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Investigating the surface characteristics of chemically modified and unmodified rice husk ash; bottom-up approach for adsorptive removal of water contaminants

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ABSTRACT

Rice ash (RHA) can be found in many agricultural countries yet the material is not utilized in its full capacity. In this research, it is attempted to chemically modify RHA and to investigate the surface chemistry of the materials considering their potential use in the removal of pollutants from water. RHA is chemically modified using acetic acid to increase the presence of –COOH functional groups on the surface. Both RHA and modified rice husk ash (MRHA) are analyzed using Fourier transform infrared spectrometry, zero point charge (pH_{zpc}) analysis, zeta potential measurement, specific surface area, particle size measurements, and quantitative determination of –COOH, to determine the changes in surface. All the studies confirm the modification process and the amount of –COOH in MRHA increases by 0.104 meq/g compared to RHA. The pH_{zpc} is lowered from 8.3 to 6.5 after modification. Zeta potential is increased from −44.50 to −36.21 mV while the specific surface area is increased from 0.52 to 2.81 m^2/g. Adsorption studies using Cu^{2+} ions as the target pollutant show 99% removal efficiency after modification compared to 95% removal efficiency before modification in 3 h reaction period. The increment in sorption efficiency may be attributed to the changes in specific surface area, –COOH groups and $pH_{zpc.}$ Possibilities of simultaneous removal of different pollutants using a mixture of RHA and MRHA are discussed.

Keywords: Acetic acid; Adsorption; Chemical modification; Functional groups; Rice husk ash

1. Introduction

Rice husk ash (RHA) is an agricultural waste which is generally not used effectively as a resource material. While RHA is widely available in many parts of the world, including South Asian countries; lack of potable water due to contamination of water bodies is a rising issue. Since RHA is readily available virtually at no cost, researching on its applicability in water treatment is worthwhile. Use of RHA (or RHA derived materials) for water treatment have been

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researched and reported in literature. Heavy metals such as Cu(II), Cd(II), Ni(II), and Hg(II) as well as organic contaminants such as dyes are among the contaminants those have been removed by adsorption onto RHA derived materials [1–7].

Chemical modifications of rice husk (mainly RHA) create different surface functional groups in addition to the readily available functional groups, or increase the amount of readily available surface functional groups. By doing so, efficiency of the risk husk derived materials can be improved. Except few reported work on chemical modification of rice husk to develop adsorbents [8,9], most of the related work are based on physical activation processes.

While research on the contaminants which could potentially be removed using rice husk derived materials is important, it would be beneficial to understand the surface chemistry and surface properties of the material. Although the chemical content of rice husk and RHA has been researched mainly in connection with studies on extracting silica from rice husk, researches on analyzing its surface chemistry are limited. Such understanding is helpful in foreseeing contaminants those can be removed using rice husk/RHA.

This paper addresses the above limitations by chemically modifying the RHA to increase the surface functional groups. In addition, surface chemistry of RHA and chemically modified rice husk ash (MRHA) are investigated to verify the modification. Such investigations help in understanding the range of contaminants those can be removed using RHA and MRHA. Adsorption efficiency and involvement of functional groups of two materials are compared and discussed using Cu^{2+} as the target contaminant.

2. Materials and methods

2.1. Materials

Rice (*Oryza sativa*) husk was obtained from a rice mill located in Anuradhapura, Sri Lanka. Sodium hydroxide, hydrochloric acid, acetic acid, sodium perchlorate, potassium bromide, methylene blue (MB), and HEPES [N-2-Hydroxyethylpiperazine-N´-ethanesulphonic acid] were purchased from Fluka (Switzerland), Merck (Germany), or BDH (UK). All chemicals were of reagent grade.

2.2. Methods

2.2.1. Preparation of adsorbent

Rice husk was washed thoroughly and sun-dried for about 8 h. After sun drying, rice husk was burned at 500°C in a box furnace for 2 h to make the RHA. Chemical treatment of RHA was carried out using acetic acid. Acid treatment was conducted by reacting 30 ml of 1 M acetic acid [CH_3COOH] with 3 g of RHA at room temperature for 24 h with stirring using a magnetic stirrer. Then it was repeatedly washed with 50 ml of distilled water to obtain constant pH value. The pH value of the solution was determined by a digital pH-meter (ORION 2 STAR pH Bench top). Finally, the MRHA sample was dried at vacuum desiccator at 60°C until constant weight was obtained.

