Study on the recycling of zeolitic imidazolate frameworks and polymer Pebax® 1657 from their mixed matrix membranes applied to CO₂ capture

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A R T I C L E   I N F O

A B S T R A C T

Mixed matrix membranes (MMMs) consisting of fillers (e.g. metal organic frameworks (MOFs)) in polymer matrix are considered as an interesting alternative for capturing post combustion CO_2 towards a sustainable development. This research is focused on the recycling of MMMs made of polymer Pebax® 1657 and MOF ZIF-94. Upon MMM preparation, characterization and testing, MMMs were dissolved to recover polymer and MOFs separately. Recovered products were characterized by SEM, EDX, FTIR, TGA, XRD, DLS, mass spectrometry and N_2 adsorption to compare their size, shape and other properties with those of fresh ones. Mean particle size of fresh and recycled ZIF-94 were 148 ± 44 nm and 164 ± 32 nm, respectively. Incorporation of recycled ZIF-94 in MMMs produced defect free membranes which was confirmed by SEM and gas separation measurements. These MMMs, with a 10 wt% ZIF-94 loading, were tested for the separation of the CO_2/N_2 mixture with a CO_2 permeability of 157 ± 6.5 Barrer (with 67 % improvement compared to fresh pure polymer membrane with 94 ± 2 Barrer) and a CO_2/N_2 selectivity of 27.5 ± 1.4 (5 % lower than that of the fresh MMM, 29.3 ± 1.8, but 20 % higher than the corresponding to the pure polymer membrane, 23 ± 2). Demonstrating its wide feasibility, the proposed methodology was also applicable for recycling of ZIF-8 from Pebax® 1657 based MMMs.

1. Introduction

Energy demands of the current world is increasing over time where fossil fuels generated power contributes major shares of the supply chain. This results in global warming and other unpredictable climatic changes [1]. Therefore, it was agreed to search for either green energy sources or capturing CO₂ from post-combustion gases or from industry exhaust (such as those related to cement and stainless steel plants) to limit the global temperature rise below 2 °C (which was set at Paris conference in 2015 [2] and confirmed at the Glasgow COP26 in 2021) [3], since a substantial increase in global energy demand is predicted by International Energy Agency (IEA) by 2030 [4]. Green hydrogen fuel, hydrothermal, wind, solar and uranium based atomic energy are the possible alternative solutions to fossil fuels for power generation but they are constrained by either affordability or geographical location. Moreover, carbon capture and storage (CCS) from flue gas is a feasible and straightforward solution over persisting concern risen from burning of fossil fuels.

Membrane separation is an environmentally friendly technology that

is expected to replace some of the thermally driven, conventional energy-intensive CCS processes such as absorption (solvent based), adsorption (solid adsorbents based) and cryogenic distillation to name a few, since they are characterized by high cost of operation [1,5]. Mixed matrix membranes (MMMs) made of integrated base polymeric matrix and a compatible inorganic micro/nano sized filler [6] show improved separation, mechanical and thermal properties [7], which enable them to be used as potential candidates for CCS application [8,9].

Metal organic frameworks (MOFs) are crystalline porous materials offering properties of both inorganic (metal ion cluster) and organic (linker) moieties often characterized by high chemical and structural flexibility and specific surface area [6]. All these properties ensure better MOF-polymer compatibility in MMMs, and hence better performance is reported [10,11]. In general, permeability of gases through MMMs and the selectivity increase compared to that of bare polymers. However, the CCS performance depends on the intrinsic compatibility between polymer and filler and on the diffusivity and solubility of a gas inside the membrane [12]. Different MOFs are reported as fillers in MMMs for CCS application such as ZIF-8, ZIF-94, ZIF-67, ZIF-71, ZIF-300, UiO-66, UiO-

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67, MIL-53(Al), to name a few [8,10,11,13–20]. ZIFs (zeolitic imidazolate frameworks) are characterized by exceptional chemical and thermal (up to 400 °C) stability, high microporosity (in general, with micropores in the 0.3–0.34 nm range) facilitating the adsorption of CO_2 [21], high specific surface area [22] and flexible pore opening when induced with guest molecules [23]. Since ZIFs are interesting for the fabrication and application of MMMs for CCS [24–26], the facile and scalable production of different ZIFs (ZIF-8, ZIF-67, ZIF-71 and ZIF-94) has been reported to make them cost effective and available for MMMs [27–31]. Pan et al. reported a green synthesis of ZIF-8 from aqueous solvent [29], whereas others have recycled mother liquors from the syntheses of ZIF-7 [32], ZIF-8 [32,33], ZIF-67 [32], ZIF-L [32], ZIF-94 [22], etc. to make the process sustainable. Moreover, Hasan et al. have reported a sustainable synthesis of ZIF-94 from mother liquor applied to fabricate MMMs with Pebax® 1657 polymer matrix which shows good CCS performance [22].

Although many attempts have been found in the literature to make the synthesis of MOFs sustainable, yet none have reported the recycling of MMMs to extract MOFs and polymer matrix to study their reusability. In fact, if this was not possible, the MMM components would be considered as a waste. Recycling of MMMs shows many advantages, such as: i) making membranes economically feasible, since extracted materials can be reused (either in membrane or in other purposes), which leads to ii) reducing loss and cost of chemicals, and finally iii) ensuring environmentally sustainable membranes, due to less waste disposition. The major component of MMM is a polymer, which is another environmental concern over CO_2 release, due to its adverse effect on soil (reducing soil fertility, crop productivity, water penetration etc.) and water (causing nano, micro and macro plastic pollution, it enters into the food chain and reduces aqueous animals productivity, etc.) [34,35]. The minor component of the MMM, the filler (i.e. MOF), creates a clear difference when comparing the MMM recycling with that of other types of plastics (e.g. agricultural plastic) [36]. MOFs contain metals which could have a higher negative impact on the environment that the polymer. Finally, in certain cases, the MMM components could not be reused, mainly when the separation process conditions would modify the physicochemical and structural nature of the components (e. g. affecting the crystallinity of the MOF, segregating the copolymer, etc.).

