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Converting polyolefin fibres into CO₂ adsorbent by radiation induced grafting

🔟 Noor Ashikin Mohamad^{a,b}, 🔟 Nur Afifah Zubair^{a,b}, 🔟 Mohamed Mahmoud Nasef^{a,b,*}, 🔟 Teo Ming Ting^c

^aMalaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia. ^bCenter of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia. ^cRadiation Processing Technology Division, Malaysian Nuclear Agency, 43000, Kajang, Selangor, Malaysia.

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ABSTRCT

Polyethylene (PE)/polypropylene (PP) bicomponent fibres were converted into three types of CO₂ adsorbents by radiation induced graft copolymerization (RIGC) of glycidyl methacrylate (GMA) and N-vinylformamide (NVF) followed by treatment of poly(GMA) grafted fibres with polyethyleneimine (PEI) or ethylenediamine (EDA) and poly(NVF) grafted counterpart with hydrolysis to yield grafted poly(vinylamine) poly(VAm). The incorporation of poly(GMA) having same degree of grafting (DG%) and their subsequently aminated samples were verified by Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). The performance of the three adsorbents was evaluated with pure CO₂ and N₂ gases and their mixtures of different ratios. The adsorbent with PEI showed CO₂ adsorption capacity of 1.03 mmol/g, which was increased to 1.43 mmol/g when it was substituted with EDA, whereas this value was raised to 1.69 mmol/g in the adsorbent containing poly(VAm) at 30 bar and room temperature. Such CO₂ adsorption capacity values were decreased when CO₂/N₂ mixtures were adsorbed, and the decrease was more profound at lower CO₂ content in all adsorbents, but the performance of poly(VAm)-containing adsorbent remained superior. It can be concluded that RIGC provides a versatile method to convert PE/PP fibres into highly selective CO₂ adsorbents with NVF grafting route is simpler and yield more efficient adsorbent for CO₂ capture.

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I. INTRODUCTION

Polyolefins are a class of polymers that include materials like polyethylene (PE) and polypropylene (PP) with high versatility making them one of the most popular plastics. Polyolefins are widely used in various industrial applications including packaging materials, pipes and fittings, automotive parts, electrical insulation, textiles, automotive parts, and consumer goods. This is due to their excellent chemical resistance, mechanical integrity including toughness and resistance abrasion in addition to hydrophobicity and low cost [1]. One of the appealing applications that has indeed been explored is the use of PE and PP fibres/nonwoven fabrics as substrates for developing functionalized adsorbents for various environmental applications. This area has gained an ever increasing attention as a means to mitigate rising levels of water and air pollution [2].

To develop SFA, specific ionic groups can be introduced to the surface of polymer substrates such as PE or PP fibres/nonwoven fabrics using graft copolymerization that can be initiated using thermal initiation, plasma treatment, redox initiation, photo-initiation in presence of UV and ionizing radiation [3, 4]. Of all methods, initiation of graft copolymerization using ionizing radiation (known as radiation induced graft copolymerization or RIGC such as γ -rays and electron beam (EB), offers several advantages, including clean and environmentally friendly approach because eliminating the detrimental residues and providing precise and uniform control over the level of grafting and its homogeneity [5].

RIGC method works on the principle of exposing polymer substrates to ionizing "radiation generates free radicals by H abstraction from polymer backbone that initiate copolymerization when the irradiated substrates are brought in contact with polar monomer molecules which can be performed with simultaneous grafting or pre-irradiation grafting. The former method involves irradiation of the polymer substrate and the monomer together under controlled conditions whereas in the latter one, the substrate is irradiated separately before being brought into contact with the monomer under controlled conditions. The grafting yield can be easily optimized by controlling the grafting conditions. Both grafting methods lead to formation of covalently bonded side chain grafts on the substrate leaving capable of hosting ionic groups either by grafting of an ionic monomer or indirectly in a post grafting reaction when a non-ionic monomer is used. These ionic groups have strong affinity that can enhance the adsorption capacity of the material for targeted pollutants. For example, functional groups such as sulfonate (-SO₃H), carboxyl (-COOH), hydroxyl (-OH) or amino (-NH₂) groups can be incorporated onto the surface imparting ionic moieties [6].

