

# Effect of Organic and Inorganic Acid Pretreatment on Structural Properties of Rice Husk and Adsorption Mechanism of Phenol

Samah B. Daffalla\*, Hilmi Mukhtar, Maizatul S. Shaharun

Chemical Engineering Department, Universiti Teknologi PETRONAS, Malaysia

\*Corresponding Author E-mail: [samahb.daffalla@gmail.com](mailto:samahb.daffalla@gmail.com)

## Abstract:

Rice husk treated with organic and inorganic acid was tested as a low cost adsorbent for the removal of phenol from artificial wastewater in batch adsorption procedure. The physical and surface properties of the developed adsorbents were characterized using FTIR and SEM. The efficiency of these adsorbents was evaluated by varying the adsorbent doses. A comparison of organic acid (citric acid) and inorganic acids (HCL, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) treatment show that rice husk treated with organic acid (a weak acid) has less removal efficiency compared to inorganic acid (stronger acid) treated rice husk. This is the result of the active sites produced by citric acid. In general, removal efficiency between 40.21-59.54%, 32.11-43.87%, 31.33-40.66% and 22.42-35.41% could be achieved after treating the rice husk with H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub> and citric acid, respectively; in comparison to the raw rice husk which is able to achieve 18.61-28.94% removal efficiency after 72hrs. The kinetics of phenol adsorption is found to follow the pseudo-second-order kinetic model. FTIR analysis shows that the -OH, C-H, C≡C, C-C, C=O, -CO, Si-OH and -Si-H groups contribute to the adsorption of phenol onto the surface of adsorbent.

**Keywords:** Acid treatment; phenol adsorption; rice husk; adsorbent functional group; adsorption mechanism; treatment of wastewater

## 1. Introduction

Aromatic organic compounds are excessively released into the environments from various industrial sectors, particularly iron-steel, coke, petroleum, pesticide, paint, solvent, pharmaceuticals, wood preserving chemicals, and paper and pulp industries [1]. Phenol, as a class of organic compounds, has been known as a common and hazardous contaminant in water environment. Phenol constitutes the 11<sup>th</sup> of the 126 chemicals, which has been designated as priority pollutants by the U.S Environmental Protection Agency (USEPA) [2]. The content of phenols in industrial wastewater is usually in the range of 0.1-6800 mg l<sup>-1</sup> [1]. The allowable discharge limit for phenol is 0.1 mg/l and 0.001 mg/l (Standard A) set by the USEPA and the Malaysia Environmental Quality Act (MEQA), 1974 respectively [3]. Human consumption of phenol-contaminated water can cause severe pain leading to damage of the capillaries and ultimately causing death. Various methods such as microbial degradation, adsorption, chemical oxidation, incineration and solvent extraction have previously been used for removal of phenol from wastewater [4-6]. Among those methods, the adsorption process has emerged as the best for removing phenolic compounds from aqueous streams.

The efficiency of the adsorption process is mainly due to the characteristic of the adsorbent such as high surface area, high adsorption capacity, microporous structure and special surface reactivity. To the present, activated carbon is the most widely used adsorbent because it has a good capacity for adsorption of phenol from wastewater [7-9]. In spite of this, it suffers from a number of disadvantages. Activated carbon is expensive, and the higher the quality the greater the cost [10]. Consequently, there has been a growing interest in developing and implementing various potential adsorbents for the removal of phenol from water, and researchers are always in a hunt for developing more suitable, efficient, cheap and easily accessible types of adsorbents, particularly from the waste materials. The abundance and availability of agricultural by-products make them good sources of cheap raw materials for natural adsorbents. Rice husk, an agricultural waste, has been reported as a good adsorbent for many metals and basic dyes [11,12]. According to the statistics compiled by the Malaysian Ministry of Agriculture, there are more than 408,000 ton of rice husk produced in Malaysia annually [13]. Rice husk consists of 32.24% cellulose, 21.44% hemicelluloses and 21.34% lignin [13,14]. The cellulose, hemicellulose and lignin are associated which each other

forming a very stable matrix structure. The inner surface of rice husk is smooth and may contain wax and natural fats that provide good shelter for the grain. On the other hand, the presence of these impurities on the inner surface of rice husk also affects the adsorption properties of rice husk, both chemically and physically [15]. Therefore, the removal of silica and other surface impurities can be expected to improve the adsorption properties of rice husk.

Chemical modification of rice husk surface is thus necessary to upgrade or improve the adsorption properties [15]. Treatment of rice husk with organic and inorganic acids has been established to improve the adsorption properties. As a result of acid wash, inorganic materials such as carbonate and silica from the surface of raw rice husk [16]. The removal of the surface impurities also improves the surface roughness of the fibers or particles, thus opening more hydroxyl groups and other reactive functional groups on the surface. The pretreatment of rice husk with acids, as one of the most effective reagents for this structural break-down, is able to remove lignin and hemicellulose, reduce cellulose crystallinity, and increase the porosity or surface area.

The present work focuses on the development and characterization of low cost adsorbents from rice husk by chemical treatment using different types of acids (organic and inorganic). The produced adsorbents were tested for removing phenol from artificial wastewater. Kinetic models were used at different adsorbent doses to identify the possible mechanisms of such adsorption process. The effects of surface functional group on the adsorption of phenol were also investigated.

