

Adsorption of Sulfur Dioxide (SO₂) Gas Using Treated Rice Husk Ash (RHA) Adsorbent

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ABSTRACT

The aim of this study was to investigate the potential of treated rice husk ash (RHA) as adsorbent to adsorb acidic SO₂ gas. The treated RHA was prepared using a water hydration method by mixing the RHA, Calcium oxide (CaO) and Sodium Hydroxide (NaOH). The addition of NaOH is to increase the dissolution of silica from the RHA to form reactive species responsible for higher desulfurization activity. The untreated and treated RHA were subjected to several characterizations and the characteristics of the adsorbents were compared. The functional groups present on the surface of the adsorbent were determined using Fourier Transform Infrared (FTIR). The chemical composition of the untreated and treated RHA was analyzed by using X-ray Fluorescence (XRF). Scanning electron microscope (SEM) analysis showed that the treated RHA has higher porosity compared to untreated RHA. Based on the SO₂ adsorption analysis, it was found that the treated RHA has higher adsorption capacity, 62.22 mg/g, compared to untreated RHA, 1.49 mg/g.

Keywords: rice husk ash, adsorbent, water hydration method, desulfurization, silica

INTRODUCTION

Air pollution is one of the phenomena that emerged due to the rapid development of the industrial activities and substantial population. The major concern of the air pollutants is the gases emitted from several industrial and production units which consist of sulfur-containing toxic gases such as SO_2 , hydrogen sulphide (H_2S), carbon disulphide and several organosulfur compounds [1]. Introduction of these sulfur-containing toxic gases to the environment will impact the quality of the environment badly. Hence, these industrial gases need to be desulfurized effectively before mixing with the environment. Many of removal methods have been developed such as wet flue gas desulfurization and dry injection desulfurization to reduce emissions of SO_2 from the flue gas. Wet-type flue gas desulfurization (FGD) technology such as lime-limestone scrubbers are extremely efficient but require large capital investment and also the production of sludge that must be disposed [2]. Therefore, dry FGD techniques would be a better option as the techniques is a way cheaper, simpler and the solid wastes generated from dry FGD techniques do not require the handling of the corrosive liquid generated like wet-type FGD [3]. Researchers recently have attracted in producing various types of dry calcium-based adsorbents having high SO_2 adsorption [4].

In order to synthesize calcium-based sorbents having a high SO_2 adsorption activity, the raw material consisting of silica needs to be activated with calcium oxide (CaO) or calcium hydroxide $\text{Ca}(\text{OH})_2$ [4]. Most of the siliceous materials reported in previous studies like coal fly ash [5], iron blast furnace slag [6], oil palm ash [7] and silica fumes [8] were reactive towards SO_2 adsorption. Coal fly ash which primarily composed of silica (SiO_2) and alumina (Al_2O_3) for instance, is a pozzolan by which in the presence of water can react with Ca-based compounds to produce calcium silicate hydrate [9]. These pozzolanic products generally are highly amorphous and have a comparably high surface area which can improve the adsorption capacity of the adsorbent [9]. A study by Keat et al. [10] has shown that higher SO_2 removal associates with higher specific surface area while Dahlan et al. [4] and Dahlan et al. [9] reported that the content of silica in the siliceous materials used to prepare the adsorbent was closely corresponding to the activity of SO_2 adsorption.

