



Fly ash as a cost-effective catalyst to promote sorbent regeneration for energy efficient CO₂ capture

Yingjie Niu^{a,1}, Ting Li^{a,1}, Francesco Barzagli^{b,*}, Chao'en Li^c, Mohammad W. Amer^d, Rui Zhang^{a,**}

^a College of Chemical Engineering, Xiangtan University, Xiangtan, Hunan, 411105, PR China

^b ICCOM Institute, National Research Council, via Madonna del Piano 10, 50019, Sesto F.no, Florence, Italy

^c CSIRO Energy, 71 Normanby Road, Clayton North, VIC, 3169, Australia

^d Department of Chemistry, School of Science, The University of Jordan, Amman, 11942, Jordan

ARTICLE INFO

Handling editor: Krzysztof (K.J.) Ptasinski

Keywords:

Fly ash
CO₂ capture
Monoethanolamine
Regeneration heat duty
Catalytic regeneration

ABSTRACT

The use of catalysts to promote sorbent regeneration is currently considered an effective method to reduce the energy required in CO₂ capture processes. Aiming at identifying stable and cost-effective catalysts with high CO₂ desorption efficiency, here we investigated the performance of fly ash (FA) during thermal regeneration of aqueous amine solutions. The desorption rate, cyclic capacity and heat duty of a CO₂-saturated aqueous ethanolamine with the addition of FA were experimentally measured, and the results were compared with those obtained for the same solution without and with eight different catalysts. Experimental results showed that catalysts significantly improved the regeneration compared to the non-catalyzed system, and FA was the most efficient of these. Further studies of CO₂ desorption at different temperatures showed that FA provided desorption performance comparable to that of the non-catalyzed system at temperatures at least 5 °C higher and always significantly reduced the heat duty at the same temperature, especially at the beginning of the process. Finally, recycling tests demonstrated that FA had good stability and its catalytic efficiency remained high even after 20 cycles. In conclusion, FA could be considered a cost-effective catalyst for energy-efficient CO₂ capture, deserving further investigation to promote its application in industrial-scale plants.

1. Introduction

The rising atmospheric concentration of carbon dioxide (CO₂) is a growing environmental concern with significant implications for the future of our planet. Increasing CO₂ emissions, mainly from the combustion of fossil fuels for energy production, are a major contributor to global warming and climate change. As the world's population continues to grow, the demand for energy also grows, exacerbating the problem [1,2]. In response, there is an urgent need to develop and deploy technologies to limit CO₂ emissions and mitigate the effects of global warming. Carbon Capture, Utilization and Storage (CCUS) technologies are gaining increasing attention as a potential solution to this problem, and are considered crucial to keeping the global temperature rise within 1.5 °C of the pre-industrial levels [3,4]. CCUS technologies have the potential to significantly control CO₂ emissions from power

plants and other industrial sources. According to the current literature, the most mature and effective technique for CO₂ capture is the use of amine-based liquid sorbents. In particular, the aqueous solution of monoethanolamine (MEA) has been extensively investigated and tested at laboratory and pilot scale [5–8]. However, MEA technology still suffers from some serious drawbacks, primarily the huge energy requirement for regeneration, which severely limits its large-scale application [9–11]. In order to identify new advanced technologies that can overcome these drawbacks and provide more efficient and cost-effective options for CO₂ capture, several innovative approaches have been developed in recent years, such as the design of new non-conventional single-atom solutions [12,13], the use non-aqueous or biphasic amine sorbents [14–17], blending different amines in water [18–23] or, as in this study, promoting CO₂ desorption by adding solid acid catalysts [24–26].

* Corresponding author.

** Corresponding author.

E-mail addresses: francesco.barzagli@iccom.cnr.it (F. Barzagli), rui Zhang@xtu.edu.cn, tange1026@163.com (R. Zhang).

¹ Yingjie Niu and Ting Li contributed equally to this work and are the co-first authors.

The costly regeneration process of amine solutions involves the decomposition of compounds formed during absorption and the release of CO₂. Shi et al. [27] proposed a two-steps mechanism for CO₂ desorption from MEA, involving the decomposition of MEA carbamate (MEACOO⁻) and the deprotonation process of protonated MEA (MEA⁺H), as shown in equations (1) and (2). Both reactions are endothermic.



As a matter of fact, the elevated energy consumption in MEA regeneration can be attributed to two main factors. First, MEA's alkalinity surpasses that of water, making proton (H⁺) transfer from MEA⁺H to H₂O a challenging process. Consequently, extra energy is required to facilitate this proton transfer reaction. Secondly, the CO₂ desorption process is inherently highly endothermic, and requires an external energy source for progression [28]. Recently, the implementation of solid acid catalysts (SAC) during the sorbent regeneration process has emerged as a promising approach to improve CO₂ desorption performance for aqueous amine solutions. The addition of SAC could provide Brønsted (B) and Lewis (L) acid sites that facilitate the reactions shown in equations (1) and (2), significantly reducing the energy consumption for CO₂ desorption [29]. A more in-depth analysis of the mechanisms involved in the catalytic regeneration of amine solutions using SAC is provided in two recent reviews on the subject [29,30]. With the addition of catalysts, sorbent regeneration can be carried out at temperatures between 85 and 100 °C, significantly lower than the 120–140 °C required in conventional processes, resulting in significant energy savings [31]. Among the various catalysts studied zeolites, metal oxides, silica materials and modified clays have demonstrated the most favorable outcomes for sorbent regeneration [32–34]. However, it is worth considering that in order to have a real impact on the cost-effectiveness of the process, the catalyst should have certain characteristics in addition to CO₂ desorption efficiency, such as thermal stability for reuse, availability and affordability [30]. Looking for a catalyst with all the above-mentioned peculiarities, we decided in the current work to thoroughly investigate the potential benefits of using the low-cost fly ash during amine sorbent regeneration. Fly ash (FA) is an abundant solid waste produced when coal is burned in power plants. Its worldwide production is estimated to be between 0.75 and 1 billion tons per year and this amount is expected to increase in the near future as the demand for affordable electricity in developing countries increases [35]. Due to the large quantities produced and the environmental and health concerns associated with its disposal, great efforts have been made for decades to recycle FA for various applications: it is currently mainly used as an additive to cementitious material, for soil amendment, as an adsorbent for gas and wastewater treatment, and as a catalyst in industrial processes [36]. The different uses of fly ash are closely related to its peculiar physical and chemical properties, which in turn depend on the type of coal from which it is obtained or the conditions under which it is generated. In general, fly ashes have a high specific surface area and are mainly composed of SiO₂, Al₂O₃, Fe₂O₃, and CaO, although their composition may vary to the extent that they have acidic or (in most cases) alkaline characteristics [36]. Recently, the use of FA for CCUS-related applications has been considered, also due to its minimal logistical requirements, as it is produced directly at the application site. Firstly, waste alkaline fly ash can be used directly and economically for CO₂ mineralization [37,38]. Due to its specific surface area and chemical composition, FA has been evaluated in different techniques to adsorb CO₂; in particular, it has been modified and used as an adsorbent material to capture CO₂ [39,40], or as a raw material for the production of zeolites and aluminosilicates [41,42], or to replace expensive products, such as MCM-41 and SBA-15, as a support material in the synthesis of amine-based solid sorbents [43]. Finally, FA can be employed as a catalyst, or catalytic support, in several CO₂ conversion processes, such

as CO₂ hydrogenation or epoxidation, due to its thermally stable metal oxide content and ease of conversion into porous materials with a high surface area [36]. As a new potential use of this cheap and widely available by-product, in this work we investigate the activity of FA as a catalyst in low-temperature desorption processes with amine sorbents. To verify the suitability of this innovative approach, we conducted a detailed study of the desorption performance of a CO₂-saturated aqueous solution of MEA (5 M), the reference sorbent of any CCUS process, with the addition of FA: its desorption rate, cyclic capacity and heat duty were measured experimentally at T = 88 °C and compared with those obtained for the same MEA solution without and with 8 other different catalysts, under the same operating conditions. The catalysts selected to compare the desorption performance of FA, namely sepiolite (SEP) [34], γ-Al₂O₃ [44], ZSM-5 [44], β-25, SBA-15 [45], SAPO-34 [46], Y-zeolite and MCM-41 [47], have already been shown to improve MEA regeneration compared to non-catalyzed system. In addition, the regeneration performance of FA (in MEA solutions) was further investigated by evaluating CO₂ desorption at different temperatures and with different amounts of catalyst. This thorough screening allows for the identification of the most advantageous operating conditions to achieve efficient desorption with the lowest energy consumption. Finally, the stability of FA in consecutive absorption and desorption cycles was evaluated to assess its catalytic effect over time after reuse.