The functionalized adsorbents based on PE and PP fibres/nonwoven fabric have several advantages. Firstly, the large surface area and porous structure of these materials provide ample contact sites to adsorb pollutants. Secondly, the presence of specific ionic groups increases the affinity between the adsorbent and target pollutants, enhancing the adsorption efficiency. The use of PE and PP fibres/nonwoven fabric as substrates also allows for easy handling, scalability, and potential reusability of the adsorbents. Particularly, these fibrous adsorbents offer crucial advantages over traditional adsorbent beads in packed-bed columns, particularly in applications involving high-pressure gas treatment, such as the removal of CO₂ from natural gas where the treated gas loses a great deal of pressure. Additionally, these adsorbents eliminate the feed channelling taking place upon using adsorbent beads in packed-bed columns [7]. The feed channelling refers to the phenomenon in which the fluid flow within the adsorption column using beads becomes concentrated in specific areas while bypassing certain regions of the bed causing an uneven feed distribution and contact time reduction leading to an inefficient adsorption process [8].

Many studies reported the development of various radiation grafted fibrous adsorbents with different functional groups. Most of such adsorbents were dedicated for wastewater treatment applications involving removal of various pollutants such as heavy metals, dyes, boron, arsenic, and oil spills [9-11]. However, less efforts were exerted to develop selective radiation grafted adsorbents to mitigate air pollution by CO₂ capture [2, 12]. Indeed, there have been some studies on using aminated electrospun nanofibrous substrates made of PP [13-15], polyacrylonitrile (PAN) [2], PAN/polystyrene (PS) [16] for application in CO₂ capture by RIGC and subsequent amine loading. Degrees of grafting (DG) above 100% were maintained in the adsorbent precursors to ensure having sufficient sites to load the desired amine groups and eventually acquire higher adsorption capacities coupled with faster kinetics than commercial resins. However, such nanofibrous adsorbents are facing challenges related to not only poor mechanical stability and textural as well as geometric properties of the nanofibrous substrates but also difficult scalability.

This work represents another part of our continuous efforts to prepare cost-effective CO₂ adsorbents in which three fibrous adsorbents containing amine were prepared using different routes involving RIGC of glycidyl methacrylate (GMA) and N-vinyl formamide (NVF) onto PE/PP bicomponent fibres in a form of nonwoven sheet followed by amine immobilization and subsequent evaluation of the material for CO₂ capture. The PE/PP bicomponent fibres were selected because they are cheap, nonpolar, hydrophobic and have radiation resistance. The properties of the

obtained adsorbents were evaluated using various analytical techniques and the performance of the samples having same degree of grafting (DG%) was tested for pure CO_2 and N_2 gases together with their mixtures at different ratios.

II. EXPERIMENTAL METHOD

The preparation of the adsorbents involves irradiation with electron beam (EB) followed by grafting of GMA or NVF monomers and subsequent incorporation desired amine. All preparation were conducted under controlled parameters. Details of chemicals used and preparation procedures, characterization and CO₂ testing are presented below:

2.1 Chemicals and reagents

PE/PP fibrous sheets were obtained from Kurashiki Co., Japan. The GMA and NVF monomers were obtained from Sigma Aldrich (Saint Louis, MO, USA). Ethylenediamine (EDA) (purity \geq 99) was purchased from Merck Millipore and was used without any further dilution. Polyethyleneimine (PEI) (purity 50 wt% aqueous solution, branched) was purchased from Acros Organics and was further diluted with dimethylformamide (DMF) and isopropanol both were of analytical grade and purchased from Merck Millipore. Deionized water (DI) was produced by Barnstead Nanopure Diamond Lab Water Purification System (ThermoFisher) and was used for washing all samples and preparation of 2 M NaOH solution required for hydrolysis reaction. Lastly, pure CO2 gas (99.8%), pure N2 (99.999%) and pure He gas (99.995%) were supplied by Alpha Gas Solution (Sdn. Bhd., Malaysia).

