Adsorption of 2-Acetyl Pyrroline Using Treated Rice Husk Char

Carla Goncalves De Oliveira Sarmento, Chi Huey Ng, Awang Bono, Duduku Krishnaiah, S M Anisuzzaman, Jidon Janaun#

Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.
#Corresponding author. E-Mail: jidon@ums.edu.my; Tel: +6088-320000; Fax: +6088-435324

ABSTRACT 2-Acetyl-1-Pyrroline (2-AP) is a main aromatic compound that gives fragrant characteristics in rice. However, 2-AP is a volatile compound that would be escaped easily with moisture from the rice during the drying operation and resulted in poorer rice quality. Therefore, the search of a material that is capable in adsorbing 2-AP and maintaining the rice quality is crucial. In this paper, two adsorbents, which are the untreated rice husk char (URHC) and treated rice husk char (TRHC) on their adsorption of 2-AP were investigated. TRHC was chosen as the adsorbent for further adsorption studies due to its high surface area and high adsorption capacity. The removal efficiency was determined at 60 min, in which 93% of 2-AP was removed by TRHC with an adsorption capacity of 625 mg/g. The adsorption isotherm was well-fitted with Freundlich model as compared to Langmuir model with correlation coefficient value of R^2 0.9952, suggesting multilayer adsorption. From the conducted adsorption kinetics study, the adsorption fitted into pseudo-second order model as compared to pseudo-first order with a R^2 value of 0.9720, indicative the occurrence of chemisorption in the adsorption process. The result demonstrated that TRHC is a promising adsorbent for the adsorption of 2-AP due to its high adsorption capacity, high removal efficiency, low cost, and environmentally friendly nature.

KEYWORDS: Adsorption; aromatic rice of 2-Acetyl -1- Pyrroline; untreated rice hush char; treated rice husk char; paddy
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INTRODUCTION

Rice is a staple food in Asia, as it provides energy and supplies essential carbohydrates to the body. As the human population increase, the demand for high-quality rice increases as well. This has thus prompted for numerous advancements in upstream and downstream processes to increase the yield of paddy production, at the same time, to improve the quality of rice. Among the important rice qualities, its aroma, which is equivalent to the sensory quality possesses direct affects toward the selling price of rice since the aromatic rice is more expensive than its non-aromatic counterpart. The compound that is responsible for the pleasant aroma in rice is 2 acetyl-pyrroline (2-AP), with the chemical formula of C_6H_9NO (Hien *et al*., 2006) with a molecular weight of 111.144 g/mol and density of 1090 kgm^{-3}. The IUPAC scientific name of 2-AP is 1- (3, 4-dihydro-2H-pyrrol-5-yl) ethenone (Yoshihashi *et al*., 2005).

The characteristic that gives fragrance to rice is the 2-AP compound where it is one of the main components of rice with typical characteristics of nutty, roasty, and popcorn scents (Routray & Rayaguru, 2018). Due to the distinctive aroma of rice, this type of rice is highly popular worldwide such as in the European countries, the United States, Middle East, and Australia with high demand and continue to command a higher price as compared to ordinary non-aromatic rice, both in the local and international markets. It was found that aromatic rice with 2-AP consisted of several different compounds such as butanol, 3-methyl butanol, pentanol, hexanol, acetaldehyde, propanal, etc (Widjaja *et al*., 1996). The aroma of 2-AP in aromatic rice was found to be fifteen times stronger in basmati rice with the value of 610 ppb, which is far higher than the non-aromatic rice with lower 6 ppb value (Buttery *et al*., 1986). Moreover, it has been discovered that the essential flavor of the aroma of 2-AP was distinguished during the cooking of the rice especially for basmati rice (Buttery *et al*., 1983). Generally, 2-AP is the main volatile aroma backbone compound that can be found in

pandan leaves where the amount of aroma in pandan leaves was found to be 10 times greater than that of the non-aromatic rice (2 -AP aroma is only 1/100 or 10%) (Yahya *et al*., 2011). Therefore, adding fresh pandan leaves improves the flavor and scent of the non-aromatic rice during cooking with the concentration of 2-AP ranging in 0.04–0.06 ppm (Buttery *et al*., 1986). 2-AP is a highly volatile compound and it easily escapes with moisture during the paddy drying operation and storage. The rapid aroma evaporation is highly disadvantaging the sensory quality of the rice (Baradi & Elepano, 2012). Hence, it is essential to overcome the problem and retain the 2-AP component in the rice.

