



Equilibrium, Kinetics, and Thermodynamic Studies Concerning the Removal of 2-chlorophenol Using Chemically Carbonized Rice Husk Waste

Duangdao Channei^{1*}, Auppatham Nakaruk², Wilawan Khanitchaidecha³

Panatda Jannoey⁴ and Sukon Phanichphant⁵

¹Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand

²Department of Industrial Engineering, Faculty of Engineering, Naresuan University, Phitsanulok 65000, Thailand

³Department of Civil Engineering, Faculty of Engineering, Naresuan University, Phitsanulok 65000, Thailand

⁴Department of Biochemistry, Faculty of Medical Science, Naresuan University, Phitsanulok 65000, Thailand

⁵Center of excellence in Materials Science and Technology, Chiang Mai University, Chiang Mai 50200, Thailand

* Corresponding author. E-mail address: duangdaoc@nu.ac.th

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Abstract

In this work, the adsorption of a harmful pollutant, 2-chlorophenol, from aqueous solution onto carbonized rice husk (C-RH) was investigated. Highly-porous adsorbent C-RH was produced in this study using chemical activation with hydrochloric acid, followed by carbonization at 550 °C. The surface morphology of C-RH by scanning electron microscope (SEM) and BET N₂ adsorption/desorption techniques showed that the results of C-RH characterization had a pore volume of 0.042 cm³/g and BET surface area of 278.90 m²/g due to the resulting silicon element contained in rice husk ash. Pore size distribution having a clear hysteresis loop belongs to type IV isotherm nature with H3-type of hysteresis loop, which is distributed by pores mainly in the mesoporous range. The batch adsorption experiments showed that the equilibrium uptake was increased with an increase in initial 2-chlorophenol concentration. The experimental isotherm data fit better with the Freundlich isotherm model, which followed an ideal multilayer adsorption with the maximum monolayer adsorption capacity (N_m) of 13.4048 mg/g obtained by Langmuir. Kinetic data was best fit to a pseudo-second order rate equation, indicating chemisorption. Thermodynamic parameter in terms of ΔG° for the adsorption showed that adsorption on the surface of C-RH at 304.15 K was spontaneous in nature. Consequently, C-RH produced from rice husk waste has the potential to serve as an alternative to commercial activated carbon for water treatment.

Keywords: Mesopore, Rice husk, Freundlich model, Adsorption, 2-chlorophenol

Introduction

Nowadays, water pollution caused by the remains of pesticide used for agricultural activities is an issue of global concern, especially in Thailand. Most pesticides such as paraquat, phenol, chlorophenols and their derivatives, which are used regularly in Thailand, fall under the US Environmental Protection Agency (EPA). This is due to various kinds of agricultural products that are exported from Thailand (Igbinsosa, Odjadjare, & Chigor, 2013; Abdelwahab & Amin, 2013; Adane, Siraj, Siraj, & Meka, 2015). With their toxicity, the contaminants are introduced as residue in the air, soil, and water, posing long-term health challenges to human organisms as well as the environment. Certain physical and chemical processes have been applied to remove chlorophenol and their derivatives in wastewater, as reported by Mahmiani, Sevim, & Gül, 2016. They showed the photocatalytic degradation of 4-chlorophenol under visible light over TiO₂ photocatalyst functionalized Co(II) or Zn(II)-phthalocyanine with 99% degradation being observed in just 30 minutes. The degradation of 4-chlorophenol under visible light using TiO₂ photocatalyst was also reported by Pirbazari (2016), with almost 50% being degraded within 90 min. Concerning the removal of organic pollutants in wastewater, the adsorption



process onto porous materials like activated carbon has gained increasing attention and interest from many researchers due to its low preparation cost, simple steps for adsorbent preparation, high surface area for adsorption, and ease of operation for the reactors in the adsorption experiment. Generally, the production of activated carbon can be prepared by following two steps: (i) activation by physical or chemical agent (H_3PO_4 , $ZnCl_2$, and KOH), and (ii) carbonization at high temperature (Bedin, Martins, Cazetta, Pezoti, & Almeida, 2016; Shamsuddin, Yusoff, & Sulaiman, 2016).