2.2 Grafting of monomers onto PE/PP fibres

PE/PP fibrous sheet was irradiated under vacuum in a sealed plastic bag by an EPS3000 electron beam accelerator operating at an acceleration voltage of 1 MeV, beam current of 10 mA and dose per pass of 10 kGy to total doses of 10 and 300 kGy. Grafting of GMA was carried out by placing the irradiated samples in an evacuated ampoule containing deoxygenated monomer of desired concentration diluted with DI and 0.5 wt% Tween-20 and reaction was allowed at 40 °C for 0.5 h. On the other hand, grafting of NVF on PE/PP was carried out in a similar manner but in toluene solvent under conditions of 300 kGy absorbed dose and 70 °C temperature for 1 h. The grafted samples were extracted and washed with methanol few times and rinsed under sonication overnight before drying in a vacuum oven followed by weighing. The degree of grafting (DG%) in samples was calculated from the sample weight gain as follows:

$$DG(\%) = \frac{W_g - W_o}{W_o} \times 100\%$$
(1)

where, W_g and W_o are weights of samples after and before grafting, respectively.

2.3 Amination of grafted PE/PP fibres

PE/PP-*g*-poly(GMA) substrate was treated with pure EDA amine in round bottom flask. The reaction was carried out at 83 °C under reflux for 24 h. Another sample of PE/PP-*g*-Poly(GMA) was treated with PEI solution diluted with a mixture of DMF and isopropanol comprising 16% and 20% of the total volume. The reaction was performed for 24 h at 90 °C under reflux. Finally, the amine functionalized substrates were removed and washed repeatedly with DI water and ethanol before drying in a vacuum oven at 60 °C for overnight. The following equation was used to calculate the amine percentage:

Amine content (%) =
$$\frac{(W_a - W_g) / M W_{amine}}{(W_a - W_o) / M W_{GMA}} \times 100\%$$
(2)

where, MW_{GMA} is the molecular weight of GMA (142.15) and MW_{amine} is the molecular weight of EDA (g/mol). W_a and W_g are the weights (g) of the PE/PP-g-poly(GMA) substrate before and after amination, respectively. The Wo is the weight of pristine PE/PP polymer before grafting. The amine content in PE/PP-g-poly(GMA)/PEI and PE/PP-g-poly(GMA)/EDA was found to be 24.3 and 23.2%, respectively.

PE/PP fibres grafted with poly(NVF) samples were fully converted into poly(VAm) group by hydrolysis with a 2 M NaOH solution. The reaction was performed on samples of known weights at 80 °C for 4 h under reflux according to the procedure reported elsewhere [5]. The treated samples were removed and the excess NaOH was washed with DI water 4 times and kept in ethanol for 24 h. The samples were removed and dried in a vacuum oven (80 °C for 16 h) before their weights were determined. The amine percentage in the hydrolysed samples was calculated taking the molar masses of NVF (71.08 g/mol) and VAm (43.07 g/mol) into consideration as reported in our previous study [17]. The conversion of the formamide to amine was found close to 100%.

2.4 Characterization of samples

The three adsorbents that were denoted as PE/PP-g-poly(GMA)/PEI, PE/PP-g-poly(GMA)/EDA and PE/PP-g-poly(VAm) were characterized using the Fourier transform infrared (FTIR, Nicolet iS50, ThermoFisher Scientific Inc.) spectroscopy and measurements were in the range of 500-4500 cm⁻¹ using 32 scans with 4 cm⁻¹ resolution. Scanning electron microscopy (SEM) images were recorded using the GEMINISEM 500 microscope (ZEISS Microscopy) with the magnification of 500x to study the surface morphological changes of the samples.

2.5 CO₂ adsorption tests

The CO₂ adsorption capacity measurements were carried out using the magnetic suspension balance (MSB) named as isoSORP® gravimetric analyser from RUBOTHERM (Germany). A blank measurement without any sample was carried out to determine the volume of the container using He gas at room temperature after evacuation. Later, the adsorbent sample was inserted in the sample container before it was pre-treated at 80 °C for 3 h under vacuum and the actual weight and volume of the sample were determined using buoyancy mode prior to adsorption tests. Finally, the adsorption measurements were carried out using pure gases of CO₂ and N₂ and their gaseous mixtures having 5, 10, 20, and 40 % CO₂ ratios at a total flow rate of 500 ml/min, a temperature of 30 °C and an ascending pressure range up to 30 bar. The equilibrium sorption was achieved in about 50 min for every pressure reading. The desorption steps for each adsorbent were carried to evaluate the remaining adsorption capacity and were carried after each adsorption measurements were completed at 30 bars. The desorption process was performed by depressurizing the vessel containing the adsorbent until reaching vacuum before heating to 80 °C for 4.5 h until no weight loss was detected in the adsorbents. All adsorption/desorption cycles experiments were repeated 3 times and the average values were reported.