## 2. Material and Methods

### 2.1 Preparation of Adsorbents

The raw material, rice husk (RH) was obtained from a nearby rice mill. The rice husk was washed thoroughly with distilled water to remove adhering soil and clay, and then dried in air at 105°C in an oven for 24 hrs. The rice husk was milled and then passed through different sieves. The particles of sizes between 500-250 µm were selected for further pretreatment. To modify the surface characteristics of rice husk, chemical treatment of RH was carried out using organic and inorganic acids:

- Organic acid: 0.6M citric acid [17]
- Inorganic acid (mineral acid): 13 M H<sub>2</sub>SO<sub>4</sub> at 175-180°C for 20 min with stirring [18], 1M HCl at 100°C for 4hrs with stirring [16] and 2M HNO<sub>3</sub> at room temperature for 1hr with stirring [19].

Then the adsorbents were washed with distilled water and dried at 50-60°C in an electrical oven until a constant weight was attained.

### 2.2 Characterization of Adsorbents

The adsorbents were characterized in terms of morphological characteristics using Scanning Electron

Microscope (SEM-EDX, model LE01430VP). In addition, the functional groups present on the adsorbent's surface were determined using a Fourier Transform Infrared spectrophotometer (FTIR, model 8400S). The spectra range chosen was from 4000 to 400 cm<sup>-1</sup>.

### 2.3 Batch Adsorption Experiments

$$\% \text{ Removal Efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$\text{Amount Adsorbed } (q_e) = \frac{(C_0 - C_e)V}{W} \quad (2)$$

(mg of adsorbate / g of adsorbant)

Where,  $C_0$  and  $C_e$  (mg l<sup>-1</sup>) are the initial and equilibrium liquid-phase concentrations of phenol, respectively,  $C_t$  (mg l<sup>-1</sup>) is the concentration of phenol at time t, V is the volume of the solution (l) and W is the mass of dry adsorbent (g).

The kinetic of the adsorption data was analyzed using three different kinetic models namely pseudo first-order, pseudo second-order and Elovich model (Table 1).

Table 1. Kinetic Equations used in this Study

Kinetic models	Equation	Parameters	Ref.
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$q_e$ (mg g <sup>-1</sup> ): equilibrium adsorption capacity $q_t$ (mg g <sup>-1</sup> ): amount of adsorbate adsorbed at time t $k_1$ (min <sup>-1</sup> ): pseudo-first-order rate constant $t$ (min): time	[20]
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ): pseudo-second-order rate constant	[21]
Elovich	$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t)$	$a$ (mg g <sup>-1</sup> min <sup>-1</sup> ): initial sorption rate constant $b$ (g mg <sup>-1</sup> ): desorption constant	[20, 22]

In order to evaluate the fitting of the experimental data and the prediction accuracy of the models utilised in the present work, the normalized standard deviation is employed,  $\Delta q_e$  (%), which is defined as [20]:

$$\Delta q_e(\%) = 100 * \sqrt{\frac{\sum[(q_{e, \text{exp}} - q_{e, \text{cal}})/q_{e, \text{exp}}]^2}{(N - 1)}} \quad (3)$$

Where N is the number of data points,  $q_{e, \text{exp}}$  and  $q_{e, \text{cal}}$  (mg g<sup>-1</sup>) are the experimental and calculated equilibrium adsorption capacity values, respectively.

### 3. Results and discussions

#### 3.1 Characterization of Adsorbent using FTIR

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. The FTIR technique is an important tool to identify the characteristic functional groups, which are instrumental in adsorption of aromatic compounds. The FTIR spectra of the raw rice husk before and after acids treatment were used to determine the vibrational frequency changes in the functional groups in the adsorbent (Table 2). The FTIR spectra of rice husk after treatment with 1M HCl, 13M H<sub>2</sub>SO<sub>4</sub>, 2M HNO<sub>3</sub> and 0.6M citric acid, are shown in Figs. 1(a-d), respectively.

As seen in this figures, the adsorption peak around 3404.31 cm<sup>-1</sup> indicates the existence of free hydroxyl groups. In RH, the C-H stretching vibration around 2925.81 cm<sup>-1</sup> indicates the presence of alkane functional group. The peaks around 1641.31-1737.74 cm<sup>-1</sup> correspond to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups [23]. The C=C stretching vibrations between 1546.80-1652.88 cm<sup>-1</sup> are indicative of alkenes and aromatic functional groups. The peaks around 1461.94 cm<sup>-1</sup> indicate the presence of CH<sub>2</sub> and CH<sub>3</sub> groups while those at 1380 cm<sup>-1</sup> are indicative of CH<sub>3</sub> [24]. A peak at 1379.01 cm<sup>-1</sup> band may be attributed to the aromatic CH and carboxyl-carbonate structures. The peaks in the 1153.35-1300 cm<sup>-1</sup>

correspond to vibration of CO group in lactones. The peaks around 1238.21, 1080.06 and 862.12-476.38 cm<sup>-1</sup>, correspond to CHOH stretching, Si-O-Si stretching and Si-H groups, respectively. The presence of polar groups on the surface is likely to provide the considerable cation exchange capacity to the adsorbent [24].