Instead of the commercial activated carbon available, low-cost porous materials are usually produced from natural and waste materials, including sugarcane bagasse, corn cob, banana peels, and olive stones (Foo, Lee, & Hameed, 2013; Nethaji, Sivasamy, & Mandal, 2013; Fasakin et al., 2018; Yakout & Sharaf El-Deen, 2016).

Lin (2017) revealed the adsorption of 2-chlorophenol by suspended biomass and biofilm-activated carbon, which is approximately 190.5 mg/L and 25.3 mg/L, respectively. The removal of 2-chlorophenol and 2, 4-dichlorophenol from water over the acid-activated bituminous shale was also done by Tütem, Apak, and Ünal (1998).

The objective of this work was to enhance the values of rice husk residues in our area for wastewater treatment applications. In this study, rice straw waste was used as a low-cost adsorbent for the removal of 2-chlorophenol from aqueous solutions. Thailand is an agricultural-based country producing large amounts of rice. As a result, large amounts of agricultural by-products are produced, such as rice husk waste. Such waste could be beneficial for use in wastewater treatment. The potential of the prepared adsorbent was analyzed with different techniques to obtain the surface morphology by scanning electron microscope (SEM), energy dispersive X-ray fluorescence (EDXRF), and Brunauer-Emmett-Teller (BET) theory. The experimental conditions to determine the 2-chlorophenol were reported in terms of equilibrium, kinetics, and thermodynamic studies.

Methods and Materials

Preparation of carbonized adsorbent derived from rice husk (C-RH)

In this study, rice husk (RH) waste was collected from an automatic rice mill plant in Sukhothai Province and Phitsanulok Province, Thailand. Approximately 500 g of RH were washed with tap water to remove any dust particles, after which they were dried at 120°C for 12 h in a hot-air oven to remove water moisture. The dried RH samples were blended into powder form using an electric blender. The sample was then chemically activated by soaking in 500 mL of 3 M HCl solution for 24 h, after which it was filtered and dehydrated in an oven at 120°C for 12 h. The impregnated sample was further treated by carbonization using a furnace at 550°C for 6 h. Subsequently, the carbonized RH adsorbent was grinded and stored in a desiccator for batch adsorption experiments, labeled as C-RH.

Characterization

The C-RH was characterized for morphology and pore structure using the scanning electron microscope (SEM, JSM-6335F, JEOL). Elemental analysis was carried out using the energy dispersive X-ray fluorescence (EDXRF) technique. The surface properties, including surface area, pore volume, and pore diameter, were characterized by N_2 adsorption-desorption isotherm based on Brunauer-Emmett-Teller theory (BET, TriStar II 3020).

**Batch adsorption experiment**

About 0.2 g (W) of C–RH was weighed and placed into a 100 mL (V) beaker filled with 20, 40, 60, 80, and 100 mg/L (ppm) of 2–chlorophenol aqueous solution (C_i). The suspensions were mixed thoroughly using a laboratory shaker. After that, 5 mL of suspension was withdrawn at different time intervals of 15, 30, 45, 60, 75, 90, 105, and 120 min and centrifuged to separate C–RH solid from the mixture. The collected supernatant liquid was measured using a double beam UV/ VIS Spectrophotometer (Shanghai mapada Instruments) at a reference wavelength of 273 nm. All the experiments were carried out twice and the average value was used for calculation. The gradual decrease in absorbance intensity at different time intervals was calculated as well as the remaining concentration of 2–chlorophenol (C_t) after the batch adsorption experiment by a standard calibration curve. Quantitative analysis of adsorption capacity (Q_t , mg/g) of C–RH and adsorption efficiency (%) was carried out using the following formulas (Aljeboree, Alshirifi, & Alkaim, 2017):

$$Q_t = \frac{(C_i - C_t) V}{W}$$

$$\text{Adsorption efficiency (\%)} = \frac{C_i - C_t}{C_i} \times 100$$

The absorptive capacity of C–RH at equilibrium (Q_e , mg/g) and the equilibrium concentration of 2–chlorophenol (C_e , mg/L) adsorbed were achieved at each equilibrium time point, obtained from the graph plotting between Q_t (mg/g) or C_t (mg/L) vs. time (t, min).

