SOLVENT-FREE SHEAR MIXING VS. WET IMPREGNATION: EVALUATION OF CLASS I POLYAMINE-BASED SORBENTS FOR CO_2 CAPTURE

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Abstract

Amine-functionalized solid adsorbents are key materials for CO_2 capture, but their practical deployment is often constrained by energy-intensive, solvent-based and time-consuming preparation methods. This study addresses that challenge by evaluating a solvent-free high-speed shear mixing (DRY) method for preparing amine-loaded adsorbents using ZEOFREE® 600, a commercially available calcium silicate. Three polyamines, branched polyethylenimine (PEI), pentaethylenehexamine (PEHA), and tetraethylenepentamine (TEPA), were impregnated at 30–60 wt.% loadings and compared with samples prepared via conventional WET impregnation. Results indicated that the DRY method yielded comparable or superior performance across multiple criteria, including morphological stability, textural properties, amine accessibility, thermal resistance, and cyclic durability, while eliminating the need for solvents and prolonged drying and requiring significantly less energy and processing time. Under simulated flue gas conditions (10% CO_2), maximum adsorption capacities reached 3.52 $mmol \cdot g^{-1}$ for TEPA60_DRY, 3.44 $mmol \cdot g^{-1}$ for PEHA60_DRY, and 3.19 $mmol \cdot g^{-1}$ for PEI60_DRY. TEPA and PEHA-based adsorbents exhibited superior uptake capacity, while PEI-based adsorbents provided enhanced thermal and cyclic stability. These findings demonstrate the suitability of ZEOFREE® 600 as a support and confirm the DRY method as a time and energy-efficient alternative for producing class I CO_2 sorbents.

Keywords: Amine, adsorption, impregnation, solvent-free shear mixing, carbon capture

1. INTRODUCTION

Amine-functionalized solid adsorbents have received significant attention for their high CO_2 selectivity, reversible chemisorption, and effectiveness under both flue gas and ultra-dilute conditions [1-3]. Early work by Satyapal et al. [4] demonstrated that polyamine-based sorbents, stabilized with polymeric supports and additives, could deliver both high capacity and long-term stability, laying the groundwork for later advances in post-combustion capture and direct air capture. In particular, solid amine sorbents continue to attract widespread research interest due to their high surface areas and tunable pore networks. Despite their promising characteristics, current preparation methods present challenges. Wet impregnation, the most widely used approach, relies on dissolving polyamines in volatile solvents, followed by lengthy drying [5]. This process is energy and time-intensive, generates toxic waste, and may lead to scalability issues. To overcome these drawbacks, recent efforts have focused on solvent-free processing. Shi et al. [6] demonstrated that low-molecular-weight amines like TEPA can be loaded onto silica via high-speed mechanical mixing. Building on this, we recently developed a solvent-free high-speed shear mixing approach using a dual asymmetric centrifuge [7].

In this study, we further explore the DRY method by impregnating PEI, PEHA, and TEPA at 30–60 wt.% onto ZEOFREE® 600, a high-surface-area commercial calcium silicate. DRY-prepared adsorbents are benchmarked against conventional WET-prepared counterparts under simulated flue gas (10% CO_2). Through morphological, textural, thermal, uptake and cyclic performance evaluations, this work aims to assess ZEOFREE® 600 as a viable support and establish the DRY method as a scalable, energy and time-efficient route for producing high-performing class I solid amine adsorbents.

2. EXPERIMENTAL

2.1 Materials

Branched polyethyleneimine, PEI (CAS-No: 25987-06-8, average M_w ~800 g·mol^{-1} by LS), pentaethylenehexamine, PEHA (CAS-No: 4067-16-7, M_w 232.37 g·mol^{-1}, technical grade), and tetraethylenepentamine, TEPA (CAS-No: 112-57-2, M_w 189.30 g·mol^{-1}, technical grade) were purchased from Sigma-Aldrich and used as received without any purification. The synthetic precipitated calcium silicate, ZEOFREE® 600, was supplied by Evonik and kindly provided by Rokospol, a.s. and dried in a vacuum oven at 90 °C under pressure of 5 mTorr for 12 hours to remove traces of moisture before the sample preparation.