2.2.2. Characterization of sorbents

Both RHA and MRHA were characterized using Fourier transform infrared (FTIR) spectrometry (Nicolet 6700 FTIR), pH of zero point charge (pH_{zpc}), zeta potential (Zeta Meter 4.0, Zeta Meter Inc.), MB absorption method for determination of specific surface area, particle size of RHA using binocular microscope (ML2000, Meiji Techno), and Boehm titration method for quantifying the –COOH groups.

2.2.2.1. FTIR spectrometry. The functional groups present in the rice husk were characterized by a FTIR spectrometer. The disks of materials under investigation were prepared with KBr by using hydraulic pressure machine (Shimadzu) at 200 Pa. The spectral range was varied from 4,000 to 400 cm^{-1}. All the spectra were obtained under transmission mode, and were analyzed by OMNIC program.

2.2.2.2. Determination of pH_{zpc}. The pH_{zpc} was determined using the batch equilibrium method. A series of pH solutions from pH 2 to 12 were prepared by adding hydrochloric acid or sodium hydroxide. A quantity of 0.05 g of RHA and MRHA materials were suspended in 25 ml of prepared pH solutions in clean glass bottles. Solutions were then shaken at 200 rpm for 24 h. Final pH values were recorded. The procedure was repeated in pH solutions with 0.05 M sodium perchlorate (i.e. with ionic strength).

2.2.2.3. Determination of zeta potential. Zeta potential of RHA and MRHA [at pH 7] was determined using the Zeta-Meter. The pH was adjusted to 7 by mixing 0.25 g of sorbent, 1 g of NaCl, 1.1915 g of HEPES, 100 ml of distilled water, and small amount of 0.5 M NaOH.

2.2.2.4. Determination of specific surface area (MB method) and particle size. MB method was used in the determination of specific surface area [10]. A series of MB solutions were prepared with different concentrations and reacted with a known amount of material. At the end of the reaction period, solutions were kept for settling and supernatants were withdrawn carefully. Supernatants were later centrifuged and tested for the residual MB concentrations using an UV–vis spectrophotometer (Shimadzu, UV-2450). The point of complete cation replacement was determined using the plot of added MB vs. absorbed MB. Specific surface area was then calculated using the equation below.

$$S_S = \left(\frac{m_{\mathrm{MB}}}{319.87}\right) \cdot A_v \cdot A_{\mathrm{MB}} \cdot \left(\frac{1}{m_s}\right) \tag{1}$$

where S_S, specific surface area, m_{MB}, mass of the absorbed MB at the point of complete cation replacement, m_s, mass of the sample, A_v, Avogadro's number (6.022×10^{23} mol), A_{MB}, area covered by one MB molecule (assumed to be 130 Å^2).

The particle size of RHA was determined by the binocular microscope. The sorbent was mixed with distilled water, a slide was prepared and observed under ×40 magnification.

2.2.2.5. Quantitative determination of –COOH (Boehm titration method). The amount of –COOH containing RHA and MRHA was determined according to the Boehm titration method [11]. A weight of 0.20 g of RHA and MRHA were suspended in a 20 ml of 0.05 M sodium bicarbonate solution separately. All samples were shaken overnight. Subsequently, samples were filtered and filtrates were titrated for the residual base concentration using 1.0 M hydrochloric solution. The –COOH concentration was derived based on the assumption that $NaHCO_3$ neutralizes only carboxylic groups.

2.2.3. Adsorption study

2.2.3.1. Adsorption efficiency. Adsorption of Cu^{2+} ions onto RHA and MRHA was investigated. RHA and MRHA (0.25 g) were suspended in 25 ml of 0.0001 M $CuSO_4$ solution (solution pH was 6.3). Solutions were then shaken for different durations without adjusting pH. At the end of shaking, the solutions were filtered. Subsequently, the amount of copper ions in the filtrates was determined using an atomic adsorption spectrophotometer (AAS–GBC 933AA).

Percentage of adsorption of Cu^{2+} was then calculated using Eq. (2):

$$\mathrm{PA} = ((C_0 - C)/C_0) \times 100\% \tag{2}$$

where C and C_0 are concentrations of Cu^{2+} in the solution at $t = t$ and $t = 0$, respectively.

The functional groups present in the RHA and MRHA residue of filtrate were elucidated using FTIR. In order to prepare pellets, the ratio of KBr: sorbent was always kept at 100:1.

2.2.3.2. Adsorption kinetics. The reaction rate constant and reaction order of the Cu^{2+} ions on RHA and MRHA were studied using pseudo-first-order and pseudo-second-order models. First-order model can be represented in the following form [12]:

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}t \tag{3}$$

where q_e is mass of solute adsorbed at equilibrium (mg/g), q_t is mass of solute adsorbed at any time "t" (mg/g), and k is the pseudo-first-order rate constant (min^{-1}).

