

Removal of Mercury (II) from Aqueous Solution by using Rice Residues

S. T. Song^a, N. Saman^a, K. Johari^a and H. B. Mat^{a,b*}

^aAdvanced Materials and Process Engineering (AMPEN) Research Group, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^bNovel Materials Research Group, Nanotechnology Research Alliance, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author: hbmat@cheme.utm.my

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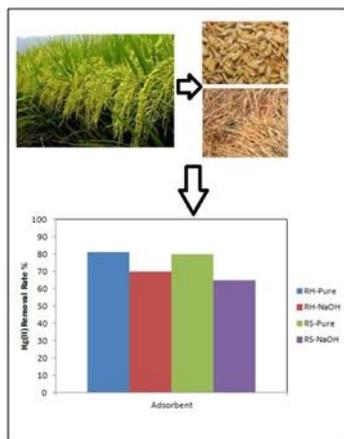
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Graphical abstract



Abstract

Sorption potential of rice residues for Hg(II) removal from aqueous solution was investigated. Rice husk (RH) and rice straw (RS) were selected and treated with sodium hydroxide (NaOH). The raw and modified adsorbents were characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and BET surface area measurements. The effects of pH, initial ion concentration, and agitation time on the removal process were studied in batch adsorption experiments. Two simple kinetic models, which are pseudo-first-order and pseudo-second-order, were tested to investigate the adsorption mechanisms. The kinetic data fits to pseudo second order model with correlation coefficients greater than 0.99 for all adsorbents. The equilibrium data fitted well with the Langmuir compared to Freundlich isotherm models. Alkali-treated adsorbent obtained larger surface area and RH-NaOH showed highest adsorption capacity followed by RS-Pure > RH-Pure > RS-NaOH. The maximum removal efficiency obtained by RH-NaOH and RS-Pure was 42 mg/l (80%) at pH 6.5 and with 2 days contact time (for 50 mg/l initial concentration and 25 mg adsorbents).

Keywords: Rice husk; rice straw; mercury ion; sorption

Abstrak

Potensi jerapan bahan sampingan padi untuk penyingkiran raksa daripada larutan telah dikaji. Padi sekam (RH) dan jerami padi (RS) telah dipilih dan diubahkan dengan natrium hidroksida (NaOH). Pencirian penjerap yang asli dan yang diubahkan telah dijalankan dengan menggunakan Mikroskop Imbasan Elektron (SEM), Spektroskopi Inframerah (FTIR) dan pengukuran kawasan permukaan BET. Pengaruh pH, kepekatan awal, dan masa pengadukan terhadap proses penyingkiran telah dikaji dengan teknik penjerapan berkelompok. Dua model kinetik, iaitu pseudo-peringkat-pertama dan pseudo-peringkat-kedua telah diuji untuk kajian mekanisma penjerapan. Data kinetik untuk semua penjerap berpadanan dengan model pseudo-peringkat-kedua dengan pekali korelasi lebih daripada 0.99. Data keseimbangan ekuilibrium berpadanan dengan model Langmuir berbanding dengan model Freundlich. Penjerap yang diubahsuaikan dengan alkali didapati mempunyai kawasan permukaan yang lebih luas dan RH-NaOH menunjukkan kapasiti penjerapan yang tertinggi diikuti oleh RS-Pure > RH-Pure > RS-NaOH. Kadar penyingkiran maksima yang dicapai oleh RH-NaOH and RS-Pure adalah 42 mg/l (80%) pada pH 6.5 dalam masa dua hari pengadukan (Kepekatan awal 50 mg/l dan 25 mg penjerap).

Kata kunci: Sekam padi; jerami padi; ion raksa; jerapan

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1.0 INTRODUCTION

Mercury is one of the common heavy metal considered as a serious toxic to both humans and the environment [1]. The major sources of mercury pollution are waste effluents from industrial facilities such as metal plating, mining operations, fertilizer industry, tanneries, and textile industries [2]. Therefore, several conventional methods have been reported for removal of mercury ions from waste streams include carbon adsorption, ion exchange, chemical precipitation, membrane filtration, adsorption, and photoreduction. Among all these methods, adsorption process is

one of the effective techniques that have been successfully employed for metal removal from wastewater [3].