Understanding all the consequences of polymer waste to Earth, more emphasis should be given to study the recyclability of polymer-based membranes before they are adopted for large scale CCS application. The objectives of this study are firstly to recycle ZIF-94 and polymer Pebax® 1657 matrix from their corresponding MMMs, and secondly to re-incorporate them into MMMs demonstrating efficient CO_2/N_2 separation performance. Finally, to validate the approach, the procedure was repeated with ZIF-8-Pebax® 1657 MMMs.

2. Experimental procedure

2.1. Materials

Zinc acetate dihydrate and 4-methyl-5-imidazolecarboxaldehyde were purchased from Acros Chemicals (98 % and 99 % purity, respectively). Methanol (99.8 %) was purchased from Honeywell, and anhydrous tetrahydrofuran (THF, ≥99.9 %) was attained from Sigma-Aldrich. Absolute ethanol was purchased from Gilca, Spain. For the membrane fabrication, commercially available Pebax® 1657 was kindly provided by Arkema, France.

2.2. Methodology

2.2.1. Recycling of ZIF-94 and a polymeric matrix from MMMs

MMMs (with 10 wt% fillers in 3 wt% polymer matrix for 10 g basis) were fabricated following a procedure described by Hasan et al. [22]. ZIF-94 was fabricated according to the methodology reported by

Johnson et al. [28]. Membranes recycled in this study were stored in between 15 days to 12 months. ZIF-94 was recovered from MMM by a two-step method: 1) initially, 3.9 ± 0.4 g of MMM sample was dissolved in 25 mL of EtOH/water (70/30 (v/v)) by stirring under reflux for 1 h, and 2) the obtained mixture was centrifuged at 9000 rpm for 20 min in order to collect ZIF-94. Next, collected ZIF-94 was washed with EtOH/water (70/30 (v/v)) under the same conditions (25 mL EtOH/H_2O, stirring with reflux for 1 h and centrifugation at 9000 rpm) to ensure the removal of remaining polymer traces (the process was repeated three times) and facilitate the subsequent characterization. The resulting ZIF-94 was dried overnight at RT. To recover a polymer matrix from MMM, dissolved polymer (supernatant) was collected from the very first centrifugation of the MMM solution. Next, centrifugation of the supernatant (polymer after removal of MOF) was repeated for three times at 9000 rpm for 20 min to remove remaining ZIF-94. Finally, the polymer solution was cast on a Petri dish and dried at 40 °C to be later re-included into MMMs. Recovery efficiency of the process was calculated following Eq. (1):

$$Recovery(\%) = \frac{Experimentaly\ recycled\ amount}{Theoretical\ amount} \cdot 100 \qquad (1)$$

where "Theoretical amount" signifies amount of polymer matrix or filler present in the fresh membrane (used for recycling) as per their composition, whereas "Experimentally recycled amount" signifies recovered amount of the polymer and ZIF-94. Similarly, "Recovery (%)" stands for the ratio of the total amount of the material recovered to the total amount of the membrane being recycled. Schematic representation of recycling of MMMs is shown in Fig. 1 and identification names of the fabricated membranes are given in Table 1.

In order to fabricate the MMMs from the recycled reagents, the required amount of fresh or recycled polymer was dissolved (3 wt% polymer in solvent) in EtOH/water (70/30 (v/v)) by stirring under reflux for 1 h. Next, 10 wt% of recycled ZIF-94 (with respect to the amount of polymer being used) was dispersed in the same solvent by repeated sonication and stirring for three times, which was later mixed with dissolved polymer and stirred overnight before casting on a Petri dish and finally placed for overnight drying at 40 °C.

2.2.2. Recycling of ZIF-8 and polymeric matrix from MMMs

To study the applicability of the prescribed recycling methodology for other MOF based MMMs, the present study also investigated ZIF-8 (synthesized according to Sánchez-Laínez et al. [14]) and Pebax® 1657 based MMMs of the same composition (10 wt% filler in 3 wt% polymer matrix for 10 g basis). Recovery (%) of both polymer and ZIF-8 was calculated using Eq. (1). The recycling conditions for ZIF-8 were maintained as for ZIF-94 which are illustrated in Fig. 1.

2.3. Characterization

The morphology of fresh and recycled ZIF-94, fresh and recycled ZIF-8, cross-sectional morphologies of Pebax® 1657 bare membrane and their MMMs were inspected by scanning electron microscopy (SEM) with back scattered electron mode using an Inspect F50 model scanning microscope (FEI) operated at 10 kV. SEM samples were coated with Pd to make them conductive. Additionally, particle size distribution of ZIF-94 was analyzed from SEM images using ImageJ software (approximately 55 particles were measured from different part of the same image). Thermogravimetric analyses (TGA) of membranes and MOFs were carried out using a Mettler Toledo TGA/STDA 851e which produces loss of weight as a function of temperature, that is characteristic for the removal of solvents and thermal degradation of the samples under investigation. For TGA analysis, a small piece of membranes or amount of MOF powder (approx. 8 mg) was placed in 70 μL alumina pans that were heated under an air flow (40 mL min^{-1}) from 35 to 700 °C at a heating rate of 10 °C min^{-1}. BET specific surface area (SSA)
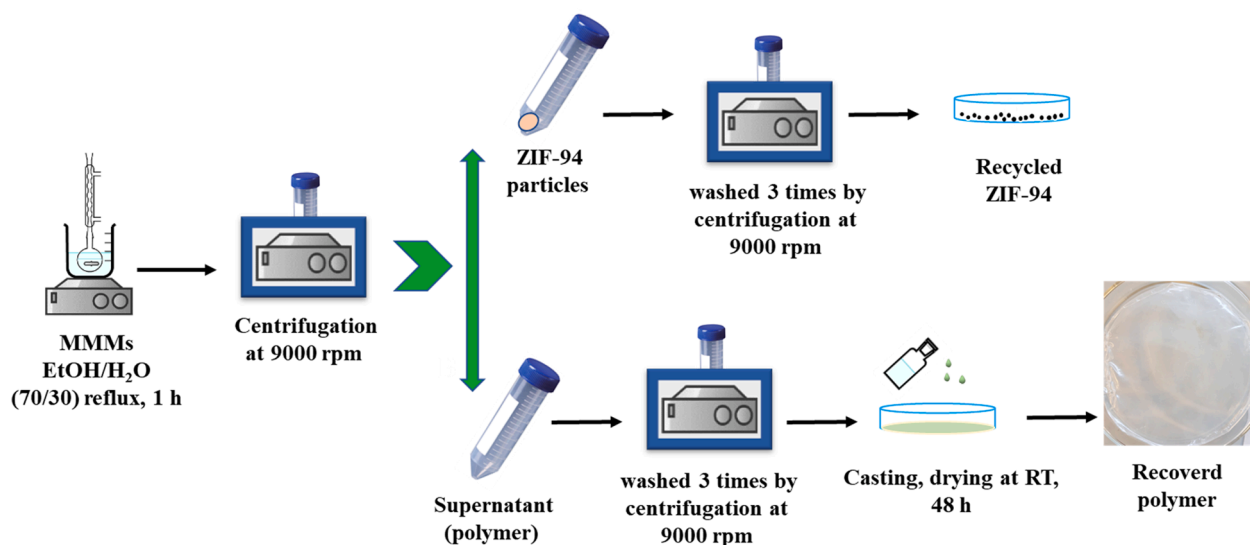
Fig. 1. Scheme of the recycling process of MMM components.