The pseudo-second-order model can be expressed as follows [13]:

$$\frac{t}{q_1} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{4}$$

where k is the pseudo-second-order rate constant (g/mg min).

The equation of the average deviation of adsorption is as follows:

$$\text{Average deviation of adsorption} = \frac{\sum\left[\frac{Q_{\mathrm{cal}} - Q_{\mathrm{exp}}}{Q_{\mathrm{exp}}}\right]}{n} \tag{5}$$

where n is number of experiments, Q_{cal} is observed mass of solute adsorbed at equilibrium (mg/g), Q_{exp} is calculated mass of solute adsorbed at equilibrium (mg/g).

2.2.3.3. Adsorption isotherms. Adsorption isotherms are important to understand the interaction of adsorbate with adsorbent, and to obtain the maximum adsorption capacities of adsorbent. Thus, two isotherm models, Freundlich and Langmuir were tested to determine the adsorption of metal ions on RHA and MRHA.

(1) The Freundlich isotherm model

The linear form of Freundlich isotherm equation is given as [12]:

$$\ln(q_{\mathrm{eq}}) = \ln(k_F) + \frac{1}{n}\ln(C_{\mathrm{eq}}) \tag{6}$$

where q_{eq} (mg/g) is equilibrium capacity of sorption, C_{eq} (mg/l) is equilibrium concentration of metal ions, k_F is a coefficient which provides an indication of the sorption capacity, and n is coefficient related to intensity of sorption.

It is assumed that sorption takes place onto a heterogeneous surface and the sorption sites are distributed exponentially with respect to heat of sorption, when Freundlich isotherm is used.

(2) The linear form of Langmuir isotherm is represented as [12]:

$$\frac{C_{\mathrm{eq}}}{q_{\mathrm{eq}}} = \frac{1}{q_{\max} b_L} + \frac{C_{\mathrm{eq}}}{q_{\max}} \tag{7}$$

where q_{eq} (mg/g) is equilibrium capacity of sorption, C_{eq} (mg/L) is equilibrium concentration of metal ions, $q_{\max}$ (mg/g) maximum monolayer sorption capacity, and b_L (L/mg) is the constant related to affinity and energy binding sites.

It is assumed that sorption takes place onto a homogeneous surface; all sites possess equal affinity for the adsorbate, when Langmuir isotherm is used.

3. Results and discussion

3.1. FTIR spectrometry

Fig. 1 shows FTIR spectra of RHA and MRHA. Both spectra have five major peaks, ranged between 4,000 and 400 cm^{-1}. RHA shows peaks at 3,443.7, 1,637.9, 1,094.4, 7,99.9, and 463.4 cm^{-1}. Similar results were reported elsewhere in the literature [14]. The broad and strong absorption peak at around 3443.7 cm^{-1} is attributed to OH group [15]. Functional groups of C=O, probably derived from carboxylate, creates the peak at 1,637.9 cm^{-1}. These two peaks indicate the presence of –COOH in RHA even prior to the modification process. The peak at 1,094.4 cm^{-1} represents OH group which is derived from deformation modes of alcohol or phenol, with a sterically hindered OH and also represents functional groups of Si–O–Si. The peak at around 463.4 cm^{-1} is also due to the simple hydroxyl compound while peaks at 799.9 and 463.4 cm^{-1} can be due to Si–H [16,17]. The intense peaks and bands at 3,443.7, 1,094.4, and 463.4 cm^{-1} are inherited as a special feature exhibited by RHA. It is exhibited as "free" OH groups, either on the surface, or embedded within a crystal lattice. Moreover, its interactions with other ions are free [16].

The above five peaks are slightly shifted to 3,447.9, 1,639.2, 1,093.1, 801.8, and 467.1 cm^{-1} after modification, possibly due to the surface modification occurred through acetic acid treatment. However, since –COOH is already present in RHA, distinguishing newly introduced –COOH groups is not possible through FTIR analysis due to the fact that the amount of materials used in the analysis are not the same. Further chemical analyses are needed to determine the actual changes that occur on the MRHA surface.

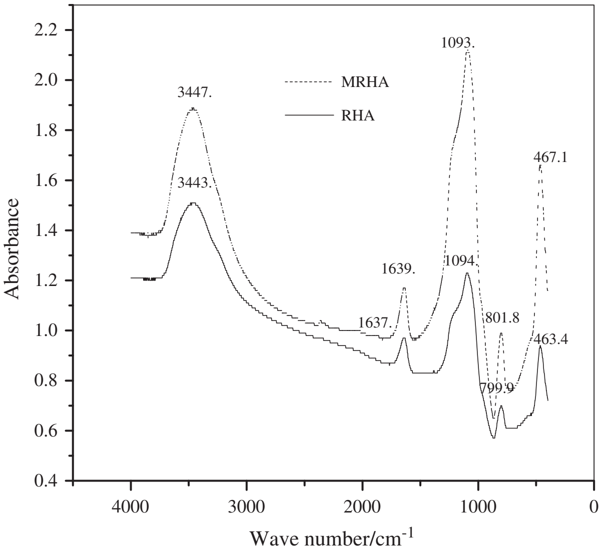

Fig. 1. FTIR spectra of RHA and MRHA.