This study aimed to compare the characteristics of agricultural waste, denoted as URHC and TRHC, in addition to evaluate the adsorption of aromatic compound 2-AP on URHC and TRHC. The adsorbents were characterized using BET, SEM, EDX, and FTIR. The adsorption of 2-AP onto the adsorbents was evaluated by investigating the effects of the initial concentration of 2-AP and the contact time toward the adsorption capacity of the adsorbents. Lastly, the adsorbent with desirable characteristics and adsorption capability was chosen for the adsorption isotherm study using Langmuir and Freundlich models, as well as kinetic study using pseudo-first order and pseudo second order kinetic models.

MATERIALS AND METHODS

Material

2-AP solution with 99% concentration was purchased from Sigma Aldrich. 2-AP with calculated weight was dissolved with 0.1 L stock solution of ethanol at desired concentrations of 100-500 mg/L. It was kept in a dry cabinet to prevent any contamination until the further experiment. The samples of raw rice husk (RRH) were collected from a local rice mill.

Preparation of Adsorbents

Raw rice husk (RRH) was initially washed with deionized water. It was dried in an oven at the temperature of 105°C for 24 h (Abang *et al*., 2016) and sieved using a 1.0 mm aperture mesh. For the TRHC, the RRH was mixed homogeneously with NaOH with the weight ratio of 1:3 and dried for 12 hours at the temperature of 120°C (Le Van & Thi, 2014). The carbonization and activation process were accomplished in a single step by carrying out the thermal decomposition of the rice husk soaked with NaOH acting as an activating agent by using a microwave operating at the power of 600 Watts for 35 minutes and was purged with purified nitrogen with the concentration of 99.95% at a flow rate of 100 ml/min. After the activation process, the adsorbent was left to be cooled to room temperature. The pyrolyzed carbon was leached with 1% HCl (v/v) for two to three hours and washed a few times with distilled water until its pH reached the value of 7. While for URHC, only the carbonization process was conducted without any treatment with NaOH. All chemicals used were of analytical grade.

Batch Adsorption

Batch adsorption study of 2-AP with the adsorbent was done by mixing well 1 g of either TRHC and URHC with 100 mL of 2-AP solution in a 250 mL volumetric flask. To optimize adsorption equilibrium, experiments were carried out by varying the initial concentrations of 2-AP between 100 to 500 mg/L, whilst keeping other parameters constant such as adsorbent dosage of 1g (Bhowmick & Science, 2015), pH of solution maintained at pH7, the temperature of 25°C and by shaking the composing sample(s) at a fixed rate, 120 rpm, which suggests for better mass transfer area for contact adsorption process (Kumar *et al*., 2010). Finally, 2-AP removal efficiency and equilibrium

capacity of the adsorption can be calculated using Equation (1) and Equation (2), respectively as shown below:

$$Removal\ efficiency\ (\%) = \frac{(Co-Ce)}{Co}.100 \quad (1)$$

$$qe = \frac{(Co-Ce)}{m}.V \quad (2)$$

where Co and Ce are the initial and final concentrations for the solution of 2-AP (mg/L), q_e is the equilibrium capacity of 2-AP (mg/g), V is the volume of solution and m is the adsorbent dosage (g).

Characterization

The specific surface area and pore volume were measured using the Brunauer-Emmett-Teller (BET) method, based on the nitrogen adsorption on the sample surface. The assays were conducted at -196.15°C in a surface area analyzer, ASAP 2020, Micromeritics. The characterization of functional groups was done using Fourier Transform Infra-red (INVENIO-R + FM FTIR Spectrometer) to analyze the sample within the wavelength range of 400-4000cm^{-1}. The morphology analyzer, Electron Scanning Microscopy (SEM) S-3400N Hitachi and elemental analysis (EDX) instrument were used for adsorption process analysis, and the samples were coated with a thin layer of the metallic gold plate under vacuum condition.