The rice husk ash (RHA) can be utilized as a source of siliceous material to synthesize adsorbent for FGD due to the high content of silica in RHA which ranges from 60-90 % [11]. In Malaysia, approximately 78 thousand tons of RHA are produced per annum [4]. Previously, RHA has been utilized in diversified applications. For instance, to remove colour such as Methylene blue [12], Crystal violet [13] and Indigo carmine [14] from liquid phase. RHA also has been used to remove heavy metals such as Pb(II) [13] and Cd(II) [15] and currently to remove antibiotics Tetracycline [16]. Besides that, the used of RHA to remove air pollutants was reported by Dahlan et al. [17]. Generally, most of the studies that were conducted by using RHA as an adsorbent often results in a good adsorption capacity in removing the pollutants. However, most of the application of RHA still remains on a laboratory scale. Therefore, a huge amount of RHA has to be disposed of, either in landfills or ash ponds [4]. Synthesis of the adsorbent from this agricultural waste material would display an attractive use of RHA for capturing SO₂ from flue gases [4]. This would help to reduce ash disposal problem and at the same time, converting a waste into a value-added product in which would bring economic benefits [18]. In this study, RHA was used as a potential adsorbent to adsorb SO₂ acidic gases. The RHA adsorbents were characterized to study the chemical composition, functional groups and surface morphology of the RHA that have high activity towards removal of SO₂.

EXPERIMENTAL

Preparation of the RHA adsorbent

The RHA was provided by Globecycle Manufacturing Sdn. Bhd. located in Padang Meha Kulim, Kedah. The RHA adsorbent was collected directly after the burning of rice husk without any pretreatment. Prior to use, the RHA was sieved to obtain ash with particle size of less than 250 µm.

The treated adsorbent was prepared using the water hydration method adopted from a study conducted by Dahlan et al. [9]. About 6.0 ± 0.1 g of CaO (Bendosen Laboratory Chemicals) was added into a 250 mL conical flask containing 100 mL deionized water and 10 mL of 0.25 M NaOH (Riendemann Shmidt Chemical).

Then, the conical flask containing the mixture was inserted into a water bath shaker at 338 K with a stirring rate of 180 rpm for 10 minutes. Upon stirring, 15.0 ± 0.1 g of the RHA was added into the slurry. The resulting slurry was heated at 338 K for 4 h of hydration period at 180 rpm. After that, the slurry was filtered and dried at 423 K for 2 h. The dried adsorbent was then crushed and sieved to obtain the particle size of less than 250 μm . The adsorbent was stored in an air tight container before using it for characterization and SO_2 adsorption analysis. This adsorbent was denoted as treated RHA.

Chemical and physical analyses

Functional groups of the RHA were characterized using a Fourier Transform Infrared (FTIR) spectrometer (Thermo Scientific Nicolet 6700 FT-IR spectrometer with ATR attached) observed under range between 4000-650 cm^{-1} . The chemical composition of the RHA was determined by using Epsilon 3 XL X-ray Fluorescence (XRF) spectrometer with a silicon drift detector. The maximum voltage supplied was 50 kV with maximum current of 3 mA. X-ray diffraction (XRD) spectra were recorded on a PANalytical X'Pert PRO, equipped with Cu $K\alpha$ radiation, $\lambda = 0.154$ nm with a step size of 0.05° from 10 to 90° (high angle) to determine the phase present in the RHA. The maximum voltage supplied was 60 kV with maximum current of 60 mA. The surface morphology of the RHA was examined using Hitachi TM3030Plus Scanning Electron Microscope (SEM) with an acceleration voltage of 5 kV and magnification of 3000x.

SO_2 adsorption analysis

SO_2 removal analysis was adopted from a study conducted by Lau et al. [3]. The desulfurization analysis was carried out in a fixed-bed reactor attached to an experimental rig. About 1.0 ± 0.1 g of the untreated RHA supported by 0.30 g glass wool was placed in a 25 mm inner diameter stainless steel tube. Then, the tube was fitted in a column and the column was inserted inside the reactor. After that, a flowing air containing SO_2 gas (1000 mg/L) at a rate of 500 mL/min was then initiated to flow pass through the adsorbent at a reaction temperature of 360 K.

The outlet gas was analysed continuously by Ultramat 23 Gas Analyzer to measure the concentration of the SO₂ in the flue gas. The same method was applied for treated RHA. Breakthrough curves for the untreated and treated RHA were plotted and the adsorption capacity of SO₂ for each of the adsorbent was calculated using Eq. (1):

$$q = \frac{(F c_0 t - \int F c dt) M}{V_m m} \quad (1)$$

Where,

F is the flow rate (L/min)

c_0 is the SO₂ concentration of the feed stream

t is the breakthrough time (min), c is the detected SO₂ concentration

M is the molar weight of SO₂ (64 g/mol)

v_m is the molar volume (assumed to be 22.4 L/mol)

m is the mass of the used adsorbent (g).