Modeling of adsorption by Langmuir and Freundlich isotherms

The adsorption data was further analyzed by fitting to the Langmuir and Freundlich models to find out how the numbers of layers of adsorbate molecule are formed on the adsorbent's surface. Linearized Langmuir and Freundlich equations are presented below, respectively (Langmuir, 1918; Freundlich & Heller, 1939).

$$\frac{C_e}{Q_e} = \frac{1}{K_L N_m} + \frac{C_e}{N_m}$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

where,

N_m = the highest monolayer formation of C–RH in adsorbing 2–chlorophenol (mg/g)

K_L and K_F = Langmuir and Freundlich equilibrium binding constants (L/mg), respectively

$1/n$ = Freundlich exponent related to the intensity of adsorption; when $1/n < 0.5$ means only a monolayer is formed, whereas $1/n > 0.5$, the adsorption is favorable for multilayer adsorption

Adsorption kinetic studies

In order to identify how quickly the reaction is occurring, the reaction rate constants (k , min^{-1}) have been compared and evaluated from the linearized pseudo–second–order plots as follows (Ho, McKay, Wase, & Foster, 2000; Kumar et al., 2011):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Moreover, the value of the linear correlation coefficient (R^2) also outlined how the chemisorption of physisorption is formed, as explained in the report by Nsami & Mbadcam, 2013.



Thermodynamic analysis (Njoku, Islam, Asif, & Hameed, 2014)

In this study, the thermodynamic parameter in terms of Gibbs free energy (ΔG°) can be calculated using the following equation to understand whether the spontaneous adsorption is favorable or unfavorable in a room-temperature experiment (304.15 K).

$$\Delta G^\circ = RT \ln K_L$$

Results and Discussion

Surface morphology of C-RH adsorbent

The SEM images in **Figure 1** represent the surface morphology, pore sizes, and porosity of C-RH. It was found that the external surfaces of the C-RH showed pores with different sizes ranging from 2 to 4 nm, related to mesopore size. The pore production on the surfaces of C-RH resulted from the evaporation of chemically activated HCl during carbonization at 550^o C, providing an area that was previously occupied by the activating agent. Due to well-established pores, the C-RH possessed a high BET surface area of roughly 278.90 m²/g with the pore volume of 0.042 cm³/g.

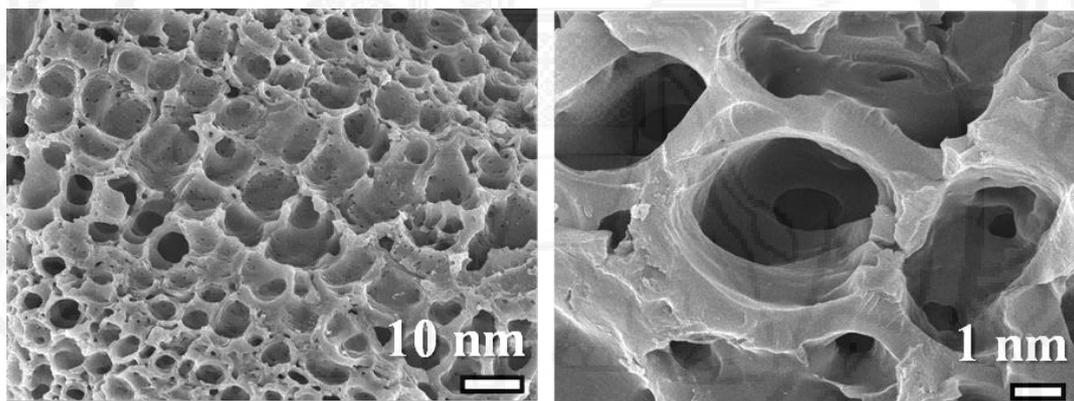


Figure 1 Scanning electron micrographs of C-RH with different magnifications

For more information on pore structure, the hysteresis loop of nitrogen adsorption/desorption isotherms was analyzed in a relatively wide pressure range (0.0–1.0). According to the IUPAC classification, different shapes of hysteresis loop were associated with a sign of porosity that have different types of pore structure (Othman, 2012). **Figure 2** shows that C-RH adsorbent having a clear hysteresis loop belongs to type IV isotherm nature with H3-type of hysteresis loop, which is indicative of the mainly slit-shaped mesopore structure, related to the reports by Qi, Tang, Wang, and Peng (2017). The inset of **Figure 2** shows the pore size distribution of the C-RH sample. The results revealed that pores with an average size of ~3.5 nm comprise the major distributor of C-RH, which is consistent with the pore size approximated by SEM images.