2. Experimental section

2.1. Materials

Ethanolamine (MEA) was purchased from Shanghai Macleans Biochemical Co. Ltd, and was used without further purification. Deionized H₂O via double distillation was used to prepare 5 M MEA aqueous solution. Pure CO₂ and N₂ (Hunan Zhongtai Hongyuan Gas Co. Ltd) were used to saturate the MEA solution and as a gas-carrier in the desorption test, respectively. Gas flow rates were adjusted and measured using two flow meters (Cole Parmer). Hydrochloric acid (HCl, 36–38%) was purchased from Hunan Huihong Reagent Co.

The FA (Grade-I) used in this work was purchased from Changsha Lvmingyuan Environmental Protection Materials Factory, while all other catalysts (sepiolite, γ-Al₂O₃, ZSM-5, β-25, SBA-15, SAPO-34, Y-zeolite and MCM-41) were purchased from Beijing InnoChem Science & Technology Co., Ltd. All catalysts were dried at 100 °C for 8 h before being added to the amine solutions, without further treatment.

2.2. Catalysts characterization

N₂ adsorption-desorption experiments are routinely used for the characterization of porous materials, providing information on surface area, pore volume, and pore size. Surface area reflects the total space available for catalytic interactions, with higher values suggesting more active sites. Pore volume indicates the diffusion capacity of the reactant, influencing catalytic activity. Pore size relates to the material's suitability for specific reactions by revealing the accessibility of reactants to active sites. Together, these parameters play a key role in evaluating and optimizing the catalytic properties of solids, shaping their applicability in diverse industrial scenarios. Here, the surface area, pore size, and pore volume for each catalyst were determined by N₂ adsorption-desorption experiments carried out at -196 °C using an ASAP2020 PLUS HD88 adsorption analyzer (Micromeritics). The Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) techniques were employed to calculate the pore size distribution and the relative surface area. Before the experiment, the sample was pretreated at 180 °C for 4 h [48]. The results are presented in Table 1.

FA analysis showed a relatively smaller surface area than the other catalysts, but relatively larger pores, similar to those of sepiolite, one of the best performing catalysts for sorbent regeneration. Fly ash, introduced as a new catalyst in this study, underwent a more detailed

Table 1
Surface area, pore volume and pore size of the catalysts selected for the experiments.

Catalyst	BET Surface Area (m ² /g)			Pore Volume (cm ³ /g)	Pore Size (nm)
	Micropore	Mesoporous	Total		
FA	2.2	0.7	3.0	0.002336	15.393
SEP	0.7	1.9	2.6	0.002906	12.015
γ-Al ₂ O ₃	9.7	137.5	147.2	0.620632	19.233
ZSM-5	253.3	71.7	325.0	0.174302	2.911
β-25	313.3	118.7	432.0	0.314095	7.867
SBA-15	23.1	467.5	490.6	1.143712	8.581
SAPO-34	527.3	-2.4	524.9	0.267191	-
Y-zeolite	627.6	28.4	656.0	0.341547	3.843
MCM-41	-	1063.69	1014.0	0.874380	3.082

investigation. The types of Brønsted (B) and Lewis (L) acid sites of the FA were assessed using infrared spectroscopy of pyridine adsorbed catalysts (Py-IR). Additionally, the number and strength of its acid and basic sites were determined through NH₃ and CO₂ temperature programmed desorption (NH₃-TPD and CO₂-TPD), respectively [34]. The results of these analyses are presented in Table 2.

The actual composition, including species content and mass percentage, of the FA was determined using X-ray fluorescence (XRF) with a Panalytical Axios spectrometer. In addition, both fresh and recycled FA were analyzed using the FT-IR technique (ALPHA spectrometer, Bruker) to compare any potential changes in the FA structure before and after the reaction. Spectra were recorded in the 4000-500 cm⁻¹ range.

2.3. CO₂ desorption experiments

Before evaluating desorption performance, a 5 M MEA aqueous solution was saturated with pure CO₂ (flow rate = 200 mL/min) at a constant temperature of 40 °C for 8 h. The CO₂ loading (mol CO₂ captured/mol MEA) was determined to be 0.53 ± 0.01 using the titration method with 1 M HCl [49]. The CO₂-loaded MEA solution was used for all catalytic and non-catalytic desorption experiments.

Desorption experiments were carried out following a well-established procedure validated in our laboratory [48,50]. The experimental setup, as depicted in Fig. 1, included a desorber (a flask connected to a condenser) and an IKA HBR 4 stirring and heating oil bath. In each experiment, 200 mL of the CO₂-loaded MEA solution (kept at 30 °C before use) was placed inside the desorber and heated to the desired temperature (temperatures ranged between 88 and 98 °C in this study). CO₂ desorption was facilitated by magnetic stirring at 800 rpm. The CO₂ released from the desorber was mixed with the gas carrier N₂ (at a constant flow rate of 500 mL/min) and sequentially passed through a concentrated sulfuric acid solution and a desiccant tube to remove any traces of escaped amine and water. Finally, the resulting CO₂+N₂ gas mixture was analyzed using a CozIR-100 infrared CO₂ sensor (GSS Ltd., UK, ±0.01% in accuracy), and the CO₂ concentration in the exhaust gas was recorded by the computer at 10-s intervals. Except for the desorption performed on the solution without catalysts (blank), a desired amount of the investigated catalyst (in the range 0.50–3.00 g) was added to the desorber before heating. Each experiment lasted 60 min, and two experiments were conducted for each catalyst, with the deviation from the mean value of the measured concentrations ranging from 0.5 to

Table 2
Results of acidity and basicity analysis for FA obtained with Py-IR, NH₃-TPD and CO₂-TPD.

B (mmol/g)		L (mmol/g)		B + L (mmol/g)		B/L	
0.119		1.362		1.481		0.087	
Acidity strength by NH ₃ -TPD (mmol/g)				Basicity strength by CO ₂ -TPD (mmol/g)			
Weak	Medium	Strong	Total	Weak	Medium	Strong	Total
0.023	0.039	0.146	0.208	0.002	0.006	0.035	0.043

1.5%. Throughout the experiments, the oil bath was connected to a digital electric energy meter (Zhejiang Tepsung Electric Co., Ltd.) to record the amount of electricity consumed for the entire regeneration process.

2.4. Assessment of desorption performance

The desorption performance of CO₂-loaded MEA solutions in the absence and presence of catalysts (including FA) was evaluated by considering the CO₂ desorption rate (V_d , molCO₂/min), the cyclic capacity, (n_{CO_2} , mol of desorbed CO₂) and the heat duty (H , kJ/mol), described by equations (3)–(5), respectively.

$$V_d = \frac{V_{N_2} \times C'}{1 - C'} \times \frac{273.15}{V_m \times T} \quad (3)$$

$$n_{CO_2} = (\alpha_{rich} - \alpha_{lean}) \times C \times V \quad (4)$$

$$H = \frac{\text{Heat input/time}}{\text{CO}_2 \text{ amount/time}} = \frac{E}{n_{CO_2}} \quad (5)$$

V_{N_2} is the nitrogen flow rate (0.5 L/min); C' is the volumetric fraction of CO₂ recorded by the sensor; V_m is the standard molar gas volume (22.4 L/mol); T is the room temperature (in K); α_{rich} and α_{lean} refer to the loading (mol CO₂/mol MEA) of the saturated and desorbed solution, respectively; V is the volume of MEA solution used (0.2 L); C is the MEA concentration in solution (5 M); E is the amount of electricity (kJ) recorded by the digital electric energy meter during the desorption process.

The heat duty, i.e. the heat needed to desorb one mol of CO₂, was determined in this study by calculating the ratio between the measured electricity consumption and the amount of CO₂ desorbed at a specific time. This approach, widely accepted for laboratory-scale testing [27, 51–53], enables a meaningful comparison to assess the catalytic performance of different catalysts through parallel testing within a single study.

It is important to emphasize that the desorption performance is strongly influenced by the instrumentation and operating procedure used, so the results obtained are only meaningful when compared to each other when obtained under the same operating conditions, as in this work. However, in order to obtain more universal results, the relative desorption energy consumption (RH, %) was calculated for each catalyst with respect to the blank MEA solution using equation (6) [48]:

$$RH(\%) = \frac{H_i}{H_0} \times 100 \quad (6)$$

where H_i is the heat duty measured with a selected catalyst and H_0 is the heat duty measured with the MEA solution without catalyst (blank).