2.2.1 Preparation of adsorbents

In the DRY method, ZEOFREE® 600 was impregnated with PEI, PEHA, and TEPA at 30, 40, 50 and 60% loadings via high-speed shear mixing using a SpeedMixer DAC 150.1 FVZ-K (Hauschild & Co KG, Germany). Specific amounts of ZEOFREE® 600 were mixed with the corresponding amounts of amine, followed by two shear mixing cycles (total two minutes) at speeds up to 3500 rpm. For comparison, a conventional WET impregnation method was also employed. In this procedure, the same amount of amine was dissolved in 20 mL of methanol at room temperature under continuous stirring for 30 minutes. The same amount of pre-dried ZEOFREE® 600 was then added to the solution, and the mixture was stirred for an additional 8-10 hours to allow gradual solvent evaporation. The resulting solids were dried overnight at 60 °C to remove any residual methanol.

2.2.2 Characterization of adsorbents

The morphologies of the synthesized adsorbents were examined using a Nova NanoSEM 450 scanning electron microscope (SEM) (Thermo Fisher Scientific, The Netherlands). Textural properties, including specific surface area and total pore volume, were determined through nitrogen adsorption/desorption isotherms measured at 77 K using a Belsorb mini II analyzer (MicrotracBEL, Japan). Prior to analysis, the samples were degassed at 100 °C for 3 hours under vacuum. Total pore volumes were determined at a relative pressure (P/P_0) of 0.99. The thermal stability and the amine loading of the synthesized adsorbents was assessed using thermogravimetric analyzer TGA Q500 (TA Instruments, USA). A small amount of sample (10-20 mg) was placed in platinum crucibles and heated from 30 °C to 800 °C at a rate of 10 °C/min under a continuous nitrogen flow of 100 mL/min.

2.4 Evaluation of CO_2 adsorption

The adsorption experiment was modified to simulate a CO_2-rich environment. A gas mixture containing 10% CO_2 was created by mixing 10 mL·min^{-1} of CO_2 with 90 mL·min^{-1} of N_2. These measurements were conducted using a thermogravimetric analyzer TGA Q500 (TA Instruments, USA). To determine the optimal adsorption temperature, samples were screened between 25 °C and 110 °C. PEI-based samples showed the highest uptake at 80 °C, while PEHA- and TEPA-based adsorbents performed best at 70 °C. For regeneration, 90 °C under N_2 atmosphere was used for all samples. To assess the long-term stability of the adsorbents, the adsorption/desorption cycle was repeated 20 times for the selected samples.

3. RESULTS AND DISCUSSIONS

3.1 Samples characteristics

Figure 1 shows the surface morphologies of amine-functionalized ZEOFREE® 600 prepared by DRY and WET methods. No major morphological differences were observed between the two methods, indicating that DRY method is effective at dispersing amines without solvents. However, notable differences emerged depending on the amine type. PEI-based samples exhibited larger and more irregular aggregates, likely due to the high viscosity and branched structure of PEI [8]. In contrast, TEPA-functionalized samples displayed finer and more uniform morphologies, reflecting better dispersion throughout the support. PEHA-modified samples showed moderate aggregation, consistent with its intermediate molecular weight and viscosity compared to PEI and TEPA. These trends suggest that TEPA enables superior amine distribution, which may contribute to its higher CO_2 uptake performance.