From the surface properties in the present work, it is confirmed that C-RH is useful for adsorption applications due to possessing high surface area, large pore volume, and suitable pore diameter for 2-chlorophenol molecules since the molecular dimensions (~0.4 x 0.6 nm) are smaller than the pore diameter of C-RH (Grabowska, Gryglewicz, & Machnikowski, 2010; Grabowska, 2016).

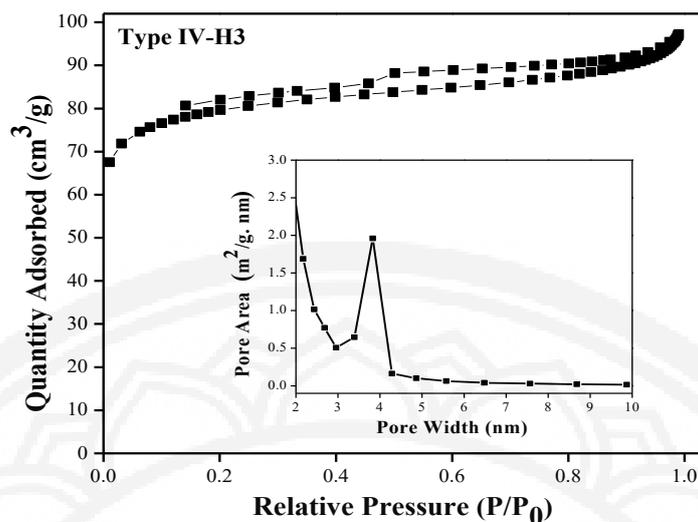


Figure 2 Nitrogen adsorption–desorption isotherms. The inset shows the pore size distributions for C–RH.

The resulting quantification was analyzed by EDXRF, as shown in Table 1. Due to the composition of rice husk, Si is contained in SiO₂ as a major element. Thus, the C–RH is able to have more adsorptive properties.

At present, SiO₂ has drawn significant attention for potential use as adsorbent due to being chemically inert and having low toxicity, a large specific surface area, and high porosity. The adsorption properties as gas purification and wastewater treatment absorbed on SiO₂ have been reported by many adsorption applications such as the adsorption of Benzene, Toluene, p-Xylene, lead (II) ions, dyes waste, and CO₂ gas (Hernández et al., 2004; Klapiszewski, Bartczak, Szatkowski, & Jesionowski, 2017; Kharat, Mohammadi Galangash, Ghavidast, & Shirzad–Siboni, 2018; Tahari & Yarmo, 2014).

Table 1 Elemental analysis of C–RH by EDXRF

Element	% w/w
Si	10.74
SiO ₂	4.38
K	1.02
S	0.80
Al	0.54
Fe	0.41

Results of adsorption equilibrium, kinetics and thermodynamics

Figures 3(a) – 3(c) show the remaining concentration (C_i) of 2–chlorophenol at different initial concentrations (20, 40, 60, 80, 100 mg/L) by the calibration curve, demonstrating a linear relationship between absorbance and concentration. It can be seen that higher 2–chlorophenol concentration resulted in less 2–chlorophenol adsorption per gram (Q_i). Adsorption occurred rapidly within 15 min and equilibrium was attained within 90 min. The increasing order of the removal rate for 2–chlorophenol in terms of C_e and Q_e from the highest to lowest concentration was recorded at equilibrium and further used to study the adsorption isotherms and kinetics (see **Table 2**).