In Figs. 1(a- d), all of the spectra for treated RH show a reduction in relative intensity of the FTIR bands at 3407.98 cm<sup>-1</sup> and 2854 cm<sup>-1</sup> identified for O-H and C-H groups, respectively, as compared to the spectrum of raw rice husk. Also for all samples treated with acid, a band at 1090-1010 cm<sup>-1</sup> attributed to silica functional group Si-O-Si, is less intense than that of the raw rice husk at 1080.06 cm<sup>-1</sup>. This indicates that as a result of acid wash inorganic materials such as carbonate and silica from the surface of raw rice husk [16]. For rice husk treated with citric acid (Fig. 1d), a peak at 1728.10 cm<sup>-1</sup> is ascribed to ester group due to the reaction of carboxylic acid with alcohol. The peak at 1633.59 cm<sup>-1</sup> may be attributed to the N=O stretching band in rice husk treated with HNO<sub>3</sub> (Fig. 1c) [25].

Table 2. Peak Identification of FTIR Spectra of Raw and Modified Rice Husk

Wave number (cm <sup>-1</sup> )	Functional group
3404.31	-OH and Si-OH
2925.81	C-H stretching of alkanes
1641.31-1737.74	C=O stretching of aromatic groups
1546.8-1652.88	C=C stretching of alkenes and aromatic
1461.94	CH <sub>2</sub> and CH <sub>3</sub>
1379.01	Aromatic CH and carboxyl-carbonate
1238.21	CHOH stretching of alcohol group
1153.35-1300	CO group in lactones
1080-1090	Si-O-Si
935.41	C-C
469-800	Si-H
580-34	-OCH <sub>3</sub>

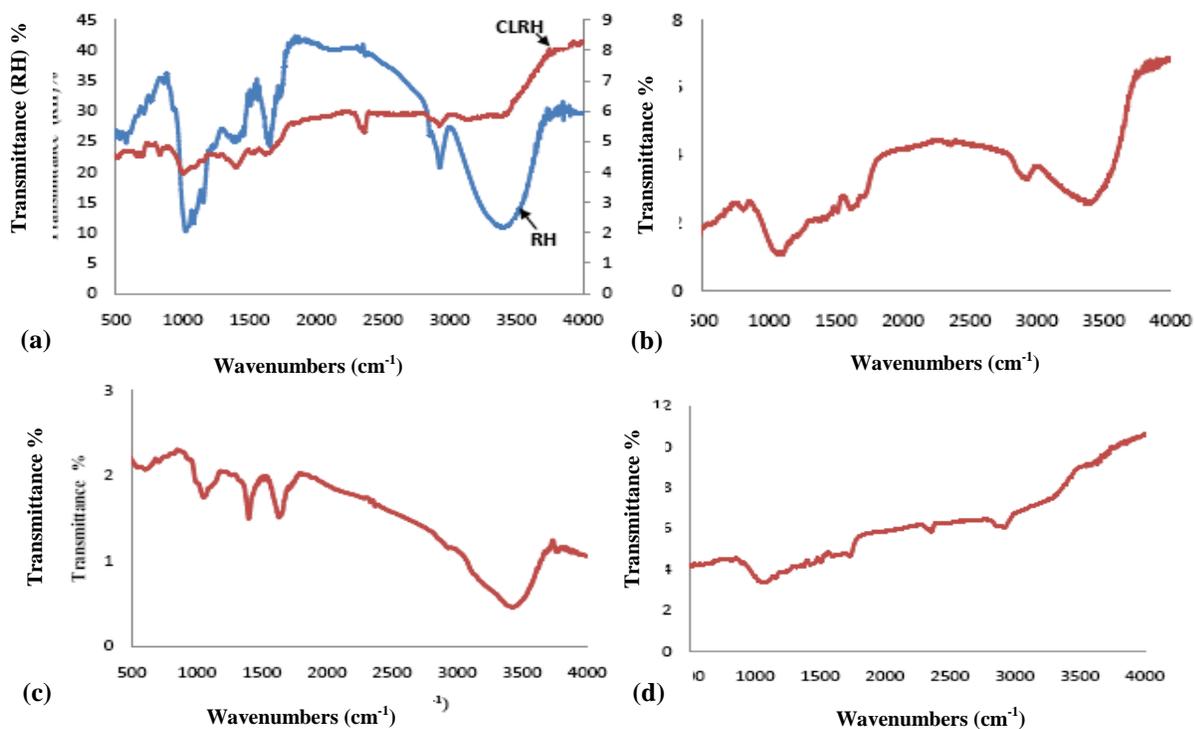


Figure 1. FTIR spectra of (a) RH and RH+ 1M HCL (CLRH), (b) RH+13M H<sub>2</sub>SO<sub>4</sub> (HRH), (c) RH+ 2M HNO<sub>3</sub> (HNRH) and (d) RH+ 0.6M citric acid (CARH)

### 3.2 Characterization of Activated Carbon using SEM

The morphological characteristic of adsorbents was observed by using scanning electron microscope (SEM). The SEM images of raw untreated rice husk and rice husks treated with HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and citric acid, respectively, are shown in Figs. 2(a-e). From the SEM