III. RESULTS AND DISCUSSIONS

3.1 Grafted PE/PP fibrous samples

PE/PP fibres were grafted with GMA and NVF to provide precursors for hosting amine groups. Figure 1 shows the variation of DG with the concentrations of GMA and NVF monomers while the rest of grafting conditions were kept unvaried. As can be seen, the DG in both grafting systems was found to increase with the rise in the monomer concentrations. For instance, the DG increased from 51 to 150% when the GMA concentration increased from 2 to 8% in the emulsion medium as depicted in Figure 1a. On the other hand, DG increased from 44 to 130% with the increase in NVF concentration in the range of 10-40% (Figure 1b). Such increasing trends in DG in both grafting systems is going along with the literature and can be attributed to the increase in the monomer diffusion and its availability in the grafting sites leading to more counts of initiation and propagations reactions [17-19]. For comparison purpose, grafted PE/PP samples from GMA and NVF with 130% DG were chosen for further functionalization with amine.



Figure 1. Variation of degree of grafting with monomer concentration (**a**) grafting of GMA on PE/PP fibres under emulsion conditions of 10 kGy absorbed dose, 40 °C temperature and 0.5 h reaction time and (**b**) grafting of NVF on PE/PP fibres in toluene solvent under conditions of 300 kGy absorbed dose, 70 °C temperature and 1 h reaction time.

3.2 Chemical and morphological changes in adsorbents

Figure 2 shows FTIR spectra of pristine PE/PP, PE/PP-*g*-poly(GMA), PE/PP-*g*-poly(GMA)/PEI, PE/PP-*g*-poly(GMA)/EDA and PE/PP-*g*-poly(NVF), and PE/PP-*g*-poly(VAm) fibres. Compared to pristine PP/PE characteristic peaks, the new peaks appeared at 751 (for C-O-C), 1161 (for C-O) and 1740 cm⁻¹ (for O-C=O) in the spectrum *b* represent epoxy and ester features of poly(GMA) chains grafted to PE/PP fibres. The emergence of –NH bands at 1658 and 1527 cm⁻¹ coupled with reduction in the intensity of ester related bands (spectra c and d) confirms the presence of EDA or PEI amines after the amination reaction [14]. The appearance of the new peak at 1650 cm⁻¹ provides evidence for the incorporation of poly(NVF) grafts into PE/PP that resembles the stretching vibration of carbonyl group (>C=O) originated from amide group (spectrum *e*). This was coupled with N-H stretching and bending vibration at 3280 and 1542 cm⁻¹ together with -CN stretching vibration at 1270 cm⁻¹ from amide. The conversion of the amide to primary amine after hydrolysis illustrated in the spectrum f was confirmed from the complete disappearance of >C=O at 1650 cm⁻¹ that was coupled with the presence of primary amine features in the range of 1542-1650 cm⁻¹ and the peak at 3360 cm⁻¹ representing NH₂ group [5]. These results confirm the incorporation of poly(NVF) grafts into PE/PP fibres and subsequent immobilization of EDA or PEI and formation of poly(NVF) grafts into PE/PP fibres and subsequent immobilization of EDA or PEI and formation of poly(NVF) grafts into PE/PP fibres and subsequent immobilization of EDA or poly(GMA) or poly(NVF) grafts into PE/PP fibres and subsequent immobilization of EDA or PEI and formation of poly(VAm).



Figure 2. FTIR spectra of (a) pristine PE/PP substrate and grafted PE/PP with (b) poly(GMA), (c) PEI, (d) EDA, (e) poly(NVF), and (f) poly(VAm).

