



Effect of Activation Condition on the Carbon Dioxide Adsorption of Triamine-Bearing Activated Rice Husk Ash

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ABSTRACT

In this study, RHA was activated by HF solution at room temperature, grafted with 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane to form an adsorbent (TRI-ARHA), and applied for adsorption of CO₂ in the gas phase. Surface analyses such as XRD, FTIR, and SEM-mapping confirmed the successful synthesis of TRI-ARHA. For CO₂ removal, adsorption results showed that TRI-ARHA is highly effective for the adsorption of CO₂ with an capacity of 178 mg/g. Moreover, its capacity strongly depended on HF content for RHA activation, where the use of 5 vol.% HF solution gave the highest adsorption capacity. Regarding temperature, the best adsorption condition was found at 80 °C with good stability after at least 10 adsorption-desorption cycles. This high adsorption capacity and stability of TRI-ARHA may be attributed to its porous structure, good dispersion of amine, enhanced transport for gases in the porous system of solid materials, and good interaction between support and amine. Thus, TRI-ARHA is great potential for carbon capture and storage, gas contaminant treatment, and other environmental treatments by adsorption.

1. INTRODUCTION

With an increase in fossil fuel prices, the use of agricultural waste as a combustion fuel is increasing in Vietnam, especially for small and medium enterprises. Among agriculture by-products, one of the most popular fuel sources in Vietnam is rice husk, which are used for boilers, furnaces, and brick kilns. As a by-product of combustion, rice husk ash (RHA) causes environmental pollution (e.g., bottom ash as solid waste in the soil and fly ash as particulate matter in the air). Many technologies have been proposed for using RHA, such as making of construction materials (e.g., brick, insulator, mortar coating, and concrete), mesoporous silica, biochar, and activated carbon, which are potential for water or gas treatment [1-5].

Due to the climate change caused by the increase of CO₂ emission (e.g., mainly from the combustion process), many researchers have focused on looking for an effective technology for the adsorption and utilization of CO₂ from the waste and the reuse of RHA for adsorption of CO₂ from rice husk combustion would be a great idea for sustainable development [6-15]. Conventionally, the rice husk is burnt

or heated at a certain level and the collected ash can be employed as a silica source [6, 7, 9, 10, 13-16] or used directly and fully [8, 11, 12] for preparation of porous material. In these studies, RHA should be activated using surfactants/templates (e.g., CTAB, PLE, and EO₂₀-PO₇₀-EO₂₀) or chemical reaction at high temperature (e.g., with NaOH or HF solution) before grafting with amine groups to form an effective adsorbent for CO₂. Therefore, developing a new and effective method for activation of RHA without the need for heating (e.g. preparation at room temperature) or surfactants (e.g. template-free) is needed. The technology should be simple, environmental-friendly, and low-cost for large-scale production.

For gas cleaning, porous nanomaterials were used with special properties such as surface acidity and basicity, pore size, pore volume, and surface area. The supporting material should possess high surface area, mesoporous pore structure, and active surface with chemical interactions between the surface and the grafted amine. The amine-grafted silica materials are attracted many researchers for environmental applications, particularly for capturing CO₂

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thanks to the amine functional groups. The grafting of amine on the silica surface is based on the silane reaction between the amine silane compound and SiO_2 on the surface of the silica via a mechanism in Fig. 1. In previous studies, RHA was used as a carrier or support to synthesize adsorbents which are capable of effectively removing many pollutant components such as organic matter [17, 18], nitrate [19], phosphate [20], and chloride [21] in water. Before being used as effective support, RHA must be activated by HF solution [22] to improve the surface area as well as to form the porous system. This activation process enhances the surface SiO_2 density, which is a very important parameter in determining the success of amine grafting on the ARHA surface through silane reaction. Therefore, in this study, we develop a facile and inexpensive route for the preparation of adsorbent from the RHA collected from a brick kiln. Here, the RHA was activated by using HF (with a concentration from 1 vol.% to 7 vol.%) at room temperature and grafted with an amine. The adsorption capacity and the recyclability of the materials were then evaluated by CO_2 adsorption using a TGA system.