3.2. pH of zero point charge

The pH$_{\mathrm{zpc}}$ describes the pH where electrical charge of a particle's surface is zero. At pH values larger than the pH$_{\mathrm{zpc}}$, particle tends to carry negative charge. At pH values lower than the pH$_{\mathrm{zpc}}$, particle carries positive charge. Depend on the charge of the surface, particles may remove different pollutants at the same pH. As such, determination of pH$_{\mathrm{zpc}}$ is important in understanding the pollutants those can be removed using a certain material. In addition, deviation in pH$_{\mathrm{zpc}}$ reveals the success of the modification process.

In this study, pH$_{\mathrm{zpc}}$ of both materials were investigated in two different electrolytes; i.e. with and without ionic strength. Fig. 2(a) and (b) shows the pH$_{\mathrm{zpc}}$ of RHA and MRHA without ionic strength and with ionic strength, respectively. Without introducing ionic strength, pH$_{\mathrm{zpc}}$ of RHA is found to be 8.3. For RHA, pH$_{\mathrm{zpc}}$ of 8.5 is reported elsewhere [2]. In MRHA, this value is changed to 6.5. However, introduction of ionic strength does not change the pH$_{\mathrm{zpc}}$ of materials significantly. Therefore, it can be seen that the pH$_{\mathrm{zpc}}$ turns acidic after the modification. Similar results were reported elsewhere in literature [18].

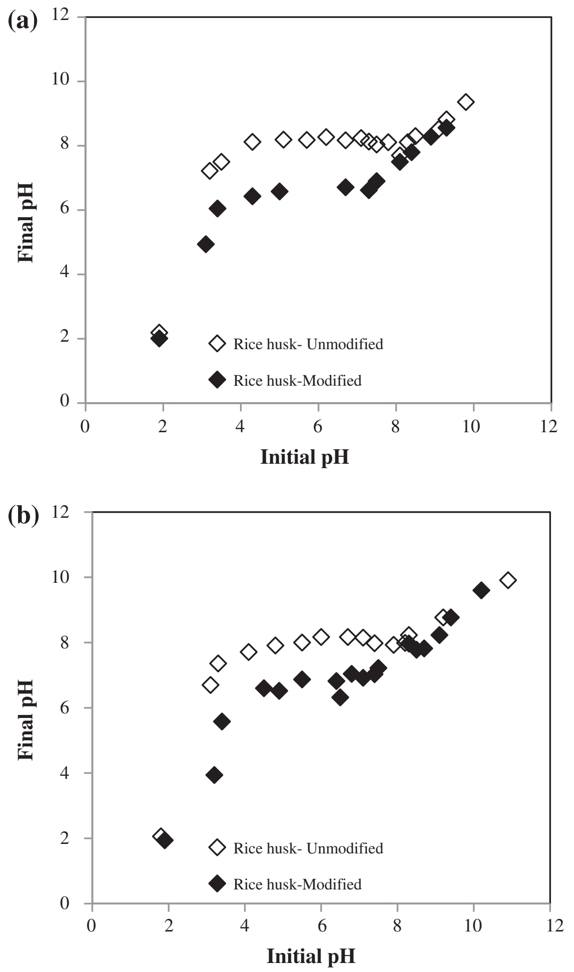

Fig. 2. pH_{zpc} of RHA and MRHA. (a) pH_{zpc} without introducing background ionic strength to the electrolyte solutions. pH_{zpc} of RHA = 8.3, pH_{zpc} of MRHA = 6.5. (b) pH_{zpc} with background ionic strength (0.05 M, $NaClO_4$) to the electrolyte solutions. pH_{zpc} of RHA = 8.3, pH_{zpc} of MRHA = 6.7.

The above discussion reveals that, based on obtained pH_{zpc} values, at neutral pH, surface of RHA is positively charged, while surface of MRHA is negatively charged. Thus, at neutral pH, RHA can be effective in removing negatively charged pollutants and MRHA can be effective in removing positively charged pollutants. This characteristic is very important in contaminant removal from natural waters. For example, RHA and MRHA can be combined in a single reactor to simultaneously remove different types of pollutants. In addition, reduction in pH_{zpc} provides strong evidence about the success of chemical modification.