RESULTS AND DISCUSSION

Characterization of the RHA

FTIR analysis

The functional groups responsible for the adsorption of SO₂ were identified by FTIR spectroscopy. The intensities of infrared bands showed some changes in the spectra obtained for untreated and treated RHA. Figure 1 shows the FTIR spectra of the untreated and treated RHA. The region between 3750.26 cm⁻¹ and 3646.97 cm⁻¹ in untreated RHA is related to the ν OH vibration of silanol groups. After hydration process, the peak was shifted to 3639.78 cm⁻¹ indicating that the hydroxyl group probably involved in the formation of a hydrogen bond with CaO. Meanwhile, the hydroxyl characterized by the band at 3750.26 cm⁻¹ do not participate in the formation of the hydrogen bond with CaO as there was no significant change of the frequency between the treated and treated RHA. In addition, it was reported by Yu et al. [19] that the vibration of hydroxyls group in portlandite is at ~3644 cm⁻¹ which is the same as the IR spectrum obtained in this study.

The peaks observed at 1031.59 cm^{-1} and 1516.34 cm^{-1} were assigned to the siloxane group in the form of $-\text{Si-O-Si-OH}$ and $-\text{C=O}$ and $-\text{C-OH}$ groups stretching from aldehydes and ketones respectively. The peak at 1417.47 cm^{-1} corresponds to the asymmetric stretching of CO_3^{2-} and weak shoulder at 872.09 cm^{-1} due to the out-of-plane bending at CO_3^{2-} . The intensity of the peak at 1031.59 cm^{-1} was considerably decreased to 963.68 cm^{-1} suggesting a progressively decreasing concentration of Si-OH group. The presence of polar groups on the surface of is likely to provide a considerable ion exchange capacity to the adsorbents [18].

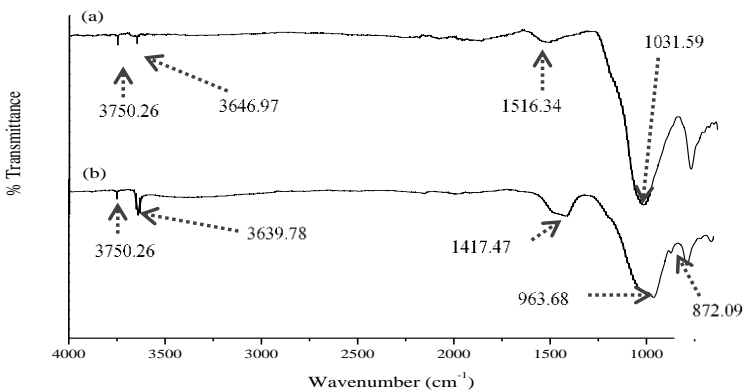


Figure 1: FTIR spectra of (a) Untreated RHA (b) Treated RHA

XRF analysis

The composition of the untreated and treated RHA obtained by XRF is shown in Table 1.

Table 1: Chemical composition of untreated and treated RHA

| Compound | Percentage (%) | |
|--------------------------------|----------------|-------------|
| | Untreated RHA | Treated RHA |
| Al ₂ O ₃ | 0.70 | 0.29 |
| SiO ₂ | 96.33 | 74.51 |
| CaO | 0.22 | 12.95 |
| MgO | 0.05 | 0.09 |
| Others | 2.70 | 12.16 |

Others: K₂O, Fe₂O₃

Based on the XRF result obtained for the untreated RHA, the major components in RHA are silica (SiO_2) and alumina (Al_2O_3). The composition of the SiO_2 and Al_2O_3 were found to reduce in treated RHA. During hydration process, SiO_2 contained in the RHA will be eluting from the RHA thus leading to the reduction in the chemical composition of SiO_2 in treated RHA.