Based on the changes in chemical composition of PE/PP after grafting and subsequent functionalization with amine, the following three plausible mechanisms presented in Figure 3 can be suggested for the preparation of the three adsorbents in the present study via grafting and amination.



Figure 3. Schematic representation of reaction mechanisms for preparation of adsorbents containing- (a) PEI, (b) EDA and (c) poly(VAm).



Figure 4. SEM images of (a) pristine PE/PP, (b) poly(GMA) grafted PE/PP, (c) PE/PP-g-poly(GMA)/EDA, (d) PE/PP-g-poly(GMA)/PEI, (e) poly(NVF) grafted PE/PP and (f) poly(VAm).

The morphology of the adsorbents with respect to average fibre diameter (AFD) was investigated to verify the changes accompanied grafting and amination. SEM images shown in Figure 4 portray the changes in the fibre diameters after grafting, amination, and hydrolysis. The AFD of pristine PE/PP was $14.0 \pm 0.3 \mu m$ (Figure 3a), which was increased after grafting with poly(GMA) to $19.3 \pm 0.2 \mu m$ (Figure 3b). After amination with EDA and PEI, the AFD was increased by ~52% and 13% reaching values of 29.3 ± 1.2 and $21.9 \pm 0.8 \mu m$, respectively (Figure 3c and d). The AFD of PE/PP was also increased to $15.2 \pm 0.3 \mu m$ after grafting with poly(NVF) and further increased after conversion of amide to amine by hydrolysis reaching $22.0 \pm 0.9 \mu m$ (Figure 3e and f). These morphological changes confirm monomers grafting and subsequent amination of the pristine PE/PP fibres [15].

3.3 Adsorption of pure CO_2 and N_2

Figure 5 (a-c) shows the adsorption isotherms of pure CO_2 and pure N_2 over the three adsorbents. The CO_2 adsorption capacity increased with pressure rise on all adsorbents. On the other hand, N₂ adsorption seems to be very tiny (negligible) at all pressures suggesting that the present adsorbents have low affinity towards N₂. The CO₂ adsorption isotherms seem to follow the type II that suggest the CO_2 uptake took place not only by a monolayer adsorption but also by multilayers adsorption with the pressure rise. For instance, the adsorbent with PEI showed CO₂ adsorption capacity of 1.03 mmol/g, which was raised to 1.43 mmol/g when EDA was immobilized on poly(GMA) grafted fibres at same pressure of 30 bar and room temperature. This value was further increased in PE/PP adsorbent containing poly(VAm) to 1.69 mmol/g at the same conditions. The increasing capacity trend with pressure is generally due to the increase in the diffusion of CO_2 gas prompting a wider access to amine groups in all adsorbents [20]. The results suggest that poly(VAm)-bearing adsorbent outperformed the other two counterparts originated from PE/PP-g-poly(GMA) fibres. This can be understood based on the amine content where the adsorbent with poly(VAm) has approximately100% degree of amination following the conversion of the amide into primary amine by hydrolysis with NaOH solution [17]. Moreover, the 63% lower performance of PEIadsorbent, which carries a substantial quantity of tertiary amines is significantly affected by presence of the bulky structure of PEI immobilized in the adsorbent impeding CO₂ access to the amine sites and thus, the adsorbent attains lower working capacity [21]. Furthermore, the 18% lower capacity of EDA-containing adsorbent than that of poly(VAm)-containing adsorbent despite having two primary amines in its structure is most likely caused by the lower degree of amination (23.2%) and low amine utilization efficiency. It can be concluded that RIGC of NVF on PE/PP fibres provide a simpler rout that is more effective for conversion of PE/PP fibres into highly selective adsorbent for CO_2 capture. It is noteworthy mentioning that the microfibrous adsorbents in this study are perfroming better than the porous polyurethane (PU)/PS electrospun nanofibrous composite membrane that was physically impregnated with PEI or trimethylamine (TMA) in adsorption of CO2. The former showed an adsorption capacity of 0.71 mmol/g when loaded with 100% PEI whereas the latter attained 0.48 mmol/g adsorption capacity upon loading with 100% TMA. Additionally, both types of nanofibrous composite adsorbents demonstrated an adsorption isotherm of type I suggesting the presence of monolayer adsorption [22].