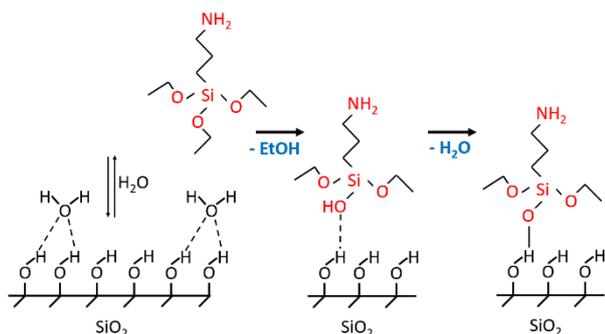


Fig. 1. The mechanism for grafting amine on SiO_2 surface.

2. MATERIAL AND METHODS

2.1. Chemicals

The rice husk ash (RHA) was from a brick kiln with Hoffman technology from Germany and a capacity of ~30,000 bricks/year in An Giang province (Vietnam). N_2 and CO_2 (99%) gases were ordered from a gas company in Vietnam.

Other chemicals were purchased from Merck or other companies in Vietnam; including HF (40 vol.%) and 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (Tech) (MW: 265.43 g/mol and liquid density: 1.03 g/mL), herein referred to as TRI.

2.2. Generation of support

The porous RHA support was prepared by a simple method of HF corrosion [22, 23]. All the processes were carried out using Teflon containers since HF is a corrosive chemical. 800 mL of aqueous HF solution (1, 3, 5, 7 vol.%) was mixed with 20 g original RHA (O-RHA) and stirred for 30 min at room condition. The remaining solid material was then

collected and repeatedly washed and centrifuged with deionized water several times (e.g., around 10 times) until reaching pH 7. After being The material was finally dried at 80 °C in a vacuum oven overnight, the black powders (i.e., activated RHA or A-RHA) were obtained.

2.3. Generation of adsorbent

The amine loading was conducted by surface grafting method reported in our previous works [23, 24]. Samples of RHA (A-RHA or O-RHA) were loaded with amines by the reaction of triaminesilane (3 mL/RHA) and water (0.3 mL/gRHA) in 150 mL of toluene at 85 °C. After grafting, the materials were washed and filtered with toluene (for removing ungrafted amines) and then pentane (for removing toluene). Finally, the TRI-A-RHA and TRI-O-RHA was collected after being dried at 100 °C for 1 h.

2.4. Characterization measurements

The produced materials were characterized by wide-angle X-ray diffraction (WAXRD, D2 Phaser XRD 300W), transmission electron microscopy (TEM, Philips Tecnai G² F20 TEM), Fourier transform infrared spectroscopy (FTIR, Alpha, Bruker), scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX, JCM-7000, JEOL), and Brunauer-Emmett-Teller (BET, Porous Materials, BET-202A).

2.5. Adsorption test

The CO_2 adsorption experiments are described in Fig. 2. The gas flow from cylinder 1 is adjusted by valve 2 before passing through column 3 containing CaCO_3 to remove water vapor present in the gas stream. After that, the dry gas stream enters the U-shaped glass tube adsorber (5) containing the adsorbent. The adsorption process takes place at a specified temperature of the furnace (4), which is controlled by the controller (6).

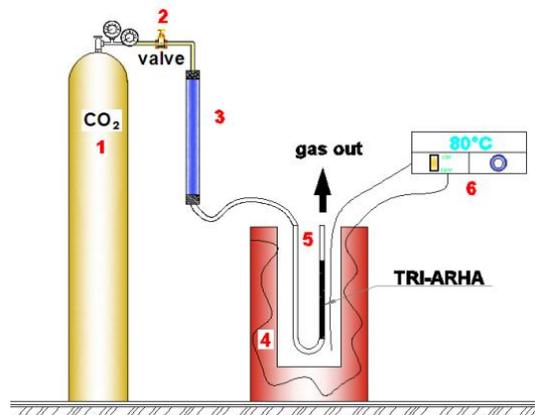


Fig. 2. CO_2 adsorption system.

(1: CO_2 cylinder, 2: valve, 3: CaCO_3 column, 4: heating furnace, 5: U-shaped glass tube adsorber, 6: temperature controller)

3. RESULTS AND DISCUSSION

3.1. Characterization of material

The raw RHA material needs to be activated before use for amine loading. The morphology of RHA before and after being activated with HF (5 vol.%) is displayed in Fig. 3. It is observed that the structure of A-RHA was much more porous than that of O-RHA, proving the corrosion of RHA by HF. The porous structure of the support is a prerequisite for good amine loading. The successful activation by HF is also evidenced by XRD results in Fig. 4. The XRD pattern of O-RHA shows mainly the presence of cristobalite crystal phase of silica in the RHA at 2θ of 22, 28.5, 31.5, and 36.3°, which is similar to those in the reports of Serra *et al.* [25] and Bhagiyalakshmi *et al.* [14]. As compared to the crystalline structure of silica in O-RHA, the structure of A-RHA is totally amorphous with a good porous system, signifying good support for amine loading.