The reactions which exist during acetic acid treatment of RHA can be depicted as in Fig. 3.

3.3. Zeta potential

When particles are suspended in water, within the diffuse layer, a hypothetical boundary can be defined where the particles and ions form a stable entity. The potential of this hypothetical boundary is known as the zeta potential. While zeta potential provides indications about particle stability, change in the zeta potential after a chemical modification provides strong evidence about the success of modification process.

In this study, zeta potentials of RHA and MRHA were determined at pH 7. The particle movement was observed through a microscope and the time taken for a particle to travel a particular distance was measured at 40 V. To minimize the error, a minimum of five particles were tracked and their average time was calculated. Results of zeta potential study are shown in Table 1. As can be seen from the table, zeta potential of RHA is −44.50 mV, while that of MRHA is −36.21 mV, which is a more positive value compared to RHA. Similar results are reported elsewhere (zeta potential—an introduction in 30 min). On the other hand, zeta potential is increased by 8.29 mV after chemical modification, indicating a successful chemical modification process. Moreover, addition of –COOH functional groups on to the surface of RHA makes the surface more negative. Subsequently, this negative surface attracts more positive ions from the surrounding water making the zeta potential more positive.

Besides, zeta potential values more negative than −30 mV in both materials indicate stable particle dispersion. This characteristic is important since the total surface area of particles can be used due to less agglomeration. Designing a reactor consisting of a suspended bed of these particles would increase the efficiency of adsorption.

3.4. Specific surface area and particle size

Specific surface area of the RHA and MRHA was determined using the MB method. MB ($C_{16}H_{18}ClN_3S$) forms a cationic dye ($C_{16}H_{18}N_3S^+$) in aqueous solutions and thus it can be absorbed onto negatively charged surfaces. Based on the assumption that MB molecule lies on its largest surface on the material under investigation covering 130 $\mathring{A}^2$, specific surface area of negatively charged surfaces can be determined [10].

Using Eq. (1) and based on the above assumptions, specific surface area of RHA and MRHA was found as 0.52 and 2.81 m^2/g, respectively. It is clear that the specific surface area is increased by more than five times after the chemical modification. This may be

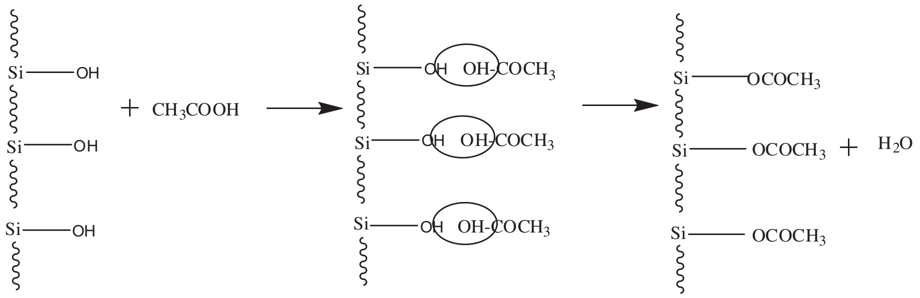

Fig. 3. Schematic diagram after acetic acid treatment of RHA.

Table 1
Zeta potential values of RHA and MRHA

Material	pH of background solution	Temperature, ℃	Zeta potential, mV
RHA	7	25	−44.50
MRHA	7	25	−36.21

due to the opening up of the pores of RHA after modification using the acid. Such increment indirectly shows the increment in surface negativity as a result of adding more –COOH groups to the surface. Increased surface area is beneficial in practical water treatment applications.

Particle size of RHA was determined using the binocular microscope. It was found that the particle size of RHA is in the range of 50–100 μm (see Fig. 4 for details).

3.5. Quantitative determination of –COOH

Boehm titration method was used in quantifying the amount of –COOH groups present in RHA and MRHA. It was found that RHA contained 2.384 meq/g of –COOH. This amount has increased to 2.488 meq/g after the modification. Thus, it can be said that the modification process is successful. Data reported by Makehelwala et al. [11] reveals the amount of –COOH present in coir pith as 0.35 meq/g. While similar studies are not found in literature for RHA, above value shows lower amount of –COOH groups on coir pith compared to RHA and MRHA. Increase in –COOH groups on the surface contributes to the reduction in pH_{zpc}, increment in zeta potential and increment in specific surface area of MRHA. Based on the above findings, it is speculated that MRHA can be more effective in removing positively charged pollutants at neutral pH. Under the similar conditions, RHA can be more effective in removing negatively charged pollutants.