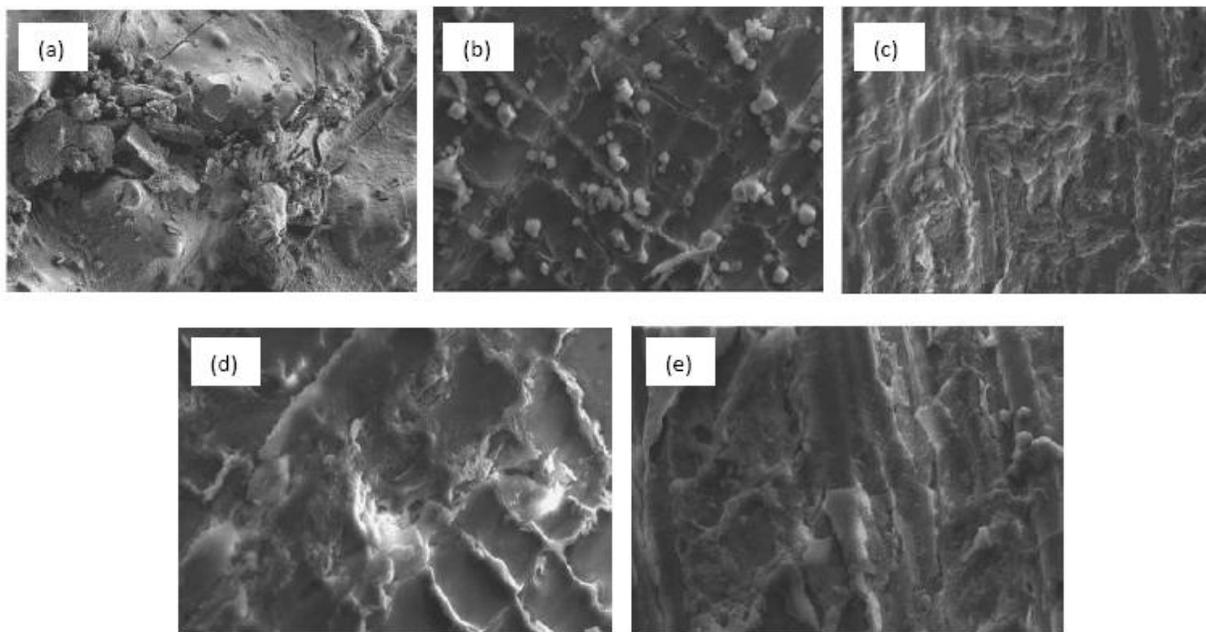


Figure2. SEM for, (a) RH, (b) RH+1M HCL , (c) RH+13MH<sub>2</sub>SO<sub>4</sub>, (d) RH+2M HNO<sub>3</sub> and(e) RH+0.6M Citric acid, magnified 1000 times.

3.3 Effect of Adsorbent Amount

Table 3 shows that, removal efficiency between 40.21-60.45%, 32.11-43.87%, 31.33-40.66% and 22.42-35.41% could be achieved after treating the rice husk with H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub> and citric acid, respectively; in comparison to the raw rice husk which is able to achieve 18.61-28.94% removal efficiency after 72hours. It is apparent that the adsorption efficiency increases by increasing the adsorbent dose. This is due to the increasing number of available adsorption sites as more adsorbent is added.

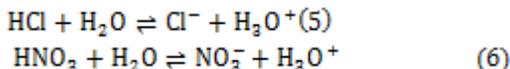
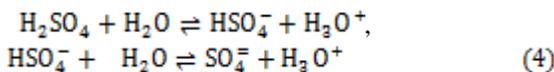
Table 3. The Effect of Adsorbent Amount on Removal Efficiency of Adsorbent Dose (1gl<sup>-1</sup>, 5gl<sup>-1</sup>, 10gl<sup>-1</sup>) after 72hrs

Adsorbent	Removal Efficiency (%)		
	1 gl <sup>-1</sup>	5 gl <sup>-1</sup>	10 gl <sup>-1</sup>
RRH	18.61	26.58	28.94
RH+H <sub>2</sub> SO <sub>4</sub>	40.21	47.74	59.54
RH+HCl	32.11	40.30	43.87
RH+HNO <sub>3</sub>	31.33	38.60	40.66
RH+CA	22.42	31.31	35.41

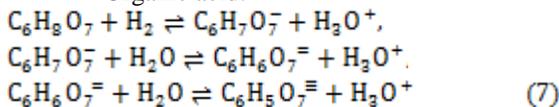
3.4 Adsorption Mechanism

Eqs. (4-7) represent the distribution of hydronium ion of acids in water [26].

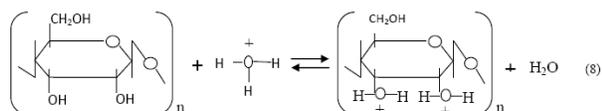
- Inorganic acid:



- Organic acid:



A lone pair electrons on the hydroxyl group at cellulose (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub> abstracts a proton from the hydronium ion to generate an oxonium ion Eq. (8) [27].



The ionic interactions results from the attraction of positive charge on the oxonium ions and negative charge of the conjugate base such as (HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, C<sub>6</sub>H<sub>7</sub>O<sub>7</sub><sup>-</sup>, C<sub>6</sub>H<sub>6</sub>O<sub>7</sub><sup>2-</sup> and C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup>) (Fig. 3)[ 26].