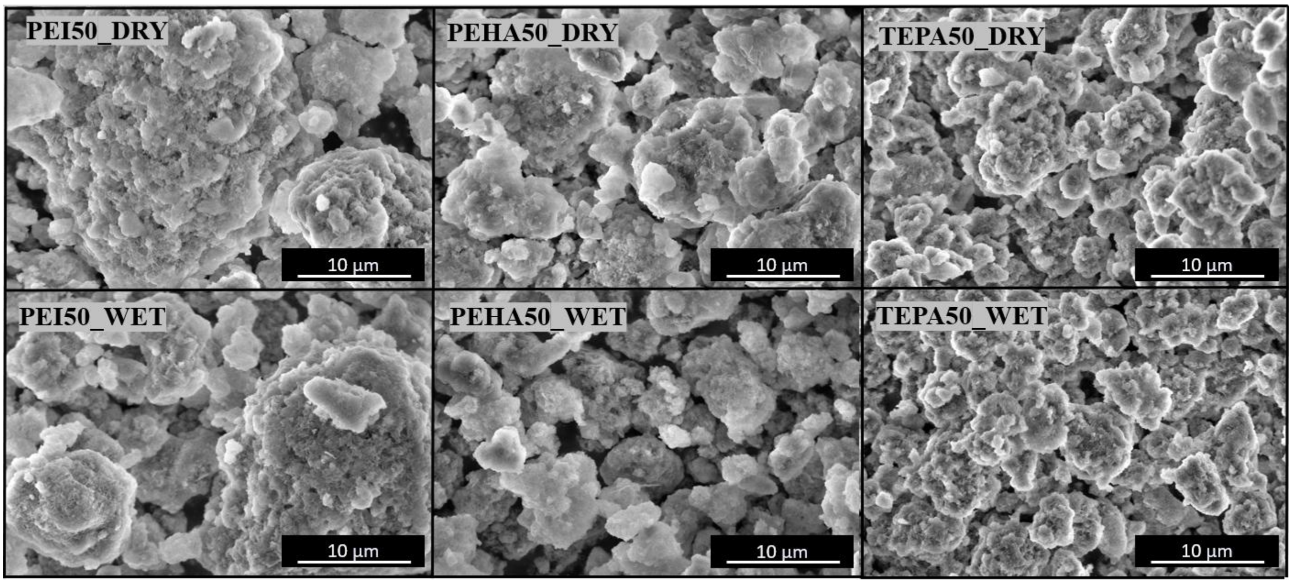

Figure 1 SEM images of amine-functionalized ZEOFREE® 600 adsorbents prepared via DRY (up) and WET (down) impregnation methods at 50 wt.% loading

Textural characteristics were evaluated using nitrogen adsorption–desorption isotherms, with the corresponding BET surface area and pore volume values summarized in **Table 1**. All materials exhibited Type III isotherm. Pristine ZEOFREE® 600 displayed a high BET surface area (167.1 m^2/g) and pore volume (1.344 cm^3/g), making it a suitable candidate for high amine loadings. Upon functionalization, a progressive decrease in surface area and pore volume was observed across all samples. PEI-loaded samples, particularly PEI60_DRY, showed the most significant reductions (5.41 m^2/g, 0.065 cm^3/g), attributed to longer entanglement of polymer chains of PEI which can lead to denser packing during mixing, thus decreasing the surface area of the adsorbent [9]. TEPA-functionalized samples retained higher textural values (e.g., TEPA60_DRY: 16.26 m^2/g, 0.2734 cm^3/g), supporting their more uniform dispersion. PEHA samples exhibited intermediate values. Additionally, almost all WET-prepared samples showed slightly higher surface areas and pore volumes than DRY-prepared ones, likely due to slower amine deposition in the presence of solvent. Nevertheless, the structural differences between the two methods remained minor.

TG/DTG analysis confirmed successful functionalization, with amine-modified samples showing higher weight loss than the support. WET samples retained more moisture due to solvent use. Regardless of the preparation route, PEI and PEHA based samples exhibited greater thermal stability compared to the more volatile TEPA based samples.

Table 1 Comparison of BET surface area, total pore volume, CO_2 adsorption capacity, and amine efficiency of DRY and WET-prepared adsorbents

Samples		**BET Surface Area (m^2/g)**		**Total Pore Volume (cm^3/g)**		**CO_2 adsorption capacity (mmol/g)**		**Amine efficiency (mmol CO_2/g amine)**	
Amine	Loading	DRY	WET	DRY	WET	DRY	WET	DRY	WET
PEI	30	51.2	56.3	0.8192	0.8984	1.47	1.46	0.21	0.21
PEI	40	35.54	40.9	0.6191	0.7014	1.86	1.81	0.2	0.19
PEI	50	21.44	21.85	0.3890	0.3498	2.39	2.25	0.2	0.19
PEI	60	5.41	9.27	0.0651	0.1497	3.19	2.64	0.22	0.18
PEHA	30	62.77	66.35	0.9336	0.9437	1.75	1.57	0.22	0.2
PEHA	40	42.75	47.26	0.6816	0.7630	2.24	2.12	0.21	0.2
PEHA	50	26.87	26.10	0.3793	0.4179	2.69	2.62	0.2	0.2
PEHA	60	8.55	13.47	0.1244	0.2290	3.44	3.24	0.22	0.19
TEPA	30	69.07	64.64	0.9552	0.9670	1.78	1.85	0.22	0.23
TEPA	40	45.87	49.15	0.7384	0.7597	2.42	2.21	0.22	0.2
TEPA	50	31.06	32.89	0.4653	0.5265	3.11	2.66	0.23	0.21
TEPA	60	16.26	16.38	0.2734	0.2613	3.52	3.22	0.22	0.2