3.6. Adsorption study

3.6.1. Adsorption efficiency

The adsorption study was performed and the results are shown in Fig. 5. Both materials achieved the maximum removal efficiencies within 3 h of contact time. However, the maximum removal efficiency of MRHA was as high as 99%, while that of RHA was 95%. The lower adsorption efficiency of RHA may be due to two related reasons. Firstly, the higher amount of –COOH groups on MRHA provides more binding sites for sorption of Cu^{2+} ions. Secondly, at the initial pH of 6.3, surface of RHA is more positively charged

Fig. 4. Binocular micrograph of RHA (magnification: ×40).

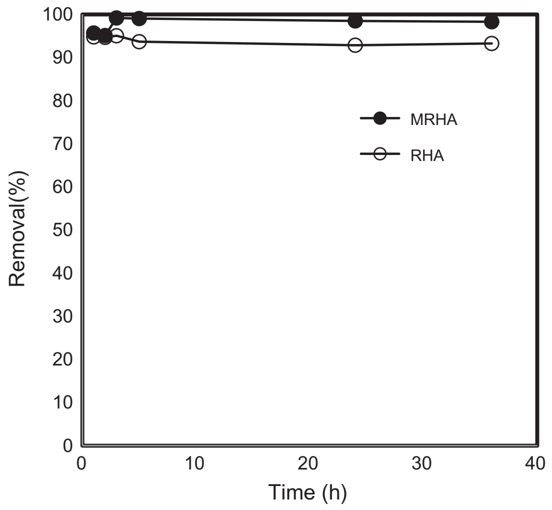

Fig. 5. Adsorptive removal of Cu^{2+} on RHA and MRHA.

compared to the surface of MRHA, providing higher repulsion to Cu^{2+} ions.

3.6.2. Adsorption kinetic study

The two different kinetic models were used to investigate the order and rate of adsorption of Cu^{2+} ions by RHA and MRHA at room temperature and the results are shown in Table 2. It is clear that the pseudo-second-order model explains the adsorption behavior better than the pseudo-first-order model. Therefore, the pseudo-second-order rate constants (k) were calculated for both RHA and MRHA. To further judge the applicability of models, the average deviation of adsorption for the different time values are listed in Table 3. The rate constant (k) obtained from the slope of the $\frac{t}{q_t}$ vs. t plot (Fig. 6) for RHA and MRHA are 0.22 and 25.12 mg/g min, respectively. It implies that Cu^{2+} ions adsorption has occurred at a higher rate after modification of RHA.

It is suggested that the adsorption of Cu^{2+} ions on the surface of RHA and MRHA is based on chemisorption process or metal complexation process, due to the applicability of pseudo-second-order model to this system [12,19]. Formation of complex between the metal ion and silanol group present at the surface of silica is the most favorable mechanism. The silanol group is formed by the hydrolysis of silicon dioxide. The equation is represented as follows [12,20]:

$$x(-SiOH) \rightarrow x(-SiO^-) + xH^+ \tag{8}$$

$$Cu^{2+} + x(-SiO^-) \rightarrow Cu(-SiO)_x^{(2-x)+} \tag{9}$$

Table 2
Regression coefficients (R^2) and adsorption kinetic constant (k) of RHA and MRHA

Material	RHA	MRHA
First-order R^2	0.937	0.012
Second-order R^2	0.998	0.962
k	0.22	25.12

Table 3
The average deviation of adsorption amount of adsorption of RHA and MRHA

Material	Average deviation of adsorption
RHA	0.068
MRHA	2.879

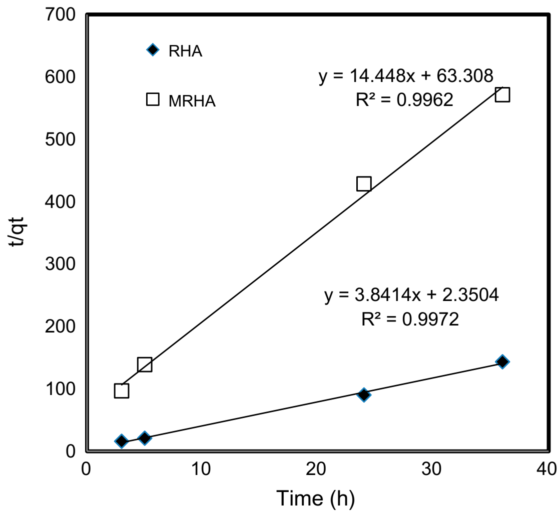

Fig. 6. Pseudo-second-order kinetic for the removal of Cu^{2+} on RHA and MRHA.