Table 1
Names of the membranes fabricated for this study and their definition.

Name	Membrane type	Description	Thickness (μm)
M1	Bare polymer	Fabricated with fresh polymer matrix	46 ± 2
M1.1	Bare polymer	Fabricated by re-dissolving and re-casting of fresh bare membrane	43 ± 5
M1.2	Bare polymer	Fabricated with polymers recovered from MMMs	45 ± 3
M2	MMM	Fresh polymer matrix + fresh ZIF-94	56 ± 4
M2.1	MMM	Recycled polymer + recycled ZIF-94	58 ± 3
M2.2	MMM	Fresh polymer + recycled ZIF-94	55 ± 4

values of ZIF-94 and ZIF-8 (for both fresh and recycled) were obtained using Micrometrics Tristar 3000 at 77 K. Before these measurements, the samples were degassed for 8 h under vacuum at 200 °C using a heating rate of 10 °C min^{-1}. Membranes and nanoparticles were also characterized by X-ray diffraction (XRD) using a Panalytical Empyrean equipment with CuK$_\alpha$ radiation ($\lambda = 0.154$ nm), over the range of 5°- 40° at a scan rate of 0.03° s^{-1}, to examine the *d*-spacing of the nanoparticles and membranes. Fresh and recycled membrane polymers were analyzed with differential scanning calorimetry (DSC) to confirm their melting temperature. Dynamic light scattering (DLS) was carried out using Brookhaven 90 plus to study polydispersity of recycled and fresh polymer solution and zeta potential of fresh and recycled MOF. Fourier-transform infrared spectroscopy (FTIR) was used to obtain absorption or transmission spectra corresponding to different functional groups present in the sample. Molecular weights of both fresh and recycled polymers were measured to study if there were any changes between the recycled and fresh products using mass spectrometer Bruker Autoflex III Smartbeam MALDI-TOF/TOF.

2.4. Gas separation measurements

Experimental set-up used for the separation of the CO_2/N_2 mixture is schematically presented in Figure S1. A small piece of the membrane was cut and placed in a module consisting of two stainless steel pieces and a 316LSS macroporous disc support (Mott Co.) with a 20 μm nominal pore size. Membranes, 2.12 cm^2 in area, were gripped inside with Viton O-rings. Temperature was controlled at 35 °C by placing the permeation module in an UNE 200 Memmert oven. Gas separation measurements were carried out by feeding the post-combustion gaseous mixture of CO_2/N_2 (15/85 cm^3(STP) min^{-1}) at 3 bar feed pressure,

controlled by two mass-flow controllers (Alicat Scientific, MC-100CCM-D). The permeate side of the membrane was swept with 2 cm^3(STP) min^{-1} of He, at atmospheric pressure (approx. 1 bar) (Alicat Scientific, MC-5CCM-D). Concentrations of CO_2 and N_2 in the outgoing streams were analyzed online by an Agilent 3000A micro-gas chromatograph. Permeability was calculated in Barrer (10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1}) once the steady state of the exit stream was reached (at least after 3 h). The separation selectivity was calculated dividing the permeability of CO_2 by that of N_2.

3. Results and discussion

3.1. Recovery and reuse of MMM components

The current study focuses on 10 wt% ZIF/polymer based MMMs since in our recent publication (related with ZIF-94/Pebax® 1657 MMMs) reported it as an optimum loading considering both CO_2 permeability and CO_2/N_2 selectivity [22]. The total amount of MMMs (3.9 ± 0.4 g) used for the recycling process produced a total recovery of 95 ± 0.5 % (Table 2). In fact, the recycling was repeated for three batches corresponding to about 12–14 membranes (of 70 mm in diameter) per batch, that is 3.8 ± 0.3 g (wt. of recovered polymer + wt. of recovered ZIF-94). This means an overall process loss of 5 ± 0.5 % (as per Eq. (1)). The prescribed process yielded 97.8 ± 0.5 % recovery of the polymer matrix from MMMs, whereas ZIF-94 recovery was 76 ± 2.5 %. Moreover, due to the fact that the recovered ZIF-94 was purified by repeated washing-centrifugation, the major loss of ZIF-94 was observed in this step. In fact, the recycled ZIF-94 obtained from first centrifugation showed a BET SSA of 270 m^2/g, whereas second and third-time washings by reflux and centrifugation increased the BET SSA to 387 m^2/g and 412 m^2/g, respectively (Table S2). However, a little fraction of the dissolved polymer was stuck on the bottom of the round flask which resulted in some loss as well (reflux was only carried out once for polymer, and centrifugation was repeated three times in one bottle, hence loss was minimum). Recycling of MMMs was repeated 3 times to confirm the recovery efficiency of the method. Similarly, ZIF-8 was also

Table 2
Mass balance of recovery polymer and ZIF-94 by recycling of MMMs.