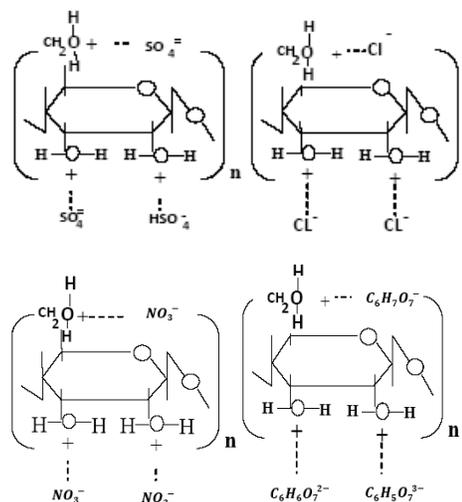
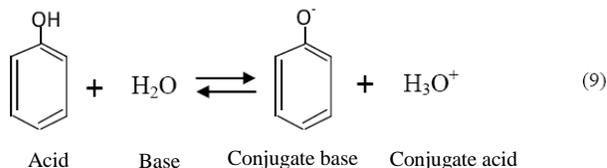


Figure 3. The interaction of intermolecular forces interaction between (a) HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, (b) Cl<sup>-</sup>, (c) NO<sub>3</sub><sup>-</sup> and (d) C<sub>6</sub>H<sub>7</sub>O<sub>7</sub><sup>-</sup>, C<sub>6</sub>H<sub>6</sub>O<sub>7</sub><sup>2-</sup> and C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup> ions and oxonium ion.

The reaction of phenol with water, as represented in Eq. (9), produces phenoxide ion with a negative charge, and hydronium ion which has a positive charge.



As we see in Table 4, the HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, C<sub>6</sub>H<sub>7</sub>O<sub>7</sub><sup>-</sup>, C<sub>6</sub>H<sub>6</sub>O<sub>7</sub><sup>2-</sup> and C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup> ions are weak bases and can be replaced by the phenoxide ion which is a stronger base [27]. The removal efficiency of rice husk treated with organic acid (a weak acid) is less than that of the rice husk treated with inorganic acids (stronger acid). This could possibly be as the result of repulsion between the C<sub>6</sub>H<sub>7</sub>O<sub>7</sub><sup>-</sup>, C<sub>6</sub>H<sub>6</sub>O<sub>7</sub><sup>2-</sup> and C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup> ions and phenoxide ion at the surface of the adsorbent.

Table 4.pKaValues for Organic and Inorganic Acids

Acid	Formula	pKa	Conjugate base
Hydrochloric acid	HCl	-7	Cl <sup>-</sup>
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	-5.2	HSO <sub>4</sub> <sup>-</sup>
Nitric acid	HNO <sub>3</sub>	-1.4	NO <sub>3</sub> <sup>-</sup>
Hydrogen sulfate ion	HSO <sub>4</sub> <sup>-</sup>	1.9	SO <sub>4</sub> <sup>2-</sup>
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	3.128	C <sub>6</sub> H <sub>7</sub> O <sub>7</sub> <sup>-</sup>
Dihydrogen citrate ion	C <sub>6</sub> H <sub>7</sub> O <sub>7</sub> <sup>-</sup>	4.77	C <sub>6</sub> H <sub>6</sub> O <sub>7</sub> <sup>2-</sup>
Hydrogen citrate ion	C <sub>6</sub> H <sub>6</sub> O <sub>7</sub> <sup>2-</sup>	6.4	C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> <sup>3-</sup>
Phenol	C <sub>6</sub> H <sub>5</sub> OH	9.95	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>

3.5 Adsorption Kinetics

Kinetic studies were conducted to determine the rate of phenol adsorption on the surface of adsorbent and to determine the equilibrium time for phenol uptake by rice husk treated with organic and inorganic acids. It was found that after 10/hrs the concentration reached the steady state Figs. 4(a-d).

In this study, the experimental equilibrium data of phenol adsorption onto chemically modified rice husk was first analyzed by the pseudo-first-order, pseudo-second-order and Elovich kinetic models (Table 1). The results of experimental data fitted with pseudo-first-order, pseudo-second-order and Elovich models are presented in Table 5. The accuracy of the models is given by the coefficient of determination ( $R^2$ ) and the normalized standard deviation,  $\Delta q_e$  (%).

It can be seen in (Table 5) that the coefficient of determination ( $R^2$ ) values for the pseudo-first order kinetic model lies in the ranges of 0.6638-0.9707. Furthermore, the experimental values ( $q_e$ ) did not agree with the calculated ones, which indicate that the pseudo-first-order equation cannot provide an accurate fit of the experimental data.

On the other hand, a better fit of the experimental data is obtained with the Elovich kinetic model as can be observed in Figs. 5(a-d). The coefficient of determination ( $R^2$ ) values for the Elovich kinetic model is in the range of 0.8298-0.9899. However, a comparison between the Elovich model and pseudo-second-order kinetic shows that the pseudo-second-order kinetic model gives a better fit between experimental and calculated data. The plots of  $t/q_t$  versus  $t$  (figure not shown) for the pseudo-second-order kinetics yielded a straight line for all adsorbent doses studied, and all the  $R^2$  values are almost equal to unity (Table 5), which indicates that the kinetics of phenol adsorption followed a second order kinetics.