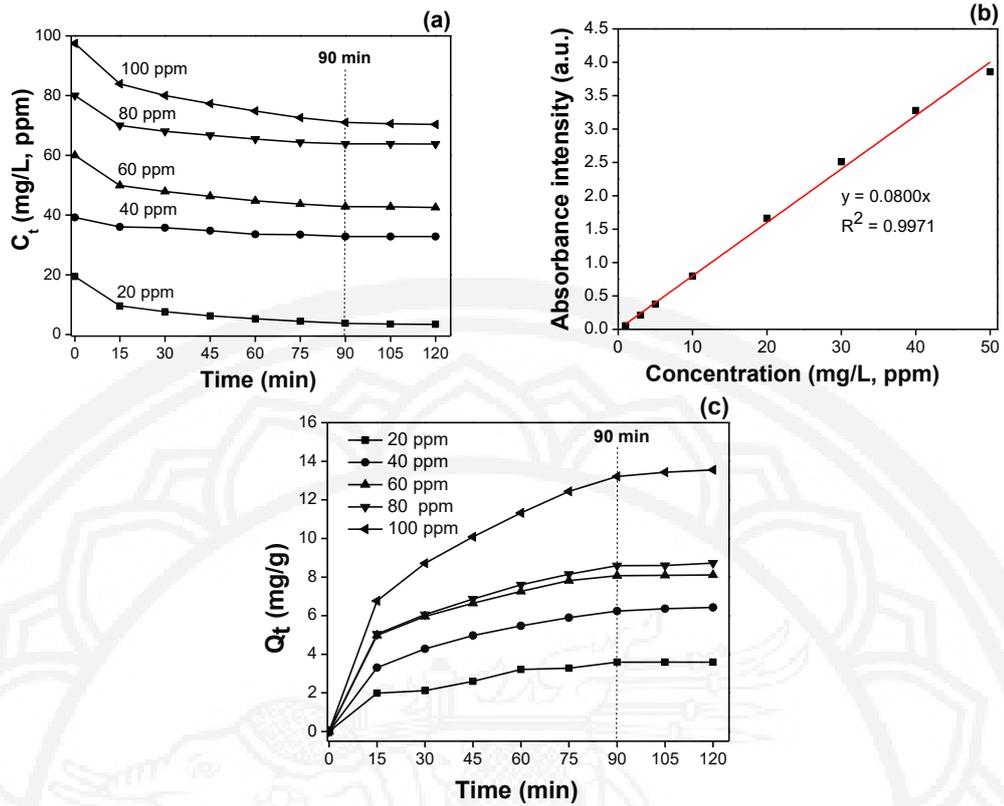


Figure 3 (a) C_t , (b) Calibration curve, and (c) Q_t

Table 2 Parameter values for the kinetic studies

Concentration (mg/L)	C_e (mg/L)	$Q_{e, exp}$ (mg/g)	Pseudo-second order		
			$Q_{e, cal}$ (mg/g)	R^2	k (min ⁻¹)
20	3.765	3.590	3.983	0.9610	0.0174
40	32.820	6.243	6.974	0.9771	0.0113
60	42.823	8.070	8.643	0.9880	0.0132
80	63.859	8.588	9.337	0.9828	0.0101
100	71.055	13.208	14.881	0.9702	0.0047

Table 3 Isotherm model parameters

Langmuir isotherm		Freundlich isotherm	
R^2	0.6426	R^2	0.8122
N_m (mg/g)	13.4048	1/n	0.5697
K_L (L/g)	0.0442	K_F (L/g)	2.073