Recently, lignocellulosic materials have been studied as low-cost adsorbent for heavy metal removal. According to Bailey *et al.* [4], an adsorbent can be considered as low-cost adsorbent if it requires little processing, abundant in nature, or by-product from another industry. Several materials including coconut pith, sawdust, rice husk, rice straw and wheat husk have been utilized for heavy metal removal and commonly they comprise with the advantages of inexpensive, environmental friendly, easy to obtain, and readily available in bulk [3,5-9]. These agro-wastes were

found to have good adsorption capacity due to their major composition of lignocellulose (hemicelluloses, lignin, and cellulose together) and also included other substances such as tannin and pectin, which contains polar functional groups (polyphenolic, aliphatic hydroxyl and carboxylic groups) [3]. These groups of lignocellulosic materials have the ability to bind heavy metals by donating an electron pair to form complexes with the metal ions in solution.

In this study, rice wastes (rice husk and rice straw) will be utilized as biosorbent in removing the mercury ions from aqueous solutions. Rice which is cultivated in more than 75 countries in the world is the most widely cultivated cereal in the world, after maize and wheat [10–11]. It is a dietary staple food of over half the world's population, mostly in Asia and Latin America. The estimation of global paddy production in 2009 by FAO points to 678 million tonnes [12]. Rice husk and rice straw are the main field based residues produced along with harvesting of paddy. The worldwide annual output of rice husk is approximately 80 million tonnes [10] and around 600–900 million tonnes of rice straw [13], which are great bulk materials. Hence, the use of rice straw as low-cost adsorbents is very essential in developing countries. From previous reviews, chemical compositions of rice waste are found to vary according to type of paddy, crop year, climatic and geographic conditions. Table 1 shows average compositions of rice straw and rice husk [14]. The main composition of the rice straw and rice husk is cellulose followed by hemicellulose and lignin.

Table 1 Average compositions of rice husk and rice straw [14]

Constituent	Composition (%)	
	Rice straw	Rice husk
Cellulose	43	35
Hemicellulose	25	25
Lignin	12	20
Crude protein (N x 6.25)	3–4	3
Ash	16–17(silica 83%)	17 (silica 94%)

Recently, Chakraborty *et al.* [15] developed NaOH-modified rice husk as low-cost adsorbent for adsorption of crystal violet dye and found that the monolayer adsorption capacity increased to be 44.87 mg/g. They found that the treatment of rice husk with NaOH breaks the covalent association between lignocellulose components, hydrolyzing hemicellulose, and depolymerizing lignin, and, hence, it enhances the adsorption capacity. Also, treatment with NaOH are proven to remove the natural fats and waxes from the cellulose fiber surfaces thus revealing chemically reactive functional groups like –OH [16].

In this study, rice husk (RH) and rice straw (RS) were selected to be modified by alkali treatment using NaOH to enhance the adsorption capacity as mercury sorbents. The effectiveness of the adsorbent was then observed in the batch adsorption of Hg (II) with respect to the initial pH, adsorption temperature, contact time, and concentration.

2.0 EXPERIMENTAL

2.1 Materials

Rice husk (RH) and rice straw (RS) were collected from local paddy field located at Kelantan. RH and RS were grinded and sieved to obtain the particle size in the range of 0.06–0.17 mm. Other chemicals such as sodium hydroxide, NaOH (99%), nitric acid, HNO₃ (36.5–38.0%) and mercury nitrate monohydrate, (Hg(NO₃)₂) were obtained from Merck (Germany) and J.T. Baker

(Europe). Deionized water (Purite Water System, U.K) was used throughout the experiments.

2.2 Synthetic Solutions

The stock solutions (1000 mg/l) were prepared in distilled water using Hg(NO₃)₂. All working solutions were prepared by diluting the stock solution with deionized water. 0.1 M HNO₃ and 0.1 M NaOH were used for adjusting the solution pH.

2.3 Surface Modification

The rice residues (RH and RS) were thoroughly washed several times with deionized water to remove surface adhered particles and water soluble materials, followed by a drying process in oven at 50°C until a constant weight was obtained. The surface modification was subjected to the alkali treatment known as mercerization. The rice samples were dipped in 5% NaOH solution for 24 hours, followed by further washed with deionized water and acetic acid [17]. The sample was then dried in oven at 50°C until a constant weight was obtained.