Parameters	Total	Pebax® 1657	ZIF-94
Initial weight (g)	3.9 ± 0.4	3.5 ± 0.3	0.40 ± 0.02
Recovered weight (g)	3.8 ± 0.3	3.4 ± 0.3	0.30 ± 0.04
Recovery (%)	95.5 ± 0.5	97.8 ± 0.5	76.0 ± 2.5

recovered following the same method where the overall recovery (polymer + MOFs) was 91 ± 0.8 % and ZIF-8 recovery was 74 ± 4 %. Mass balance for ZIF-8 recovery and change in SSA with centrifugation cycle are presented in Tables S1 and S2, respectively. This demonstrates the generalization of the methodology for at least two different MOFs.

SEM images of fresh and recycled ZIF-94 are presented in Fig. 2 (A) and (B), respectively. No significant difference in terms of particle shape between this couple of MOFs is observed. Cross section images of MMMs containing both fresh and recycled ZIF-94 within the polymer matrix are shown in Fig. 2 (C) and (D), correspondingly. The fabricated membranes show homogenous distribution of both MOFs. Membranes are also found without apparent defects and cracks, which justifies the reusability of recycled ZIF-94 in imperfection free MMMs. ImageJ was used to calculate particle size from SEM images for both fresh and recycled ZIF-94. Counts of particle diameters were taken arbitrarily from different parts of the SEM images resulting in ZIF-94 particle size in the range of 74–258 nm with mean value of 148 ± 44 nm, as shown in the Gaussian distribution in Fig. 3 (A). Analogously, particle size of recycled ZIF-94 was found in the range of 97–246 nm with a mean value of 164 ± 32 nm (Fig. 3 (B)). Similarly, fresh and recycled ZIF-8 were analyzed with SEM which is represented in Figure S2. Gaussian distributions of ZIF-8 and recycled ZIF-8 are presented in Fig. 3 (C) and (D). Analysis of SEM images with ImageJ shows that mean particle sizes of the fresh and recycled ZIF-8 correspond to 120 ± 30 nm and 110 ± 20 nm (Table 3), respectively. Even if particle size changes fall within the range of the experimental error, it can be speculated on an explanation dealing with the different ZIF chemistry. In general, ZIF-94 is hydrophilic, whereas, ZIF-8 is hydrophobic. Consequently, ZIF-94 is less interactive to polymer justifying some agglomeration of recycled ZIF-94 particles due to interparticle chemical interaction (i.e., hydrogen bonding, etc.), in line with in the increase in particle size observed. However, hydrophobic ZIF-8 may present better interaction with polymer, causing deagglomeration of the MOF particles, resulting in a decrease in particle size.

N_2 adsorption – desorption mediated BET analysis added another analogous information between this set of MOFs: BET SSA values for fresh ZIF-94 and recycled ZIF-94 are 427 ± 7 m^2/g and 412 ± 6 m^2/g, respectively. These values are comparable and in the range of those published in the literature (415–480 m^2/g) [22,37,38]. N_2 adsorption – desorption isotherms are shown in Figure S3 which mainly correspond to type I isotherms, in agreement with the fact that both MOFs are microporous [39,40]. Additionally, DLS analysis was performed to study zeta potential which confirmed some remaining polymer coating on recycled ZIF-94. On DLS, which determines surface charge of the nanoparticles, fresh ZIF-94 produced a zeta potential response of 16.8 ± 0.5 mV whereas recycled ZIF-94 showed 6.6 ± 1.1 mV which are presented in Table 3. This descending trend of zeta potential suggests the polymer coating (which reduces surface charge on fillers) on the recycled ZIF-94. This argument agrees with Herynek et al. results who reported that polymer coating on iron oxide (maghemite) nanoparticles reduced zeta potential score as compared to that of the uncoated [41]. To justify the applicability of this methodology for other MOFs, ZIF-8 was also recycled from its Pebax® 1657 matrix based MMM (10 wt% loading as well). Zeta potential response of recovered ZIF-8 was expectedly lower than that of fresh ZIF-8, whereas BET SSAs of both
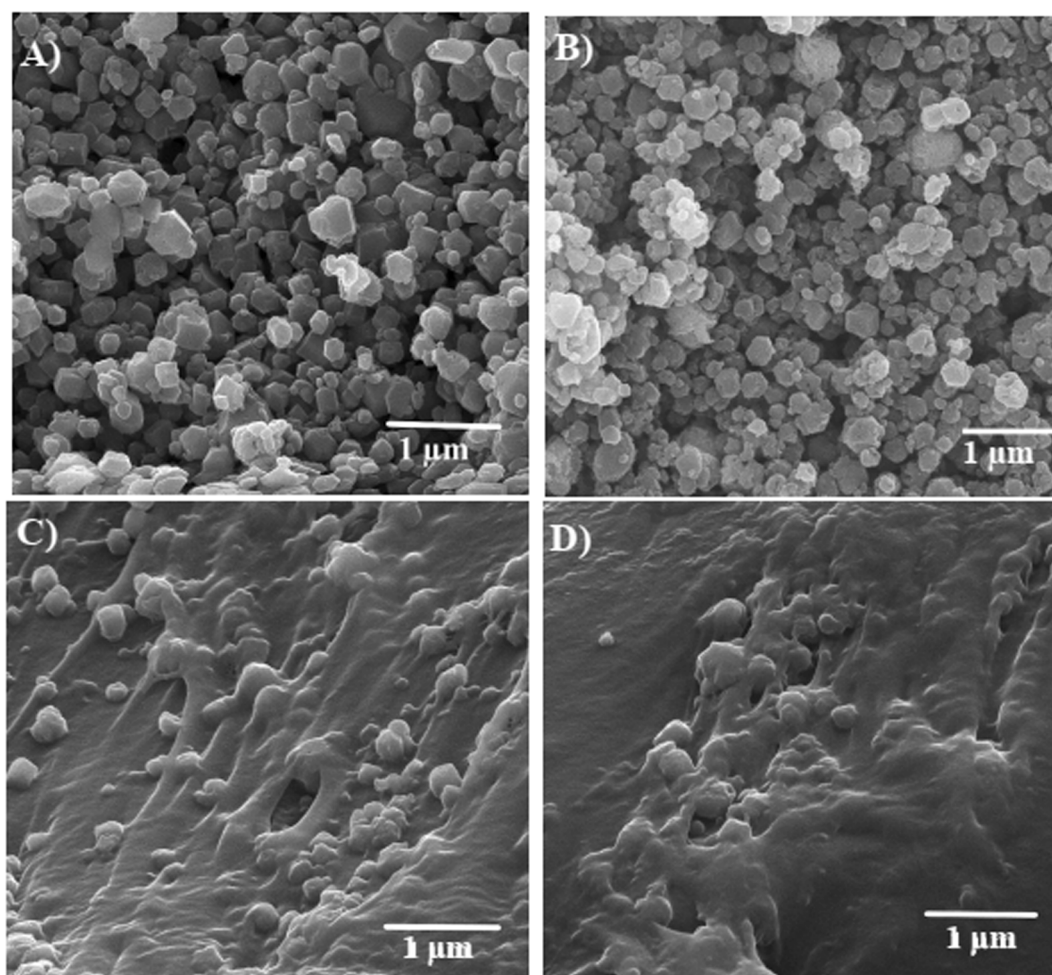