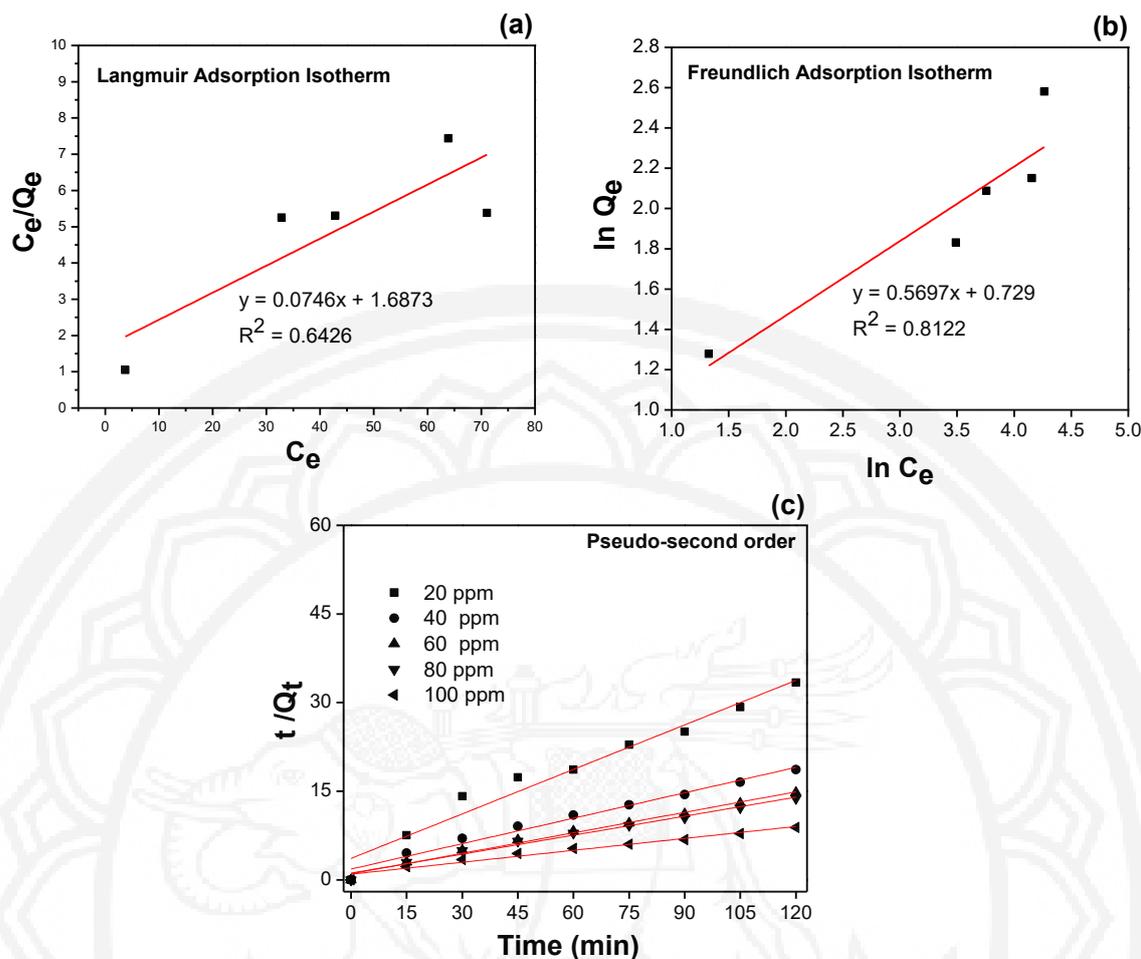


Figure 4 (a) Langmuir plots, (b) Freundlich plots, and (c) Pseudo-second order kinetic model for 2-chlorophenol adsorption on C-RH

The experimental data for various 2-chlorophenol concentrations at equilibrium time was used to fit into the adsorption isotherm models proposed by Langmuir and Freundlich. **Figure 4** shows that the 2-chlorophenol experimental data was better fitted in the Freundlich adsorption model than in the Langmuir isotherm model with relatively higher R^2 values (see **Table 3**). This described the multilayer adsorption of 2-chlorophenol onto C-RH surface. Moreover, favorable adsorption tends to correspond with Freundlich isotherm with the Freundlich exponent $1/n > 0.5$, which indicates identical adsorption energies for all sites of multilayer adsorption.

The kinetics of adsorption for 2-chlorophenol on C-RH were tested using pseudo-second order, as shown in **Figure 4(c)**. The results showed clearly that the pseudo-second order rate constant (k) depended on the initial concentration, as mentioned previously in **Table 2**. The value of rate constant was found to decrease from 0.0174 to 0.0047 min^{-1} as the initial concentration increased from 20 to 100 mg/L, likely due to the increased mobility of the 2-chlorophenol solute and enhanced diffusion at low concentration. In addition, increasing 2-chlorophenol concentration reduced the diffusion of 2-chlorophenol in the boundary layer and enhanced the diffusion in the adsorbent.