RHA had the oxides of K, Fe and Mg which can influence the reaction of the adsorbent with SO_2 . These oxides were found to increase after the treatment of the RHA. Oxides of K would result in the formation of KOH which reacts with SO_2 to form sulphite salts reducing SO_2 from the flue gas [20]. Meanwhile, the oxides of Fe and Mg are expected to provide the catalytic ability to enhance the desulfurization reaction between Ca in the adsorbents and SO_2 [20].

XRD analysis

The phase present in the untreated and treated RHA were determined using XRD and the spectra were shown in Figure 2 (a) and (b). The SiO_2 (cristobalite) was the only compound detected in untreated RHA. The result agrees well with the XRF findings which indicate that SiO_2 was the major components in the untreated RHA. The XRD diffraction peaks of untreated RHA corresponding to SiO_2 were at $2\theta = 21.9^\circ, 28.4^\circ, 31.3^\circ, 36.1^\circ, 48.4^\circ$ and 56.9° . The main phases identified by the XRD of treated RHA were SiO_2 ($2\theta=22.4^\circ, 42.8^\circ, 43^\circ$) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) or portlandite at $2\theta=18.2^\circ, 34.4^\circ, 83.9^\circ$. The presence of portlandite in this XRD analysis was consistent with FTIR result for treated RHA.

It was found that there was a significant change of the intensity of SiO_2 (cristobalite) peaks observed for the treated RHA when comparing both the XRD patterns. The intensity of the amorphous silica in untreated RHA greatly reduced from 3500 to 600 in the treated RHA. The reduction of the intensity was about 82.9 %. According to Jung, et al. [21], the lower the intensity of the peak, the more amorphous is the product. In addition, Dahlan, et al. [9].reported that the reduction in the intensity of the peaks indicates that the amorphous silica has reacted to form highly amorphous compounds that cannot be detected by XRD.