Figure 5. Adsorption isotherms of pure CO_2 and pure N_2 over prepared adsorbents (a) PE/PP-g-poly(GMA)/EDA, (b) PE/PP-g-poly(GMA)/PEI, and (c) PE/PP-g-poly(VAm).

3.4 Adsorption of CO₂ and N₂ mixtures

Figure 6 shows the adsorption isotherms of CO_2/N_2 gas mixtures having composition ratios up to 40% on the adsorbents. The EDA- and poly(VAm)-containing adsorbents were chosen based on their higher performance as illustrated in Figure 6a. The CO₂ adsorption capacity at all CO₂ ratios was found to increase with the applied pressure but attained values lesser than those of pure CO₂ adsorption. Similar trends with respect to pressure dependancy and lower CO₂ adsorption capacities were observed for the three adsorbents when a mixture of CO_2/N_2 with a ratio of 40% CO₂ was used. This behaviour can be attribuated to the competitive diffusion between CO₂ and N₂ gases leading to a partial hinderance in the accessibility of amine groups for CO₂ molecules.

In Figure 6b, the PEI-containing adsorbent showed the lowest adsorption capacity values with CO_2/N_2 mixtures compared to the other two counterparts in a way resembling the adsorption trend of pure CO_2 . Unlikely, the poly(VAm)-containing adsorbent showed the highest adsorption capacity compared to its counterparts containing PEI and EDA for all CO_2 ratios and pressure values. This further confirms the superiority of poly(VAm) adsorbent compared to PEI- and EDA-containing adsorbents suggesting that the poly(VAm) adsorbent has a high amine

utilization efficiency and high competitive adsorption capacity compared to other adsorbents in this study. However, the CO₂ adsorption capacity of PEI- and EDA-containing adorbents was found to be lower than radiation grafted dsorbents containing poly(GMA)/ethanolamine (EA) based on electrospun nanofibres of PP [13-15], PAN/PS [16] and PAN [23]. This can be understood taking into account not only the greater surface area of nanofibrous structure but also the higher DG and amine utilization efficiency in these adsorbents.



Figure 6. Isotherms for adsorption of CO_2/N_2 gas mixtures having composition ratio (a) the range of 5-20% CO_2 and (b) ratio of 40% CO_2 on various adsorbents.

The stability of the three adsorbents were evaluated using several adsorption/desorption cycles as illustrated in Figure 7. The three adsorbents showed negligible losses in their CO₂ adsorption capacity after 8 cycles suggesting the presence of an excellent stability. This further confirms that the grafting step with RIGC was efficient in covalently bonding the poly(GMA) or poly(NVF) side chain grafts to PE/PP fibrous backbone before functionalization with amine. The trend of stability and regeneration of adsorbents in this study is similar to that of tetraethylenepentamine-containing adsorbent prepared by RIGC of GMA onto PE/PP microfibres followed by amination reported earlier [11]. Tetraethylenepentamine-containing adsorbent with optimized amination efficiency based on grafted polyolefin microfibrous substrate for CO2 adsorption [12]. On the other hand, aminated adsorbents with electrospun nanofibrous networks such as ethanolamine (EA)-containing PP scaffolds [15], aminated (PEI and TMA) PU/PS nanofibers [22] and EA-containing PU/PAN nanofibers grafted with GMA [16] along with its counterpart-based pristine PAN nanofibers [23] showed higher rate of loss in adsorption capacity

compared to the marginal loss in the three adsorbents in the present study. This certainly, indicate that aminated adsorbents based on microfibrous PE/PP have more practical advantages than nanofibrous counterparts.



Figure 7. Variation of CO2 adsorption capacity with number of adsorption/desorption cycles of three adsorbents.