2.4 Characterization of Adsorbents

2.4.1 Fourier-Transform Infrared (FTIR) Spectroscopy

The IR spectra of untreated and modified rice residues (RH and RS) were recorded using FTIR Perkin Elmer Model 2000. The FTIR analysis was done in order to elucidate the functional groups existed in these rice residues samples. The measurements were carried out over 4000–370 cm⁻¹ using the KBr disc method [18].

2.4.2 Scanning Electron Microscopy (SEM)

In order to evaluate the changes in the surface morphology, the adsorbent were analyzed by using JEOL model JSM-6390LV scanning electron microscope.

2.4.3 Surface Area Analysis

Single point BET (Brunauer, Emmett and Teller) surface area of the adsorbent was measured at temperature of 77 K using Micromeritics Pulse Chemisorb 2705.

2.5 Adsorption Experiment

Adsorption experiments were performed in batch adsorption method. The mercury stock solutions were prepared for each experiment from Hg(NO₃)₂. In equilibrium adsorption experiment, 25 mg adsorbent was suspended in 25 ml aqueous Hg(II) solution having concentration of 50mg/l. The pH of the mixture solution was adjusted to the desired value (2–14) by adding HNO₃ or NaOH solutions, accordingly. The mixture solution was shaken at 200 rpm using shaker for 2 days at 30°C. Two days of shaking time was sufficiently long enough for the mixture solution to achieve equilibrium conditions. The mixture solution was filtered using nylon membrane filters (0.80 μm) to remove adsorbent in the solution that might interfere in mercury determination by using atomic absorption spectrophotometer (Perkin-Elmer precisely HGA 900).

The effects of Hg (II) concentration, adsorption temperature and agitation time were also conducted according to the same procedure. The initial Hg (II) concentrations used ranged from 25 to 200mg/l. The temperature were set on 30°C, 40°C, 50°C and

60°C. The effect of agitation time on Hg (II) adsorption was monitored up to 3 days.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

The identification of some characteristic functional groups capable of adsorbing metal ions was performed using FTIR in the range of 4000-370 cm⁻¹. The results was shown in Figures 1 and 2. The IR-spectra of untreated RH and RS showed the structural similarity in between 3410-3620 cm⁻¹ and 2910-2923 cm⁻¹ due to O-H stretching and C-H stretching vibrations, respectively [3,19-21]. This stretching of OH groups can be associated to silanol groups (Si-OH) which adsorb water on the rice surface.