The FTIR spectra of RHA, A-RHA, TRI-ARHA, and CO₂-adsorbed TRI-ARHA are shown in Fig. 5. The spectrum of A-RHA is simpler than that of RHA. These two materials are characterized by vibrations of -OH (3450 cm⁻¹), C=O (1730 cm⁻¹), C=C (1600 cm⁻¹), and Si-O-Si (1100 cm⁻¹) [18, 19, 26]. In TRI-ARHA material, vibration peaks were observed at around 3442 cm⁻¹ for -OH (silanol groups on ARHA surface) and 1480 cm⁻¹ for amine groups [19] along with characteristic peaks of -OH (3420 cm⁻¹), C-H (2930 cm⁻¹), C=C (1650 cm⁻¹), Si-O-Si (1030-1130 cm⁻¹), and Si-H (650-840 cm⁻¹) [26], confirming the successful loading of amine on the SiO₂ sites of TRI-ARHA.

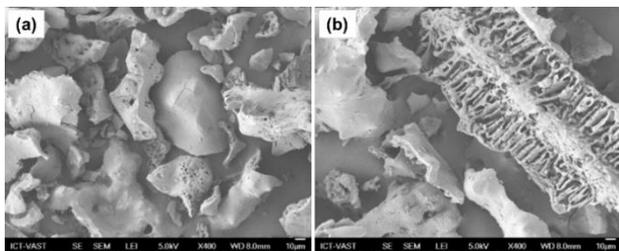


Fig. 3. SEM images of (a) O-RHA and (b) A-RHA materials.

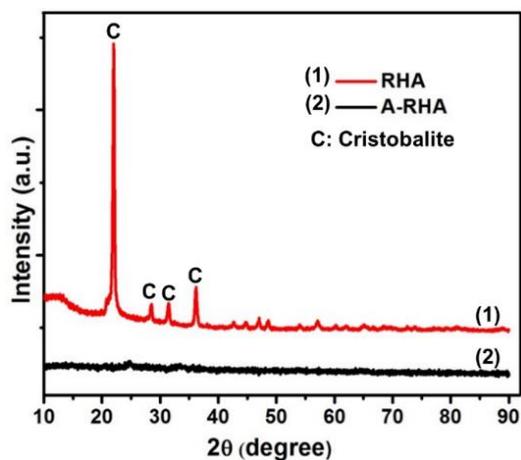


Fig. 4. XRD patterns of (1) RHA and (2) A-RHA materials.