Thus, the net reaction can be represented as:

$$Cu^{2+} + x(-SiOH) \rightarrow Cu(-SiO)_x^{(2-x)+} + xH^+ \tag{10}$$

3.6.3. Isotherm study

Linear plots of the Freundlich and Langmuir models for adsorption of Cu(II) on RHA and MRHA are shown in Fig. 7(a, b) and isotherm constants and other relevant parameters are presented in Table 4. It is found that the Langmuir isotherm model best fitted the experimental results for adsorption of Cu(II) on both RHA and MRHA than Freundlich model with correlation coefficient (R^2) 0.993 and 0.991, respectively. This finding reveals the monolayer adsorption of Cu(II) ions on both adsorbents. The similar outcome was reported by Hsu and Pan [21].

The maximum sorption capacities, $q_{\max}$, of Cu(II) RHA and MRHA are 1.22 and 3.83 mg/g, respectively. Thus, adsorption capacity is three times higher in MRHA than RHA. These results reveal that modifying the RHA markedly increases the adsorption capacity to adsorb Cu(II).

Table 4
Freundlich and Langmuir isotherms parameters and correlation coefficients

Isotherm model	RHA	MRHA
Freundlich model		
R^2	0.005	0.027
Langmuir model		
R^2	0.993	0.991
$q_{\max}$	1.22 mg/g	3.83 mg/g

3.6.4. FTIR study

The goal of this study was to quantitatively delineate the changes of functional groups before and after adsorption of Cu^{2+} ions. For that, pellets were made by mixing equal ratio of KBr and sorbent materials. Fig. 8(a, b) and Table 5 reveal the changes in the absorption peaks of the surface functional groups of RHA and MRHA after Cu^{2+} adsorption onto the surface of the sorbent within 1 and 3 h. Since hydroxyl

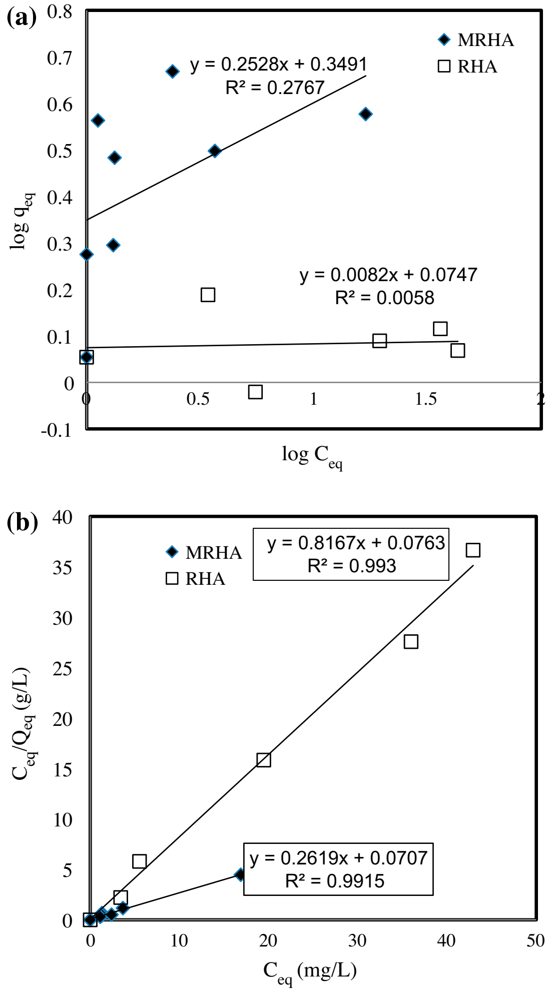

Fig. 7. Adsorption of Cu(II) ions by RHA and MRHA. (a) Freundlich isotherm model and (b) Langmuir isotherm model. Adsorbent dosage = 10 g/l, contact time = 36 h.