2.5. Cyclic test for the catalyst stability

To assess the cyclic stability of fly ash as a catalyst, after the first

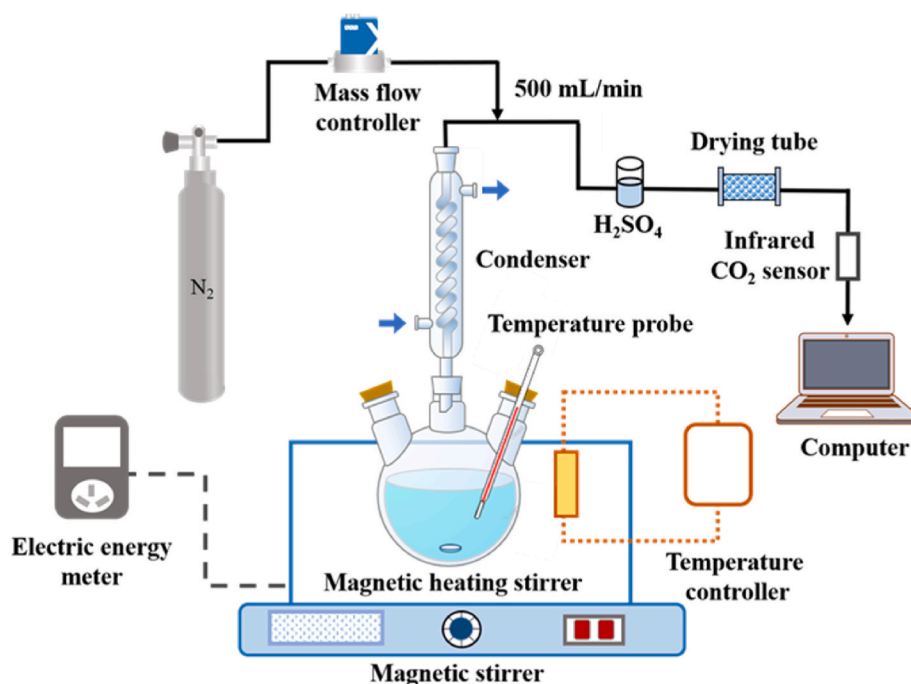


Fig. 1. Illustration of the instrumentation used for CO₂ desorption experiments.

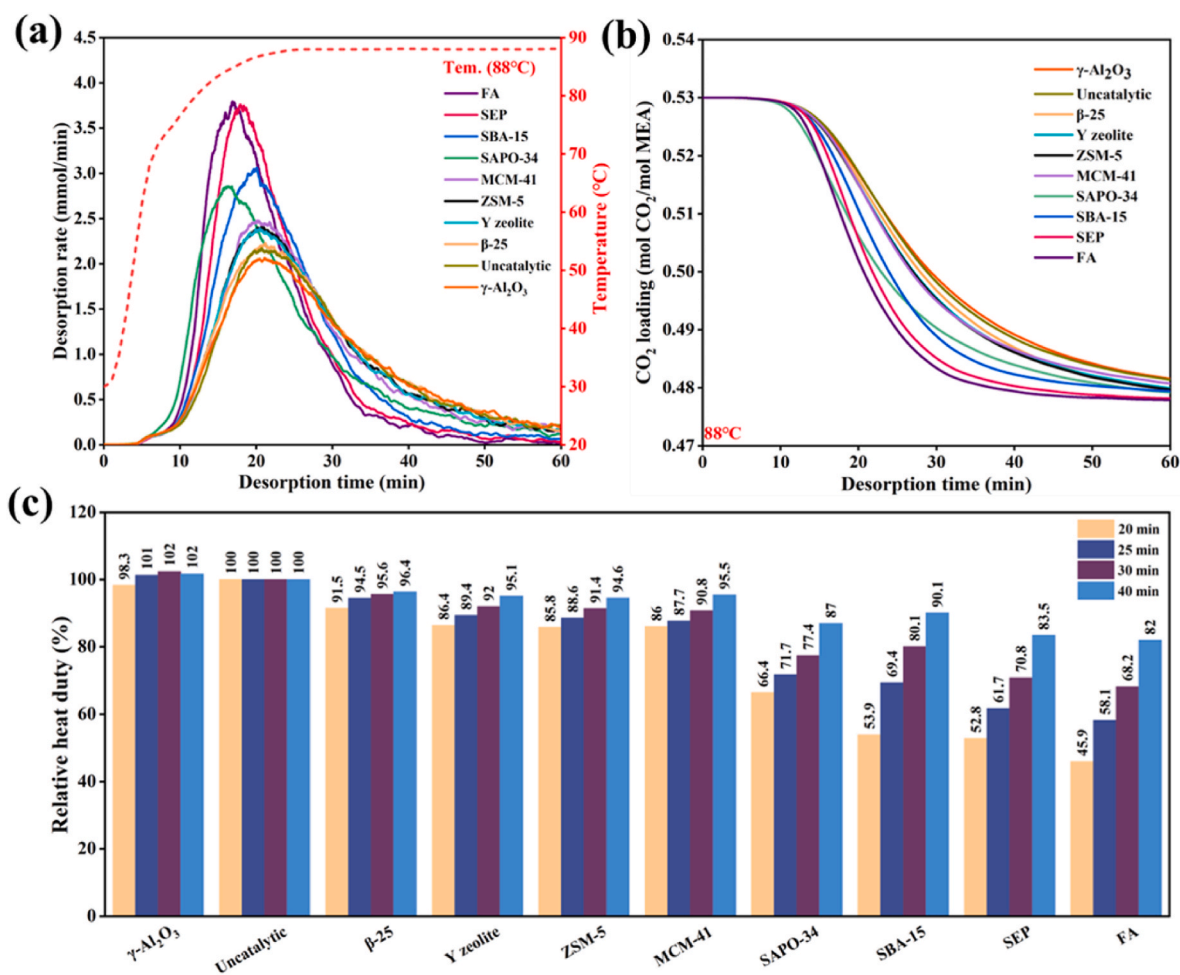


Fig. 2. CO₂ desorption performance with and without catalysts, reported as CO₂ desorption rate (a), CO₂ loading (b) and relative heat duty (c) as a function of the desorption time. Experimental conditions: desorption temperature = 88 °C, amount of catalyst = 0.50 g, volume of MEA solution = 200 mL.

desorption experiment at $T = 88\text{ }^{\circ}\text{C}$, the desorbed lean amine solution was cooled to ambient temperature and re-saturated with CO_2 , using a total flow rate of 500 mL/min of mixed CO_2+N_2 gas (CO_2 : 300 mL/min, N_2 : 200 mL/min). After 60 min of absorption, the rich amine solution was again subjected to the desorption experiment (again at $88\text{ }^{\circ}\text{C}$). Absorption and desorption were repeated 20 consecutive times to test the cyclic stability performance of the FA catalyst.

3. Results and discussion

3.1. Evaluation of FA desorption performance compared to other catalysts

This study investigates the catalytic effect of fly ash on the regeneration process of aqueous amine sorbents. Experimentally, the desorption performance of a CO_2 -saturated solution of MEA was measured both in the absence and presence of the solid catalyst FA. In addition, the obtained results were compared with those achieved under the same operating conditions using eight different catalysts previously demonstrated to be efficient in this process [34,44–47]. Each desorption experiment was conducted using 200 mL of a CO_2 -saturated MEA solution (CO_2 loading = 0.53) at a temperature of $88\text{ }^{\circ}\text{C}$, following the procedure described in Section 2.3. Except for the uncatalyzed system (blank), 0.50 g of catalyst (mass ratio of catalyst to amine solution of 0.25:100) was added at the beginning of the process. The time-dependent trends of CO_2 desorption rate, CO_2 loading, and relative heat duty are shown in Fig. 2.

As can be seen from Fig. 2a, almost all the catalysts tested allow higher CO_2 desorption rates than the uncatalyzed system (blank), with the sole exception of $\gamma\text{-Al}_2\text{O}_3$, which under the operating conditions used here does not appear to have any significant effect. On the contrary, the use of the FA catalyst allows the maximum value of the CO_2 desorption rate to be obtained, which is significantly higher than that of all other catalysts (only SEP achieves a similar value) and which is almost double that of the blank. It should also be noted that the maximum value of desorption rate is reached faster with FA than with both the blank and the other catalysts (with the exception of SAPO-34, which, however, has a significantly lower absolute value). This implies that regeneration conducted with the addition of FA will feature a greater release of CO_2 in a shorter time, indicating a higher degree of regeneration.