IV. CONCLUSIONS

Three different adsorbents containing PEI, EDA, and poly(VAm) for CO₂ capture were successfully prepared by modification of PE/PP fibres with poly(GMA) and poly(NVF) grafts using RIGC followed by amination reactions. The adsorption of pure CO₂ and its mixtures with N₂ at different ratios showed increasing trends with pressure rise. The adsorption capacity of pure CO₂ gas at room temperature and 30 bar was 1.03, 1.43 and 1.69 mmol/g for PEI-, DEA- and poly(VAm)-containing adsorbents, respectively. Such values were reduced when various CO₂/N₂ mixtures of different CO₂ ratios were absorbed on the same adsorbents and the decrease is more profound at low CO₂ content in the gas mixture suggesting that N₂ partially blocked the access to some amine sites despite its low affinity towards amine. All the adsorbents were proven to be highly selective to CO₂ and have excellent adsorption/desorption stability. Finally, it can be concluded that RIGC provide distinctive tool for converting PE/PP fibres into efficient adsorbents and poly(VAm)-containing fibrous adsorbent has the best CO₂ capture performance. Hence, this adsorbent has a high potential for CO₂ capture from CO₂/N₂ mixtures resembling post combustion flue gas.

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REFERENCES

[1] Jang KS (2018) Exploring polyethylene/polypropylene nonwoven fabrics derived from two-dimensionally coextruded composites: Effects of delamination, consolidation, drawing and nanoparticle incorporation on mechanics, pore size and permeability, Composites Sci Technol 165: 380-387. https://doi.org/10.1016/j.compscitech.2018.07.022

[2] Tourzani AA, Hormozi F, Asadollahzadeh M, Torkaman R (2023) Effective-CO₂ capture by using poly(acrylonitrile) nanofibers based on the radiation grafting procedure in fixed-bed adsorption column. Sci Rep 13: 6173. <u>https://doi.org/10.1038/s41598-023-33036-y</u>

[3] Ishihara R, Asai S, Saito K (2020) Recent progress in charged polymer chains grafted by radiation-induced graft polymerization: adsorption of proteins and immobilization of inorganic precipitates. Quantum Beam Sci 4: 20. <u>https://doi.org/10.3390/qubs4020020</u>

[4] Bhattacharya A, Misra BN (2004) Grafting: a versatile means to modify polymers, Techniques, factors and applications, Prog Polym Sci 29: 767-814. <u>https://doi.org/10.1016/j.progpolymsci.2004.05.002</u>

[5] Zubair NA, Nasef MM, Mohamad NA, Abouzari-Lotf E, Ting TM, Abdullah EC (2020) Kinetic studies of radiation induced grafting of N-vinylformamide onto polyethylene/polypropylene fibrous sheets and testing its hydrolysed copolymer for CO_2 adsorption. Radiat Phys Chem 171: 108727. https://doi.org/10.1016/j.radphyschem.2020.108727

[6] Zubair, NA, Moawia, RM, Nasef MM, Hubbe M, Zakeri M (2022) A critical review on natural fibers modifications by graft copolymerization for wastewater treatment, J Polym Environ 30: 1199-1227. https://doi.org/10.1007/s10924-021-02269-1

[7] Nasef MM, Ting TM, Abbasi A, Layeghi-moghaddam A, Sara Alinezhad S, Hashim K (2016) Radiation grafted adsorbents for newly emerging environmental application. Rad Phys Chem 118: 55-60. https://doi.org/10.1016/j.radphyschem.2015.02.025

[8] Rezaei F, Mosca A, Webley P, Hedlund J, Xiao P (2010) Comparison of traditional and structured adsorbents for CO₂ separation by vacuum swing adsorption, Ind Eng Chem Res 49: 4832 - 4841. http://doi.org/10.1021/ie9016545.

[9] Dong D, Wang Y, Wen D, Peng J, Zhao L, Zhai M (2022) Recent progress in environmental applications of functional adsorbent prepared by radiation techniques: A review. J Hazard Mater 424: 126887. https://doi.org/10.1016/j.jhazmat.2021.126887

[10] Nasef MM, Guven O (2012) Radiation-grafted copolymers for separation and purification purposes: status, challenges and future directions, Prog Polym Sci 37: 1597-1656. http://doi.org/10.1016/j.progpolymsci.2012.07.004

[11] Torkaman R, Maleki F, Gholami M, Torab-Mostaedi M, Asadollahzadeh M (2021) Assessing the radiationinduced graft polymeric adsorbents with emphasis on heavy metals removing: A systematic literature review, J Water Process Eng 44: 102371. <u>https://doi.org/10.1016/j.jwpe.2021.102371</u>