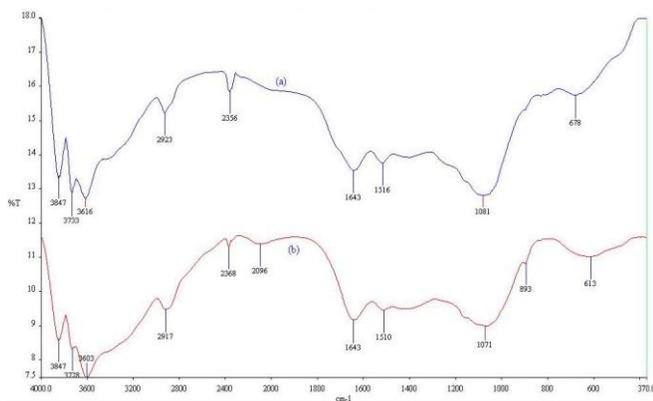


Figure 1 FTIR spectrum of (a) RH-Pure and (b) RH-NaOH

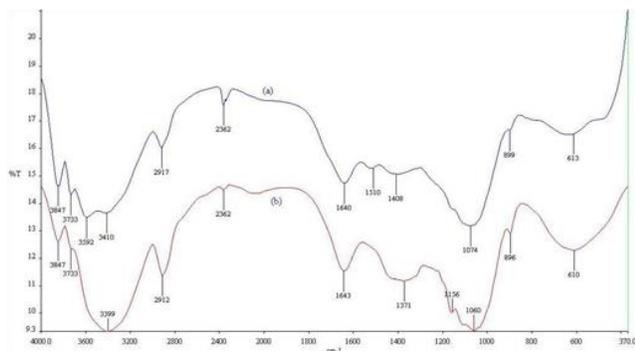


Figure 2 FTIR spectrum of (a) RS-Pure and (b) RS-NaOH

The IR-spectra of RH-Pure and RH-NaOH show an asymmetric absorption band at 3603 and 3616 cm⁻¹, which are attributed to the hydrogen bonding O-H stretching vibrations from the cellulose structure of the rice husk. Additionally, the typical absorption band at 2917 and 2923 cm⁻¹ stands for other OH groups bound to methyl radicals which are common in the lignin structure. It also indicates the C-H stretching vibration of cellulose/hemicelluloses. Spectra of RH-Pure and RH-NaOH which showed peaks at 1643 cm⁻¹, indicative of C=O stretching vibrations in conjugated aryl ketone, and 1510-1516 cm⁻¹ render to guaiacyl and syringyl lignin characteristic peaks. The band at 1375 cm⁻¹ for RH-Pure and 1380 cm⁻¹ for RH-NaOH arise from aliphatic C-H bending vibration.

In Figure 2(a) RS-Pure showed the peaks at 3410 cm⁻¹ (O-H stretching in hydroxyl group), 2917 cm⁻¹ (C-H stretching in methyl and methylene groups), 1640 cm⁻¹ (C=O stretching in

conjugated aryl ketone), 1408-1510 cm⁻¹ (guaiacyl and syringyl lignin characteristic peaks), and 1074 cm⁻¹ (aromatic C-H in-plane deformation) [22-23]. All these bands disappeared or decreased in RS-NaOH (shown in Figure 2b). These results highlight the delignification effect of the alkali treatment process. Other peaks detected on RS-NaOH located at 1371, and 1156 cm⁻¹, respectively, indicated to aliphatic C-H bending vibration and C-O-C stretching.

Figures 3a, 3b, 4a and 4b show the SEM images for RH-Pure, RH-NaOH, RS-Pure, and RS-NaOH samples, respectively. It can be observed from Figures 3 and 4, some imperfections such as breakages on the surface of the rice wastes wall were verified after treatment. The morphology of untreated and modified rice reveals the changes on the surfaces due to the different chemical bonds formed on the surface during treatment. The surface modification of rice husk and rice straw was prepared according to Sreekala *et al.* [17] by using alkali (NaOH) treatment known as mercerization. The effect of this treatment indicates the increasing amount of amorphous cellulose at the expense of crystalline cellulose. This treatment process also improves the fiber surface adhesive characteristics by removing natural and artificial impurities and produced a rough surface [17].

The BET surface area of RH-Pure, RH-NaOH, RS-Pure and RS-NaOH was determined from the N₂ adsorption data and values was found to be 10.08 m²/g, 23.86 m²/g, 8.46 m²/g and 12.38 m²/g, respectively.

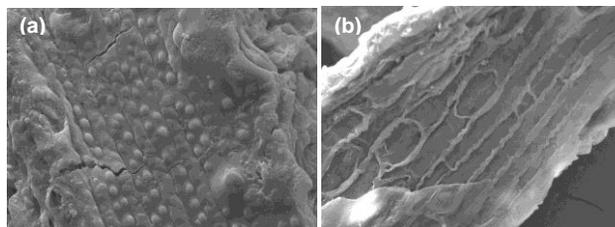


Figure 3 SEM images of (a) RH-Pure and (b) RH-NaOH (magnification x1000)

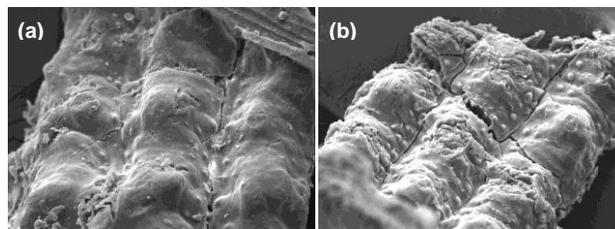


Figure 4 SEM images of (a) RS-Pure and (b) RS-NaOH (magnification x1000)

3.2 Adsorbent Adsorption Characteristics

3.2.1 Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [3]. The effect of pH on the adsorption of Hg(II) onto different adsorbents RH-Pure, RH-NaOH, RS-Pure, and RS-NaOH was studied. The experiment was carried out at different initial pH ranging from 2.0 to 14.0 and the results are presented in Figure 5.