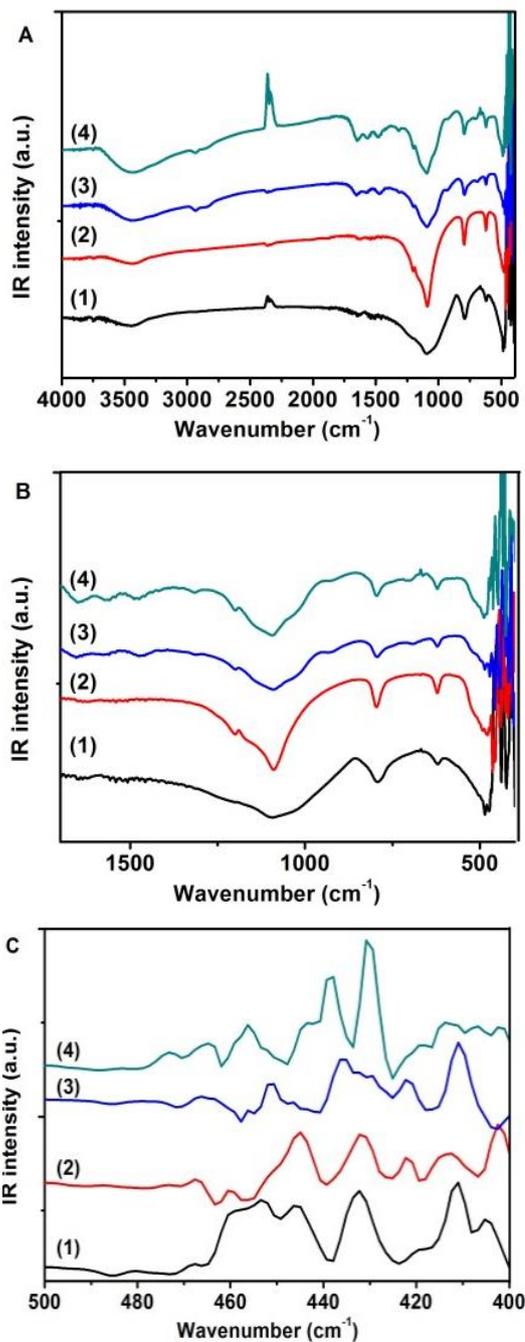


Fig. 5. FTIR spectra of (1) O-RHA, (2) A-RHA, (3) TRI-A-RHA, and (4) TRI-A-RHA-CO₂ materials.

Table 1 summarizes the surface properties (e.g., amine content, surface area, and Si/C ratio) of TRI-ARHA and ARHA. For ARHA samples, the surface area continuously increases from 98 to 415 m²/g when HF concentration increases from 1% to 5%, and then decreases to 342 m²/g with further increase of HF concentration to 7%. Moreover, the EDX results (not shown) give the same trend of surface Si/C ratio, which increases from 0.27 to 0.71 in HF concentration range of 1-5% and decreases to 0.43 at HF concentration of 7%. This signified that 5% could be the best condition for activation of RHA. This condition creates the

porous structure of ARHA and exposes more Si atoms onto the material surface for effective amine grafting. As predicted, the surface area (measured by BET) and the amine content (determined by TGA, Fig. 6) of TRI-ARHA show similar trends to those of the surface area and Si/C ratio of ARHA. The surface area and amine content of TRI-ARHA increase from 94 to 402 m²/g and 5.86 to 7.51 mg/g, respectively, when HF concentration increases from 1 to 5%, and then decrease to 335 m²/g and 6.7 mg/g, respectively, at HF concentration of 7%. EDX-mapping results of the TRI-ARHA material activated at an HF concentration of 5% are presented in Fig. 7, showing a homogenous distribution of Si and N on the surface of the material. These indicate that the activation of RHA by HF at 5% generates ARHA with the best porous structure and exposed Si atom on the surface. It is effective for the grafting of amine functional groups, which could be the best material for CO₂ adsorption.

Table 1. Composition and surface area of ARHA and TRI-ARHA samples

ARHA samples			TRI-ARHA samples		
Sample	Surface area (m ² /g)	Ratio of Si/C	Sample	Surface area (m ² /g)	Amine content (wt.%)
ARHA (1% HF)	98	0.27	TRI-ARHA (1% HF)	94	5.86
ARHA (3% HF)	214	0.38	TRI-ARHA (3% HF)	212	6.66
ARHA (5% HF)	415	0.71	TRI-ARHA (5% HF)	402	7.51
ARHA (7% HF)	342	0.43	TRI-ARHA (7% HF)	335	6.70

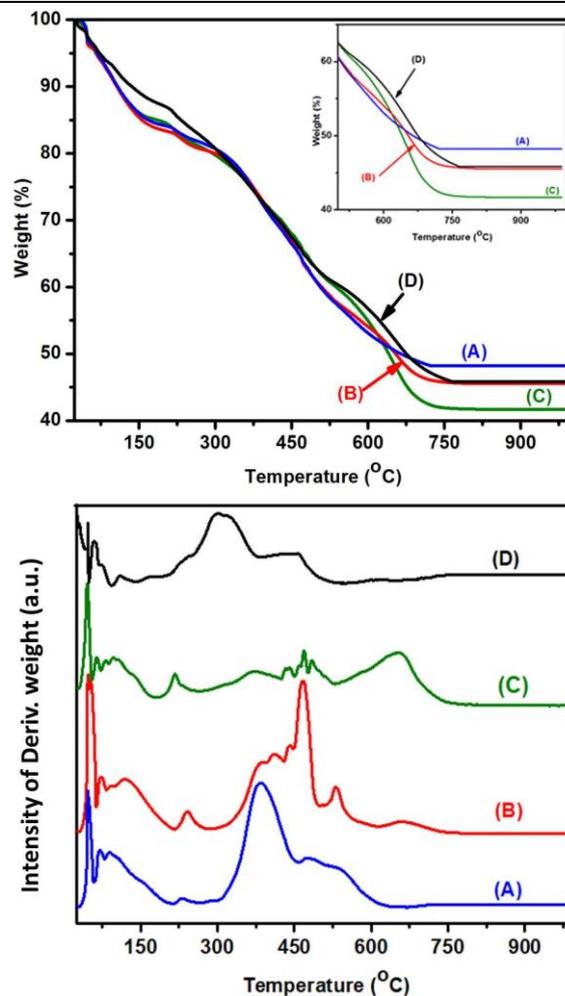


Fig. 6. TGA results of TRI-ARHA activated from different HF concentration: (A) 1%, (B) 3%, (C) 5%, and (D) 7%.