[12] Mohamad NA, Nasef MM, Nia PM, et al (2021) Tetraethylenepentamine-containing adsorbent with optimized amination efficiency based on grafted polyolefin microfibrous substrate for CO₂ adsorption. Arab J Chem 14:103067. <u>https://doi.org/10.1016/j.arabjc.2021.103067</u>

[13] Abbasi A, Nasef MM, Faridi-Majidi R, et al (2018) Highly flexible method for fabrication of poly (Glycidyl Methacrylate) grafted polyolefin nanofiber. Rad Phys Chem 151: 283-291.
https://doi.org/10.1016/j.radphyschem.2018.07.002

[14] Abbasi A, Nasef MM, Babadi FE, Faridi-Majidi R, Takeshi M, Abouzari-Lotf E, Choong T, Somwangthanaroj A, Kheawhom (2019) Carbon Dioxide Adsorption on Grafted Nanofibrous Adsorbents Functionalized Using Different Amines. Front Energy Res 7: 1-14. <u>https://doi.org/10.3389/fenrg.2019.00145</u>

[15] Abbasi A, Nasef MM, Kheawhom S, Faridi-Majidi R, Takeshi M, Abouzari-Lotf E, Choong T (2019) Amine functionalized radiation induced grafted polyolefin nanofibers for CO₂ adsorption. Rad Phys Chem 156: 58-66. https://doi.org/10.1016/j.radphyschem.2018.10.015

[16] Imanian Z, Hormozi F, Torab-Mostaedi M, Asadollahzadeh M (2022) Highly selective adsorbent by gamma radiation-induced grafing of glycidyl methacrylate on polyacrylonitrile/polyurethane nanofiber: Evaluation of CO₂ capture. Sep Purif Technol: 289, 120749. <u>https://doi.org/10.1016/j.seppur.2022.120749</u>

[17] Rojek T, Gubler L, Nasef MM, Abouzari-lotf E (2017) Polyvinylamine containing adsorbent by radiation induced grafting of N-vinylformamide onto UHMWPE films and hydrolysis for CO2 capture. Ind Eng Chem Res 56: 5925-5934. <u>https://doi.org/10.1021/acs.iecr.7b00862</u>

[18] Hidzir, NM, Hill DJT, Martin D, Grondahl L (2012) Radiation-induced grafting of acrylic acid onto expanded poly(tetrafluoroethylene) membranes. Polym 53: 6063–71. <u>https://doi.org/10.1016/j.polymer.2012.10.042</u>

[19] Afolabi HK, Nasef MM, Nordin NAH, Ting TM, Harun NY, Abbasi A (2021) Facile preparation of fibrous glycidol-containing adsorbent for boron removal from solutions by radiation-induced grafting of poly(vinylamine) and functionalisation. Rad Phys Chem 188: 109596. <u>https://doi.org/10.1016/j.radphyschem.2021.109596</u>

[20] Ahmed S, Ramli R, Yusup S (2017) Development of polyethylenimine-functionalized mesoporous Si-MCM41 for CO2 adsorption. Fuel Process Technol 167: 622-630. <u>https://doi.org/10.1016/j.fuproc.2017.07.036</u>

[21] Mafra L, Čendak T, Schneider S, Wiper PV, Pires J, Gomes JRB, Pinto ML (2017) Amine functionalized porous silica for CO2/CH4 separation by adsorption: Which amine and why. Chem Eng J 336: 612–621. https://doi.org/10.1016/j.cej.2017.12.061

[22] Zain G, Babar AA, Iqbala N, Wang X, Yu JY, Ding B (2018) Amine-impregnated porous nanofiber membranes for CO₂ capture, Comp Commun 10: 45-51. <u>https://doi.org/10.1016/j.coco.2018.06.005</u>

[23] Tourzani AA, Hormozi F, Asadollahzadeh M, Torkaman R (2023) Effective CO₂ capture by using poly (acrylonitrile) nanofibers based on the radiation grafting procedure in fixed-bed adsorption column, Sci Reports 13: 6173. <u>https://doi.org/10.1038/s41598-023-33036-y</u>