This can easily be seen from Fig. 2b, which shows that the CO_2 loading decreases much more rapidly with FA and SEP than with the other catalysts, reaching its minimum value in approximately 35–40 min. The potential benefits of faster desorption are explicitly illustrated in Fig. 2c, presenting a comparison of different energy costs, expressed in terms of relative heat duty (%), using uncatalyzed desorption as a reference. All the catalysts tested reduce the cost of regeneration, with the exception of $\gamma\text{-Al}_2\text{O}_3$, which shows no significant effect on desorption under the chosen operating conditions. Among the catalysts, FA provides the best performance, with a 54.1% decrease in energy consumed (energy to desorb 1 mol of CO_2) after 20 min and a 31.8% after 30 min. To highlight the different performance achievable with the different tested catalysts, Table 3 presents the average CO_2 desorption rate, cyclic capacity, and heat duty measured after 25 min of desorption at $88\text{ }^{\circ}\text{C}$. Under the selected operating conditions, FA proves to be the best-performing catalyst.

3.2. Regeneration performance of FA as a function of temperature and amount of catalyst

The total energy consumption consists of heat of reaction, sensible heat, and evaporation heat. As mentioned in the previous section, FA exhibited superior catalytic performance than the other catalysts tested for CO_2 release at the same desorption temperature of $88\text{ }^{\circ}\text{C}$. Furthermore, since the use of FA enables CO_2 desorption at a lower temperature than the non-catalytic system, the resulting reduction in sensible heat could potentially lead to a further decrease in total energy cost.

Table 3

Average CO_2 desorption rate, cyclic capacity and heat duty based on the first 25 min for 5 M MEA solution regeneration at $88\text{ }^{\circ}\text{C}$ with and without catalysts.

Catalysts	Average desorption rate ($\times 10^{-3}$ mol/min)	Cyclic capacity ($\times 10^{-3}$ mol)	Heat duty (kJ/mol)
blank	0.92	23.32	4939.12
$\gamma\text{-Al}_2\text{O}_3$	0.93	23.03	5003.03
$\beta\text{-25}$	0.99	24.68	4667.18
Y-zeolite	1.04	26.08	4416.58
ZSM-5	1.05	26.32	4377.47
MCM-41	1.06	26.59	4332.78
SAPO-34	1.34	33.62	3543.48
SBA-15	1.30	32.51	3426.75
SEP	1.51	37.80	3048.01
FA	1.60	40.11	2872.10

Therefore, the CO_2 desorption performance at different desorption temperatures with and without the FA catalyst was also investigated in this work, and the results are shown in Fig. 3.

Fig. 3a reports the variation of the CO_2 desorption rate as a function of regeneration time. When comparing systems with and without catalyst at the same temperature, it is evident that the addition of FA led to higher desorption rates achieved in a shorter time, resulting in faster desorption. Furthermore, a higher temperature generally resulted in a higher CO_2 desorption rate than a lower temperature (both with and without FA support), as the CO_2 desorption process is an endothermic reaction. These considerations are reflected in the variation of CO_2 loading over time (Fig. 3b), where it is evident that the total amount of CO_2 desorbed is temperature-dependent, while the rate at which loading decreases is strongly influenced by the presence of the catalyst. The final loading value, which is almost the same at the same temperature both with and without FA support, emphasizes that the catalyst does not change the equilibrium of the reaction but accelerates its rate.

To assess the energy efficiency of the CO_2 desorption process, the heat duty was calculated (equation (5)) at successive stages of the desorption process (i.e., after 20, 25, 30 and 40 min of heating) at different temperatures, with and without FA. The results are shown in Fig. 3c, which also shows, for each stage, the amount (mol) of CO_2 desorbed. With the assistance of FA, more CO_2 can be desorbed from the rich amine solution at the same CO_2 desorption stage and temperature. It is worth noting that the difference in the amount of desorbed CO_2 with and without catalyst decreases as desorption proceeds. This is because FA only play the role of activating the CO_2 desorption rate while the reaction reaches equilibrium for the given temperature. The heat duty is related to the amount of CO_2 desorbed; a smaller (or larger) amount of CO_2 released leads to a larger (or smaller) heat duty. Consequently, the difference in heat duty between the process with and without FA decreases as the regenerative process proceeds. Fig. 3c also shows that, for the same desorption stage, to release equal amounts of CO_2 , the advantage of low-temperature catalysis over high-temperature non-catalytic systems in terms of heat duty gradually decreases, and the corresponding advantage in temperature difference also decreases: for example, the advantage in temperature decreases from about $7\text{ }^{\circ}\text{C}$ in the 20-min desorption stage to about $2\text{ }^{\circ}\text{C}$ in the 40-min desorption stage. The greater the advantage in temperature difference, the lower the sensible heat demand in the regeneration process for the catalytic system, contributing to a reduction in the total heat consumption of sorbent regeneration.

Numerous studies have demonstrated the significant impact of the amount of added catalyst on the CO_2 desorption process [29,30]. In order to identify the optimal amount of catalyst under our operating conditions (volume of the CO_2 -loaded MEA solution = 200 mL; desorption temperature = $88\text{ }^{\circ}\text{C}$), we evaluated the desorption performance using quantities of FA in the range between 0.10 and 3.00 g. Fig. 4 shows the variation of CO_2 desorption rate (Fig. 4a) and CO_2 loading (Fig. 4b) as a function of time. As a first general observation, it is

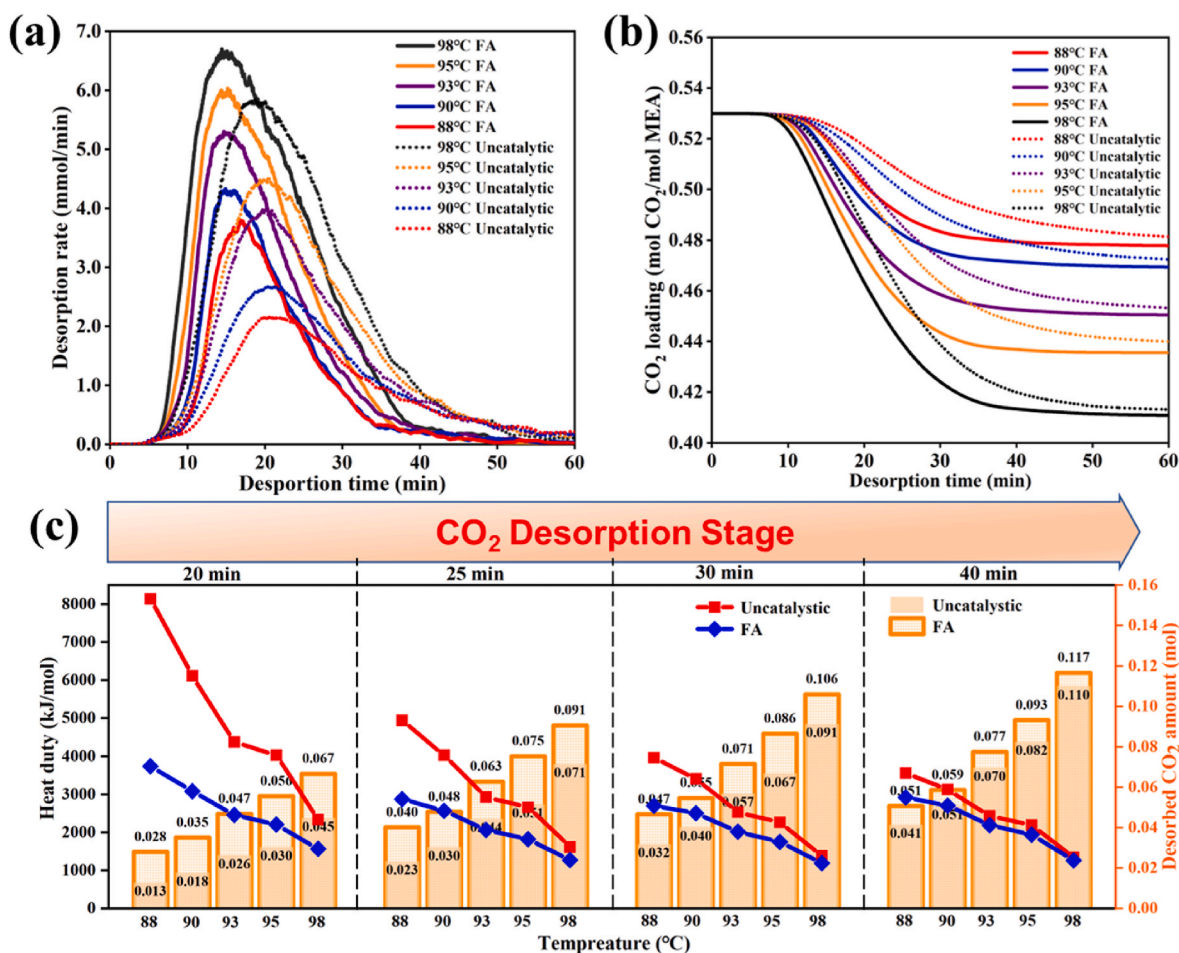


Fig. 3. CO₂ desorption performance of FA catalyst at different temperatures, reported as CO₂ desorption rate (a) and CO₂ loading (b) as a function of the desorption time, and (c) heat duty and amount of CO₂ desorbed at the desorption stages of 20, 25, 30 and 40 min. Experimental conditions: desorption temperature = 88–98 °C, amount of FA = 0.50 g, volume of MEA solution = 200 mL.