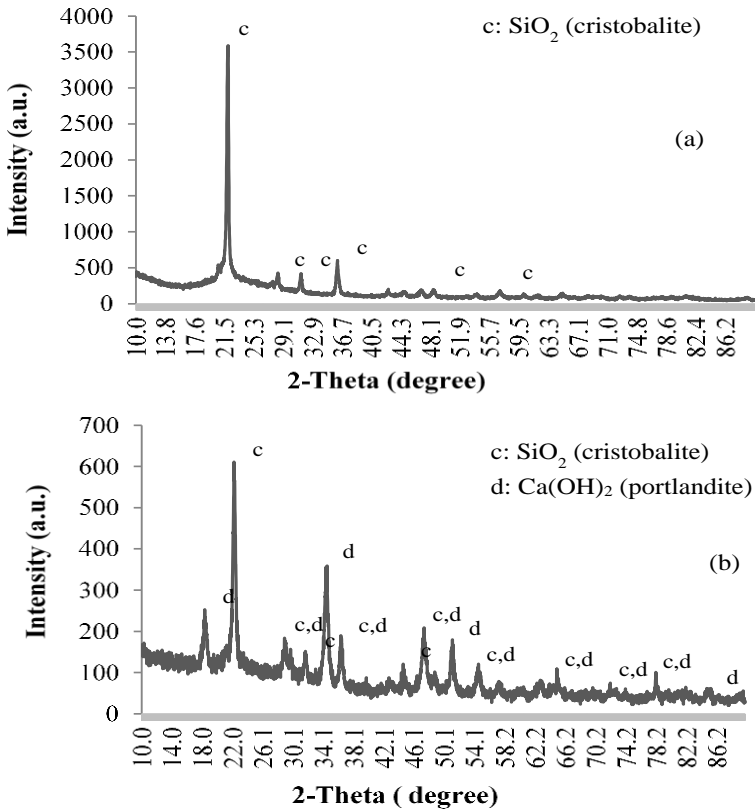


Figure 2: XRD pattern for (a) untreated RHA (b) treated RHA

SEM analysis

The morphological differences between the untreated and treated RHA were observed by SEM and presented in Figure 3 (a) and (b). These images reveal the surface texture and porosity of the untreated and treated RHA. It was observed that the untreated RHA had less porous structure, smooth surface with many small granular particles attached to the surface. However, after hydration process, more porous structure has been developed on the surface of the adsorbent and the particles. According to Lee et al. [22], during the hydration process, silica and/ or alumina will elute from the ash to react with CaO to form calcium aluminum silicate hydrate compounds and thus have a positive effect on the adsorbent surface area leading to higher porous structure compared to the untreated RHA.

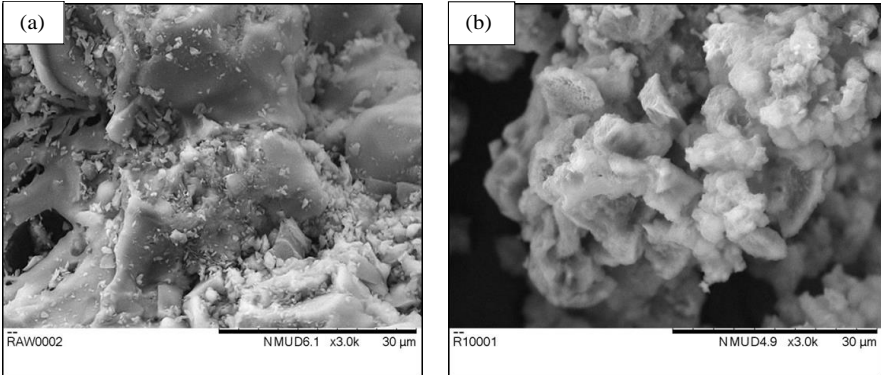


Figure 3: SEM micrograph for (a) Untreated RHA (b) Treated RHA

Characterization of the RHA SO₂ adsorption analysis

Breakthrough curves analysis

The untreated and treated RHA were subjected to desulfurization analysis at reaction temperature 360 K. The breakthrough curves of the adsorbents were shown in Figure 4 in terms of dimensionless concentration of SO₂ versus time.

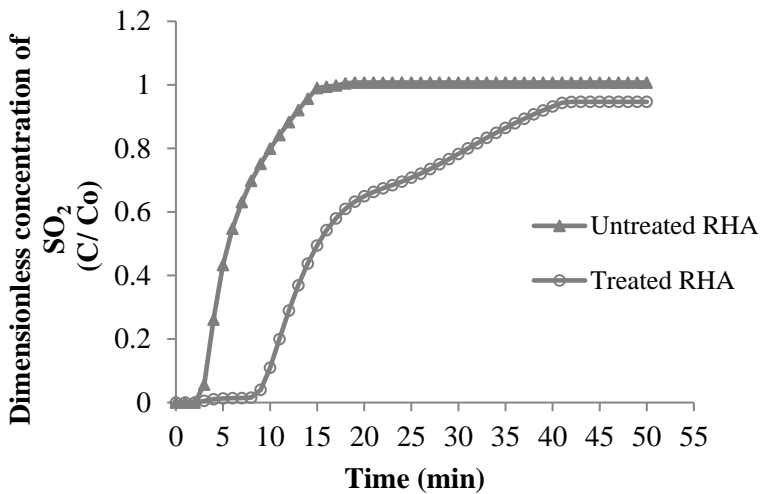


Figure 4: Breakthrough curves for untreated and treated RHA

In Figure 4, the untreated RHA had very low desulfurization activity as they could maintain 100% removal of SO₂ from the feed gas for only the first 2 minutes. Conversely, treated RHA exhibited higher desulfurization activity compared to the untreated RHA as it could completely remove SO₂ from the feed gas for the first 8 minutes. Beyond 8 minutes of reaction time, the concentration of SO₂ gradually increased until there was no more SO₂ adsorption activity in the adsorbent. This is when the concentration of SO₂ from the reactor is the same as the inlet concentration.