RESULTS AND DISCUSSION

Characterizations

Both adsorbents of the TRHC and URHC show a huge amount of nitrogen. It was adsorbed by TRHC owing to its high surface area (210 m^2/g), pore diameter (22.19 nm), and pore volume (0.122 cm^3/g). Meanwhile, the smaller surface area (8.020 m^2/g), pore diameter (20.6 nm), and pore volume (0.015 cm^3/g) properties of URHC demonstrated a lower nitrogen adsorption rate. The superiority of TRHC against the URHC could be attributed to the activation process using NaOH, which is expected to have facilitated the development of mesoporosity of TRHC where the pore volume of TRHC increased, in accompanied with the formation of mesoporous with an average pore size of 2 μm to 8 μm (Chuah *et al.*, 2005).

In addition, stark morphologies differences were observed from URHC and TRHC. The chemical impregnation of NaOH: RRH was in the ratio of 3g: 1g into the mesoporous and microporous layers of activated carbon of the testing sample resulted in the morphology of URHC and TRHC showing nearly similar features but after natural process analysis, it was found that these surfaces were irregular due to its very porous characteristic. The morphology of the sample TRHC was shown to be very porous as compared to URHC due to untreated small cells and lower sorption process (Liou & Wu, 2009) from the cross-linking between the NaOH and its chemical reaction with a hydroxyl group.

The elemental composition of URHC and TRHC surfaces was determined by EDX analysis. According to (Hayes *et al.*, 2019) organic elements that are mostly found in adsorbents of rice husk char are C, O, H and N. However, for the sample of TRHC, a new element, which is the sodium (Na) was detected due to the alkali treatment process. Table 1 shows the results obtained from EDX analysis for URHC and TRHC where the composition unit is in wt.%.

Table 1. Elemental compositions of TRHC and URHC using EDX.

Sample	Elemental content (wt.%)			
	C	Na	O	Si
URHC	82.3	-	3.52	1.27
TRHC	61.6	3.55	11.0	3.56

Table 2 shows the functional groups of URHC and TRHC obtained from FTIR from the wavelengths of 400-4000cm^{-1}. Functional groups of aromatic, carboxylic group, and silica group were found in the sample of URHC before and after adsorption. Whilst, for the TRHC sample, all peaks found in URHC are being detected, except for the silica group owing to the NaOH treatment. It was discovered that only aromatic and carboxylic groups were presented before the adsorption on TRHC. However, after the adsorption of 2-AP on the TRHC, hydroxyl group was detected, which might be due to the activation process with NaOH that has facilitated the adsorption of 2-AP. Furthermore, methyl groups were also detected in TRHC sample after the adsorption of 2-AP, which could be ascribed to the presence of methyl group on 2-AP. The enhancement of TRHC could be credited to the NaOH treatment where it removed the natural fats and waxes from the cellulose fiber surfaces, thus gave rise to a rougher fibers surface and the revealing of chemically reactive functional groups such as –OH and other reactive functional groups for the adsorption of 2-AP (Ndazi *et al.*, 2007).

Table 2. Functional groups of TRHC and URHC.

Sample	Functional group					
	O-H	C-H	C-C	Methyl C-H	Si-O-Si	Si-O
URHC	-	2325	1591	-	1064	788-447
TRHC	3392	1986	1554	1360	1040	-

Equilibrium Adsorption Isotherms

The equilibrium adsorption experiment was conducted at different initial concentrations ranging from 100-500 mg/L of 2-AP for TRHC and URHC at the temperature of 25°C. For the equilibrium adsorption experiments, it was found that adsorption rate of TRHC increased rapidly and the optimal removal efficiency achieved up to 93% within 60 min with an adsorption capacity of 625 mg/g. Whereas, the removal efficiency and adsorption capacity of URHC were significantly lesser, 72% and 238 mg/g, respectively. From the results of the study, it was discovered that the amount of adsorbed 2-AP increases with time, as well as an increased in initial concentration of 2-AP due to the filling up of vacant binding sites (Kumar *et al.*, 2010). From the results of this equilibrium adsorption study, TRHC was selected for further adsorption isotherm and kinetics studies due to its high removal efficiency and adsorption capacity as compared to URHC.