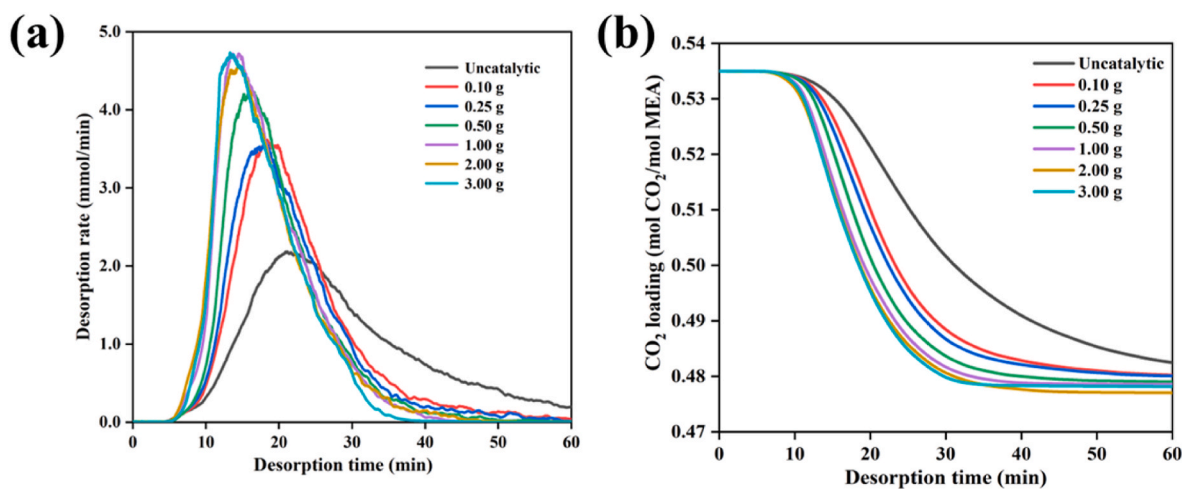


Fig. 4. CO₂ desorption rate (a) and CO₂ loading (b) as a function of the desorption time for different amounts of FA catalyst ($T_{des} = 88$ °C).

clear that the regeneration performance improves significantly even with the smallest addition of FA (0.10 g), compared to the non-catalytic system. Fig. 4a shows that as the amount of FA used increased, the CO₂ desorption rate grew faster and reached higher values. However, the maximum values obtained with 1.00, 2.00 and 3.00 g of FA were almost equal to each other, suggesting that beyond a certain amount, the

further addition of catalyst does not lead to a further improvement of the desorption kinetics. These observations are further supported by Fig. 4b, where it is evident that the decrease in CO₂ loading was faster and greater with increasing amounts of FA. Since that the differences in performance diminish for higher quantities of FA, and considering that the maximum amount of CO₂ desorbed was obtained with 2.00 g of FA

(Fig. 4a), resulting in a minimum CO₂ loading value (Fig. 4b), we considered 2.00 g of fly ash as the optimal amount of catalyst to continue with further investigations under the experimental conditions used.

Fig. 5 shows the CO₂ desorption performance achieved with and without 2.00 g FA in the temperature range of 88–103 °C. In this series of experiments, the solution used for desorption is the usual CO₂-loaded MEA solution (loading 0.53). The chosen temperature range covers the evaporation heat of water and also increases the difference of the experimental temperatures to further explore the catalytic CO₂ desorption performance of FA at relatively high temperatures. Fig. 5a highlights the significant increase in the amount of desorbed CO₂ when the temperature was 103 °C, both with and without catalyst, compared to other temperatures below 100 °C. Furthermore, it appears clear that the addition of the catalyst promoted the release of CO₂ from the MEA-rich solution from the first minutes of heating, significantly more rapidly than the corresponding non-catalyzed process at the same temperature. Fig. 5b instead shows that the heat requirement increased with the increase in desorbed CO₂, and all catalytic systems required less heat consumption than non-catalytic systems to desorb the same amount of CO₂. Furthermore, it can be observed that the heat requirement increased sharply towards the end of the process, when most of the CO₂ had already been desorbed, and prolonged heating did not lead to a substantial improvement in sorbent regeneration.

Finally, similar to Fig. 3c and 5c shows that the effect of the FA catalyst is particularly impactful, especially in the first heating phase. As the desorption process progressed, the advantage of low-temperature catalysis over the high-temperature non-catalyzed system gradually

diminishes. As a further comparison, it is observed that when the amount of FA increased from 0.50 g (Fig. 3c) to 2.00 g (Fig. 5c), the advantage in temperature difference increased relatively little, e.g. from about 7 °C to about 10 °C in the 20-min desorption stage.

3.3. Cyclic use of the FA catalyst

The stability of catalysts is a key factor for their widespread application in the industry. In order to assess the cyclic stability of FA catalyst, 20 consecutive absorption-desorption experiments were conducted in this study, following the procedure described in section 2.5. The cyclic capacities (calculated using equation (4)) for each consecutive cycle are shown in Fig. 6a. As evident, during the 20 cycles, the amount of CO₂ desorbed remains essentially stable, with minor variations above or below the average.

To further confirm the stability of the catalyst, after completing the last desorption cycle, FA was recovered from the regenerated amine solution through filtration, washing, and drying processes. Subsequently, fresh FA and recovered FA were analyzed and compared by FT-IR (Fig. 6b). As shown, the two spectra obtained are nearly identical. Notably, characteristic signals can be identified, such as the broadened signal in the 3200–3600 cm⁻¹ region indicating the presence of -OH groups, the stretching band of the T-O bond (where T = Si or Al) at 1078 cm⁻¹, the quartz peak band at 796 cm⁻¹, and the mullite peak band at 555 cm⁻¹. The peak at 457 cm⁻¹ corresponds to the stretching of the Si-O band, the primary component of FA (as confirmed by XRD analysis). Comparison of the FT-IR spectra reveals that the catalyst structure