Fig. 2. SEM images: (A) fresh ZIF-94, (B) recycled ZIF-94 from MMM, (C) cross section image of MMM (M2) incorporated with fresh ZIF-94, (D) cross section image of MMM (M2.1) incorporated with recycled ZIF-94.
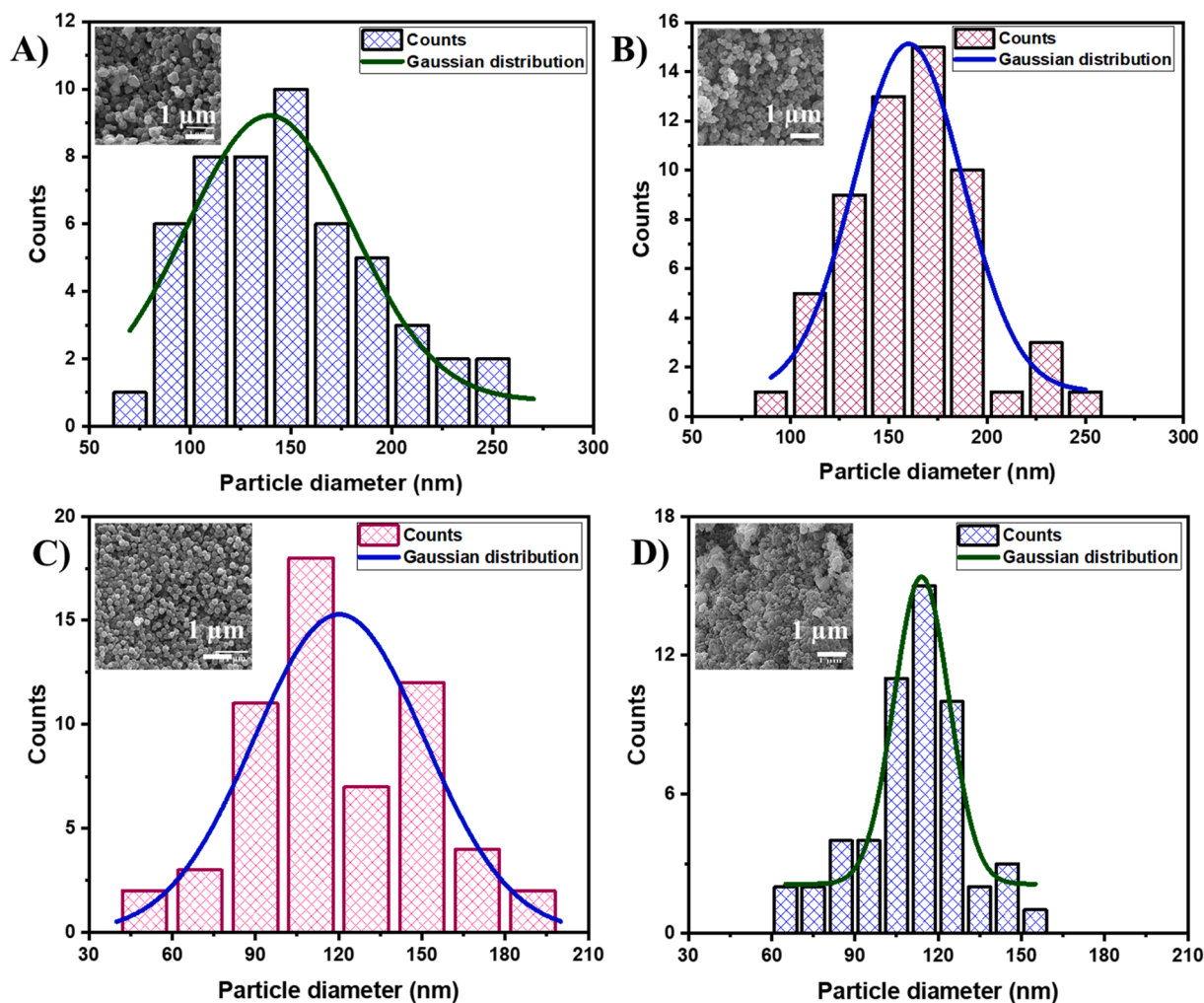
Fig. 3. Particle size distributions: (A) fresh ZIF-94, (B) recycled ZIF-94, (C) fresh ZIF-8 and (D) recycled ZIF-8.

Table 3
Zeta potential, BET specific surface area (SSA) and particle size of fresh and recycled ZIF-94.

