity of nitrate, indicating also that the surface charge may play a major role in the adsorption of nitrate. The adsorption of nitrate on RHB is similar to RH; hence, surface area does not play a major role in nitrate adsorption unlike that of the adsorption of ammonia. Increasing the positive charge of the surface by using a positive charge surfactant could attract the negatively charged nitrate ion through electrostatic interaction. This is similar to the results of Xi et al. (2010) who showed

that nitrate can be electrostatically attracted by a cationic surfactant modified organo-clay and surface area was not a key factor controlling adsorption.

Comparison of the  $\text{NO}_3\text{-N}$  adsorption capacity of adsorbent in this study with other studies (Table 5) showed that RH is similar to the unmodified palm kernel shell (Adebayo et al. 2016), while the result of RHB is better than the wheat straw biochar, corn straw biochar and peanut-shell biochar (Gai et al. 2014). The modification of rice husk and rice husk biochar with CTAB could increase adsorption capacity by 10–49 times which is in the range of other surfactant modification studies (8–123 times). In addition, the adsorption capacity of C-RH (277.78 mgN/g) and of C-RHB (212.77 mgN/g) were higher than the commercial resin Duolite A 171 (123.63 mg/g or 27.92 mgN/g) (Sowmya and Meenakshi 2013). Surface modification using a surfactant shows the best increase in adsorption capacity compared with other modification techniques. This demonstrates an advantage of using household chemicals with simple modification technique.

## Conclusions

A surfactant modification technique was not suitable for ammonium adsorption because the surfactant can clog the pores thereby lowering the specific surface area. Pyrolysis, however, was a more suitable technique to increase ammonium adsorption on rice husk by providing a more specific surface area and a more negatively charged surface. Pyrolysis also gave a satisfactory increase in ammonium adsorption capacity in biomass adsorbent with greater cost effectiveness as compared to other reviewed techniques: NaOH pretreatment, carboxylic acid modification, acid treatment. A cationic surfactant modification technique was suitable for nitrate adsorption because rice husk and rice husk biochar have neutral to negative charge; hence increasing the surface charge by a positive charge surfactant enhances nitrate attraction. In addition, surfactant modification seems to give the highest efficiency in improving nitrate adsorption capacity as compared to other reviewed techniques: acid treatment, acid with thermoactivation, surfactant modification, and cross-linking with epichlorohydrin. This study shows the alternative way of using rice husk to adsorb ammonium and nitrate with low cost which is advantage for wide practical application in the agricultural and industrial sectors. The further study on the desorption and plant uptake is interesting to examine in order to apply as nitrogen rich fertilizer and fertilizer retention.

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## Compliance with ethical standards

**Conflict of interest** The authors have no conflict of interest.

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