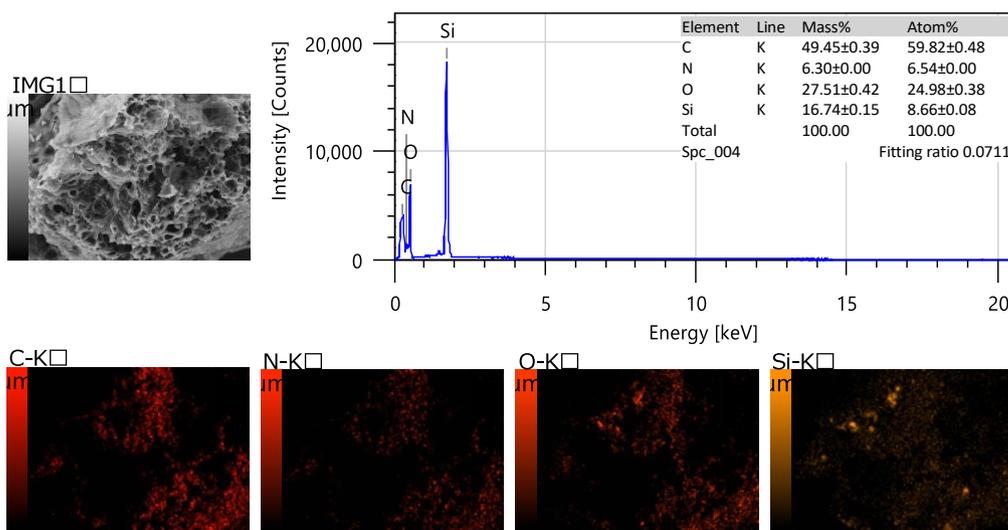


Fig. 7. EDX mapping of elements in TRI-A-RHA at HF concentration of 5% for RHA activation.

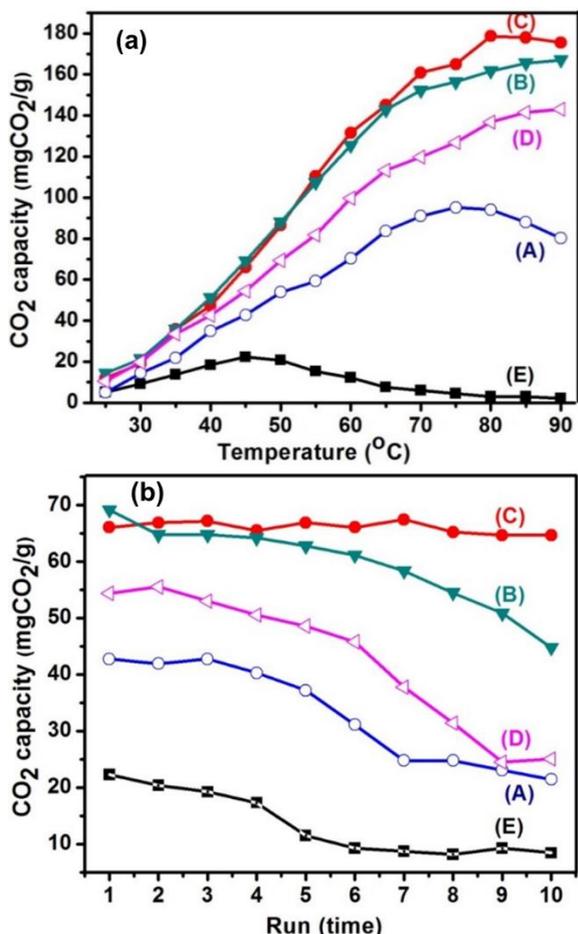


Fig. 8. CO₂ adsorption capacity of TRI-A-RHA with different HF concentrations (A) 1%, (B) 3%, (C) 5%, and (D) 7% and (E) A-RHA (5% HF) at different temperatures (a) and cyclic test at 45 °C (b).