Parameters	Zeta potential (mV)	BET SSA (m²/g)	Mean particle size (nm)
Fresh ZIF-94	16.8 ± 0.5	427 ± 7	148 ± 44
Recycled ZIF-94	6.6 ± 1.1	412 ± 6	164 ± 32
Fresh ZIF-8	19.7 ± 0.3	1507 ± 30	120 ± 30
Recycled ZIF-8	7.6 ± 0.7	1325 ± 26	110 ± 19

recycled (1325 ± 26 m²/g) and fresh (1507 ± 30 m²/g) ZIF-8 are comparable and are presented in Table 3. ZIF-8 has been reported with a wide range of BET SSA (700–1946 m²/g) [42–45] which agrees with the BET SSA values of fresh and recycled ZIF-8. Additionally, SEM images and N_2 adsorption – desorption isotherms of fresh and recycled ZIF-8 are presented in Figure S2 and Figure S4, respectively.

In addition to the MOFs, polymer matrix was also recovered from MMMs by the recycling process. Cross-section images of both fresh bare membrane and recycled bare membrane are presented in Figure S5 (A) and (B), respectively. Presence of ZIF-94 was not found in the membrane (Figure S5 (B)), while the cross-section is defect free and identical to that of the fresh bare membrane. Further confirmation of removal of MOFs was obtained by EDX analysis of polymers (obtained by recycling of ZIF-94 and ZIF-8 based MMMs), as presented in Figures S6 and S7. EDX analyses confirmed the removal of Zn below its detection limit, while a

certain Pd percentage appeared since samples were made conductive by coating them with it. DSC analyses of both fresh and recycled polymeric membranes are presented in Fig. 4 (A) which reveal that fresh (M.1), re-cast (M1.1) and recycled polymer (M1.2) produced similar response to calorimetry analysis. Those measurements confirm identical melting temperature for the polyamide segment of fresh, re-cast and recycled membranes, that is $T_m = 205$ °C which was already justified by Martinez-Izquierdo et al. [46]. Moreover, no significant difference was observed in terms of DLS polydispersity between this set of polymers. Polydispersity is an important index for nanomaterial research, which suggests heterogeneity of the sample based on their particle size. Poly-dispersity can arise due to agglomeration or aggregation of the particles under investigation during their isolation or analysis [47]. Although mean particle diameter of dissolved recycled polymer was higher (580 $\pm$ 30 nm) compared to that of fresh polymer (464 ± 41 nm), both of them showed identical polydispersity (0.22 and 0.21, respectively), which suggests that both polymers agree in terms of heterogeneity (Table 4). Moreover, it is clear that polymer chains are much smaller than the aggregates that the DLS detects [48]. In any event, the larger DLS particle diameter suggests a lower solubility of the recycled poly-mer. This can be due to the remains of MOF (i.e. small MOF nano-particles from the relatively wider particle size distribution harder to remove) or MOF components creating chemical interaction (i.e., hydrogen bonding, van der Walls interaction, etc.) within primary polymer constituents.

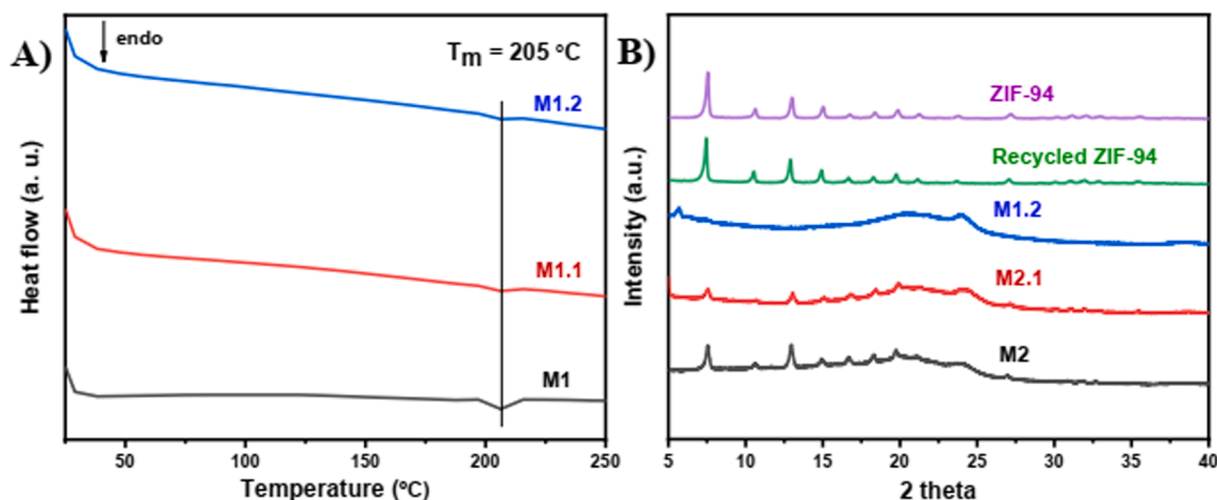XRD analysis outcomes are presented in Fig. 4 (B) where fresh and

Fig. 4. (A) DSC analyses of fresh and recycled and re-cast bare polymer membrane, (B) XRD patterns of fresh ZIF-94, recycled ZIF-94, fresh MMM (M2), recycled MMM (M2.1) and recycled polymer matrix from MMM (M1.2).

Table 4
DLS analyses of fresh (M1) and recycled (M1.2) Pebax® 1657 polymer.

	DLS particle diameter (nm)	Polydispersity
Polymer M1	464 ± 41	0.21 ± 0.04
Polymer M1.2	580 ± 30	0.22 ± 0.03

recycled ZIF-94 show identical response, which justifies similarity in crystalline structure of both MOFs. This confirms that the complex process carried out of MOF recycling did not alter its crystallinity. Correspondingly, fresh and recycled MMMs also produced similar peaks, whereas peaks of ZIF-94 are not observed for recycled polymer from MMMs which suggests complete removal of MOFs from membranes. Additionally, Fig. 5 depicts FTIR spectra for pure polymer, recycled polymer, MMMs and both fresh and recycled ZIF-94 and ZIF-8. No significant changes were observed in the polymer functionalities, while apparent absence of fillers in the recycled polymer and vice-versa are evident. Molecular weight analysis of both fresh and recycled polymers dissolved in the same 70/30 ethanol/water mixture used to prepare the membranes was performed with the results presented in Figure S8 (A)

and (B), respectively. No significant difference was observed between them, showing the expected molecular weight distribution corresponding to polyethylene oxide with 44 as repeated unit (m/z). All these compared characterizations justify the possibility of recovered polymers for reuse in MMMs if they satisfy the gas separation performance expectations. However, we cannot discard the presence of traces of MOF nanoparticles (or their components) in the recycled polymer below the detection limits of the characterization techniques (XRD, EDX, FTIR, etc.) used in this work.