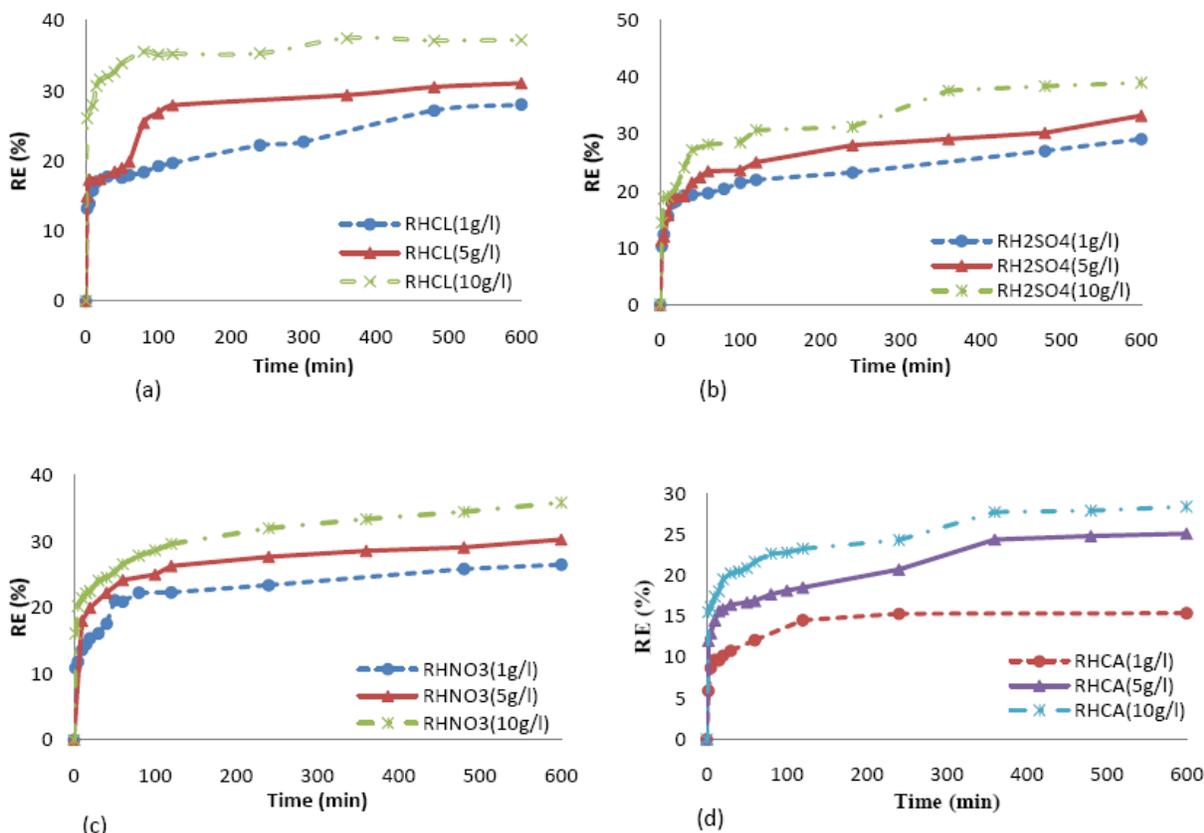


Figure 4. Effect of contact time(t) on percent removal(RE) of phenol for rice husk treated with organic and inorganic acids, (a)RH+HCl, (b) RH+H<sub>2</sub>SO<sub>4</sub>, (c)RH+HNO<sub>3</sub> and (d) RH+CA (adsorbent dose = 1 g l<sup>-1</sup>, 5g l<sup>-1</sup> and 10 g l<sup>-1</sup>)