The changes in pH of the solution shows that adsorption of Hg(II) was found to increase with the pH increased up to pH 6-7, and after that decreased. The pH that gave the maximum Hg(II) adsorption for RH-Pure was observed at pH 9.5, however, for RH-

NaOH, RS-Pure and RS-NaOH was at pH 7.12, 6.68 and 6.71, respectively. It can be observed from Figure 5, the adsorption efficiency of rice wastes were the highest around pH 6.5-7.0. The increments may be due to the increase of negative sites and addition of surface functional groups during the thermo-chemical reactions with NaOH, increased the Hg(II) ion sorption capacity of the sorbents. The formations of negatively charged hydrolyzed ions decrease again the sorption of metal ions at higher pH [5].

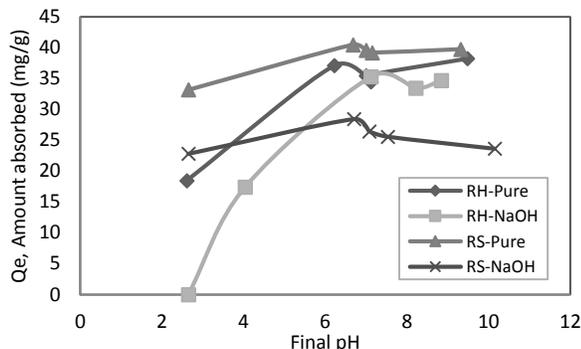


Figure 5 Effect of pH on Hg(II) adsorption by RH-Pure, RH-NaOH, RS-Pure and RS-NaOH sorbents (Initial concentration of Hg(II): 50mg/l)

3.2.2 Effect of Initial Concentration

Figure 6 shows that at the constant pH, increasing the initial concentration of Hg ion solutions from 25-300 mg/l increased the sorption amount of Hg ions by sorbents. It can be observed that for the RH-Pure and RS-Pure, the adsorption of Hg(II) increases linearly with the increase of Hg(II) concentration and showing saturation behaviour after 200mg/l. For RH-NaOH, the same adsorption results are obtained but the saturation behaviour showed after 200mg/l and for RS-NaOH, where the amount of Hg(II) adsorbed increase with increasing of initial Hg(II) concentrations but having lowest Hg(II) adsorption capacity was observed. Overall results show that RH-NaOH gave highest adsorption capacity and this may be due to the better surface morphology with the additional of active site and larger surface area. However, RS-NaOH showed least adsorption capacity than the untreated RS-Pure and RH-Pure. Considering these results and the BET values could be asserted that mercury removal was due not only to a physical mechanism. Also, it was not always true that materials with higher surface area were more efficient than others with lower one. The reduction in the amount adsorbed as affected by modification means that the mercerization may blocks some of the micro-pores making it difficult for the metal ions uptake [24].

3.2.3 Effect of Agitation Time

Figure 7 shows the effect of agitation time on the adsorption of Hg(II) on sorbents (RH-Pure, RH-NaOH, RS-Pure, and RS-NaOH). It can be observed from the figure that the amount of Hg(II) adsorbed increases with an increase in agitation time. These results revealed that the Hg(II) adsorption was fast at the initial stages of the contact period, and thereafter it became slow when near to the equilibrium. Almost 50% of Hg(II) was adsorbed within 30 minutes to 1 hours for RH-Pure, RH-NaOH, RS-Pure and RS-NaOH sorbents. This may be due to the fact that a large number of vacant surface sites were available for adsorption during the initial stage. After certain time the remaining vacant surface sites were difficult to absorb due to repulsive forces between the solute molecules on the solid and bulk phases [25].

The final equilibrium time showing the sorbents reaches saturation with no further adsorption take places approximately about 6 hours.