TGA analysis outcomes of the materials under investigation are represented in Fig. 6. Fresh bare membrane (M1) and recycled bare membrane (M1.2) show identical response on thermal degradation analysis. Both of them are stable up to 250 °C, then they start to undergo a first weight loss. Weight loss of these two membrane samples become intense after 400 °C due to thermal decomposition which, through a second step, continues up to 530 °C with a residual lower than 2 % of initial weight. Similarly, fresh MMM (M2) and recycled MMM (M2.1) show analogous response on TGA. They also exhibit a rapid thermal degradation after 400 °C and continue until 550 °C with residues of 3.5 % and 4 %, respectively, due to the ZnO generated from the MOF since TGA was carried out in air [49]. Fresh and recycled ZIF-94 were also studied with TGA to compare their thermal behavior. Both of them start
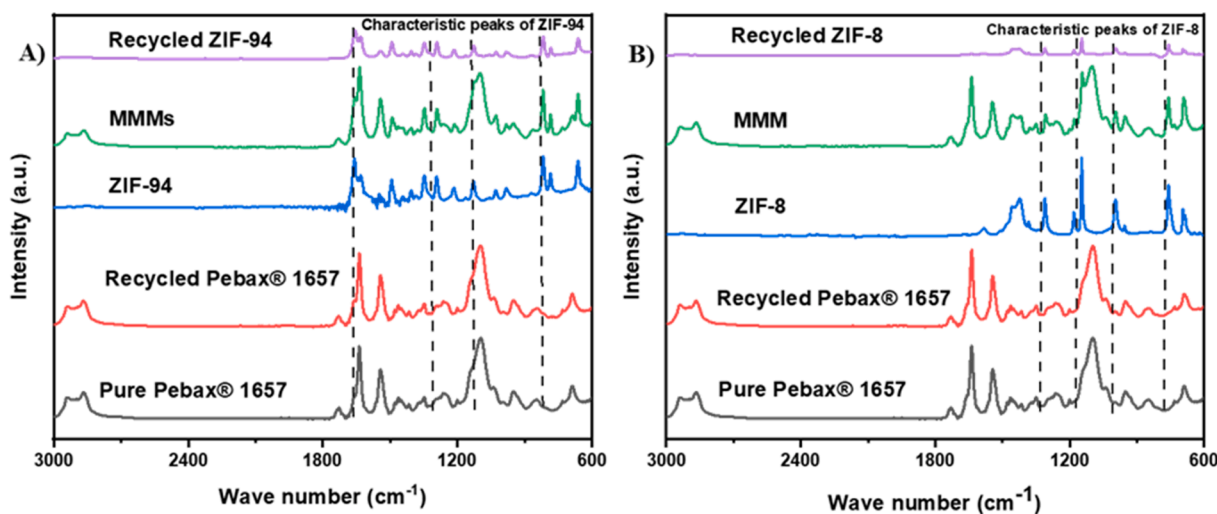

Fig. 5. FTIR analyses: A) of pure polymer, fresh ZIF-94, fresh MMM with ZIF-94 and recycled products from ZIF-94 based MMM, B) of pure polymer, fresh ZIF-8, fresh MMM with ZIF-8 and recycled products from ZIF-8 based MMM.
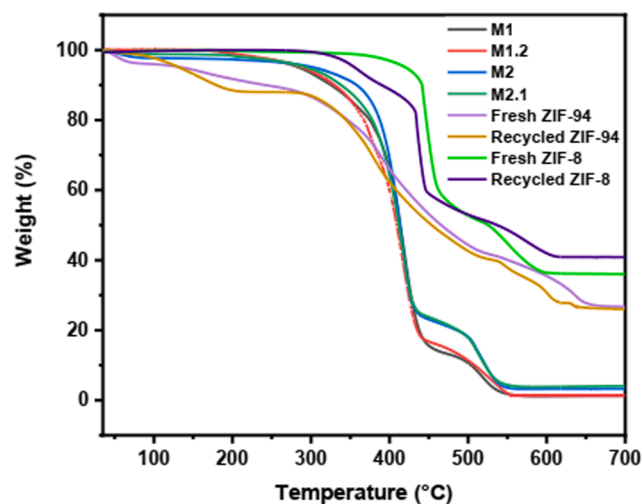
Fig. 6. TGA analyses in air of fresh and recycled ZIF-94, their membranes and fresh and recycled ZIF-8 (see Table 1).

losing weight before 100 °C which is due to the loss of moisture and solvents from inside of the micropores which ends at ca. 300 °C. Rapid thermal degradation of both fresh and recycled MOFs starts after 300 °C which continues up to 600 °C generating ZnO. Recycled ZIF-94 shows comparatively small amount of extra weight loss than the fresh MOF and finally gives a 0.7 % less residue. This tendency agrees with the presence of traces of polymer coating on the MOF surface (since this polymer decomposes between 400 and 530 °C as seen above), also responsible for the small loss of BET SSA quoted above for the two MOFs ZIF-94 and ZIF-8. Finally, typical membrane characterization techniques have been applied in this work without discarding the utility of other tools (e.g. evaluation of mechanical properties) and approaches dealing, for instance, with cost evaluation and life cycle analysis.