3.2. CO₂ adsorption performance

The activation of RHA by HF is a key step for the formation of mesoporous structure in the A-RHA material, which should strongly affect the amine loading and the CO₂ adsorption ability, as discussed above in the TGA results. The effect of HF concentration in the activation step on the CO₂ adsorption capacity is demonstrated in Fig. 8. The temperature of the adsorption test in this study was investigated in the range of 25 to 90 °C, which is a typical range for flue gas temperature in Vietnam after a heat recovery system. Without amine, the adsorption capacity of A-RHA was very low and the maximum capacity reached 20 mg/g at the temperature of 45 °C. Once grafting with amine, the adsorption ability of the TRI-A-RHA increased remarkably, as demonstrated by curves E and C in Fig. 8(a). This proved that amine grafting is a key step that provides high CO₂ absorption performance. Additionally, the adsorption capacity was strongly impacted by the HF concentration during the activation process. One can see that the adsorption capacity of TRI-A-RHA increased when HF concentration increased from 1% to 5%, then decreased with a further increase of HF concentration from 5% to 7%. The

maximum CO₂ adsorption capacity can reach 178 mg/g for TRI-A-RHA activated by HF at a concentration of 5%. This adsorption result is consistent with the physico-chemical properties of this material with the best condition of surface area, Si/C ratio, and amine contents as discussed previously.

The performance of the materials for adsorption was significantly influenced by temperature as well. It is typical for the adsorption capacity to rise with temperature in the region of 25 to 90 °C. The optimum temperatures for the highest CO₂ adsorption capacity are determined to be 45 °C, 75 °C, and 80 °C for A-RHA, TRI-A-RHA (HF 1%), and TRI-A-RHA (HF 5%), respectively. The comparison of CO₂ capacity with other adsorbents from the literature is summarized in Table 2. These studies also used rice husk ash as a silica source and loaded with amine for CO₂ adsorption. The data shown in this table are the highest capacity in each study. It is clear that our material was superior for CO₂ adsorption compared with those published in the literature. Among them, the result from Zeng and Bai is comparable with ours since they also use HF for activation of RHA and their obtained capacity reached 159 mg/g [11]. However, it is noted that in the preparation process of PEI/PSNs, the RHA activation by HF was conducted at 100 °C for 30 min as compared to room temperature (without any heating) in our study.

Table 2. Comparison of CO₂ capacity with other adsorbents from literature

Material	Temp. for CO ₂ adsorption (°C(method))	CO ₂ capacity (mgCO ₂ /g)	References
TREN/MCM-41	75 (TGA)	70.0	[15]
3-CPA/SBA-15	25 (15.21% CO ₂)	74.8	[14]
	75 (15.21% CO ₂)	57.2	
APTS/MCM-48	50 (TGA, 100% CO ₂)	3.0	[10]
	70 (TGA, 100% CO ₂)	2.7	
TEPA/MS-400	75 (10% CO ₂)	173	[13]
PEI/ZSM-5	120 (100% CO ₂)	86.2	[6]
	90 (100% CO ₂)	61.6	
PEI/PSNs	75 (15% CO ₂)	159	[11]
TRI/PE-MCM-41	110 (5% CO ₂)	62	[16]
TRI/ARHA	80 (TGA, 100% CO ₂)	178	This study

It is also important to test the stability of TRI-A-RHA for CO₂ adsorption under long-term use. Therefore, all the materials were employed for the CO₂ adsorption-desorption

test under 10 cycles at a temperature of 45 °C and the results are presented in Fig. 8(b). Most of the materials showed a decline in adsorption capacity during 10 cycles test. However, TRI-A-RHA activated with 5% HF had a very stable adsorption capacity of ~ 65% (with a loss of ~ 3 %) after 10 adsorption-desorption cycles. This indicates that the grafting of TRI amine in A-RHA is very stable (as also proven by TGA results) and suitable for the adsorption of CO₂ in the actual environment.

4. CONCLUSIONS

RHA was successfully activated by using HF without any heating or use of surfactants. The activated RHA was grafted with TRI amine and applied for CO₂ adsorption. Results showed that the condition of HF activation has a significant impact on the material's characteristics such as surface area, surface Si/C ratio, and amine content. Therefore, the adsorption capacity depended on the concentration of HF and the adsorption temperature with optimum conditions of 5% HF solution and 80 °C, respectively. At these conditions, the CO₂ adsorption capacity can reach 178 mg/g. The adsorption ability of the material was stable for at least 10 cycles of adsorption-desorption and could be a very effective adsorbent for the capture of CO₂ in the flue gas.

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