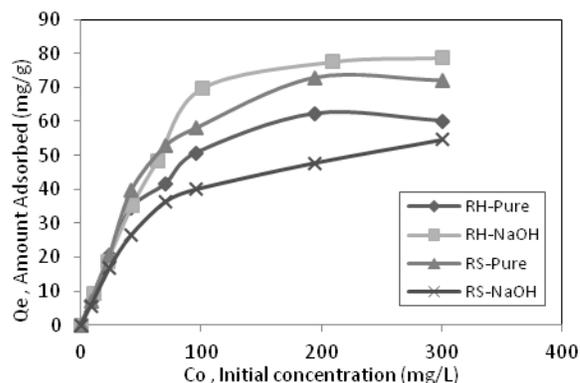


Figure 6 The effect of Hg(II) initial concentration on the Hg(II) adsorption by sorbents (pH 6.5)

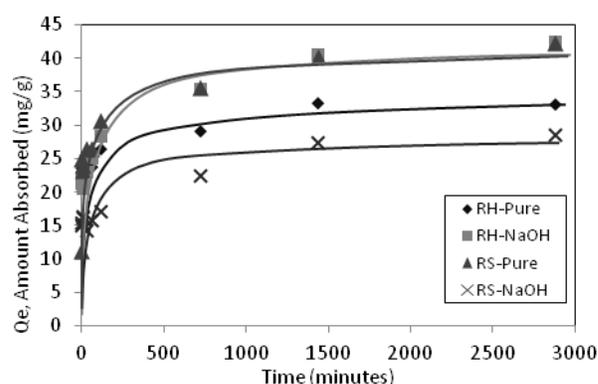


Figure 7 The effect of agitation time on the Hg(II) adsorption by sorbents (Initial concentration of Hg(II): 50mg/l, pH 6.5)

3.3 Adsorption Isotherms

Adsorption isotherm studies are important in determining the maximum adsorption capacity of any sorbents [26]. The equilibrium adsorption isotherm is described as the variation of the adsorption capacity, Q_e of the any adsorbent-fluid systems at various adsorbate concentrations at given temperature.

The Langmuir and Freundlich isotherm models were applied to analyze the adsorption isotherm of Hg(II) for untreated or modified RH and RS sorbents (as shown in Figure 8). In Langmuir isotherm, the adsorption data were analyzed according to a linear form of Langmuir equation (Equation 1) [27-30].

$$C_e/Q_e = 1/(Q_0b) + C_e/Q_0 \quad (1)$$

where C_e is the equilibrium mercury concentration in the liquid phase, C_e (mg/l), Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The linear plot of (C_e/Q_e) versus C_e for Hg(II) adsorption onto adsorbents give the constant values of Q_0 and b (Table 2). The essential characteristics of Langmuir isotherms can be expressed by a dimensionless equilibrium parameter, R_L which is defined by Equation 2 [21,31].

$$R_L = 1/(1 + bC_0) \quad (2)$$

where b is the Langmuir constant and C_0 is the initial concentration (mg/g). The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich adsorption model, which assumes that the adsorption occurs on the heterogeneous surfaces, can be expressed using Equation 3 [28,31-32].

$$\log Q_e = \log K_F + (1/n) \log C_e \quad (3)$$

where, Q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), and K_F and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [33].

Table 2 summarizes all the constants and correlation coefficients, R^2 of the two models used. It can be observed that, the Langmuir model yielded the best fit with higher R^2 value of 0.9976 and 0.9991 for RH-Pure and RH-NaOH sorbents on the adsorption of Hg(II), respectively. Moreover, the Q_e values predicted from the Langmuir model agreed well with the experimental values. The R_L values were found to be between 0 and 1, indicates to the favourable adsorption of Hg(II) adsorption on RH-Pure, RH-NaOH, RS-Pure and RS-NaOH. The results show the homogenous nature of rice husk and rice straw, untreated and modified surface had equal adsorption activation energy. It also implies that the adsorption process was taking place at the formation of monolayer at the outer surface of rice husk and rice straw [27].