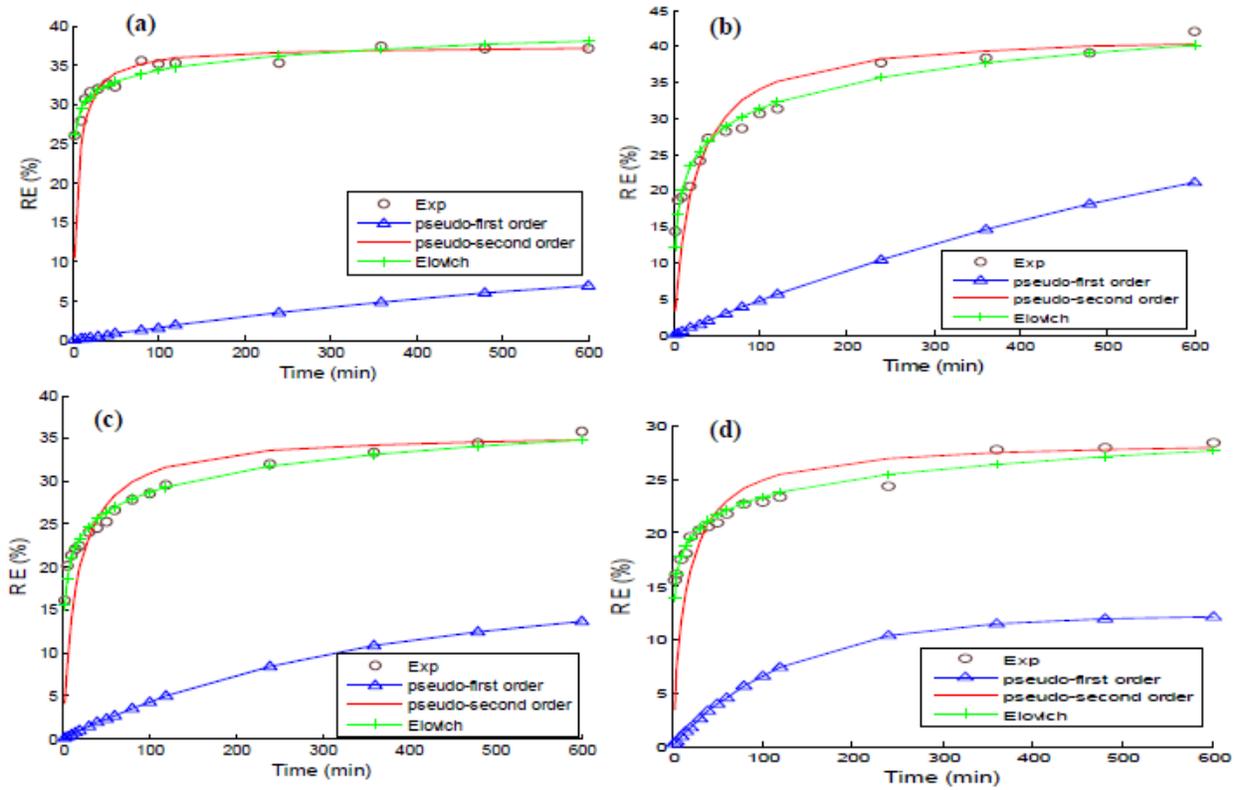


Figure 5. Comparison of experimental and calculated RE(%) values of (a) RH+HCl, (b) RH+H<sub>2</sub>SO<sub>4</sub>, (c) RH+HNO<sub>3</sub> and (d) RH+CA (adsorbent dose = 10 g l<sup>-1</sup>).

Table 5. Pseudo-first-order, Pseudo-second-order and Elovich model, constant and correlation coefficient for adsorption of phenol on rice husk treated with organic and inorganic acids (adsorbent dose = 1 g l<sup>-1</sup>, 5 g l<sup>-1</sup> and 10 g l<sup>-1</sup>)

Model	Parameters	RH+HCl			RH+H <sub>2</sub> SO <sub>4</sub>			RH+HNO <sub>3</sub>			RH+CA		
		1g/l	5g/l	10g/l	1g/l	5g/l	10g/l	1g/l	5g/l	10g/l	1g/l	5g/l	10g/l
Pseudo -first order	q <sub>e,exp</sub> (mg g <sup>-1</sup> )	34.442	9.17	4.792	29.64	6.616	4.264	34.516	8.18	6.404	21.71	5.35	3.032
	q <sub>e,cal</sub> (mg g <sup>-1</sup> )	16.669	4.76	1.21	12.27	3.096	1.760	18.096	3.57	3.077	12.19	3.29	1.298
	K <sub>1</sub> (min <sup>-1</sup> )	0.0011	0.0015	0.0017	0.002	0.009	0.007	0.0017	0.001	0.0009	0.002	0.01	0.008
	R <sup>2</sup>	0.7987	0.719	0.685	0.803	0.757	0.955	0.7460	0.846	0.8395	0.774	0.73	0.949
Pseudo -second order	Δq <sub>e</sub> (%)	14.312	13.86	20.732	16.25	14.22	16.29	13.194	18.79	14.406	14.62	10.3	14.76
	q <sub>e,cal</sub> (mg g <sup>-1</sup> )	25.060	6.991	4.263	25.99	6.539	4.286	27.036	6.473	4.498	16.39	5.27	3.046
	K <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	0.0035	0.0086	0.0453	0.003	0.013	0.017	0.0025	0.009	0.0196	0.005	0.009	0.022
	R <sup>2</sup>	0.9984	0.9978	0.9997	0.998	0.998	0.999	0.9981	0.998	0.9949	0.997	0.993	0.997
Elovich	Δq <sub>e</sub> (%)	7.555	6.851	3.06	3.413	0.314	0.143	6.01	6.977	8.253	8.171	0.382	0.115
	q <sub>e,cal</sub> (mg g <sup>-1</sup> )	24.483	6.792	4.334	26.30	6.726	4.335	27.067	6.442	4.374	16.27	4.915	2.940
	a(mg g <sup>-1</sup> min <sup>-1</sup> )	1.4×10 <sup>3</sup>	21.316	3.3×10 <sup>4</sup>	100.7	15.16	7.991	33.653	31.04	1.5×10 <sup>3</sup>	25.28	34.09	40.22
	b (g mg <sup>-1</sup> )	0.5306	1.447	4.205	0.382	1.406	2.129	0.325	1.599	3.41	0.556	2.178	3.894
	R <sup>2</sup>	0.9544	0.8307	0.9411	0.971	0.958	0.986	0.9509	0.989	0.9594	0.979	0.931	0.962
Δq <sub>e</sub> (%)	8.0198	7.478	2.65	3.129	0.444	0.459	5.985	7.102	8.791	8.351	2.174	0.781	

3.6 Characterization of Adsorbent Using FTIR After Adsorption Experiments

The effects of surface functional group on phenol adsorption were analyzed by observing the shifting of the FTIR peaks after the adsorption experiment. Figs. 6(a-d) and Tables 6-9, show the characterizing peaks of all the

adsorbents before and after phenol sorption for raw rice husk modified by 1M HCl, 13M H<sub>2</sub>SO<sub>4</sub>, 2M HNO<sub>3</sub> and 0.6M Citric acid, respectively. The FTIR spectra of acid modified rice husk show that shifting occurs at lower and higher wave numbers.