The adsorption isotherms were determined using the two most popular adsorption models, which are the Langmuir and Freundlich, as shown in Equation (3), Equation (4), and Equation (5).

$$\frac{1}{qe} = \frac{1}{Qmax} + \frac{1}{b.Qmax} \cdot \frac{1}{Ce} \quad (3)$$

$$\log q_e = \log K_F + (1/n)\log C_e \quad (4)$$

$$R_L = \frac{1}{1+K_L.Co} \quad (5)$$

where C_o and C_e are the initial and final concentration of 2-AP (mg/L), q_e is the amount of 2-AP adsorbed per unit mass of adsorbent (mg/g), Q_{max}, b and K_L= are the Langmuir constant associated with the rate of maximum adsorption capacity (L/mg), RL= dimensionless constant or known as separation factor, K_F is constants of adsorption capacity and n= adsorption intensity, respectively.

The details of the experimental results were explicated in Table 3. These models were used to differentiate the monolayer and multilayer adsorption of the TRHC surface at a constant temperature. Results showed that the isotherm model was fitted well with the Freundlich model; with a higher value of R^2, 0.9952, implies an effective adsorption capability of multilayer adsorbents on the heterogeneous surface.

Table 3. Isotherm parameters for the two models, Langmuir and Freundlich.

Isotherm model	Langmuir				Freundlich			
Parameter	Qm(mg/g)	b	RL	R^2	KF	n	1/n	R^2
	625	0.001	0.557	0.9925	1.027	0.939	1.064	0.9952

Adsorption Kinetics

The adsorption mechanism reaction rate of the adsorbate uptake was calculated by selecting different types of kinetic models such as the pseudo-first order and pseudo-second order models which are expressed in Equation (6) and Equation (7), respectively.

$$\log [qe - qt] = \log qe - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e} \quad (7)$$

q_e is the amount of adsorbed adsorbate (mg/g) at equilibrium, q_t is the amount of adsorbed (mg/g); t is the time (min); k_1 is the first-order rate constant (min), k_2 is the second-order rate constant (min), respectively. To calculate the slope and intercept for pseudo-first order, slope =k_1/2.303, intercept=log q_e and for the pseudo second order, slope =1/q_e and intercept= 1/ $k_2 q_e^2$.

Experimental data of various initial concentrations (100-500 mg/L) of the 2-AP solution obtained were elucidated in the adsorption kinetic studies. Kinetic models were used to investigate the adsorption mechanism including estimation of the kinetic parameters, as shown in Table 4. These results showed that pseudo-second order could best describe for the adsorption of 2-AP towards TRHC, suggesting the occurrence of chemisorption during the adsorption process (Kumar *et al.*, 2010).

Table 4. First order and second order kinetics isotherm data for TRHC.

Kinetic Isotherm	First order			Second order		
Parameter	K_1(l/h)	Q_e(mg/g)	R^2	K_2(l/h)	Q_e(mg/g)	R^2
	0.050	0.102	0.8474	19.95	47.39	0.9720

CONCLUSION

The activation process of rice husk produced treated rice husk char with high surface area, 210 m^2/g, pore-volume, 0.047 cm^3/g, and pore radius of 3.364 nm. The treated rice husk char showed high adsorption towards 2-AP. For the adsorption isotherm study, it was found that the adsorption of 2-AP onto the TRHC was fitting well to the Freundlich model, implies a multilayer adsorption. While the adsorption kinetics was best fitted with Pseudo-second order, suggests the occurrence of chemisorption during the adsorption process. In summary, treated rice husk char is proved to be a good adsorbent towards the adsorption of 2-AP.

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