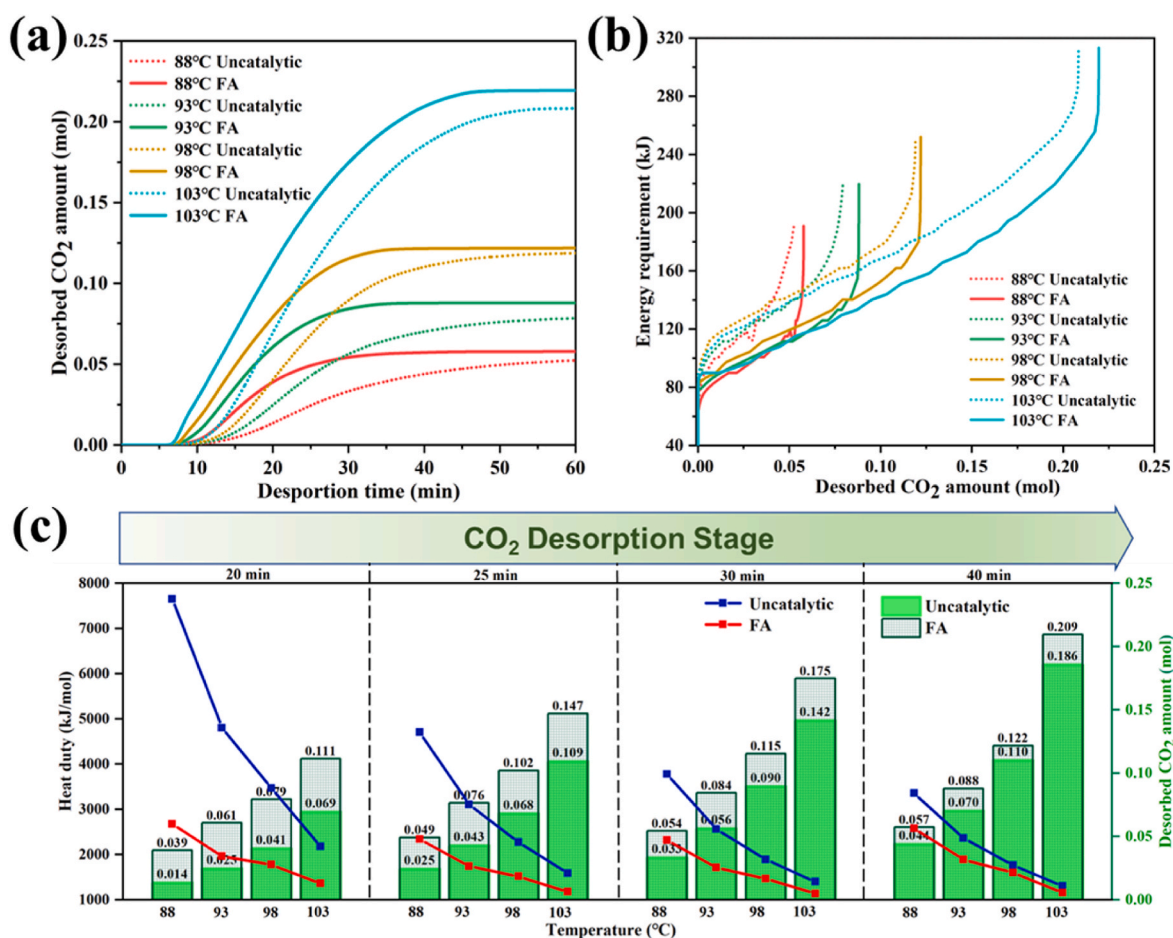


Fig. 5. CO₂ desorption performance of FA catalyst at different temperatures, reported as (a) amount of CO₂ desorbed, (b) energy requirement, and (c) heat duty and amount of CO₂ desorbed at the desorption stages of 20, 25, 30 and 40 min. Experimental conditions: desorption temperature = 88–103 °C, amount of FA = 2.00 g, volume of MEA solution = 200 mL.

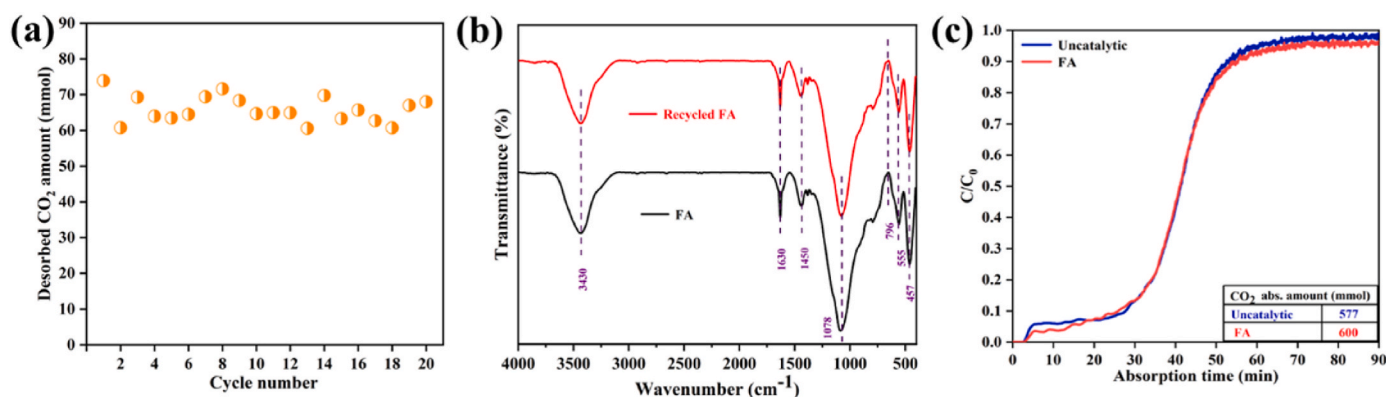


Fig. 6. (a) Stability of the FA catalyst in 20 consecutive cycles, (b) FT-IR spectra of fresh and recycled FA catalyst, (c) evaluation of the effect of the FA catalyst on CO₂ absorption performance.

remains almost unchanged before and after desorption at 88 °C, indicating good stability of the catalyst.

As a further analysis, the possible changes in structure of FA after recycling were analyzed using XRF characterization technology, and the results are shown in Table 4.

The fresh FA we used was primarily composed of SiO₂ (50.4%), Al₂O₃ (24.5%), Fe₂O₃ (9.4%) and CaO (6.4%), with lower levels of K₂O, TiO₂ and P₂O₅, as well as trace elements such as manganese, strontium, barium, chlorine, vanadium, zirconium, chromium, nickel, zinc and copper. XRF results indicate that the elemental content of FA remained essentially stable before and after use, with a slight decrease in Fe₂O₃ and CaO to 4.2% and 2.1%, respectively.

Finally, we investigated whether the FA catalyst could have an effect not only during regeneration, but also on the subsequent absorption process, considering that sorbents must be continuously reused. Two absorption experiments were conducted on 5 M MEA solutions with and without the addition of the FA catalyst to assess any possible positive or negative impact on the CO₂ absorption rate and capacity. During the absorption experiment, a gas mixture with a total flow rate of 500 mL/min (CO₂: 300 mL/min; N₂: 200 mL/min) was bubbled into 200 mL of the MEA solution for a total time of 90 min, sufficient to reach a condition close to equilibrium. As depicted in Fig. 6c, the two absorptions are nearly equal, and it can be observed that with the addition of the FA catalyst, absorption increases more rapidly in the first few minutes, with the final amount of CO₂ captured being slightly higher (by about 4%). This small variation could be attributed to the fact that FA, as a solid particle, generates small bubbles during the absorption process, increasing the gas-liquid contact area. This facilitates the transfer of CO₂ from the gas phase to the liquid phase, thereby improving the absorption rate and, consequently, the total amount of CO₂ captured in non-equilibrium systems. In any case, this indicates that the FA catalyst not only significantly improves the CO₂ desorption performance, but also has no negative effect on subsequent reuse in absorption, and may even have a small beneficial effect.

4. Conclusions

In order to develop energy-efficient industrial CO₂ capture processes, this study explores the possibility of utilizing inexpensive and readily available fly ash (FA) as a catalyst to enhance the regeneration process of CO₂-saturated sorbents. The desorption performance of FA was

experimentally measured in terms of CO₂ desorption rate, cyclic capacity and heat duty at a temperature of 88 °C from a CO₂-saturated aqueous solution of MEA 5 M. The results were compared with those obtained for the same solution without catalyst and with eight other different catalysts (previously validated in other studies), under identical operating conditions. The findings indicate that FA enable significantly higher desorption performance compared to the blank system, and proves to be the most efficient catalyst. In particular, the use of FA allows achieving the maximum CO₂ desorption rate value, which is significantly higher than that of all the other catalysts and almost double that of the blank system. Additionally, FA also allows most substantial reduction in energy consumed (energy required to desorb 1 mol of CO₂), with relative heat duties (compared to the blank) of 45.9% after 20 min and 68.2% after 30 min.

Subsequently, the performance of FA in the regeneration of CO₂-loaded MEA solution was further investigated. Particularly, variations in performance as a function of the desorption temperature (ranging from 88 to 103 °C) and amount of catalyst added (ranging from 0.10 to 3.00 g) were evaluated. Even with the smallest addition of FA, the catalytic effect is evident and significantly improves desorption compared to blank system. The highest performance was achieved by adding 2.00 g of FA to 200 mL of MEA solution. Furthermore, the results also indicate that the use of FA provides desorption performance comparable to that of the blank system at temperatures at least 5 °C higher, and that at different temperatures it is always able to significantly reduce the heat duty, especially in the early stages of the process. Finally, recycling tests demonstrated that the catalytic efficiency of FA remained almost unchanged after 20 continuous cycles of absorption and desorption. In conclusion, owing to its low cost (essentially a solid waste), wide availability and ease of use, FA could be considered an economically advantageous catalyst for energy-efficient CO₂ capture processes, warranting further investigation to assess its feasibility on a larger scale.