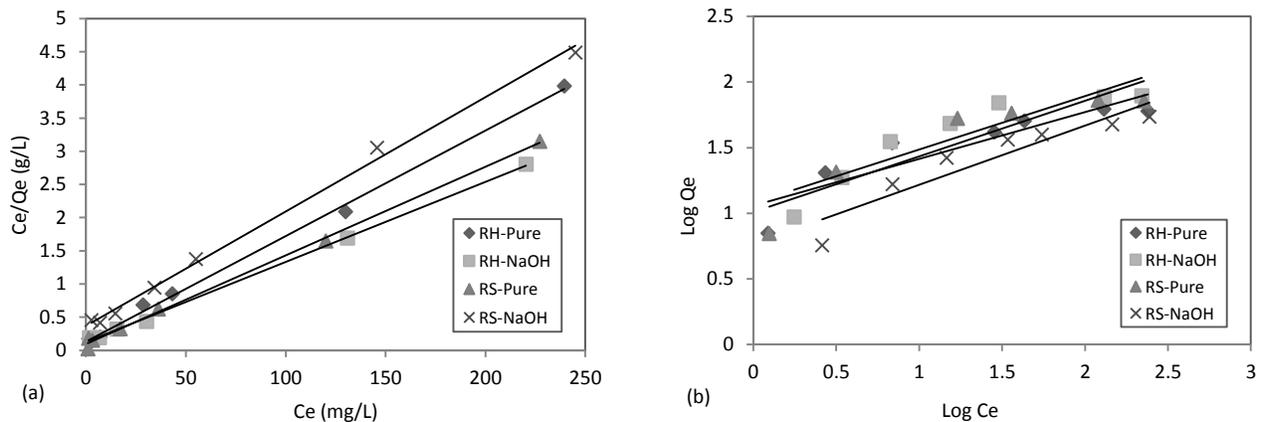


Figure 8 Langmuir plots (a) and Freundlich plots (b) for the adsorption of Hg(II) onto RH-Pure, RH-NaOH, RS-Pure and RS-NaOH sorbents

Table 2 Langmuir and Freundlich isotherm constants for the adsorption of Hg(II) onto rice wastes sorbents

Adsorbent	Langmuir			Freundlich		
	R^2	Q_0 (mg/g)	b (L/mg)	R^2	$1/n$	K_F (mg ^(1-1/n) L ^{1/n} /g)
RH-Pure	0.9976	62.89	0.1196	0.8200	0.3565	11.431
RH-NaOH	0.9991	82.64	0.0982	0.8326	0.4080	11.965
RS-Pure	0.9920	75.19	0.1368	0.9095	0.4243	10.198
RS-NaOH	0.9053	58.14	0.0465	0.8712	0.4503	5.844

3.4 Adsorption Kinetics

The kinetics of adsorption describes the rate of adsorbate adsorbs at the solid-liquid interface which controls the equilibrium time. The kinetics of Hg (II) ion adsorption on the untreated and modified RH and RS were analyzed using different kinetic models namely the pseudo-first-order and pseudo-second order models (Figures 10a and 10b).

3.4.1 Pseudo-first-order Kinetic Model

The pseudo-first-order kinetic model has been widely used to predict adsorption kinetics. The adsorption kinetic data of mercury are analyzed using Equation 4 [29,34-35].

$$\log (Q_e - Q_t) = \log Q_e - k_1 t \quad (4)$$

where Q_e and Q_t (mg/g) are the amounts of mercury adsorbed at equilibrium and at time t (min), respectively (mg/g) and k_1 is the Lagergren rate constant of the first order adsorption (min^{-1}). The plot of $\log (Q_e - Q_t)$ versus t gave a linear relationship, which the values of Q_e and k_1 can be determined from the slope and intercept of the plot (Figure 9a). The values of k_1 , Q_e and correlation coefficient, R^2 obtained from the plot are given in Table 3. It was found that the theoretical Q_e values do not agree with the experimental Q_e values. This shows that the adsorption of Hg (II) onto the sorbents (RH-Pure, RH-NaOH, RS-Pure, and RS-NaOH) does not follow the first-order kinetic model.