3.2 Analysis of CO_2 adsorption capacity and amine efficiency

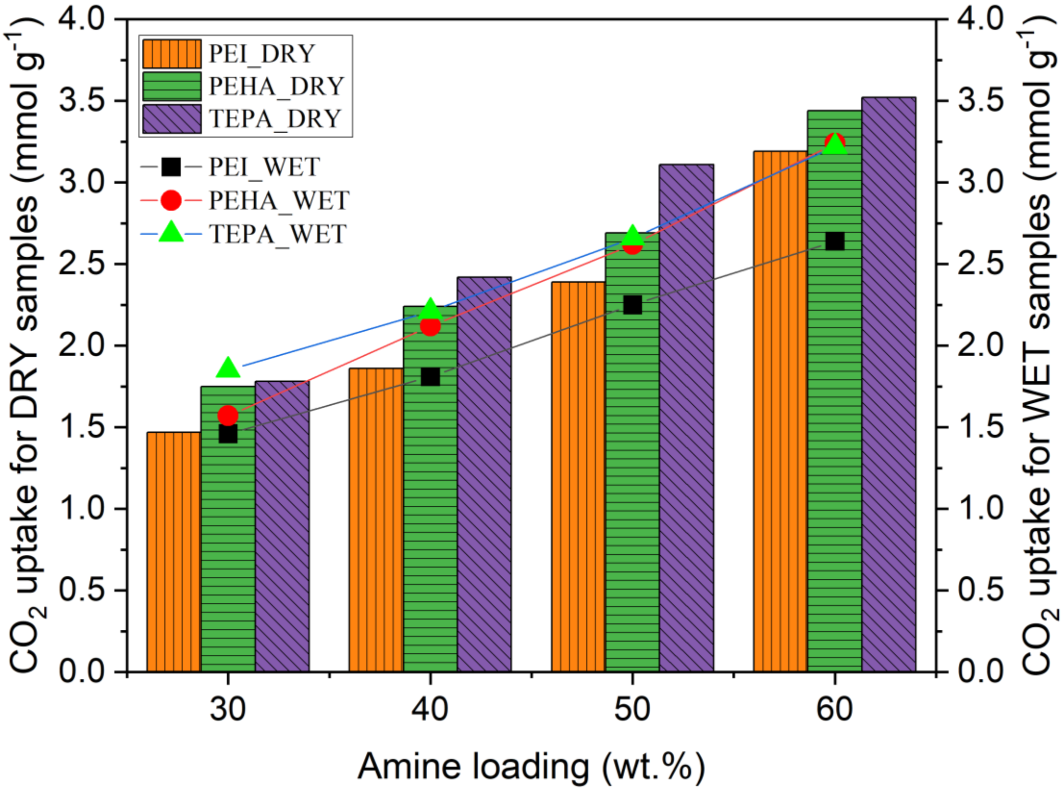

Figure 2 CO_2 adsorption capacity of all prepared samples.

CO_2 adsorption capacity and amine efficiency are key indicators of the performance of solid amine-based adsorbents. As shown in **Figure 2**, DRY-prepared samples exhibited higher CO_2 uptake than their WET counterparts. This improvement can be attributed to the absence of solvent residues and the formation of more open pore networks, which facilitate faster diffusion and greater accessibility of active amine sites [6]. The uptake trend followed TEPA > PEHA > PEI based samples for all loadings and preparation routes, which agrees with literature data [10]. Notably, at comparable loadings DRY samples not only delivered higher CO_2 capacities but also maintained similar or slightly better amine efficiencies than WET samples, demonstrating that higher uptake did not come at the expense of amine utilization. Amine efficiency, defined as mmol CO_2 captured per gram of amine, is also presented in **Table 1**. Three distinct regimes of amine loading and performance emerged. (i) Low loadings (30 wt.%): Amine efficiency was relatively high across all samples, with TEPA and PEHA based samples slightly outperforming PEI, reflecting better dispersion, minimal pore blockage. (ii) Moderate loadings (40–50 wt.%): A slight decline in efficiency occurred with increased loading, likely due to partial pore blockage or diffusion limitations. Nevertheless, TEPA50_DRY achieved the highest efficiency (0.235 mmol g^{-1} amine), may indicate an optimal balance between amine content and accessibility at this loading. (iii) High loading (60 wt.%): Efficiency stabilized or increased slightly for DRY samples, suggesting that the denser but well-dispersed amine layers created by shear mixing may still allow good CO_2 accessibility, whereas WET samples showed a more pronounced drop.