CRediT authorship contribution statement

Yingjie Niu: Investigation, Writing – original draft. **Ting Li:** Investigation, Writing – original draft. **Francesco Barzagli:** Funding acquisition, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Chao'en Li:** Funding acquisition, Supervision. **Mohammad W. Amer:** Funding acquisition, Supervision. **Rui Zhang:** Conceptualization, Funding acquisition, Supervision, Writing – original

Table 4

The actual species content (mass %) of FA catalyst, before and after use, from XRF analysis.

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	TiO ₂	P ₂ O ₅	others
FA	50.4	24.5	9.4	6.4	2.7	2.1	1.1	3.4
Recycled FA	50.3	37.6	4.2	2.1	1.5	1.1	0.3	2.7

draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (22008204), the Natural Science Foundation of Hunan Province (2023JJ30580), the Research Start-up Foundation of Xiangtan University (21QDZ56) and the CNR/HCST/NCRD bilateral project Italy-Jordan (B95F21000050005).

References

- [1] IPCC. Climate change 2014: synthesis report. Contribution of working groups I, II and III to the Fifth Assessment report of the Intergovernmental Panel on climate change. 2014. Geneva, Switzerland.
- [2] Cao M, Zhao L, Xu D, Ciora R, Liu PKT, Manousiouthakis VI, et al. A carbon molecular sieve membrane-based reactive separation process for pre-combustion CO₂ capture. *J Membr Sci* 2020;605:118028. <https://doi.org/10.1016/j.memsci.2020.118028>.
- [3] UNFCCC - United Nations Framework Convention on ClimateChange. The Glasgow climate Pact – key outcomes from COP26. 2021. <https://unfccc.int/process-and-meetings/the-paris-agreement/the-glasgow-climate-pact-key-outcomes-from-cop26>.
- [4] UNFCCC - United Nations Framework Convention on ClimateChange. The Paris Agreement. 2015. <https://unfccc.int/process/the-paris-agreement/the-paris-agreement>.
- [5] El Hadri N, Quang DV, Goetheer ELV, Abu Zahra MRM. Aqueous amine solution characterization for post-combustion CO₂ capture process. *Appl Energy* 2017;185:1433–49. <https://doi.org/10.1016/j.apenergy.2016.03.043>.
- [6] Bui M, Adjiman CS, Bardow A, Anthony EJ, Boston A, Brown S, et al. Carbon capture and storage (CCS): the way forward. *Energy Environ Sci* 2018;11:1062–176. <https://doi.org/10.1039/c7ee02342a>.
- [7] Feron PHM, Cousins A, Jiang K, Zhai R, Garcia M. An update of the benchmark post-combustion CO₂ capture technology. *Fuel* 2020;273:117776. <https://doi.org/10.1016/j.fuel.2020.117776>.
- [8] Chen G, Chen G, Peruzzini M, Barzagli F, Zhang R. Investigating the performance of ethanolamine and Benzylamine blends as promising sorbents for postcombustion CO₂ capture through ¹³C NMR speciation and heat of CO₂ absorption analysis. *Energy Fuels* 2022;36:9203–12. <https://doi.org/10.1021/acs.energyfuels.2c01930>.
- [9] He X, He H, Barzagli F, Amer MW, Li C, Zhang R. Analysis of the energy consumption in solvent regeneration processes using binary amine blends for CO₂ capture. *Energy* 2023;270:126903. <https://doi.org/10.1016/j.energy.2023.126903>.
- [10] Idem R, Wilson M, Tontiwachwuthikul P, Chakma A, Veawab A, Aroonwilas A, et al. Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the boundary dam CO₂ capture demonstration plant. *Ind Eng Chem Res* 2006;45:2414–20. <https://doi.org/10.1021/ie050569e>.
- [11] Oh SY, Binns M, Cho H, Kim JK. Energy minimization of MEA-based CO₂ capture process. *Appl Energy* 2016;169:353–62. <https://doi.org/10.1016/j.apenergy.2016.02.046>.
- [12] Zhang C, Zhou C, Li Y, Yu Y, Zhang J, Zhang Z, et al. Single atom solutions for carbon dioxide capture. *J Chem Phys* 2023;158:84309. <https://doi.org/10.1063/5.0132627>.
- [13] Zhou C, Zhang C, Zhang T, Zhang J, Ma P, Yu Y, et al. Single-atom solutions promote carbon dioxide capture. *Appl Energy* 2023;332:120570. <https://doi.org/10.1016/j.apenergy.2022.120570>.
- [14] Zhou X, Shen Y, Liu F, Ye J, Wang X, Zhao J, et al. A novel dual-stage phase separation process for CO₂ absorption into a biphasic solvent with low energy penalty. *Environ Sci Technol* 2021;55:15313–22. <https://doi.org/10.1021/acs.est.1c01622>.
- [15] Yu Y, Shen Y, Zhou X, Liu F, Zhang S, Lu S, et al. Relationship between tertiary amine's physical property and biphasic solvent's CO₂ absorption performance: quantum calculation and experimental demonstration. *Chem Eng J* 2022;428:131241. <https://doi.org/10.1016/j.cej.2021.131241>.
- [16] Shen Y, Gong Y, Sun L, Chen P, Zhang Q, Ye J, et al. Machine learning-driven assessment of relationship between activator properties in phase change solvent and its absorption performance for CO₂ capture. *Sep Purif Technol* 2023;309:123092. <https://doi.org/10.1016/j.seppur.2022.123092>.
- [17] Barzagli F, Bhatti UH, Kazmi WW, Peruzzini M. Solid acid catalysts for low-temperature regeneration of non-aqueous sorbents: an innovative technique for energy-efficient CO₂ capture processes. *Carbon Capture Sci Technol* 2023;8:100124. <https://doi.org/10.1016/j.ccsst.2023.100124>.
- [18] Shi H, Cheng X, Peng J, Feng H, Yang X, Quan L, et al. Structure-activity correlation analyses of MEA + 3A1P/MAE isomers with a coordinative effect study. *Ind Eng Chem Res* 2022;61:3091–103. <https://doi.org/10.1021/acs.iecr.1c02726>.
- [19] Shi H, Yang X, Feng H, Fu J, Zou T, Yao J, et al. Evaluating energy-efficient solutions of CO₂ capture within tri-solvent MEA+BEA+AMP within 0.1+2+2–0.5+2+2 mol/L combining heterogeneous acid–base catalysts. *Ind Eng Chem Res* 2021;60:7352–66. <https://doi.org/10.1021/acs.iecr.1c00545>.
- [20] Zhang R, Li Y, He X, Niu Y, Li C, Amer MW, et al. Investigation of the improvement of the CO₂ capture performance of aqueous amine sorbents by switching from dual-amine to trio-amine systems. *Sep Purif Technol* 2023;316:123810. <https://doi.org/10.1016/j.seppur.2023.123810>.
- [21] Zhang R, Liu H, Liu R, Niu Y, Yang L, Barzagli F, et al. Speciation and gas-liquid equilibrium study of CO₂ absorption in aqueous MEA-DEEA blends. *Gas Sci Eng* 2023;119:205135. <https://doi.org/10.1016/j.gscge.2023.205135>.
- [22] Zhang R, Liu R, Barzagli F, Sanku MG, Li C, Xiao M. CO₂ absorption in blended amine solvent: speciation, equilibrium solubility and excessive property. *Chem Eng J* 2023;466:143279. <https://doi.org/10.1016/j.cej.2023.143279>.
- [23] Liu H, Qu J, Bhatti AH, Barzagli F, Li C, Bi J, et al. A generic machine learning model for CO₂ equilibrium solubility into blended amine solutions. *Sep Purif Technol* 2024;334:126100. <https://doi.org/10.1016/j.seppur.2023.126100>.
- [24] Shi H, Cheng X, Peng J, Feng H, Tontiwachwuthikul P, Hu J. The CO₂ absorption and desorption analysis of tri-solvent MEA + EAE + AMP compared with MEA + BEA + AMP along with “coordination effects” evaluation. *Environ Sci Pollut Res* 2022;29:40686–700. <https://doi.org/10.1007/s11356-022-18792-0>.
- [25] Zhang B, Peng J, Li Y, Shi H, Jin J, Hu J, et al. Evaluating CO₂ desorption activity of tri-solvent MEA + EAE + AMP with various commercial solid acid catalysts. *Catalysts* 2022;12:723. <https://doi.org/10.3390/catal12070723>.
- [26] Bhatti UH, Alivand MS, Barzagli F, Sanku MG, Gascon J, Mumford KA. Functionalized carbon spheres for energy-efficient CO₂ capture: synthesis, application, and reaction mechanism. *ACS Sustainable Chem Eng* 2023;11:11955–64. <https://doi.org/10.1021/acssuschemeng.3c02069>.
- [27] Shi H, Naami A, Idem R, Tontiwachwuthikul P. Catalytic and non catalytic solvent regeneration during absorption-based CO₂ capture with single and blended reactive amine solvents. *Int J Greenh Gas Control* 2014;26:39–50. <https://doi.org/10.1016/j.ijggc.2014.04.007>.
- [28] Liang Z (Henry), Rongwong W, Liu H, Fu K, Gao H, Cao F, et al. Recent progress and new developments in post-combustion carbon-capture technology with amine based solvents. *Int J Greenh Gas Control* 2015;40:26–54. <https://doi.org/10.1016/j.ijggc.2015.06.017>.
- [29] Alivand MS, Mazaheri O, Wu Y, Stevens GW, Scholes CA, Mumford KA. Catalytic solvent regeneration for energy-efficient CO₂ capture. *ACS Sustainable Chem Eng* 2020;8:18755–88. <https://doi.org/10.1021/acssuschemeng.0c07066>.
- [30] Li T, Yu Q, Barzagli F, Li C, Che M, Zhang Z, et al. Energy efficient catalytic CO₂ desorption: mechanism, technological progress and perspective. *Carbon Capture Sci Technol* 2023;6:100099. <https://doi.org/10.1016/j.ccsst.2023.100099>.
- [31] Srisang W, Pouryousefi F, Osei PA, Decardi-Nelson B, Akachuku A, Tontiwachwuthikul P, et al. Evaluation of the heat duty of catalyst-aided amine-based post combustion CO₂ capture. *Chem Eng Sci* 2017;170:48–57. <https://doi.org/10.1016/j.ces.2017.01.049>.
- [32] Bhatti UH, Kazmi WW, Muhammad HA, Min GH, Nam SC, Baek IH. Practical and inexpensive acid activated montmorillonite catalysts for energy-efficient CO₂ capture. *Green Chem* 2020;22:6328–33. <https://doi.org/10.1039/d0gc01887b>.
- [33] Bhatti UH, Sultan H, Min GH, Nam SC, Baek IH. Ion-exchanged montmorillonite as simple and effective catalysts for efficient CO₂ capture. *Chem Eng J* 2021;413:127476. <https://doi.org/10.1016/j.cej.2020.127476>.
- [34] Zhang R, Li Y, Zhang Y, Li T, Yang L, Li C, et al. Energy-saving effect of low-cost and environmentally friendly sepiolite as an efficient catalyst carrier for CO₂ capture. *ACS Sustainable Chem Eng* 2023;11:4353–63. <https://doi.org/10.1021/acssuschemeng.2c06739>.
- [35] Yao ZT, Ji XS, Sarker PK, Tang JH, Ge LQ, Xia MS, et al. A comprehensive review on the applications of coal fly ash. *Earth Sci Rev* 2015;141:105–21. <https://doi.org/10.1016/j.earscirev.2014.11.016>.
- [36] Dindi A, Quang DV, Vega LF, Nashef E, Abu-Zahra MRM. Applications of fly ash for CO₂ capture, utilization, and storage. *J CO₂ Util* 2019;29:82–102. <https://doi.org/10.1016/j.jcou.2018.11.011>.
- [37] Montes-Hernandez G, Pérez-López R, Renard F, Nieto JM, Charlet L. Mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash. *J Hazard Mater* 2009;161:1347–54. <https://doi.org/10.1016/j.jhazmat.2008.04.104>.
- [38] Tamilselvi Dananjayan RR, Kandasamy P, Andimuthu R. Direct mineral carbonation of coal fly ash for CO₂ sequestration. *J Clean Prod* 2016;112:4173–82. <https://doi.org/10.1016/j.jclepro.2015.05.145>.
- [39] Sreenivasulu B, Sreedhar I, Reddy BM, Raghavan KV. Stability and carbon capture enhancement by coal-fly-ash-doped sorbents at a high temperature. *Energy Fuels* 2017;31:785–94. <https://doi.org/10.1021/acs.energyfuels.6b02721>.
- [40] Uliasz-Bocheńczyk A, Mokrzycki E. The potential of FBC fly ashes to reduce CO₂ emissions. *Sci Rep* 2020;10:9469. <https://doi.org/10.1038/s41598-020-66297-y>.
- [41] Czuma N, Casanova I, Baran P, Szczurowski J, Zarębska K. CO₂ sorption and regeneration properties of fly ash zeolites synthesized with the use of differentiated methods. *Sci Rep* 2020;10:1825. <https://doi.org/10.1038/s41598-020-58591-6>.