3.2. Gas separation performance

Due to its higher CO_2 adsorption capacity, already discussed in the introduction section, ZIF-94 was chosen for the MMM fabrication. As shown in Fig. 7, gas permeation analysis reveals that the re-cast bare membrane (M1.1) and fresh bare membrane (M1) produced similar CO_2 permeabilities which are 94 ± 2 Barrer and 90 ± 3 Barrer, respectively. However, the re-cast membrane (M1.1) sacrificed 21 % of CO_2/N_2

Fig. 7. Gas permeation results of the membranes when applied to the separation of the CO_2/N_2 mixture at 35 °C. At least 3 different membrane samples were tested for each membrane type.

selectivity compared to fresh bare membrane (M1) with values of 18 ± 1 and 23 ± 2, respectively. Analogously, the bare membrane made with polymer recycled from 10 wt% ZIF-94 MMM (M1.2) performed lower in terms of selectivity (18.5 ± 0.8) but outperformed in terms of permeability (106 ± 2 Barrer) than the fresh bare membrane (M1, 90 ± 3 Barrer). Such improvement of CO_2 permeability can be due to the existence of traces of MOFs in the recovered polymer (below the detection limits of FTIR, XRD and TGA) and in any event agrees with the larger DLS particle size which may produce an increase of free volume (responsible in turn of the CO_2/N_2 selectivity decrease). However, recovered polymer can be reused in MMMs which is evidenced from the gas separation performance of MMM M2.1 presented in Fig. 7. This recycled MMM improved fresh MMM M2 in terms of permeability with a trade-off in selectivity. The permeability and selectivity values corresponding to M2.1 are 174 ± 3 Barrer and 25.6 ± 0.6, respectively, whereas M2, which is called fresh MMM, produced a permeability of 137 ± 3 Barrer with a selectivity of 29.0 ± 1.8. Such performance of M2.1 follows the general phenomena: an increase in the permeability costs selectivity and vise-versa. In addition, M2.1 prepared with reused materials still outperformed the fresh bare membrane (M1) in terms of both permeability and selectivity. Similar performance of pure polymer and MMM containing fresh ZIF-94 and Pebax® 1657 matrix has been reported by several authors [22,50]. Moreover, when recycled ZIF-94 was incorporated into fresh polymer matrix (MMM M2.2) the selectivity of the membrane went down to 27.5 ± 1.4 (5 % lower than M2) but the permeability increased to 157 ± 6.5 Barrer which is still 67 % higher than that of fresh bare polymer (M1) and 15 % higher than that of M2. The separation performances and thicknesses of all the membranes are shortlisted in Table S3.

4. Conclusions

In this work, a methodology was developed to recycle ZIF-94 and Pebax® 1657 polymer components from their MMM which was also applicable for the recycling of ZIF-8. The recycled nanocrystals were undistorted in terms of size, shape and crystallinity. The reported methodology is excellent in terms of recovery yield for both polymer (97.8 ± 0.5 %) and MOF ZIF-94 (76 ± 2.5 %). Fresh and recycled ZIF-94 have quite similar BET SSA values which are of 427 ± 7 m^2/g and 412 ± 6 m^2/g, whereas respective mean particle sizes of 148 ± 44 nm and 164 ± 32 nm seem to be within the experimental error. Similarly, fresh ZIF-8 and recycled ZIF-8 show BET specific surface areas of 1507 ± 30 m^2/g and 1325 ± 26 m^2/g, respectively, and their mean particle sizes correspond to 120 ± 30 nm and 110 ± 20 nm, corroborating the applied method with two different MOFs. It should be pointed out that ZIF-8 and ZIF-94, belonging to the same MOF family, share many characteristic; however, new difficulties might arise when trying to recycle other kinds of MOFs (e.g. carboxylate type MOFs).

Additionally, the recovered polymer was found highly selective to the CO_2/N_2 mixture with a comparable CO_2 permeability to that of the fresh bare membrane. All these remarks validate the reported approach for the recycling of MMMs to obtain ZIF-94 and polymer matrix. The MMMs containing recovered MOFs and fresh polymer matrix produced an acceptable gas separation performance with CO_2 permeability and CO_2/N_2 selectivity of 174 ± 3 Barrer and 25.6 ± 0.6, respectively. These values are comparable to those achieved with MMMs obtained from totally fresh MOF and polymer materials (permeability of 134 ± 6 Barrer and selectivity 29 ± 0.8).

These parameters suggest successful recovery of precious components (MOFs) from MMMs. Additionally, recovered polymer matrices, with no traces of MOF according to the characterization tools used, are still selective, suggesting that they could be used in other applications (i. e. plastic bags). This work reinforces the environmental friendly industrial application of MMMs establishing the principles for the recovery and reuse of their individual components. Although recycled materials are found compatible for the CCS membrane application, still,
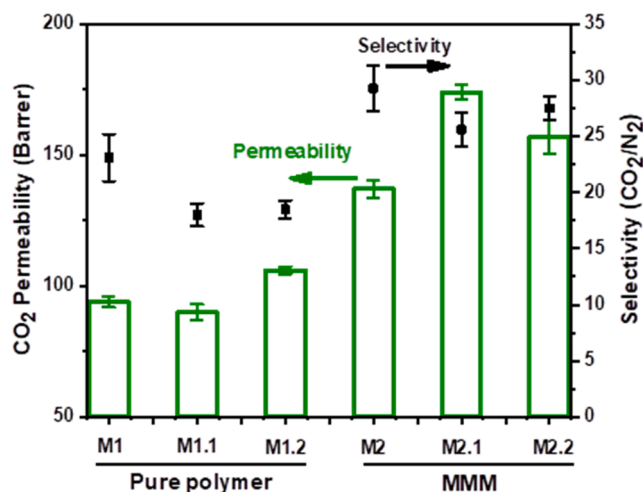
estimation of energy consumption, recycling of the solvents and life cycle assessment are considered as future objectives of the project which will reveal the complete insight of the recycling of MMMs. Moreover, this new approach suggests a way for membrane and MMM researchers to make their investigations cheaper and more sustainable.

CRediT authorship contribution statement

Md Rafiul Hasan: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Visualization, Data curation, Writing - original draft, Writing - review & editing. **Andoni Moriones:** Investigation, Methodology, Validation, Writing - original draft. **Magdalena Malankowska:** Conceptualization, Supervision, Writing - original draft, Writing - review & editing. **Joaquín Coronas:** Conceptualization, Supervision, Funding acquisition, Writing - original 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

Data will be made available on request.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2022.122355.

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