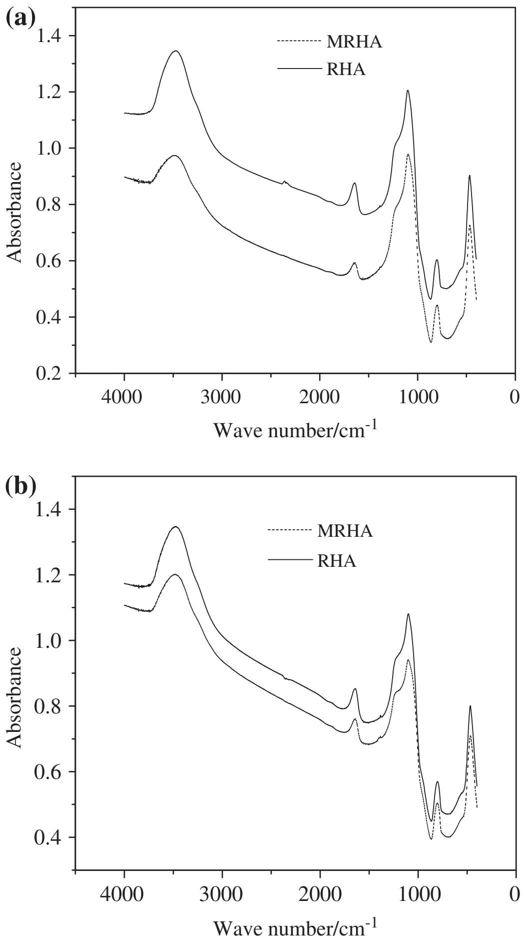

Fig. 8. FTIR spectra of MRHA residue after adsorption study at (a) 1 h and (b) 3 h (the ratio of KBr: sorbent = 100:1).

Table 5
Peaks values of FTIR spectra of residue at 1 and 3 h after adsorption

	RHA		MRHA	
Reaction time, h	Wave number, cm^{-1}	Absorbance	Wave number, cm^{-1}	Absorbance
1	3473.6	1.346	3483.3	0.974
	1643.5	0.872	1638.0	0.592
	1100.6	1.204	1097.4	0.976
	803.2	0.604	800.7	0.440
	466.4	0.901	466.9	0.727
3	3483.0	1.345	3475.4	1.200
	1641.8	0.850	1641.1	0.760
	1100.5	1.079	1101.8	0.939
	803.6	0.568	803.3	0.503
	467.2	0.797	465.7	0.709

(–OH) groups are already present in RHA, distinguishing the changes of –OH groups are identified through differences in peak heights (please note that for this study the amount of materials used were kept the same). Following FTIR spectra, (Fig. 8(a) and (b)) show that –OH groups of RHA have higher absorbance than MRHA. Moreover, MRHA has narrower peaks than RHA. This may be attributed to the fact that more –OH groups on MRHA are attached with Cu^{2+} ions, providing higher efficiency in adsorption.

Table 5 shows that –OH group of MRHA at 1 h has lower absorbance than 3 h after the process of adsorption. It indicates that more –OH groups on MRHA are attached with Cu^{2+} ions at maximum removal efficiency than initial stage of adsorption. This data provides strong evidence about the success of the absorption study. Comparisons between RHA and MRHA (Fig. 8(a) and (b) and Table 5) show minor shifts in the wave numbers of hydroxyl groups indicating the involvement of –OH groups in the process of adsorption.

4. Conclusions

The main aim of this study was to investigate the surface chemistry and properties of RHA and MRHA. Such investigation would help understanding the range of contaminants those can be removed using two materials. In addition, adsorption efficiency and involvement of functional groups of two materials were compared using Cu^{2+} as the target contaminant.

In order to accomplish this main aim, firstly, the surface of RHA was modified with acetic acid. Modification was confirmed by several characterization processes. The FTIR spectrum of MRHA was shifted from the FTIR spectrum of RHA confirming the surface modification on RHA. Analysis of FTIR showed the presence of –COOH functional group on both RHA and MRHA.

The pH_{zpc} of RHA and MRHA were found as 8.3 and 6.5, respectively. No significant impact on pH_{zpc} value was found by changing the ionic strength. These results confirmed the modification process and showed the possibility of simultaneous removal of different contaminants if the two materials are mixed together. Moreover, zeta potential of RHA and MRHA were found as −44.50 and −36.21 mV, respectively, indicating an increment of 8.29 mV. This finding further confirmed the modification process and provided important data on surface chemistry of RHA and MRHA. The MB method showed that the specific surface area of RHA increased from 0.52 to 2.81 m^2/g after modification. Boehm titration showed that the amount of –COOH has increased by 0.104 meq/g after the modification. RHA showed a 95% removal of Cu^{2+} ions within a reaction time of 3 h. MRHA further increased the removal efficiency to 99% in 3 h, indicating the effects of increase in surface area, increase in –COOH functional groups and reduction in pH_{zpc} after chemical modification. The results show that adsorption of Cu^{2+} ions on both RHA and MRHA have followed pseudo-second-order kinetics. Involvement of –COOH in removal of Cu^{2+} ions was confirmed through FTIR analysis.

With this remarkable characteristic, RHA, a waste product in agricultural countries can be proposed as an excellent alternative for removing contaminants from water. In addition, chemical modification process proposed in this study increases the range of contaminants those can be removed using RHA through changing the surface chemistry of RHA.

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