- [42] Kumar V, Labhsetwar N, Meshram S, Rayalu S. Functionalized fly ash based aluminosilicates for capture of carbon dioxide. *Energy Fuels* 2011;25:4854–61. <https://doi.org/10.1021/ef201212h>.
- [43] Sarmah M, Baruah BP, Khare P. A comparison between CO₂ capturing capacities of fly ash based composites of MEA/DMA and DEA/DMA. *Fuel Process Technol* 2013;106:490–7. <https://doi.org/10.1016/j.fuproc.2012.09.017>.
- [44] Liang Z, Idem R, Tontiwachwuthikul P, Yu F, Liu H, Rongwong W. Experimental study on the solvent regeneration of a CO₂-loaded MEA solution using single and hybrid solid acid catalysts. *AIChE J* 2016;62:753–65. <https://doi.org/10.1002/aic.15073>.
- [45] Gao H, Huang Y, Zhang X, Bairq ZAS, Huang Y, Tontiwachwuthikul P, et al. Catalytic performance and mechanism of SO₄²⁻/ZrO₂/SBA-15 catalyst for CO₂ desorption in CO₂-loaded monoethanolamine solution. *Appl Energy* 2020;259:114179. <https://doi.org/10.1016/j.apenergy.2019.114179>.
- [46] Zhang X, Zhang X, Liu H, Li W, Xiao M, Gao H, et al. Reduction of energy requirement of CO₂ desorption from a rich CO₂-loaded MEA solution by using solid acid catalysts. *Appl Energy* 2017;202:673–84. <https://doi.org/10.1016/j.apenergy.2017.05.135>.
- [47] Zhang X, Huang Y, Yang J, Gao H, Huang Y, Luo X, et al. Amine-based CO₂ capture aided by acid-basic bifunctional catalyst: advancement of amine regeneration using metal modified MCM-41. *Chem Eng J* 2020;383:123077. <https://doi.org/10.1016/j.cej.2019.123077>.
- [48] Zhang R, Li T, Zhang Y, Ha J, Xiao Y, Li C, et al. CuO modified KIT-6 as a high-efficiency catalyst for energy-efficient amine solvent regeneration. *Sep Purif Technol* 2022;300:121702. <https://doi.org/10.1016/j.seppur.2022.121702>.
- [49] Zhang R, Zhang Y, Cheng Y, Yu Q, Luo X, Li CC, et al. New approach with universal applicability for evaluating the heat requirements in the solvent regeneration process for postcombustion CO₂ capture. *Ind Eng Chem Res* 2020;59:3261–8. <https://doi.org/10.1021/acs.iecr.9b05247>.
- [50] Bhatti UH, Ienco A, Peruzzini M, Barzagli F. Unraveling the role of metal oxide catalysts in the CO₂ desorption process from nonaqueous sorbents: an experimental study carried out with ¹³C NMR. *ACS Sustainable Chem Eng* 2021;9:15419–26. <https://doi.org/10.1021/acssuschemeng.1c04026>.
- [51] Xing L, Wei K, Li Q, Wang R, Zhang S, Wang L. One-step synthesized SO₄²⁻/ZrO₂-HZSM-5 solid acid catalyst for carbamate decomposition in CO₂ capture. *Environ Sci Technol* 2020;54:13944–52. <https://doi.org/10.1021/acs.est.0c04946>.
- [52] Sun Q, Li T, Mao Y, Gao H, Sema T, Wang S, et al. Reducing heat duty of MEA regeneration using a sulfonic acid-functionalized mesoporous MCM-41 catalyst. *Ind Eng Chem Res* 2021;60:18304. https://doi.org/10.1021/ACS.IECR.1C03671/ASSET/IMAGES/LARGE/IE1C03671_0010.JPEG. –15.
- [53] Bhatti UH, Shah AK, Hussain A, Khan HA, Park CY, Nam SC, et al. Catalytic activity of facilely synthesized mesoporous HZSM-5 catalysts for optimizing the CO₂ desorption rate from CO₂-rich amine solutions. *Chem Eng J* 2020;389. <https://doi.org/10.1016/j.cej.2019.123439>.