3.3 Analysis of cyclic capacity and stability

Long-term stability is a key requirement for practical CO_2 adsorbents. To assess this, 20 thermal swing cycles were conducted under 10% CO_2 using DRY and WET samples loaded with 50 wt.% amine, as shown in **Figure 3**. PEI-based samples exhibited excellent stability, with only ~5% capacity loss and less than 1% mass loss over 20 cycles. This behavior aligns with PEI's higher thermal stability and branched macromolecular structure, which likely resists degradation during repeated heating and gas exposure [5]. PEHA-based sorbents followed closely, with PEHA50_DRY and PEHA50_WET showing capacity losses of 5.25% and 4.39%, respectively, and mass losses below 2%. Although slightly less thermally robust than PEI, PEHA still demonstrated strong resistance to degradation and the DRY sample exhibited a higher average CO_2 capacity across cycles (2.81 mmol·g^{-1} vs. 2.61 mmol·g^{-1} for WET), indicating better accessibility or retention of active sites. In contrast, TEPA-based adsorbents degraded more significantly over time. TEPA50_DRY and TEPA50_WET showed capacity losses of 20.7% and 17.1%, along with 8.8% and 6.8% mass loss, respectively. These results suggest that TEPA, being the most volatile and lowest molecular weight amine among the three, is more prone to evaporation or decomposition under cyclic conditions.

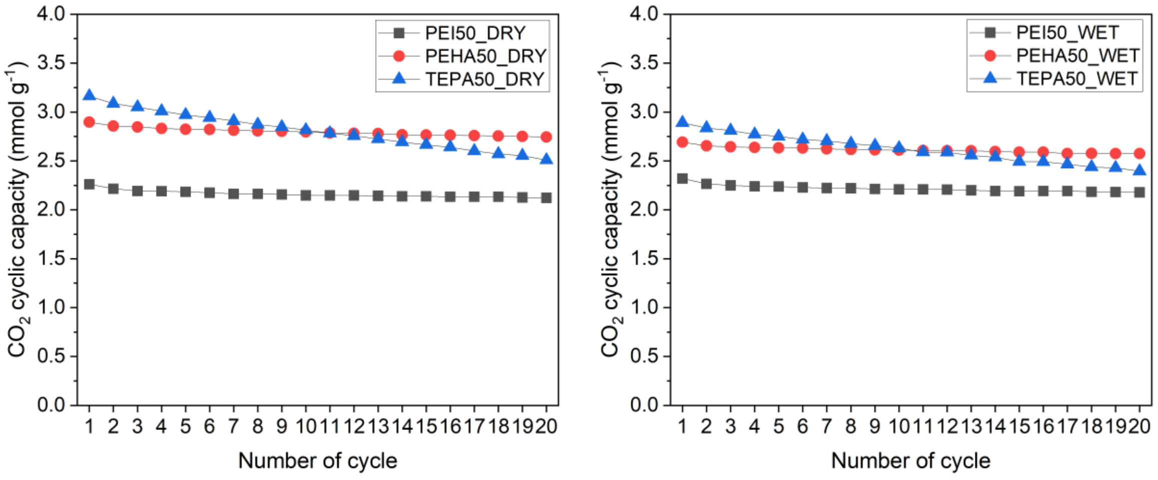

Figure 3 CO_2 cyclic results over 20 cycles for 50 wt.% loaded PEI, PEHA, and TEPA samples prepared by DRY (left) and WET (right) impregnation methods.

4. CONCLUSION

This work demonstrated the successful preparation of amine-functionalized ZEOFREE® 600 adsorbents via a solvent-free DRY method, offering a simple, sustainable, and time-efficient alternative to conventional WET impregnation. Across various amine types and loadings, the DRY approach produced materials with comparable or superior performance in terms of morphology, CO_2 uptake, cyclic, and stability. TEPA and PEHA-based samples achieved higher CO_2 capacities, while PEI-based sorbents exhibited enhanced thermal and cyclic durability. Among them, PEHA-based adsorbents emerged as the most balanced candidate, combining good uptake with long-term stability. Overall, the DRY method proves to be an effective and may scalable strategy for producing solid CO_2 adsorbents without compromising material performance.

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