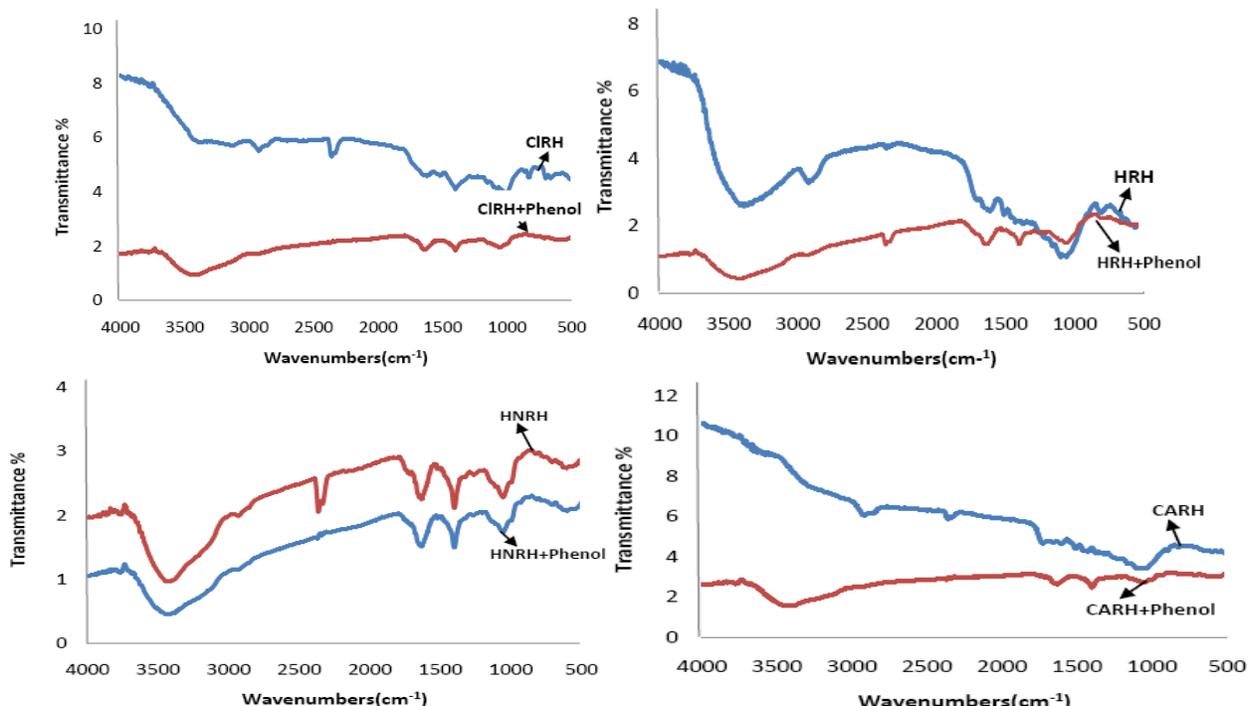


Figure 6. FTIR spectra of (a) RH+1M HCl (CIRH), (b) RH+13M H<sub>2</sub>SO<sub>4</sub> (HRH), (c) RH+2M HNO<sub>3</sub> (HNRH) and (d) RH+0.6M Citric acid (CARH) before and after phenol sorption

Table 6. FT-IR Spectra of RH+1M HCL Before and After Phenol Sorption

Adsorbent	SiOH,-OH	C-H	C≡C	C=O	Si-O-Si	Si-H
CIRH	3423.41	2923.88	2362.64	1630	1006.77	700.11
CIRH after Phenol sorption	3417.63	2925.81	2370.35	1633.59	1000.99	705.9

Table 7. FT-IR spectra of RH+13M H<sub>2</sub>SO<sub>4</sub> Before and After Phenol Sorption

Adsorbent	SiOH,-OH	C-H	C≡C	C=O	Si-O-Si	Si-H
HRH	3363.6	2920.03	2350.05	1608.52	1099.35	563.18
HRH after Phenol sorption	3408.9	2929.67	2364.57	1633.59	1101.28	561.25

Table 8. FT-IR spectra of RH+2M HNO<sub>3</sub> before and after phenol sorption

Adsorbent	SiOH,-OH	C-H	C≡C	C=O	C-O	Si-H
HNRH	3425.34	2931.6	2372.28	1743.53	1267.14	703.97
HNRH after Phenol sorption	3413.77	2929.67	2364.57	1737.74	1259.43	707.83

Table 9. FT-IR spectra of RH+0.6M Citric Acid Before and After Phenol Sorption

Adsorbent	SiOH,-OH	C-H	C≡C	C=O	Si-O-Si	Si-H
CARH	3272.98	2921.96	2360.71	1600.81	1093.56	898.77
CARH after Phenol sorption	3421.48	2931.6	2370.35	1618.17	1103.21	875.62

#### 4. Conclusions

The present investigation has shown that higher phenol removal efficiency can be obtained by using rice husk treated with either organic or inorganic acids compared to using raw rice husk. Acid treatment of raw rice husk removes the surface impurities such as silica and carboxylic compounds, which blocks reactive chemical groups at the surface of the rice husk. The adsorption of phenol is also found to increase by increasing the adsorbent dose and contact time.

A comparison between organic and inorganic acids shows that the removal efficiency of rice husk after treatment with organic acid (a weak acid) is less compared to that after treatment with inorganic acids (stronger acid). This is the result of the active sites produced by citric acid. In general, removal efficiency between 40.21-59.54%, 32.11-43.87%, 31.33-40.66% and 22.42-35.41% could be achieved after treating the rice husk with H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub> and citric acid, respectively; in comparison to the raw rice husk which is able to achieve 18.61-28.94% removal efficiency after 72hrs.

Although Elovich kinetic model gave a good fit of the experimental data, the pseudo-second-order model is the best model to describe the adsorption of phenol onto the surface of acid treated rice husk as the *R*<sup>2</sup> values were almost equal to unity. The FTIR analysis shows that the –OH, C–H, C≡C, C–C, C=O, –CO, Si–OH and –Si–H groups contribute to the adsorption of phenol onto the surface of adsorbent.

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