3.4.2 Pseudo-second-order Kinetic Model

The adsorption kinetic data can also be described by pseudo-second-order chemisorption kinetics given by Equation 5 [28,33-34].

$$t/q = 1/k_2Q_e^2 + t/Q_e \quad (5)$$

where k_2 (g/ mg min) is the rate constant of second order adsorption. The values of k_2 and Q_e were calculated from the linear plots of t/Q versus t shown in Figure 8b. Comparison of Q_e data in Table 4 shows that the theoretical Q_e values of the second order equation are generally closer to that of the experimental Q_e values compared to the theoretical Q_e values of the first order equation. Thus, the kinetics of the Hg(II) adsorption could be better described by the second-order kinetic model over the whole range of adsorption process [21]. This differs from the first-order kinetics which only describes the sorption sites and not the whole adsorption process [36]. The correlation coefficients for the

second-order kinetics gave the higher values (above 0.99), indicating that the rate limiting step of the adsorption process might be the chemical sorption or chemisorption involving the force through the sharing or exchange of electrons between the heavy metals and biosorbents.

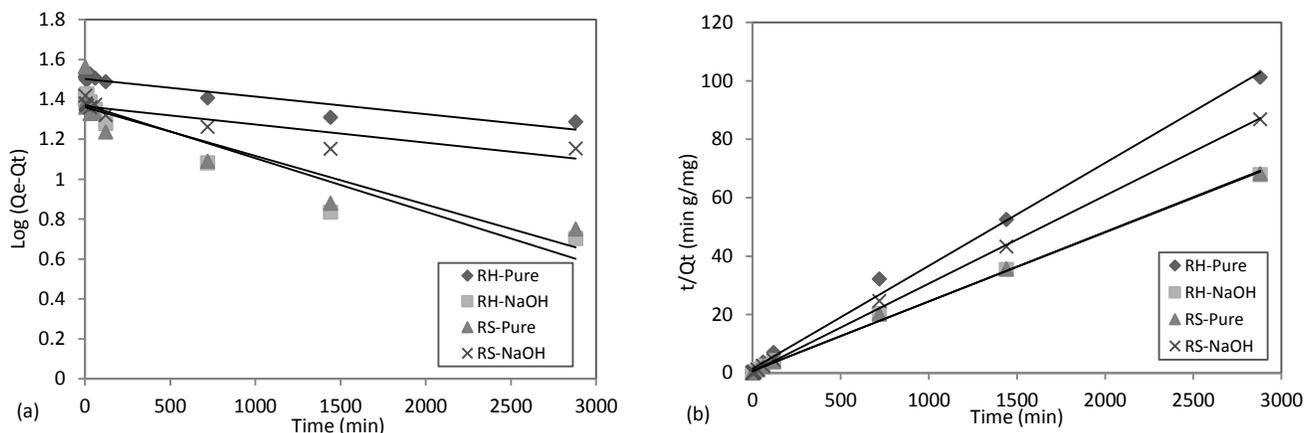


Figure 9 (a) Pseudo-first-order kinetic model plots and (b) Pseudo-second-order kinetic model plots for different sorbents (RH-Pure, RH-NaOH, RS-Pure and RS-NaOH)

Table 3 Pseudo-first-order and pseudo-second-order rate constants for the adsorption of Hg(II) onto untreated and modified RH and RS sorbents

Adsorbent	Q_e (mg/g), Experimental	Pseudo-first-order			Pseudo-second-order		
		Q_e (mg/g)	R^2	K_1	Q_e (mg/g)	R^2	K_2
RH-Pure	33.00	23.18	0.8159	0.0001	33.22	0.9989	0.0017
RH-NaOH	42.50	23.57	0.9119	0.0003	42.19	0.9978	0.0007
RS-Pure	42.00	22.90	0.8468	0.0002	42.02	0.9980	0.0008
RS-NaOH	28.50	31.77	0.8885	0.0001	28.41	0.9959	0.0008

4.0 CONCLUSION

The untreated and NaOH-treated rice husk and straw were successfully used as Hg(II) sorbents. The modified RH showed significant improvement of adsorption capacity to that of the untreated RH. However, there are no increments of sorption capacity by NaOH-treated RS compared to untreated RS. This may be due to the blockage on pore structure for metal ions uptake. The highest adsorption of Hg (II) was observed for RH-NaOH and RS-Pure. The adsorption data fitted well to the Langmuir isotherm model and pseudo-second-order kinetics model, suggesting that the uptake of Hg(II) onto the adsorbents were monolayer and predominately through the chemisorption process. This study significantly reveals that the solution pH, time, initial concentration and precursors are influential factors for mercury adsorption using alkali treated rice residues.

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