Adsorption capacity of the RHA

The SO₂ adsorption capacity of the adsorbent is expressed by the weight of the SO₂ captured from the flue gas per gram adsorbent. The SO₂ adsorption capacity of the untreated and treated RHA was 1.49 mg/g and 62.22 mg/g, respectively. It was found that after the treatment of the RHA, the SO₂ adsorption capacity of the treated RHA was greatly enhanced (see Figure 5). Higher reactivity towards SO₂ attributed to the presence of active species on the adsorbents. Hydration process with addition of NaOH promote higher dissolution rate of silica to form more reactive species that enhance the adsorbent activity. The increased of the adsorption capacity of the RHA after the treatment was due to the presence of Si-OH groups that can interact in different way and are responsible for adsorption properties [23]. In opposition to this, Lee, et al. [22] believed that the active species in the sorbents that reacts with SO₂ is the calcium (Ca) ions only and the role of the high surface area hydrated compound is basically to make the Ca ions contained in the adsorbent more accessible to SO₂ during the desulfurization reaction.

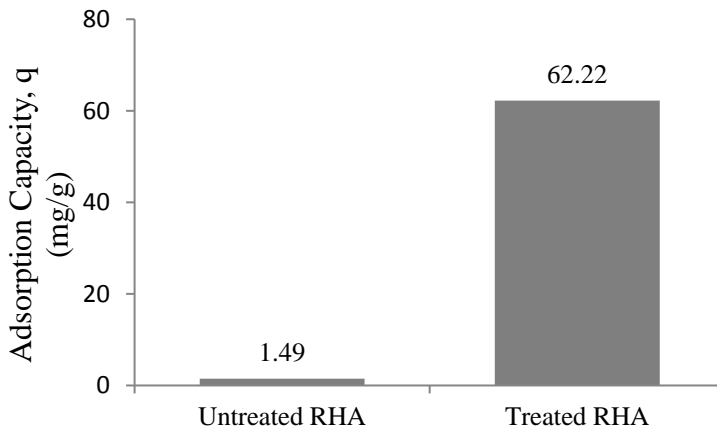


Figure 5: Adsorption capacity of the untreated and treated RHA

CONCLUSION

The RHA was treated with CaO and NaOH to improve the SO₂ adsorption capacity of the adsorbent. The untreated and treated RHA were subjected for several characterizations and the characteristics of the adsorbents were compared between the untreated and treated RHA. Functional groups present on the adsorbents were determined by using FTIR. From the FTIR spectroscopy analysis, the peaks observed at 3646.97 cm⁻¹ and 1031.59 cm⁻¹ corresponding to hydroxyl and siloxane groups were responsible for high activity for SO₂ adsorption of the adsorbents. Besides that, the chemical composition of silica and alumina in the untreated RHA was found to reduce greatly and this was confirmed by using XRF. Presence of metal oxides on the surface of the untreated RHA was found to increase after the treatment may explain the high adsorption capacity obtained by treated RHA. The XRD spectra and SEM micrographs showed that the differences in the adsorption capacity of the untreated and treated RHA are due to the different phases present in the adsorbent and also due to the higher porous structure of the treated RHA compared to untreated RHA. From the characterization analyses, it was found that after hydration process, there were significant changes in the properties of the adsorbent including its chemical composition, chemical phase and surface morphology. It can be concluded that the treated RHA displayed characteristics of a good adsorbent that would have high adsorption capacity.

The adsorption capacity of the untreated and treated RHA is 1.49 mg/g and 62.22 mg/g, respectively. The adsorption capacity of the adsorbent was greatly affected by the presence of the active species and porous structure of the adsorbent. The presence of hydroxyls and Si-OH on the surface of the adsorbents had greatly enhanced the adsorption capacity as these functional groups are responsible for adsorption properties. Besides, the phase of the adsorbent also played an important role in the desulfurization activity of the adsorbent. Higher content of amorphous silica in treated RHA was confirmed by XRD analysis.

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