It is apparent that the calculated adsorbed amounts ($Q_{e, \text{cal}}$) obtained from the linear plot of pseudo-second order kinetic model increased from 3.983 to 14.881 mg/g as the initial concentration varied from 20 to 100 mg/L, respectively. These values correspond closely to the experimental adsorbed amounts ($Q_{e, \text{exp}}$), indicating



that this type of kinetic plot for the adsorption system is acceptable. The general explanations for this type of kinetic model basically supports chemisorption with the heterogeneous active sites in C-RH, which is likely responsible for 2-chlorophenol uptake (Ngulube, Gumbo, Masindi, & Maity, 2017).

Thermodynamic parameters are expressed in terms of Gibbs free energy (ΔG°). The relationship between ΔG° of the adsorption process and the Langmuir constant ($K_L = 0.0442 \text{ L/g}$) is presented using the equation $\Delta G^\circ = -RT \ln K_L$, as explained in the previous part. The calculated ΔG° was determined by a negative value of -7.887 kJ/mol at 304.15 K , indicating the adsorption processes at a given temperature occurred spontaneously in nature (He, Hong, Zhang, Gan, & Ho, 2010).

In order to compare the adsorption capacities of C-RH as an adsorbent, their maximum monolayer adsorption capacities (N_m) based on the Langmuir isotherm were compared with other adsorbents reported in previous research. In Table 4, it can be observed that the maximum adsorption capacity of C-RH in this study was approximately 13.4 mg/g , which is higher than the highest adsorption capacity reported for Surfactant-modified natural zeolite, *Azolla filiculoides* biomass, and *Ricinus communis* pericarp. Meanwhile, the adsorption capacity of C-RH was less than Fluted activated carbon and Bagasse. However, the difference in the adsorption performance of the adsorbents not only depends on the sources of precursor for the adsorbents, but also the intrinsic and extrinsic parameters such as preparation process, initial pollutant concentration, contact time, surface area, pore volume, surface charge, and pH of aqueous solution. Additionally, the temperature of the system cannot be neglected.

The produced C-RH prepared from rice husk waste in this study can be considered an effective adsorbent for wastewater treatment, which could eventually replace expensive, commercial activated carbon.

Table 4 Comparison of the maximum monolayer adsorption capacities of chlorophenol compounds on various adsorbents

Adsorbent	Adsorption capacity (N_m , mg/g)	Temperature (K)	Contact time (min)	References
C-RH (in this study)	13.4	304	120	-
Surfactant-modified natural zeolite	12.7	293	480	Kuleyin (2007)
<i>Azolla filiculoides</i> biomass	8.24	298	75	Zazouli, Balarak, and Mahdavi (2013)
<i>Ricinus communis</i> pericarp	71.43	303	120	Adane et al. (2015)
Fluted activated carbon	47.62	303	140	Ekpete, Horsfall, Tarawou, and Nepal (2011)
Bagasse	52.5	303-333	450	Shah, Taylor, and Shah (2011)

Conclusion and Suggestions

This study successfully prepared highly-porous adsorbent from low-cost agricultural waste, namely rice husk, which could effectively remove 2-chlorophenol from an aqueous solution. The resulting silicon element



contained in rice husk ash resulted in highly-specific surface area, pore volume and mesopore size, which had a beneficial effect on the adsorption process of 2-chlorophenol. The maximum adsorption capacity for 2-chlorophenol by C-RH was 13.4048 mg/g with 120 min of reaction time. Adsorption equilibrium was reached in 90 min. Further, the adsorption process followed the pseudo-second order kinetic model with the isothermal data fitting well in the Freundlich model, indicating chemisorption of multilayer adsorption. Hence, the production of C-RH from rice husk waste could be adapted to any environment with local agricultural residue using an inexpensive and simple process to provide an alternative to expensive commercial activated carbon for water treatment as well as water purification. Some suggestions for future work as well as their adsorption activities for real wastewater need to be tested.

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